

HESLOP  
ROBINSON

Inorganic  
Chemistry

THIRD  
EDITION

ELSEVIER

THIRD  
EDITION

R. B. HESLOP/P. L. ROBINSON

Inorganic  
Chemistry

A GUIDE TO ADVANCED STUDY

ELSEVIER

# INORGANIC CHEMISTRY

*A Guide to Advanced Study*

*by*

R. B. HESLOP

*Senior Lecturer in Chemistry,  
The University of Manchester Institute of Science and Technology*

*and*

P. L. ROBINSON

*Emeritus Professor in the University of Durham  
and in the University of Newcastle upon Tyne;  
formerly Professor of Inorganic Chemistry,  
King's College, Newcastle upon Tyne  
and later Principal Scientific Officer,  
Atomic Energy Research Establishment, Harwell*

THIRD, COMPLETELY REVISED EDITION



ELSEVIER PUBLISHING COMPANY

AMSTERDAM LONDON NEW YORK

1967

ELSEVIER PUBLISHING COMPANY  
335 JAN VAN GALENSTRAAT, P.O. BOX 211, AMSTERDAM

AMERICAN ELSEVIER PUBLISHING COMPANY, INC.  
52 VANDERBILT AVENUE, NEW YORK, N.Y. 10017

ELSEVIER PUBLISHING COMPANY LIMITED  
RIPPLESIDE COMMERCIAL ESTATE, BARKING, ESSEX

*First Edition April 1960*  
*Reprinted September 1960*  
*Reprinted December 1960*  
*Reprinted November 1961*  
*Reprinted February 1962*  
*Second Edition November 1962*  
*Reprinted June 1963*

LIBRARY OF CONGRESS CATALOG CARD NUMBER 67-11549  
WITH 400 ILLUSTRATIONS AND 155 TABLES

ALL RIGHTS RESERVED  
THIS BOOK OR ANY PART THEREOF MAY NOT BE REPRODUCED IN ANY FORM  
INCLUDING PHOTOSTATIC OR MICROFILM FORM  
WITHOUT WRITTEN PERMISSION FROM THE PUBLISHERS

PRINTED IN THE NETHERLANDS

### **From the Preface to the First Edition (1960)**

This book is addressed to students and intended to provide in a single small volume an outline of current inorganic chemistry sufficient for basic reading up to honours degree standard. The approach is general and reasonably fundamental, so that some of the material is suitable for advanced level and scholarship pupils in schools and for non-specialist students in universities and technical colleges. Suggestions are made for further reading. Teachers may find it useful in planning their instruction to classes at all stages. An endeavour has been made to select factual matter of topical interest and to present the theoretical foundations rigorously enough to make advance possible by addition rather than correction.

Inorganic chemistry is descriptive in the sense that many branches of chemistry remain essentially descriptive. But the emphasis falls increasingly upon a description of its phenomena in terms of the discoveries of atomic physics, quantum mechanics, and theoretical and physical chemistry. Accordingly the earlier chapters seek to provide a minimum background for the rational understanding of chemical observations.

The main body of the work has three objects. First to provide clear-cut, readily assimilated information about the elements, presented in a comparative way, usually, but not exclusively, under the appropriate periodic sub-groups; secondly to cross-link related material by short discussions of particular topics; and thirdly to emphasise, by reiteration and repeated page reference, applications of theory developed in the earlier chapters. By these modes of association, it is hoped the student will both acquire a useful body of information and appreciate the growing integration which now characterises inorganic chemistry.

### **From the Preface to the Second Edition (1963)**

Four further impressions of this book have been called for since it was published in April 1960. This fact and much encouraging comment suggest that the selection of material and the manner of its presentation have met with general approval. We are grateful for many helpful criticisms—made personally and in reviews—all of which have been carefully considered. Wherever possible, modifications to meet them have been made in this second edition.

### **Preface to the Third Edition**

One of the consequences of the rapid expansion of chemical knowledge has been its impact on the teaching of chemistry at all levels. Ideas of structure, chemical bonding and energetics have been successfully intro-



duced at an early stage and this instruction has undoubtedly proved a sound basis for more advanced study. The CBA and Chemical Materials Study Projects in the United States of America and the Nuffield Project in Britain are examples of the new spirit in pre-university instruction.

The first edition itself attempted a fresh presentation of the subject and its cordial reception led us to hope that it did something to stimulate the healthy change in teaching now so widely recognised. But in the nine years since the original text was planned and written, major discoveries and a more sophisticated examination of older problems have appreciably altered the present subject matter of inorganic chemistry. All this, together with certain welcome alterations in emphasis, have made more coherent honours courses possible. The third edition seeks to meet these changes by making a smooth integration of the new facts and recent theory. It still remains a text-book addressed to undergraduates and one designed to give a broad picture of the subject which is neither too long nor too detailed for the time at their disposal.

In addition to a careful revision of all remaining text, some rearrangements, and much rewriting, the reader familiar with the earlier editions will find new chapters on bonding in transition-metal complexes, organometallic compounds and reaction mechanisms. He will see that a move has been made from the valence-bond description of bonding to the crystal-field and molecular-orbital approaches; these have the advantage of illuminating its more quantitative aspects. Without entering into details about current physico-chemical methods of investigation, we have made use of the results they have provided. By adequate cross-references the unity of inorganic chemistry which these discoveries further emphasise is brought home to the reader. Most of the space required for the new material has been found by omitting topics that now have less relevance.

The arrangement of the revised chapters on the elements is still according to that of the groups in the Periodic Table. This sequence, supported by special treatment of significantly related elements and by abundant cross-references, remains, in our opinion, the most satisfactory method of presenting the information. Chemistry has always gained by the recognition of its applications in other sciences and technology; where it seemed appropriate brief mention has been made of such applications.

To most of the chapters is appended a selected list of further reading. Because a student's time is limited and his requirement is a wide balanced view of the subject, books, monographs and review articles, rather than original papers, have mainly been cited.

February 1967

R. B. H.

P. L. R.

# Contents

	Page
<i>From the Preface to the First Edition</i> . . . . .	v
<i>From the Preface to the Second Edition</i> . . . . .	v
<i>Preface to the Third Edition.</i> . . . . .	v
<i>Chapter</i>	
1 Modern Inorganic Chemistry . . . . .	1
2 The Atomic Nucleus: Genesis of the Elements . . . . .	5
3 Radiochemistry . . . . .	36
4 Electronic Structures of Atoms. The Periodic Table . . . . .	50
5 Valency; Nature and Classification of Chemical Bonding . . . . .	93
Electronic Theory of Bonding, 94	
The Ionic Bond, 99	
The Covalent Bond, 107	
Non-localised and Metallic Bonding, 129	
Long-Range Bonds, 134	
6 Structure and Shape of Molecules . . . . .	137
7 Bonding and Structure in Compounds of Non-transition Elements . . . . .	145
8 Bonding in Transition-Metal Complexes . . . . .	153
General, 153	
Crystal Field Theory, 154	
High-Spin and Low-Spin Complexes, 160	
Absorption Spectra of Transition-Metal Complexes, 166	
Evidence for Covalent Bonding in Transition-Metal Complexes, 173	
Molecular Orbital Theory of Metal-Ligand Bonding, 177	
9 The Solid State . . . . .	187
Experimental Evidence on Structure, 187	
Structure and Properties, 189	
Crystal Growth, 217	
10 Oxidation-Reduction: Redox Reactions . . . . .	222
11 Acids and Bases . . . . .	237
12 Hydrogen. . . . .	254
13 The Hydrides . . . . .	264
General, 264	
The Saline Hydrides, 265	
The Metallic Hydrides, 266	
The Covalent Hydrides, 267	
14 The Noble Gases (Group 0) . . . . .	295
15 The Alkali Metals (Group IA) . . . . .	308
16 Beryllium, Magnesium and the Alkaline Earth Metals (Group IIA) . . . . .	321

17	Boron and Aluminium . . . . .	336
18	Gallium, Indium and Thallium (Group IIIB) . . . . .	354
19	Carbon and Silicon . . . . .	363
	Metal Carbonyls, 383	
20	Organometallic Compounds . . . . .	393
21	Germanium, Tin and Lead (Group IVB) . . . . .	407
22	Nitrogen and Phosphorus . . . . .	420
23	Arsenic, Antimony and Bismuth (Group VB) . . . . .	459
24	Oxygen, Sulphur, Selenium, Tellurium and Polonium (Group VIB) . . . . .	470
25	The Oxides . . . . .	494
26	Peroxides and Peroxo-Compounds. . . . .	504
27	The Halogens (Group VIIB) . . . . .	515
28	The Halides and Pseudohalides . . . . .	537
	The Halides, 537	
	The Pseudohalogens and Pseudohalides, 551	
29	The Transition Metals . . . . .	554
30	Complex or Co-ordination Compounds and Ions. . . . .	565
	General, 565	
	Nomenclature of Complex Compounds, 579	
	Complexes in Aqueous Solution, 582	
31	Substitution Reactions of Metal Complexes . . . . .	590
32	The Lanthanides, Scandium and Yttrium (Group IIIA) . . . . .	605
	The Lanthanides, 605	
	Scandium and Yttrium, 615	
33	The Actinides . . . . .	617
34	Titanium, Zirconium and Hafnium (Group IVA) . . . . .	633
35	Vanadium, Niobium and Tantalum (Group VA). . . . .	646
36	Chromium, Molybdenum and Tungsten (Group VIA) . . . . .	657
37	Manganese, Technetium and Rhenium (Group VIIA) . . . . .	674
38	Iron, Cobalt and Nickel. . . . .	690
	General Features of Group VIII, 690	
	Group VIII: The First Triad, 690	
39	The Platinum Metals . . . . .	708
	Group VIII: The Second and Third Triads, 708	
40	Copper, Silver and Gold (Group IB) . . . . .	726
41	Zinc, Cadmium and Mercury (Group IIB) . . . . .	743
	<i>Appendix: The Elements: Atomic Weights and Other Data . . . . .</i>	<i>758</i>
	<i>Subject Index. . . . .</i>	<i>761</i>

## *Chapter 1*

# **Modern Inorganic Chemistry**

The ambit of inorganic chemistry is well established; it comprises the natural occurrence and artificial preparation of the elements, their properties and reactions, and those of their compounds, together with a rational correlation and theoretical interpretation of the phenomena.

Although the oldest discipline in chemistry, inorganic chemistry continues to excite increasing interest as a subject of pure and applied research and is finding manifold applications in industry. It is the foundation of vast endeavour in fine and heavy chemicals, in ceramics, in the production of glass and building materials, and in extraction metallurgy. There is hardly an element which is not being investigated from some aspect at the present time. It is concerned in the preparation of catalysis and has made, and is making, contributions which facilitate the production and exploitation of atomic energy. Inorganic chemists have continued to call attention to much in this vast field which awaits exploration, and this book will have failed in its purpose if something of the enthusiasm and confidence which inspires them is not reflected in its pages. A few of the exciting themes dealt with are: current interpretation of chemical bonding and structure with the modern physicochemical evidence, non-stoichiometry, electron-deficient compounds, complex compounds, organometallic compounds, materials with exceptional properties (such as great hardness, high melting points, corrosion resistance), noble gas compounds. Most of the compounds of carbon with non-metallic elements lie outside inorganic chemistry, but organometallic compounds (p. 393) form one of its most important current topics.

The advances of the last two decades have taken inorganic chemistry right out of the stage of being a mass of arbitrarily chosen facts brought into some relationship by the Periodic Table. Although modern inorganic chemistry remains in a measure descriptive and pictorial (as do the other branches of the subject) the pictures have grown in precision and the descriptions have become more quantitative. Hence an historical approach is now inappropriate because the subject has developed to a point which makes entry from the level of present theoretical and physico-chemical knowledge desirable; such an entry has the advantage of being both easier

and more lively. For this reason earlier work on the structure of the atom, culminating in 1913 with Bohr's atomic model, and other classical material has not been included.

### Approach to the subject

Quantum theory has provided a picture of the atom that allows an immediate approach to valency and molecular structure while furnishing a far more secure basis for the periodic arrangement of the elements than selected physical and chemical properties. This is not to overlook the achievements of Thomson, Rutherford and Bohr in atomic structure, or of Newlands, Lothar Meyer, Mendeleeff, Bohr and others in evolving the Periodic Law, but rather to seize upon developments which their prescient work made possible. Readers will find it easier to assimilate and remember the facts embodied in the Periodic Classification when these are seen to emerge from the systematic development of electronic structure with increasing atomic number.

The description of atoms and molecules which is used—that of one or more positive nuclei surrounded by a cloud of electrons which, for many purposes, is equivalent to a smeared-out negative charge—presents in pictorial form the results of thirty years of quantum mechanics. All available evidence suggests that this general picture is unlikely to suffer substantial modification. Theoretical chemistry accepts the Schrödinger equation and is largely concerned with finding the most direct mathematical path to a unified explanation of the physico-chemical properties of molecules. This description has been adopted and used in the interpretation of valency theory, including metal-ligand bonding, and in discussing structure generally. A brief account of the nucleus is included because not only does it determine the extra-nuclear structure of the atom, but is also the seat of radioactivity and the source of nuclear energy. Some knowledge of it is necessary in order to follow present ideas on the synthesis of elements taking place in the stars.

The kinetic and thermodynamic aspects of reactions are stressed wherever the data are available, and examples are worked out which should enable the reader to understand and acquire facility in these essential calculations.

So much of inorganic matter is crystalline that once a means of investigating the structure of solids became available it was eagerly applied. The result has made it necessary to include a short account of the solid state. With this goes a little about the growth of crystals and the way atoms in their lattices suffer dislocation.

### Suggestions

This book is a brief epitome of modern inorganic chemistry and the reader may usefully begin anywhere, since liberal cross-references provide a constant link with definitions and the underlying theory. These appear mainly in the earlier chapters which need not be mastered before the rest of the book can be understood, and their assimilation by repeated reference will be repaid by a fuller appreciation of what follows. It is idle to suppose that a real appreciation of any branch of chemistry can be had without two things—adequate theory and sufficient facts. The best way to grasp theory is to apply it constantly, and the easiest way to remember facts is to seek their theoretical relationship.

Appended to every chapter is a short list of references which will be found useful in extending the reader's knowledge of particular aspects of the subjects treated. In order to keep up to date he may consult *Chemistry in Britain*, *Education in Chemistry*, *Journal of Chemical Education*, *School Science Review*, *Quarterly Reviews of the Chemical Society*, and *Chemical Reviews*.

### Symbols and Abbreviations

1. Chemical symbols and formulae have been frequently used in place of names to save space and often to secure clarity. Where an arrow ( $\rightarrow$ ) from the donor atom appears, it does not imply that the bond is different from the rest.
2. Where there can be no confusion as to the temperature scale,  $^{\circ}\text{C}$  is indicated by the degree sign only after a number.
3. For pressure, mm signifies mm of mercury.
4. The numerical values of properties are intended for comparative purposes; they are given to no greater accuracy than this requires.
5. Atomic radius, density and atomic volume data are for the form stable at  $25^{\circ}$  and 1 atmosphere, except where otherwise stated.
6. Symbols which appear frequently are:

Avogadro's number	$N$	Heat capacity	$C$ (cal mole $^{-1}$ deg $^{-1}$ )
Gas constant	$R$ (cal mole $^{-1}$ )	Internal energy	$U$ (cal)
Faraday's constant	$F$ (coulombs)	Entropy	$S$ (cal deg $^{-1}$ )
Charge on an electron	$-e$ (coulombs)	Heat content (Enthalpy)	$H$ (cal)
Planck's constant	$h$ (erg sec)	Gibbs free energy	$G$ (cal)
Frequency	$\nu$ (sec $^{-1}$ )	Atomic number	$Z$
Wave number	$\lambda^{-1}$ (cm $^{-1}$ )	Atomic mass number	$A$
Wave length	$\lambda$ (Ångstrom units)	Concentration of X	$[X]$ moles l. $^{-1}$
		Activity of X	$a_x$ or $\{X\}$
		Specific reaction rate	$k$
		Equilibrium constant	$K$
		Activation energy	$E$ (cal)

Subscripts and superscripts when used with these symbols, are explained in the text. The units of  $h$  and  $K$  are variable.

7. The most frequently used abbreviations are:

g	gram	amu	atomic mass unit
kg	kilogram	AO	atomic orbital
l.	litre	MO	molecular orbital
ml	millilitre	b.p.	boiling point
cm	centimetre	m.p.	melting point
Å	Ångstrom unit ( $10^{-8}$ cm.)	u.v.	ultraviolet
V	volt	i.r.	infrared
eV	electron volt	atm.	atmosphere (pressure)
MeV	million electron volts	dens.	density
$I(1)$	ionisation potential (first)	s.g.	specific gravity
$E^\circ(M^+/M)$	standard electrode potential for $M^+/M$ couple in volts	$^\circ K$	degree Kelvin
e.m.f.	electromotive force (volts)	Gp. II. etc.	Periodic Group Two etc.
$H$	magnetic field strength	$\ln x$	logarithm of $x$ to base $e$
cal	calorie	n.m.r.	nuclear magnetic resonance
kcal	kilocalorie	n.q.r.	nuclear quadrupole resonance
h.c.p.	hexagonal close-packed	B.M.	Bohr magneton
b.c.c.	body-centred cubic	e.s.r.	electron spin resonance
f.c.c.	face-centred cubic		
At. Vol.	atomic volume		

Other abbreviations used in the text are explained where they occur.

## Chapter 2

# The Atomic Nucleus: Genesis of the Elements

The chemical properties of an element depend on the nature of its atoms, and many advances in chemistry are directly attributable to knowledge of their structure provided by atomic physics during the last half century.

An atom comprises an extremely small, positively charged, central *nucleus* which occupies about  $10^{-15}$  of its volume, has a radius of  $10^{-12}$  cm, and accounts for nearly all its mass, surrounded by a region of negative charge produced by the *electrons*. The free unexcited atom is electrically neutral, electrons balancing protons. The nucleus contains positive *protons* and uncharged *neutrons*, both particles having about the same mass. Other particles are known to emerge from radioactive nuclei (*e.g.* electrons p. 23 and positrons p. 24) but are not primary constituents and are only observable when released by some nuclear change. This apparent paradox is a manifestation of the Uncertainty Principle (p. 52): if the position of an electron is known within extremely narrow limits (as in a nucleus) its momentum can be known only within extremely wide limits; this means an electron known to be within a nucleus at one instant has

TABLE I  
CONSTITUTION OF SOME NUCLEI

<i>Element</i>	<i>Z</i>	<i>N</i>	<i>A</i>	<i>Symbols</i>	<i>Properties</i>
Hydrogen	1	0	1	${}^1_1\text{H}$ p	Stable
Deuterium	1	1	2	${}^2_1\text{H}$ d	Stable
Tritium	1	2	3	${}^3_1\text{H}$ t	Radioactive
Helium	2	1	3	${}^3_2\text{He}$	Stable
	2	2	4	${}^4_2\text{He}$ $\alpha$	Stable
Lithium	3	3	6	${}^6_3\text{Li}$	Stable
	3	4	7	${}^7_3\text{Li}$	Stable
Sodium	11	11	22	${}^{22}_{11}\text{Na}$	Radioactive
	11	12	23	${}^{23}_{11}\text{Na}$	Stable
	11	13	24	${}^{24}_{11}\text{Na}$	Radioactive



a high probability of escaping during the next instant. Thus it cannot be regarded as a permanent constituent of the nucleus. The number of protons in the nucleus determines the nature of an element; as indicated, it equals the number of electrons in the atom, which, in turn, fixes its chemical character. An atom with eight protons is oxygen, one with seventeen protons, chlorine. This number, the *atomic number*  $Z$ , fixes the place of the element in the Periodic Table. Except for hydrogen (protium,  ${}^1\text{H}$ ), all nuclei also contain a number of neutrons,  $N$ . The sum of  $Z$  and  $N$  is the *mass number*,  $A$ . Protons and neutrons are known collectively as *nucleons*, and thus  $A$  is the number of nucleons (see Table 1).

An atom has three noteworthy features: (i) the enormous density of the nucleus, about  $5 \times 10^{12}$  times as dense as uranium; (ii) the small volume of the nucleus, about  $10^{-15}$  of that of the atom, (iii) the large volume of the negatively charged cloud, about  $10^{15}$  times that of the nucleus. Nevertheless atoms have diameters which do not differ greatly, the largest being only seven times greater than the smallest (caesium in the metal is  $2 \times 2.65$  Å and hydrogen in the hydrogen molecule is  $2 \times 0.37$  Å).

TABLE 2

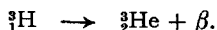
APPROXIMATE DATA FOR NUCLEUS, ELECTRON CLOUD AND ATOM

	<i>Nucleus</i>	<i>Electron cloud</i>	<i>Atom</i>
Charge (coulombs)	$1.6 \times 10^{-19} Z$	$1.6 \times 10^{-19} Z$	—
Mass (amu)	$A$	$Z/1837$	$A$
Diameter (cm)	$1.4 \times 10^{-13} A^{\frac{1}{2}}$	$10^{-8}$	$10^{-8}$
Density (g/cm <sup>3</sup> )	$10^{14}$	$2 \times 10^{-4} Z$	$0.4 A$
Charge density (coulombs/cm <sup>3</sup> )	$5 \times 10^{18}$	$4 \times 10^4 Z$	—

### Isotopes

There are three kinds of hydrogen atoms; these are the *isotopes*  ${}^1\text{H}$ ,  ${}^2\text{H}$  and  ${}^3\text{H}$  and, unlike any other isotopes, they have names: *protium*, *deuterium*, *tritium*. In the commonest, protium, the nucleus is a proton. Terrestrial hydrogen is usually combined with other elements, but whether free or combined one atom of this hydrogen in six thousand is deuterium and has a nucleus containing a neutron as well as a proton. This isotope was separated from ordinary hydrogen in 1931 by Urey, Brickwedde and Murphy, who were able to do this because it has slightly different properties from the latter. The third isotope, tritium, is produced by bombarding an isotope of lithium ( ${}^6\text{Li}$ ) with slow neutrons. Tritium is unstable, its

atom reverting to a helium atom of the same mass by the loss of a  $\beta$ -particle (p. 23), an electron of nuclear origin:



In a process of this kind the neutron decays into a proton and an electron.

In the respective formulations,  ${}^1_1\text{H}$ ,  ${}^2_1\text{H}$  and  ${}^3_1\text{H}$ , the superscript is the mass number,  $A$ , and the subscript the atomic number,  $Z$ . These isotopes occupy the same place as hydrogen in the Periodic Table. Helium has two natural isotopes  ${}^3_2\text{He}$  and  ${}^4_2\text{He}$ , the former very rare, and lithium also two,  ${}^6_3\text{Li}$  and  ${}^7_3\text{Li}$ , occurring in the ratio of about 1:13. Though the mass number precedes the symbol, the isotopes are spoken of as lithium-*six* and lithium-*seven*. There is only one natural isotope of sodium,  ${}^{23}_{11}\text{Na}$ ; the other two,  ${}^{22}_{11}\text{Na}$  and  ${}^{24}_{11}\text{Na}$ , are artificial and unstable, the lighter emitting positrons (p. 24) and the heavier electrons. Many elements have more than two natural isotopes.

Though it is proper to refer to lithium-6 and lithium-7 as isotopes of lithium, an individual atomic species, such as lithium-6, should be called a *nuclide*. The hundred or so elements have furnished about sixteen hundred nuclides.

Isotopes were first recognised in the natural radioactive series which comprise heavy elements, but positive ray analysis soon showed that light elements also had isotopes and the development of the mass spectrograph enabled all the elements to be examined for isotopes. The operation of the mass spectrograph is based on the deflection of collimated beams of positively charged particles, cations, in electric and magnetic fields of known strength. The ions are formed as an anode ray of positively charged particles, by evaporating from a hot filament or, as in Aston's earliest apparatus, by passing a discharge through a vapour. Adjustment of the strength of the fields enables particles of the same charge to mass ratio to be focussed as slit images. With such a beam from an element possessing isotopes, the several images are brought to different foci, and from their positions the masses of the individual isotopes may be determined with an accuracy of 0.01% or better.

Molecules have rotational and vibrational energies (p. 138) which are quantised, taking only certain discrete values which depend in magnitude on the masses of the atoms involved and are therefore different for molecules containing different isotopes of the same element, for instance  ${}^1\text{H}^{35}\text{Cl}$  and  ${}^1\text{H}^{37}\text{Cl}$ . Changes in rotational energy are characterised by the absorption of radiation in the far infrared, and in vibrational energy by absorption in the near infrared; they give rise to lines in these spectral regions. Particular lines which occur singly when one nuclide is present

appear in groups when there are several nuclides. From the small differences in frequency both the presence and relative masses of the nuclides may be inferred. By this sensitive method Giauque and Johnson (1929) showed that oxygen contained molecules of  $^{16}\text{O}^{17}\text{O}$  and  $^{16}\text{O}^{18}\text{O}$ . The existence of oxygen-17 and oxygen-18 had not been revealed by the mass spectrograph.

### Natural isotopic ratios — Atomic mass standard

The mass spectrometer is a mass spectrograph in which the positive ions are produced at a steady rate and the photographic plate, by means of which the positions of the ion images were formerly observed, is replaced by a slit behind which is a collector connected to devices for amplifying and measuring the ion current. The slit scans the spectrum and the ion current shows as a series of peaks. Every peak indicates an isotope and its height represents the relative number of ions (Fig. 1). The design of these

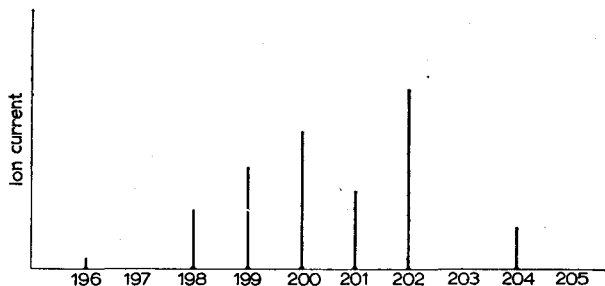


Fig. 1. Ion current peaks in the mass spectrograph of mercury.

instruments now allows an accuracy of 0.001%, making the method better than that of chemical analysis for the determination of atomic mass—the weighted mean of the masses of the isotopes.

The relative abundance of isotopes from different sources may vary a little. Atmospheric oxygen is slightly richer in oxygen-18 than the combined oxygen in sea water, and the relative abundance in water from different sources is not constant. Elementary sulphur in the Texas deposits has a different isotopic composition from that of the combined sulphur in the surrounding rocks. A range of 3.8% has been observed in the ratio of boron-10 and -11 from various sources but no difference in the ratio of silicon-28, -29 and -30 in material of widely spaced terrestrial origin.

## The Mole

Atomic masses are expressed in units based on the carbon-12 scale. The atomic mass unit, amu, is  $1.6604 \times 10^{-24}$  g, one twelfth of the mass of a  $^{12}\text{C}$  atom. Its reciprocal,  $6.0228 \times 10^{23}$ , the Avogadro number, is the number of atoms in 12 g of the carbon-12 nuclide.

For comparison of quantities in chemistry it is convenient to define as a mole the amount of substance containing the same number of molecules (or atoms, or radicals, or ions, or electrons as the case may be) as there are atoms in 12 g of carbon-12. Mole has been used in this sense throughout this book. It is a less restricted term than gram molecule, which was applied only to molecular species.

## Separation of isotopes

### (i) Gaseous diffusion

Gases of different density,  $\rho$ , diffuse at different rates: rate  $\propto 1/\sqrt{\rho}$ . Uranium hexafluoride made from natural uranium contains one part of  $^{235}\text{UF}_6$  in 140 parts of  $^{238}\text{UF}_6$ . The ratio of the densities is 1.0086, of diffusion rates 1.0043. A process of successive diffusion through a series of porous partitions was developed at Oak Ridge, Tennessee (1945), and has been modified and used elsewhere. In these the lighter fraction passes a barrier and becomes the feed for a later stage while the heavier fraction is returned to an earlier stage.

### (ii) Thermal diffusion

When two gases of different densities are in a vertical tube which is cool and has an electrically heated wire down the axis, the lighter gas diffuses preferentially towards the hot wire where it rises in a convection current, while the heavier streams downwards on the surface of the tube. The principle is applicable to isotopes and, with a column of 100 feet and a temperature difference of  $600^\circ$ , an almost complete separation of  $^{35}\text{Cl}$  from  $^{37}\text{Cl}$  was effected as early as 1938.

### (iii) Electromagnetic method

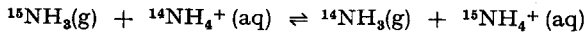
A perfect separation is possible with a mass spectrograph in which the positive ions of the different isotopes pass into collectors, but the quantities would be small. About 1943, however, a large-scale apparatus, the calutron, was constructed in which an ideal rigorous separation was sacrificed to yield, since the ions in beams of heavy current repel one another and cause spreading. The method has been further refined and is extensively used.

*(iv) Molecular distillation*

In 1921 the isotopes of mercury were partially separated by distillation in a high vacuum with a distance between the evaporating and condensing surfaces equal to about the mean free path of the atoms. The rates at which the isotopes evaporate is inversely proportional to the square roots of their masses so that the condensate is a little richer in the lighter isotopes.

*(v) Chemical methods*

Isotopes are not absolutely identical in chemical properties (p. 38), but the difference is observable only in the light elements where the ratio of the mass of the isotopes is large, for instance  $^1\text{H}$  and  $^2\text{H}$ . Thode and Urey (1939) concentrated nitrogen-15 in ammonium nitrate, to the extent of 70%, by allowing a solution of the salt to flow down a column against a counter current of ammonia. The equilibrium constant for



has a value of about 1.033.

*(vi) Gas chromatography*

This technique enables gases to be separated by the selective adsorption of one or more from a mixture on a suitable packing in a column. The adsorbed gas, should that be required, may be subsequently recovered by elution or other means. Though only partially successful when applied to the isotopes of neon because the difference in their adsorption coefficient on charcoal is small, the method has enabled deuterium to be separated from a 1 : 1 deuterium-hydrogen mixture. The column is packed with palladium-black on asbestos which preferentially adsorbs the hydrogen and allows the deuterium to pass on.

**Exact masses of nuclides**

Precise determinations of the masses of nuclides have shown that they are not simply the sums of the individual masses of their component protons and neutrons. When these units, or nucleons, combine to form a nucleus there is a change of potential and kinetic energy which appears as a change in mass. Einstein showed the energy created by the destruction of mass and the mass destroyed to be related thus:

$$E = mc^2.$$

The velocity of light  $c$  is  $\sim 3 \times 10^{10}$  cm.sec $^{-1}$  and a mass of 1 g is thus equivalent to about  $9 \times 10^{20}$  ergs.

A unit of energy, the *electron-volt*, is used in discussing energy changes in nuclei. It is the kinetic energy acquired by an electron in falling through a potential difference of 1 V.

$$\begin{aligned} 1 \text{ eV} &= 1.60 \times 10^{-12} \text{ ergs,} \\ 1 \text{ million eV, } 1 \text{ MeV} &= 1.60 \times 10^{-6} \text{ ergs,} \\ \therefore \text{ a mass of } 1 \text{ g} &= 5.61 \times 10^{26} \text{ MeV,} \\ 1 \text{ amu} &= 931 \text{ MeV.} \end{aligned}$$

An obvious result of Einstein's deduction is that the separate principles of conservation of mass and conservation of energy are replaced by the single principle of conservation of mass-energy. Furthermore, both mass and energy may be expressed in electron-volts, ergs or grams.

The atomic mass or exact mass,  $M$ , of a nuclide is the weight of its atom, which includes the extra-nuclear electrons, expressed in atomic mass units, amu.  $M$  is very slightly different from the mass number,  $A$ , in every instance except the standard, carbon-12. With sulphur-32, for instance,  $M = 31.97207$  amu.

### Binding energy

When nucleons coalesce into a nucleus there is a loss of energy, shown as an equivalent decrease in mass; the binding energy,  $BE$ , is given by

$$\begin{aligned} BE &= \Delta M \\ &= Z \times (\text{mass of proton}) + N \times (\text{mass of neutron}) - \text{Mass of nucleus} \\ &= Z \times (\text{mass of H atom}) + N \times (\text{mass of neutron}) - \text{Mass of atom } (M) \end{aligned}$$

The mass of the hydrogen atom = 1.00782 amu

The mass of the neutron = 1.00866 amu

For oxygen-16,  $Z = N = 8$ , and  $M = 15.99491$  amu

$$\begin{aligned} BE &= 8(1.00782) + 8(1.00866) - 15.99491 \text{ amu} \\ &= 0.1370 \text{ amu} \\ &= 0.1370 \times 931 \text{ MeV} = 128 \text{ Mev.} \end{aligned}$$

Thus the  $BE$  per nucleon =  $\frac{128}{16} = 8 \text{ MeV}$ .

The nuclear binding forces are strong attractive forces, independent of charge and of very short range. Just as an individual extra-nuclear energy level holds two electrons (Pauli principle (p. 69)) so an individual nuclear energy level appears to hold two protons and two neutrons. This probably accounts for the stability of the  $\alpha$ -particle (p. 23) which is the  ${}^4_2\text{He}$  nucleus, and those nuclides with even numbers of protons and neutrons. Oxygen-16 and carbon-12 are outstanding examples, and the majority of the stable (non-radioactive) nuclides are further instances.

### Nuclear models

Nuclear models have been devised as an aid in the discussion of nuclear properties; they have been very useful but must not be taken as an accurate picture of real nuclei, about the structure of which much remains to be known. Two important models are the *Shell model* in which the emphasis is on the individual particles, and the *Liquid Drop model* in which there is the idea of a surface tension that must be overcome for fission to take place.

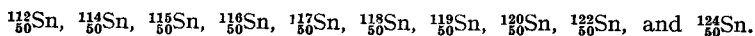
In the shell model it is assumed that the energy of a system of nucleons is capable of taking only certain discrete values, *i.e.* it is quantised; the possible values of the energy cannot be reliably calculated by quantum mechanics, however, because the nature of the nuclear forces is not fully known. It is further assumed that the spins of protons and of neutrons are paired, each to each, and moreover that there is a coupling between the orbital angular momentum and the spin leading to a splitting in levels. These levels account for the experimental fact of the magic numbers of either protons or neutrons (2, 8, 20, 28, 50, 82, 126), so called because they represent especially stable nuclei. There is a broad resemblance between the shell model of the nucleus and the electron shells of the extra-nuclear structure (p. 66), but the nucleons are extremely closely packed. Acceptance of the shell model implies an assumption that each nucleon moves in an average central field provided by all the others, rather as the extra-nuclear electrons move in the electrostatic field of the nucleus.

The evidence for a shell structure associated with the special stability of nuclei containing 2, 8, 20, 28, 50, 82, or 126 of either protons or neutrons rests upon the following facts:

(i) The elements with unusually large numbers of stable isotopes and with the greatest range of mass are calcium and tin; these have the stable isotopes:



and



Similarly lead,  $Z = 82$ , is the final stable isotope of all the natural radioactive series.

(ii) Energies of radioactive-decay products show the *BE* of neutrons to have a 2.2 MeV discontinuity at 126 neutrons, and the *BE* of protons to have a discontinuity of 1.6 MeV at 82 protons.

(iii) Nuclei with 50 or 82 neutrons are particularly abundant.

(iv)  ${}_{36}^{87}\text{Kr}$  and  ${}_{54}^{137}\text{Xe}$  are neutron emitters—very few are known. They

have 51 and 83 neutrons respectively. The last neutron is evidently weakly held.

(v) Neutrons are absorbed with difficulty—the absorption cross sections are low—by nuclei with 50, 82 or 126 neutrons.

(vi) Experimental nuclear masses and semi-empirically calculated ones often differ. The largest of these differences can be explained by assuming that nuclei with 50 and 82 neutrons are particularly stable.

### Nuclear spin

Measurement of the energy emitted in radioactive changes (p. 21) and of the magnetic properties of nuclei (p. 14) indicate that some nuclei possess spin (p. 19) which depends on the energy state. Since in nuclei there is pairing, only nuclei which have an unpaired proton or neutron show spin.

The nuclear shell model has allowed the prediction of energy levels and spins for nuclei in which  $N$  or  $Z$  is near one of the magic numbers. For example,  $^{123}_{51}\text{Sb}$  has an even number of neutrons which produce no net spin, but the odd proton as expected gives nuclear spin for the nucleus in its ground state in agreement with experiment.

The shell model is less successful in predicting energy levels for nuclei as  $N$  and  $Z$  depart from the magic numbers. Bohr and Mottleson, in their *Collective model* of the nucleus (a kind of combination of Shell and Liquid Drop models) interpret the deviations as due to the existence of low-energy vibrations and rotations in non-spherical nuclei (p. 19).

### Deviations in binding energy per nucleon

In spite of the repulsion of positively charged protons at long range, within the nucleus, at the close range of about  $10^{-13}$  cm, they exert a strong attractive force probably by means of the exchange of  $\pi$  mesons. The same is true of neutrons and, as the density of all nuclei is the same, these forces must be saturated. Moreover, except for the very light nuclei the binding energy averages about 8 MeV, ranging from 7.5 to 8.5 MeV.

However, in the lighter nuclei, where the ratio of surface to mass becomes high, the surface energy reduces the binding energy per nucleon below the average. The binding energy per nucleon in deuterium is 1.1 and in tritium 2.8 whereas it is 7.1 MeV in helium-4; fusion of very light nuclei thus involves an increase in binding energy and the release of energy.

Nuclei which have even numbers of both protons and neutrons are particularly stable (Table 3) and those with equal as well as even numbers



of both (for instance  ${}^4_2\text{He}$ ,  ${}^{12}_6\text{C}$ ,  ${}^{16}_8\text{O}$  and  ${}^{40}_{20}\text{Ca}$ ) have high binding energies relative to those of adjacent nuclei (Fig. 2). The fall in binding energy per nucleon at high mass numbers is largely due to an increased coulombic repulsion between the protons and because the extra neutrons have to occupy high-energy levels in the nucleus.

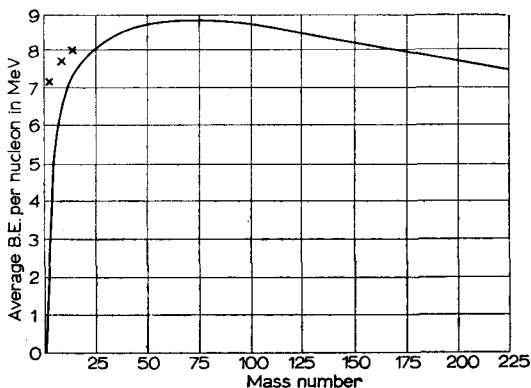


Fig. 2. Binding energy per nucleon related to mass number. Smoothed curve for stable nuclides. The binding energies of  ${}^4\text{He}$ ,  ${}^{12}\text{C}$  and  ${}^{16}\text{O}$ , indicated by the crosses, show the abnormal stabilities of these even-even nuclides.

Energy is also released when a heavy nucleus, such as uranium-235, suffers fission.

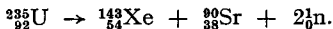


TABLE 3

CONSTITUTION AND STABILITY OF NUCLIDES

$Z$	$N$	$A$	<i>Number of stable nuclides</i>
Even	Even	Even	164
Even	Odd	Odd	55
Odd	Even	Odd	50
Odd	Odd	Even	4

### Nuclear magnetic resonance spectroscopy

#### *Physical principles*

Those atomic nuclei which have an odd number of either protons or neutrons, or odd numbers of both, possess intrinsic magnetic moments.

The nuclear spin quantum number,  $I$ , analogous to the electron spin quantum number  $s$  (p. 65) differs from it in being able to take various integral and half-integral values. Examples are:

$$\begin{aligned} I = 0 & \text{ for } {}^{12}_6\text{C and } {}^{16}_8\text{O.} \\ I = \frac{1}{2} & \text{ for } {}^1_1\text{H, } {}^{19}_9\text{F and } {}^{31}_{15}\text{P.} \\ I = 1 & \text{ for } {}^2_1\text{H and } {}^{14}_7\text{N.} \\ I = 3/2 & \text{ for } {}^{35}_{17}\text{Cl and } {}^{37}_{17}\text{Cl.} \end{aligned}$$

Magnetic nuclei placed in a magnetic field,  $H$ , acquire an energy of magnetic interaction

$$E = \mu_H H$$

where  $\mu_H$  is the component of the nuclear moment in the field direction

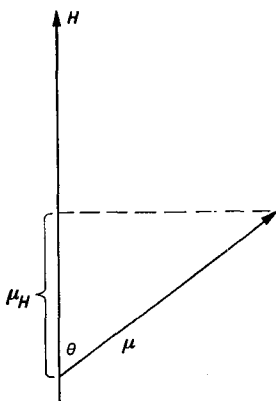


Fig. 3. Magnetic moment,  $\mu$ , represented as a vector.

(Fig. 3). Quantum mechanics (p. 50) restricts the orientations to those for which

$$\mu_H = \frac{m\mu}{\sqrt{I(I+1)}} \text{ and } \theta \text{ is therefore } \cos^{-1} \frac{m}{\sqrt{I(I+1)}}$$

where  $m = I, I - 1, I - 2 \dots -I$ . It also restricts the energy changes, which can arise when the nucleus interacts with electromagnetic radiation, to those for which  $\Delta m = \pm 1$ .

Thus for the absorption of radiation with a frequency of  $\nu \text{ sec}^{-1}$ .

$$E = h\nu = \frac{\mu}{\sqrt{I(I+1)}} H$$

$$\therefore \nu = \left\{ \frac{\mu}{h\sqrt{I(I+1)}} \right\} H$$

The fraction in braces is characteristic of a particular nucleus.

For magnetic fields of  $10^3$  to  $10^4$  gauss, absorption frequencies are in the range 1–50 Megacycles per second, so that measurements are in the radiofrequency range. The energy which is absorbed causes the nuclear magnets, which precess round the direction of the applied field, to tilt, so that  $\theta$  increases in value. The precession may be indicated as shown in Fig. 4.

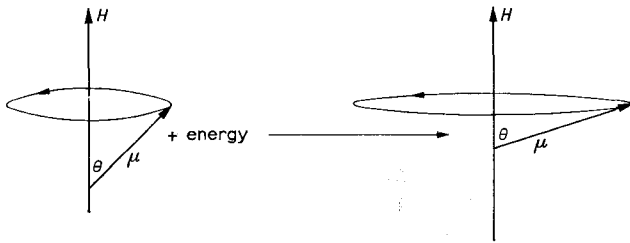


Fig. 4.

Thus identical nuclei, irradiated at a particular frequency, would be expected to absorb energy at the same strength of applied field.

Chemical interest in n.m.r. spectroscopy arises from the fact that the field  $H$  round the nucleus depends on the field due to its surrounding electrons and to adjacent nuclei as well as on the external field produced by the laboratory magnet.

$$H = H_a + H_b + H_c + H_d$$

$H_a$  = applied field due to laboratory magnet;

$H_b$  = a field due to currents induced by  $H_a$  in electrons around the nuclei;

$H_c$  = a field due to neighbouring magnetic nuclei, large in solids, but absent in liquids and gases where random molecular motion occurs;

$H_d$  = a field due to neighbouring nuclei in the same molecule but unlike  $H_c$  in being indirect, depending on currents induced in electrons by the adjacent nuclei, and also in not being averaged to zero by random molecular motion in liquids and gases.

#### *Measurement of internuclear distances in solids*

In solids,  $H_b$  and  $H_d$  may be neglected in relation to  $H_c$ . The strength of the applied field  $H_a$  required to produce resonance absorption in a solid is therefore related to  $H$  and the spectrum has the form shown in Fig. 5.

The shape of the absorption curve reflects the range and distribution of local fields which depend on the distances of nuclear separation. From

it, nuclear distances may be determined with a higher degree of precision than by other methods: for instance in  $\text{NH}_4\text{Cl}$ ,  $r_{\text{N-H}} = 1.038 \pm 0.004 \text{ \AA}$  by n.m.r. spectroscopy and  $1.03 \pm 0.02 \text{ \AA}$  by neutron diffraction.

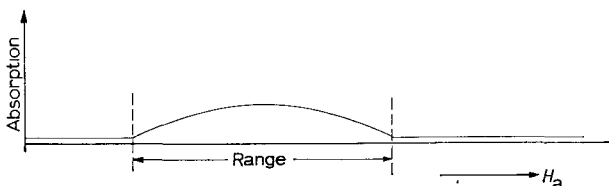


Fig. 5. Nuclear magnetic resonance spectrum for a solid.

#### *Application to molecular structure determination*

Nuclear magnetic resonance spectroscopy is also used to determine molecular structure in liquids and gases.  $H_b$  and  $H_a$  (unlike  $H_c$ ) take discrete values, and the plot of absorption against  $H_a$  shows fairly sharp bands. Usually  $H_b$  has a larger value than  $H_a$ , and spectra obtained at low resolution can be interpreted in terms of  $H_b$  variations. The ratio  $H_b/H_a$  is characteristic of a particular environment in a molecule. The value of  $H_b/H_a \times 10^6$ , referred to standard environment structure is termed the 'chemical shift' characteristic of a particular environment. In the  $^{31}\text{P}$  resonance spectrum of the tetrapolyphosphate ion, for example, there are two absorption bands of equal intensity (Fig. 6).

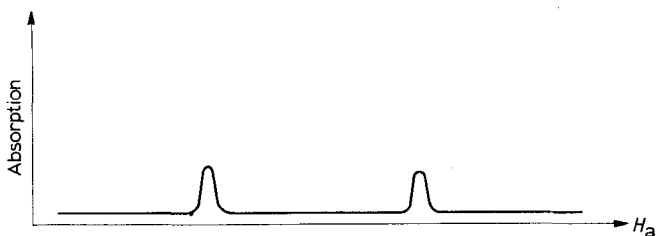
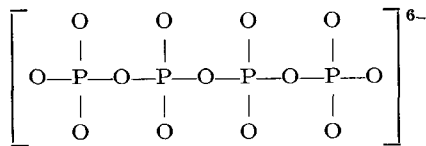


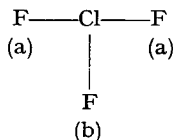
Fig. 6. Low-resolution  $^{31}\text{P}$  resonance spectrum of  $\text{P}_4\text{O}_{13}^{6-}$  ion.

One arises from the two central P atoms, which both have the same type of environment; the other from the two terminal P atoms, which both lie in a rather different environment:



*Spin-spin coupling and its value in interpreting structure*

The field  $H_d$ , which unlike  $H_b$  is independent of the strength of the externally applied field  $H_a$ , arises from other magnetic nuclei in the same molecule, particularly ones distinct in position and function. In these the adjacent nuclear magnets induce circulatory currents; the number of possible local fields depends on the orientations of the neighbouring nuclear magnets. In the T-shaped  $\text{ClF}_3$  molecule, two F atoms ( $F_a$ ) have one kind of environment, and the other ( $F_b$ ) has a different environment



Each  $^{19}\text{F}$  ( $I = \frac{1}{2}$ ) may have two effective orientations (*i.e.* averaged over all precession angles)

→  
or  
←

$F_b$  experiences three different  $H_d$  fields due to the two nuclei  $F_a$  (I and II)

→ I	→ I	← I
→ II	← II	← II
	← I	
	→ II	

1/4 of the molecules      1/2 of the molecules      1/4 of the molecules

But the two  $F_a$  atoms experience only two  $H_d$  fields due to  $F_b$ , according as to whether its spin is → or ←.

At a low temperature ( $-50^\circ\text{C}$ ) the absorption, which can only be recorded by a high-resolution instrument, is therefore of the form shown in Fig. 7.

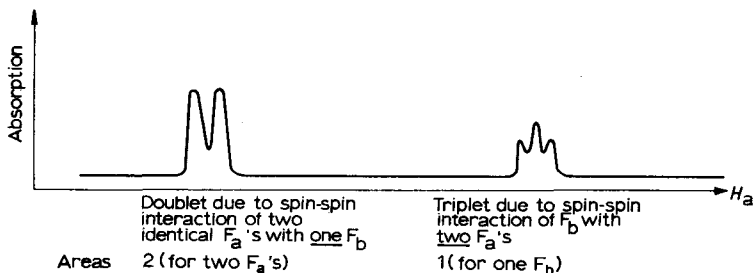


Fig. 7. High-resolution  $^{19}\text{F}$  resonance spectrum of  $\text{ClF}_3$  at  $-50^\circ$ .

The area under an absorption band indicates the number of paramagnetic nuclei in a particular environment; the number of peaks (for the  $I = \frac{1}{2}$  case) in a multiplet band is *one* greater than the number of nuclei with which spin-spin interaction occurs. The method is of obvious value in determining structure. (See pp. 449, 481 for other examples.)

#### *Applications to study of fast exchange reactions*

At about  $60^\circ\text{C}$ , the n.m.r. spectrum of  $\text{ClF}_3$  has a single  $^{19}\text{F}$  band because of rapid exchange of fluorine atoms between the two environments. As the temperature is decreased the band broadens and eventually splits into the doublet and triplet shown above. From this behaviour information on the kinetics of the fluorine exchange may be deduced. The techniques can often be applied to other processes such as this which involve no net chemical change (p. 592).

### Nuclear quadrupole coupling

#### *Principles*

Where the spin quantum number  $I$  of a nucleus exceeds  $\frac{1}{2}$ , the distribution of its positive charge is non-spherical. The electric quadrupole moment,  $Q$ , measures the extent to which the distribution of positive charge deviates from spherical symmetry (Fig. 8).

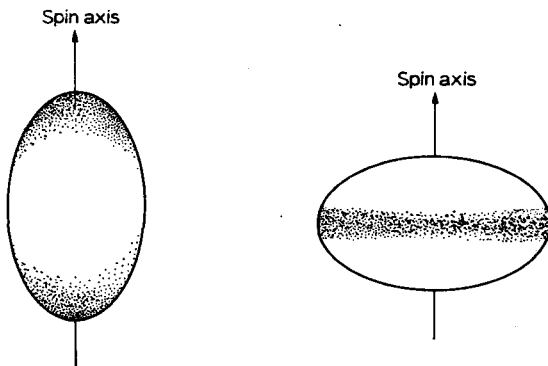


Fig. 8. Left: Prolate spheroid of +ve charge. Greatest charge density at poles. Right: Oblate spheroid of +ve charge. Greatest charge density at equator.

In atoms and molecules the nuclei are enveloped in an electronic cloud. When the electrons round a quadrupolar nucleus produce a non-spherical charge distribution, there is interaction between the nuclear field and the field due to the electrons; as a result the nucleus has a potential energy

which depends on the orientation of its quadrupole moment to the electronic field (quadrupole coupling energy). The possible orientations of the spin axis of a nucleus relative to the rotation axis of the molecule as a whole represent quantised energy levels and produce rotational lines with nuclear quadrupole fine structure. The quadrupole coupling-energy of a single nucleus is proportional to  $eQq$ ; where  $e$  is the charge on the proton;  $Q$  is the nuclear quadrupole moment;  $q$  is the field gradient, being equal to  $\frac{\partial^2 V}{\partial z^2}$  where  $V$  is the potential at the nucleus arising from all the charges outside it and  $z$  is a co-ordinate referred to a fixed axis. The nuclear quadrupole coupling constant,  $eQq$ , can be calculated from the hyperfine structure of rotational lines in the microwave range—for gases—or from the nuclear quadrupole resonance spectrum of solids in the radiofrequency range. In the latter case only the modulus of  $eQq$  is obtained.

#### *Application in chemistry*

Since  $s$  electrons and filled inner shells have spherical symmetry, and since  $d$  and  $f$  electrons do not penetrate close to the nucleus, the field gradient depends largely on the  $p$  electrons in the valence shell. Quadrupole coupling constants therefore provide information about the character of chemical bonds; a quadrupolar nucleus can be imagined as a kind of built-in probe giving information about the electronic field around it.

#### *Nuclear quadrupole coupling constants and the ionicity of bonds*

Some values for  $eQq$  of  $^{35}\text{Cl}$  in chlorine compounds are:

	$eQq$ (Mc. sec <sup>-1</sup> )
BrCl	-103.6
ICl	- 82.5
SiF <sub>3</sub> Cl	- 43.0
TiCl	- 15.8
KCl	+ 0.04

(In the case of solids, the sign is arrived at by analogy).

The numerical value of  $eQq$  for KCl is small because the  $\text{Cl}^-$  ion, with an  $s^2p^6$  structure, has a symmetrical arrangement of  $p$  electrons. The large value for BrCl indicates that the field due to the  $p$  electrons is asymmetric; some of the  $p$  electrons take part in covalent bonding. For TiCl the field due to the  $p$  electrons of the Cl is evidently only slightly asymmetric; the compound is essentially ionic in character.

*Coupling constants in relation to the distribution of covalent bonds*

The quadrupole coupling constants of  $^{14}\text{N}$  in some of its compounds are:

	$eQq$ Mc. sec $^{-1}$
HCN	-4.58
$\text{CH}_3\text{CN}$	-4.40
$\text{NH}_3$	-4.08
$\text{CH}_3\text{NC}$	+0.5

The low numerical value for the  $^{14}\text{N}$  coupling constant in  $\text{CH}_3\text{NC}$  indicates a fairly uniform p-electron distribution around the N atom—it is therefore essentially quadrivalent—compared with the asymmetric arrangement around the trivalent nitrogens in the other compounds.

Clearly the measurement of nuclear quadrupole coupling constants is valuable in elucidating the nature of valency bonds. Furthermore, being particularly sensitive to the electronic distribution near the nucleus the coupling constants provide information about the adequacy of wave functions in that region. By contrast, bond energies and dipole moments give information mainly about the overlap region of the valence bond.

### Radioactivity

The manifestations of radioactivity are the emission from the nucleus of  $\alpha$ -particles ( $\frac{4}{2}\text{He}$  nuclei moving with high kinetic energies),  $\beta^-$ -particles (electrons of nuclear origin) and  $\beta^+$ -particles (positrons, p. 24). Particle emission is often accompanied by  $\gamma$ -radiation, energy in the form of electromagnetic waves of very high frequency. The energies involved in a radioactive change are so great that the change is unaffected in rate by alterations of temperature of several thousand degrees. Individual emissions are governed by statistical laws, and are generally accompanied by a characteristic radiation.

The probability of a nucleus disintegrating in unit time is the *decay constant*,  $\lambda$ . For  $N$  nuclei

$$\frac{dN}{dt} = -\lambda N, \quad \text{and} \quad N = N_0 e^{-\lambda t},$$

where  $N_0$  is the original number of nuclei and  $N$  the number left after time  $t$  (in convenient units).

A useful constant is the half-life,  $t_{1/2}$ , the time taken to halve the number of atoms of the nuclide.



$$\text{Substituting } \frac{N}{N_0} = \frac{1}{2} \text{ above: } \lambda = \frac{\ln 2}{t_{\frac{1}{2}}} = \frac{0.693}{t_{\frac{1}{2}}}$$

The specific activity,  $S$ , of a nuclide is the number of disintegrations per unit of mass in unit time, usually expressed in curies per g (1 curie =  $= 3.7 \times 10^{10}$  disintegrations per second).

Generally for any nuclide

$$S = \frac{1.34 \times 10^8}{At_{\frac{1}{2}}} \text{ curies per g}$$

where  $A$  is the mass number,  $t_{\frac{1}{2}}$  being expressed in days.

The activity of a specimen is measured by comparing the number of impulses which it produces per minute in a Geiger counter with that produced by a substance of known specific activity, say uranium oxide, in the same position in the same counting equipment.

### Natural radioactivity

There is no difference in principle between natural and artificial radioactivity. The classical disintegration series (Table 4) stem from radionuclides with long half-lives, exceeding  $10^8$  years. Their decay is almost entirely by  $\alpha$ - and  $\beta$ -emissions.

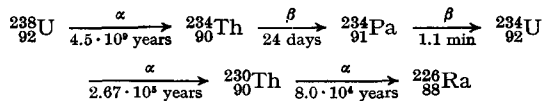


Fig. 9.

Figure 9 represents changes at the beginning of the Uranium series, designated the  $4n + 2$  series because the expression, with  $n$  integral, gives the mass number. Loss of an  $\alpha$ -particle reduces the atomic number by 2 and the mass number by 4. Loss of a  $\beta$ -particle increases the atomic number by one but leaves the mass number unchanged.

TABLE 4

THE DISINTEGRATION SERIES

<i>Series</i>	<i>Parent nuclide</i>	<i>Half-life of parent</i>	<i>Type</i>
Thorium	${}^{232}\text{Th}$	$1.4 \times 10^{10}$ years	$4n$ (natural)
Neptunium	${}^{237}\text{Np}$	$2.25 \times 10^6$ years	$4n + 1$ (not natural)
Uranium	${}^{238}\text{U}$	$4.5 \times 10^9$ years	$4n + 2$ (natural)
Actinium	${}^{235}\text{U}$	$7.0 \times 10^8$ years	$4n + 3$ (natural)

### $\alpha$ -Emission

The  $\alpha$ -particle is a helium atom which has lost two electrons and become  $\text{He}^{2+}$ . Its emission depends on the probability of the  $\alpha$ -particle penetrating the potential energy barrier arising from the nuclear interactions. Thus the greater the energy of the particle in relation to the energy barrier the higher the decay constant. The energies of  $\alpha$ -particles, though not identical for a particular species, usually lie within a narrow range and are high, generally greater than 4.5 MeV. Because of their size and charge,  $\alpha$ -particles do not penetrate far into matter. Their energies can be roughly assessed by observing their penetration, or can be measured from their response to magnetic and electric fields.

Certain nuclides give  $\alpha$ -particles which have different energies. For instance,  $^{212}_{83}\text{Bi}$  emits five groups with energies 6.084, 6.044, 5.762, 5.620 and 5.601 MeV, the first group comprising 27% and the second 70% of the total. Such *spectra* are accounted for by the existence of definite energy levels in the atomic nucleus. The nuclide  $^{212}_{83}\text{Bi}$  is ordinarily in its ground state, but the emission of an  $\alpha$ -particle, according to its energy, gives  $^{208}_{81}\text{Tl}$  in the ground state or in one of its four excited states.

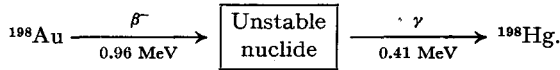
### $\beta$ -Emission

The energy of a  $\beta$ -particle, or electron of nuclear origin, on emission can be calculated approximately from the mass lost in the disintegration producing it.

In the nuclear change  $^{12}_6\text{C} \rightarrow ^{12}_7\text{N} + \beta + \text{neutrino}$ :

$$\begin{aligned} M \text{ for } ^{12}_6\text{C} &= 14.003242 \text{ amu} \\ M \text{ for } ^{12}_7\text{N} &= 14.003074 \text{ amu} \\ \text{Difference} &= 0.000168 \text{ amu} \\ &= 0.000168 \times 931 \text{ MeV} \\ &= 0.155 \text{ MeV} \end{aligned}$$

Thus the change is accompanied by the release of 0.155 MeV, as kinetic energy of  $\beta$ -particle and neutrino. The neutrino, which has no charge and a very small mass, shares the available energy with the  $\beta$ -particle; hence the energy of  $\beta$ -particles from a particular type of nuclide can vary. A neutrino has spin which enables the angular momentum to be conserved in the disintegrating process. The energy is approximately assessed by the depth the particle penetrates into aluminium. Sometimes the  $\beta$ -emission is accompanied by  $\gamma$ -emission.



In these circumstances an unstable nucleus is generally produced by the first change and stabilised by the second. The energy of the  $\gamma$ -radiation can be measured, after filtering out the  $\beta$ -particles with aluminium foil, by either its ionising or penetrating effects.

Alternative processes often occur. Such a one is illustrated in Fig. 10 in which chlorine-38 produces three  $\beta$ -particles, in the proportions and of the energies shown. Conversion to a stable argon atom is completed by low energy  $\beta$ -emission being followed by  $\gamma$ -radiation; but this is not necessary after high energy  $\beta$ -emission.

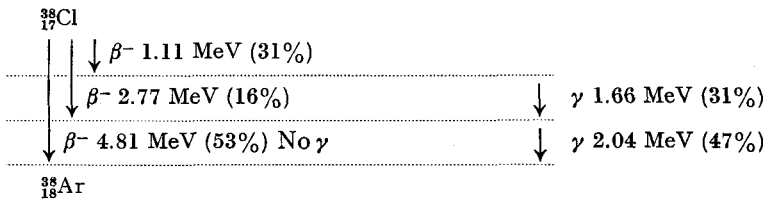


Fig. 10.

Frequently disintegration processes are far more complicated.

### Positrons: $\beta^+$ -emission

Dirac (1928) showed theoretically that a particle of the mass of an electron may have an energy less than  $-mc^2$  or greater than  $+mc^2$  but not of an intermediate value, and proposed the following hypothesis. The negative states are normally all filled and give an all-pervading, uniform density of negative charge whose presence cannot be detected experimentally: for otherwise ordinary electrons would spontaneously disappear by falling into the lower energy states and taking on the properties of particles of negative mass (negative kinetic energy). Such particles would, for instance, move *against* an applied force instead of with it. A perfect vacuum is thus a *sea* of electrons in a negative energy state (not to be confused with a negative charge), and only *changes* in this background are observable. If, however, a particle in the sea is given enough energy ( $> 2mc^2$ ) it can go into a positive energy state and is observed as an ordinary electron. When an electron goes into this state it leaves a 'hole' and this is also observed, but as something with positive energy (for to fill the 'hole', and make it disappear, negative energy must be added) and with positive

charge (being a missing negative charge in the uniform sea). Excitations of this kind are actually observed, with energy absorption of at least  $2mc^2$  or 1.02 MeV, and the process is described as *pair production*. The 'hole' behaves like a positive 'electron' and is called a *positron*. The reverse process also occurs, an electron and a positron annihilating each other with the liberation of the same amount of energy as that required in pair production. Both processes require the presence of a nucleus—as 'catalyst'—in order that momentum conservation conditions are satisfied.

Anderson (1932) discovered the positron in a study of cosmic rays, using the Wilson cloud chamber. Blackett (1933) confirmed his findings.

Curie and Joliot obtained positron-electron pairs from heavy metals bombarded with high energy (5 MeV)  $\gamma$ -rays derived from beryllium mixed with polonium. The average life of the positron is about  $10^{-9}$  sec. On colliding with an electron both are annihilated and  $\gamma$ -radiation—the annihilation radiation—is emitted. The formation and annihilation of a positron-electron pair may be represented thus:

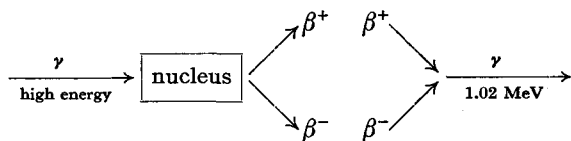


Fig. 11.

The energy of a  $\beta^+$ -particle at the instant of emission can be found by considering copper-64. This nuclide, in one of its transitions, emits a positron with a maximum energy of 0.66 MeV, giving nickel-64.

For $^{64}\text{Cu}$	$M = 63.92976$ amu
$^{64}\text{Ni}$	$M = 63.92796$ amu
Difference	$\Delta M = 0.00180$ amu
	$= 1.68$ MeV
Energy required to create a $\beta^+$	$= 1.02$ MeV
Maximum kinetic energy available to the positron	$= 0.66$ MeV.

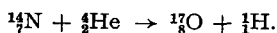
### Electron capture

Besides  $\beta^-$  and  $\beta^+$ -emission, a third form of nuclear change is possible; in it the nucleus captures an extra-nuclear, usually a K electron, and  $A$  remains unaltered. This change is not accompanied by radiation unless the daughter nucleus emits a  $\gamma$ -ray, all the energy of transition being retained.

### Nuclear reactions

#### (i) $\alpha$ -Induced reactions

Rutherford (1919) noticed that high energy  $\alpha$ -particles from bismuth-214, on passing through nitrogen gas, produced protons of long range:

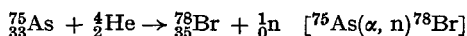


This nuclear reaction, in which an  $\alpha$ -particle induces the loss of a proton, is known as an  $(\alpha, p)$  reaction and represented by  ${}^{14}_7\text{N}(\alpha, p){}^{17}_8\text{O}$ .

For ${}^{14}_7\text{N}$	$M = 14.003074$ amu
${}^4_2\text{He}$	$M = 4.002603$ amu
Total mass	18.005677 amu
For ${}^{17}_8\text{O}$	$M = 16.999133$ amu
${}^1_1\text{H}$	$M = 1.007825$ amu
Mass after reaction	18.006958 amu

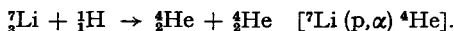
Since the mass is increased by 0.001281 amu (1.19 MeV), only high energy  $\alpha$ -particles are capable of bringing about the change. All elements from boron to potassium, except carbon and oxygen, undergo  $\alpha$ -induced reactions.

Although heavy nuclei repel the  $\alpha$ -particles more strongly, some of these have been broached by  $\alpha$ -particles highly energised (up to 300 MeV) in the cyclotron. An example is

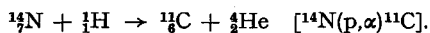


#### (ii) Proton-induced reactions

Cockcroft and Walton (1932) disrupted lithium with low energy protons ( $\sim 10^5$  eV, cf. natural  $\alpha$ -particles  $\sim 10^7$  eV) produced in a linear accelerator:

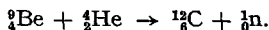


This reaction liberated 17.3 MeV, the mass afterwards being 0.0186 amu less than before. Beryllium, fluorine, sodium and magnesium provide nuclides which undergo proton-induced reactions. Nitrogen-14 yields carbon-11, a positron-emitter with a half-life of twenty minutes.

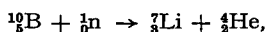


#### (iii) Neutron-induced reactions

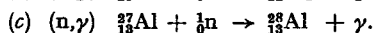
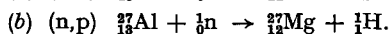
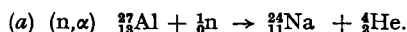
Chadwick (1932) produced neutrons by bombarding beryllium with natural  $\alpha$ -particles:



The yield is very small, thirty neutrons per million  $\alpha$ -particles. As the neutron is non-ionising it is detected by its action on a nuclide such as boron-10,



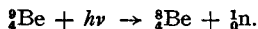
the  $\alpha$ -particle produced being readily observable. This is an  $(n, \alpha)$  reaction. The neutron is a versatile participator in nuclear reactions; its freedom from charge enables it to penetrate into nuclei resistant to high-energy  $\alpha$ -particles and protons. Fermi discovered the three main types of neutron-induced reactions illustrated.



Fast neutrons favour the first (a), medium speed, the second (b), and slow, the third (c). The capture reaction (c) is important in the heavy elements (p. 621).

(iv) *Reactions induced by high energy  $\gamma$ -rays*

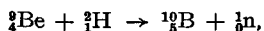
One of the best-known of these is



It takes place when antimony-124, which emits  $\gamma$ -rays of 2.04 MeV, is intimately mixed with powdered beryllium, and furnishes an easily accessible source of neutrons.

(v) *Deuteron-induced reactions*

Deuterons may be sufficiently accelerated in the cyclotron to cause nuclear reaction; examples of this are:



### Stellar energy

The recognition of the enormous energy set free in nuclear reaction has suggested the source from which the stars draw their energy. At the exceedingly high temperatures prevailing ( $\sim 10^8$  °C) the nuclei are stripped of electrons and attain velocities comparable with those of particles from the cyclotron, thus making possible thermonuclear reactions. Weizsäcker and Bethe independently (1938) proposed the *carbon cycle* of six reactions in

the sequence shown (Fig. 12), in which four protons are converted into one alpha particle, a process accompanied by the release of 30 MeV.

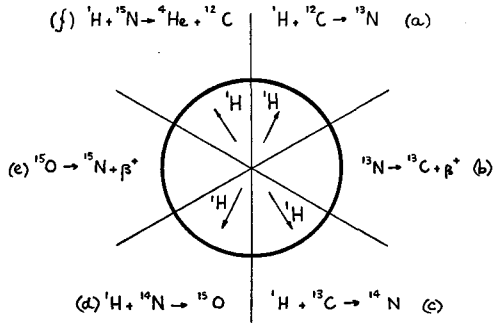
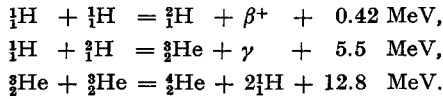


Fig. 12. The stellar carbon cycle.

On the other hand the energy of cooler stars like the sun ( $\sim 10^7$  °C) appears to emerge from a proton-proton cycle:

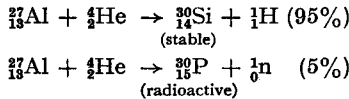


Four protons are converted into an  $\alpha$ -particle with the release of 26.6 MeV, including the annihilation energy of an electron-positron pair.

### Artificial radioactivity

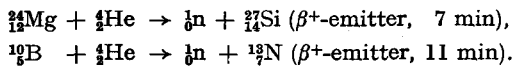
#### (i) $\alpha$ -Bombardment

Curie and Joliot (1934) produced a radioactive light element by bombarding aluminium with  $\alpha$ -particles.

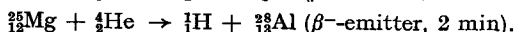
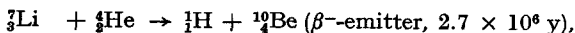


The silicon is inactive but phosphorus-30 is a  $\beta^+$ -emitter. When the irradiated aluminium is dissolved in hydrochloric acid, all the radioactivity goes with the hydrogen, presumably as phosphine. Aqua regia oxidises it to phosphoric acid which can be precipitated as radioactive zirconium phosphate.

Many of the lighter nuclides including potassium-39 undergo this ( $\alpha, n$ ) transformation to give radionuclides.



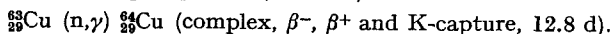
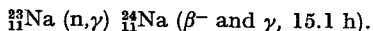
It is also possible for  $\alpha$ -bombardment of these light elements to cause ( $\alpha, p$ ) changes.



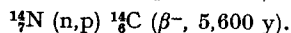
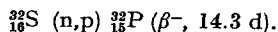
(ii) *Neutron bombardment*

Most of the light radioactive nuclides which are being produced for radiochemical work are made by the action of neutrons on suitable materials in an atomic pile (p. 620). In such a reactor there is a high flux of slow and fast neutrons and also abundant  $\gamma$ -rays. Fast neutrons cause ( $n, \alpha$ ) and ( $n, p$ ), and the slow ones ( $n, \gamma$ ) reactions. As a rule the products are  $\beta^-$ -emitters.

( $n, \gamma$ ) Reactions produce a nuclide isotopic with the parent, which cannot be separated therefrom, so the latter acts as a diluent or isotopic *carrier*,



( $n, p$ ) Reactions brought about by fast neutrons, however, give non-isotopic products which may be separated chemically and produced almost carrier-free.

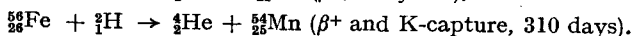
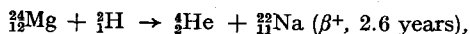


Aluminium nitride, for example, is converted into  $\text{Al}_4^{14}\text{C}_3$  carbide from which  ${}^{14}\text{CH}_4$  may be liberated by acid.

( $n, \alpha$ ) Reactions occur only to a limited extent even with fast neutrons. Chemical separation again produces a carrier-free product of high specific activity.

(iii) *Bombardment with deuterons or protons (from cyclotron)*

Some radioactive nuclides which do not result from neutron attack can be made in the cyclotron by bombarding suitable targets with deuterons or protons.



(iv) *Fission products*

When a uranium-235 atom undergoes neutron-induced fission two atoms are produced, one of mass about 95, the other about 140, together with neutrons.

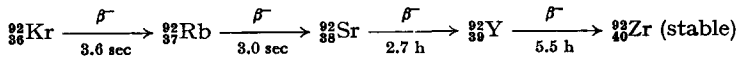
The actual nuclides formed may be  ${}^{92}_{36}\text{Kr}$  and  ${}^{142}_{56}\text{Ba}$ ,





but these reactions usually release two or three neutrons. The nuclides have high  $A/Z$  ratios and undergo  $\beta^-$  changes which increase their stability.

This applies to all the fission products:



While a reactor is working the uranium-235 or plutonium-239 is slowly converted into fission products. The materials are intensely radioactive. Their separation is described later (p. 621).

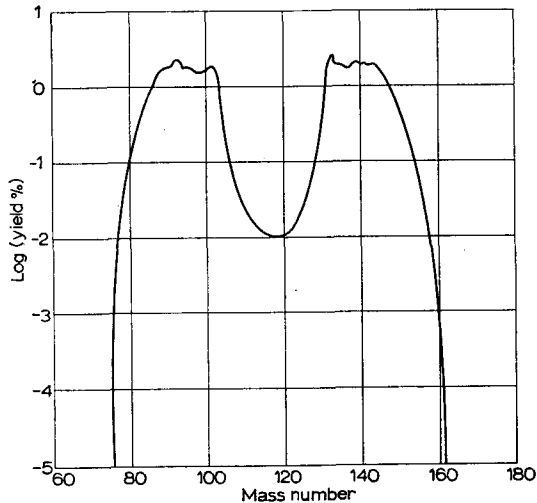


Fig. 13. Spread of primary products from the thermal neutron fission of  ${}^{235}\text{U}$ .

The yield of primary fission products from the fission of uranium-235 by thermal neutrons in relation to their mass number is shown in Fig. 13. Most of the radioactive fission products have short half-lives, but some decay slowly; technetium-99 has  $t_{\frac{1}{2}}$   $2.2 \times 10^5$  yr and promethium-147, 2.6 yr. Two of the most useful fission products obtained in the operation of a pile are caesium-137 ( $\beta^-$ , 33 yr) and strontium-90 ( $\beta^-$ , 22 yr). The former is used in medicine and the latter in medicine and industry; both are separated from shorter-lived material.

### Some commonly accepted elementary particles

It is generally believed that all matter and energy (except gravitation) consist of fundamental entities. The more important of these are the photon,

the electron, the proton, the neutron, six species of hyperon (charged particles with masses greater than the proton), four species of meson (charged particles with masses between the mass of the proton and electron), the muon and the neutrino. With the exception of the mesons all the particles have spin. Only four, however, are stable, namely, the photon, electron, proton and neutrino. The free neutron (half-life  $\sim 20$  min) decays to a proton, an electron and a neutrino.

A number of particles with properties opposite in some respect to those mentioned are known, for instance the positron (electron) and the anti-proton. More of these anti-particles are likely to be observed in work with high power ( $\sim 10^{10}$  eV) accelerators.

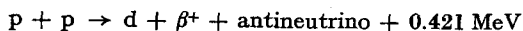
### Genesis and abundance of the elements

Many estimates have been made of the relative abundance of the elements in the Universe, notably by Goldschmidt (1931), Brown (1949) and Urey (1952). The logarithm of the estimated abundance, taking  $\log A_{\text{SI}} = 6$  as standard, is plotted against atomic number in the diagram (Fig. 14). The points of interest are:

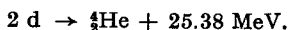
- (i) the higher abundance values for the even elements,
- (ii) the rapid fall in abundance with atomic number up to element 45 after which the variations are smaller,
- (iii) the surprisingly low abundance of Li, Be and B,
- (iv) the high values for elements with  $Z$  around 26, 54 and 78,
- (v) the abnormal abundance of iron.

Various theories have been advanced to explain the relative abundance of the elements. In recent years knowledge has accumulated of the types of nuclear transformations occurring in stars. A continuous process of synthesis and consumption of elements (Burbidge, Burbidge, Fowler and Hoyle, 1957) accounts for the observed differences in composition of stars of different ages and also such abnormalities as the presence of technetium in S-type stars.

Except in catastrophic phases a star has a self-governing energy balance, the temperature attained depending on the nuclear fuel available. The consumption of hydrogen is responsible for the production of energy on a large scale, and the nuclear reactions employed in the changes do not require such a high temperature as other stellar processes. Cyclic processes synthesise He and those isotopes of C, N, O, F, Ne and Na not produced by He consumption or  $\alpha$ -processes:



and, probably,



The conversion of helium to  $^{12}\text{C}$ ,  $^{16}\text{O}$  and  $^{20}\text{Ne}$  occurs in stars whose temperatures are about  $10^8$  °C.

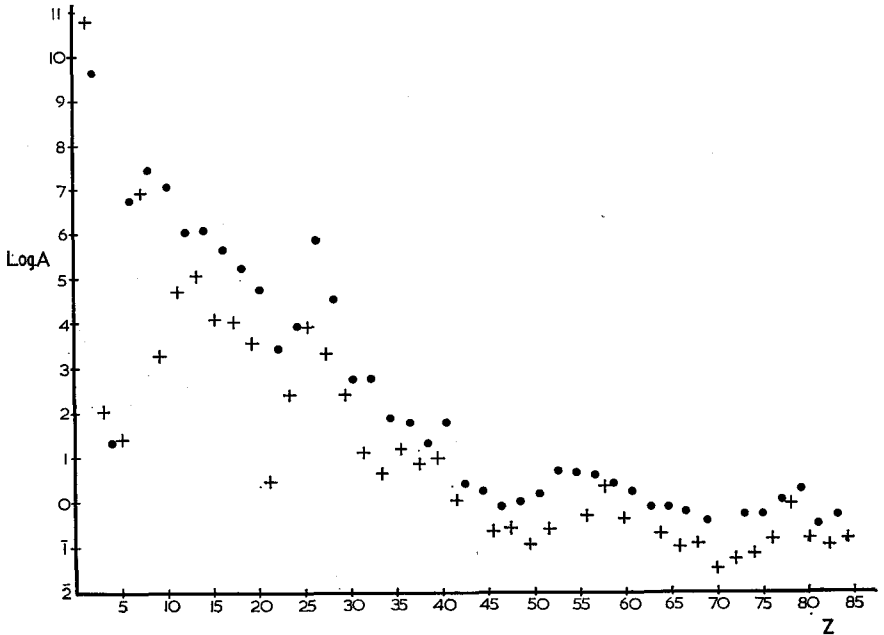
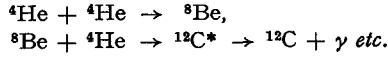
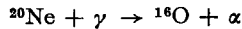


Fig. 14. Cosmic abundance of elements compared with silicon ( $10^8$ ) (Suess and Urey).  
 • Even atomic numbers.  
 + Odd atomic numbers.

At temperatures of about  $2 \times 10^8$  °C the so-called  $\alpha$ -process also becomes possible. Under these conditions the  $\gamma$ -rays produced in the helium consumption are sufficiently energetic to bring about the change



and for the  $\alpha$ -particle released to have the energy necessary for such reactions as  $^{20}\text{Ne}(\alpha, \gamma)^{24}\text{Mg}$  and  $^{24}\text{Mg}(\alpha, \gamma)^{28}\text{Si}$ , in which the  $\alpha$ -addition goes on certainly as far as  $^{40}\text{Ca}$ , and possibly to  $^{48}\text{Ti}$ . The high abundance of nuclei with mass numbers divisible by four compared with that of their neighbours is due to the remarkable efficiency of the He consumption and  $\alpha$ -processes. The C,N cycle (p. 28) belongs to this stage; it results in the catalytic conversion of hydrogen into helium until the hydrogen is exhausted.

Elements of the first transitional period are synthesised at about  $3 \times 10^9$ °C in the so-called e-process. The nuclear reactions operating are of many types ( $\gamma, \alpha$ ) ( $\gamma, p$ ) ( $\gamma, n$ ) ( $\alpha, \gamma$ ) ( $p, \gamma$ ) ( $n, \gamma$ ) ( $p, n$ ) but they always lead to a preponderance of elements belonging to the iron group. The strongly-marked peak in the abundance curve at  $^{56}\text{Fe}$  is due to the e-process, which occurs when stellar evolution is at an advanced stage.

Two nuclear reactions involving neutron capture are responsible for the production of the majority of nuclides. The s-process, in which ( $n, \gamma$ ) reactions occur on a time-scale of  $10^3$  to  $10^5$  years per neutron capture, gives rise to most of the nuclides in the mass-range 23–46 which are not formed in the  $\alpha$ -process, together with a large proportion of those in the range 63 to 209. The s-process is responsible for peaks in the abundance curve at mass numbers 90, 138 and 208. The r-process also involves ( $n, \gamma$ ) reactions but with a time-scale of 0.01 to 10 sec per neutron capture. It is responsible for very many nuclides in the mass range 70 to 209, and for Th and U. Peaks in the abundance curve are produced at mass numbers 80, 138 and 194. The advanced stage of stellar evolution necessary to build up elements of such high mass numbers is uncommon in the Universe and accordingly the heavier elements are relatively rare.

The p-process is one of proton capture ( $p, \gamma$ ) or of gamma-ray absorption with neutron emission ( $\gamma, n$ ), and is responsible for many proton-rich nuclides of low abundance, generally derived from iron-group elements. Finally, an x-process is responsible for the synthesis of D, Li, Be and B which are unstable at the temperatures reached inside stars, where they are converted to helium by a large number of processes including  $^2\text{D}(p, \gamma)^3\text{He}$ ,  $^6\text{Li}(p, \alpha)^3\text{He}$  and  $^{11}\text{B}(p, \alpha)^8\text{Be} \rightarrow 2\ ^4\text{He}$ .

The rarity of D, Li, Be and B compared with H, He, C, N, and O is due partly to the inefficiency of their production and partly to their consumption in processes such as those just set out.

The composition of the Earth differs from that of the Universe by having a much lower proportion of hydrogen and helium; these elements comprise about 90% and 9% respectively of the currently accepted grand total of matter. The small planets, Venus, Mercury and Mars, appear to have compositions similar to that of the Earth. Presumably their masses are too small for them to attract and retain the lighter particles in the form of an atmosphere as they move through space. Jupiter, however, has a core of iron and siliceous material surrounded by ice, solid methane and ammonia and finally by hydrogen and helium.

Apart from the small values for hydrogen and helium, the Earth's composition is not remarkable, the percentages by weight of the commonest elements, taking hydrosphere and lithosphere together, are:

O	49.20	Mg	1.93	C	0.08
Si	25.67	H	0.87	S	0.06
Al	7.50	Ti	0.58	Ba	0.04
Fe	4.71	Cl	0.19	N	0.03
Ca	3.39	P	0.11	F	0.03
Na	2.63	Mn	0.08	Sr	0.02
K	2.40			All others	0.47

The composition of the atmosphere at sea level in moles per million moles is:

N <sub>2</sub>	7.8 × 10 <sup>5</sup>	Ne	1.8 × 10 <sup>1</sup>	N <sub>2</sub> O	0.5
O <sub>2</sub>	2.1 × 10 <sup>5</sup>	He	5.2	H <sub>2</sub>	0.5
Ar	9.3 × 10 <sup>3</sup>	CH <sub>4</sub>	1.5	O <sub>3</sub>	0.4
CO <sub>2</sub>	3 × 10 <sup>2</sup>	Kr	1	Xe	0.08

#### FURTHER READING

- J. G. CUNINGHAME, *Introduction to the Atomic Nucleus*, Amsterdam, Elsevier, 1964.
- S. GLASSTONE, *Sourcebook on Atomic Energy*, 2nd ed., Princeton, Van Nostrand, 1958.
- J. D. ROBERTS, *Nuclear Magnetic Resonance*, New York, McGraw-Hill, 1959.
- W. J. ORVILLE-THOMAS, *Nuclear Quadrupole Coupling and Chemical Bonding*, Quart. Rev. (London), 11 (1957) 162.
- G. R. BURBIDGE, E. M. BURBIDGE, W. A. FOWLER AND F. HOYLE, *Synthesis of the Elements in Stars*, Revs. Mod. Phys., 29 (1957) 547.

## Relative abundance of naturally-occurring isotopes

(Hydrogen to Nickel)

Z	Element	Nuclide	Percentage	Z	Element	Nuclide	Percentage
1.	Hydrogen	<sup>1</sup> H	99.985	17.	Chlorine	<sup>35</sup> Cl	75.4
		<sup>2</sup> H	0.015			<sup>37</sup> Cl	24.6
		* <sup>3</sup> H	~ 0	18.	Argon	<sup>36</sup> Ar	0.34
2.	Helium	<sup>3</sup> He	0.00013			<sup>38</sup> Ar	0.06
		<sup>4</sup> He	~ 100			<sup>40</sup> Ar	99.60
3.	Lithium	<sup>6</sup> Li	7.4	19.	Potassium	<sup>39</sup> K	93.08
		<sup>7</sup> Li	92.6			* <sup>40</sup> K	0.012
4.	Beryllium	<sup>9</sup> Be	100			<sup>41</sup> K	6.91
		5.	Boron	<sup>10</sup> B	18.7	20.	Calcium
<sup>11</sup> B	81.3			<sup>42</sup> Ca	0.64		
6.	Carbon	<sup>12</sup> C	98.9	<sup>43</sup> Ca	0.13		
		<sup>13</sup> C	1.1	<sup>44</sup> Ca	2.13		
		* <sup>14</sup> C	~ 10 <sup>-10</sup>	<sup>46</sup> Ca	0.0032		
7.	Nitrogen	<sup>14</sup> N	99.63	<sup>48</sup> Ca	0.18		
		<sup>15</sup> N	0.37	21.	Scandium	<sup>45</sup> Sc	100
8.	Oxygen	<sup>16</sup> O	99.76			22.	Titanium
		<sup>17</sup> O	0.037	<sup>47</sup> Ti	7.4		
		<sup>18</sup> O	0.20	<sup>48</sup> Ti	73.4		
9.	Fluorine	<sup>19</sup> F	100	<sup>49</sup> Ti	5.6		
		<sup>20</sup> F	~ 10 <sup>-10</sup>	<sup>50</sup> Ti	5.4		
10.	Neon	<sup>20</sup> Ne	90	23.	Vanadium	<sup>50</sup> V	0.25
		<sup>21</sup> Ne	0.3			<sup>51</sup> V	99.75
		<sup>22</sup> Ne	9.7	24.	Chromium	<sup>50</sup> Cr	4.4
11.	Sodium	<sup>23</sup> Na	100			<sup>52</sup> Cr	83.7
		<sup>24</sup> Na	~ 10 <sup>-10</sup>			<sup>53</sup> Cr	9.5
12.	Magnesium	<sup>24</sup> Mg	79.0			<sup>54</sup> Cr	2.4
		<sup>25</sup> Mg	10.0	25.	Manganese	<sup>55</sup> Mn	100
		<sup>26</sup> Mg	11.0				
13.	Aluminium	<sup>27</sup> Al	100	26.	Iron	<sup>54</sup> Fe	5.9
14.	Silicon	<sup>28</sup> Si	92.18			<sup>56</sup> Fe	91.6
		<sup>29</sup> Si	4.70			<sup>57</sup> Fe	2.2
		<sup>30</sup> Si	3.12			<sup>58</sup> Fe	0.33
15.	Phosphorus	<sup>31</sup> P	100			27.	Cobalt
16.	Sulphur	<sup>32</sup> S	95.04	28.	Nickel		
		<sup>33</sup> S	0.74			<sup>60</sup> Ni	26.2
		<sup>34</sup> S	4.24			<sup>61</sup> Ni	1.2
		<sup>36</sup> S	0.017			<sup>62</sup> Ni	3.7
						<sup>64</sup> Ni	1.0

\* Radioactive isotopes.

### Chapter 3

## Radiochemistry

The operation, since 1945, of nuclear reactors has made available radioisotopes of most elements. The isotopes are useful in a variety of chemical investigations, including those concerned with solubility, diffusion, reaction mechanism and structure. They have given rise to new analytical techniques, such as isotopic dilution and radioactivation analysis. In industry also, they have a wide and rapidly expanding application. All this is made possible by the ease with which small quantities of the nuclides can be detected, often remotely, and quantitatively determined by commercially available and easily operated equipment.

### Detection

The most common measurement is  $\beta$ -counting with a Geiger-Muller tube. A potential difference of some hundreds of volts is applied between an axial wire and the cylindrical wall. When an ionising particle enters through the mica end-window the gas inside, usually neon, is ionised; acceleration of the ions towards the electrodes, causing further ionisation, gives rise to a pulse which is amplified and finally counted by a suitable electronic device. The thickness of the window prevents penetration by  $\beta$ -particles of low energy.

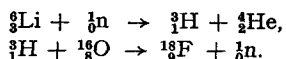
Scintillation methods are increasing in importance. A  $\gamma$ -photon falling on a single sodium iodide crystal produces a flash of light which causes emission of photo-electrons from the light-sensitive surface, or photocathode, of a photomultiplier tube. Suitable voltages applied to the intermediate electrodes, or dynodes, of the tube cause electron multiplication and the current pulses so produced are counted by a scalar circuit. The energy as well as the intensity of radiation can be recorded, and a mixture of several  $\gamma$ -emitters can be resolved into its components, without chemical separation, by means of a  $\gamma$ -scintillation spectrometer. The sodium iodide phosphor can be replaced by ZnS for  $\alpha$ -counting or an anthracene crystal for  $\beta$ -counting. Such scintillators as *p*-terphenyl may be dissolved in toluene to provide liquid scintillating systems which are particularly useful for counting low-energy  $\beta$ -particles from carbon-14 and tritium.

An activity of about  $10^{-9}$  curie can be detected by ordinary counting equip-

ment. The quantity of radioactive material corresponding to this activity depends on the specific activity, and hence the half-life, of the nuclide involved. Phosphorus-32 ( $\beta^-$ , 14.3 days) has a specific activity of  $3.3 \times 10^7$  curies per gram;  $10^{-16}$  g of this nuclide gives about 300 counts per minute with equipment of moderate efficiency. A comparison of this limit of measurement with those of other methods shows its advantage, for instance with gravimetric ( $10^{-6}$  g), emission spectroscopy ( $10^{-8}$  g), polarography ( $10^{-10}$  g), and radiochemical ( $10^{-16}$  g).

### Production

Radioactive nuclides are produced principally in the nuclear reactor as the result of (n,  $\gamma$ ), (n, p) and (n, d) reactions (p. 26). When a high specific activity is required an (n,  $\gamma$ ) preparative reaction is unsuitable because the product is necessarily diluted by the parent isotope, from which separation is always difficult and generally impossible, as in the  $^{23}\text{Na}(n, \gamma) ^{24}\text{Na}$  conversion.  $^{18}\text{F}$  is conveniently made by irradiating LiOH in a reactor:



Another useful source of radionuclides, particularly those with mass number from 80 to 140, is the fission occurring in uranium fuel in a reactor. From the fission products  $^{90}\text{Sr}$  of high specific activity is obtainable. Certain nuclides can, however, only be made by proton or deuteron bombardment in the cyclotron. An example is  $^{24}\text{Mg}(d, \alpha) ^{22}\text{Na}$  (2.6 yr); and another route to  $^{18}\text{F}$  is provided,  $^{18}\text{O}(p, n) ^{18}\text{F}$  (112 min).

### Tracers: suitability of nuclides

For physical and chemical investigation by means of radioactive material minute quantities of the active isotopes, termed *tracers*, are used. Generally the nuclide employed is isotopic with the inactive atoms whose behaviour is to be studied.

The choice of isotopic tracer for a particular experiment depends upon two things:

1. The duration of the experiment. A nuclide with a half-life shorter than this is clearly unsuitable. This limitation is marked with nitrogen and oxygen whose longest-lived active isotopes are the cyclotron-produced  $^{13}\text{N}$  (10.1 min) and  $^{15}\text{O}$  (2.1 min). For these elements the stable  $^{15}\text{N}$  and  $^{18}\text{O}$  are used, their behaviour being followed by means of the mass-spectrograph. Helium, boron and aluminium are other elements which are without active isotopes suitable for tracer work.



2. Whether the radiation emitted by the tracer is suitable for measurement under the conditions of the experiment. For instance  $^{35}\text{S}$  cannot be used when the operation calls for a liquid counter since the  $\beta$ -energy (max. 0.17 MeV) is too low to penetrate the glass walls of the counter. Again the very low  $\beta$ -energy of  $^3\text{H}$  (0.018 MeV) demands special counting techniques for this particular nuclide.

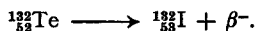
There are two assumptions implicit in the use of isotopic radioactive tracers. First, that the radioactive nuclide behaves in a manner identical with that of its non-radioactive isotopes in chemical reactions. Actually the difference in mass has some effect, the isotope effect, which, although usually negligible, must be taken into account where the ratio of the masses is large; for instance when tritium,  $^3\text{H}$ , is substituted for protium,  $^1\text{H}$ . Secondly, that the chemical and physical properties of the bulk compound are unaffected by the radiation from the nuclide. But only at very high specific activities would there be significant radiation damage of this kind, and in well-designed tracer experiments the effect is negligible.

A radionuclide used merely as a physical label, to trace the escape of gas from a pipe, for example, need not be isotopic with an element in the system. In the absence of this requirement the choice of radio-tracer is widened considerably.

### Separation of tracers from non-isotopic fission products

The non-isotopic products of  $(n, p)$  and  $(n, \alpha)$  reactions, usually from high-energy neutrons in atomic reactors, are separable from the parent. Both physical and chemical methods are available for the purpose.

(i) *Volatilisation.* Iodine-132 is produced spontaneously by tellurium-132, a fission product of uranium, and is readily volatilised from the involatile parent:



(ii) *Solvent extraction.* Cobalt-59 reacts with fast neutrons to give iron-59. The metals are converted to  $\text{FeCl}_3$  and  $\text{CoCl}_2$ , the former being quantitatively extractable with ether.

(iii) *Electrodeposition.* Copper-64 is made from zinc-64 by an  $(n, p)$  reaction. Electrolysis of a sulphate solution of the product deposits the copper preferentially.

(iv) *Ion exchange.* Carrier-free material can be obtained by this method. Praseodymium-143 has been separated from cerium by absorbing the dilute chloride solution on Dowex 50 in its ammonium form. Elution with a 5% nitrate solution buffered at pH 3 gave, in the first four litres of eluate, 94% of the praseodymium and no cerium.

(v) *Precipitation.* These methods of separation are usually carried out with the aid of carriers.

### Carriers

Most of the radionuclides produced in the pile have high specific activities. One millicurie of  $^{32}\text{P}$  represents only about  $10^{-8}$  g of phosphate. A safely-handled quantity of this nuclide would be the amount adsorbed on the surface of the containing vessel. About  $10^{-4}$  g of inert phosphate is added as an isotopic carrier for each millicurie of activity, and, in subsequent chemical operations, the  $^{32}\text{P}$  accompanies the added phosphorus.

*Hold-back carriers* are those used to prevent the adsorption of an active nuclide on precipitates. For instance in the separation of  $^{90}\text{Sr}$  and  $^{140}\text{La}$  from fission products, precipitation of the  $^{90}\text{Sr}$  as sulphate occurs only when sufficient inert strontium ion has been added to exceed the solubility product of the sulphate. But, under these conditions, nearly all the lanthanum would also be removed from solution as ions adsorbed on the precipitate; to avoid this ordinary lanthanum ions must be added to provide a non-active adsorbate and thereby 'hold back' in solution most of the active species, lanthanum-140.

Non-isotopic carriers have their uses as in the recovery of strontium-89 which is made from  $^{89}\text{Y}$  by an (n, p) reaction. The addition of a lead salt followed by fuming nitric acid precipitates lead and strontium together as nitrates and leaves the yttrium in solution. The lead, having thus acted as a non-isotopic carrier, may be precipitated as sulphide from a solution of the lead and strontium salts. Here again a hold-back carrier of inactive strontium ions is necessary to prevent adsorption of most of the  $^{89}\text{Sr}$  on the  $\text{PbS}$ .

Precipitates such as iron(III) hydroxide, with a large specific surface, adsorb certain ions preferentially. Thus phosphate ion can be separated from sulphate ion by adding a soluble iron(III) salt to the solution and then precipitating it as hydroxide. The method is used to separate  $^{32}\text{PO}_4^{2-}$  from  $^{35}\text{SO}_4^{2-}$ , the former being completely, and the latter but slightly adsorbed. Such precipitates as the iron(III) hydroxide are known as *scavenging carriers*.

### Chemical applications of tracers

(i) *Diffusion.* Radioactive tracers are particularly suitable for studying self-diffusion in both liquids and solids. Gold containing  $^{198}\text{Au}$  when pressed against inactive gold has been shown to diffuse, the extent being found by machining successive thin slices from the originally inactive metal and making counts. The diffusion coefficient of chromium-51 into a titanium

bar has been measured either by machining or by dissolving off thin layers and making counts, or by autoradiography.

(ii) *Solubility and Partition.* The measurement of solubility is facilitated by tracer techniques. The solid is labelled, usually by precipitating it from a solution containing active material (*e.g.* strontium sulphate from a solution containing some  $^{90}\text{Sr}^{2+}$ ) and the specific activity of the dry solid is determined. It is then shaken with the solvent until equilibrium is established, when the solution shows an activity proportional to the solubility.

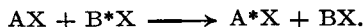
Measurement of partition coefficients of immiscible layers is particularly easy; an example is the addition of  $^{131}\text{I}$  to inactive iodine to observe the distribution between an organic solvent and water. The partition coefficient,  $K = \text{activity per ml in the aqueous layer} / \text{activity per ml in the organic layer}$ .

(iii) *Precipitation and entrainment in precipitates.* The completeness of the separation of, say, a phosphate can be found by precipitating it from a phosphate carrier solution containing some  $^{32}\text{P}$  phosphate. A count-rate is made on the original solution and on a solution made by dissolving the precipitate after it has been filtered off, appropriate volumes of each and the same liquid counter being used. The efficiency of the separation = count-rate from redissolved precipitate/count-rate from original solution. The method is especially useful for assessing the efficacy of different precipitants; in this instance magnesia mixture, molybdate, and zirconium nitrate, or the same reagent under different conditions of perhaps pH and temperature.

The entrainment of foreign ions in precipitates may also be measured. For example a precipitate of tin(II) sulphide carries down some cobalt ions when they are present, and the extent of this can be ascertained by means of a trace of  $^{60}\text{Co}$  and the comparative count-rates of the original solution and the dissolved precipitate.

### *Exchange reactions*

Isotopic exchange is possible in both homogeneous and heterogeneous conditions and the commonest form is represented by



A knowledge of the rate of exchange is necessary in tracer investigations since it should be negligible in relation to the duration of the experiments.

The free-energy change in an isotopic exchange reaction is always negative since

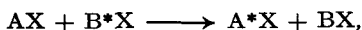
$$\Delta G = \Delta H - T\Delta S,$$

in which  $\Delta H$  is zero because there is no chemical change and  $\Delta S$  is positive because there is an increasing randomness in the distribution of the isotopic

atoms. Nevertheless, exchange reactions are often extremely slow on account of the high entropy of formation of the activated complex.

Exchange rates are found by mixing the two species AX and BX, one labelled with a suitable radioisotope of X, taking portions at suitable time intervals, separating the two species, analysing the fractions and counting the activities. The separation may be made by (i) precipitation, (ii) solvent extraction, or (iii) ion exchange, but it has to be remembered that chemical reaction may induce exchange by producing a labile species.

For the reaction



the rate can be obtained from the equation

$$\ln(1 - F) = -Rt \frac{a + b}{ab}$$

where  $a$  and  $b$  are the total concentrations of both active and inactive X in AX and BX respectively at time  $t$ , and  $R$  is the rate of exchange of X.

$$F \text{ (the fractional change at time } t) = \frac{\text{specific activity of AX at time } t}{\text{specific activity of AX at equilibrium}}$$

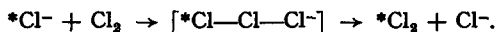
For the time of half-exchange,  $t_{\frac{1}{2}}$ ,

$$R = \frac{ab}{a + b} \times \frac{0.693}{t_{\frac{1}{2}}}$$

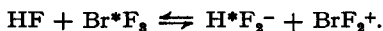
Exchange between inorganic ions of different charge is often rapid: examples are  $\text{Cu}^+$ ,  $\text{Cu}^{2+}$ ;  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ;  $\text{Co}^{2+}$ ,  $\text{Co}^{3+}$ ;  $\text{MnO}_4^-$ ,  $\text{MnO}_4^{2-}$ ;  $\text{Fe}(\text{CN})_6^{3-}$ ,  $\text{Fe}(\text{CN})_6^{4-}$ . In other instances, the time of half-reaction is measurable and sometimes long:  $\text{Mn}^{2+}$ ,  $\text{Mn}^{3+}$  ( $t_{\frac{1}{2}} = 20$  sec);  $\text{Co}(\text{en})_3^{2+}$ ,  $\text{Co}(\text{en})_3^{3+}$  ( $t_{\frac{1}{2}} = 30$  h);  $\text{Ce}^{3+}$ ,  $\text{Ce}^{4+}$  ( $t_{\frac{1}{2}} = 11$  min);  $\text{Co}(\text{NH}_3)_6^{2+}$ ,  $\text{Co}(\text{NH}_3)_6^{3+}$  ( $t_{\frac{1}{2}} = 80$  days). Other ions present in solution may affect the speed of reaction; thus at corresponding concentrations for  $\text{Tl}^+$ ,  $\text{Tl}^{3+}$  in HCl,  $t_{\frac{1}{2}} = 10$  days and in  $\text{HClO}_4$ ,  $t_{\frac{1}{2}} = 25$  min.

In trying to explain exchange between ions of the same sign it is always necessary to seek a mechanism which allows of electron-transfer without demanding contact between the ions. The possible intermediates are: (i) solvent molecules, (ii) ions of opposite sign, and (iii) neutral molecules (p. 602).

Exchange rates between ions and neutral molecules also vary widely. Chlorine exchanges with aqueous  $\text{Cl}^-$  ion too rapidly for measurement, but not at all with the anions  $\text{ClO}_3^-$  or  $\text{ClO}_4^-$  in slightly acid solution. The rapidity with  $\text{Cl}^-$  is probably due to the ready formation and decomposition of the complex ion shown in brackets:



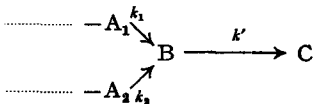
A similar mechanism is advanced for the rapid exchange between dissolved sulphur and  $S^{2-}$  ions in polysulphide solutions. The fast exchange between HF and interhalogen fluorides has been accounted for by ionisation:



Heterogeneous exchange processes are more complicated. Solid-liquid interchange depends not only on the rate of exchange between the solution and the solid surface, but also on the slower rate of diffusion into the solid, and, to a lesser extent, on any recrystallisation which is proceeding. An aged precipitate, with its small specific surface area and more perfect lattice, undergoes exchange more slowly than a fresh precipitate. Thus freshly precipitated lead sulphate exchanged lead ions completely with lead nitrate ( $^{212}\text{Pb}$  tracer) solution in about 3 minutes. But after the precipitate had stood in its mother liquor 48 hr, exchange in the same time was only 35% of the previous value, presumably because of a decrease in available surface.

#### *Finding the course of reaction by radioactive tracer*

Suppose  $A_1$  and  $A_2$  are possible precursors of B in a reaction chain:

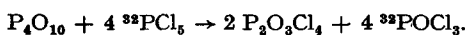


To identify the precursor, labelled  $A_1$  and unlabelled B are added to the reaction mixture. The specific activity of  $A_1$  should decrease and that of B increase if B is formed from  $A_1$ . The specific activity of B eventually reaches a maximum,  $a_1$ ; if the specific activity of  $A_1$  is  $a_1$ , then the rate constant  $k_2$  is zero showing that B is formed only from  $A_1$ , not from  $A_2$ .

When ethylene is oxidised over metallic oxides at  $220^\circ$  both ethylene oxide and carbon dioxide are produced. However, when  $^{14}\text{C}$ -labelled ethylene is used the  $\text{CO}_2$  has a higher specific activity than the ethylene oxide, showing the  $\text{CO}_2$  to be derived, not through the ethylene oxide but direct from the ethylene itself.

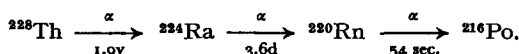
The labelling of compounds with radioactive atoms has enabled the course of reactions to be followed. The reaction between  $\text{P}_4\text{O}_{10}$  and  $\text{PCl}_5$  forms an excellent route to pyrophosphoryl chloride,  $\text{P}_2\text{O}_3\text{Cl}_4$ . The manner in which the yield depends on the  $\text{P}_4\text{O}_{10}:\text{PCl}_5$  ratio suggested that the P—O—P links were not formed during the reaction and that the phosphorus atoms of pyrophosphoryl chloride were derived entirely from the phosphorus(V) oxide.

This has been confirmed by the use of  $^{32}\text{P}\text{Cl}_5$  and inactive  $\text{P}_4\text{O}_{10}$ ; the  $\text{P}_2\text{O}_3\text{Cl}_4$  produced was inactive.



### The uses of natural radionuclides

(i) *Emanation*. The texture of solids has been investigated by incorporating a source of radon or thoron in them. The latter is introduced either by co-precipitation with  $^{228}\text{Th}$ , or by mixing the dry solids with a thorium compound so that the thoron is distributed by recoil.



The *emanating power* of a solid is defined as the fraction of radioactive-gas atoms which escapes and is measured by the ratio of rate of escape to rate of formation.

The emanating power of freshly formed, dry iron(III) hydroxide is high and falls by only about 2% a year. Digestion in water quickly reduces the emanating power, indicating a rapid ageing.

Structural changes in a solid can be detected by changes in emanating power. For instance, that of anhydrous  $\text{BaCl}_2$  increases with temperature to  $540^\circ$  and then falls a little, but again begins to rise and reaches a maximum at  $925^\circ$ . The first maximum is associated with the change from a porous form to the monoclinic  $\alpha$ -form, the second with one from the monoclinic  $\alpha$ -form to the cubic  $\beta$ -form.

(ii) *Geochronometry*. Improvement in the precision of physico-chemical measurements has increased the use of natural nuclides for the dating of natural objects and artifacts. Some of the radioactive clocks, as they may be termed, with remote ranges are based on the extent to which one or other of the following changes have been found to have occurred in the material which is being dated:  $^{87}\text{Rb} \rightarrow ^{87}\text{Sr}$ ;  $^{40}\text{K} \rightarrow ^{40}\text{Ar}$ ;  $\text{U, Th} \rightarrow \text{Pb}$ .

The first change enables the age of a mineral which contains rubidium but is unlikely to have originally contained strontium to be deduced. The mineral is analysed and from the Rb : Sr ratio and the radioactive decay constant of Rb its age is found. The last change, U, Th  $\rightarrow$  Pb comprises four clocks in one, (1)  $^{238}\text{U} \rightarrow ^{206}\text{Pb}$ , (2)  $^{235}\text{U} \rightarrow ^{207}\text{Pb}$ , (3)  $^{232}\text{Th} \rightarrow ^{208}\text{Pb}$ , (4) the ratio  $^{206}\text{Pb} : ^{207}\text{Pb} : ^{208}\text{Pb}$ . Of these, (4) enables the age of a mineral to be determined even when some of the lead has been leached out of it, because the isotopic ratio is independent of the amount so removed, depending only upon the duration of the lead-producing process.

Radiocarbon dating has been exceedingly useful. It is based on the fact that carbon-14 is produced in the upper atmosphere by cosmic-ray bombardment of nitrogen-14. It is oxidised to carbon dioxide and eventually absorbed and incorporated in the tissues of plants and animals. The time taken for a carbon atom to complete such a carbon-cycle and return to the upper atmosphere is, on average, about 500 years. As the half-life of  $^{14}\text{C}$  is 5568 years, the specific activity of carbon in the carbon cycle is roughly constant. But carbon removed from this life-embracing cycle by conversion to, and retention in, a solid such as wood, bone or shell loses activity at a rate determined by the decay constant for  $^{14}\text{C}$ . Thus the specific activity of carbon in a piece of wood, bone, shell or ancient artifact gives its age. The measurements are not easy because of the low specific activities but are of considerable and improving accuracy. They are limited to about 24,000 years.

Measurement with carbon assumes that the rate of cosmic activation has remained constant over the period involved. Though doubts have been cast on this assumption, there is no evidence that it is not a safe one to make; the datings found have agreed well with those fixed by other scales.

Tritium has been used similarly, since water, free to move to and from the upper atmosphere had also a constant specific activity. The position is however changing with the release of tritium from nuclear reactions. Because of its shorter half-life (12.5y) it is adopted for even shorter-range dating, such as finding the age of a wine.

### Radiochemical methods of analysis

(i) *Radiometric analysis.* This is used to find the amount of a nuclide of long half-life and known specific activity in a material; it is based on the premise that the mass present is proportional to the activity. Because it is impossible to observe all disintegrations the count-rate from a sample is compared with that from the same weight of a standard, the same geometry being ensured by the use of the same counting equipment.

The potassium content of a fertiliser can be determined by comparing its activity with a pure potassium salt. However, as  $^{40}\text{K}$ , about 0.01% of natural potassium, has a specific activity of only  $7 \times 10^{-6}$  curies/g, the count-rate is low (20 c.p.m. for 1 g of  $\text{K}_2\text{SO}_4$ ), accordingly the background-count must be reduced to a minimum.

(ii) *Isotope dilution analysis.* This has been used for the determination of amino acids in protein hydrolysates, and it has also been applied to the analysis of mixtures of lanthanides. In both instances quantitative separation into pure species is wellnigh impossible. But when an active specimen of one of the species is uniformly incorporated in the original and some of the

mixture is put through the purification process, then

$$\frac{\text{specific activity of additive}}{\text{specific activity of purified specimen}} = \frac{\text{weight of species originally present} + \text{additive}}{\text{weight of additive}}$$

For the protein hydrolysate a  $^{14}\text{C}$  acid is added which suffers dilution by the inactive acid already present. The extent of the dilution, measured radio-metrically, indicates the amount of the particular acid in the hydrolysate.

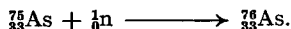
By adding in turn an active form of all the amino acids present a complete analysis is possible.

(iii) *Radioactivation analysis*. This requires an atomic reactor or other strong neutron source. It is specially useful for measuring trace impurities; an example is copper in aluminium. The aluminium under examination and a pure copper standard are irradiated together and subsequently dissolved, the solution of the latter being diluted up to  $10^5$  times. Portions of both solutions, after the addition of a copper carrier, are precipitated. (Sometimes a hold-back carrier is required at this stage to remove high-activity products which would interfere in the counting of the copper activity). The two precipitates are dried and weighed and their activities are compared. Then

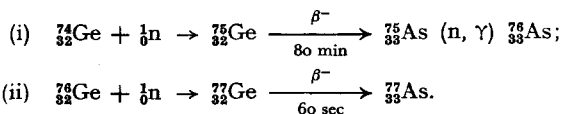
$$\frac{\text{activity of copper in aluminium}}{\text{activity in standard}} = \frac{\text{mass of copper in aluminium}}{\text{mass in standard}}$$

The method enables impurities to be assessed with an accuracy greater than one part per million without recourse to micro methods. Care must be exercised in its application, for in a high neutron flux spurious impurities may arise.

The estimation of traces of arsenic in germanium provides a problem of this kind. Irradiation of  $^{75}\text{As}$  with neutrons gives rise to the 27-hour  $\beta$ -emitter  $^{76}\text{As}$ :



But both this nuclide and the 40-hour  $^{77}\text{As}$  can arise from the irradiation of the germanium itself:



The amount of spurious  $^{76}\text{As}$  is small because of the comparative complexity of process (i), but considerable amounts of  $^{77}\text{As}$  can be produced. The interference of  $^{77}\text{As}$  is overcome by the use of proportional counting techniques which distinguish between the different  $\beta$ -energies, 0.7 MeV for  $^{77}\text{As}$  and



3.1 MeV for  $^{76}\text{As}$ . Choice of suitable time of irradiation and neutron flux can minimise the yield of spurious  $^{76}\text{As}$ , making possible the determination of as little as 0.01 ppm As in  $\text{GeO}_2$ .

Neutron activation analysis without previous chemical separation is possible when the contaminating element and the principal constituent have

- (i) large differences in their cross-section for neutron capture,
- (ii) large differences in the half-life of the products of irradiation,
- (iii) product-nuclides with very different emission characteristics.

As an example of (i) gold has a cross-section of 96 barns for slow-neutron capture, lead one of only  $5 \times 10^{-4}$  barns. Irradiation, while hardly affecting the lead, changes the gold into an active form. The gold content of lead can thus be found.

Traces of osmium in rhodium can be determined because of (ii). Irradiation produces  $^{198}\text{Os}$  (32 hr) and  $^{104}\text{Rh}$  (4.4 min). When the irradiated specimen is kept for some hours the activity due to the rhodium decays and makes possible the measurement of the osmium activity.

The estimation of iridium in palladium is feasible because of (iii). All the isotopes of palladium are pure  $\beta$ -emitters but  $^{197}\text{Ir}$  produces  $\gamma$  radiation as well as  $\beta$  particles. Measurement of the  $\gamma$  activity after absorption of the  $\beta$  radiation gives the iridium content.

## The Mössbauer effect

### *Principle and method*

This effect, increasingly applied in chemistry, concerns the resonance fluorescence of recoil-free gamma radiation from radioactive nuclei. Atoms of a nuclide like  $^{57}\text{Co}$  which have been allowed to diffuse into platinum or stainless steel emit  $\gamma$  rays of almost identical energy, the recoil momentum in every event being taken up by the solid as a whole. The decay scheme for cobalt-57 can be represented as in Fig. 15.

The lower of the two excited states of  $^{57}\text{Fe}$  has a lifetime of about  $1.0 \times 10^{-7}$  sec giving a line width, in accordance with the Heisenberg uncertainty principle, of about  $4.8 \times 10^{-9}$  eV, that is  $3.3 \times 10^{-14}$  of the resonance frequency. It is therefore possible to measure small changes in the position of these resonances caused, for example, by internal electric fields in solids.

The apparatus consists of a source such as  $^{57}\text{Co}$  in steel, an absorber containing the daughter nuclide,  $^{57}\text{Fe}$  in this case, and a  $\gamma$ -scintillation counter (Fig. 16).

If  $\gamma$  radiation from the source strikes an absorber in which  $^{57}\text{Fe}$  nuclei are in the same electronic environment as in the source there is resonance absorption by which these nuclei are raised to the excited state. But if

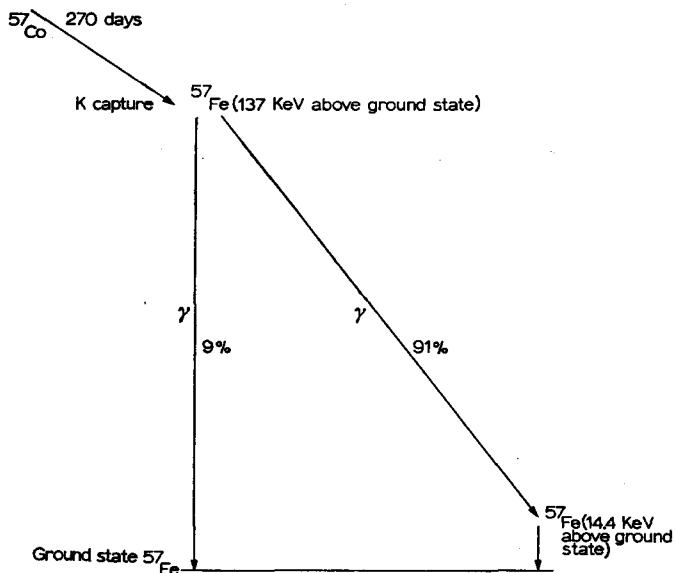


Fig. 15. Decay scheme for cobalt-57.

$^{57}\text{Fe}$  atoms in the absorber are in a different state of chemical combination from those in the source, the absorber must be moved at a steady speed relative to the source to fulfil the conditions for resonance, the Doppler shift in frequency just compensating for the frequency change induced in the absorbing nucleus by its electronic environment.

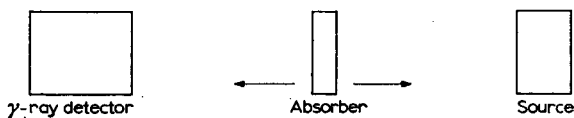


Fig. 16. Arrangement of source, absorber and detector for Mössbauer spectrometry.

The shifts, known as isomer shifts, are measured in mm per second and can be positive or negative. The extent of the isomer shift depends largely on the s-electron density around the absorbing nucleus, in which the positive charge becomes differently distributed on excitation. In  $\text{Fe}^{2+}$  ( $d^6$ ) there is rather more screening of the 3s electrons from external influences than in  $\text{Fe}^{3+}$  ( $d^5$ ). The isomer shift is

$$\sim 1.0 \text{ mm sec}^{-1} \text{ for } \text{Fe}^{2+} \text{ salts}$$

$$\sim 0.1 \text{ mm}\cdot\text{sec}^{-1} \text{ for } \text{Fe}^{3+} \text{ salts}$$

The resonant rays are often emitted as a pair of frequencies because of interaction between the field round the nucleus and the nuclear quadrupole (p. 19) of  $^{57}\text{Fe}$ . For  $^{57}\text{Fe}^{3+}$  the quadrupole splitting is small but for  $^{57}\text{Fe}^{2+}$  with an extra electron, it is larger.

In  $\text{Fe}(\text{CN})_6^{4-}$ , for instance, with a symmetrical electron distribution, quadrupole splitting does not occur, but in  $\text{Fe}(\text{CN})_6^{3-}$ , with one 3d orbital singly occupied, there is splitting which is strongly temperature-dependent.

#### *Applications in Chemistry*

In recent years, observation of the resonant absorption of the 14.1 KeV  $\gamma$  ray from the first excited state of iron-57 has been used for the investigation of several iron compounds in the solid state. Measurements of the isomer shifts have been valuable in determining oxidation states, as the values for ions of different charge fall within different characteristic ranges. The existence of  $\text{Fe}^+$  in solid solution in NaCl, of  $\text{Fe}^{4+}$  in  $\text{Sr}_2\text{FeO}_4$ , and of  $\text{Fe}^{3+}$  in non-stoichiometric FeO (p. 695) have been substantiated. The mixed oxide  $\text{FeVO}_3$  has been shown to contain  $\text{Fe}^{3+}$  but not  $\text{Fe}^{2+}$ .

In potassium ferrate,  $\text{K}_2\text{FeO}_4$ , the isomer shift is smaller than predicted for a  $3d^2$  electron configuration, evidently because the electron density in the 3d orbitals is augmented by  $d^3s$  hybridisation in the tetrahedral  $\text{FeO}_4^{2-}$  ion, and the s-electron density close to the nucleus is thereby weakened.

Mössbauer studies have been extended to other metals with low-lying excited states. Possible target nuclei include iridium-191, which absorbs the 129 KeV  $\gamma$  rays from osmium-191 ( $\beta$ , 16d), and also  $^{61}\text{Ni}$ ,  $^{119}\text{Sn}$  and  $^{197}\text{Au}$ .

#### FURTHER READING

- A. C. WAHL AND N. A. BONNER, *Radioactivity Applied to Chemistry*, New York, Wiley, 1951.
- G. FRIEDLANDER AND J. KENNEDY, *Nuclear and Radiochemistry*, 2nd ed., New York, Wiley, 1964.
- M. HAISSINSKY AND J. P. ADLOFF, *Radiochemical Survey of the Elements*, Elsevier, Amsterdam, 1965.
- R. T. OVERMAN AND H. M. CLARK, *Radiosotope Techniques*, New York, McGraw-Hill, 1960.
- J. SHARPE, *Nuclear Radiation Detectors*, 2nd ed., London, Methuen, 1964.
- S. C. CURRAN, *The Determination of Geological Age by means of Radioactivity*. Quart. Rev. (London), 7 (1953) 1.
- D. R. STRANKS AND R. G. WILKINS, *Isotopic Tracer Investigations of Mechanism and Structure in Inorganic Chemistry*, Chem. Rev., 57 (1957) 743.
- E. N. JENKINS AND A. A. SMALES, *Radioactivation Analysis*, Quart. Rev. (London), 10 (1956) 83.

- D. L. BAULCH AND J. F. DUNCAN, *Quantitative Nuclear Chemistry*, Quart. Rev. (London), 12 (1958) 133.
- E. FLUCK, W. KERLIN AND W. NEUWIRTH, *The Mössbauer Effect and its Significance in Chemistry*, Angew. Chem., Internat. Ed. Engl., 2 (1963) 277.
- W. F. JOHNSON, E. EICHLER AND G. D. O'KELLEY, *Nuclear Chemistry*, Interscience, New York, 1963.
- D. J. CARSWELL, *Introduction to Nuclear Chemistry*, Amsterdam, Elsevier, 1967.
- E. FLUCK, *The Mössbauer Effect and its Application in Chemistry*, in H. J. EME-LÉUS AND A. G. SHARPE, *Advances in Inorganic Chemistry and Radiochemistry*, London, Academic Press, Vol. 6 (1964) 433.

## Electronic Structures of Atoms. The Periodic Table

### Wave mechanics

#### *Classical and atomic physics*

Two main sets of experimental phenomena are inconsistent with concepts of classical physics.

(i) Changes in the internal energy of an atom accompanying emission or absorption of light are not continuous but occur in discrete amounts. Moreover spectroscopic evidence shows an atom exists only in certain discrete energy states characteristic of the element. The change from an energy state  $E$  to one  $E'$  is accompanied by emission (when  $E > E'$ ) or absorption (when  $E < E'$ ) of light, whose frequency  $\nu$  is related to the energy change thus:

$$|E - E'| = h\nu$$

where  $h$  (Planck's constant) =  $6.624 \times 10^{-27}$  erg sec (the dimensions of action).

(ii) A beam of electrons shows interference effects exactly as does a beam of light. A diffraction pattern is obtained when light is reflected or diffracted from a grating. The regularly spaced atoms in a crystal provide a grating which diffracts not only X-rays but also electron beams. Hence wave properties must be associated with the electron.

#### *Particulate and wave properties of the electron*

The occurrence of discrete energy states of a 'bound' electron in an atom and the co-existence of wave and particle properties in a free electron, can be accounted for on the basis of *wave mechanics* (Schrödinger, 1926). Observation of the diffraction patterns produced when electrons of known energy encounter crystals of known atomic spacing shows that the wave length,  $\lambda$ , associated with an electron of velocity,  $v$ , is given by

$$\lambda = h/mv.$$

Wave and particle properties can then be reconciled by the following argument.

Normally, a wave motion is a disturbance which varies at any point with a *frequency*,  $\nu$ , and is propagated with some *phase velocity*,  $u$ . The *wavelength*,  $\lambda$ , is then given by the relationship  $\lambda\nu = u$ , and represents the distance, along the direction of propagation, between points where the variation is exactly similar or *in phase*. A train of waves of this kind extends over space as long as the source goes on emitting energy; it describes a steady state. But if a wave is to be associated with a localised particle, it is necessary to consider a travelling *pulse* or *wave packet*. Such a pulse can be described only by combining a group of wave trains whose phase velocities (and hence also wave lengths) depend on frequency, varying slightly about their mean values: it travels with a *group velocity*,  $v_g$ , given by

$$v_g = \frac{d\nu}{d(\frac{1}{\lambda})}$$

Now for the electron,  $\lambda = h/mv$  (experimentally) and therefore

$$v_g = \frac{h}{m} \frac{d\nu}{dv};$$

but if the wave packet, which carries the energy, is always to stay with the particle,  $v_g$  must be the same as the actual particle velocity  $v$  and the frequency  $\nu$  must then satisfy the equation

$$\frac{d\nu}{dv} = \frac{m}{h} v.$$

The solution is simply  $\nu = E/h$ , where  $E (= \frac{1}{2}mv^2)$  is the energy of the particle, say an electron.

#### *Wave packet and material particle*

The equivalence  $\nu = E/h$  expresses Planck's law relating the energy of a pulse of radiation, a *light quantum*, to its frequency. Thus the law acquires a more general significance and enables us to associate a wave packet with a *material particle*, its frequency being similarly related to the energy of the particle. Such a wave has to be associated with a particle simply in order to describe its behaviour; it is not necessarily real in the same sense as an electromagnetic wave. Its interpretation must now be examined.

### Interpretation

#### *Some definitions*

Let  $\psi$  be the amplitude, varying from point to point in space, of the wave associated with a moving particle. Relative amplitudes at different

points can then be calculated just as in optical diffraction theory; and in all diffraction experiments the degree of darkening of a photographic plate at different points depends on the relative values of  $\psi^2$ , the *intensity*, at these points. Now, on a particle picture, this effect must depend on the *number of particles* landing at the different points, and since one particle can arrive only at one point, it is necessary to make a *statistical* interpretation. The *probability* of a particle being found in a given small region is proportional to the square of the amplitude of the associated *wave function* in that region. Since this probability is also proportional to the size of the region the actual probability must be  $\psi^2 d\tau$ , where  $d\tau$  is the volume element and  $\psi^2$  is a *probability density*.

### *Stationary patterns*

In the diffraction of a free particle, the probability density changes with time as the wave packet progresses, but the interpretation turns out to be quite general. In other situations, where the particle is bound within a certain region of space, *stationary patterns* occur (like the standing waves on a vibrating string, where the actual profile is fixed, instead of travelling along the string as it does in a whip), and again  $\psi^2$  determines the probability of finding the particle at a given point. Stationary patterns are of supreme importance in molecular theory since they describe an electron bound in an atom or molecule. They are invoked throughout this book and their calculation is taken up in a later section.

## The Uncertainty Principle

### *Especially in relation to the electron*

The need to associate a wave packet with a moving particle has another important consequence. In the one-dimensional case of plane waves representing a particle moving in the  $x$ -direction, the extension of the wave packet,  $\Delta x$ , is determined by the range of wavelengths admitted in the packet and this, in turn, by the momentum range,  $\Delta p_x$ . It can then be shown that

$$\Delta x \Delta p_x \sim h.$$

This is one consequence of the famous Uncertainty Principle, which relates the simultaneous uncertainties in certain pairs of measurable quantities. Similar relationships exist for the  $y$  and  $z$  co-ordinates and momentum components. If the wave packet associated with the electron is very compact ( $\Delta x$  small) it must be very 'impure', containing a mixture of wave trains corresponding to a considerable range of momenta ( $\Delta p_x$  large); it is then

known fairly accurately where the electron is at a given time, but only roughly what momentum to associate with it. When, however, the momentum of the electron is measured more and more precisely, the width of the wave packet must increase, and there is a corresponding loss of precision in possible knowledge of its position. However, since  $h$  is very small, these uncertainties, except in atomic physics, are often negligible. The position of a particle weighing 1 g can be determined optically without sensibly disturbing its momentum, but even in principle this is not true for an electron.

### The wave equation

Any disturbance  $\Psi$  (e.g. the displacement of an elastic string or the height of a water wave) which is propagated along the  $x$ -direction with velocity  $u$ , satisfies a simple partial differential equation, the *wave equation*:

$$\frac{\partial^2 \Psi}{\partial x^2} = \frac{1}{u^2} \cdot \frac{\partial^2 \Psi}{\partial t^2}.$$

Here  $\Psi$  depends on both position and time,  $\Psi = \Psi(x, t)$ . More generally for a three-dimensional disturbance,

$$\nabla^2 \Psi = \frac{\partial^2 \Psi}{\partial x^2} + \frac{\partial^2 \Psi}{\partial y^2} + \frac{\partial^2 \Psi}{\partial z^2} = \frac{1}{u^2} \cdot \frac{\partial^2 \Psi}{\partial t^2},$$

where  $\Psi = \Psi(x, y, z, t)$ .

Proceeding immediately to the stationary patterns, a particular type of one-dimensional solution is, for example,

$$\Psi(x, t) = \psi(x) \sin 2\pi\nu t,$$

where  $\psi(x)$  is the amplitude, which depends only on position, and the disturbance at a point varies between  $+\psi(x)$  and  $-\psi(x)$ , oscillating  $\nu$  times per unit time owing to the time-dependent factor which has extreme values  $\pm 1$ . In this case substitution in the wave equation shows that  $\psi(x)$  must satisfy a time-independent amplitude equation:

$$\frac{d^2 \psi}{dx^2} = \frac{4\pi^2 \nu^2}{u^2} \psi.$$

### The wave function

It is customary to call  $\psi$  the 'wave function', though strictly it is only the amplitude of the wave function  $\Psi$ , the time-dependent quantity. Provided the medium is uniform, so that  $u$  is constant, the last equation has solutions of the form

$$\sin \frac{2\pi\nu}{u} x \quad \text{and} \quad \cos \frac{2\pi\nu}{u} x,$$



and these stationary patterns (standing waves) are repeated when  $x$  increases by  $\lambda = u/v$ , the wave length.

Returning to the case of an electron with kinetic energy  $E$ , the associated wave function is known to have a wavelength

$$\lambda = \frac{h}{mv} = \frac{h}{\sqrt{2mE}},$$

and the amplitude equation then becomes

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2mE}{h^2} \psi = 0.$$

*The bound electron has quantised energy*

In the first instance, the last equation applies only to a particle with constant kinetic energy. Nevertheless, it shows with unexpected clarity the origin of *quantisation*—namely, the fact that a particle bound within a certain region of space can exist only in certain discrete energy states. For if the particle is now confined to a certain region, by means of barriers a distance  $l$  apart,  $\psi$  must vanish at and outside the end points and these 'boundary conditions' require that the region contains an integral number of half waves, *i.e.*  $n(\frac{1}{2}\lambda) = l$ . Substituting for  $\lambda$ , the only possible values of  $E$  are

$$E = \frac{h^2}{8ml^2} n^2, \quad \text{where } n = 1, 2, 3, \dots$$

Thus a particle moving back and forth within definite limits can exist in states described by a stationary probability pattern only for certain discrete values of the energy.

The Schrödinger equation (1926) represents a generalisation to the case in which there is an external potential field and the kinetic energy is no longer constant. The kinetic energy, which might be expected to take the place of  $E$  in the above equation, is now (classically)  $E - V$ , where  $E$  is the total energy and  $V = V(x)$  is the potential energy, which in general varies from place to place. The final wave equation for determining the stationary wave patterns associated with a particle in an arbitrary potential field is then

$$\nabla^2\psi + \frac{8\pi^2m}{h^2} (E - V) \psi = 0.$$

Although the historical derivation sketched above depends largely on suggestive analogies, more profound derivations have since been given, and the equation itself is now regarded as entirely satisfactory so long as extremely small relativistic effects are neglected. On physical grounds (and  $\psi^2$

has a physical meaning) it is assumed that the only solutions which mean anything are well-behaved. That is they are everywhere finite, smoothly varying, and vanishing at infinity. This requirement alone leads automatically to the quantisation so foreign to classical physics.

Sometimes the wave equation is rewritten in the form

$$\left[ \frac{1}{2m} \left( \frac{-\hbar^2}{4\pi^2} \right) \nabla^2 + V(x, y, z) \right] \psi = E\psi.$$

The quantity in square brackets is an 'operator'—the Hamiltonian operator. All *eigenvalue equations* have this form; and there are solutions  $\psi$  only for certain *eigenvalues* of the factor  $E$  on the right hand side. This form immediately suggests the final generalisation from 1 to  $n$  electrons. Since the classical energy expression is

$$E = \frac{1}{2}mv^2 + V(xyz) = \frac{1}{2m} (p_x^2 + p_y^2 + p_z^2) + V(xyz)$$

where  $p_x = mv_x$  etc. are components of momentum, the 1-electron equation may be obtained by replacing  $p_x^2$  etc. by the differential operators

$$-\frac{\hbar^2}{4\pi^2} \frac{\partial^2}{\partial x^2}, \text{ etc.}$$

letting the resultant operator (in square brackets above) operate on a wave function  $\psi$ , and equating the result to  $E\psi$ . The same recipe, applied to a system of  $N$  particles with masses  $m_1, m_2, m_3 \dots m_N$ , gives

$$\left[ \frac{1}{2m_1} \left( \frac{-\hbar^2}{4\pi^2} \right) \nabla_{(1)}^2 + \frac{1}{2m_2} \left( \frac{-\hbar^2}{4\pi^2} \right) \nabla_{(2)}^2 + \dots V \right] \psi = E\psi,$$

where  $V$  and  $\psi$  are now functions of the co-ordinates of all the particles and there is a  $\nabla^2$  for every particle.  $\psi^2 d\tau_1, d\tau_2 \dots d\tau_n$  is then the probability of simultaneously finding particle 1 in volume element  $d\tau_1$ , particle 2 in volume element  $d\tau_2$ , etc.

### Applications of wave mechanics to the hydrogen atom

In the hydrogen atom, an electron of charge  $-e$  moves about a proton of charge  $+e$ . If the distance between them is  $r$ , its potential energy is expressed by

$$V = -\frac{e^2}{r}$$

and

$$\nabla^2 \psi + \frac{8\pi^2 m}{\hbar^2} \left( E + \frac{e^2}{r} \right) \psi = 0.$$

One type of solution follows on taking  $\psi = f(r)$  and assuming that, as the potential is spherically symmetrical, there must be a solution dependent only on  $r$ ; in which case

$$\frac{\partial \psi}{\partial x} = \frac{d\psi}{dr} \frac{\partial r}{\partial x} \text{ etc.}$$

Then since  $r = \sqrt{x^2 + y^2 + z^2}$ ,

$$\left(\frac{\partial r}{\partial x}\right)_{y,z} = \frac{1}{2} \frac{2x}{\sqrt{x^2 + y^2 + z^2}} = \frac{x}{r}$$

and

$$\frac{\partial \psi}{\partial x} = \frac{x}{r} \frac{d\psi}{dr}$$

Differentiating again:

$$\frac{\partial^2 \psi}{\partial x^2} = \frac{1}{r} \frac{d\psi}{dr} - \frac{x^2}{r^3} \frac{d\psi}{dr} + \frac{x^2}{r^2} \frac{d^2 \psi}{dr^2}$$

$\frac{\partial^2 \psi}{\partial y^2}$  and  $\frac{\partial^2 \psi}{\partial z^2}$  may be found similarly. Adding, and using  $x^2 + y^2 + z^2 = r^2$ ,

$$\nabla^2 \psi = \frac{3}{r} \frac{d\psi}{dr} - \frac{1}{r} \frac{d\psi}{dr} + \frac{d^2 \psi}{dr^2} = \frac{2}{r} \frac{d\psi}{dr} + \frac{d^2 \psi}{dr^2}$$

As  $\nabla^2 \psi$  reduces to this form if  $\psi$  is a spherically symmetrical function, it follows that spherically symmetrical solutions must satisfy the equation

$$\frac{d^2 \psi}{dr^2} + \frac{2}{r} \frac{d\psi}{dr} + \frac{8\pi^2 m}{h^2} \left(E + \frac{e}{r}\right) \psi = 0.$$

A standard trial solution is  $\psi = e^{-ar}$ , for the exponential factor remains on differentiation, and can be extracted as a common factor.

Thus

$$\frac{d\psi}{dr} = -a e^{-ar} \quad \text{and} \quad \frac{d^2 \psi}{dr^2} = +a^2 e^{-ar},$$

and substitution gives

$$e^{-ar} \left[ a^2 - \frac{2}{r} a + \frac{8\pi^2 m}{h^2} \left(E + \frac{e}{r}\right) \right] = 0.$$

If this is to be true for all values of  $r$ , the constant term and the term in  $\frac{1}{r}$  must both vanish: thus

$$a^2 + \frac{8\pi^2 m E}{h^2} = 0, \quad \text{and} \quad -2a + \frac{8\pi^2 m e}{h^2} = 0, \quad \therefore a = \frac{4\pi m^2 e^2}{h^2};$$

and the  $E$  value for this state is  $E_1 = \frac{-a^2 h^2}{8\pi^2 m} = -\frac{2\pi^2 m e^4}{h^2}$ .

*The ionisation energy of  $H \rightarrow H^+$*

Two important points arise. First,  $E_1$  is negative and hence the electron is bound within the atom and, secondly  $E_1$  is expressed in terms of universal constants and is itself a useful constant. The energy  $-E_1$  is the ionisation energy necessary to remove the electron entirely from the hydrogen atom. Its actual value derived from spectroscopic measurements, 13.60 eV, agrees with that calculated from the equation above.

*The radius of the hydrogen atom*

We have seen that the value of  $\psi^2 dr$  is proportional to the probability of finding an electron in an element of volume  $dr$ . The probability of one electron being somewhere is obviously one, and it is necessary to multiply  $\psi$  by a constant so that

$$\int_{-\infty}^{+\infty} \psi^2 dr = 1$$

The wave amplitude  $\psi$  is then said to be *normalised*. For the case under discussion, where  $\psi$  depends only on  $r$ , the probability of an electron being at a distance between  $r$  and  $r + dr$  from the nucleus (*i.e.* in a shell of radius  $r$  and thickness  $dr$ , and therefore of volume  $4\pi r^2 dr$ ) must be  $4\pi r^2 \psi^2 dr$ . When the radial probability density,  $4\pi r^2 \psi^2$  is plotted against  $r$  (Fig. 17)

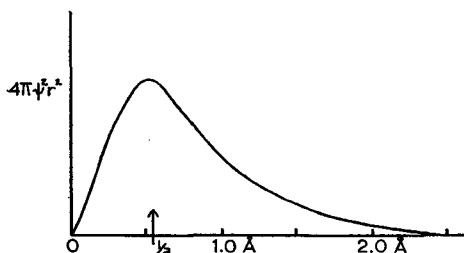


Fig. 17. Radial probability density,  $4\pi r^2 \psi^2$ , in ground state hydrogen atom.

there is a maximum at  $r = 1/a$ . This is the radius of the thin spherical shell which has a greater probability of holding the electron than any equally thin spherical shell of larger or smaller radius. The radius,  $1/a$ , can be calculated in terms of  $m$ ,  $e$  and  $h$  and equals  $h^2/4\pi^2 m e^2 = 0.5292 \text{ \AA}$ . This is the Bohr radius of the semiclassical approach (1913) and is often adopted as the atomic unit of length. The electron has a maximum probability of being at this distance from the nucleus but a good chance of being anywhere within a very considerable volume.

The probability density  $\psi^2$  is commonly represented pictorially by density of shading (Fig. 18) or, more simply, by sketching a bounding contour (on which all points have the same value of  $\psi^2$ ) enclosing, say, 95% of the density. The  $\psi$ -function, indicated by this bounding surface, is called an *atomic orbital*, being the wave-mechanical counterpart of the classical orbit (Figs. 18, 19).

#### *The s electron*

An electron, like that in the unexcited hydrogen atom, whose orbital is spherically symmetrical is called an s electron.

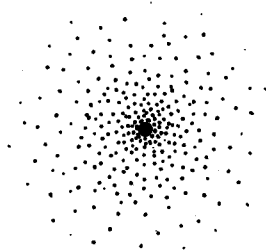


Fig. 18. Electron probability density represented by density of shading

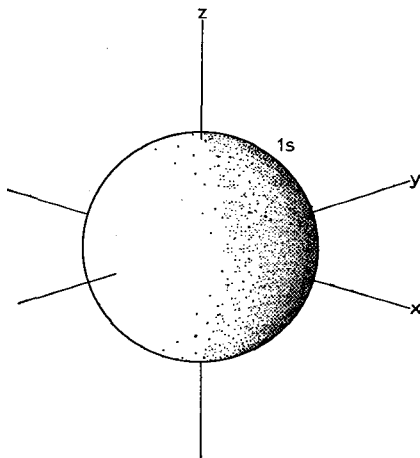


Fig. 19. Atomic orbital represented by spherical bounding surface.

#### *Excited states: the hydrogen spectrum*

In addition to the state of lowest energy  $E_1$ , there are *excited states* with greater energies  $E_2, E_3, \dots, E_n$ , for which it can be shown that

$$E_n = \frac{-2\pi^2me^4}{h^2} \frac{1}{n^2} = \frac{E_1}{n^2},$$

$n$  being an integral quantum number. When  $n$  is very large,  $E_n$  approaches zero. For the free electron  $E \geq 0$ .

The energy set free when an electron falls from an energy level  $n$  to the energy level 2 is

$$\begin{aligned} E_n - E_2 &= -\frac{2\pi^2me^4}{h^2} \left( \frac{1}{n^2} - \frac{1}{2^2} \right), \\ &= +\frac{2\pi^2me^4}{h^2} \left( \frac{1}{2^2} - \frac{1}{n^2} \right). \end{aligned}$$

In this form the equation relates the wave number of lines in the visible hydrogen spectrum (Balmer, 1885) to the change in energy state of the electron. The wave number  $\lambda^{-1}$  is simply the number of waves per unit length:

$$\lambda^{-1} = \frac{1}{\lambda} = \frac{\nu}{c},$$

where  $c$  is the velocity of light. Since

$$E_n - E_2 = \Delta E = h\nu = h\lambda^{-1}c,$$

$$h\lambda^{-1}c = \frac{2\pi^2me^4}{h^2} \left( \frac{1}{2^2} - \frac{1}{n^2} \right),$$

$$\lambda^{-1} = \frac{2\pi^2me^4}{h^3c} \left( \frac{1}{2^2} - \frac{1}{n^2} \right) = R \left( \frac{1}{2^2} - \frac{1}{n^2} \right).$$

The constant  $R$  agrees, within the limits of experimental error, with the empirical one found by Rydberg (1889).

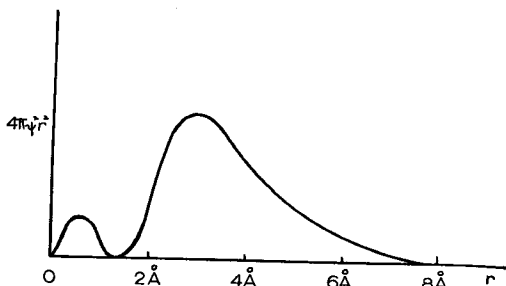


Fig. 20. Radial density distribution of charge for electron of energy  $E_2$ .

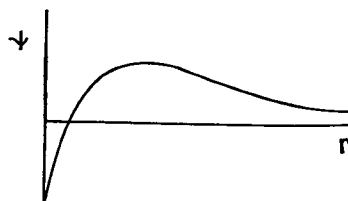


Fig. 21. Relation of  $\psi$  to  $r$  for electron of energy  $E_2$ .

The radial density distribution of the charge of an electron of energy  $E_2$  is shown by plotting  $4\pi\psi^2r^2$  against  $r$ , as in Fig. 20. The corresponding

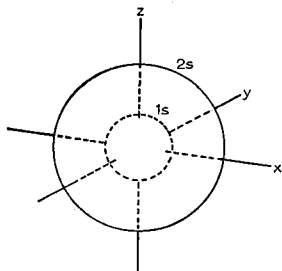


Fig. 22. Boundary surface for 2s electron, compared with that for 1s.

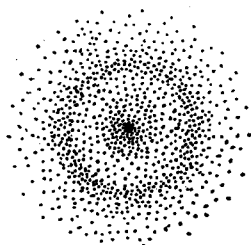


Fig. 23. Representation of probability density for electron of energy  $E_2$ .

relationship of  $\psi$  itself to  $r$  is shown in Fig. 21. Alternative pictorial representations of both  $\psi$  and  $\psi^2$  are given in Fig. 22 and Fig. 23, the former obscuring the details but indicating schematically the general size and shape of the orbital. In the latter the density of the dots is intended only to show where  $\psi$  is large.

### p Functions

Though the potential  $V$  in the Schrödinger equation depends only on  $r$ , there are solutions which depend on  $x$ ,  $y$  and  $z$  separately, e.g.  $\psi = xf(r)$ . Wave functions of this type are p functions and there are three solutions for the same energy value. As a result of the spherical symmetry of the potential  $V$ , the orbitals which are not themselves spherically symmetrical occur in groups, the members of a given group having the same value of  $E$  but quite independent  $\psi$ -patterns. Solutions in the same group are described as *degenerate*, their number being the *degree of degeneracy*, and different orbitals of the same group are often said to be *equivalent*, that is energetically alike.

For the special case where  $V(r) = -e^2/r$ , substitution in the Schrödinger equation shows the p-type solution of lowest energy to give

$$E = -\frac{2\pi^2me^4}{h^2} \frac{1}{2^2} = E_2.$$

$E_2$  is the energy of the second-lowest s state. For the single-electron hydrogen atom this energy level is fourfold degenerate, corresponding to one s and three p orbitals.

### The *p* and *d* electrons

All other elements have atoms with more than one electron and, accordingly, an electron in them moves, roughly speaking, in the field created by the nucleus and the other electrons together. This field is not of a simple inverse distance form; and in such atoms *s* electrons differ in energy from *p* electrons and from *d* electrons when these are present.

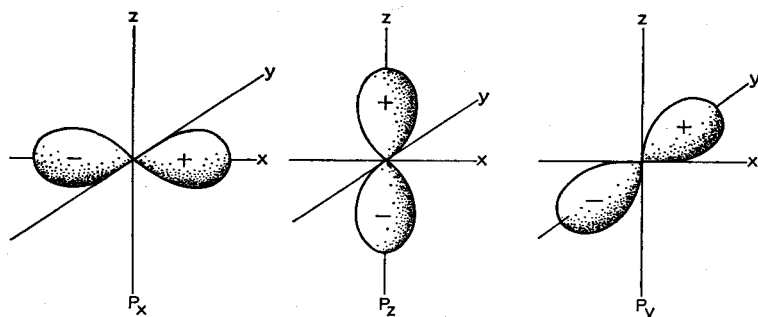


Fig. 24. Boundary surfaces for *p* electrons.

The number of higher energy solutions is infinite, their 'atomic' character disappearing for  $E \rightarrow 0$ , when the electron becomes free. Some of the higher atomic orbitals are represented by boundary surfaces including most of the probability density, in Fig. 24 for *p* electrons and in Fig. 25 for *d* electrons. The figures do not strictly show surfaces of constant  $\psi$  ( $\psi$  vanishes

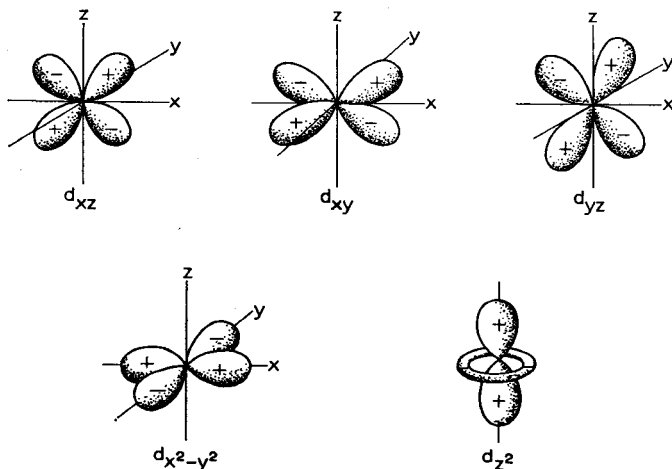


Fig. 25. Boundary surfaces for *d* electrons.



at the nucleus) but rather their general disposition in relation to one another, and for clarity the different parts of the separate lobes are joined up into a single pattern. The pattern indicates simply the sign of  $\psi$  and the regions where it is large, the different regions being separated by nodal surfaces in which  $\psi = 0$ . The sevenfold degenerate f states are less easy to represent pictorially.

The terminology s, p, d, f, ... is a legacy from the Bohr theory which attempted to classify the 'sharp', 'principle', 'diffuse' and 'fundamental' series of classical spectroscopy.

### Orbital angular momentum

The *angular momentum* of a particle about a point O is a quantity  $M = \rho mv$  where  $\rho$  is the perpendicular distance from O to the line of motion and  $mv$  is the ordinary momentum; the quantity is associated with an axis through O, namely the normal to the plane in which the motion is taking place (Fig. 26). The angular momentum is thus a vector quantity and can be

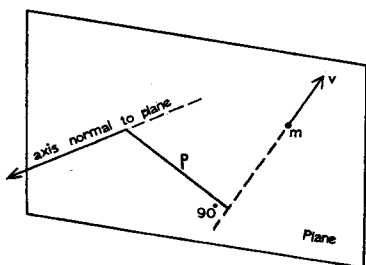
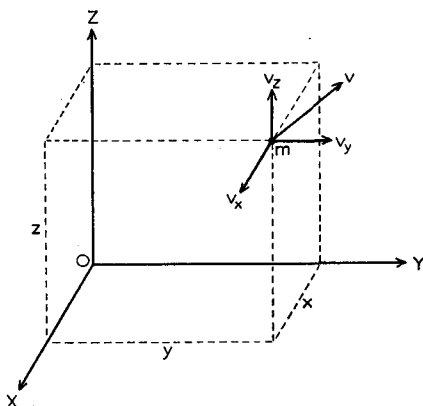


Fig. 26. Illustrating angular momentum.

Fig. 27. Components of angular momentum.



described in terms of components parallel to the three axes. Its units are erg sec (the dimensions of action and also those of  $h$ , Planck's constant). The magnitude of the vector is

$$M = \sqrt{M_x^2 + M_y^2 + M_z^2},$$

and the direction (*i.e.* the axis) makes angles

$$\cos^{-1} \frac{M_x}{M}, \quad \cos^{-1} \frac{M_y}{M}, \quad \cos^{-1} \frac{M_z}{M}$$

with the three co-ordinate axes. Here for instance  $M_x = y(mv_z) - z(mv_y)$  and is seen from Fig. 27 to be the total momentum of the  $y$  and  $z$  momentum components about the  $x$  axis, the contributions being counted positive for anticlockwise and negative for clockwise motion.  $M_y$  and  $M_z$  follow by cyclic rearrangement,  $xyz \rightarrow yzx \rightarrow zxy$ .

*Orbital angular momentum is quantised*

Now  $M$  and its three components are all observable dynamical quantities just as is the energy  $E$ . It turns out that, in a definite energy state,  $M$  and one of its components can simultaneously have definite, quantised values. Thus if a particular direction in space is singled out, by means of an applied magnetic field for example, the component in this direction can take only certain quantised values, while the other two components must remain uncertain. It is customary to call the particular axis the  $z$  axis. The definite allowed values of  $M_z$  are then integral multiples of  $h/2\pi$ ,

$$M_z = m_l (h/2\pi); \text{ where } m_l = 0, \pm 1, \pm 2, \dots \pm l$$

those of  $M$  itself being

$$M = \sqrt{l(l+1)} \frac{h}{2\pi}; \text{ where } l = 0, 1, 2, \dots$$

The s, p, d, f electrons have angular momenta corresponding to  $l = 0, 1, 2, 3$  respectively, and the different degenerate states can be classified according to the simultaneously definite values of  $M_z$ .

Thus there are three p orbitals, corresponding to  $m_l = -1, 0, +1$ ; five d orbitals, corresponding to  $m_l = -2, -1, 0, +1, +2$ ; and in general  $(2l+1)$  orbitals, corresponding to  $m_l = -l, \dots, 0, \dots, +l$ , for an angular momentum  $M$  with quantum number  $l$ . This classification suggests a *vector model* (Fig. 28) in which different states correspond to different settings of a vector of length  $l$ , representing the angular momentum. This model goes

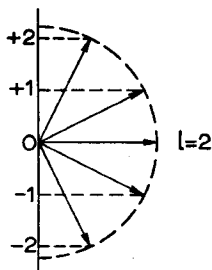


Fig. 28. Representation of angular momenta.

back to the early days of quantum theory, when it was found empirically necessary to assume the rather curious angular momentum value  $\sqrt{l(l+1)}$  (in units  $\hbar/2\pi$ ) instead of the  $l$  employed in the semi-classical vector diagram. The wave mechanical treatment is in fact capable of bringing theoretical and experimental results into perfect agreement.

### *The Zeeman effect*

The quantisation of angular momentum components in a given direction is experimentally realised in the Zeeman effect. Here the unique direction is fixed by an applied magnetic field; the states with different electronic angular momentum components in this direction correspond to slightly different energy values since the circulating charge behaves like a small magnet, whose component along the field is proportional to  $m_l$ . The splitting of the initially degenerate level, due to the different coupling energies, is spectroscopically observable. Quantitative discussion of this magnetic effect is deferred (p. 86). The Zeeman effect does, however, provide a very powerful tool in the interpretation of atomic spectra.

### *Mixtures of degenerate solutions of the wave equation*

At this stage, it must be stressed that any mixture of two or more degenerate solutions is also a solution of the wave equation, and is an equally satisfactory description of an electron with a given energy and angular momentum; but, for example, an equal mixture of solutions with common  $E$  and  $l$  but with  $m_l = +1$  and  $-1$ , respectively, would describe a state in which  $M_x$  was uncertain and, if observed, would be equally likely to yield either result. This arbitrariness disappears only if the spherical symmetry of the problem is destroyed by fixing an axis (e.g. by an applied field); for when this is done the only stationary states are those compatible with this axis of symmetry, and such states correspond to definite values of the third characteristic,  $M_x$ . To make this clear, consider the three  $p$  orbitals, describing electrons with the same energy, and with  $l = 1$ , but with  $m_l = -1, 0, +1$ . These orbitals, which are called  $p_{-1}$ ,  $p_0$  and  $p_{+1}$ , describe the stationary states when a feeble magnetic field (just sufficient to reduce the symmetry) is applied along the  $z$  axis; but they may be mixtures of the  $p$  orbitals  $p_x$ ,  $p_y$ , and  $p_z$ , which were introduced before any reference was made to symmetry or angular momentum. In fact  $p_z$  which is symmetrical about the  $z$  axis, does coincide with  $p_0$ : but  $p_{-1}$  and  $p_{+1}$  are mixtures of  $p_x$  and  $p_y$  (and *vice versa*) which can be interpreted, somewhat naively, as permitting the 'jumping' of an electron from one orbital to the other, so as to give respectively clockwise or anticlockwise circulation. On the other hand,  $p_x$  and  $p_y$  correspond to standing waves (this time 'ro-

tational') built up from  $p_{-1}$  and  $p_{+1}$  which are oppositely directed travelling waves. The same situation arises with the d electrons. Five 'travelling wave' solutions can be used which all give electron distributions completely symmetrical about a particular axis, or five standing wave solutions which are less symmetrical but more easily visualized. This ambiguity need cause no alarm; the freedom of choice simply means it is possible to work with those orbitals most suitable for a given application. In describing the spectroscopic states of free atoms (spherical symmetry), and of linear molecules (axial symmetry), it is often advantageous to employ the functions which correspond to definite  $M_x$  values; but this is not so in systems of lower symmetry in which there is no such thing as quantised angular momentum. And in discussing molecular structure where the atomic orbitals are employed only as 'building bricks' for constructing molecular wave functions, it is usually quite immaterial which type of orbital is used. The mixtures such as  $p_x, p_y, p_z$ , have, however, an important practical advantage. Unlike the travelling wave solutions, they can be directly represented by stationary patterns with a fixed orientation in space, and permit a pictorial approach to the construction of molecular wave functions.

### Electron spin. Fine structure

The interpretation of the Zeeman effect provided by the theory of orbital angular momentum is incomplete. Anomalous Zeeman splittings are observed (indeed, the so-called 'normal' splitting is found to be the exception) and require a further development of the theory. The difficulty first arises in the one-electron (hydrogen-like) system already considered, for even an s electron, with *no* angular momentum, is found to have two accessible energy states in the presence of a magnetic field. This led Goudsmit and Uhlenbeck (1925) to postulate an intrinsic angular momentum due to *spin* of the electron itself. Treating this on the same footing as orbital angular momentum the observed *doublet splitting* of an s state requires a spin quantum number,  $s = \frac{1}{2}$ , such that there would be two possible  $z$  components (separated by an integral multiple of  $h/2\pi$ ) namely  $+\frac{1}{2}$  and  $-\frac{1}{2}$  (*cf.* Fig. 28).

The general interpretation of the Zeeman effect for a one-electron system then calls for an extension of the vector picture. Consider an electron in a p state, denoting  $z$  components of the orbital and spin angular momenta, in units of  $h/2\pi$ , by  $m_l$  and  $m_s$ , respectively. The possibilities are  $m_l = -1, 0, +1$  and  $m_s = -\frac{1}{2}, +\frac{1}{2}$ ; thus the possible values of the total angular momentum  $z$  components are  $(-1 \pm \frac{1}{2}), (0 \pm \frac{1}{2}), (+1 \pm \frac{1}{2})$ . These correspond to different  $z$  components of total angular momentum with quantum

number  $j$ , where  $j$  can take the values  $l + \frac{1}{2} = \frac{3}{2}$  and  $l - \frac{1}{2} = \frac{1}{2}$ . The two vector diagrams for the allowed states are shown in Fig. 29, along with the composition of the orbital and spin vectors, the spin being parallel or anti-parallel to the orbital vector. The method of composition is applicable for arbitrary orbital angular momentum with quantum number  $l$ ,  $j$  taking values  $l + \frac{1}{2}$  and  $l - \frac{1}{2}$ .

The alternative couplings of orbital and spin angular momentum give rise to another experimentally observable phenomenon. The magnetic field associated with  $l$  performs in effect a Zeeman experiment on the spinning electron and, even in the absence of an external field, the two couplings correspond to slightly different energies which are revealed in the fine structure of spectral lines. Thus p, d, f... states are always resolved into

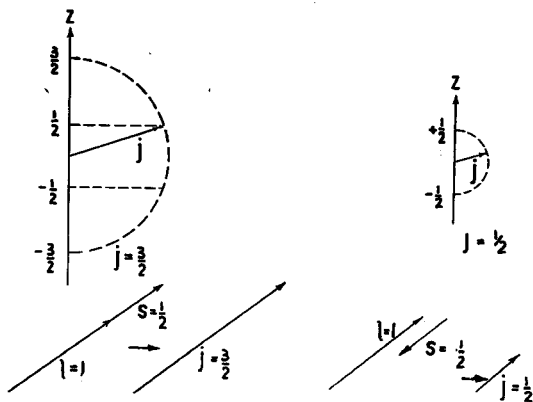


Fig. 29. Vector addition of orbital and spin angular momenta.

doublets by the electron spin, while the s state is single, being unresolved because the orbital magnetic moment is then zero. Further resolutions should occur when an external field is applied and these are in complete accord with the observed Zeeman splittings. A rigorous justification of this semi-classical vector model comes from quantum mechanics. The pictorial interpretation must not be taken too literally (in getting quantitative results, for instance, angular momenta with quantum numbers,  $l$ ,  $j$  etc. have magnitudes  $\sqrt{l(l+1)}$ ,  $\sqrt{j(j+1)}$  etc.); nevertheless, the pictorial model is extremely useful in the general classification and understanding of spectra.

### Many-electron systems

The wave equation for several electrons in the presence of a central nucleus may be taken over from p. 55—where now  $m_1 = m_2 = \dots = m$ ,

the electron mass. Abbreviating the co-ordinates of the electrons from  $(x_1, y_1, z_1), (x_2, y_2, z_2), \dots$  to 1, 2... the wave function is then represented by  $\Psi(1, 2, \dots, N)$ , and  $V(1, 2, \dots, N)$  contains the potential energy of each electron in the field of the nucleus together with interaction terms representing the mutual repulsion of the electrons. This partial differential equation cannot be solved in closed form, that is to give formulae for wave functions and energy levels, even for the helium atom. But highly developed approximation methods yield numerical values of the energy in essentially perfect agreement with experiment (1 part in 50,000), which leaves little doubt of the general validity of the wave equation itself.

When approximate solutions are extended to heavier atoms and to molecules, the accuracy is rather lower (e.g. 1 to 2%). The most fruitful approximation method is that of Hartree (1928), later justified and refined by Slater (1930) and Fock (1930). This is suggested by first neglecting the electron repulsion and observing that the probability function  $P(1, 2, \dots, N)$  must then be approximated by the product  $P_1(1) P_2(2) \dots P_N(N)$ , for then the probability of any configuration of the electrons is a product of the probabilities of  $N$  independent events. Since  $P = \Psi^2$ , this means the many-electron wave function must also be a product.

$$\Psi(1, 2, \dots, N) = \psi_1(1) \psi_2(2) \dots \psi_N(N),$$

in which electron 1 is described by orbital  $\psi_1$  and probability pattern  $P_1 = \psi_1^2$ , electron 2 by orbital  $\psi_2$  and probability pattern  $P_2 = \psi_2^2$ , and so on. Pictorially, each electron occupies its own orbital, as if it alone were being considered. The probability of finding electron 1 at a given point  $(x, y, z)$  is proportional to  $P_1(x, y, z)$ , that of finding electron 2 at the same point is proportional to  $P_2(x, y, z)$  and by addition the probability  $P$  of finding an electron (*i.e.* any of the  $N$  electrons) at the point  $(x, y, z)$  is

$$P(x, y, z) = P_1(x, y, z) + P_2(x, y, z) \dots + P_N(x, y, z).$$

Thus the probability density in the system, to this approximation, is obtained simply by pictorially superimposing contributions from individual electrons, each described by its own orbital. The orbitals  $\psi_1, \psi_2 \dots \psi_N$  are, however, not necessarily the orbitals of the one-electron problem in which all electrons but one are literally ignored, for it is possible to choose all the orbitals in such a way that the resultant wave function closely approaches the exact solution. These best orbitals then represent the motion of an electron in an *effective* field. This is the Hartree field produced by the nucleus together with the remaining electrons, severally regarded as a smeared-out negative charge with a density equal to that of its probability function.

Certain restrictions are imposed on this picture by the fact that electrons are indistinguishable and by the existence of electron spin. Indistinguishability implies that  $P(1, 2 \dots N)$  shall be unchanged in value if the positions of any two particles are interchanged, and this in turn implies that  $\psi$  can at most change sign. For electrons, the wave function must be an anti-symmetric sum of products,

$$C[\psi_1(1)\psi_2(2)\psi_3(3)\dots\psi_N(N) - \psi_1(2)\psi_2(1)\psi_3(3)\dots\psi_N(N) + \dots]$$

whose sign reverses in any interchange (the constant  $C$  being chosen to normalise the probability function so that the chance of finding all particles somewhere is unity). Fortunately, this does not destroy the simplicity of the picture; the electron probability density  $P(x, y, z)$  is given by exactly the same sum-rule as for a single product. But there is now a fundamental restriction on the choice of orbitals. It might have been expected that every electron added to a nucleus would, in the lowest energy or ground state, be described by the lowest energy solution of the one particle wave equation. However the requirement of antisymmetry rules out this possibility because an antisymmetric  $\Psi$  vanishes if any two orbitals (e.g.  $\psi_1, \psi_2$  above) are identified. The orbitals occupied by the electrons must therefore all be different and in the ground state the tendency will be for  $N$  electrons to occupy the first  $\frac{1}{2}N$  orbitals, in ascending energy order, of the one-electron problem.

The existence of spin calls for a further slight modification. An orbital such as  $\psi_1$  describes the spatial distribution of an electron in a given energy state. If, in addition to given energy, a particle has one of two given spin components, this must also be indicated in its orbital description by adding a factor  $\alpha$ , which is unity if the particle has spin  $s_z = \frac{1}{2}$  and vanishes otherwise, or  $\beta$ , which is likewise unity or 0 according as  $s_z = -\frac{1}{2}$  or not. The set of orbitals is therefore in effect duplicated, becoming  $\psi_1\alpha, \psi_1\beta, \psi_2\alpha, \psi_2\beta \dots$ . At the same time  $\psi_1\alpha$  and  $\psi_1\beta$ , having the same spatial part  $\psi_1$ , lead to identical contributions to the electron density.

#### *Wave mechanical form of the exclusion principle*

The effect of indistinguishability, which denies the occupation of two orbitals which are alike in every respect (including now the spin), may consequently be stated in modified form. Any orbital  $\psi$  can be empty or occupied by either 1 or 2 electrons, appearing once with each spin factor in the second instance, but not by more than 2. The conclusion is that the electron density is of the form

$$P(x, y, z) = n_1 P_1(x, y, z) + n_2 P_2(x, y, z) + \dots n_N P_N(x, y, z),$$

where each of the 'occupation numbers'  $n_1, n_2, \dots$  may be 1 or 2, and an orbital is said to be 'filled' when it is 2. This is the wave-mechanical form of the Pauli exclusion principle.

### Electronic configurations of atoms

In the ground states of atoms, the lowest energy orbitals are doubly occupied but some of those of higher energy, which may be degenerate, may be only singly occupied. Later it will be seen that the occupied orbitals of highest energy are the *valence orbitals*, responsible for the chemical behaviour of the atom. Whereas the lower energy orbitals are tightly localised about the nucleus, the higher ones are much more diffuse, and when a whole set of orbitals is occupied the resultant electron density falls into 'shells' (Fig. 30), giving the wave-mechanical analogue of the

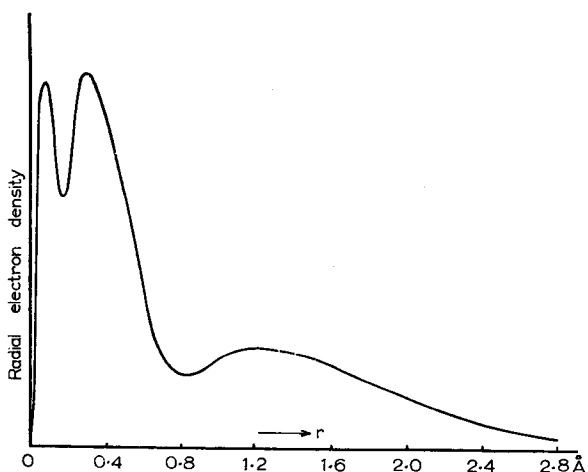


Fig. 30. Shell structure. Charge distribution in argon (after Hartree).

shells of Bohr theory. The shells are determined by the *principal* quantum number  $n$ , and orbitals in the individual shells are distinguished by the *subsidiary* quantum numbers  $l$  and  $m_l$ . (When the orbitals are not strictly hydrogen-like,  $n$  can still be defined as the number of nodes in an orbital minus one). This classification is general, depending only on the spherical symmetry of the system, but it must be stressed that orbitals in the same shell but with different  $l$  values do not have quite the same 'spread', and for  $n \geq 3$  the division into shells is not very clear-cut.



*Departures from the hydrogen-like form*

The nature of departures from the hydrogen-like form must now be discussed. It is the essence of the Hartree method that each orbital describes one electron in the field of the nucleus *and* all the other electrons (each regarded as 'smeared out' according to its orbital). Thus when there are two electrons in a 1s orbital and one in a 2s orbital, outside a nucleus of charge  $+3e$ , the 2s electron will 'feel', roughly speaking, an effective nuclear charge of little more than  $+1e$ . The simplest way of improving hydrogen-like orbitals, in order to take into account electron repulsion, is to use 'screening rules' (Slater, 1931) to estimate an effective nuclear charge for each orbital. In better approximation, the orbitals are obtained by numerical solution of the equations given by Hartree and Fock. But since each depends, through the field arising from the charge distribution, upon the forms of *all* the occupied orbitals, tedious repetition is necessary to get a *self-consistent field*. Fortunately, the main features of atomic orbitals can be understood in terms of the screening due to various groups of electrons and the non-Coulombic form of the resultant field. In particular, this is responsible for a separation of the energy levels of orbitals in the same shell but with different  $l$  values, the order becoming  $s < p < d < f \dots$

*Estimating the effective nuclear charge*

The effective nuclear charge,  $Z^*$ , acting on an electron is given by  $Z^* = Z - \sigma$ , where  $Z$  is the atomic number and  $\sigma$  is a screening constant.

To determine  $\sigma$ , divide the electrons into the respective orbital groups:

1s  
2s and 2p  
3s and 3p  
3d  
4s and 4p  
4d  
4f  
5s and 5p

Then  $\sigma$  is the sum of the contributions:

- (a) Zero from any orbital group outside the one considered.
- (b) 0.35 in general, but 0.30 in the case of the 1s, from every other electron in the orbital group considered.
- (c) 0.85 from every electron in the quantum level immediately below (nearer to the nucleus) than the electron considered, and 1.00 from every electron in levels still nearer the nucleus, provided that the electron considered is in an s or a p orbital. If the electron considered is in a d or f

orbital, every electron in lower orbital groups contributes 1 towards the value of  $\sigma$ .

Thus for an electron in the 3s or 3p shell in silicon  $1s^2, 2s^2, 2p^6, 3s^2 3p^2$ . ( $Z = 14$ )

$$\begin{aligned}\sigma &= 3 \times 0.35 \text{ (for the 3 other electrons in 3s and 3p)} \\ &\quad + 8 \times 0.85 \text{ (for the 8 electrons in 2s and 2p)} \\ &\quad + 2 \times 1 \text{ (for the 2 electrons still nearer the nucleus)} \\ &= 9.85\end{aligned}$$

$$\therefore Z^* = Z - \sigma = 4.15$$

The method is useful for orbitals with principle quantum numbers up to 4, but for orbitals of higher energy it is progressively less accurate.

#### *Prediction of the electron configurations of simple unexcited atoms*

It is now possible to predict the electron configurations of simple atoms by adding  $Z$  electrons to a central nucleus, filling the available orbitals in ascending energy order in accordance with the Pauli principle. This is because the total electronic energy is a sum of the characteristic energies of the occupied orbitals (counted once or twice according to occupation) along with a smaller electron interaction term. Consequently the normal or *ground state* occurs when the electrons occupy the orbitals of lowest energy, with not more than 2 in each. Thus, the atoms from H to B have electron configurations which may be indicated by H ( $1s^1$ ), He ( $1s^2$ ), Li ( $1s^2 2s^1$ ), Be ( $1s^2 2s^2$ ), B ( $1s^2 2s^2 2p^1$ ). At this point a difficulty arises. In the next atom, carbon, there are 2 electrons outside the  $1s^2 2s^2$  group, but there are three 2p orbitals all of equal energy into which the electrons may go. This ambiguity is admitted by writing the configuration C ( $1s^2 2s^2 2p^2$ ) without specifying which of the equivalent 2p orbitals are occupied. Corresponding to such a configuration there are several states whose energies differ somewhat. We are interested primarily in the lowest of these, which is the ground state, and in its spectroscopic character. Before proceeding further in 'building up' the atoms of the Periodic Table it is therefore necessary to classify the states associated with a given electron configuration and to decide which is lowest.

### Spectroscopic states

After specifying the configuration in terms of the occupation of orbitals of given  $(n, l)$ , without reference to  $m_l$ , which labels different equivalent orbitals, the possible states may be classified according to angular momentum. We shall therefore summarise and extend the vector scheme (p. 66), using the carbon  $1s^2 2s^2 2p^2$  configuration in illustration.

- (1) s, p, d, ... orbitals describe electrons with angular momentum quantum numbers 0, 1, 2 ... For any value of  $l$  there are  $2l + 1$  equivalent orbitals, corresponding to  $z$ -components of  $m_l = l, l - 1, \dots -l$ .
- (2) Each electron has a spin with quantum number  $s = \frac{1}{2}$  and possible  $z$ -components  $m_s = +\frac{1}{2}, -\frac{1}{2}$ .
- (3) The orbital and spin vectors may be separately combined to give *total* angular momenta with orbital and spin quantum numbers (for 2 electrons)  $L = (l_1 + l_2), (l_1 + l_2 - 1) \dots (l_1 - l_2)$  and  $S = s_1 + s_2 (= 1), s_1 + s_2 - 1 (= 0)$ ; and  $z$ -components  $M_L = L, L - 1, \dots -L$  and  $M_S = S, S - 1, \dots -S$ . The possibilities are indicated, for carbon, in Fig. 31. The greatest possible  $L$  is simply the maximum value of

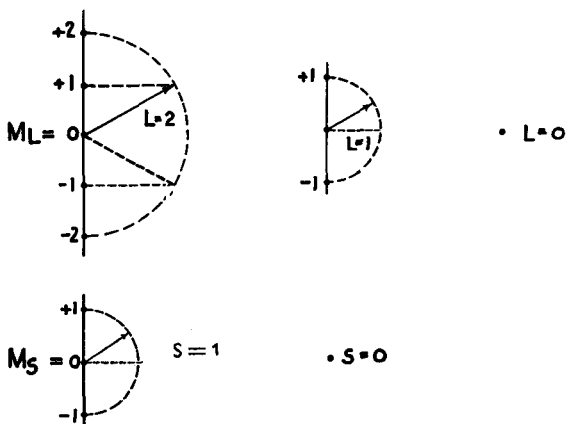


Fig. 31. Resultant orbital and spin angular momentum for configuration  $2p^2$ .

$M_L$ , which is  $m_{l_1} + m_{l_2}$ ; but the latter has a maximum value  $l_1 + l_2$  and the greatest possible  $L$  is thus  $L = l_1 + l_2 = 2$ . The other  $L$  values correspond to different couplings in which  $M_{L(\max)}$  and hence  $L$  are reduced by unit steps. The allowed total angular momenta therefore correspond to  $L = 2, 1, 0$ , each with its  $2L + 1$  possible  $z$ -components. Atomic states are classified according to  $L$  value in essentially the same way as orbitals in terms of  $l$  value. Those in which  $L$  has the value 0, 1, 2, 3, ... are called S, P, D, F, ... states. For instance, S, P and D states are associated with the  $1s^2 2s^2 2p^2$  configuration of carbon

- (4) The total orbital angular momentum and the total spin, described by  $L$  and  $S$ , may be coupled exactly as in the one-electron case (p. 66). Their resultant total angular momentum is described by a quantum number  $J$ , with possible values  $L + S, L + S - 1, \dots L - S$ ; and for each  $J$  there are  $2J + 1$  possible  $z$ -components  $M_J = J, J - 1, \dots -J$ .

There are  $2S + 1$  possible couplings of  $L$  and  $S$  if  $S < L$  (or  $2L + 1$  if  $L < S$ ) and, since these introduce slightly different coupling energies, a state of given  $L$  is always a *multiplet*, with multiplicity  $2S + 1$  (or  $2L + 1$  if  $L < S$ ). Since for carbon,  $S = 1$  or  $0$ , we expect S, P and D states of multiplicity 1 and 3 to appear. It is customary to indicate these singlet and triplet states by  $^1S$ ,  $^1P$ ,  $^1D$  and  $^3S$ ,  $^3P$ ,  $^3D$ . Not all these states occur. Thus  $^3D$  would require two electrons in the same orbital with the same spin and this, by the Pauli principle, is inadmissible. In fact only  $^1S$ ,  $^3P$  and  $^1D$  are found. The individual states of a multiplet may be labelled (when necessary) by adding their  $J$  values as subscripts. The states comprising the triplet P level of carbon are  $^3P_2$ ,  $^3P_1$ ,  $^3P_0$ . States of given  $J$  are not resolved further (according to  $M_J$ ) unless a magnetic field is applied, when each shows a Zeeman splitting into  $2J + 1$  components.

By the use of this vector model it is possible to recognise and classify observed atomic states and to associate them with definite electron configurations. It will be noticed that mention has not been made of the doubly occupied orbitals of closed shells; these together give a zero contribution to the angular momenta, and consequently spectral data provide direct information about the outer, singly-occupied orbitals. Later this will be seen to be of the utmost importance (p. 95). Briefly, the valency of an atom, that is the number of *covalent* bonds in which it can participate (p. 97), is the number of singly occupied outer orbitals, and this is shown by the fact that a configuration with  $n$  such orbitals gives rise to states with a maximum multiplicity of  $p = 2S + 1 = n + 1$ . Hence the valency of an atom whose electron configuration gives states of maximum multiplicity  $p$  is  $p - 1$ . Even at this stage, important conclusions can be drawn. Thus, the lowest energy configuration of carbon is observed to give states of maximum multiplicity  $p = 3$ . Carbon is not however bivalent; and the implication is that the normal quadrivalence must in some way involve an excitation, from a ground state with *two* singly-occupied p orbitals (the theoretically expected  $1s^2 2s^2 2p^2$ ) to an excited state with *four* (namely,  $1s^2 2s 2p^3$ ). The energy order of the various states cannot be predicted from the vector model, but rules are available for this purpose.

Finally, it must be remembered that the vector model gives only an approximate description of the electronic structure. According to (4) the present picture is one of  $L$ - $S$  (or Russell-Saunders) coupling. For heavy atoms this picture is often inadequate, the  $L$ - $S$  coupling being broken (*cf.* p. 87).

### Hund's rules. The Landé $g$ -factor

The order of the energy levels arising from any configuration can be predicted, when  $L$ - $S$  coupling is operative, by rules proposed by Hund (1925):

- (1) The state of maximum multiplicity lies lowest. The electrons then occupy equivalent orbitals singly, as far as possible, with parallel spins.
- (2) For a given multiplicity, the state of maximum  $L$  lies lowest.
- (3) For a given  $S$  and  $L$ , the state of maximum or minimum  $J$  lies lowest, according as the set of equivalent orbitals is more or less than half filled. When the set is exactly half-filled  $J$  is equal to  $S$ .

The first two rules are of greatest chemical importance. From them it follows immediately that the lowest energy states of the carbon atom lie in the order  $^3P$ ,  $^1D$ ,  $^1S$ ; carbon has a  $^3P$  ground state.

Ground states for the elements following carbon are tabulated in Table 5.

TABLE 5  
GROUND STATES FOR ELEMENTS 7 TO 10

	<i>Electronic configuration</i>	<i>Unpaired electrons</i>	$S$	$2S + 1$	$L$	$J$	<i>Spectroscopic State</i>
N	$1s^2 2s^2 2p^3$	3	$3/2$	4	0	$3/2$	$^4S_{3/2}$
O	$1s^2 2s^2 2p^4$	2	1	3	1	2	$^3P_2$
F	$1s^2 2s^2 2p^5$	1	$\frac{1}{2}$	2	1	$3/2$	$^2P_{3/2}$
Ne	$1s^2 2s^2 2p^6$	0	0	1	0	0	$^1S_0$

At a later stage (p. 87) we shall also need to know precisely what magnetic moment is associated with an atom in a given angular momentum state, this determining the Zeeman splitting of the levels. The magnetic moment is proportional to the angular momentum, but experiment indicates that the proportionality factor is twice as great for spin as for orbital angular momentum. When both contributions occur, the formula for the effective magnetic moment,  $\mu$ , is consequently less simple: it is

$$\mu = g \sqrt{J(J+1)} \mu_B$$

where

$$g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)},$$

and

$$\mu_B = \frac{e\hbar}{4\pi mc} = 9.273 \times 10^{-21} \text{ erg/gauss}$$

is the *Bohr magneton*. This  $g$ -factor was first proposed on experimental grounds by Landé and later derived theoretically.

### The 'Aufbau' principle and the Periodic Table

It is now possible to work through the Periodic Table, predicting ground state electronic configurations and spectroscopic states, by adding  $Z$  electrons to each successive nucleus, filling the available orbitals in ascending energy order and observing the Pauli principle and Hund's rules. The principles already discussed, upon which this process is based, are known collectively as the *aufbau principle*. It is, of course, necessary to know the energy order of the orbitals, but fortunately their relative positions change gradually and systematically throughout the Periodic Table. The variation which exists is caused mainly by the screening effect of electrons near the nucleus and is clearly revealed in the ionisation energies, which are numerically equal to the orbital energies. Thus, in filling the shell with principal quantum number  $n = 2$ , we start with Li, the  $1s^2$  'core' of which

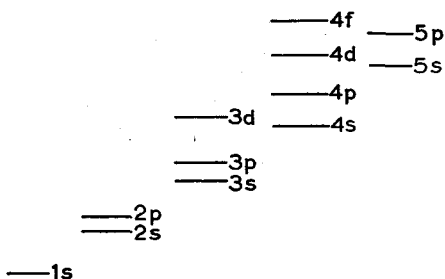


Fig. 32. Energy levels in a heavy atom.

has an effective nuclear charge  $3 - 2(0.85) = +1.30 e$  and end with Ne, in which  $2s$  and  $2p$  electrons move under the influence of an effective nuclear charge of  $10 - 2(0.85) - 7(0.35) = +5.85 e$  (Slater's rules, p. 70). Accordingly, ionisation energies tend to increase as each shell is filled, increasing from  $I = 5.4 eV$  for Li to  $I = 21.6 eV$  for Ne. For the same reason, a second ionisation is much more difficult to achieve than the first. On the other hand, nearly filled shells usually accept an extra electron quite readily owing to the relatively small change in screening which results. Thus, F readily accepts one electron but  $F^-$  has a closed shell and repels a second electron which could only be accommodated outside; consequently fluorine forms only a singly-charged anion.

The energies associated with the occupied orbitals of a typical heavy atom follow the trend shown in Fig. 32. The separations of the energies depend upon atomic number, but the *order* of the levels rarely differs from that shown. It should be noticed that the energy levels associated with different shells overlap after  $n = 2$ . For instance, the  $4s$  orbital has a lower

energy than the 3d, and this is a general feature of the atoms of the fourteen elements from nitrogen to calcium inclusive. It is simply a result of the different shapes of the 4s and 3d orbitals and their different degrees of penetration into the inner shells, a 4s electron spending considerably more time within the *L*-shell (where screening is relatively small and binding high) than a 3d electron. The fact that the order of the energy levels is preserved in going from one atom to another, with only a few exceptions, means that the order of filling, as *z* is increased and electrons are added, is pre-determined. This order is indicated in Fig. 33. The diagram is slightly over-simplified; in fact one 5d electron is found in lanthanum before the 4f orbitals begin to fill, and there are one or more 6d electrons in actinium (and possibly in Th and Pa) before any 5f. Fig. 34 gives a more detailed

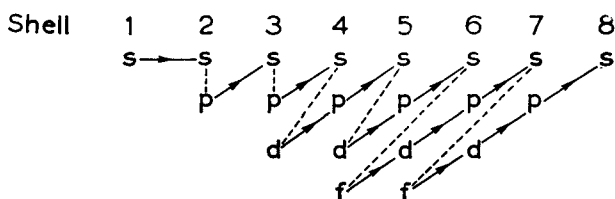


Fig. 33. Order of filling orbitals.

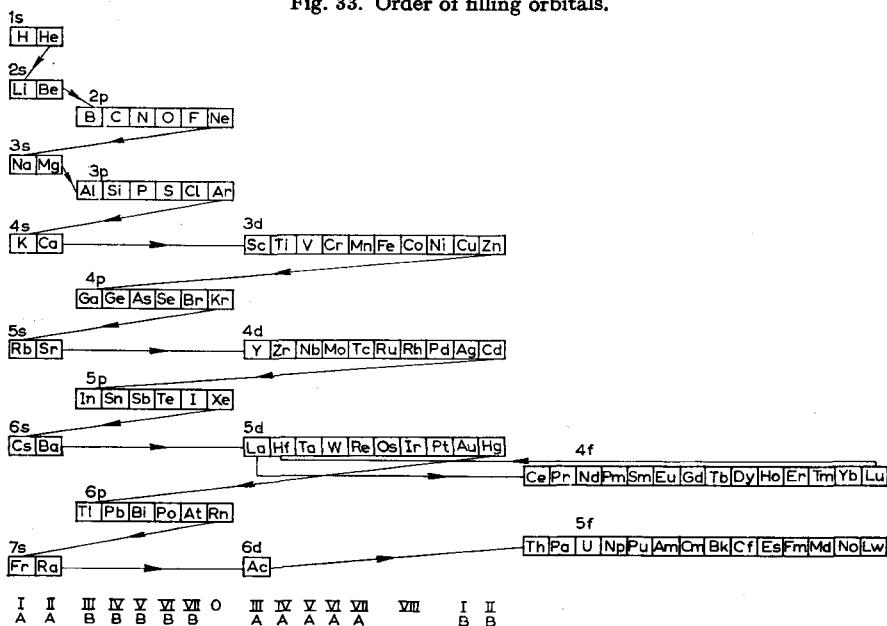
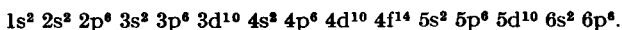


Fig. 34. The 'Aufbau' principle.

picture of the building-up process, but again the order is not adhered to strictly. A chromium atom in its ground state has five 3d electrons and only one 4s, and a copper atom has ten 3d electrons and only one 4s. This is because a half-filled or a completely-filled d-shell, that is a set of equivalent orbitals, gives a particularly stable state.

Various types of structure can be distinguished:

(i) *The group O gases.* In the gaseous elements He, Ne, Ar, Kr, Xe, Rn all the sets of p, d, f orbitals which occur are filled to capacity, radon for example having the structure



The  $ns^2 np^6$  arrangement is common to all these gases except helium and confers particularly great stability on their atoms. Such atoms have spherically symmetrical electron distributions and  $^1S$  ground states.

(ii) *The 'representative' elements forming Gps. IA, IIA and Gps. IIB to VIIB.* These elements have atoms in which the singly occupied orbitals are confined to the outermost shell. All the underlying levels are filled to capacity. This type of electronic structure is found in all the non-metals.

(iii) *The transition elements forming Gps. IIIA through to IB.* In these elements, of which there is a *first, second and third series*, the hitherto empty d orbitals of an inner shell begin to fill. The elements would be expected to have an outer electronic structure ranging from  $(n-1)d ns^2$  to  $(n-1)d^9 ns^2$ , but they do not show a rigid adherence to the  $ns^2$  arrangement. Chromium and copper, already mentioned, and gold have reasonably stable  $ns^1$  states. These  $ns^1$  states also occur in the second transition series; for instance, although zirconium has  $4d^2 5s^2$ , its successor, niobium, has  $4d^4 5s^1$ , and in the following elements the d orbitals continue to fill until ruthenium with a  $4d^8 5s^1$  structure is reached. Palladium differs from the rest in not having an electron in the 5s level. The third transition series is regular, but is interrupted between La and Hf by the development, within it, of an inner transition series—the lanthanides.

(iv) *The inner transition elements.* These comprise two series of elements: the lanthanides and actinides. They have not only unfilled d orbitals, but also underlying, unfilled f orbitals. The f orbitals fill up almost regularly as the two series develop (pp. 78–80). Again, as for d orbitals, configurations in which all the f orbitals are either singly or doubly occupied are particularly stable. Thus the  $4f^7$  and  $4f^{14}$  shells found in Eu and Yb tend to persist in the elements which follow them, for instance Gd has  $4f^7 5d^1$  rather than  $4f^8$ . The similarity of the configurations of the outermost energy levels causes the transition elements, and particularly the inner transition elements, to have very similar properties (p. 554).



### Electron configurations of the elements

Ground states of the free atoms

Atomic No.	Element	K		L		M			N				
		1s	2s	2p	3s	3p	3d	4s	4p	4d	4f		
1	H	1											
2	He	2											
3	Li	2	1										
4	Be	2	2										
5	B	2	2	1									
6	C	2	2	2									
7	N	2	2	3									
8	O	2	2	4									
9	F	2	2	5									
10	Ne	2	2	6									
11	Na	2	2	6	1								
12	Mg	2	2	6	2								
13	Al	2	2	6	2	1							
14	Si	2	2	6	2	2							
15	P	2	2	6	2	3							
16	S	2	2	6	2	4							
17	Cl	2	2	6	2	5							
18	Ar	2	2	6	2	6							
19	K	2	2	6	2	6				1			
20	Ca	2	2	6	2	6				2			
21	Sc	2	2	6	2	6	1			2			
22	Ti	2	2	6	2	6	2			2			
23	V	2	2	6	2	6	3			2			
24	Cr	2	2	6	2	6	5			1			
25	Mn	2	2	6	2	6	5			2			
26	Fe	2	2	6	2	6	6			2			
27	Co	2	2	6	2	6	7			2			
28	Ni	2	2	6	2	6	8			2			
29	Cu	2	2	6	2	6	10			1			
30	Zn	2	2	6	2	6	10			2			
31	Ga	2	2	6	2	6	10			2	1		
32	Ge	2	2	6	2	6	10			2	2		
33	As	2	2	6	2	6	10			2	3		
34	Se	2	2	6	2	6	10			2	4		
35	Br	2	2	6	2	6	10			2	5		
36	Kr	2	2	6	2	6	10			2	6		
		2	8		18								

**Electron configurations of the elements (continued)**

Ground states of the free atoms

Atomic No.	Element	K	L	M	N				O				P	
					4s	4p	4d	4f	5s	5p	5d	5f	6s	
37	Rb	2	8	18	2	6			1					
38	Sr	2	8	18	2	6			2					
39	Y	2	8	18	2	6	1		2					
40	Zr	2	8	18	2	6	2		2					
41	Nb	2	8	18	2	6	4		1					
42	Mo	2	8	18	2	6	5		1					
43	Tc	2	8	18	2	6	6		1					
44	Ru	2	8	18	2	6	7		1					
45	Rh	2	8	18	2	6	8		1					
46	Pd	2	8	18	2	6	10							
47	Ag	2	8	18	2	6	10		1					
48	Cd	2	8	18	2	6	10		2					
49	In	2	8	18	2	6	10		2	1				
50	Sn	2	8	18	2	6	10		2	2				
51	Sb	2	8	18	2	6	10		2	3				
52	Te	2	8	18	2	6	10		2	4				
53	I	2	8	18	2	6	10		2	5				
54	Xe	2	8	18	2	6	10		2	6				
55	Cs	2	8	18	2	6	10		2	6			1	
56	Ba	2	8	18	2	6	10		2	6			2	
57	La	2	8	18	2	6	10		2	6	1		2	
58	Ce	2	8	18	2	6	10	1	2	6	1		2	
59	Pr	2	8	18	2	6	10	2	2	6	1		2	
60	Nd	2	8	18	2	6	10	3	2	6	1		2	
61	Pm	2	8	18	2	6	10	4	2	6	1		2	
62	Sm	2	8	18	2	6	10	5	2	6	1		2	
63	Eu	2	8	18	2	6	10	6	2	6	1		2	
64	Gd	2	8	18	2	6	10	7	2	6	1		2	
65	Tb	2	8	18	2	6	10	8	2	6	1		2	
66	Dy	2	8	18	2	6	10	9	2	6	1		2	
67	Ho	2	8	18	2	6	10	10	2	6	1		2	
68	Er	2	8	18	2	6	10	11	2	6	1		2	
69	Tm	2	8	18	2	6	10	12	2	6	1		2	
70	Yb	2	8	18	2	6	10	13	2	6	1		2	
71	Lu	2	8	18	2	6	10	14	2	6	1		2	
					32									

**Electron configurations of the elements** (*continued*)

Ground states of the free atoms

Atomic No.	Element	K	L	M	N	O				P			Q
						5s	5p	5d	5f	6s	6p	6d	7s
72	Hf	2	8	18	32	2	6	2		2			
73	Ta	2	8	18	32	2	6	3		2			
74	W	2	8	18	32	2	6	4		2			
75	Re	2	8	18	32	2	6	5		2			
76	Os	2	8	18	32	2	6	6		2			
77	Ir	2	8	18	32	2	6	7					
78	Pt	2	8	18	32	2	6	9		1			
79	Au	2	8	18	32	2	6	10		1			
80	Hg	2	8	18	32	2	6	10		2			
81	Tl	2	8	18	32	2	6	10		2	1		
82	Pb	2	8	18	32	2	6	10		2	2		
83	Bi	2	8	18	32	2	6	10		2	3		
84	Po	2	8	18	32	2	6	10		2	4		
85	At	2	8	18	32	2	6	10		2	5		
86	Rn	2	8	18	32	2	6	10		2	6		
87	Fr	2	8	18	32	2	6	10		2	6		1
88	Ra	2	8	18	32	2	6	10		2	6		2
89	Ac	2	8	18	32	2	6	10		2	6	1	2
90	Th	2	8	18	32	2	6	10		2	6	2	2
91	Pa	2	8	18	32	2	6	10	2	2	6	1	2
92	U	2	8	18	32	2	6	10	3	2	6	1	2
93	Np	2	8	18	32	2	6	10	4	2	6	1	2
94	Pu	2	8	18	32	2	6	10	6	2	6		2
95	Am	2	8	18	32	2	6	10	7	2	6		2
96	Cm	2	8	18	32	2	6	10	7	2	6	1	2
97	Bk	2	8	18	32	2	6	10	8	2	6	1	2
98	Cf	2	8	18	32	2	6	10	10	2	6		2
99	Es	2	8	18	32	2	6	10	11	2	6	2	
100	Fm	2	8	18	32	2	6	10	12	2	6		2
101	Md	2	8	18	32	2	6	10	13	2	6		2

**The Periodic Classification**

The above considerations give rise to the Periodic Law, a general regularity in the succession of properties of the elements, established empirically by Mendeleev. They determine the modern form of the Periodic Table (Table 6).

TABLE 6  
THE PERIODIC TABLE

The First Three Periods								
<i>s orbitals filling</i>			<i>p orbitals filling</i>					
Group	I	II	III	IV	V	VI	VII	O
Period								
1	H						(H)	He
2	Li	Be	B	C	N	O	F	Ne
3	Na	Mg	Al	Si	P	S	Cl	Ar

All the Periods																	
<i>d orbitals filling</i>							<i>p orbitals filling</i>										
Group	I	II	IIIA	IVA	VA	VIA	VIIA	VIII	IB	IIB	IIIB	IVB	VB	VIB	VII B	O	
Period																	
1	H														(H)	He	
2	Li	Be									B	C	N	O	F	Ne	
3	Na	Mg									Al	Si	P	S	Cl	Ar	
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn				Kr	
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	Ga	Ge	As	Se	Br
6	Cs	Ba	La*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	In	Sn	Sb	Te	I
7	Fr	Ra	Ac†										Tl	Pb	Bi	Po	At

*f orbitals filling*

6	*	Lanthanides	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
7	†	Actinides	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lw

This particular tabulation is one of many that have been proposed and has the advantage over some of affording quick reference to the periods (horizontal with Arabic numerals) and the groups (vertical with Roman numerals) and of showing the relation of the transition elements to the rest. Major features to note are:

(i) There are only two elements, hydrogen and helium, in the first period. Two electrons are sufficient to fill the first quantum level. Because hydrogen can form both a cation and an anion it is placed at the head of Group I and also, in parenthesis, at the head of Group VII. Helium falls naturally in Gp. 0 above neon.

(ii) Gp. 0, the noble gases, lie between the halogens which give uninegative ions and the alkali metals which give unipositive ions.

(iii) Gps. IA, IIA and Gps. IIB to VIIB are the non-transition elements and they flank the transition elements which occupy the centre of the Table. They include all the non-metals, except the noble gases.

(iv) The transition metals include the lanthanides and actinides and are all in the centre of the Periodic Table from Periods 4 to 7. Of the inner-transition elements only lanthanum and actinium actually appear in the Table, to show where their respective series begin.

The Periodic Table is a useful basis from which to begin a comparison of the properties of individual elements because those elements with similar electronic configurations (pp. 78–80) are found in the same groups. For example, the configuration of the atoms C, Si, Ge, Sn, Pb, excluding the filled inner shells, are  $2p^2$ ,  $3p^2$ ,  $4p^2$ ,  $5p^2$  and  $6p^2$  respectively; all the elements have the same spectroscopic ground state as carbon, namely  $^3P$ , and the similarity of their outermost structure is responsible for a family relationship in chemical properties.

### Ionisation energies

The energy required to withdraw an electron from an atom against the attraction of the nuclear charge is the first *ionisation energy* of the atom.

The value of the ionisation energy depends on:

(i) the quantum level of the electron of highest energy in the ground state of the atom

(ii) the effective nuclear charge acting on that electron.

The first ionization energies of elements 1 to 36 (H to Kr) are shown diagrammatically in Fig. 35.

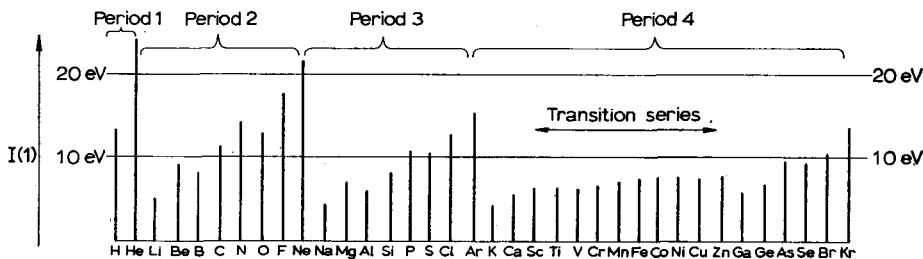


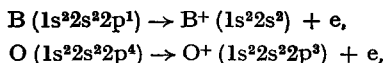
Fig. 35. First ionisation energies in Periods 1 to 4.

Periodicity in the values of the first ionisation energies is evident; the changes arise from the following causes:

(i) Much energy is required to remove an electron from a completely filled outer quantum shell, for instance, from the atom of a Gp. 0 gas.

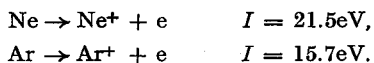
(ii) The first ionisation energy of an alkali metal is low because the outer s electron is heavily screened from the  $Z$  positive charges on the nucleus by  $Z - 1$  electrons in relatively compact orbitals. The screening constant is high and the effective nuclear charge is low.

(iii) The effective nuclear charge on the outer shell increases through a period and with it the first ionisation energy also increases, but the upward trend is not smooth. When the removal of an electron leaves an ion with a spherically symmetrical shell, for instance in the following examples:



the energy required is usually somewhat less than the ionisation energy of the preceding element. The 'staggered' rise in ionisation energies through a short period is supporting evidence for the existence of s- and p-type orbitals.

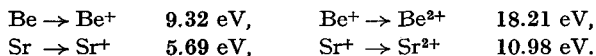
(iv) For a particular group, an electron is more easily withdrawn from an atom in a later period than from an atom in an early period:



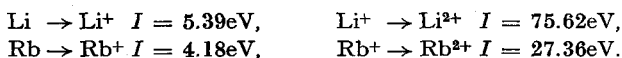
In this example the ionisation energy is lower in the second case largely because the outermost electrons of Ar belong to a higher quantum level, and therefore have a higher energy, than those of Ne.

### *Second ionisation energies*

The energy required to remove a second electron from a unipositive ion is the second ionisation energy. For Gp. IIA metals it is about twice the first ionisation energy.



This difference is because the effective nuclear charge has been increased by the removal of the first electron. For Gp. IA elements the second ionisation energies are very large indeed. For instance:



This is because of (a) the lower energy-state and (b) the far weaker shielding of the electrons in the complete  $s^2 p^6$  shell.

For transition and inner transition elements there is little variation ( $7.4 \pm 0.6$  eV for a transition series and  $5.9 \pm 0.3$  for the lanthanides). The metals following the lanthanides are exceptions to the general rule of decreasing ionisation energy down a group. In them the screening effect of the rather diffuse d shell is outweighed by the increasing nuclear charge.

Ag	7.87 eV	Cd	8.99 eV
Au	9.22 eV	Hg	10.43 eV

Elements of B subgroups have higher ionisation energies than those of the corresponding A subgroups.

K	4.34 eV	Cu	7.72 eV
Ca	6.11 eV	Zn	9.39 eV

The increased binding of the electron due to the penetration of its orbital into orbitals nearer the nucleus is greater with 18 than with 8 electrons immediately beneath it, since it comes into the region of a positive charge greater by 10 units.

### Electron affinities

The energy released when an extra electron is taken up by an atom is its electron affinity, *A*. This is generally estimated indirectly by applying the Born-Haber cycle to ionic compounds (p. 103).

In the halogens, except for fluorine, the smaller the atom the greater the electron affinity and the ease of anion formation:

F	3.74,	Cl	4.02,	Br	3.78,	I	3.44 eV.
---	-------	----	-------	----	-------	---	----------

In Gp. VI the values for two electrons are

O	-7.28	S	-3.44	Se	-4.21 eV.
---	-------	---	-------	----	-----------

Once an electron has been received by an atom the uninegative ion which is formed repels further electrons; hence the negative affinities displayed by oxide, sulphide and selenide binegative ions.

### Magnetic properties

A few materials, termed *ferromagnetic*, attract a magnetic field very strongly and can themselves become magnetic, for example iron, cobalt alloys, magnetite. With these we are not further concerned here.

Other substances are *diamagnetic*, tending to move to the weakest part of a non-uniform magnetic field, or *paramagnetic*, tending to move to the strongest part (Fig. 36).

The *magnetic permeability*,  $B/H$ , is the ratio of the flux,  $B$ , (*i.e.* number of lines of force per unit cross section) in the substance to that,  $H$ , in a vacuum. The ratio is greater than unity for a paramagnetic substance and less, but not much less, than unity for a diamagnetic one (Fig. 37).

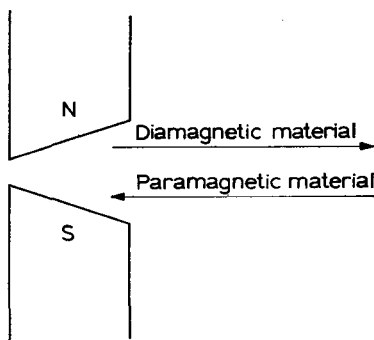


Fig. 36. Movement of diamagnetic and paramagnetic materials in a non-uniform field.

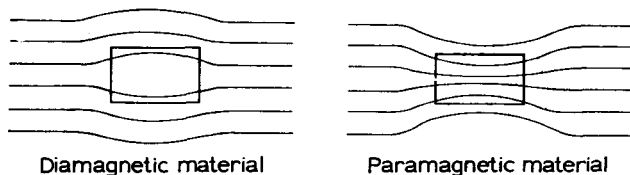


Fig. 37. Lines of force through diamagnetic and paramagnetic materials.

The *volume susceptibility*,  $\kappa$ , is related to  $B/H$ :

$$B/H = 1 + 4\pi\kappa$$

A quantity  $\kappa/\rho = \chi$ , where  $\rho$  is the density, is the *gram susceptibility*, but in magnetochemistry the most useful quantities are  $\chi_M$ ,  $\chi_A$  and  $\chi_I$  the susceptibility for molecule, atom and ion respectively. These are obtained by multiplying the gram susceptibility by the molecular or atomic weight.

The value of  $\chi$  is independent of field strength. It may be found by many methods, for instance by suspending the material from a balance in a non-uniform magnetic field. A sample of powdered material, usually sealed in a glass tube, is suspended from a balance between the poles of a magnet. The lower end of the tube is in a strong field ( $\sim 10,000$  gauss) and the upper in a negligible field. The force exerted on the specimen is

$$\frac{1}{2} H^2 A \kappa$$

where  $\kappa$  is the volume susceptibility,  $H$  the field strength in gauss, and  $A$  the cross-sectional area of the sample in  $\text{cm}^2$ . The force is measured by first counterpoising the sample without the magnetic field and then adding



weights to restore the balance after the field has been applied. The volume susceptibility is given by:

$$\kappa = \frac{2g\Delta w}{H^2 A}$$

For strongly paramagnetic substances  $\Delta w$  may be several hundred mg when the cylindrical sample has a diameter of 5 to 10 mm, and an ordinary balance is sufficiently sensitive. For measurements on weakly paramagnetic materials a microbalance or electrodynamic balancing should be substituted.

### *Diamagnetism and paramagnetism*

The fact that an electron in an orbital produces a magnetic field proportional to its angular momentum has already been discussed. The application of an external field causes, in classical language, a precession which produces a field opposed to that originally applied and results in a negative susceptibility for all atoms. It is, however, almost completely obscured by the much stronger positive susceptibility when this is present. Thus observable negative susceptibility characterises a diamagnetic material; it increases numerically with atomic number, is always weak compared with paramagnetic susceptibility and is independent of temperature.

Paramagnetism, on the other hand, is restricted to certain materials and completely overshadows the relatively feeble diamagnetism also present. In general, paramagnetism arises from the presence of a permanent (*i.e.* not induced) magnetic moment associated with a state of definite angular momentum. The magnetic moment,  $\mu$ , arising from total angular momentum with quantum number  $J$  may be represented pictorially by a vector of length  $Jg\mu_B$ , where  $\mu_B$  is the Bohr magneton and  $g$  the Landé  $g$ -factor (p. 74), although, as usual, a strict analysis gives  $\sqrt{J(J+1)}$  instead of  $J$ . The components of magnetic moment along the field direction can take only the values  $M_J g$  ( $M_J = J, J-1, \dots, -J$ ) and when the field strength is  $H$  these  $(2J+1)$  energy levels are separated by intervals  $g\mu_B H$ .

For atoms in S states,  $L=0$ ,  $J=S$ , and therefore  $g=2$ ; but in all other states  $g < 2$ . Consequently observed  $g$  values indicate whether the paramagnetic moment arises from both orbital and spin momentum or from spin only. In the latter instance, observation of the maximum  $J$  arising from a given electron configuration indicates the number,  $n$ , of unpaired spins,  $J_{\max} = S_{\max} = \frac{1}{2} n$ .

Since the magnetic moment of an assembly of atoms depends on statistical averaging over all possible  $z$  components, thermal agitation opposing regular orientation, the relationship between  $\mu$  and the observed quantity  $\chi_A$  must

involve the temperature. For  $\mu H \ll kT$ , it can be shown that  $\chi_A \propto 1/T$  (Curie's law) and that  $\mu = 2.839 \sqrt{\chi_A T}$ . More accurately  $\chi_A \propto 1/(T - \theta)$ , a result due to Weiss, where  $\theta$  is the *Curie temperature* and is small for most paramagnetics. When other small effects are taken into account (e.g. the small opposing diamagnetism) magnetic moments determined in this way agree well with those inferred from spectroscopy.

### Paramagnetic ions

There are three principal types of paramagnetic ion.

- (i) The inner-transitional (lanthanides and actinides), in which the separation between states with different  $J$  values is large compared with  $kT$  (strong  $L$ - $S$  coupling). For these ions

$$\mu = g \sqrt{J(J+1)} \quad (\text{in Bohr magnetons}).$$

- (ii) The iron group, in which the orbital contribution to the magnetic moment is 'quenched', owing to the destruction of spherical symmetry by the strong field of neighbouring ions. This occurs only when the unpaired electrons occupy the outermost orbitals. The magnetic moment is calculated from the 'spin-only' formula with  $n$  singly occupied orbitals:

$$\mu_s = \sqrt{4S(S+1)} = \sqrt{n(n+2)}.$$

Thus for the  $\text{Fe}^{3+}$  ion, with a  $3d^5$  configuration,  $\mu = \sqrt{5(5+2)} = 5.9$  Bohr magnetons, in agreement with experiment.

- (iii) Ions in which the separation of states with different  $J$  values is small compared with  $kT$  (weak  $L$ - $S$  couplings). Here the orbital contribution is not quenched but is 'uncoupled' from the spin so that a resultant  $J$  does not occur. The resultant moment is

$$\mu_{s+L} = \sqrt{4S(S+1) + L(L+1)}.$$

The bivalent ions  $\text{Co}^{2+}$  and  $\text{Fe}^{2+}$  are of this type and the good agreement with experiment confirms that orbital angular momentum contributes to the permanent moment.

Finally, it must be stressed that Hund's rules (p. 74) (and indeed the whole  $L$ - $S$  coupling picture) do not generally apply well to heavy atoms. However, magnetic measurements confirm their approximate validity in the transition series Sc to Fe.

Table 7 shows the magnetic moments of some Period 4 transition-metal ions, calculated from the spin-only formula ( $\mu_s$ ) and from the formula in (iii) above ( $\mu_{s+L}$ ) and also as observed experimentally:

TABLE 7  
MAGNETIC MOMENTS OF SOME TRANSITION-METAL IONS

d-Shell occupancy	S	L	Spectroscopic symbol	$\mu_S$	$\mu_{S+L}$	Observed	Example
d <sup>1</sup>	1/2	2	${}^2D_{\frac{3}{2}}$	1.73	3.00	1.7–1.8	Ti <sup>3+</sup>
d <sup>2</sup>	1	3	${}^3F_2$	2.83	4.47	~ 2.8	V <sup>3+</sup>
d <sup>3</sup>	3/2	3	${}^4F_{\frac{3}{2}}$	3.87	5.40	~ 3.8	Cr <sup>3+</sup>
d <sup>4</sup>	2	2	${}^5D_0$	4.90	5.49	~ 4.9	Mn <sup>2+</sup>
d <sup>5</sup>	5/2	0	${}^6S_{\frac{5}{2}}$	5.92	5.92	~ 5.9	Fe <sup>3+</sup>
d <sup>6</sup>	2	2	${}^5D_4$	4.90	5.49	5.0–5.4	Fe <sup>2+</sup>
d <sup>7</sup>	3/2	3	${}^4F_{\frac{3}{2}}$	3.87	5.20	4.1–5.2	Co <sup>2+</sup>
d <sup>8</sup>	1	3	${}^3F_4$	2.83	4.47	2.8–4.0	Ni <sup>2+</sup>
d <sup>9</sup>	1/2	2	${}^2D_{\frac{3}{2}}$	1.73	3.00	1.7–2.2	Cu <sup>2+</sup>

### Electron spin resonance

#### General principles

Any atom or molecule with an incompletely paired system of electrons has a magnetic moment. In a magnetic field the moment acquires an interaction energy which depends upon its orientation relative to the field. In a field of about  $10^4$  gauss the interval between the quantised energy levels is about  $10^{-4}$  eV, and transitions may be induced by irradiation with microwaves of wavelength 0.5 to 5 cm. The consequent absorption spectrum arises from electron spin resonance.

In a non-linear molecule containing one unpaired electron, the electronic orbital motion makes no contribution to the magnetic moment, and

$$\mu = g\sqrt{S(S+1)}\beta$$

$\beta$  is the Bohr magneton;  $S$  is the spin quantum number which is  $\frac{1}{2}$  for a system containing one unpaired electron; and  $g$  is the Landé splitting factor. Here we must use a more exact value derived from relativistic quantum mechanics, in which  $g$  is 2.00229 in this idealised case.

In a magnetic field,  $H$ , the energy of interaction is

$$E = \mu_H H,$$

$\mu_H$  being the component of the magnetic moment vector in the field direction. The values of  $\mu_H$  are restricted to  $gM\beta$ , with  $M$  equal to  $S, S-1, S-2, \dots -S$ . A transition between states is permitted if  $\Delta M = \pm 1$ . As absorptive

transitions to higher energy states are more numerous than radiative transitions downwards, measurements are made for the  $\Delta M = +1$  case

$$\therefore \Delta E = g\beta H = h\nu$$

$$\therefore \nu = \frac{g\beta H}{h} = \eta H$$

To determine their electron spin resonance, the molecules are irradiated with monochromatic microwaves of frequency about  $10^{10} \text{ sec}^{-1}$ , while the magnetic field applied on them is varied. According to the derivation above, all paramagnetic species should absorb at exactly the same field strength when irradiated at equal frequencies; for example, 3566 gauss for  $10^{10} \text{ sec}^{-1}$  radiation. But if this were the case, e.s.r. spectroscopy would be without chemical interest.

However there are deviations from constant  $\nu/H$  because  $g$  can vary from the value 2.00229. For paramagnetic molecules, deviations are small but usually sufficient to separate the absorptions of different species. Whereas for paramagnetic ions,  $g$  can vary considerably (p. 86). Not only is the position of the absorption variable, but so also is its nature. Absorption in a single band is rare; there is usually a symmetrical multiplet.

### Applications

(1) The spectrum of a chloroform solution of  $\text{KSO}_3 \cdot \text{NO} \cdot \text{SO}_3\text{K}$  (containing one unpaired electron) consists of three bands of equal intensity, equally spaced by 13 gauss. The middle one corresponds to  $g = 2.0054$ , which is rather higher than the spin-only value because of incomplete quenching of an orbital contribution to the magnetic moment. There are three bands because one of the nuclei present,  $^{14}\text{N}$ , is paramagnetic (p. 15) with nuclear spin quantum number  $I = 1$ . ( $M_N$  is therefore  $+1$ ,  $0$  or  $-1$ .) As the moment of the electron can have two values represented by  $M_e = +\frac{1}{2}$  or  $-\frac{1}{2}$ , six possible energy states arise from the possible combinations of electronic and nuclear moments (Fig. 38).

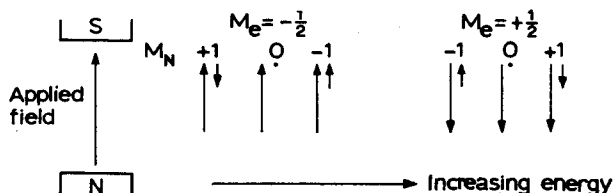


Fig. 38. Possible combinations of electronic ( $M_e$ ) and nuclear ( $M_N$ ) moments for nitrogen-14 atoms.

An antiparallel arrangement of moments represents a lower energy than a parallel one, the extent of the difference increasing with the probability of finding the unpaired electron at the nitrogen. The energy level diagram has the form shown in Fig. 39.

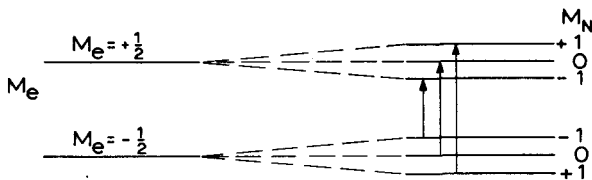


Fig. 39. Energy levels and allowed transitions for nitrogen-14 atom in a negative field.

The selection rules are  $\Delta M_e = +1$  and  $\Delta M_N = 0$ . The three possible energy transitions are as shown. From the splitting, the unpaired electron density at the nitrogen can be calculated.

(2) The absorption due to transition metal ions also shows multiplet structure due to nuclear magnetism. For example, the spectrum of a benzene solution of bis(cyclopentadienyl)vanadium has eight equally intense bands associated with  $^{51}\text{V}$ , which has  $I = \frac{7}{2}$ , and  $2I + 1 = 8$  components of magnetic moment.

(3) More important than the nuclear splitting, however, is the observed deviation from  $g = 2.00229$ , arising from the orbital contribution to the electronic magnetic moment which provides information on crystal-field and spin-orbital coupling effects. In free atoms or monatomic ions

$$\mu = g\sqrt{J(J+1)} \text{ Bohr magnetons,}$$

$J$  is the spin-orbital quantum number and

$$g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$

For the  $\text{Ti}^{3+}$  ( $d^1$ ) the values are:

$$S = \frac{1}{2}, L = 2 \text{ and } J = \frac{3}{2}$$

$$\therefore g = 0.8.$$

But when the  $\text{Ti}^{3+}$  ion is surrounded by other ions in a crystal the  $d$  orbital energy levels are split (p. 157); the effect of this is to destroy the significance of  $L$  and the orbital contribution is quenched by the crystal field (p. 154) or, of course, by molecule formation. If  $L = 0$ , then  $S = J$  and  $g$  is therefore 2, the spin-only value; actually 2.00229 after relativistic correction. A further modification to the energy states and to the wave

functions, which has the effect of restoring some significance to the orbital contributions to magnetic moments, is made by spin-orbit coupling.

### *Spin-orbit coupling*

An electron tends to align its spin anti-parallel to its orbital angular momentum. Thus, when it has orbital angular momentum, this is maintained by being weakly coupled to the spin; furthermore, the spin itself tends to generate orbital angular momentum. As a result, there is competition between the quenching effect of the ligands—the crystal field (p. 154)—and the sustaining effect of the spin-orbit coupling. The spin-orbit coupling constant,  $\lambda$ , expressed in energy units, depends on the atomic number, on the number and type of outer electrons, and on the values of  $L$  and  $S$  for the ion in the particular state.

For an octahedral arrangement of ligands (p. 153) round a central  $d^1$  ion:

$$g = 2.00229 - \frac{8\lambda}{\Delta_0}$$

where  $\Delta_0$  is the crystal-field splitting (p. 157) and  $\lambda$  is the spin-orbit coupling constant.

The moment of an ion in which spin-orbit coupling is effective is given by:

$$\mu = \mu_s \left( 1 - \alpha \frac{\lambda}{\Delta_0} \right)$$

where  $\mu_s$  is the spin-only moment and  $\alpha$  is a constant which depends upon the spectroscopic state of the free ion. For high-spin ions of the first transition series:

$$\begin{array}{ll} \alpha = 0 \text{ if } L = 0 & (d^5) \\ \alpha = 2 \text{ if } L = 2 & (d^1, d^4, d^6, d^9) \\ \alpha = 4 \text{ if } L = 3 & (d^2, d^3, d^7, d^8) \end{array}$$

The value of  $\lambda$  is positive for ions with fewer than five d electrons, and negative for those with six or more:

$$\begin{array}{lll} \text{Ti}^{2+}(d^2) + 61, & \text{V}^{2+}(d^3) + 56, & \text{Cr}^{2+}(d^4) + 57 \text{ cm}^{-1} \\ & \text{Mn}^{2+}(d^5) \text{ zero,} & \\ \text{Fe}^{2+}(d^6) - 102, & \text{Co}^{2+}(d^7) - 177, & \text{Ni}^{2+}(d^8) - 315 \text{ cm}^{-1} \end{array}$$

The first group have observed moments slightly lower than the spin-only value; the last have moments significantly larger (Table 7, p. 88), the effect being greatest when the crystal field is weakest.

## FURTHER READING

- R. M. HOCHSTRASSER, *The Behavior of Electrons in Atoms*, New York, Benjamin, 1964.
- G. HERZBERG, *Atomic Spectra and Atomic Structure*, 2nd ed., New York, Dover, 1944.
- H. EYRING, J. WALTER AND G. E. KIMBALL, *Quantum Chemistry*, London, Wiley, 1960.
- J. W. LINNETT, *Wave Mechanics and Valency*, London, Wiley, 1960.
- B. N. FIGGIS AND J. LEWIS, *The Magnetochemistry of Complex Compounds*, in J. LEWIS AND R. G. WILKINS, *Modern Co-ordination Chemistry*, New York, Interscience, 1960.
- B. N. FIGGIS AND J. LEWIS, *The Magnetic Properties of Transition Metal Complexes*, in F. A. COTTON, *Progress in Inorganic Chemistry*, Vol. 6, New York, Interscience, 1964, p. 37.

## Chapter 5

# Valency

## Nature and Classification of Chemical Bonding

### Introduction

In principle, the existence of stable compounds could be predicted by solving the wave equation for systems of nuclei (masses  $M_1, M_2, \dots$ ) and electrons (mass  $m$ ). Solutions would occur for certain most probable nuclear configurations, and would correspond to lower energy values than when the systems were separated into neutral atoms at rest. This has never been attempted. Fortunately it is not necessary because the large mass ratio (usually  $> 10,000:1$ ) of nuclei and electrons makes it permissible to discuss separately the electron distribution and the relatively sluggish motion of the nuclei. To an exceedingly good approximation, the nuclei may be regarded as moving in a 'cloud' of electrons whose distribution is determined by a wave function depending on the instantaneous positions of the nuclei. This general picture is adopted universally in the electronic interpretation of valency, the stability of different configurations being discussed as though the nuclei were at rest.

Another guiding principle of great value was derived theoretically by Feynman and Hellmann (1939). It states that the forces which hold together the positive nuclei in a molecule or crystal are just those which they would experience if they were embedded in a static distribution of negative charge of density  $P$ ,  $P(x, y, z)$  being the probability density for finding an electron at the point  $x, y, z$ . This principle at once provides immediate physical insight into the nature of bonding and its classification. Briefly, all bonds can be interpreted electrostatically in terms of a charge cloud, provided this is determined wave-mechanically rather than classically. Usually, the form of the charge cloud is inferred from experimental, intuitive and theoretical considerations.

When internuclear distances are large compared with molecular distances, every nucleus has its normal complement of electrons fairly tightly localised about it. At molecular distances, the inner shells remain in this condition, but the outermost electrons are affected in varying degrees, ranging from a slight distortion of their orbitals to an electron transfer from one atom to another.



## ELECTRONIC THEORY OF BONDING

## The Aufbau or 'building-up' approach

The simplest of all molecules is the ion  $H_2^+$  since it possesses two nuclei and but one electron. If orbitals can be found to describe the states of the one electron in a two-centre field of this kind, it should be possible to develop an aufbau theory of diatomic molecules, exactly as in the one-centre instance (p. 75). And there is no reason why this should not be extended to a many-centre example. The one-electron orbitals, which extend over all nuclei, are called *molecular orbitals*; or in the case of a crystal, *crystal* or *Bloch* orbitals. In the aufbau approach, the available molecular orbitals are filled in ascending energy order and the resultant electron density is, in this approximation, again just a sum of the orbital contributions. And again, as in the Hartree method, the picture will be a good one when each orbital is chosen so as to take account of the various nuclear charges, the screening effect of electrons in inner orbitals, and the average disposition of electrons in the other molecular orbitals.

## Forms of molecular orbitals

In 1927 Burrau determined accurately the molecular orbital of lowest energy for the system  $H_2^+$  and found, by considering a range of internuclear distances, that at 1.06 Å there was an energy minimum which was 2.777 eV lower than that of a system comprising a normal H atom and a distant proton. This bond length and the theoretical dissociation energy agree excellently with spectroscopic values. The electron density calculated by Burrau is indicated in Fig. 40; it clearly substantiates the Feynman-Hellmann principle by showing a considerable piling up of charge in the bond region. Burrau's results form the true starting point of an aufbau theory of molecular structure. They were, however, almost immediately overshadowed by those of Heitler and London, who considered the normal hydrogen molecule and later developed a general theory of *two*-electron bonds so closely in accord with the accepted ideas of G. N. Lewis (1916) that it won universal popularity. It was not for some time that the relationship between the two approaches was appreciated.

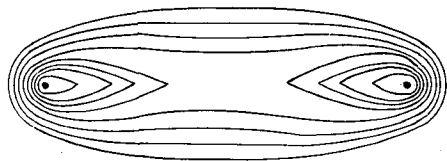


Fig. 40. Electron density in  $H_2^+$  is mainly between the nuclei (after Burrau).

*Linear combination of atomic orbitals*

Since accurate calculations are not usually feasible, it is necessary to find means of securing fair approximations to *molecular orbitals* and of estimating their relative energies. The simplest way is to build them up out of *atomic orbitals*, taking

$$\psi = c_1\varphi_1 + c_2\varphi_2 + c_3\varphi_3 + \dots$$

where the  $\varphi$ 's are suitable atomic orbitals put together with numerical coefficients  $c_1, c_2, \dots$ . This is called the *linear combination of atomic orbitals* approximation. Using abbreviations, we employ an LCAO approximation to the MO's. Returning to  $\text{H}_2^+$ , an approximate MO would be  $\psi = c_a\varphi_a + c_b\varphi_b$ , where  $\varphi_a$  and  $\varphi_b$  are 1s orbitals on the nuclei  $a$  and  $b$ . Since the AO's fall off exponentially,  $\psi$  at a point near nucleus  $a$  will be essentially  $c_a\varphi_a$ , that is a solution of the wave equation for an electron of atom  $a$ . In the same way  $\psi$  behaves correctly when the electron is near  $b$ . It remains to determine the values of  $c_a$  and  $c_b$  in order to get as good an approximation of this form as possible. There are standard mathematical methods for this, which give sets of coefficients and energies, not only for the lowest state, but for as many states as there are AO's.

*Bonding and anti-bonding molecular orbitals*

Here, however, where the two centres are identical,  $P = \psi^2$  is symmetrical which means that  $c_a = \pm c_b$ . The two solutions are then

$$\psi_1 = N_1(\varphi_a + \varphi_b) \quad \text{and} \quad \psi_2 = N_2(\varphi_a - \varphi_b),$$

where the constants  $N_1$  and  $N_2$  are chosen so that the functions are correctly normalised (p. 57). The values of  $\psi_a$  and  $\psi_b$  across an axis through two nuclei,  $a$  and  $b$ , obtained by the L.C.A.O. method, are shown graphically in Fig. 41.

In the first case there is considerable electron density, proportional to  $\psi_1^2$ , between the nuclei  $a$  and  $b$ . In the second case the electron density mid-way between  $a$  and  $b$  (proportional to  $\psi_2^2$ ) is zero.

The shapes of these MO's are indicated in Fig. 42, and it is clear that  $\psi_1$  must approximate to Burrau's ground state solution and  $\psi_2$  represents an excited state. In fact  $\psi_1$ , in error by only a few percent, still suffices to predict a stable molecule; but the excited state, giving repulsion at all internuclear distances, indicates spontaneous dissociation. The two MO's are described as *bonding* and *anti-bonding* partners; they are designated by  $\sigma$ ls and  $\sigma^*$ ls, being built out of 1s AO's, where  $\sigma$  indicates their symmetry about the molecular axis and the asterisk distinguishes the anti-bonding from the bonding MO.

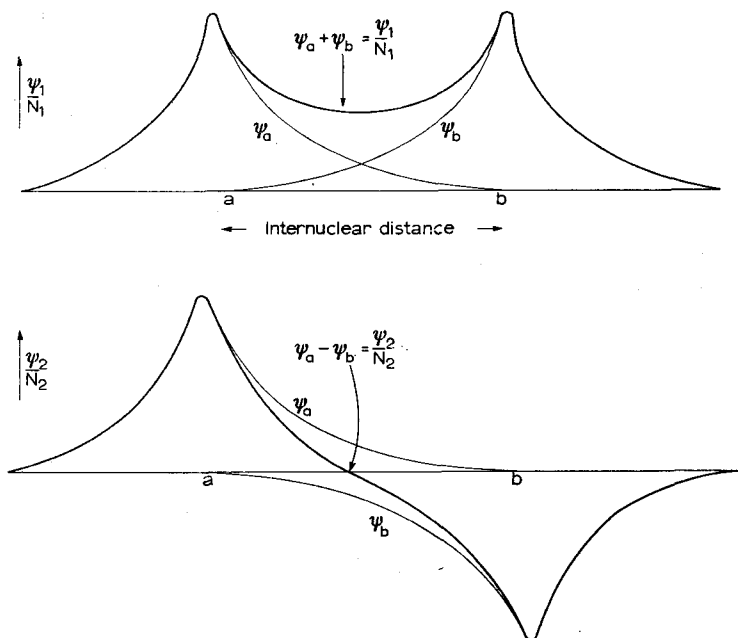


Fig. 41. Linear combinations of 1s orbitals.

As with AO's, the set of solutions of the *two*-centre wave equation is infinite;  $\sigma_{1s}$  and  $\sigma^*_{1s}$  are the two of lowest energy. Some of the solutions would lead to certain MO's with more than one node across the bond, others with nodal planes through both nuclei, and so on. The main features of all these MO's can be quite well reproduced in LCAO approximation, as is indicated schematically in Fig. 42, where the names of the orbitals are also given.

The symmetry of an MO is specified by the number of nodal planes containing the molecular axis. The types with 0, 1, 2, ... such planes are designated by  $\sigma$ ,  $\pi$ ,  $\delta$ , ... by analogy with the AO notation s, p, d, ... Again, these numbers correspond to quantised values of the angular momentum—momentum around the molecular axis— $\lambda(\hbar/2\pi)$ , where  $\lambda = 0, \pm 1, \pm 2, \dots$ . Orbitals other than those of  $\sigma$  type thus occur in degenerate pairs, corresponding to circulation in one sense or the other; and MO's such as  $\pi 2p_x$  and  $\pi 2p_y$  are mixtures of equal parts of those representing states of definite angular momentum ( $\lambda = \pm 1$ ), and are the counterparts of the AO's  $2p_x$  and  $2p_y$ , which were adopted in place of  $2p_{+1}$  and  $2p_{-1}$  (p. 64). There is thus a close similarity throughout with the classification of AO's though this

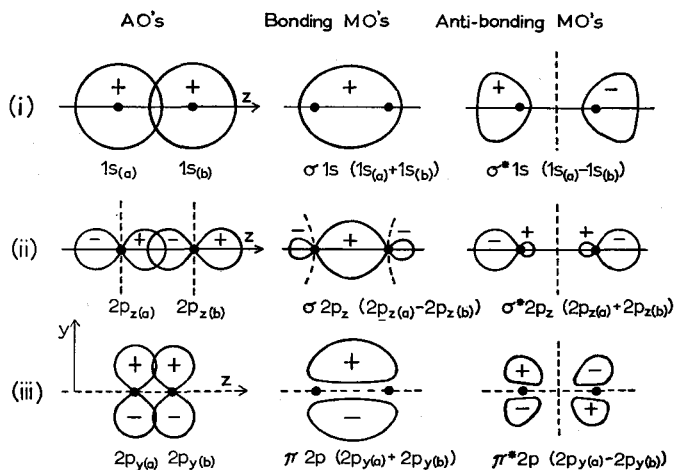


Fig. 42. Molecular orbitals in LCAO approximation (nodes indicated by broken lines).

extends only to linear molecules. The LCAO MO method can in fact be applied to any polyatomic molecule or crystal.

### The two-electron bond

#### *In the hydrogen molecule*

The two lowest energy MO'S of a homonuclear diatomic molecule are  $\sigma 1s$  and  $\sigma^* 1s$ . The relative energies of the MO's and the AO's from which they arise are shown in Fig. 43, which is for  $H_2$ :

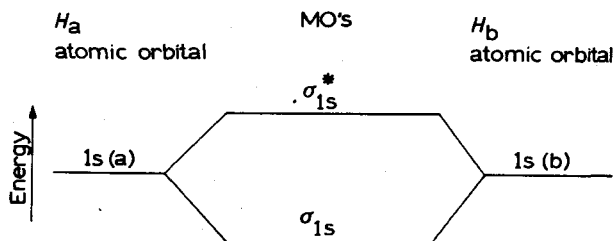


Fig. 43. Relative energies of MO's and the  $1s$  AO's from which they are formed.

The valence orbitals of the combining atoms,  $H_a$  and  $H_b$ , which have the same coulombic energy, are placed directly opposite one another. The energies of the MO's appear in the middle of the diagram. The  $\sigma 1s$  MO is more stable than the combining  $1s$  valence orbitals, the  $\sigma^* 1s$  is correspondingly less stable.

According to the aufbau approach, the electronic configuration of the normal molecule  $H_2$  would be written  $H[(\sigma 1s)^2]$ . The charge cloud would be very similar in shape to that in  $H_2^+$ , only twice as dense and, by exerting a correspondingly greater attraction upon the nuclei, would lead to a shorter and stronger bond. But, on the other hand, further addition of electrons would weaken the bond. Thus the hypothetical molecule  $He_2$  would have the structure  $He[(\sigma 1s)^2(\sigma^* 1s)^2]$  and the bonding effect of the  $\sigma 1s$  electrons would be offset by the anti-bonding effect of the others. If the charge clouds (*cf.* Fig. 42) are superimposed, it turns out that there is no accumulation of charge in the bond region, the final density being roughly that of two unmodified helium atoms. More precisely, there is a slight repulsion which grows rapidly when the closed shells are pushed together. The saturation property of chemical binding is thus immediately interpreted: an atom with one or more *singly* occupied orbitals has a corresponding number of valencies, but one with only *doubly* occupied orbitals is inert.

*In molecules generally: the principle of maximum overlap*

Nearly all strong chemical bonds are *two-electron bonds*, and in the aufbau picture both electrons occupy a bonding MO whose antibonding partner is empty. All two-electron bonds can be explained in this way, but their characters and strengths vary widely according to the form of the charge density. The bonding MO, whatever its type, gives a density contribution

$$\psi^2 = c_a^2 \varphi_a^2 + c_b^2 \varphi_b^2 + 2c_a c_b \varphi_a \varphi_b,$$

where the first two terms are AO charge clouds with 'weight factors'  $c_a^2$  and  $c_b^2$ . The third term is best described as an overlap density, since it can be large only in the 'overlap region' between the atoms where both  $\varphi_a$  and  $\varphi_b$  are large. Now when  $c_a$  and  $c_b$  are roughly equal (they are exactly so for all homonuclear systems) the charge will spread more or less evenly over the two atoms and the binding will arise mainly from the attraction exerted by the overlap density between them. This density depends jointly on the *amount* of charge described by the overlap function  $\varphi_a \varphi_b$  and upon its weight factor  $2c_a c_b$ ; the amount is clearly greater the greater the overlap of the AO's, but the weight-factor (fixed so that  $\psi$  is normalised) is not very sensitive to overlap. Consequently, in a 'homopolar' situation ( $c_a \simeq c_b$ ), the strength of a bond involving two given AO's is determined largely by their overlap, the larger the overlap the stronger the bond. This conclusion, embodied in the *principle of maximum overlap*, is corroborated by a great weight of chemical evidence. When, however, the bonded atoms have very different electron affinities,  $c_a$  and  $c_b$  may be of different orders of magnitude, describing the much greater chance of finding an electron on one nucleus rather than on

the other. The change of bond type can be seen from the limiting case  $c_a \rightarrow 1$ ,  $c_b \rightarrow 0$ : for then the MO degenerates into an AO  $\varphi_a$  and this acquires both electrons of the two-electron bond; the overlap density of the covalent bond disappears and the charge cloud becomes that of two oppositely charged ions. There is clearly a perfectly smooth transition from covalent to ionic binding, the amount of ionic character being reflected in the disparity between the MO coefficients and in a 'lopsided' bond orbital.

To summarise: two-electron bonds occur when the singly occupied AO's of different atoms overlap in pairs; these bonds are strong when the overlap is large. The combination of AO's which are doubly occupied, or which overlap only weakly, need not in general be considered. The bonding MO's lean towards the more electronegative atom, approaching the form of an AO of that atom in extreme cases. These principles, as will be seen later, apply with little modification to polyatomic molecules and crystals, the only difference being that strong overlapping is not confined to *one pair* of AO's.

## THE IONIC BOND

### Energy changes in the formation of ionic bonds

Suppose that in their power of attracting electrons (their electronegativities (p. 127)) two atoms *a* and *b* are so different that the singly occupied AO's  $\psi_a$  and  $\psi_b$  give a bonding MO which is almost purely  $\psi_a$ . The electron configuration in the molecule then contains  $\psi_a^2$  instead of  $\psi_a^1\psi_b^1$ . A typical ionic bond arising in this way is indicated in Fig. 44. The binding force in these circumstances comes predominantly from the attraction of oppositely charged ions, whose outer orbitals are all doubly occupied. The equilibrium position occurs when these filled orbitals begin to interpenetrate, the situation then resembling that in a hypothetical molecule such as  $\text{He}_2$  (p. 98). The repulsive force which arises is of short range, corresponding to a potential energy which can be represented fairly well by a term  $ar^{-n}$ , where *r* is the internuclear distance, *a* is a constant and *n*, the Born exponent, is a number which depends on the electron configuration of the ion:

Type of electron configuration	Born exponent, <i>n</i>
He	5
Ne	7
Ar and $\text{Cu}^+$	9
Kr and $\text{Ag}^+$	10
Xe and $\text{Au}^+$	12

If cation and anion are of different types, for example  $\text{Na}^+$  (Ne type) and  $\text{Cl}^-$  (Ar type) the mean value, 8 in this case, is taken. Because when one atom loses  $z_1$  electrons and the other gains  $z_2$  electrons the Coulomb potential energy is  $-z_1 z_2 e^2 / r$ , the net *interaction energy* of the two ions at distance  $r$  is

$$E_{int} = ar^{-n} - z_1 z_2 e^2 / r.$$

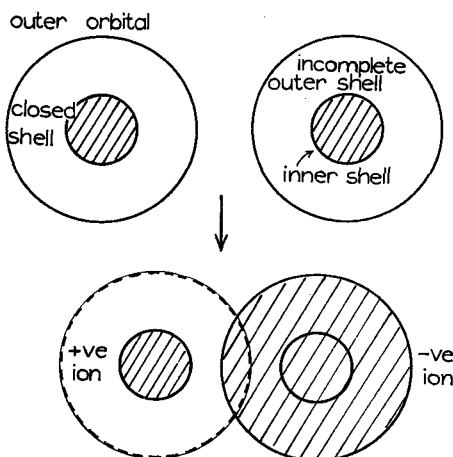
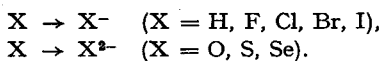


Fig. 44. Ionic binding.

### Factors determining the formation of ions

A simple anion is formed when a non-metal accepts one or two electrons:



Anions formed from single atoms all have the Gp. 0 gas structures  $1s^2$  or  $ns^2 np^6$ . On the other hand, cations are formed when a metal loses one, two, three or even four electrons. Various electron configurations occur (see Table 8).

Both anions and cations are stable when they have a closed shell (or subshell, *e.g.*,  $nd^{10}$ ) of electrons, since the electrons outside such a shell are heavily screened from the nuclear charge and therefore loosely bound. Moreover, as the effective nuclear charge upon the outer electrons is increased by the removal of electrons and decreased by their addition, successive ionisations become increasingly difficult.

TABLE 8  
CONFIGURATIONS OF CATIONS

<i>Kinds of ion</i>		<i>Electron configuration (term in brackets indicates a Gp. 0 gas inner shell)</i>		
(i) No electrons	H <sup>+</sup>			
(ii) Two electrons	Li <sup>+</sup> , Be <sup>2+</sup>	1s <sup>2</sup>		He type
(iii) '8-electron' structures	Na <sup>+</sup> , Mg <sup>2+</sup> , Al <sup>3+</sup> K <sup>+</sup> , Ca <sup>2+</sup> , Sc <sup>3+</sup>	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> (Ne) 3s <sup>2</sup> 3p <sup>6</sup>		Ne type Ar type
(iv) '18-electron' structures	Cu <sup>+</sup> , Zn <sup>2+</sup> , Ga <sup>3+</sup> Ag <sup>+</sup> , Cd <sup>2+</sup> , In <sup>3+</sup> Au <sup>+</sup> , Hg <sup>2+</sup> , Tl <sup>3+</sup>	(Ar) 3d <sup>10</sup> (Kr) 4d <sup>10</sup> (Xe) 5d <sup>10</sup>		
(v) 'Inert pair' structures	In <sup>+</sup> , Sn <sup>2+</sup> , Sb <sup>3+</sup> Tl <sup>+</sup> , Pb <sup>2+</sup> , Bi <sup>3+</sup>	(Kr) 4d <sup>10</sup> 5s <sup>2</sup> (Xe) 5d <sup>10</sup> 6s <sup>2</sup>		
(vi) Transition ions	V <sup>3+</sup> Fe <sup>3+</sup> Fe <sup>2+</sup> Ni <sup>2+</sup>	(Ar) 3d <sup>3</sup> (Ar) 3d <sup>5</sup> (Ar) 3d <sup>6</sup> (Ar) 3d <sup>8</sup>		

### *Types of cation*

Of the various types of cation, those with the Gp. 0 gas structure are by far the most stable. They do not show appreciable tendency to share their electrons with other atoms or ions. Cations with the '18-electron' configuration are moderately stable, although the Cu<sup>+</sup> ion can lose a second electron to form Cu<sup>2+</sup>, a transition type of coloured ion with 3s<sup>2</sup> 3p<sup>6</sup> 3d<sup>9</sup> structure. But the 3d<sup>10</sup> group is stabilised by an increase of nuclear charge, and the further ionisation of zinc from Zn<sup>2+</sup> to Zn<sup>3+</sup> does not occur. The unexpected, though not great, stability of the 'inert pair' structures is due to the outer s electrons penetrating the rather diffuse 18-electron shell immediately beneath them. The effect increases with higher shells; thus the ions of the third long period show greater stability than those of the second; Pb<sup>2+</sup> is, for instance, much more stable than Sn<sup>2+</sup>. However, large singly charged ions with an inert pair, such as Tl<sup>+</sup>, show some of the properties of the alkali metals, though the bonds they form are by no means purely ionic. The least stable ions are those of the transition metals; in these variable charge number is common. Cobalt (3s<sup>2</sup> 3p<sup>6</sup> 3d<sup>7</sup> 4s<sup>2</sup>) forms cobalt(II), Co<sup>2+</sup>, and, less easily, cobalt(III), Co<sup>3+</sup>, ions, but nickel (3s<sup>2</sup> 3p<sup>6</sup> 3d<sup>8</sup> 4s<sup>2</sup>) only Ni<sup>2+</sup>, the tendency



to lose 3d electrons falling with increasing nuclear charge. The more highly charged ions, particularly of the transition elements, are frequently invoked in describing molecular complexes (p. 153); but then the purely ionic picture is not very satisfactory as the bonds often possess considerable covalent character.

### Lattice energies of ionic crystals

The energy of a system of spherical ions is at a minimum when each is surrounded by as many others of opposite charge as possible (p. 193); this number of nearest neighbours is the *crystallographic co-ordination number* of the ion. Thus in sodium chloride (Fig. 45, p. 104) the ions are in a regular lattice and every ion has the co-ordination number six.

When  $N$  ions (one mole) of each kind are brought together to form a crystal the interaction energy is clearly not just that of  $N$  pairs of ions. The formula on p. 100 is replaced by

$$E_{\text{int}} = br^{-n} - z_1 z_2 e^2 N A_a r^{-1}$$

where  $A_a$ , the Madelung constant, depends on the crystal geometry, and the  $br^{-n}$  term represents the total repulsion energy. Now the equilibrium value of  $r$ , the distance separating the two kinds of ion, occurs when  $E_{\text{int}}$  is a minimum; putting

$$\frac{dE_{\text{int}}}{dr} = 0,$$

the first term may be eliminated, and the drop in energy on assembling the ions in the crystal (*i.e.*  $-E_{\text{int}}$ ) is then given by the equation

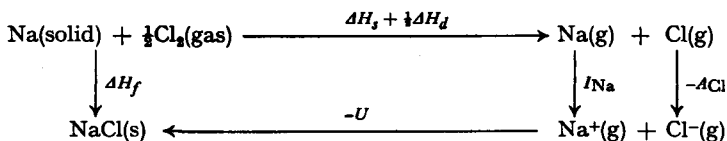
$$U = \frac{z_1 z_2 e^2 N A_a}{r} \left( 1 - \frac{1}{n} \right).$$

This drop in energy,  $U$ , is the *lattice energy*.  $A_a$  may be chosen so that  $U$  is given directly in kcal. mole<sup>-1</sup> when  $e$  is in e.s.u. and  $r$  in Å. Some representative values are:

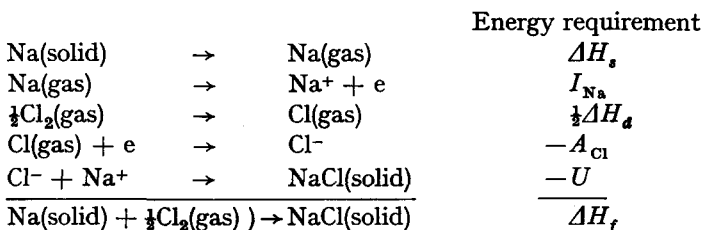
NaCl lattice,  $A_a = 1.748$ ; Wurtzite lattice,  $A_a = 1.641$ ; Corundum,  $A_a = 25.03$ .

The inter-ionic distance  $r$  and the type of lattice are found from determinations of crystal structure (p. 187).

The lattice energy may be deduced from experimental thermochemical data by considering a suitable cycle of changes (Born and Haber, 1919). The cycle for formation of sodium chloride, with the energy changes occurring at each step shown alongside the arrows, is:



It may also be conveniently set out thus:



$\Delta H_s$  is the heat of sublimation of sodium to free atoms,  $\Delta H_d$  the heat of dissociation of chlorine molecules to atoms,  $\Delta H_f$  is the heat of formation of sodium chloride from the elements; these, with the ionisation energy of sodium,  $I_{\text{Na}}$ , and the electron affinity of chlorine,  $A_{\text{Cl}}$ , refer to one mole of material.

Thus:

$$\Delta H_f = \Delta H_s + \frac{1}{2}\Delta H_d + I_{\text{Na}} - A_{\text{Cl}} - U.$$

Therefore

$$U = \Delta H_s + \frac{1}{2}\Delta H_d + I_{\text{Na}} - A_{\text{Cl}} - \Delta H_f.$$

### Ionic radii

The meaning and determination of ionic radius can be illustrated by reference to the alkali metal halides. Their crystal structure and internuclear distance are found by X-ray analysis (p. 187). Most of them have the same type of crystal lattice as sodium chloride (Fig. 45) but their inter-ionic distances differ. Cubic arrangement of ions in NaCl indicates 6-co-ordination of both anions and cations. The internuclear distance,  $r$  for a number of similar lattices is given:

	<i>Internuclear distance</i>		<i>Internuclear distance</i>
KCl	3.14 Å	NaCl	2.76 Å
KF	2.69 Å	NaF	2.31 Å

These distances represent the sum of the radii of neighbouring, spherical ions. The method most generally used to deduce ionic radii from internuclear distance is that due to Pauling (1927), and is applicable only to isoelectronic

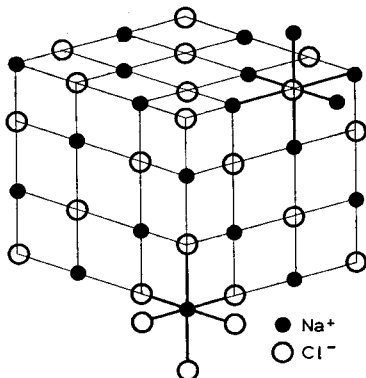


Fig. 45. Arrangement of  $\text{Na}^+$  and  $\text{Cl}^-$  ions in the sodium chloride lattice.

pairs. To obtain the ionic radius of the singly charged, isoelectronic ions  $\text{K}^+$  and  $\text{Cl}^-$  (both with Ar configuration) in potassium chloride the distance between their nuclei is divided in the inverse ratio of the effective nuclear charge exerted on the outer electron shell of each ion. The screening constant  $\sigma$  (p. 70) is given by

$$\begin{aligned} \sigma &= 8 \times 0.35 && (3s \text{ and } 3p \text{ electrons}) \\ &+ 8 \times 0.85 && (2s \text{ and } 2p) \\ &+ 2 \times 1.0 && (1s) \\ &= 11.6 \end{aligned}$$

Thus for  $\text{K}^+$  ( $Z = 19$ )  $Z^* = 7.4$ ,

and for  $\text{Cl}^-$  ( $Z = 17$ )  $Z^* = 5.4$ .

The radius of the  $\text{Cl}^-$  ion,  $r_{\text{Cl}^-}$ , is given by

$$\frac{7.4}{5.4 + 7.4} \times 3.14 = 1.81 \text{ \AA}$$

$$\text{and that of } \text{K}^+ = \frac{5.4}{5.4 + 7.4} \times 3.14 = 1.33 \text{ \AA}$$

Similar treatment of the data for NaF gives

$$r_{\text{F}^-} = \frac{6.5}{6.5 + 4.5} \times 2.31 = 1.36 \text{ \AA},$$

$$r_{\text{Na}^+} = \frac{4.5}{6.5 + 4.5} \times 2.31 = 0.95 \text{ \AA}.$$

The sum of  $r_{\text{Na}^+}$  and  $r_{\text{Cl}^-}$  should therefore be  $0.95 + 1.81 = 2.76 \text{ \AA}$ , in agreement with the X-ray determination.

*Pauling's method for ions of charge greater than one*

For an ion of charge  $z$ , Pauling's method is to calculate first the hypothetical 'univalent' radius,  $r_1$ , that the ion would possess provided it retained its electron configuration but suffered coulombic attraction as though it carried unit charge. Then  $r_z$  for the actual ion is computed from the equation

$$r_z = \frac{r_1}{z^{2/(n-1)}}$$

where  $n$  is the Born exponent (p. 99).

TABLE 9  
IONIC RADII  
Radii in crystals with 6-co-ordination

		H <sup>-</sup>	Li <sup>+</sup>	Be <sup>2+</sup>	B <sup>3+</sup>		
		2.08	0.60	0.31	0.20		
N <sup>3-</sup>	O <sup>2-</sup>	F <sup>-</sup>	Na <sup>+</sup>	Mg <sup>2+</sup>	Al <sup>3+</sup>	Si <sup>4+</sup>	P <sup>5+</sup>
1.71	1.40	1.36	0.95	0.65	0.50	0.41	0.34
P <sup>3-</sup>	S <sup>2-</sup>	Cl <sup>-</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Sc <sup>3+</sup>	Ti <sup>4+</sup>	V <sup>5+</sup>
2.12	1.84	1.81	1.33	0.99	0.81	0.68	0.59
			Cu <sup>+</sup>	Zn <sup>2+</sup>	Ga <sup>3+</sup>	Ge <sup>4+</sup>	As <sup>5+</sup>
			0.96	0.74	0.62	0.53	0.47
As <sup>3-</sup>	Se <sup>2-</sup>	Br <sup>-</sup>	Rb <sup>+</sup>	Sr <sup>2+</sup>	Y <sup>3+</sup>	Zr <sup>4+</sup>	Nb <sup>5+</sup>
2.22	1.98	1.95	1.48	1.13	0.93	0.80	0.70
			Ag <sup>+</sup>	Cd <sup>2+</sup>	In <sup>3+</sup>	Sn <sup>4+</sup>	Sb <sup>5+</sup>
			1.26	0.97	0.81	0.71	0.62
Sb <sup>3-</sup>	Te <sup>2-</sup>	I <sup>-</sup>	Cs <sup>+</sup>	Ba <sup>2+</sup>	La <sup>3+</sup>	Ce <sup>4+</sup>	
2.45	2.21	2.16	1.69	1.35	1.15	1.01	
			Au <sup>+</sup>	Hg <sup>2+</sup>	Tl <sup>3+</sup>	Pb <sup>4+</sup>	Bi <sup>5+</sup>
			1.37	1.10	0.95	0.84	0.74

As stated, these values are for 6-co-ordinated ions. To calculate the ionic radius for an ion in a crystal when its co-ordination number is  $a$ , the following formula is used.

$$r_a = \left(\frac{a}{6}\right)^{\frac{1}{n-1}}$$

Thus for 8-co-ordinated Cl<sup>-</sup> ( $n = 9$ )

$$\begin{aligned} r_8 &= r_6 \times \left(\frac{8}{6}\right)^{\frac{1}{8}} \\ &= 1.81 \times 1.038 = 1.88 \text{ \AA} \end{aligned}$$

and for 4-co-ordinated Cl<sup>-</sup>

$$r_4 = r_6 \times \left(\frac{4}{6}\right)^{\frac{1}{8}} = 1.72 \text{ \AA}$$

### Interpretation of lattice energies

The experimental (Born-Haber) and theoretical (Born-Mayer) estimates of lattice energy agree well for typically ionic solids such as the Gp.IA halides, and show that the theoretical picture of complete electron transfer is satisfactory. Values for salts of '18-electron' type cations, however, often show considerable discrepancies. Representative differences between  $U_{\text{expt}}$  and  $U_{\text{calc}}$  are: RbI, 4 kcal; CdI<sub>2</sub>, 86 kcal; PbO<sub>2</sub>, 212 kcal. These indicate a gradual departure from the purely ionic condition found in NaCl; the small cations such as Pb<sup>4+</sup> tend to retain some hold on their electrons and the binding acquires considerable covalent character.

Deviations of this kind used to be ascribed to the 'polarisation' of the large anions by the small cations, the charge density of the former being deformed by the strong electric field of the latter. Although such effects undoubtedly occur, the deviations can most readily be accounted for along the lines already indicated. The electron transfer from a small cation which has a correspondingly great electron-attracting power is never complete, and the bonds that such a cation forms may exhibit considerable covalent character. Nevertheless, the term 'polarisation' is convenient and continues to be used to describe this effect. Moreover, the effect, always accompanied by an abnormally high heat of formation and lattice energy, is not confined to '18-electron' ions. Thus, although there is no discrepancy between  $U_{\text{expt}}$  and  $U_{\text{calc}}$  for BaO, the difference for MgO is 20 kcal, in accord with the smaller size and higher electron-attracting power of the Mg<sup>2+</sup> ion.

### Lattice energy and solubility

Water consists of polar molecules (dipole moment 1.8 D) with a strong tendency to form hydrogen bonds, and has a high dielectric constant ( $\sim 78$ ). Its molecules orient themselves around cations with the oxygen atoms pointing inwards, the complex so formed being stabilised by a *hydration energy* arising from electrostatic attraction between the cation and the excess of negative charge on the oxygen. Consequently, water is a good solvent for ionic compounds but a poor one for non-electrolytes whose molecules are without strong charges. The process of dissolution is easier the higher the dielectric constant of the solvent; for, in an ideal (continuous) medium, of dielectric constant  $\epsilon$ , the solvation or hydration energy of an ion of radius  $r$  and charge  $e$  would be  $(e^2/r)(1 - 1/\epsilon)$ .

The more ionic the character of the bonds in crystals, the more easily they dissolve in water. Where there is considerable polarisation, the spread-

ing out of the electron cloud, which accompanies the increase in covalence, leads to a screening of the positive-ion field and a reduction of the attraction of water molecules, with a corresponding fall in solubility.

## THE COVALENT BOND

### Simple diatomic molecules

The electron configuration of simple diatomic molecules can be readily discussed in terms of the MO's described on p. 97. It is only necessary, in the aufbau approach, to know the energy order of the various orbitals, and for homonuclear molecules where the difference in energy between the 2s and 2p orbitals is large (taking the bond as the  $z$  axis) this is:

$$\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \sigma 2p_z < \left( \begin{matrix} \pi 2p_x \\ \pi 2p_y \end{matrix} \right) < \left( \begin{matrix} \pi^* 2p_x \\ \pi^* 2p_y \end{matrix} \right) < \sigma^* 2p_z \dots$$

Where the energy difference between 2s and 2p orbitals in the atoms is small, the 2s and 2p<sub>z</sub> orbitals must be considered together in an LCAO scheme. The effect of this *sp hybridisation* is to stabilise the  $\pi 2p_x$  and  $\pi 2p_y$  orbitals relative to the  $\sigma 2p_z$ . All homonuclear diatomic molecules for which there is reliable evidence have a  $\sigma 2p_z$  orbital less stable than the  $\pi 2p_x$  and  $\pi 2p_y$ .

A more flexible but less explicit notation, due to Mulliken, is also employed. Here the MO's are simply labelled  $z, y, x, w, v, u, \dots$ , in ascending energy order, the symmetry symbols  $\sigma, \pi, \delta, \dots$  being added as required. Thus, for example,  $z\sigma$  is used for the  $\sigma 2s$  MO, inner shells being omitted. With this notation and the principles already put forward, electronic structures may be described along the following lines:

**Lithium.**  $2\text{Li}(1s^2 2s^1) \rightarrow \text{Li}_2(\text{KK } z\sigma^2)$

Here the two 'K-shell' (1s) electrons on each nucleus are indicated in the molecular configuration simply by the two K's, the inner shells being more or less undisturbed, and the two valence electrons give a typical single bond.

**Nitrogen.**  $2\text{N}(1s^2 2s^2 2p^3) \rightarrow \text{N}_2(\text{KK } z\sigma^2 y\sigma^2 x\pi^4 w\sigma^2)$

Here  $z\sigma$  is bonding and  $y\sigma$  is its anti-bonding partner, so there is little net effect from this pair of MO's. The first bonding effect comes from the  $x\pi^4$  which comprises two pairs of electrons in the two degenerate, that is

equivalent,  $2p\pi$ -type bonding MO's. These describe densities which vanish on the axis itself but which have maxima some distance to either side of it (Fig. 42). The two orbitals differ by rotation through  $90^\circ$ , but when put together their density contributions give an axially symmetrical resultant. This is a hollow 'tube' of charge, densest in the region between the nuclei (Fig. 46). In addition there is a  $w\sigma$  bonding orbital containing two electrons which is a  $\sigma 2p$  MO formed from  $2p$  AO's, with some  $s$  contribution, pointing towards each other and describing an electron density which is greatest along the bond axis.

The nitrogen molecule has thus three bonds—one  $\sigma$  and two  $\pi$ , which is the maximum for an  $A_2$  molecule. This electronic arrangement accounts for the unusual thermal stability of  $N_2$ , its extraordinarily large dissociation energy of  $225 \text{ kcal mole}^{-1}$ , its very short internuclear distance of  $1.10 \text{ \AA}$ , its lack of chemical reactivity, and its diamagnetism.

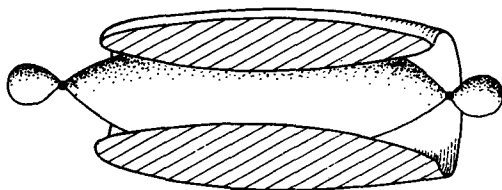
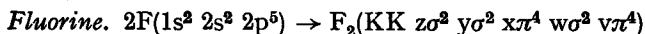
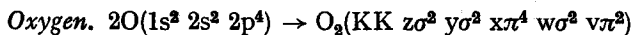


Fig. 46. Diagram showing schematically the general disposition of charge in  $N_2$  (cylindrical density due to two  $\pi$  bonds cut away to reveal  $\sigma$  bond).



Here the situation resembles that in nitrogen until the last four electrons are added; these fill the  $v\pi$  MO's which are the anti-bonding partners of the  $x\pi$  MO's. Thus the two  $\pi$  bonds of the nitrogen-like configuration are 'undone' when the extra electrons are provided, and only a single bond remains. This electronic structure is consistent with the weakness of the F-F bond ( $37 \text{ kcal mole}^{-1}$ ), the long internuclear distance ( $1.42 \text{ \AA}$ ) and the diamagnetism of fluorine.



This is intermediate between nitrogen and fluorine; the anti-bonding  $v\pi$  orbitals contain only two electrons and leave effectively one  $\pi$  bond. More precisely, by Hund's rules, the two  $v\pi$  MO's are each singly occupied, half-cancelling the effect of a  $x\pi$  electron pair. There is thus a  $\sigma$  bond and two 'half'  $\pi$  bonds, their resultant density being axially symmetrical as in

nitrogen but being much 'thinner'. Since the two odd electrons have parallel spins the molecule is paramagnetic.

The bond energy is 118 kcal mole<sup>-1</sup> and the internuclear distance 1.21 Å. When an electron is removed to leave the O<sub>2</sub><sup>+</sup> ion the bond length decreases to 1.12 Å, consistent with the removal of an antibonding electron, but the addition of an electron to form O<sub>2</sub><sup>-</sup> increases the bond length to 1.26 Å as expected, since the extra electron must enter an antibonding orbital.

### Energy level diagrams

The molecular-orbital energy-level diagrams for homonuclear diatomic molecules like N<sub>2</sub>, O<sub>2</sub> and F<sub>2</sub> have the general form shown in Fig. 47.

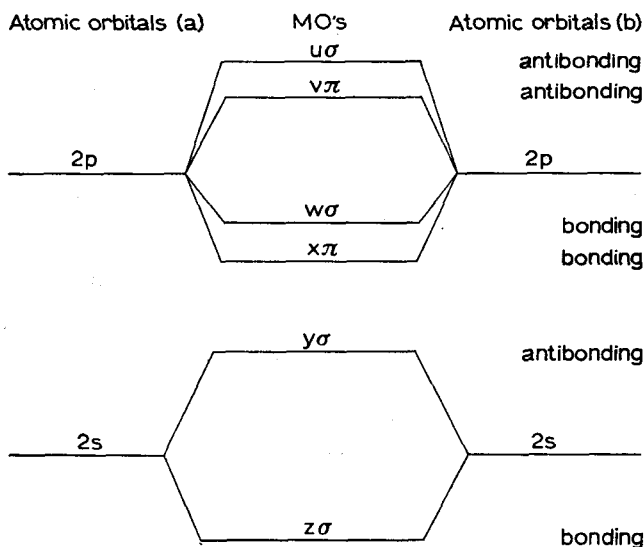


Fig. 47. Energy levels of MO's in N<sub>2</sub>, O<sub>2</sub> and F<sub>2</sub> molecules (not to an exact energy scale).

In N<sub>2</sub> only the four lowest MO's are filled, in O<sub>2</sub> the two additional electrons are in the vπ, in F<sub>2</sub> all but the uσ are filled.

### Hybridisation

Although simple pairing of the AO's on different atoms suggests MO forms which account surprisingly well for the general properties of many diatomic



molecules, its limitations soon become apparent as when the mixing of 2s and 2p contributions cause the reversal of MO energy levels. It must be remembered that the best MO's are solutions of a wave equation and that simple LCAO forms are rather rough approximations only. However, by building an MO out of a number of AO's instead of just a pair, a better approximation can be obtained. It will appear later that this refinement is often quite indispensable, even in qualitative descriptions.

### *The hydrogen fluoride molecule*

Consider, as first example, the hydrogen fluoride molecule (Fig. 48).

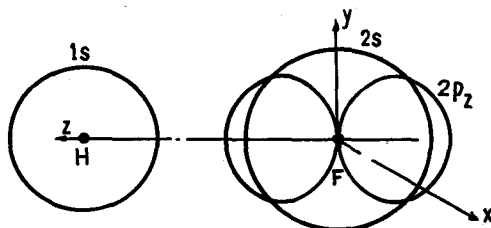
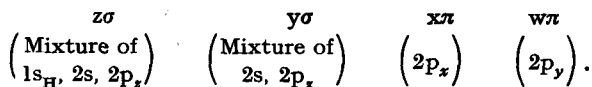
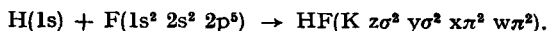


Fig. 48. Hydrogen fluoride with the  $2s + 2p_x$  atomic orbitals of fluorine shown. The  $2p_x$  and  $2p_y$  atomic orbitals, normal to the  $z$  axis, are omitted for clarity.

Omitting the fluorine K shell, the two atoms provide eight electrons, and the lowest energy AO's are  $1s_{\text{H}}$  (hydrogen),  $2s$ ,  $2p_x$ ,  $2p_y$  and  $2p_z$  (fluorine). The question is what are the lowest energy molecular orbitals which may be built from these AO's? Actual calculation yields an answer of the following kind in which the MO's are in ascending energy order:



The  $z\sigma$  MO is of bonding type, concentrating charge between the nuclei, though it may lean more towards the fluorine atom. The  $y\sigma$  MO contains an inappreciable amount of  $1s_{\text{H}}$  and is hardly a molecular orbital at all; it leans to the 'rear' of the fluorine atom, away from the hydrogen. The other two orbitals are pure fluorine AO's each of which has its distinctive symmetry and, in the absence of other low-lying AO's of similar type, improved mixtures cannot be formed. The structure is:



There is thus a normal  $\sigma$  bond, although it cannot be well represented by less

than 3 AO's, which is densest at the fluorine end, and 3 doubly occupied non-bonding orbitals. The latter give a striking picture of the three lone pairs of the octet on the fluorine atom; one projects to the rear while the other two combine to give an axially symmetrical charge distribution, in form something like a doughnut with the fluorine nucleus in the hole (Fig. 49).

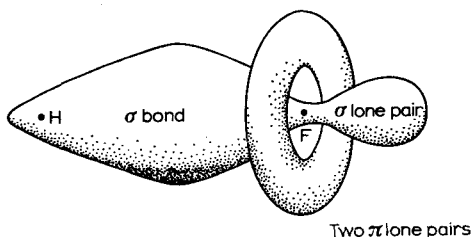


Fig. 49. Principal regions of high charge density in HF (schematic).

### Hybrid atomic orbitals

By examining the MO's more carefully it is now possible to retrieve the simple picture in which MO's are approximated by overlapping suitable pairs of orbitals derived from the different atoms. For clearly the  $\sigma$  MO could be regarded as being formed by combining the 1s orbital of the hydrogen with a modified fluorine orbital which is itself a *mixture* of the 2s and  $2p_x$  on the same (fluorine) atom. Such modified orbitals, which are still essentially atomic though not pure AO's, are called *hybrid* AO's. They are an immense aid to description because they make it possible to retain the pair picture in which bonds are associated with strongly overlapping pairs of AO's (now including hybrid as well as pure AO's), one on each of two atoms. The general forms of the hybrid orbitals which can be achieved by mixing are easily inferred. Thus the 2s and  $2p_x$  AO's in the hydrogen fluoride example yield an infinite range of hybrid pairs, the most symmetrical being

$$h_1 = \frac{1}{\sqrt{2}}(\varphi_{2s} + \varphi_{2p_x}) \quad \text{and} \quad h_2 = \frac{1}{\sqrt{2}}(\varphi_{2s} - \varphi_{2p_x}).$$

These are illustrated in Fig. 50 and are called *digonal* sp hybrids; they are exactly similar or 'equivalent' except in orientation. Clearly, a plausible description of the  $\sigma$  MO in HF could be obtained by overlapping  $h_1$  with the hydrogen 1s AO and using  $h_2$  as the lone pair orbital,  $\sigma$ . This would not be the best description because there is no reason, here, for choosing a pair of exactly similar hybrids; but it is still qualitatively useful. More generally,

departures from symmetry are permissible, but the most acceptable pairs are related so that they overlap as little as possible. If the  $2s$  content of  $h_1$  is increased and its  $2p_z$  content decreased, then the  $2s$  content of  $h_2$  must decrease and its  $2p_z$  content increase.

It is probable that  $sp$  hybridisation of this kind is significant in a large number of diatomic molecules, but its importance depends on a number of delicately balanced factors. It is favoured by the fact that overlap in a bond region (that is where the electrons are attracted by *two* nuclei) may be in-

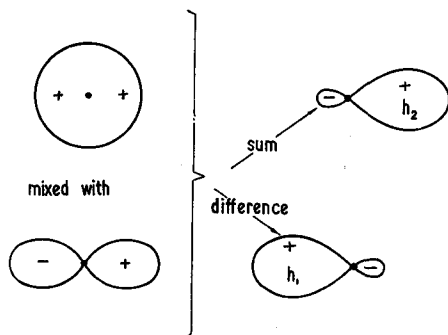
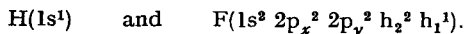


Fig. 50. Representing combination of  $s$  and  $p$  atomic orbitals to give  $sp$  hybrids.

creased. It occurs most easily when the  $p$  orbital is not much higher in energy than the  $s$  but is opposed by, for instance, an increasing  $p$  character in a lone pair orbital. Hybridisation also accounts most readily for the fact that electrons repel one another and tend to stay apart, particularly (owing to the exclusion principle) when each has the same spin. It will be seen later that the forms and disposition of hybrid orbitals can be discussed in terms of repulsions between the different pairs of bonding and lone pair electrons. This more detailed analysis of the electronic energy helps to give some understanding of the factors determining molecular geometry.

### Valence states. Promotion

In discussing bonds involving hybrid AO's it is necessary to introduce 'atomic valence states'. Accepting the above description (p. 111) we can discuss the energy of the hydrogen fluoride molecule. The bond is formed by overlapping  $h_1$  and  $1s_{\text{H}}$ , each contributing one electron, where the atoms, supposing they could be taken apart without changing the orbital forms, would be in the respective states



The hydrogen would be in a 'true atomic' state and the fluorine in a 'valence' state. The latter state is hypothetical, because  $h_1$  and  $h_2$  would, in fact, go smoothly into  $2s$  and  $2p_z$  orbitals as the nuclei were being separated; it does, however, allow the energy changes to be visualised. As Fig. 51 shows, the net binding energy is the 'gross binding energy' minus the 'valence state excitation energy'. The latter, which is characteristic of the valence state considered and constant from one molecule to another, accordingly forms an exceedingly useful datum. The high excitation energy involved is often completely offset by the more satisfactory overlap of the hybrid AO's, so that the net binding energy becomes considerably larger than could be accounted for without invoking hybridisation.

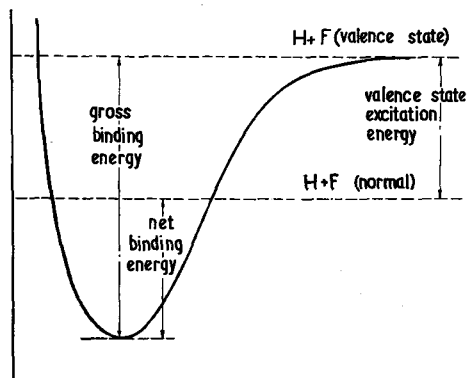
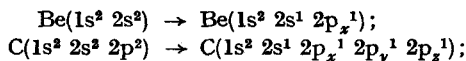


Fig. 51. Energy relationships in HF molecule (energy  $v$  distance between nuclei).

*Ineffective mixing of atomic orbitals: beryllium and carbon, electron promotion*

There are many instances in which a mixing of the AO's occupied in the ground state of an atom does nothing to improve its capacity for bond formation. Beryllium, for example, has the ground state structure  $\text{Be}(1s^2 2s^2)$  and, being without singly occupied orbitals, should be zero-valent. Carbon, with the structure  $\text{C}(1s^2 2s^2 2p^2)$ , should be bivalent; mixing the singly occupied  $2p$  orbitals is found merely to change their orientation. The bonds formed by these atoms can best be understood in terms of valence states in which 'electron promotion' has occurred. The promotions envisaged are



where the  $x$ ,  $y$ , and  $z$  directions are chosen in terms of the molecular environment of the atom. These valence states would serve to describe bivalent beryllium and quadrivalent carbon but, since two types of AO appear, would not account for the formation of the sets of *identical* bonds found in the linear molecule  $\text{BeCl}_2$  and the tetrahedral molecule  $\text{CH}_4$ . The difficulty disappears when the possibility of hybridisation is introduced; for mixing a  $2s$  and  $2p$  orbital has already been seen to yield, among other possibilities, precisely equivalent hybrid orbitals (Fig. 50) pointing in opposite directions. Promotion and hybridisation are employed freely to set up atomic valence states which give the best account of bond formation in specific molecular situations. With the help of these ideas it is possible usefully to discuss the bonding in really complicated polyatomic molecules.

### Localised MO's. Polyatomic molecules

Above (p. 97), the AO's of atoms were paired, according to symmetry and degree of overlap, to yield MO's of various type, all describing a two-electron bond. Essentially similar considerations may be employed in dealing with polyatomic molecules; but then the bonds, instead of being superimposed (e.g.  $\sigma$  and  $\pi$  bonds), may lie in different regions of space, uniting different pairs of atoms. If there are 'obvious' pairs of strongly overlapping AO's, or if such pairs can be formed by invoking not unreasonable valence states, it is possible to obtain a fairly satisfactory picture of the molecular electronic structure in terms of the 'localised' MO's which result. As with the diatomic molecule (p. 107), this description succeeds in explaining the accumulation of electron density in a number of localised bond regions. The application of these ideas is best illustrated by reference to specific molecules.

*Beryllium Chloride,  $\text{BeCl}_2$ .* This is a linear molecule in which both Be—Cl bonds are equivalent. The appropriate valence state of the Be atom is thus  $\text{Be}(1s^2 h_1^1 h_2^1)$ , where  $h_1$  and  $h_2$  are the digonal hybrids of Fig. 50. The relevant orbitals on the chlorine atoms are the singly occupied  $3p_z$  AO's ( $z$  referring to the molecular axis),  $3s$ ,  $3p_x$  and  $3p_y$ , containing lone pairs. It is likely also that some digonal hybridisation would occur at the chlorine atoms, the incorporation of some  $3s$  character strengthening the overlap in the bonds and pushing one of the lone pairs to the rear of each chlorine. The resulting situation, shown in Fig. 52, should be compared with that in HF (Fig. 49).

Heavier atoms with the same  $ns^2$  ground state configurations, for example zinc, cadmium and mercury, form linear dichlorides and dibromides whose electronic structures must be closely similar.

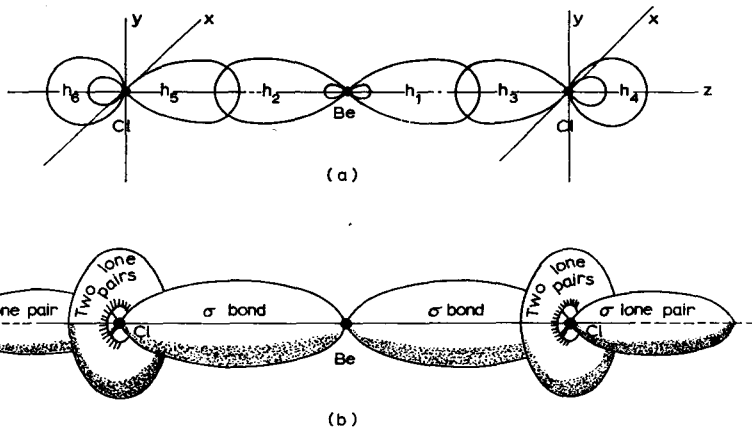


Fig. 52. Beryllium chloride: (a) Hybrid orbitals of the  $\sigma$  bonds and  $\sigma$  lone pairs ( $2p_x$  and  $2p_y$  orbitals omitted), (b) Regions of maximum charge density (schematic).

*Acetylene*,  $\text{C}_2\text{H}_2$ . This molecule is also linear. Again digonal valence states are appropriate, each carbon having the prepared configuration  $\text{C}(1s^2 h_1^1 h_2^1 2p_x^1 2p_y^1)$ . A  $\sigma$  C—C bond and two  $\sigma$  C—H bonds, all collinear, arise from obvious pairings (Fig. 53); the singly occupied carbon  $2p$  AO's overlap laterally to give two  $\pi$  bonds, exactly as in the diatomic molecule  $\text{N}_2$ . Consequently, there is a carbon-carbon triple bond.

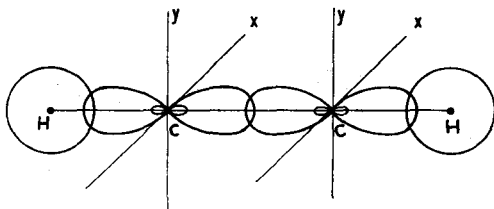


Fig. 53. Hybrid orbitals of the  $\sigma$  bonds in  $\text{C}_2\text{H}_2$  ( $2p_x$  and  $2p_y$  orbitals omitted).

*Water*,  $\text{H}_2\text{O}$ . This is a non-linear molecule, the H—O—H angle being about  $105^\circ$ . Hybridisation occurs somewhat less easily in oxygen than in carbon. By neglecting it altogether, it is still possible to get a rough explanation of the molecular shape. A strong overlap occurs between the singly occupied oxygen  $2p$  orbitals and the hydrogen  $1s$  AO's and suggests localised MO's at about  $90^\circ$ . But the overlap can be improved and the lone pairs better separated, thus lowering their repulsion energy, by admitting a fair amount of  $2s$ - $2p$  mixing (p. 119).

*Boron Trichloride, BCl<sub>3</sub>.* Here the molecule is planar, with the boron atom at the centre of an equilateral triangle of chlorine atoms (Fig. 54). The valence state must be described in terms of three similar hybrid AO's pointing towards the corners of the triangle. Such orbitals can be formed by mixing the 2s AO and two 2p AO's, say 2p<sub>y</sub> and 2p<sub>x</sub>; they lie in the yz plane of the latter and are precisely equivalent (Fig. 55). If the so-called *trigonal* hybrids are denoted by h<sub>1</sub>, h<sub>2</sub> and h<sub>3</sub>, the appropriate boron valence state must be B(1s<sup>2</sup> h<sub>1</sub><sup>1</sup> h<sub>2</sub><sup>1</sup> h<sub>3</sub><sup>1</sup>). The hybrid AO's overlap chlorine 3p AO's, directed towards the boron atom, to form localised MO's similar to those in beryllium chloride.

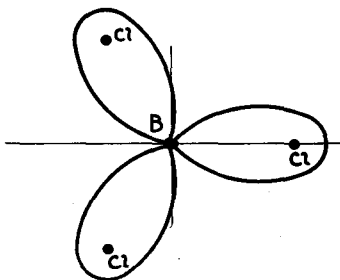


Fig. 54. Localised molecular orbitals in BCl<sub>3</sub>.

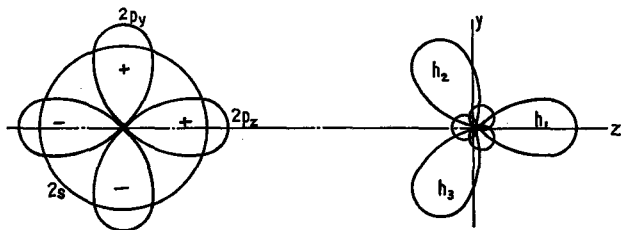


Fig. 55. Mixing of 2s, 2p<sub>y</sub> and 2p<sub>x</sub> atomic orbitals to form three equivalent hybrid atomic orbitals, h<sub>1</sub>, h<sub>2</sub>, h<sub>3</sub>. (Cf. Fig. 50, except that here the possibilities are superimposed instead of being shown separately.)

*Methyl radical, CH<sub>3</sub>.* The trigonal hybridisation just mentioned is indicated whenever an atom forms three identical bonds directed at 120° with each other. In carbon the valence state entails promotion and also hybridisation: it is C(1s<sup>2</sup> 2p<sub>x</sub><sup>1</sup> h<sub>1</sub><sup>1</sup> h<sub>2</sub><sup>1</sup> h<sub>3</sub><sup>1</sup>), where the third 2p AO, mainly 2p<sub>x</sub>, is not involved in the mixing and lies perpendicular to the plane of the hybrids. Three C—H bonds in the planar methyl radical are accounted

for by an overlap of  $h_1$ ,  $h_2$  and  $h_3$  with the three hydrogen  $1s$  AO'S. The free radical character of the system arises from the singly occupied  $2p_x$  orbital.

*Ethylene,  $C_2H_4$ .* This molecule is also flat, and the bonds from each carbon atom make very nearly  $120^\circ$  with each other. Assuming the same trigonal valence state as in the methyl radical, four C—H bonds and a central C—C bond are readily accounted for; and, when the two  $CH_2$  groups are rotated about the C—C bond until their singly occupied  $2p$  AO's are parallel, they overlap laterally to give a normal  $\pi$  bond (Fig. 56). The planar configuration is thus stabilised by  $\pi$  bonding and any twisting between the two  $CH_2$  groups would lead to a reduction in binding energy.

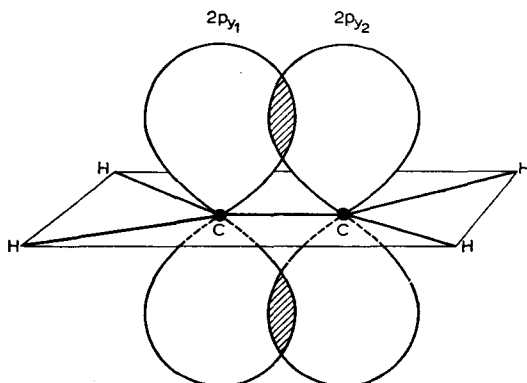


Fig. 56. Formation of a  $\pi$  bond in ethylene ( $\sigma$  bonds omitted). If the two  $2p$  orbitals are parallel there is substantial lateral overlap giving a  $\pi$  bond: rotation of the  $CH_2$  groups lessens the binding energy.

*Methane,  $CH_4$ .* The hydrogen atoms are at the corners of a regular tetrahedron, with the carbon at the centre. A carbon valence state with four identical, singly occupied hybrid AO's can be set up by allowing the mixing of  $2s$  and *all* the  $2p$  AO's. When they are denoted by  $h_1$ ,  $h_2$ ,  $h_3$ , and  $h_4$ , the carbon valence state is  $C(1s^2 h_1^1 h_2^1 h_3^1 h_4^1)$ . The pairing of AO's, describing four identical strong bonds, is then obvious (Fig. 57(a) and (b)). This *tetrahedral* hybridisation occurs whenever carbon forms four single bonds; thus it is appropriate to ethane and indeed to all the paraffins and their derivatives. The possibility of free rotation about the bonds leads to long, flexible chains.



### The wide occurrence of hybridisation

Consideration of the bonds formed by atoms with  $s$  and  $p$  electrons in their valence shells has brought to light three principal types of valence state. Although their realisation may require promotion and hybridisation, it often leads to strongly directed bonds with a very high net binding energy.

The principal types of hybrid which occur are:

- (i) Digonal or  $sp$  hybrids, formed from an  $s$  and *one*  $p$  orbital and pointing in opposite directions along the axis of the  $p$  orbital;
- (ii) Trigonal or  $sp^2$  hybrids, formed from an  $s$  and *two*  $p$  orbitals and inclined at  $120^\circ$  in the plane of the  $2p$  orbitals;
- (iii) Tetrahedral or  $sp^3$  hybrids, formed from an  $s$  and *three*  $p$  orbitals and inclined at about  $109.5^\circ$  (the tetrahedral angle).

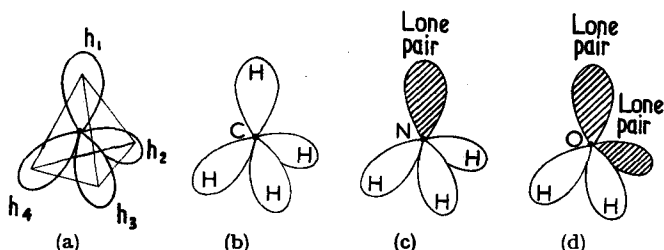


Fig. 57. Tetrahedral hybridisation in a series of iso-electronic molecules.

It is important to remember that, as already recognised, these types are exactly appropriate only in symmetrical situations (*e.g.*  $\text{BeCl}_2$ ,  $\text{BCl}_3$ ,  $\text{CH}_4$ ) and that departures from them are frequent. It is now generally believed that hybridisation is much more widely appropriate than was at first thought. It is interesting to consider, for example, what would happen if one of the protons in  $\text{CH}_4$  were transferred to the carbon nucleus. The resulting system,  $\text{NH}_3$ , is iso-electronic with the original, differing from it only in an increase of 1 in the central charge and a loss of symmetry. But the four  $\text{C—H}$  MO's have become three  $\text{N—H}$  MO's together with a lone pair orbital,  $h_1$  say. The tetrahedral valence state is therefore a plausible description of the nitrogen atom in ammonia, although at first sight hybridisation does not appear to be necessary; for the pyramidal form of the molecule (Fig. 57(c)) could be accounted for simply by overlapping three hydrogen orbitals with the three singly occupied  $2p$  orbitals of the nitrogen ground state. The  $\text{H—N—H}$  angle is, however,  $106.7^\circ$  which is neither the tetrahedral nor the right angle. The hybrid  $h_1$  has increased its  $s$  content, thereby lowering the energy of the lone pair electrons (which are no longer attracted by another nucleus), and

at the same time decreasing the s content of the other hybrids. This allows their approach towards the right-angled set of three pure p orbitals—an effect which is helped by repulsion from the concentrated lone-pair charge. The equilibrium configuration results from a quite fine energy balance, involving the mutual repulsions of all four electron pairs.

A tetrahedral disposition of four hybrids appears to give a much better description of the actual electronic structure than could be achieved without hybridisation, largely because it puts individual electron pairs in different regions of space. The same is true for  $\text{H}_2\text{O}$  where the system can be imagined as having been formed from the iso-electronic  $\text{CH}_4$  by the shrinking of two protons into the carbon nucleus. Then a tetrahedral oxygen valence state becomes more reasonable, the two lone pairs being well separated (as in Fig. 57 (d)) instead of being superimposed in one 2s and one 2p orbital.

The electron-donor property of nitrogen and the hydrogen-bonding property of oxygen are both connected with the existence of localised and strongly directed lone pairs of this kind. Later (p. 147), it will be seen how a great deal of stereochemistry may similarly be interpreted in terms of a theoretically reasonable distribution of electron pairs.

### Covalency maxima

Earliest ideas on covalence were based largely on the view that the atom under consideration attained a Gp. 0 gas structure by sharing electrons. Faced with such compounds as  $\text{PCl}_5$  and  $\text{SF}_6$ , in which sulphur and phosphorus share 10 and 12 electrons respectively, Sidgwick added the suggestion that every element had a certain maximum covalency which depended on atomic number (see Table 10).

TABLE 10

MAXIMUM COVALENCY AS IT DEPENDS ON ATOMIC NUMBER

<i>Atomic number</i>	<i>Period</i>	<i>Maximum number of shared pairs</i>
1	1	1 ( 2 electrons)
3 — 9	2	4 ( 8 electrons)
11 — 35	3 and 4	6 (12 electrons)
37 — 92	5, 6 and 7	8 (16 electrons)

The maximum covalency is by no means always reached, being shown by many elements only in their fluorides, and clearly represents the number of orbitals in the outermost, partially filled, shell which might be invoked in

forming valence states. It is 1 for hydrogen, 4 for elements of the second period, 6 for those of the third and fourth periods and 8 for the rest of the elements. The last group of elements, having s, p and d orbitals ( $1 + 3 + 5 = 9$ ) available, might be expected to exhibit a maximum covalency of 9. But the outermost electronic shells become less defined with increasing principal quantum number and the amount of promotion which can take place is restricted. A covalency of 4 is common in the third period, though there is a limited d orbital participation in spite of the d orbitals being unoccupied in the ground states.

### Hybridisation with d orbitals

With the admission of d orbitals the number of principal types of hybridisation is increased from 4 (pure p, digonal, trigonal, tetrahedral) to over 40; fortunately only a few of these lead to systems of strong bonds.

*Bipyramidal,  $sp^3d$ .* A typical bipyramidal molecule is phosphorus pentachloride,  $PCl_5$ , which is monomeric in the vapour and has the form shown in Fig. 58. The hybridisation in the central plane could be  $sp^2$ , giving the three bonds at  $120^\circ$  with one another. And the third p orbital could be mixed with the appropriate d orbital, since both are symmetrical about the central axis, to give one hybrid directed up and another down as in Fig. 59. In these circumstances two chlorine atoms would be expected to

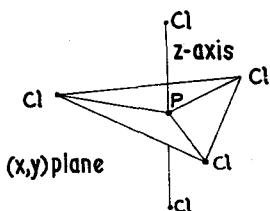


Fig. 58. Bipyramidal structure of  $PCl_5$ .

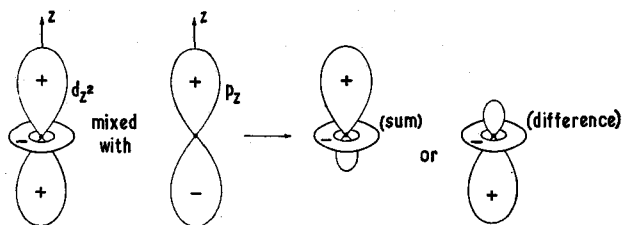


Fig. 59. One type of pd hybridisation.

be bound somewhat differently from the other three; the bond above and below the plane are in fact slightly longer. The corresponding element of the first short period, nitrogen, forms no such compound because there are no 2d AO's and the 3d AO's are too high in energy to allow of appreciable mixing. Thus  $NF_5$  is the highest fluoride.

*Octahedral,  $sp^3d^2$ .* A molecule of this kind is  $SF_6$ , which has four bonds lying at right angles in the plane of the sulphur and the other two pointing up and down from the plane (Fig. 60). The two vertical bonds are formed essentially as in a bipyramidal molecule, but the in-plane bonds are best

described in terms of hybrids incorporating a second d orbital. The mode of formation of one of the in-plane hybrids is indicated in Fig. 61. Here the four hybrids so formed would not be quite equivalent to the other two,

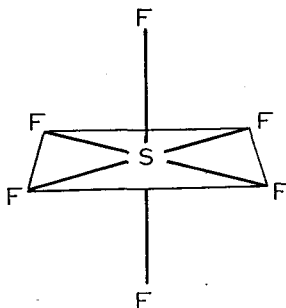


Fig. 60. Octahedral structure of  $\text{SF}_6$ .

but, if slight mixing is permitted, a strictly equivalent set of six can be found; these point to the corners of a regular octahedron.

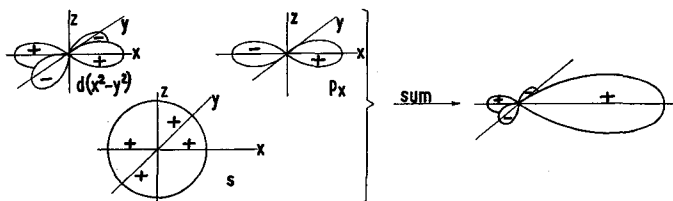


Fig. 61. One type of spd hybridisation.

*Square planar,  $dsp^2$ .* Certain ions have four planar orbitals directed towards the corners of a square without atoms above or below the plane. Examples of 'square' ions are  $\text{Ni}(\text{CN})_4^{2-}$  and  $\text{PtCl}_4^{2-}$ . The hybridisation shown in Fig. 61 is again appropriate. In planar ions of this kind, however, it is possible for the primary system of hybrid bonds to be supplemented by a secondary system involving the remaining orbitals of the valence shell. In the plane square instance, the secondary system can be formed from the out-of-plane orbitals (one p and three d) as in Fig. 62. Such orbitals have a node in the molecular plane and therefore have  $\pi$  character. They can overlap with p orbitals on the atoms to which they point, to give a  $\pi$  bond superimposed on the primary  $\sigma$  bond. Double bonding of this kind is almost certainly important in planar complexes when sufficient electrons are available.

It should be noted that the orbitals which are mixed belong, in the first two examples, to the same quantum shell (3s, 3p, 3d). Often, however, the

d orbital belongs to a lower-quantum shell (e.g. 4s, 4p, 3d) and this is indicated by writing the d orbital first. In the last example (Ni, Pt) we therefore refer to  $dsp^2$  hybridisation.

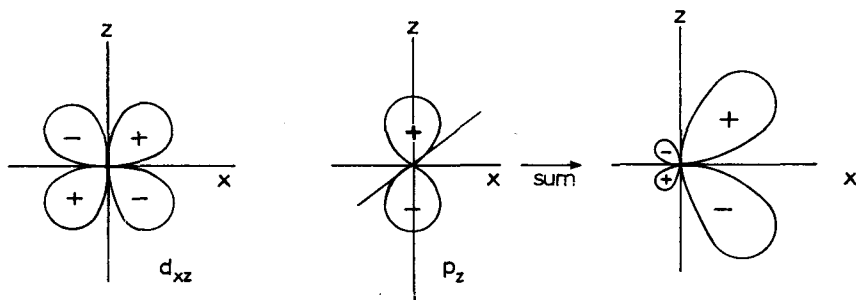


Fig. 62. Secondary hybrid suitable for  $\pi$ -bond formation.

Compounds in which the maximum covalency is exhibited are naturally very stable. Thus, for instance,  $CCl_4$  and  $SF_6$  are unreactive towards water, whereas  $SiCl_4$  and  $PCl_5$  are easily hydrolysed because the valency of each central atom is capable of being increased.

### Covalent radii

The nature of the electron cloud about a nucleus makes it difficult to define the size of an atom. However, the distance between a nucleus and its nearest neighbour is a precisely measurable quantity, and from it the atomic radius may be deduced. Internuclear distances in solids and bond lengths in molecules can be determined by a variety of methods, such as X-ray or electron diffraction and band spectroscopy. Inter-nuclear distances in solids depend to some extent on the way the atoms are packed. In diamond, however, the C-C distance (1.542 Å) is very nearly the same as it is in a saturated hydrocarbon (1.52 to 1.55 Å). The covalent radius of carbon for tetrahedral bonding is thus 0.77 Å. In silicon the Si-Si distance is 2.34 Å, indicating a covalent radius of 1.17 Å. Thus the C-Si distance in a compound should be  $0.77 + 1.17 = 1.94$  Å, which proves to be the measured value in tetramethylsilane,  $Si(CH_3)_4$ .

For hydrogen, uniquely as it happens, the covalent radius varies considerably when the element is in different states of combination, from, for instance, 0.28 Å in the halogen halides to 0.37 Å in the hydrogen molecule,  $H_2$ .

From a comparison of a large number of covalent bond distances we can assign to atoms single-bond covalent radii which, when added together,

successfully predict internuclear distances for bonds of this type. The radii depend to some extent on the number and spatial distribution of the bonds, but the variations thus caused are usually less than 0.05 Å.

*Double bond and triple bond radii*

The existence of  $\pi$ -bonding as well as a sigma bond between two nuclei shortens the internuclear distance. In alkenes the distance between the 'doubly bound' carbon atoms is  $1.34 \pm 0.02$  Å; hence, carbon has been assigned a double-bond radius of 0.67 Å. The carbon triple-bond radius deduced from the spectra of alkynes is 0.60 Å. For nitrogen the triple-bond radius is 0.55 Å. In HCN, the C-N distance is 1.15 Å, which is the sum of the carbon and nitrogen triple-bond radii. It should be emphasised, however, that many compounds have bonds which cannot be described, even to a first approximation, simply as single, double or triple. The description implied by the formulation  $N \equiv C-C \equiv N$  for the bonding in cyanogen is a poor one because the C-C distance is only 1.37 Å. Clearly the electron density in the region between these two atoms must be nearly as high as that in the double bond of an alkene.

TABLE 11  
SINGLE-BOND COVALENT RADII (Å)

Group											
IA	IIA	IIIA	IVA	IB	IIB	IIIB	IVB	VB	VIB	VIIB	
Li	Be					B	C	N	O	F	
1.34	0.90					0.82	0.77	0.75	0.73	0.72	
Na	Mg					Al	Si	P	S	Cl	
1.54	1.30					1.18	1.11	1.06	1.02	0.99	
K	Ca	Sc	Ti	Cu	Zn	Ga	Ge	As	Se	Br	
1.96	1.74	1.44	1.36	1.38	1.31	1.26	1.22	1.19	1.16	1.14	
Rb	Sr	Y	Zr	Ag	Cd	In	Sn	Sb	Te	I	
2.11	1.92	1.62	1.48	1.53	1.48	1.44	1.41	1.38	1.35	1.33	
Cs	Ba	La	Hf	Au	Hg	Tl	Pb	Bi	Po	At	
2.25	1.98	1.69	—	1.50	1.49	1.48	1.47	1.46	—	—	

### Trends in ionic and covalent radii

An ion may be looked upon as a sphere with a radius which depends on (a) the quantum level of its outermost electrons and (b) the effective nuclear charge acting on those electrons. Ionic radii can be derived as indicated on p. 103, and they show clear trends through the Periodic Table. Within a group there is an increase in radius with atomic number which is due to the increasing energies of the successive outermost electrons, the effective nuclear charge on these electrons remaining about the same:

Li <sup>+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Rb <sup>+</sup>	Cs <sup>+</sup>
0.60	0.95	1.33	1.48	1.69 Å
F <sup>-</sup>	Cl <sup>-</sup>	Br <sup>-</sup>	I <sup>-</sup>	
1.36	1.81	1.95	2.16 Å	

Within a period the sizes of the positive ions decrease as the effective nuclear charges increase with atomic number, the quantum level of the outermost electrons remaining the same:

Cs <sup>+</sup>	Ba <sup>2+</sup>	La <sup>3+</sup>
1.69	1.35	1.15 Å

For corresponding reasons a 2-positive ion is larger than a 3- or 4-positive one:

Fe <sup>2+</sup>	0.76	Fe <sup>3+</sup>	0.64 Å
Pb <sup>2+</sup>	1.20	Pb <sup>4+</sup>	0.84 Å

Across a transition series, for a series of ions of equal charge, the increase in effective nuclear charge with atomic number as electrons enter an inner d shell is rather small, and the radii of the ions remain about constant:

Mn <sup>2+</sup>	Fe <sup>2+</sup>	Co <sup>2+</sup>	Ni <sup>2+</sup>
0.80	0.76	0.78	0.78 Å

The minor variations are due to ligand field effects (p. 164).

In the lanthanides an increase of 14 in atomic number occurs as the 4f shell is filled up; these f electrons exert only weak screening and the ionic radii fall from 1.15 (La<sup>3+</sup>) to 0.93 Å (Lu<sup>3+</sup>). This, the *lanthanide contraction*, affects the size of the ions of the elements which follow in the Periodic Table.

However the sizes of atoms cannot be compared as easily as those of ions. The *Van der Waals radius* is that of the spherical, non-bonded atom in a crystal of the solid element; it can be measured only for the noble gases, although estimates of its value can be made for some other atoms. Pauling has assumed that in directions other than that of a covalent bond

the electrons of an atom are in almost the same environment as those of the corresponding anion: thus, for instance, since the anion  $F^-$  has a radius of 1.36 Å, the Van der Waals radius of the fluorine atom must be about the same. The single-bond covalent radius of fluorine is, of course, much smaller. Thus a fluorine molecule can be represented as a pair of spherical atoms fused together (Fig. 63):

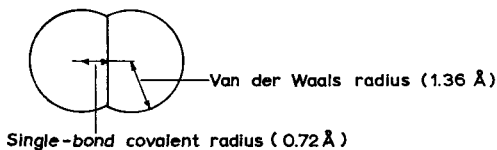


Fig. 63. Diagrammatic representation of  $F_2$  molecule.

In view of what has been said (p. 107) about the nature of covalent bonding, this picture obviously gives an over-simplified representation of the electron densities in the molecule. Nevertheless, the Van der Waals radii can account satisfactorily for effects such as steric hindrance between parts of a molecule not directly bonded to each other (p. 600).

As Van der Waals radii can be measured only for the noble gases, and estimated only for those elements which form simple anions, some other criterion of size is necessary for the atoms of metals. The *metallic radius* obtained by halving the internuclear distance in the solid metal is not the same as a Van der Waals radius because neighbouring atoms cannot be considered as non-bonded. The concept of metallic radius is of limited value; in many metals (*e.g.* zinc, p. 197) the internuclear distances differ in the different crystal planes. Nevertheless two generalizations can be made.

(a) When a metal forms compounds in which the bonds can be described as covalent single bonds, the covalent radius assigned to the metal is less than its metallic radius. Thus for aluminium the single-bond covalent radius in the alkyls is inferred to be 1.18 Å; whereas the metallic radius in the face-centred cubic lattice of the metal is 1.43 Å. But the ionic radius of  $Al^{3+}$ , 0.50 Å, is very much less than either the metallic radius or the covalent radius, as would be expected from the larger effective nuclear charge acting on the outer electrons.

(b) Trends in metallic radii, like those in single-bond covalent radii and also in Van der Waals radii as far as these are known, are similar to the trends in ionic radii. Sizes increase down a group in the Periodic Table:

	Li	Na	K	Rb	Cs
Metallic radius	1.55	1.90	2.35	2.48	2.67 Å
Covalent radius	1.34	1.54	1.96	2.11	2.25 Å



But sizes decrease along a period:

	Na	Mg	Al
Metallic radius	1.90	1.60	1.43 Å
Covalent radius	1.54	1.30	1.18 Å

As for ions, the trends can be explained in terms of the energies of the outermost electrons and the effective nuclear charges acting upon them.

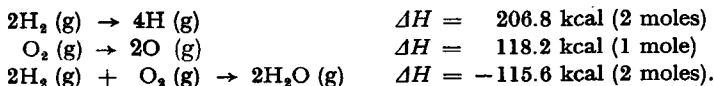
### Bond energies

Strictly, what has been said in the discussion of valency refers to an idealised situation in which all the atomic nuclei are at rest in equilibrium positions. Such a situation is not realised even at the absolute zero of temperature, because there still remains the zero-point energy of vibration. The electronic binding energy, that is the energy required to separate a molecule into its component atoms in their ground states and at rest, is thus not directly measurable. What can be measured is the 'dissociation energy', which is the energy required for separation of the atoms under specified conditions (*e.g.* referred to standard temperature and pressure). The two quantities differ by the energies of vibration, rotation and translation; the latter two are usually small, but the vibrational energy may amount to a substantial fraction of the binding energy. For a diatomic molecule, the dissociation energy is often called the 'bond energy' and

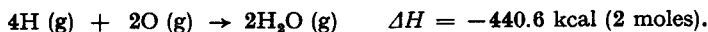


Energies of dissociation can be found by spectroscopic methods ( $\text{H}_2$ , p. 258) from heats of sublimation, and from thermochemical measurements ( $\text{I}_2$ ). For polyatomic molecules the last method is usually employed, the heats of reaction being generally used. Thus [the heat of dissociation of the water molecule can be found from

- (i) the heat of dissociation of  $\text{H}_2$  (103.4 kcal/mole),
  - (ii) the heat of dissociation of  $\text{O}_2$  (118.2 kcal/mole),
  - (iii) the heat of formation of  $\text{H}_2\text{O}$  (57.8 kcal/mole),
- by considering the reactions



Subtracting the first two equations from the third gives



The heat of dissociation is thus  $-\Delta H = 220.3$  kcal/mole. Since in a gas reaction the  $p\Delta V$  term in  $\Delta H = \Delta U + p\Delta V$  is usually negligible, the energy of dissociation is  $D_0 \sim 220.3$  kcal/mole.

Now it is found experimentally that the dissociation energy of a polyatomic molecule can be fairly accurately represented as a sum of the bond energies of every individual bond broken and, moreover, that the energies of the bonds between particular elements do not vary much from one molecule to another. Thus, the dissociation energy of the water molecule is the sum of the two O—H bond energies,  $E_{\text{O-H}} = 110.2$  kcal/mole. This is a remarkable empirical fact, for the electronic energy of a molecule must depend considerably on its size and shape and the existence of characteristic bond properties must, in a general way, be a consequence of the strong localisation of the orbitals describing individual bonds. Tables of bond energies have been drawn up and have been of considerable value, more particularly in organic chemistry where molecules often contain large numbers of bonds but relatively few different types (very common ones are C—H, C—C, C—O, C—N). However, the additivity rule breaks down when systems whose atoms adopt different valence states are compared; for the gross or 'intrinsic' bond energy (*cf.* p. 113) will be offset by different excitation energies in different situations. In these circumstances, it would be preferable to use an equation of the form

$$-\Delta U = \Sigma E_{\text{A-B}} - \Sigma V_{\text{A}}$$

for the dissociation energy—a sum of intrinsic bond energies minus a sum of atomic valence state excitation energies—but valence state data are at present limited.

### The electronegativity scale

In discussing bonds between unlike atoms, it is convenient to associate with every atom a quantity,  $x$ , representing its electron-attracting power in a bond, such that the ionic character of a bond A—B is determined by  $x_{\text{A}} - x_{\text{B}}$ . The equality  $x_{\text{A}} = x_{\text{B}}$  would describe a 'pure covalent' situation in which there is no tendency for electrons to drift in either direction. Mulliken takes  $\frac{1}{2}(I + A)$  as the absolute electronegativity of an atom. Pauling (1932) constructed an electronegativity scale from bond-energy data. For atoms whose electronegativities are about the same, it is found that the bond energy  $E_{\text{A-B}} \sim \sqrt{E_{\text{A-A}}E_{\text{B-B}}}$  (the geometric mean). But for atoms with electronegativities that are different the bond energy is greater than the geometric mean by an amount proportional to  $(x_{\text{A}} - x_{\text{B}})^2$ . By

suitable choice of the proportionality factor is it therefore possible to arrange that the 'ionic stabilisation energy' is given by

$$A_{AB} = (x_A - x_B)^2$$

The Mulliken method of finding electronegativity has the disadvantage that few electron affinities are known, and the Pauling method suffers from the fact that bond-dissociation energies for the elements can be determined in relatively few instances. Another method, due to Allred and Rochow, which is of far wider applicability, brings into use the effective nuclear charge,  $Z^*$  (p. 70).

*The Allred-Rochow method*

In this method the electron-attracting power of an atom is considered to be proportional to  $Z^*/r^2$ , where  $Z^*$  is the effective nuclear charge exerted in the outer shell of the atom and  $r$  is the covalent radius. The Allred-Rochow value for the electronegativity,  $x$ , is given by

$$x = \frac{0.359Z^*}{r^2} + 0.744$$

Here  $r$  is in Å and the constants are chosen to give  $x_H = 2.1$ , a value which was the basis of the earlier, widely accepted, Pauling scale.

TABLE 12

TABLE OF ELECTRONEGATIVITIES (Allred-Rochow scale)

F	4.10	P	2.06
O	3.50	Ge	2.02
N	3.07	B, Te	2.01
Cl	2.83	Ga, Sb	1.82
Br	2.74	Si	1.74
C	2.50	Transition metals	1.7 → 1.2
Se	2.48	Lanthanides	1.1 → 1.0
S	2.44	Alkaline earths	1.04 → 0.97
I, As	2.20	Alkali metals	0.97 → 0.86
H	2.10		

The actual electron-attracting power of an atom depends on its environment, accordingly the electronegativity ascribed to an element can only be a mean value for the element in its most common valence and oxidation states. The higher the charge number (p. 230) of an atom in a compound the greater the electronegativity displayed by the element.

It is useful to note that the dipole moment of the bond P—Q, in debyes, is usually within a few percent of the difference  $x_A - x_B$ . Electronegativity differences determine charge shifts along bonds and this fact will be seen later (p. 249) to be of considerable significance.

### Effect of electronegativity difference on bond length

Where two atoms connected by a bond differ considerably in electronegativity the bond length is shorter than the sum of the covalent radii. Thus in ClF the bond length is 1.63 Å, that is 0.08 Å shorter than the sum of the radii of Cl and F.

The empirical equation: Internuclear distance

$$r_{A-B} = r_A + r_B - 0.09(x_A - x_B),$$

due to Schomaker and Stevenson, is an attempt to relate bond length to bond polarity. It should be stressed, however, that the shortening of a bond can rarely be proved to be entirely due to its polar nature; there is usually the possibility of some double-bond character which would contribute to the shortening.

## NON-LOCALISED AND METALLIC BONDING

### Non-localised orbitals

It has been possible to represent all the bonds thus far considered by using localised MO's built up from pairs of AO's (or hybrid AO's). But Fig. 64

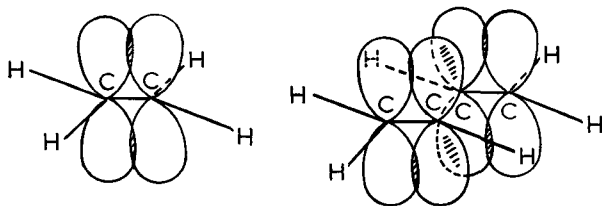


Fig. 64. Singly occupied 2p orbitals in ethylene and butadiene. The  $\sigma$ -bonded framework is omitted. (For clarity the greater extent of the actual overlap has not been shown.)

shows that unique pairs cannot always be found. In ethylene there is no ambiguity, the highest occupied orbital providing a normal  $\pi$  bond; but in butadiene, where there is a very similar ' $\sigma$ -bonded framework', the electrons of the 2p AO's normal to the molecular plane are less easily accommodated. In instances of this kind, which occur throughout organic chemistry, every such AO overlaps *two* or *three* neighbours (end atoms excepted), and if *one* is

admitted in a  $\pi$ -type MO then *all* must be admitted. Hence the so-called ' $\pi$  electrons' must be accommodated in MO's which extend over the whole molecule, the restricted 'pairing' approximation being no longer valid.

The coefficients of the individual AO's, in the LCAO approximation to any  $\pi$ -type MO, can, as always, be determined by standard methods. Fig. 65

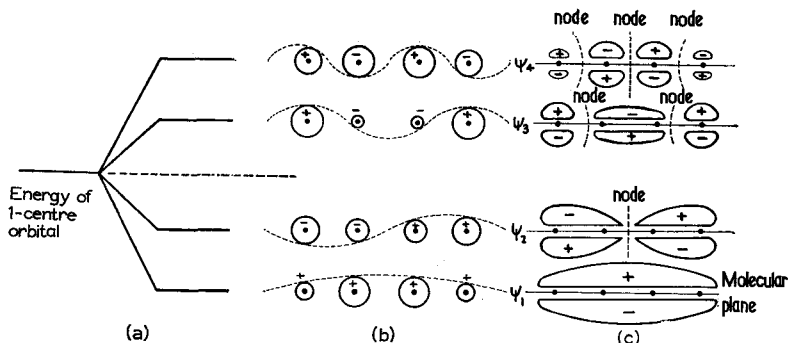


Fig. 65. Energy levels and  $\pi$ -orbitals for a chain of 4 atoms.

- (a) MO energies, relative to that of electron confined to one centre.  
 (b) Coefficients in LCAO approximation—indicated by size of circles.  
 (c) Regions where  $\psi$  is greatest, separated by nodes.

indicates their values in the butadiene MO's and illustrates some general properties of *non-localised MO's*. Clearly the orbitals may be classified as bonding ( $\psi_1$  and  $\psi_2$ ) or anti-bonding ( $\psi_3$  and  $\psi_4$ ) on energetic grounds, and their character is reflected in their charge density contributions—the highest energy MO putting a node across every bond, and the lowest leading to a pile-up of charge in every bond. The wave-like pattern followed by the coefficients is also typical; the non-localised orbitals for any long chain would be similar and the allowed energies would behave as in Fig. 66.

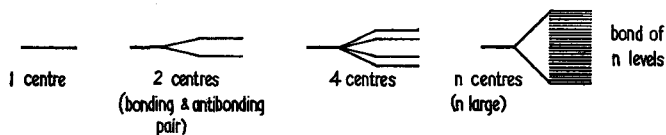


Fig. 66. Energy levels for a chain of atoms, showing origin of energy bands.

Generally, for every energy state of an electron moving about one centre there are  $n$  related states in a crystal of  $n$  such centres. The energies of these states lie within a *band* whose width depends on the strength of the interaction between neighbours.

In foregoing sections the one-centre orbitals described have fallen into *pairs*, interaction between different pairs being so small that each pair could be considered by itself, but in conjugated molecules and in metals there is no alternative but to admit complete non-localisation. This non-localisation is essential to an understanding of the characteristic properties of such systems.

### Electronic structure of conjugated molecules

Butadiene shows features common to all 'conjugated' molecules, that is those in which the double bonds of classical chemistry cannot be uniquely allocated. According to the aufbau approach, its electronic structure, apart from that of the  $\sigma$ -bonded framework, would be  $(\psi_1)^2(\psi_2)^2$ . The extra stabilisation due to these 'mobile'  $\pi$  electrons is in fact greater than that which could be provided by two ethylenic  $\pi$  bonds. The difference in the stabilisation which accompanies the increased delocalisation of the same number of electrons, is the 'resonance' energy. If the system is twisted about its centre link it does indeed, from the point of view of the  $\pi$  electrons, break into two ethylenic halves, because interaction between the central 2p AO's diminishes to zero as they are rotated (*cf.* Fig. 56, p. 117). It is accordingly the resonance energy which keeps such systems flat.

More insight into the  $\pi$ -electronic structure can be gained from the coefficients indicated in Fig. 65. As stated earlier (p. 98), the squares of these coefficients, and therefore the *areas* of the circles in Fig. 65 (b), represent the amounts of charge associated with corresponding atoms in each MO. The electrons in  $\psi_1$  and  $\psi_2$  are associated mainly with internal and end atoms, respectively; but, on adding up the contributions, each atom gets just the same share, one electron, and the charge is thus uniformly distributed. This is true for a large class of hydrocarbons though non-uniformities arise when hetero-atoms are introduced and when ionisation occurs; thus, for example, the removal of an electron from  $\psi_2$  would give a net positive charge mainly on the *end* atoms. On the other hand, the electron density *between* the atoms is determined (p. 99) by products of adjacent AO coefficients. More precisely,  $p_{1-2} = 2 \sum_{\text{occupied MO's}} c_1 c_2$  measures the  $\pi$ -bond density in link 1-2; it has the

value 1 for ethylene (with 1  $\pi$  bond), but is fractional in other molecules. For butadiene, the  $\pi$  bond orders are about 0.45 for the central, and 0.89 for the outer bonds. These substantial differences in  $\pi$ -bonding in different regions of the molecule are reflected in the extent to which the underlying  $\sigma$  bonds are strengthened and shortened. It has in fact proved possible to interpret both bond lengths and bond properties in terms of bond orders.

### Electronic structure of metals

Metals are generally distinguished from non-metals by (a) their excellent thermal and electrical conductivity and (b) their great mechanical strength and ductility. These properties are a direct result of the non-localised nature of the bonding in metals; the electrons are mobile, like the  $\pi$  electrons and, furthermore, in a true metal there are no underlying directed bonds.

Lorentz first suggested that a metal consists of an array of cations in a sea of free electrons, and Sommerfeld put the idea on a wave-mechanical basis, describing the electrons by standing waves. Fig. 65, which refers to the prototype of a one-dimensional crystal, shows that the standing wave description is not inappropriate even when the presence of the cations is explicitly recognised. But a more accurate picture shows more. The energies of the allowed 'standing waves', the Bloch orbitals, fall into characteristic *bands*, one associated with each atomic level, whose widths and positions can be correlated with a range of non-structural (*e.g.* electric and magnetic) properties.

The true metals comprise the elements of Gps. IA, IB, IIA, and the transition elements, including lanthanides and actinides. With the exception of manganese and uranium they all have one of the three simple structures:

- (i) Body-centred cubic (Fig. 67), *e.g.* Na, K, Mo, Fe;
- (ii) Face-centred cubic (Fig. 68, 70), *e.g.* Cu, Ag, Au, Fe;
- (iii) Close-packed hexagonal (Fig. 69, 70), *e.g.* Be, Mg, Zr.

In (i) the number of nearest neighbour atoms, *viz.* the crystal co-ordination number, is 8. Obviously there are insufficient electrons to account for the binding in terms of normal electron-pair covalencies. For instance, the one valence electron of sodium cannot, in any conceivable way, provide

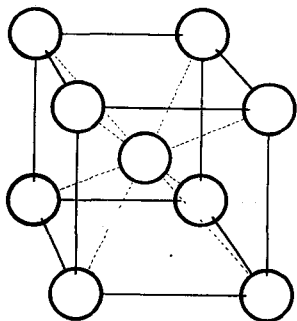


Fig. 67.  
Body-centred cubic packing.

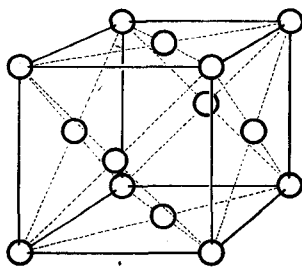


Fig. 68.  
Face-centred cubic packing.

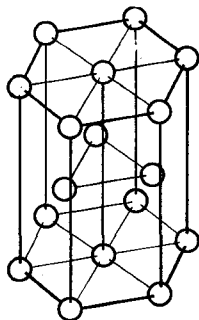


Fig. 69. Close-packed hexagonal packing.

covalent bonds with its near neighbours. The necessary sharing, which results in 'partial' bonds, is strictly comparable with that which occurs in butadiene (4 electrons giving 3 partial  $\pi$  bonds) or benzene (6 electrons giving 6 partial  $\pi$  bonds); but the spreading out must be much more complete in a metal and the crystal bond orders must be relatively small.

*Passage from metals to non-metals across the Periodic Table*

It is largely because the formation of a close-packed metallic structure demands a fairly easy removal of electrons that the metals lie at the left hand side of the Periodic Table (p. 81). Such elements pool their valence electrons readily, having low ionisation potentials, and the large de-localisation energy then easily leads to a net binding. Proceeding to the right along every period,

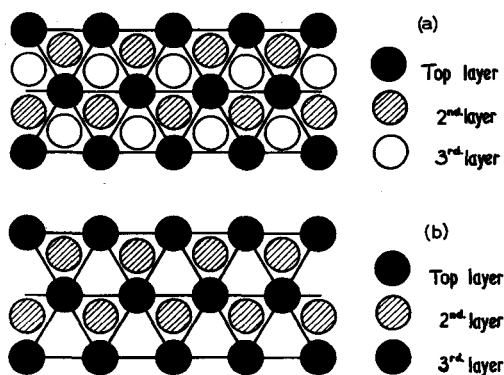


Fig. 70. (a) Face-centred cubic packing (shown in depth). (b) Hexagonal close-packing (shown in depth).

metallic properties become feebler and the tendency towards covalently-bonded structures increases. Carbon, for instance, does not allow its valence electrons to escape but readily shares them covalently with 4 neighbours. The open tetrahedral structure of diamond, with its strongly directed bonds (which make it brittle), is thus energetically preferred to a close-packed metallic structure. In diamond, carbon completes its octet in the usual sense—a sense which entirely breaks down in the true metals—and in this context is said to satisfy the  $(8 - N)$  rule. Every atom is bound covalently to  $8 - N$  others,  $N$  being the number of its group in the Periodic Table.

Silicon, germanium and grey tin have diamond-like structures and, although the latter two are metallic to a considerable degree, their bonding is largely covalent, the localisation merely being less complete than in, say, diamond. Other structures are also possible. Graphite consists of well-



separated layer planes in which every carbon has three neighbours (as in a giant polycyclic hydrocarbon), but the absence of a fourth covalent bond is compensated for by non-localised  $\pi$  bonding which makes graphite into a 'two-dimensional metal' (the conductivity being primarily along the single planes). Other elements conforming to the  $(8 - N)$  rule are arsenic, antimony and bismuth ( $N = 5$ ) with three nearest neighbours, and selenium and tellurium ( $N = 6$ ) with only two. In the latter, the atoms are connected in spiral chains which are held together by much weaker forces. In iodine ( $N = 7$ ) the essential units are simply diatomic molecules.

Thus a gradual breakdown of metallic properties is observed in passing along the various periods, together with a growing tendency to form covalently bonded units. Thermal and electrical conductivity diminish, density decreases, and the materials become hard but brittle. In the intermediate region of the Periodic Table are included the metals of Gps IIB and IIIB, where there is still a tendency to obey the  $(8 - N)$  rule, but their atoms lose electrons with a readiness approaching that of the true metals. Their atoms are sometimes said to be in an 'incompletely ionised' condition, and their structures are distorted forms of the simple lattices.

## LONG-RANGE BONDS

### Electrostatic bonds

The forces which hold together well-separated units such as the individual molecules in ice or naphthalene are weak compared with covalent bonds. The strongest of them are often termed 'electrostatic' bonds, signifying that the forces can be attributed to an interaction of the unmodified, static charge distributions of the separate systems. Examples are the *ion-dipole*

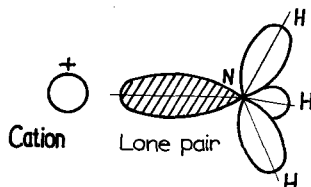


Fig. 71. Ion-dipole interaction.

bonds which occur in hydrates and ammoniates. These are usually weaker than ordinary covalent bonds and relatively easily break on heating. The binding force arises (Fig. 71) from the attraction between the positive ion and the lone-pair electron density. Appreciable mixing of the lone pair

orbitals with those on the other atom is not required, overlap being small. The attraction arises mainly from a very asymmetrical charge distribution *within* the separate systems, but some mixing (covalency) also contributes to it.

### Hydrogen bonds

Similar forces account for the *hydrogen bond* between hydrogen, already bonded to one atom, and the lone pair on a strongly electronegative element such as fluorine, oxygen or nitrogen. Of these, the  $\text{H}\cdots\text{F}$  bond is the strongest, with an energy about one tenth that of a  $\sigma$  bond and a length about twice as great. Such bonds are responsible for the open tetrahedral structure of ice (p. 289), in which every hydrogen (with a net positive charge) attaches itself through the lone pair to a neighbouring oxygen atom. It is the persistence of this structure, in the liquid state, which makes the boiling point of water higher than that of other non-metallic hydrides. The boiling points of ammonia and hydrogen fluoride are high in relation to other hydrides of Gps. V and VII for the same reason. Similar  $\text{O}\cdots\text{H}$  bonds occur in many polymers; thus, in non-polar solvents, they bind carboxylic acids into dimers (Fig. 72). And in *o*-hydroxy aromatic aldehydes and *o*-nitrophenols (Fig. 73) *intramolecular*  $\text{O}\cdots\text{H}$  bonds prevent the characteristic  $\text{O}-\text{H}$  vibrations which are normally revealed in infrared spectra and reduce the solubility of the compounds in water. The *m*- and *p*-isomers which give the normal  $\text{O}-\text{H}$  frequencies are much more soluble.

Electrostatic effects are undoubtedly of importance in molecular crystals, but, as heats of sublimation show, they are small and packing considerations must be put first. When electrostatic effects are weak, owing to high symmetry of the interacting systems, other forces must be sought.

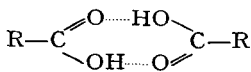


Fig. 72. Dimeric bonding in carboxylic acids.

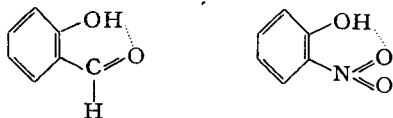


Fig. 73. Prevention of  $\text{O}-\text{H}$  vibration by  $\text{O}\cdots\text{H}$  bonds.

### Polarisation and dispersion forces

Electrostatic interactions between the atoms of a Gp. 0 gas, which are very symmetrical, are exceedingly small. But weak long-range forces do

operate in both gases and liquids. To account for these *Van der Waals* forces, it is necessary to introduce a more refined treatment which recognises the disturbance of one charge density by another. Each electronic system can induce a weak dipole in the other, giving a *polarisation* force which depends on the polarisability of the system and falls off as the sixth power of the distance. At the same time a correlation of the electronic motions of the two systems provides further attractive force. London first suggested that the latter was like the force between rapidly varying electric dipoles. He called it a *dispersion force*. It is now known that dispersion forces operate over considerable distances and that they are strongest when (a) one system is in an excited state and (b) the systems are identical (the case of 'resonance' interaction). Van der Waals forces between atoms or small molecules are well accounted for in this way; those between large molecules are, as yet, but partly understood. Forces of this type always occur as a 'higher order' effect, and also play their part in determining the cohesive properties of molecular crystals and many other non-metallic solids. These forces are usually completely masked by those associated with true chemical valence and will not be considered further.

#### FURTHER READING

- H. B. GRAY, *Electrons and Chemical Bonding*, New York, Benjamin, 1964.  
C. A. COULSON, *Valence*, 2nd ed. Oxford, University Press, 1961.  
L. C. PAULING, *The Nature of the Chemical Bond and the Structure of Molecules and Crystals*, 3rd ed., Ithaca, N.Y., Cornell University Press, 1960.  
A. L. ALLRED AND E. G. ROCHOW, *J. Inorg. Nucl. Chem.*, 5 (1958) 264.  
C. J. BALLHAUSEN AND H. B. GRAY, *Introductory Notes on Molecular Orbital Theory*, New York, Benjamin, 1965.  
T. L. COTTRELL, *The Strengths of Chemical Bonds*, 2nd ed., London, Butterworths, 1958.

## Structure and Shape of Molecules

### EXPERIMENTAL METHODS

The structure of crystalline solids is investigated by a diffraction method, usually the diffraction of X-rays (p. 187), but in special cases that of neutrons. For molecules in the gas phase, electron diffraction is used (p. 188). Furthermore, useful information about the presence of particular bonds, of bond lengths and of bond angles in molecules can be obtained from absorption spectra, particularly infrared absorption spectra.

#### Infrared absorption spectra

Infrared radiation is of lower energy and longer wave length than ordinary light. Absorption in the range  $1\mu$  to  $200\mu$  ( $1\mu = 10^4 \text{ \AA}$ ), which is from  $50 \text{ cm}^{-1}$  to  $10^4 \text{ cm}^{-1}$  on the wave-number scale, is due to molecules absorbing quanta of energy and thereby increasing their rotational and vibrational energy.

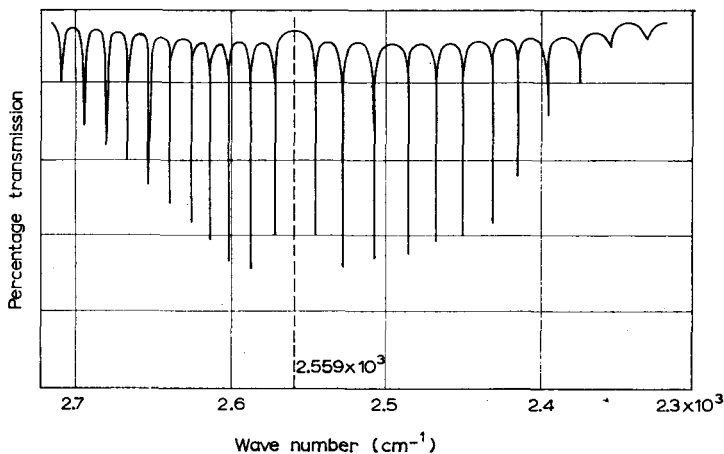


Fig. 74. Fundamental absorption band for HBr gas, showing rotational fine structure.

The fundamental absorption band (p. 139) of gaseous HBr in the infrared (Fig. 74) shows the many simultaneous changes brought about in the vibrational and rotational energy of that molecule. The fine structure of the spectrum is associated with changes in rotational energy.

Generally, for a molecule of moment of inertia  $I$ , the energy of rotation

$$= \frac{\hbar^2}{8\pi^2 I} \times J(J + 1),$$

where  $J$  is a rotational quantum number 0, 1, 2, 3... Thus the energy increase between two lines in the fine structure represents

$$\Delta E = \frac{2\hbar^2}{8\pi^2 I} = \hbar^2/4\pi^2 I.$$

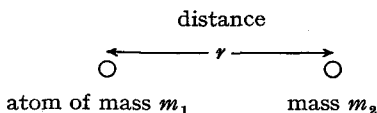


Fig. 75. Representation of heteronuclear diatomic molecule.

For a diatomic molecule (Fig. 75):

$$I = \frac{m_1 m_2}{m_1 + m_2} \times r^2 = \mu r^2$$

( $\mu$  = the reduced mass of the molecule =  $\frac{m_1 m_2}{m_1 + m_2}$ ).

Thus if  $m_1$ ,  $m_2$  and  $I$  are known, the internuclear distance  $r$  can be found. For molecules with more atoms, such as  $\text{NH}_3$ , both bond angles and internuclear distances have to be considered and the calculation is more involved.

### Fundamental frequency and force constant of bond

The middle of the absorption band for HBr, corresponding to  $2559 \text{ cm}^{-1}$ , represents the energy,  $\Delta E$ , absorbed in lifting the vibrational energy of the H-Br bond from its lowest quantum level ( $v = 0$ ) to the next ( $v = 1$ ). This is the *fundamental frequency* of the bond. A quantity called the *force constant* of the bond,  $k$ , which is a measure of the resistance of the bond to stretching, is given by

$$k = \left\{ \frac{2\pi(\Delta E)}{\hbar} \right\}^2 \mu$$

TABLE 13

FUNDAMENTAL VIBRATIONAL ABSORPTIONS AND FORCE CONSTANTS FOR SOME DIATOMIC MOLECULES

<i>Molecule</i>	<i>Fundamental absorption band (cm<sup>-1</sup>)</i>	<i>Force constant (dynes cm<sup>-1</sup>)</i>
HF	2907	$9.7 \times 10^5$
HCl	2886	$4.8 \times 10^5$
HBr	2559	$4.1 \times 10^5$
HI	2230	$3.2 \times 10^5$
NO	1876	$15.3 \times 10^5$
CO	2143	$18.4 \times 10^5$

A comparison of these force constants (Table 13) indicates that the HF bond resists stretching more than does the bond in HCl and the other hydrogen halides. Furthermore the  $\pi$ -bonded molecules NO and CO show greater rigidity than the single-bonded molecules.

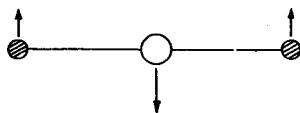
The value of a stretching frequency depends on two factors:

- (a) the masses of the atoms,
- (b) the strength of the bond.

The frequency of the infrared absorption increases as the masses are reduced and the bond strengths are increased:

	Wave number
$\text{>C-H stretch}$	$\sim 2900 \text{ cm}^{-1}$
$\text{>C-O stretch}$	$\sim 1100 \text{ cm}^{-1}$
$\text{>C=O stretch}$	$\sim 1750 \text{ cm}^{-1}$

In molecules with three or more atoms, bond-bending vibrations also occur:

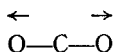


These are of lower frequency than the stretching vibrations.

For a molecule to be infrared-active the vibrational change must cause a change in dipole moment (p. 142). This can be illustrated by reference to the  $\text{CO}_2$  and  $\text{H}_2\text{O}$  stretching frequencies, both of which have symmetric and asymmetric stretching.

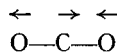
For the  $\text{CO}_2$  molecule the former is without net change in dipole moment and is infrared inactive; there is a single peak near  $2400 \text{ cm}^{-1}$ .

(a) Symmetric stretching



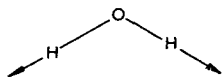
No net change in dipole moment  
Infrared inactive

(b) Asymmetric stretching

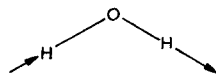


A net change in dipole moment  
Infrared active

But for the angular  $\text{H}_2\text{O}$  molecule there is a net change in dipole moment, whether both hydrogen atoms move away from the oxygen atom, or one hydrogen atom moves towards it as the other moves away from it.



(a) Symmetric stretching

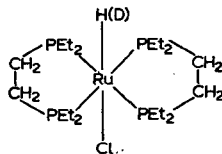


(b) Asymmetric stretching

Accordingly,  $\text{H}_2\text{O}$  has a double peak in the stretching frequency absorption in the region of  $3700\text{ cm}^{-1}$ .

Various groups present in molecules give rise to characteristic frequencies for the stretching and bending of bonds. These frequencies are altered only slightly by the presence of other groups and can therefore be used for diagnostic purposes. For instance carbon monoxide has a fundamental absorption band at  $2143\text{ cm}^{-1}$ . For metal carbonyls, however, the stretching frequencies are in the range  $1850\text{--}2100\text{ cm}^{-1}$ , indicating some reduction of electron density in the C–O bond in carbonyls. The manganese carbonyl,  $\text{Mn}_2(\text{CO})_{10}$ , has only one C–O stretching band, showing all the C–O groups are terminal ones, but the iron carbonyl,  $\text{Fe}_2(\text{CO})_9$ , has a band at  $1830\text{ cm}^{-1}$ , indicating the presence of bridging groups,  $>\text{C}=\text{O}$ , in addition to the band near  $2000\text{ cm}^{-1}$  ascribed to terminal CO groups.

What was said above about the effect of atomic masses on stretching frequencies makes it evident that the substitution of deuterium for hydrogen in a compound will show at once whether an observed frequency is due to a bond between hydrogen and another atom. The infrared spectrum of



has a band at  $1938\text{ cm}^{-1}$ , but in the deuterio analogue this band disappears and a new one appears at  $1410\text{ cm}^{-1}$ . The energy is about  $\sqrt{2}$  times less because of the approximately twofold increase in  $\mu$ .

The effect of the chlorine atom on the Ru-H stretching frequency in this molecule can be studied by replacing it by Br, when the band moves to  $1945\text{ cm}^{-1}$ , or by CN, when the band moves to  $1803\text{ cm}^{-1}$ . Clearly, electron density is withdrawn from the Ru-H bond by *trans* substituents in the order  $\text{CN} > \text{Cl} > \text{Br}$ .

### Microwave spectra

Very accurate measurements of the moments of inertia, and hence the bond angles and bond lengths of gaseous molecules, can be obtained by observing absorption in the microwave (radar wave) region of the spectrum. That is around  $1\text{ cm}$  wavelength. For this purpose, the gas is put in a long tube through which microwaves pass to a receiver which records the absorption at particular frequencies. These frequencies correspond to transitions between possible rotational states of the molecule. The equation

$$hr = \Delta E = \frac{h^2}{4\pi^2 I}$$

enables the moments of inertia for all the possible rotational modes of the molecule to be determined, and hence, in suitable cases, the bond lengths and bond angles.

### Raman spectra

When monochromatic light is passed through a gas or liquid some of it is scattered. A small fraction of the scattered light has a slightly different wave length because quanta are absorbed by molecules and, having lost some of their energy in inducing vibrational or rotational change in these molecules, are emitted as quanta of lower energy, that is as light of lower frequency than the incident radiation. The Raman spectra (1928) of the scattered radiation supply the same kind of information as does absorption in the infrared but have two advantages:

- (i) the source frequency can be chosen to give an easily photographed spectrum;
- (ii) homonuclear diatomic molecules which do not give rotational lines in the infrared region are often active in the Raman.

Ions in solution may be readily recognised by their Raman spectra. Thus all metal nitrates give an  $\text{NO}_3^-$  line; a line which is also shown by nitric acid with maximum intensity in a  $7M$  solution of the acid. More concentrated nitric acid contains fewer  $\text{NO}_3^-$  ions and more  $\text{HNO}_3$  molecules.



A Raman line is produced by  $\text{Cd}^{2+}$  ions in solution. This disappears on the addition of an excess of bromide ion probably because  $\text{CdBr}_4^{2-}$  is formed, since a new line appears similar in energy increment to that of  $\text{SnBr}_4$ .

The addition of  $\text{SnCl}_4$  to  $\text{SnBr}_4$  gives rise to new lines which are presumably due to such species as  $\text{SnClBr}_3$  and  $\text{SnCl}_2\text{Br}_2$ . The chlorides of carbon and silicon do not behave in this way; evidently tin-halogen bonds are more labile. But  $\text{PFCl}_2$  and  $\text{PBr}_2$  produce a new line on mixing, probably because of the formation of  $\text{PFClBr}$ .

### Electric dipole moments

When a non-conductor is placed between the two plates of a condenser a capacitance change is produced from which the dielectric constant of the medium can be calculated. The increase in capacitance is caused by polarisation of the molecules in the electric field and  $P_M$ , the molar polarisation, is given by

$$P_M = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{M}{\rho}$$

where  $\epsilon$  is the dielectric constant,  $M$  the molecular weight and  $\rho$  the density.  $P_M$  is the sum of  $P_\mu$ , the orientation polarisation due to the alignment in the field of molecules with permanent dipoles, and  $P_D$ , the induced polarisation due to distortion of molecules by the field.

When  $P_M$  is plotted against  $1/T$  straight lines are obtained (Fig. 76).  $P_D$  is temperature-independent because thermal collisions may disturb the direction of a molecule but not that of an induced dipole; on the other hand  $P_\mu$  decreases with temperature because random collisions interfere with the *lining up* of permanent dipoles in the field.

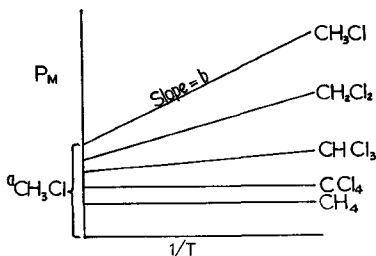


Fig. 76. Variation of molar polarisation,  $P_M$ , with the reciprocal of absolute temperature.

The slope of the graph, which is a measure of the permanent dipole of the molecule, is given by

$$b = \frac{4\pi N\mu^2}{9k}$$

$$\text{Hence } \mu = \sqrt{\frac{9kb}{4\pi N}}$$

$$= 1.282 \times 10^{-20} \sqrt{b} \text{ esu}$$

$$= 0.01282 \sqrt{b} \text{ debye units } (10^{-18} \text{ esu}),$$

where  $\mu$  is the dipole moment per molecule,  $k$  the Boltzmann constant, and  $N$  the Avogadro number.

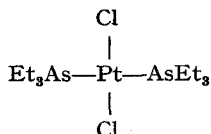
The dipole moment per molecule, (debye units), is given for representative molecules:

HCl	1.03	SO <sub>2</sub>	1.61
HBr	0.78	CO <sub>2</sub>	0
HI	0.38	BCl <sub>3</sub>	0
H <sub>2</sub> O	1.85	<i>p</i> -dichlorobenzene	0
NH <sub>3</sub>	1.49	quinol	1.64

Four illustrations of how dipole moments provide information about bonding and structure follow:

- (i) In HI the inter-atomic distance is 1.87 Å. As the electronic charge is  $4.8 \times 10^{-10}$  e.s.u., the calculated moment of H<sup>+</sup>—I<sup>-</sup> is  $1.87 \times 10^{-8} \times 4.8 \times 10^{-10}$  e.s.u. = 9.0 D. The actual moment is 0.38 D. This indicates that the bonding electrons are displaced only slightly towards the iodine and that the bond is predominantly covalent.
- (ii) The zero dipole moment of CO<sub>2</sub> must arise from the polarities of the two bonds cancelling one another exactly. This implies a linear molecule O=C=O. By the same token, H<sub>2</sub>O and SO<sub>2</sub> must be angular as they both have considerable dipole moments. BCl<sub>3</sub> has zero dipole moment because the molecule is planar with Cl—B—Cl angle of 120°; whereas NH<sub>3</sub>, with its appreciable moment, has a pyramidal molecule.
- (iii) *p*-Dichlorobenzene has a zero moment and quinol an appreciable one. Evidently Cl atoms of the first are coplanar with the benzene ring but the OH groups of the second are not.
- (iv) An important application of electric dipole moments is to distinguish between isomers. For example, consider the compound PtCl<sub>2</sub> · 2Et<sub>3</sub>As which has two forms: one is white, m.p. 142°, sparingly soluble in benzene; the other is yellow, m.p. 121°, very soluble in benzene. The white isomer has a dipole moment of about 10 D and could be either

tetrahedral or *cis* planar. The yellow one is practically without dipole moment and must be *trans* planar, thus:



#### FURTHER READING

- G. M. BARROW, *The Structure of Molecules*, New York, Benjamin, 1963.
- W. J. ORVILLE-THOMAS, *The Structure of Small Molecules*, Amsterdam, Elsevier, 1966.
- P. W. ATKINS AND M. C. R. SYMONS, *The Structure of Inorganic Radicals: An Application of Electron Spin Resonance to the Study of Molecular Structure*, Amsterdam, Elsevier, 1967.
- R. E. DODD, *Chemical Spectroscopy*, Amsterdam, Elsevier, 1962.
- F. A. COTTON, *The Infrared Spectra of Transition Metal Complexes*, in J. LEWIS AND R. G. WILKINS (Eds.) *Modern Co-ordination Chemistry*, New York, Interscience, 1960.
- P. J. WHEATLEY, *The Determination of Molecular Structure*. Oxford, Clarendon Press, 1959.
- K. NAKAMOTO, *Infrared Spectra of Inorganic and Co-ordination Compounds*, London, Wiley, 1961.
- M. DAVIES (Ed.), *Infrared Spectroscopy and Molecular Structure*, Amsterdam, Elsevier, 1963.

## Bonding and Structure in Compounds of Non-transition Elements

### General principles

The forces holding atoms together in molecules and crystals have been interpreted (p. 94) in terms of located electron density. There are further theoretical principles which make it possible to account for the shapes of molecules.

#### *Localized molecular orbitals*

Although the forces on the nuclei depend on the charge density  $P$  (that is the probability density for finding an electron at the given point (p. 95)), their equilibrium configuration is determined by the total energy of the system, and to understand the factors on which it depends, the *interaction* between different electrons must be examined. The interaction energy depends on the probability of two electrons being a given distance apart and accordingly on how their motions are *correlated*. Fortunately, this correlation is mainly associated with the exclusion principle (p. 68), which prevents electrons of like spin from occupying the same orbital or, more generally, the same region of space. If the various doubly occupied orbitals are chosen so as to be localised essentially in different parts of space, this correlation requirement is automatically met—for then electrons with the same spin are obviously always well separated. Thus, by working in terms of localised MO's, it is possible to get a picture not only of where an electron is *on the average* (the charge density) but also of where different electrons are *at the same instant*.

The water molecule provides a good example. In the true molecular orbital approach, the electrons responsible for bonding would occupy orbitals extending over the whole molecule (Fig. 77 (a)): but in the earlier discussion of valency (p. 114) the electrons were supposed to occupy localised MO's (Fig. 77 (b)). The two descriptions are, however, exactly equivalent, provided the two types of MO are related by

$$\psi_1 = \frac{1}{\sqrt{2}} (\psi_a + \psi_b) \quad \text{and} \quad \psi_2 = \frac{1}{\sqrt{2}} (\psi_a - \psi_b).$$

It is easily seen, for instance, that they give the same charge density contribution; for, when the orbitals are each doubly occupied, the density is

$$2\psi_1^2 + 2\psi_2^2 = (\psi_a^2 + 2\psi_a\psi_b + \psi_b^2) + (\psi_a^2 - 2\psi_a\psi_b + \psi_b^2) = 2\psi_a^2 + 2\psi_b^2.$$

But, by allocating the electrons to the localised MO's, we can describe, without mathematical analysis, the fact that two electrons with the same spin tend at any instant to occupy different regions of space. Different electron pairs have, in fact, an interaction energy which can be closely estimated by regarding each as a smeared-out charge.

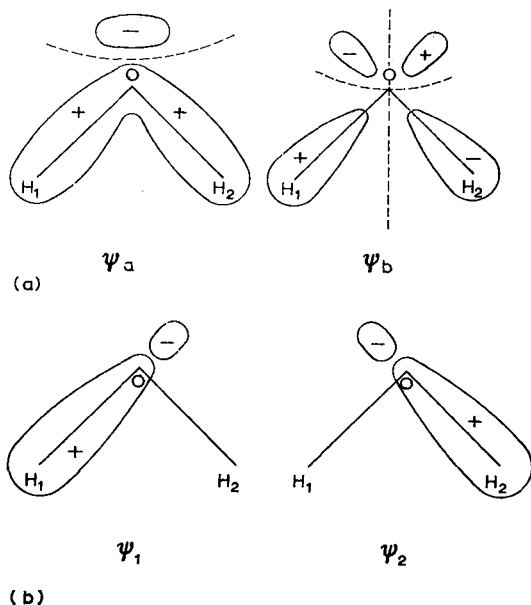


Fig 77. (a) Molecular orbitals (each with two electrons) for the bonding electrons in H<sub>2</sub>O (nodal surfaces indicated by broken lines).

(b) Localised molecular orbitals (bond orbitals each with two electrons) for the bonding electrons in H<sub>2</sub>O.

The energy of interaction of different electron pairs plays an important role in determining the equilibrium shapes of molecules. Broadly speaking, its effect will be minimised when the different pairs (either lone pairs or bond pairs) are as far apart as possible. This idea is strongly supported by the observed spatial arrangement of the valencies of multivalent atoms; it was, indeed, formulated on empirical grounds by Sidgwick and Powell in 1940.

### Shapes of molecules and ions of non-transitional atoms

Beryllium has two valency electrons. It is in the  $sp$  valence state in its covalent compounds which have collinear  $\sigma$  bonds (Fig. 52, p. 115), the electron pairs of the two bonds being as far from each other as possible. This linear form is the shape of the covalent halides of all metals with two electrons only in the valency shell, *e.g.*  $HgCl_2$ .

Boron, with three valency electrons, forms a planar trichloride, the boron being in an  $sp^2$  valence state (Fig. 54, p. 116). Again the electron pairs of the three bonds are arranged at the greatest possible distances from one another. Tin in tin(II) chloride has also three pairs of electrons round the central atom but their disposition is no longer symmetrical since one of the valence states (roughly  $sp^2$ ) holds a lone pair. The individual molecules observed in the vapour are therefore V-shaped (Fig. 78). The  $Cl-Sn-Cl$  angle is less than  $120^\circ$ , indicating that the lone pair repels the bonding pairs more strongly than they repel each other.

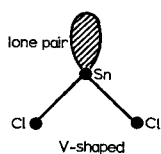


Fig. 78. Single molecule of tin(II) chloride.

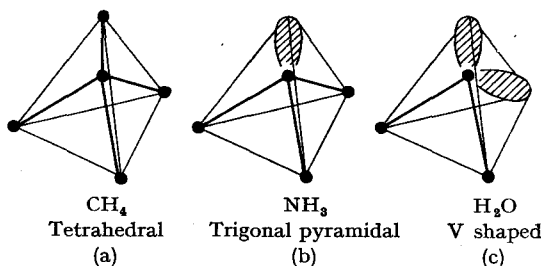


Fig. 79. Shapes of methane, ammonia, and water molecules.

When there are four pairs of electrons round a non-transitional atom they tend to be arranged in a tetrahedral configuration. This dictates the shapes of the methane, ammonia and water molecules (Fig. 79 (a), (b), (c)), already considered in some detail (p. 118). The bond angle in  $CH_4$  is  $109.5^\circ$ , in  $NH_3$   $106.7^\circ$  and in  $H_2O$   $104.5^\circ$ , showing again the strong repulsion exerted by lone pairs on bonding pairs.

More than four electron pairs may be arranged about an atom only when  $d$  orbitals are used. As usual, it is convenient to work in terms of the orbitals  $d_{z^2}$ ,  $d_{x^2-y^2}$ ,  $d_{xy}$ ,  $d_{yz}$ ,  $d_{zx}$  (p. 61): the lobes of the first two are along the  $z$  axis and the  $x$  and  $y$  axes, respectively, and of the other three in the co-ordinate planes but falling between the axes. The two types are often referred to as  $e_g$  and  $t_{2g}$ , respectively. It is the  $s$  and  $p$  orbitals which can be mixed to give strongly directed hybrids; towards the corners of a trigonal bipyramid for  $sp^3d$  (p. 120), the corners of a square for  $sp^2d$  (p. 121), and

the corners of an octahedron for  $sp^3d^2$  (p. 121). The  $t_2$  orbitals give tetrahedral hybrids (more important in the transition elements), which are suitable for  $\sigma$  bonding when mixed with  $s$ ; when mixed with  $p$ , they commonly participate in  $\pi$  bonding (*cf.* Fig. 62, p. 122). As expected, five pairs tend to adopt the trigonal bipyramidal configuration and six pairs the octahedral.

The resulting shapes of molecules containing a central (non-transitional)

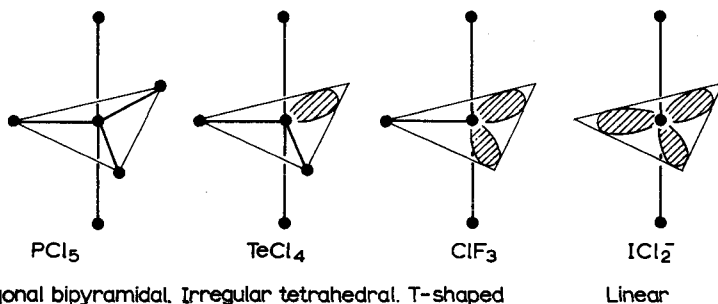


Fig. 80. Shapes arising from the disposition of five electron pairs round a central atom. (In  $TeCl_4$  and  $ClF_3$  the two bonds are inclined from the vertical away from the lone pair(s).)

atom, about which there are five electron pairs, are shown in Fig. 80. In fact, all the covalent compounds of non-transitional elements with five electron pairs which have been investigated have the trigonal bipyramidal structure or one of these derived forms. Other shapes are possible but are ruled out if lone-pair-bond-pair repulsions are assumed to be stronger than bond-pair-bond-pair. Thus, in  $TeCl_4$ , lone-pair-bond-pair repulsion is minimised when the lone pair lies at about  $120^\circ$  to two of the bonds and about  $90^\circ$  to the other two. In the trigonal pyramid (Fig. 81) the lone pair would

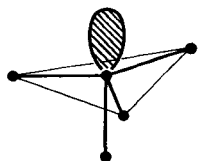


Fig. 81. Trigonal pyramid. (Permitted by  $sp^3d$  hybridisation but not observed).

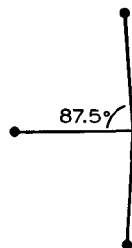


Fig. 82. Bond angles in  $ClF_3$ .

be close to three (instead of two) bond pairs and electron repulsion energy would be higher; this alternative does not occur.

For similar reasons  $\text{ClF}_3$  is T-shaped, not triangular. A triangular molecule involves six lone-pair-bond-pair angles of  $90^\circ$ , whereas a T-shaped molecule contains four lone-pair-bond-pair angles of  $90^\circ$  and two lone-pair-bond-pair angles of  $120^\circ$ . The latter is the more stable structure. The  $\text{F}-\text{Cl}-\text{F}$  angle is actually only  $87.5^\circ$  because of the strength of the lone-pair-bond-pair repulsions (Fig. 82).

TABLE 14

SHAPES OF MOLECULES WITH NON-TRANSITIONAL ELEMENT AS CENTRAL ATOM  
(No  $\pi$ -bonding)

<i>Number of electron pairs in valence shell</i>	<i>Bonding pairs</i>	<i>Lone pairs</i>	<i>Shape of molecule</i>	<i>Example</i>
2	2	0	Linear	$\text{BeCl}_2(\text{vap})$
3	3	0	Triangular	$\text{BCl}_3$
	2	1	V-shaped	$\text{SnCl}_2(\text{vap})$
4	4	0	Tetrahedral	$\text{CH}_4$
	3	1	Trigonal pyramidal	$\text{NH}_3$
			V-shaped	$\text{H}_2\text{O}$
5	5	0	Trigonal bipyramidal	$\text{PCl}_5(\text{vap})$
	4	1	Irregular tetrahedron	$\text{TeCl}_4$
			T-shaped	$\text{ClF}_3$
	6	2	3	Linear
6		0	Octahedral	$\text{SF}_6$
5		1	Square pyramidal	$\text{IF}_5$
			Square	$\text{ICl}_4^-$

The arrangement of six pairs of electrons about the atom of a non-transitional element is basically octahedral, but there again lone pairs tend to adopt positions in which their repulsive energy is a minimum (Fig. 83).

A most important principle to recognise is that the shapes of molecules and ions formed by non-transitional elements are determined mainly by the number of electron pairs round the central atom and by the repulsions between them. Lone-pair-lone-pair repulsion is strongest, lone-pair-bond-pair next and bond-pair-bond-pair weakest.



Another factor affecting bond angles is the electronegativity of the central atom. Thus the bond angle in  $\text{H}_2\text{O}$  is  $104.5^\circ$  but in  $\text{H}_2\text{S}$  only  $92.5^\circ$ , corresponding to a fall in electronegativity from 3.5 in oxygen to 2.5 in sulphur. The bond pairs lie nearer to the O in  $\text{H}_2\text{O}$  than to the S in  $\text{H}_2\text{S}$ , so that in  $\text{H}_2\text{O}$  the bond-pair-bond-pair repulsion is greater and the effect of the lone

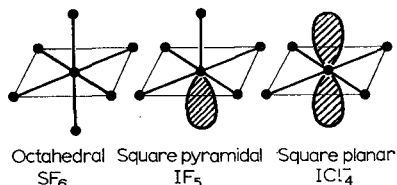


Fig. 83. Shapes based on octahedral disposition of electron-pairs round a central atom.

pairs on the angle between the bonds less than in  $\text{H}_2\text{S}$ . In terms of the molecular-orbital theory there is a greater  $p$ -orbital contribution to the bonding orbitals. If the bonding were truly ionic the configuration would become tetrahedral, possessing 4 equivalent lone pairs.

### Molecules with $\pi$ bonds

The description of  $\pi$  bonding already adopted (p. 108) apparently conflicts with the fact that electron pairs tend to stay apart, for the  $\pi$  pair is superimposed on the  $\sigma$  pair. But, as on p. 146, the same wave function can be built out of alternative orbitals which do lie in different regions. In, for instance, ethylene (Fig. 56, p. 117) we can choose

$$\psi_1 = \frac{1}{\sqrt{2}}(\psi_\sigma + \psi_\pi) \quad \text{and} \quad \psi_2 = \frac{1}{\sqrt{2}}(\psi_\sigma - \psi_\pi),$$

where  $\psi_\sigma$  and  $\psi_\pi$  are the  $\sigma$  bond and  $\pi$  bond MO's. The configurations  $(\psi_1)^2(\psi_2)^2$  and  $(\psi_\sigma)^2(\psi_\pi)^2$  both reproduce the same charge density, but the former also indicates the simultaneous dispositions of the two pairs. There is here striking resemblance to the *bent bond* picture of Bayer's *strain theory*; and indeed the bent bond orbitals, one lying above the molecular plane and one below, could have been approximated by overlapping tetrahedral hybrids.

#### *$\sigma$ -Bonding influence in determining molecular shape*

Nevertheless, it is simpler, and usually satisfactory, to employ the  $\sigma$ - $\pi$  description, regarding the less strongly bound  $\pi$  electrons as of secondary importance in determining molecular shape. (There are, however, certain transition-metal complexes for which this generalisation is untrue (p. 185)).

The basic configuration is settled by  $\sigma$  electron pairs; any remaining ambiguity is then resolved by  $\pi$  bond considerations. Thus in  $\text{CO}_2$  the two single bonds formed by the central carbon adopt the linear configuration typical of bivalent metals, and the superimposed  $\pi$  bonding does not affect this shape. But in ethylene the pair of plane triangular  $\text{CH}_2$  groups could rotate about the central bond were it not for the presence of  $\pi$  bonding. In  $\text{SO}_2$  the sulphur may, in the first instance, be regarded as  $\text{sp}^2$  hybridised, providing two

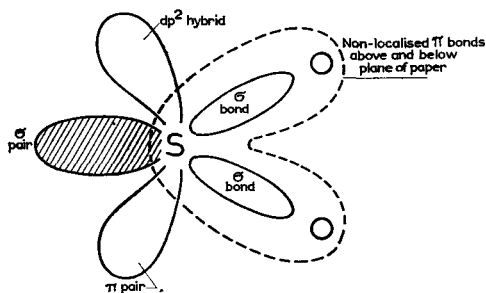


Fig. 84. Bonding in  $\text{SO}_2$ .

single bonds and a lone pair with a second lone pair in the remaining 3p orbital; this gives the plane triangular form. If then  $\text{pd}^2$  hybridisation is admitted, the 3p lone pair may be replaced by three  $\pi$ -type hybrids (Fig. 84) two of which overlap oxygen 2p orbitals, describing  $\pi$  bonds, while the

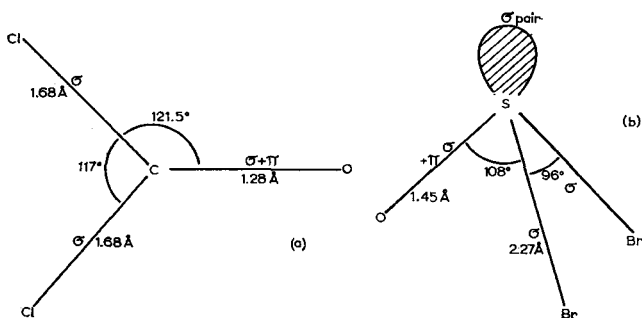


Fig. 85. (a) Plane triangular carbonyl chloride molecule. (b) Irregular pyramidal shape of thionyl bromide molecule.

third accommodates the original lone pair. Again, the  $\pi$  stabilisation does not affect the plane triangular form. Similarly, the plane triangular and irregular pyramidal forms of carbonyl chloride and thionyl bromide (Fig. 85) are associated with three and four electron pairs, respectively, and the  $\pi$  bonding is again relatively unimportant in determining the shapes of the molecules.

An examination of bond angles shows that  $\pi$  bonding may be assumed merely to increase the repelling power of the bond pair on which it is superimposed. This is natural since the  $\pi$  bond supplements the electron density of the underlying  $\sigma$  bond.

#### FURTHER READING

R. J. GILLESPIE AND R. S. NYHOLM, *Quart. Rev.*, 7 (1957) 339.

A. W. SEARCY, *J. Chem. Phys.*, 31 (1959) 1.

H. A. JAFFÉ AND M. ORCHIN, *Symmetry in Chemistry*, New York, Wiley, 1965.

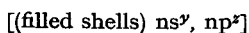
## Bonding in Transition-Metal Complexes

### GENERAL

#### Electron configuration

##### *Non-transition elements*

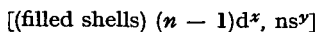
The non-transitional elements are characterised by electron configurations of the type



in which the number of valence electrons  $y + z$ , varies from 1 to 8 and hybridisation involves  $ns$  and  $np$  orbitals and, less commonly,  $nd$  orbitals. The metals with  $y = 1$  or  $2$ ,  $z = 0$ , have small electronegativities and readily form ionic bonds. As  $z$  increases electrons are lost less easily, ionic character diminishes, and the atom holds near itself up to 4 electron pairs; this number may be increased to 6 by  $d$  hybridisation and acceptance of electrons.

##### *Transition elements*

In the transition elements the electron configuration is



in which  $y = 1$  or  $2$  and  $x$  goes from 1 to 10. They resemble the Gp.I and Gp. II metals in having low electronegativity; but, owing to the incomplete  $d$  shell, the number of electrons available for bonding is potentially much larger. The  $(n - 1)d$ ,  $ns$ ,  $np$  and even the  $nd$  orbitals may lie so close together that promotion and hybridisation occur freely. The transition elements are accordingly distinguished by having a high and variable valency. Often, however, all the  $d$  orbitals are not free to participate in hybridisation; they may describe a stable sub-shell, not affected by bonding. The valence properties of a transition metal are thus controlled to some extent by the stability of incomplete  $d$  shells. This in turn is determined largely by the strength and symmetry of the electric field imposed by the attached atoms, ions or groups, known collectively as *ligands*.

A molecular orbital treatment of metal-ligand bonding has been developed (p. 177) which is of particular value in giving a picture of what is happening in highly covalent complexes such as carbonyls; but although it is the most fundamental approach, it is not always easy to apply. For

many complexes, however, a sufficiently accurate theoretical explanation of the observed phenomena may be obtained by allocating electrons to atomic orbitals. In doing so we imply a limiting, purely ionic model. This is the basis of the electrostatic *crystal field theory* outlined below. A modification of the theory which makes allowance for some orbital mixing (covalence) is known as the *ligand field theory*.

## CRYSTAL FIELD THEORY

First we note that in transition metal ions all the orbitals except the highest d-orbitals are either completely full or quite empty. Then that in an ionic crystal or a mononuclear complex, the metal cation is symmetrically surrounded, as nearest neighbours, either by negative ions or dipoles both of which direct electrons towards it. The five d-orbitals described on p. 61, although distinct, all have the same energy in a free atom or ion—they are degenerate (p. 60). But the presence around the cation of negative charges due to ligands splits this degeneracy. The precise effect of this on the d-orbital energies depends on the arrangement of the ligands, and a simple pictorial representation of it is possible for a square complex.

### The square complex

Consider a cation with d electrons, situated centrally between four ligands lying on the  $x$ - and  $y$ -axes. As the ligands are either negative ions, or

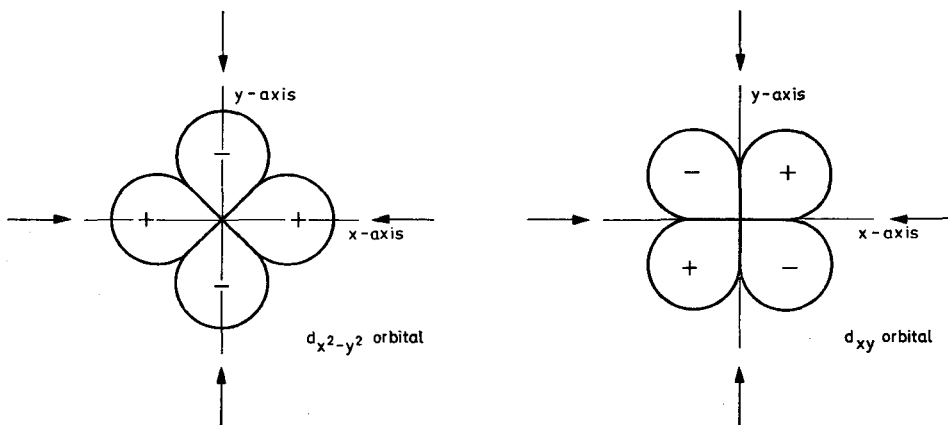


Fig. 86. Positions of ligands on  $x$  and  $y$  axes in relation to  $d_{x^2-y^2}$  and  $d_{xy}$  orbitals.

dipoles aligned with their most negative regions towards the metal ion, the electrostatic field which they create tends to repel electrons of the metal ion from the vicinity of its  $x$ - and  $y$ -axes (Fig. 86). Because the lobes of a  $d_{x^2-y^2}$  orbital of the cation are directed towards the ligands, an electron in this orbital must suffer considerable electrostatic repulsion from them;

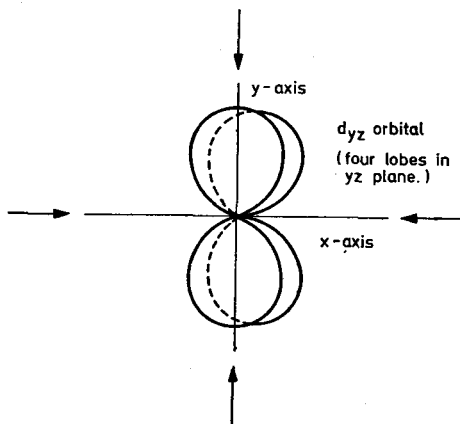


Fig. 87. Position of ligands on  $x$  and  $y$  axes in relation to  $d_{yz}$  orbital.

accordingly the energy of this orbital is raised. But an electron in a  $d_{xy}$  orbital tends to occupy lobes lying between the co-ordinate axes, thus the energy of this orbital is raised less by the ligand electrons than is that of the  $d_{x^2-y^2}$  orbital.

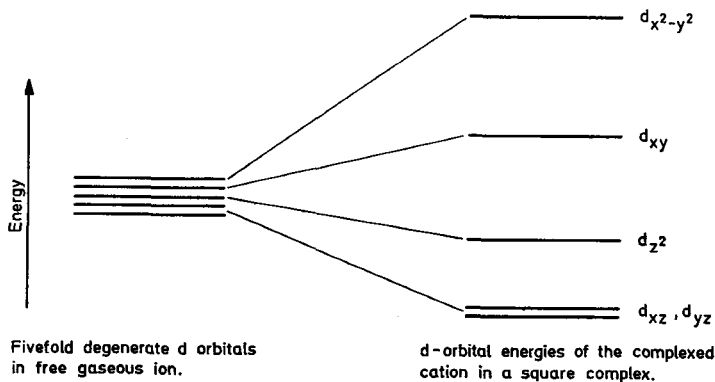


Fig. 88. Splitting of degeneracy of d orbitals in field produced by ligands on  $x$  and  $y$  axes.

Moreover, the energy of a  $d_{yz}$  or  $d_{xz}$  orbital is raised very little by ligands on the  $x$ - and  $y$ -axes (Fig. 87).

The influence of the ligands on the  $d_x^2$  cannot be pictured quite so simply, but the energy of this orbital is known to lie slightly above the  $d_{yz}$  and  $d_{xz}$  in such an environment. As a consequence of these orbital energy changes, the original five-fold  $z$  degeneracy is split into a doublet and three distinct singlet levels (Fig. 88). It is only for convenience that the mean energy of the perturbed orbitals is placed, as shown (Fig. 88), equal to the energy of the degenerate  $d$  orbitals of the free ion. The crystal field theory of metal-ligand bonding is concerned essentially with differences in energy, although all the  $d$ -orbital energies are, of course, raised by the presence of the ligands.

### Octahedral arrangement of ligands

The most common geometrical symmetry in complexes is octahedral. Ligands arranged symmetrically around a central metal ion in the directions of the  $x$ -,  $y$ - and  $z$ -axes cause the five degenerate  $d$  orbitals to be split into two groups, the high-energy  $d_{x^2-y^2}$  and  $d_z^2$ , the lower-energy  $d_{xy}$ ,  $d_{xz}$  and  $d_{yz}$  (Fig. 89).

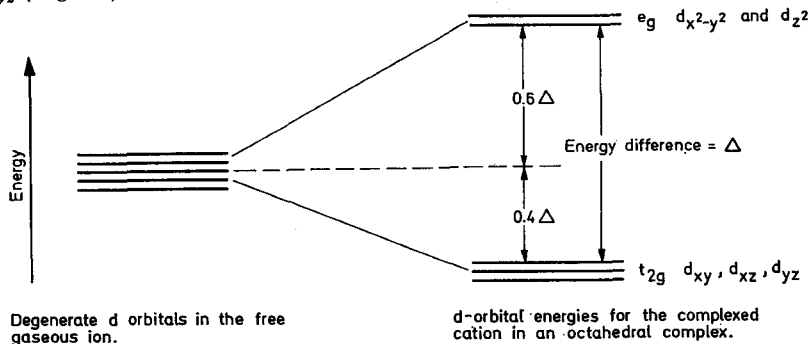


Fig. 89. Splitting of  $d$ -orbital energies in an octahedral ligand field.

The  $d_x^2$  orbital behaves in the same way as the  $d_{x^2-y^2}$ ; it is in fact a linear combination of  $d_{x^2-x^2}$  and  $d_{x^2-y^2}$ , which, by symmetry, must behave as the  $d_{x^2-y^2}$  does. The  $d_{x^2-y^2}$  and  $d_x^2$  are known as  $e_g$  orbitals, the  $d_{xy}$ ,  $d_{xz}$ ,  $d_{yz}$  as  $t_{2g}$  orbitals. These symbols are taken from group theory;  $e$  indicates twofold degeneracy,  $t$ , threefold. The subscript  $g$  (gerade = even) denotes that the wave function  $\psi$  does not suffer change in sign on inversion through the origin (Fig. 90). Orbitals where the sign of  $\psi$  changes on inversion are ungerade (odd), and carry the subscript  $u$ .

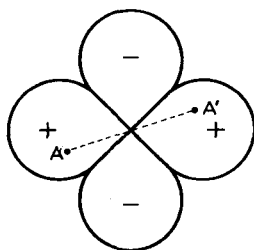


Fig. 90. Sign of  $\psi$  unchanged by inversion of  $d$  orbital. Amplitude  $\psi$  the same at all points related as  $A$  is to  $A'$ .

The reader may wonder how the picture given above would have been altered had the choice of axes been different. Although we should have needed to consider linear combinations of the five fundamental  $d$  orbitals, detailed analysis would have led to the same combinations of  $e_g$  and  $t_{2g}$  for the octahedral group.

### Ligand-field splitting

The difference in energy between the  $t_{2g}$  and  $e_g$  orbitals is represented by the symbol  $\Delta_0$ , the ligand-field splitting, the energy of which can be expressed in eV, kcal per mole or  $\text{cm}^{-1}$ .

$$1 \text{ eV} \equiv 23 \text{ kcal} \equiv 8.07 \times 10^3 \text{ cm}^{-1}$$

$$1 \text{ kcal} \equiv 350 \text{ cm}^{-1}$$

The value of  $\Delta_0$  depends on the interaction between the ligands and the  $d$  electrons of the ion. For octahedral complexes  $\Delta_0$  is in the range 25–100 kcal per mole, depending on the metal ion and the ligands.

The principles involved in the measurement of the ligand-field splitting are most simply explained when there is one  $d$  electron. This occurs in the  $\text{Ti}(\text{H}_2\text{O})_6^{3+}$  the purple colour of which is due to an absorption of light

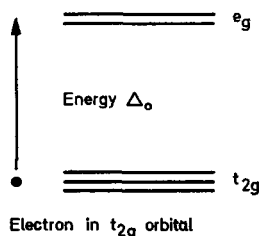


Fig. 91. Representation of energy required to promote an electron from a  $t_{2g}$  orbital to an  $e_g$  orbital.



energy to raise the electron, normally located in a  $t_{2g}$  orbital, to an  $e_g$  orbital (Fig. 91).

The absorption band for the  $\text{Ti}(\text{H}_2\text{O})_6^{3+}$  ion in aqueous solution has the form shown in Fig. 92.

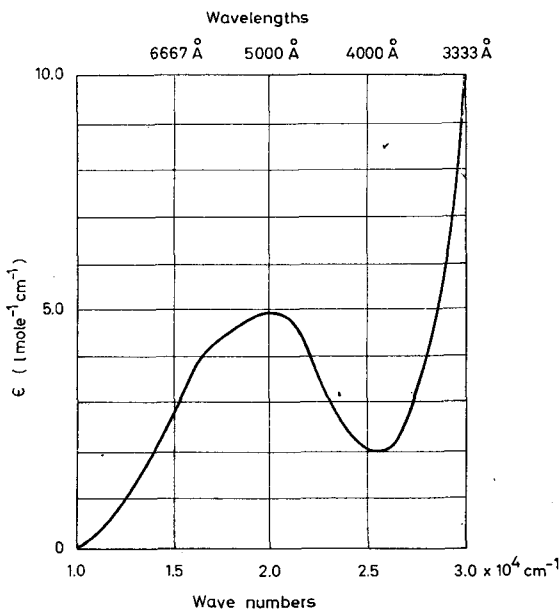


Fig. 92. Absorption spectrum of  $\text{Ti}(\text{H}_2\text{O})_6^{3+}$  ion.

The band with a maximum absorption at  $4900 \text{ \AA}$  ( $20,400 \text{ cm}^{-1}$ ) represents the energy absorbed in promoting the d electron from a  $t_{2g}$  orbital to an  $e_g$  orbital. [The strong absorption in the near ultraviolet is probably due to a charge-transfer process (p. 184).] The absorption at  $4900 \text{ \AA}$  is not a thin line but a band, because electronic excitation is accompanied by vibrational excitations spread over several thousand wave numbers. Octahedral complexes of  $\text{Ti}^{\text{III}}$  formed by ligands other than the water molecule show maximum absorption at different wave-lengths. The size of the energy difference  $\Delta_0$  is very simply related, in this one-electron case, to the wave-number of the absorption maximum.

Transition from  $t_{2g}$  to  $e_g$  in a ligand field of strength  $\Delta_0$  gives rise to an absorption maximum at  $\Delta_0 \text{ cm}^{-1}$  (Fig. 93).

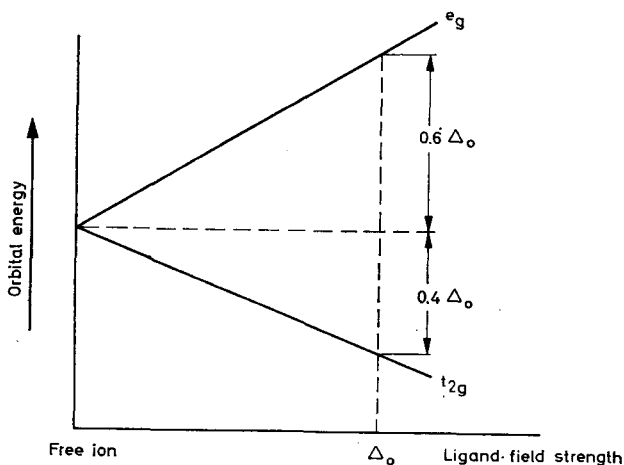
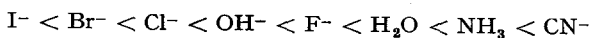


Fig. 93. Energy diagram for  $d^1$  ion.

### The spectrochemical series

The strength of the field depends on the intensity of the electron density placed by the ligands into the regions covered by the different d orbitals. It will be large when the lone pairs offered by the ligands occupy well directed orbitals, but smaller for those ligands, such as halide ions, without strongly directed lone-pair electrons. For a given cation, the extent of the splitting increases with ligands along the sequence:



This is known as the *spectrochemical series*. The position of an absorption band of a compound shifts towards the blue (shorter wave length) as one ligand is replaced by a successor which exerts a stronger ligand field.

With more than one d electron, the factors governing the positions of absorption maxima are more complicated (p. 170) but, nevertheless, the ligand-field strengths can usually be determined from the spectra. The spectrochemical series is almost independent of the choice of central ion, although the precise value of  $\Delta_0$  does, of course, depend on this choice.

### Other factors affecting ligand-field strengths

Three empirical rules on d orbital splitting (indicating ligand-field strength) emerge:

- (i) For a given ligand and a given oxidation state of the cation, it has

a small range for metals in the same period. For  $M(H_2O)_6^{2+}$  in Period 4,  $\Delta_0$  varies from  $7,800\text{ cm}^{-1}$  (22 kcal) for  $Mn^{II}$  to  $11,000\text{ cm}^{-1}$  (31 kcal) for  $Cr^{II}$ .

- (ii) For a given ligand, it is larger for a higher oxidation state than for a lower oxidation state of the same metal.

$$\Delta_0 \text{ for } Fe(H_2O)_6^{2+} \text{ is } 10,400\text{ cm}^{-1} \quad (30\text{ kcal})$$

$$\Delta_0 \text{ for } Fe(H_2O)_6^{3+} \text{ is } 13,700\text{ cm}^{-1} \quad (39\text{ kcal})$$

- (iii) For a given ligand and a given oxidation state, it is about 30% larger for metals in Period 5 than for metals in Period 4. And for metals in Period 6,  $\Delta_0$  is about 30% larger again.

## HIGH-SPIN AND LOW-SPIN COMPLEXES

### Octahedral complexes

In an octahedral complex of  $Ti^{III}$ , the single d electron occupies a  $t_{2g}$  (low-energy) orbital in the unexcited ion. In a similar  $Cr^{III}$  complex, the three d electrons, their spins orientated parallel, occupy the three  $t_{2g}$  orbitals, and the system is stable for three reasons:

- (i) the electrons occupy the d orbitals of lowest energy;
- (ii) the electrons are in different d orbitals and thus the coulombic repulsion between them is small;
- (iii) the electrons have parallel spins and thus their quantum mechanical exchange energy is low.

In a  $d^4$  ion such as  $Mn^{3+}$  there are two possible orientations (Fig. 94).

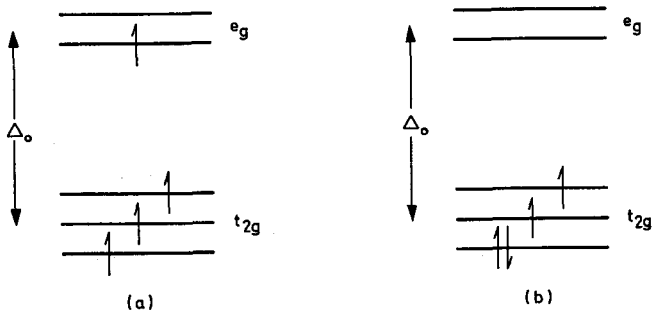


Fig. 94. Two possible distributions of four d electrons in an octahedral field.

In (a) the coulombic repulsion is a minimum, and the existence of six ( ${}^4C_2$ ) pairs of electrons with parallel spin further stabilises the ion. It must be remembered that the orbitals are quite diffuse and that there is a finite

chance of one electron changing places with another of the same spin. In effect there are six ways in which electrons can exchange with each other without causing a net energy change; the greater the possibility of such exchange the more the system is stabilised—the effect is called *exchange stabilisation*. But always there is one electron in a high-energy  $e_g$  orbital.

In (b) the coulombic repulsion is greater because two electrons occupy the same orbital, and there are only three ( ${}^3C_2$ ) pairs with parallel spins. But the high-energy  $e_g$  orbital is unoccupied.

Whether in a  $Mn^{III}$  complex the electrons are arranged as in (a) or as in (b) depends on the value of  $\Delta_0$ . In the strong ligand field exerted by six  $CN^-$  ions, the energy drop occasioned when the electron falls from an  $e_g$  to a  $t_{2g}$  orbital more than compensates for the increase in coulombic energy and exchange energy. Hence, the d orbitals in  $Mn(CN)_6^{3-}$  are occupied as in (b), the magnetic moment is that due to two unpaired spins only, and the complex is a low-spin complex. The ligand acetylacetonate, however, exerts a weaker field,  $\Delta_0$  is small, and the complex is a high-spin complex with a magnetic moment due to four unpaired spins as shown in (a). The energy drop if the  $e_g$  electron fell into a  $t_{2g}$  orbital would not be large enough to compensate for the increase in coulombic and exchange energy.

In a  $d^5$  ion such as  $Fe^{3+}$ , a strong octahedral ligand field will cause both  $e_g$  electrons to fall to  $t_{2g}$  orbitals (Fig. 95). The orbital energy released is

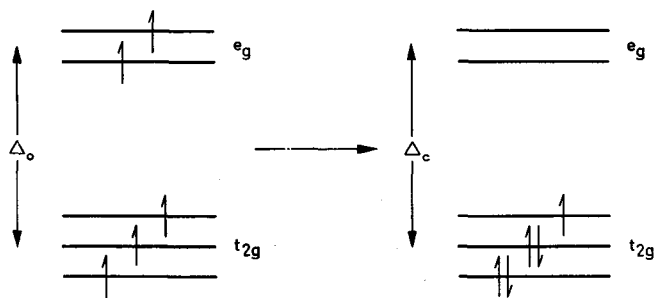


Fig. 95. Spin-pairing induced by strong ligands placed octahedrally around a  $d^5$  ion.

$2\Delta_0$ . The number of parallel pairs falls from 10 ( ${}^5C_2$ ) to 4 ( ${}^3C_2 + {}^2C_2$ )—a difference of 6; accordingly there is a considerable loss of exchange stabilisation and the field has to be a strong one to induce spin-pairing. Cyanide ions exert a field strong enough to cause spin-pairing and the  $Fe(CN)_6^{3-}$  ion has a magnetic moment due to 1 unpaired electron. It is a *low-spin complex*. But the field exerted by water molecules is too weak to cause spin-pairing and the hydrated ion  $Fe(H_2O)_6^{3+}$  has a magnetic moment

indicative of five unpaired spins. (Note that the intermediate case of 3 unpaired spins never occurs.)

Ions with  $d^6$  structure can also form high- and low-spin complexes (Fig. 96). The release of orbital energy is again  $2\Delta_0$ ; but, as the number of

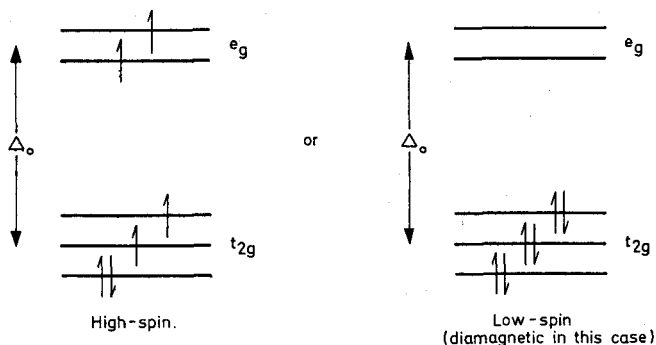


Fig. 96. Two possible arrangements of six d electrons in an octahedral ligand field.

parallel pairs is reduced by only four ( ${}^5C_2 - 2 \times {}^3C_2$ ), the value of  $\Delta_0$  required to force spin-pairing does not need to be so large, and even the  $\text{NH}_3$  molecule exerts a strong enough field to do this in the  $\text{Co}(\text{NH}_3)_6^{3+}$  ion, which is diamagnetic.

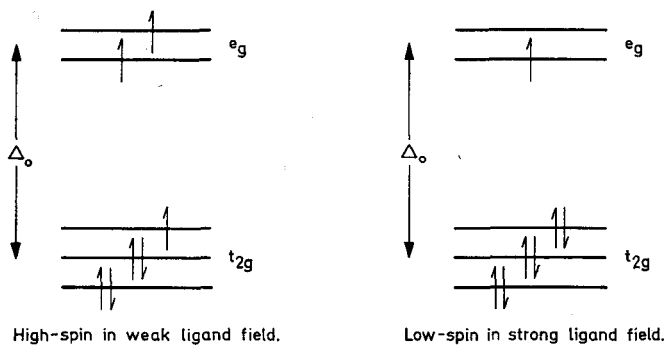


Fig. 97. Two possible arrangements of seven d electrons in an octahedral ligand field.

Ions with  $d^7$  configurations also form both high-spin and low-spin octahedral complexes (Fig. 97). Octahedral  $d^8$  ions of necessity have two electrons, and  $d^9$  ions have three electrons, in the  $e_g$  orbitals; because of this the strength of the ligand field is without effect on the extent of spin-pairing.

### Summary of the magnetic effect of the ligand field

The effect of the ligand field on the magnetic properties of a transition metal ion can now be summarised;

- (i) For a given metal ion there is a critical value of  $\Delta_0$  at which the state of lowest energy ceases to be the high-spin form and becomes the low-spin form.
- (ii) Since for a given ligand  $\Delta_0$  is greatest for Period 6 metals and for high oxidation states, low-spin complexes are most likely to be formed by highly charged ions of heavy transition metals.
- (iii) Because there is a comparatively small decrease in exchange stabilisation in the  $t_{2g}^4 e_g^2 \rightarrow t_{2g}^6$  transition, spin-pairing in  $d^6$  ions is caused by comparatively weak fields. Ions containing four or five d electrons undergo spin-pairing less readily than  $d^6$  ions, and  $d^7$  ions still less readily.

Thus, according to simple electrostatic theory, spin-pairing is most likely to be caused by ligands to the left of the spectrochemical series in the octahedral complexes of ions such as  $\text{Ir}^{3+}$  ( $d^6$ ) and, particularly,  $\text{Pt}^{4+}$  ( $d^6$ ).

### Tetrahedral complexes

When ligands are arranged tetrahedrally around an ion the five degenerate d orbitals are split into two groups of different energy but here the  $d_{xy}$ ,  $d_{xz}$  and  $d_{yz}$  orbitals have the higher energy. The directions of these orbitals lie closer to the ligands than do those of the  $d_z$  and  $d_{x^2-y^2}$  (Fig. 98).

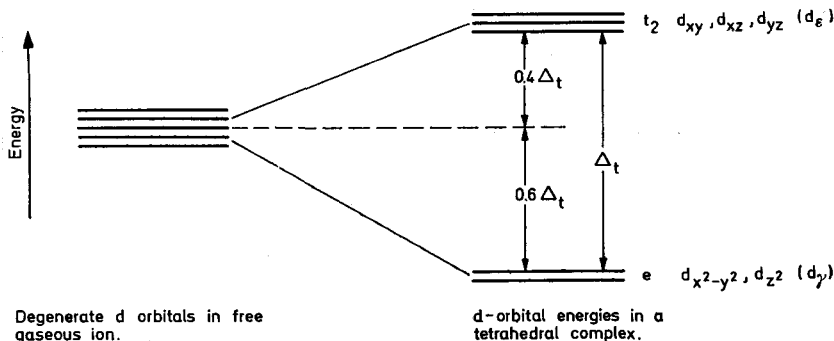


Fig. 98. Splitting of d-orbital degeneracy in a tetrahedral ligand field.

According to simple electrostatic theory,  $\Delta_t$ , the ligand-field splitting of the d electrons for a tetrahedral field should be  $\frac{4}{9}\Delta_0$ , where  $\Delta_0$  is the splitting

produced by an octahedral field exerted by the same ligands at the same metal cation.

Moreover, according to theory, transition metal cations with 3, 4, 5, or 6 d electrons should be capable of existence in either the high-spin or low-spin state in tetrahedral complexes. In fact there is no evidence of any metal forming a low-spin tetrahedral complex. Presumably the value of  $\Delta_t$ , even with strong ligands, is too small.

### Square complexes

In the field exerted by ligands lying on  $x$  and  $y$  axes of a central ion, the energy of the  $d_{x^2-y^2}$  orbital is raised to a high level (p. 155). The energy release in the transition of an electron from this orbital to a  $d_{xy}$  orbital is about the same as in an octahedral field of the same strength. The strong tendency for  $d^8$  ions ( $\text{Ni}^{2+}$ ,  $\text{Pd}^{2+}$ ,  $\text{Pt}^{2+}$ ) to form square complexes is because the unfavourably situated  $d_{x^2-y^2}$  orbital can be left empty while considerable energy is released as the electron falls to the  $d_{xy}$  level (Fig. 99).

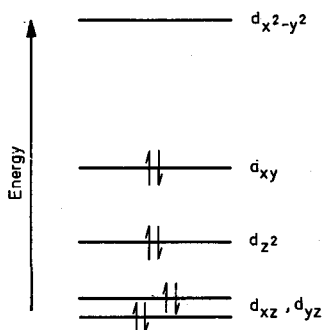


Fig. 99. Occupancy of d orbitals in a square  $\text{Pd}^{\text{II}}$  complex.

### Tetragonal complexes

Symmetrical non-linear molecules cannot remain in equilibrium in an orbitally degenerate state but must be distorted in some way which will destroy the degeneracy. This effect, which is found whenever the electron configuration of such a central atom contains unequally occupied, degenerate orbitals, was predicted by Jahn and Teller in 1937.

In an octahedral  $\text{Ti}^{\text{III}}$  complex the single d electron occupies a triply degenerate  $t_{2g}$  orbital level, making the system unstable. The resulting distortion converts the octahedral arrangement into a tetragonal one by

either expansion or compression along the  $z$  axis. The effect of compression will be to raise the  $d_{xy}$  and  $d_{yz}$  levels relative to the  $d_{xz}$  (Fig. 100). The effect of expansion along the  $z$ -axis will be to lower the  $d_{xz}$  and  $d_{yz}$  and raise the  $d_{xy}$ . In either case the degeneracy of the  $t_{2g}$  level is split by the movement of  $z$ -axis ligands towards or away from the central atom.

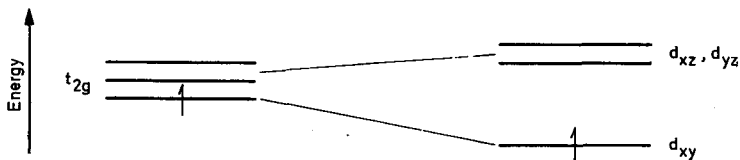
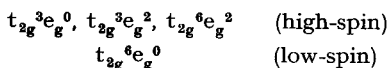


Fig. 100. Splitting of the degeneracy of  $t_{2g}$  orbitals when only one is occupied.

The effect is small for ions containing only  $t_{2g}$  electrons, since the  $t_{2g}$  orbitals lie between the directions of the ligands. Nevertheless, even for  $Ti^{III}$  complexes there is sufficient splitting of the  $t_{2g}$  level to cause a slight asymmetry in the absorption curve (p. 158).

There is no Jahn-Teller effect at all when the  $t_{2g}$  and  $e_g$  orbitals are occupied by symmetrical arrangements of  $d$  electrons, for example:



But for  $t_{2g}^3 e_g^1$ ,  $t_{2g}^6 e_g^1$  and  $t_{2g}^6 e_g^3$  arrangements, where the  $e_g$  orbitals directed towards the ligands are not symmetrically occupied, there is appreciable distortion from octahedral symmetry. For the  $Cu^{2+}$  ( $d^9$ ) ion, the energy in an octahedral field will be reduced when the ligands on one axis move outwards and those on the others move symmetrically inwards.

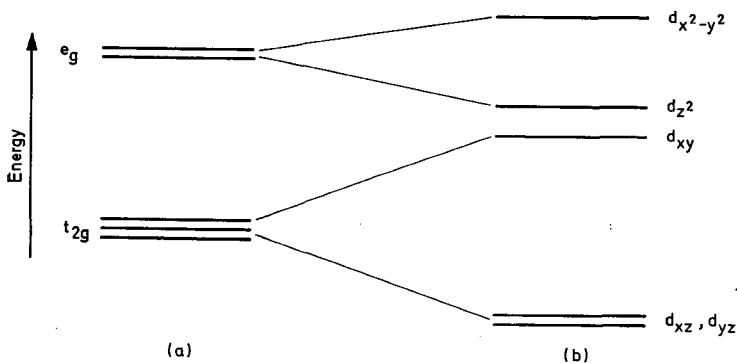


Fig. 101. Splitting of  $d$ -orbital energies in (a) octahedral, (b) tetragonal ligand fields.



As a consequence, the octahedral disposition of ligands changes spontaneously to one of tetragonal form. For instance,  $\text{CuF}_2$  has a distorted rutile structure in which there are two  $\text{F}^-$  ions at 2.27 Å and four at 1.93 Å from the  $\text{Cu}^{2+}$ . The effect on the orbital energies is to split the degeneracy of the  $t_{2g}$  and  $e_g$  orbitals (Fig. 101). In a very strong ligand field the energy of the  $d_{z^2}$  orbital may fall below that of the  $d_{xy}$  and the order of energies is the same as for a square complex (p. 155). In fact the ligands on the  $z$  axis are sometimes withdrawn altogether to give square complexes; an example of this is the  $[\text{Cr}(\text{H}_2\text{O})_4]^{2+}$  ion ( $t_{2g}^3 e_g^1$ ).

Jahn-Teller distortion of octahedral complexes usually produces tetragonal arrangements with one long ( $z$ ) axis and two short ( $x$  and  $y$ ) axes, but there are instances where one axis is short and the two others are longer. At present it is not possible to predict which of these arrangements should be the more stable.

### Distortion of tetrahedral complexes

Equally filled degenerate orbitals are also present in the perfectly tetrahedral complexes  $[\text{FeO}_4]^{2-}$  ( $d_y^2$ ),  $[\text{FeCl}_4]^-$  ( $d_y^2 d_e^3$ ),  $[\text{CoCl}_4]^{2-}$  ( $d_y^4 d_e^2$ ),  $[\text{ZnCl}_4]^{2-}$  and  $[\text{Zn}(\text{acac})_2]$  ( $d_y^4 d_e^6$ ). Slightly distorted tetrahedra occur less frequently, probably, for example, in the vanadium tetrahalides, ( $d^1_y$ ). Usually a complete transition to the planar square form takes place. A spin-free arrangement  $d_y^2 d_e^2$  in a tetrahedral field would incur strong distorting forces; these are completely relieved in the square system, both degenerate pairs of orbitals being uniformly filled.

## ABSORPTION SPECTRA OF TRANSITION-METAL COMPLEXES

A solution of a transition-metal compound owes its colour to the absorption of light at certain wave-lengths in the visible range. The absorption for a particular wavelength is expressed as a molar extinction coefficient ( $\epsilon$ ):

$$\epsilon = \frac{l}{cd} \log_{10} \frac{I_0}{I} \quad (\text{l mole}^{-1} \text{ cm}^{-1})$$

where  $c$  is the concentration of the solution in  $\text{mole l}^{-1}$ ,  $I_0$  is the intensity of the incident light and  $I$  the intensity of the light transmitted after passing through  $d$  cm of the solution.

The radiant energy absorbed by these compounds is used to promote

electrons from low-lying d orbitals to higher ones. The principles involved in the simplest case of an octahedral  $d^1$  complex have already been described (p. 159). Because the wave-lengths of absorption bands are of importance for the determination of ligand field strengths, we shall discuss the general principles applying to complexes with more than one d electron.

*Forbidden transitions may appear in complexes*

As already explained under atomic spectra (p. 59), not all electron transitions are allowed by quantum mechanics. Conditions under which certain forbidden electron transitions may occur are indicated below:

(i) Transitions in which the multiplicity,  $(2S + 1)$ , changes are forbidden.

Since  $S = \frac{n}{2}$ , where  $n$  is the number of unpaired electron spins, another way of expressing this is to say that transitions which cause a change in the number of unpaired spins are forbidden. Nevertheless, weak absorption ( $\epsilon_{\text{Max}} < 1$ ) can occur, even with high-spin  $d^5$  (for example  $\text{Mn}^{2+}$ ) complexes, where any transition between d orbitals must involve a change in  $n$ , because of the weak coupling of spin and orbital angular momenta.

(ii) According to Laporte's selection rule, for any electron transition  $\Delta l = \pm 1$ . Thus transitions from one d orbital to another ( $\Delta l = 0$ ) are 'Laporte forbidden'. Although this rule applies to free gaseous ions, there is always some low-intensity absorption ( $\epsilon_{\text{Max}} < 50$ ) by ions in complexes because the d orbitals are to some extent mixed with p or f orbitals.

(iii) Actually, nearly all transition metal compounds owe their colour to absorption due to 'forbidden' transitions. At shorter wave-lengths, in the ultraviolet, there are usually intense absorption bands ( $\epsilon_{\text{Max}} < 10^4$ ) arising from 'allowed' transitions. But in a few instances these 'allowed' transitions cause strong absorption in the visible spectrum; an example is the  $\text{Fe}^{\text{III}}$  thiocyanato complex formed in the thiocyanate test for  $\text{Fe}^{3+}$  ions.

### Energy level diagrams for ions with more than one d electron

(i)  $d^2$  ions

In an ion containing two d electrons the energy levels are affected not only by the field due to the ligands but also by the interaction between the two electrons themselves under the influence of the field. We shall consider the effect of ligands on the Russell-Saunders states (p. 74) of the free ion.

The free  $V^{3+}$  ion has as its lowest energy state a  ${}^3F$  state (Hund's rules, p. 74). Ligands octahedrally round the metal ion split the energy of the  ${}^3F$  state into three components, denoted by the symbols  ${}^3A_2$ ,  ${}^3T_2$  and  ${}^3T_1$ .

The excited states lying next above the  ${}^3F$  state in a free  $d^2$  ion are  ${}^1D$  and  ${}^3P$ . We shall consider here only the triplet state, because we are concerned with transitions between the lowest energy state, a triplet state in this case however strong the field, and states of the same multiplicity; other transitions are strongly forbidden and give rise to very weak absorption. The energy-level diagram for a  $d^2$  ion in an octahedral field has the form shown in Fig. 102.

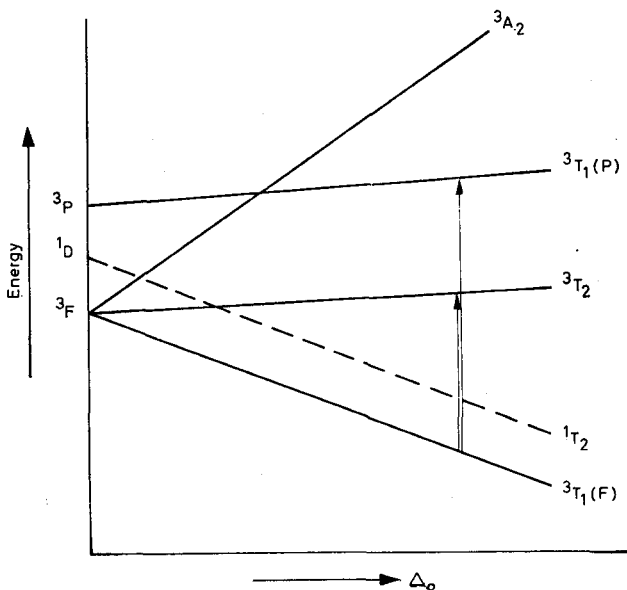


Fig. 102. Energy diagram for  $d^2$  ion in an octahedral field. The two transitions which are illustrated give rise to two absorption bands.

Only the lowest singlet state  ${}^1D$  is drawn, merely to show that it always lies above the lowest triplet state. The  ${}^3P$  state gives rise to only one state,  ${}^3T_1(P)$  in the field.

The spectrum of  $[V\overline{Ox}_2]^{3-}$  has two absorption bands at  $1.7$  and  $2.4 \times 10^{-4}$   $\text{cm}^{-1}$ . As the energy diagram shows, these energies correspond to transitions from a  ${}^3T_1$  state to  ${}^3T_2$  and  ${}^3T_1(P)$  respectively, at a point where the ligand-field splitting,  $\Delta_0$ , is  $1.78 \times 10^4$   $\text{cm}^{-1}$ . The transition  ${}^3T_1 \rightarrow {}^3A_2$  is unlikely because it represents a movement of both electrons simultaneously.

*(ii) d<sup>9</sup> ions*

The visible absorption spectrum of a d<sup>9</sup> system in an octahedral field can be interpreted by means of an energy level diagram which is effectively the d<sup>1</sup> diagram (p. 158) inverted (Fig. 103). The d<sup>9</sup> ion can be imagined

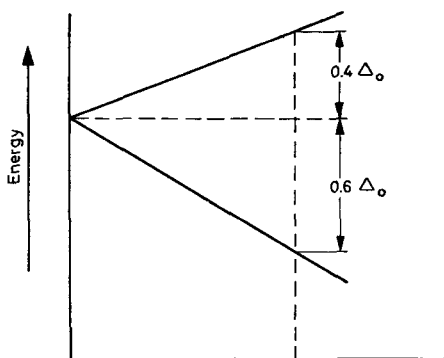


Fig. 103. Energy diagram for d<sup>9</sup> ion in an octahedral field.

as a d<sup>10</sup> ion with a hole where an electron is missing. Thus, as far as differences between the two energy levels are concerned, the treatment is the same as for a system containing one positron capable of being excited from an e<sub>g</sub> orbital to a t<sub>2g</sub> orbital by energy equivalent to Δ<sub>o</sub>.

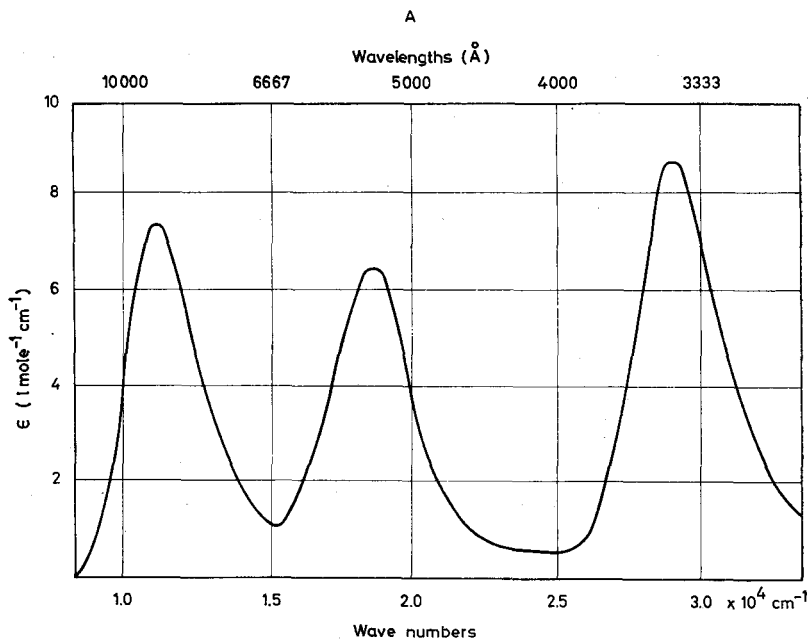
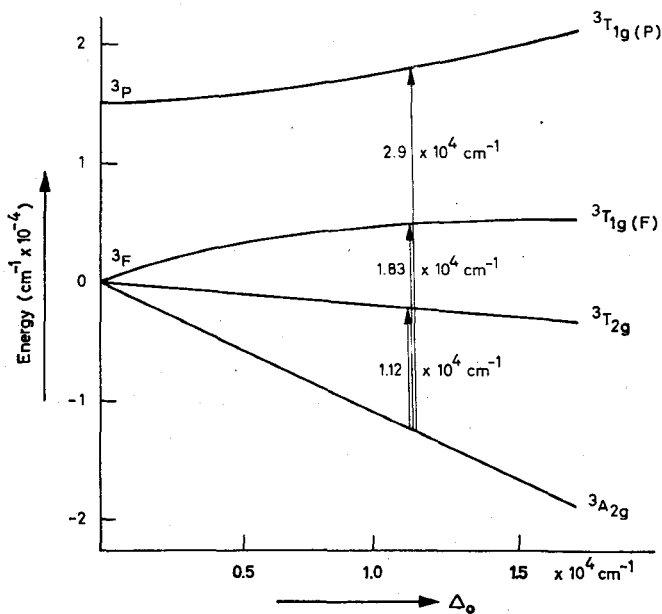
In fact the absorption spectrum of a Cu<sup>II</sup> complex does not consist of a single symmetrical band because the e<sub>g</sub> and t<sub>2g</sub> levels are split in Jahn-Teller distortion (p. 164), much more so than in the Ti<sup>3+</sup>(d<sup>1</sup>) case.

*(iii) d<sup>8</sup> ions*

The absorption spectra of Ni<sup>II</sup> compounds have excited considerable attention. The spectrum of the Ni(en)<sub>3</sub><sup>2+</sup> ion has three almost symmetrical absorption peaks (Fig. 104). This energy diagram for Ni<sup>II</sup> in an octahedral field, shown in Fig. 105, with singlet states omitted, resembles that of the d<sup>2</sup> system V<sup>III</sup>.

The <sup>3</sup>F state splits in the field into three components but their energies are inverted in relation to those in a d<sup>2</sup> system. The <sup>3</sup>P, as in the d<sup>2</sup> ion, gives only a <sup>3</sup>T<sub>1</sub> state in the ligand field, and as before (p. 168) the <sup>1</sup>D state always lies above the lowest triplet state.

Thus the three absorption bands are due to transitions from the <sup>3</sup>A<sub>2</sub> state to the <sup>3</sup>T<sub>2</sub>, the <sup>3</sup>T<sub>1</sub>(F) and the <sup>3</sup>T<sub>1</sub>(P) states respectively. For energy transitions of 1.12, 1.83 and 2.9 × 10<sup>4</sup> cm<sup>-1</sup> the value of Δ<sub>o</sub> is 1.12 × 10<sup>4</sup> cm<sup>-1</sup>.

Fig. 104. Absorption spectrum of  $\text{Ni}(\text{en})_3^{2+}$ .Fig. 105. Energy as a function of  $\Delta_o$  for  $\text{Ni}^{II} (d^8)$  system.

*(iv) d<sup>5</sup> ions*

Hydrated manganese(II) salts contain the octahedral  $\text{Mn}(\text{H}_2\text{O})_6^{2+}$  ion. In common with other high-spin  $d^5$  complexes—the  $\text{Fe}(\text{H}_2\text{O})_6^{3+}$  ion is another example—the hydrated  $\text{Mn}^{2+}$  ion is almost colourless; absorption in the visible range is very weak indeed. The absorption spectrum of this ion has been thoroughly studied, and because it illustrates some important principles, it is reproduced in Fig. 106.

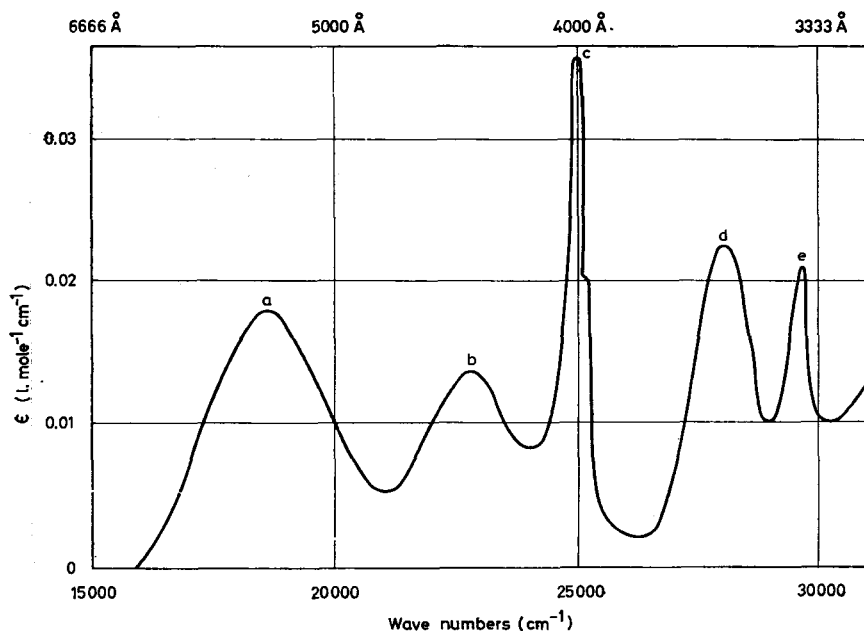


Fig. 106. Visible and near-ultraviolet spectrum of  $\text{Mn}(\text{H}_2\text{O})_6^{2+}$  ion in aqueous solution.

The first point of interest about this spectrum is that the maximum extinction coefficient is less than  $0.04 \text{ l mole}^{-1} \text{ cm}^{-1}$ , only about one-hundredth of the usual absorption caused by  $d-d$  transitions in octahedral transition-metal complexes. The reason is that all five  $3d$  orbitals are singly occupied in the  ${}^6\text{S}$  ground state by electrons of parallel spin. Promotion of an electron from one  $d$  orbital to another of higher energy must involve a change in spin and the multiplicity must be reduced from six to four. Thus every possible  $d-d$  transition is multiplicity-forbidden (p. 167) and the absorption is therefore very weak.

The second point of interest is that there are many bands in the spectrum

(*cf.*  $\text{Ti}(\text{H}_2\text{O})_6^{3+}$ , p. 158 and  $\text{Ni}(\text{en})_3^{2+}$ , p. 170). The reason is apparent from the energy diagram, Fig. 107, which shows the energies of the four quadruplet states relative to the  ${}^6\text{S}$  state in the free, gaseous  $\text{Mn}^{2+}$  ion and in ligand fields of increasing strength. There are numerous energy states lying sufficiently close together to cause a number of absorptions in the

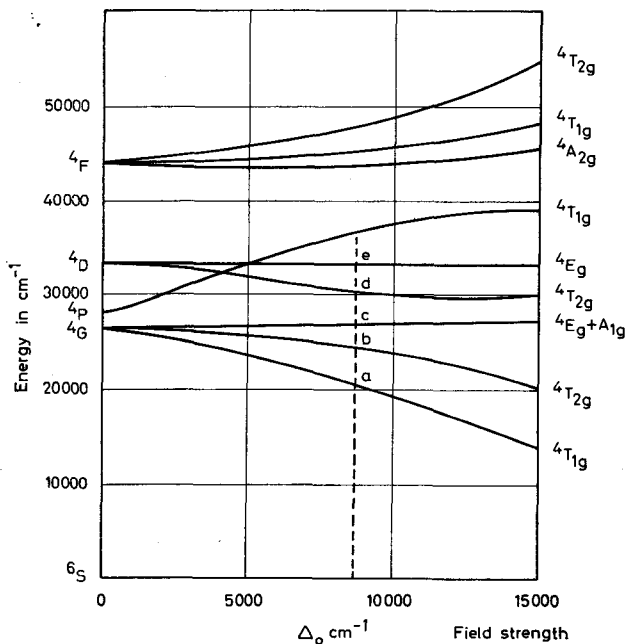


Fig. 107. Energies of the quadruplet states of  $\text{Mn}(\text{H}_2\text{O})_6^{2+}$ , relative to the  ${}^6\text{S}$  state of the free gaseous  $\text{Mn}^{2+}$  ion.

visible and the near ultraviolet. The energy transitions from  ${}^6\text{S}$  which are responsible for the absorption peaks are lettered for easy comparison with Fig. 107; the value of  $\Delta_o$  which fits the observed bands is  $\sim 8,600 \text{ cm}^{-1}$ .

The third point of interest is that bands c and e in Fig. 106 are much sharper than the others. Comparison with Fig. 107 indicates that these bands are due to d-d transitions in which the energy difference is affected very little by ligand field strength—the lines (*e.g.*  ${}^4\text{D}-{}^4\text{E}_g$ ) are about parallel to the  ${}^6\text{S}$  base line. In these transitions the electron 'jump' brought about by the absorption of energy is from one  $t_{2g}$  orbital to another. In an octahedral field the difference in energy between two  $t_{2g}$  orbitals is affected

much less by the field strength than is the difference between a  $t_{2g}$  and an  $e_g$  orbital. For transition of the  $t_{2g}-t_{2g}$  type the energy absorbed is therefore affected very little by the lengths of the vibrating metal-ligand bonds at the moment the electron jumps. Unlike the  $t_{2g}$  orbitals which lie between the octahedrally disposed ligands, the  $e_g$  orbitals lie opposite them and their energies are sensitive to changes in metal-ligand bond length (*i.e.* to changes in  $\Delta_0$ ) which occur as the bonds vibrate. In  $t_{2g}-e_g$  transitions the size of the energy absorption therefore depends a good deal on the lengths of the metal-ligand bonds at the moment the electron jumps; there is a wide spread of energy transition and a broad absorption band (a, b and d, Figs. 106 and 107).

The fourth point of interest in the absorption spectrum is the 'shoulder' on the peak at  $25000\text{ cm}^{-1}$ . The  ${}^4G$  state of the free  $\text{Mn}^{2+}$  ion gives rise to four symmetry states in the complexed ion. Of these the  ${}^4E_g$  and  ${}^4A_{1g}$  are almost, but not exactly degenerate; the line in Fig. 107 should actually divide very slightly.

#### (v) Other $d^n$ ions

The spectra of other  $d^n$  systems are not treated in detail; but, in general, it may be said that an octahedral  $d^n$  system has an energy level diagram resembling that of an octahedral  $d^{10-n}$  system, except that the order of levels coming from each Russell-Saunders state of the free ion is reversed (Figs. 93 and 103).

### Splitting of energy levels in tetrahedral fields

The energy level diagram for a  $d^n$  system in a tetrahedral field has the same form as that for a  $d^{10-n}$  system in an octahedral field. The values of  $\Delta_t$  can be determined in a similar way to those of  $\Delta_0$ .

## EVIDENCE FOR COVALENT BONDING IN TRANSITION-METAL COMPLEXES

Although the explanation just given of metal-ligand bonding in terms of electrostatic interaction is sufficient to account for the general form of the spectra arising from d-d transitions, the frequencies of the absorption peaks do not always coincide with those calculated from the theory. Furthermore, an ionic model cannot account for the order of ligands in the spectrochemical series. This is because there is always a degree of covalent



bonding between metal and ligand. The presence of covalence can be shown by several methods.

- (i) How the Landè splitting factor,  $g$ , varies under the influence of crystal-field and spin-orbital coupling effects has been described (p. 91). A  $d$  electron which spends only some of its time on the transition metal atom in a complex will contribute only in part to the orbital component of magnetic moment. From an experimental determination of the  $g$ -value, the mean distribution of the electrons which cause the magnetism can be calculated. The result shows that the  $d$ -electrons in transition metals are always delocalised to some extent. Even in octahedral fluorocomplexes, where a purely electrostatic interaction of  $M^{n+}$  and  $F^-$  ions might be expected to give an accurate representation of the bonding, the evidence is that the  $d$  electrons of the metal spend up to 5% of their time on the fluorines.
- (ii) How the unpaired electron density round an atom can be found from the nuclear splitting in the e.s.r. spectrum has been described for an odd-electron molecule (p. 89). The same principles can be applied to the finding of electron densities round atoms in paramagnetic ions. For instance, the e.s.r. spectrum of the interesting  $[(NH_3)_5CoO_2Co-(NH_3)_5]^{5+}$  complex shows eleven lines in the hyperfine splitting, indicating that the unpaired electron is in an MO which gives it an equal probability of being on each cobalt. Moreover, all metal nitrosyls have three-line e.s.r. spectra due to nitrogen splitting ( $I = 1$  for nitrogen), indicating considerable covalent character in the M-N bond.
- (iii) An unpaired electron in an orbital about a paramagnetic nucleus has a very large effect on the magnetic field at that nucleus. Measurement of the  $^{19}F$  chemical shift (p. 17) in the n.m.r. spectra of fluorocomplexes of  $Mn^{II}$  and  $Ni^{II}$  shows that the  $t_{2g}$  and  $e_g$  electrons of the metal spend more than a negligible part of their time around the fluorines.
- (iv) Shifts in the n.q.r. spectra (p. 19) of halide ions in various complexes can be related to the so-called percentage ionic character of the bonds (p. 20). Analysis of the quadrupole resonance spectra of square and octahedral complexes of Pd and Pt shows that the metal-halogen bonds are only partly ionic (Table 15, p. 175).
- (v) The energy-level diagrams on pp. 168, 172, etc. are based on the assumption that the energy separations between Russell-Saunders states (p. 74) in a complexed  $M^{n+}$  ion are the same as in a free, gaseous  $M^{n+}$  ion. In fact, the actual positions of lines in the  $d-d$  absorption spectra always indicate that there is less interaction between the  $d$  electrons themselves in a complexed ion than in a free gaseous ion. Presumably the ligands provide outlets by which  $d$  electrons can to some extent

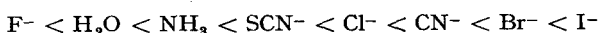
TABLE 15

PARTIAL IONIC CHARACTER OF METAL-HALIDE BONDS FROM D.Q.T. SPECTRA

Complex	Shape	Ionic character of $M-X$ (%)
$\text{PdBr}_4^{2-}$	square	60
$\text{PtBr}_4^{2-}$	square	57
$\text{PdBr}_6^{2-}$	octahedral	37
$\text{PtBr}_6^{2-}$	octahedral	38

(Note: the greater the oxidation number of the metal the more covalent the metal-halogen bond).

escape from the metal; indeed the ligands effectively increase the size of the d-electron cloud. An arrangement of ions and molecules in order of their 'cloud-expanding' or nephelauxetic effect:



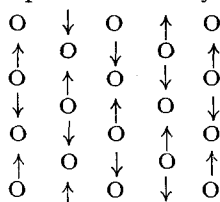
is almost independent of the central metal ion involved, as also is the arrangement in the spectrochemical series (p. 159). But the order of ligands for the nephelauxetic effect, unlike that for the spectrochemical series, appears to be closely related to the increasingly covalent character of the metal-ligand bond.

- (vi) In some solids which contain paramagnetic ions, the moments of the separate ions tend to align themselves parallel. However, the effect is small above the Curie temperature (p. 87) of the solid because the thermal vibrations are sufficiently great to upset the alignment, but up to this point the susceptibility rises rapidly with temperature. Such solids are termed *ferromagnetic*. In another class of solids, called *antiferromagnetic*, which also exhibit normal paramagnetic behaviour at high temperatures, the moments of the separate ions in the crystal lattice tend to align themselves antiparallel; for these materials, at temperatures below a characteristic temperature called the Néel point, the susceptibility falls rapidly because thermal agitation is insufficient to prevent antiparallel alignment of the ionic moments.

Some transition-metal oxides such as  $\text{MnO}$  and  $\text{NiO}$  are antiferromagnetic for another reason. In them the metal ions retain their moments but these line up in the  $\text{NaCl}$  type crystal lattice with one half in one direction and one half in the other, as is shown in the diagram on the next page. The moments of the metal ions almost certainly do not interact directly with one another but through the oxide ions.

The antiferromagnetism can be explained if we suppose some sharing of electrons between  $\text{O}^{2-}$  and adjacent  $\text{Mn}^{2+}$  ions (Fig. 108).

## 010 plane in MnO crystal



Alignment of magnetic moments of  $\text{Mn}^{2+}$  ions in MnO crystal.

↑  $\text{Mn}^{2+}$  showing direction of its magnetic moment.

O =  $\text{O}^{2-}$  ion.

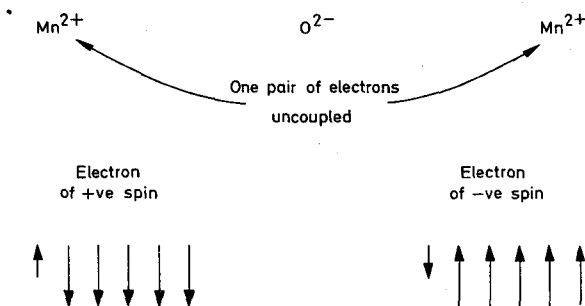


Fig. 108. Representation of the effect of an uncoupled electron pair from an oxide ion upon neighbouring  $\text{Mn}^{2+}$  ions.

Single electron occupancy of a metal d orbital makes the electron with which it pairs align with antiparallel spin and all the other unpaired d electrons align similarly to maintain the maximum exchange stabilisation (p. 161). Thus the spins, and the magnetic moments due to them, are aligned in opposition on two metal ions separated by an oxygen. The immediate point of this is that the explanation of antiferromagnetism implies a certain amount of covalent character in the bonding of these metal oxides.

Obviously when the delocalisation of metal d-electrons is slight, the results from crystal field theory need only slight modification to give calculated values of  $\Delta$  which agree with experimental results. However, a more satisfactory energy level diagram can be constructed if we accept that (a) the spin-orbit coupling constant (p. 91) and (b) the energy differences between the Russell-Saunders states are not the same for a complexed ion as for a free gaseous ion. Generally  $\lambda$  is 15–30% less in a complex than in a free ion. The energy difference between two states of the same

symmetry arising from two Russell-Saunders states of the free ion, for example the  ${}^3T_{1g}(F)$  and  ${}^3T_{1g}(P)$  states in the  $d^8 Ni^{2+}$  system (Fig. 105), is usually about 30% less than for the transition ( ${}^3F \rightarrow {}^3P$  in this case) in the free ion.

When the smaller values for  $\lambda$  and for the separations of the energies of the Russell-Saunders states are used, the simple electrostatic theory can give good agreement between the calculated and experimental values of  $\Delta$ . This is the method of the ligand field theory; in it a basically electrostatic theory is modified to allow for electron delocalisation, in other words, for some covalent character in the metal-ligand bonding. When, however, the metal-ligand bonding in a complex is largely covalent, the best treatment is provided by the molecular orbital theory.

## MOLECULAR ORBITAL THEORY OF METAL-LIGAND BONDING

### Octahedral complexes

In general the LCAO-MO method applied to complexes is the same as that for simple molecules (p. 95). There are three steps.

*The first step.* In this we seek to pick out the valency AO's of the atoms in the molecule under consideration. For a transition metal of Period 4, the valence atomic orbitals are 3d, 4s and 4p. The ligands may have  $\sigma$  and  $\pi$  valence orbitals; for example in fluorine the  $\sigma$  valence orbital is composed of 2s and  $2p_z$ , the  $\pi$  valence orbitals are  $2p_x$  and  $2p_y$ .

*The second step.* The next stage is to construct the proper linear combinations of valence AO's for the molecule. For this a knowledge of the molecular symmetry is required. The  $\sigma$  valence orbitals in an octahedral complex, classified according to symmetry, are

$$\begin{array}{cccc} 4p_x & 4p_y & 4p_z & (t_{1u}) \\ & 4s & & (a_{1g}) \\ 3d_{z^2} & 3d_{x^2-y^2} & & (e_g) \end{array}$$

The symmetry classifications on the right are derived from group theory, the symbol  $a$  indicates nondegeneracy, the other letters have the meanings explained on p. 156.

The linear combinations of ligand  $\sigma$  orbitals which can bond with the  $t_{1u}$ ,  $e_g$  and  $a_{1g}$  metal orbitals must have the same symmetry properties as the metal orbitals. For example, the linear combination which has the same symmetry as the  $4p_x$  metal orbital has a positive value in the  $+x$  direction

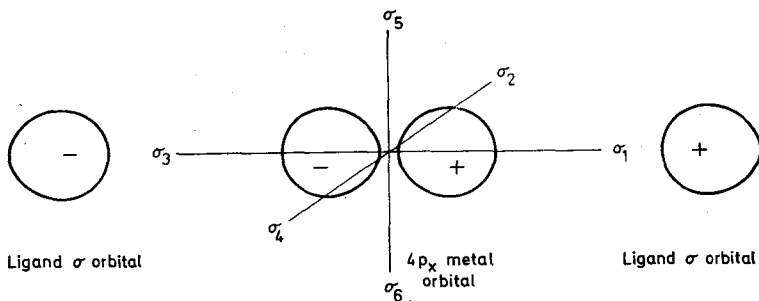


Fig. 109. Linear combination of  $4p_x$  orbital on metal with  $\sigma_1 - \sigma_3$  ligand orbitals.

and a negative value in the  $-x$  direction (Fig. 109). This is the combination  $\sigma_1 - \sigma_3$ . Similarly the combination  $\sigma_2 - \sigma_4$  has the correct symmetry for overlap with  $4p_y$  and the combination  $\sigma_5 - \sigma_6$  for overlap with  $4p_z$ . The  $4s$  metal orbital, positive in all directions, combines with  $\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4 + \sigma_5 + \sigma_6$ . The  $3d_{x^2-y^2}$  orbital, the lobes of which have alternately positive and negative  $\psi$  values, matches the  $\sigma_1 - \sigma_2 + \sigma_3 - \sigma_4$  in symmetry (Fig. 110).

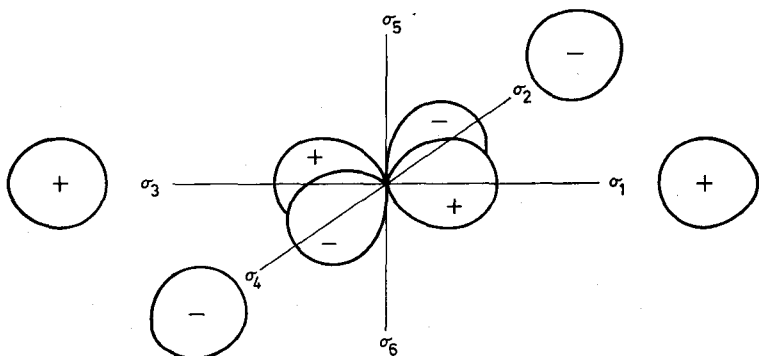


Fig. 110. Combination of  $d_{x^2-y^2}$  with  $\sigma_1 - \sigma_2 + \sigma_3 - \sigma_4$ .

The ligand  $\sigma$  orbital combination for  $3d_{x^2}$  presents more difficulty; it is in fact  $2\sigma_5 + 2\sigma_6 - \sigma_1 - \sigma_2 - \sigma_3 - \sigma_4$ .

For  $\pi$ -bonding the appropriate metal orbitals are

$$\begin{array}{lll} 3d_{xy}, & 3d_{xz}, & 3d_{yz} \quad (t_{2g}), \\ 4p_x, & 4p_y, & 4p_z \quad (t_{1u}). \end{array}$$

The  $4p$  orbitals are involved in both  $\sigma$ - and  $\pi$ -bonding. The proper  $t_{1u}(\pi)$  and  $t_{2g}(\pi)$  ligands can be written down as for the  $\sigma$  LCAO's (see Fig. 111).

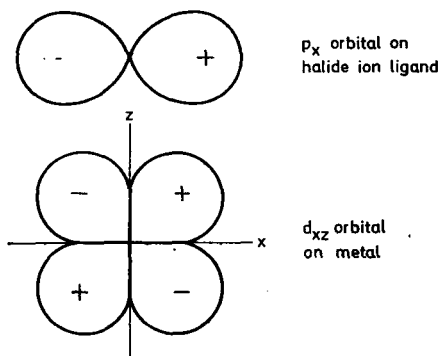


Fig. 111. Example of metal and ligand orbitals with suitable symmetry for  $\pi$ -bonding.

Fig. 112 shows the co-ordinate system for  $\pi$ -bonding in an octahedral complex, relative to the  $\sigma$ -bond directions.

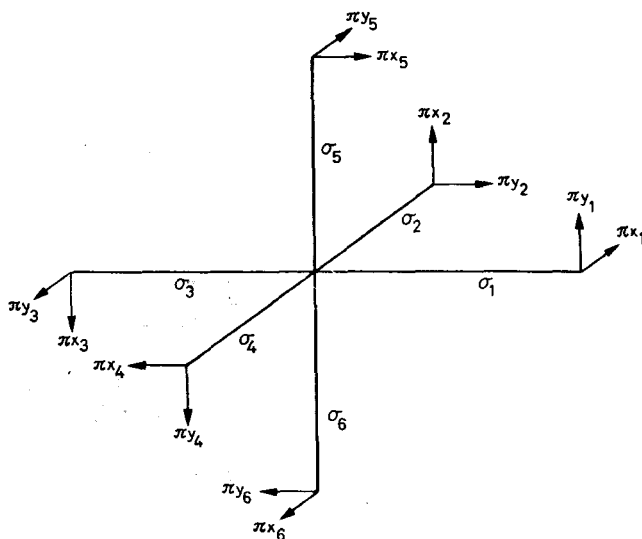


Fig. 112. Co-ordinate system for  $\sigma$  and  $\pi$  bonds in an octahedral complex.

In addition to the six ligand  $\pi$ -orbital combinations given in Table 16, there are six more made up of the same  $\pi$  orbitals as the  $t_{1u}$  and  $t_{2g}$  but with the signs of the second and fourth terms changed. These are the  $t_{2u}$  and  $t_{1g}$  respectively. These are non-bonding because there are no metal orbitals of the same symmetry, so that overlap is not possible.

TABLE 16

PROPER METAL- AND LIGAND-ORBITAL COMBINATIONS FOR OCTAHEDRAL COMPLEXES

Symbol	Metal orbital	Combination of ligand orbitals
<i>(i) For sigma bonds</i>		
$a_{1g}$	s	$\frac{1}{\sqrt{6}} (\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4 + \sigma_5 + \sigma_6)$
$e_g$	$d_{z^2}$	$\frac{1}{2\sqrt{3}} (2\sigma_5 + 2\sigma_6 - \sigma_1 - \sigma_2 - \sigma_3 - \sigma_4)$
	$d_{x^2-y^2}$	$\frac{1}{2} (\sigma_1 - \sigma_2 + \sigma_3 - \sigma_4)$
$t_{1u}$	$p_x$	$\frac{1}{\sqrt{2}} (\sigma_1 - \sigma_3)$
	$p_y$	$\frac{1}{\sqrt{2}} (\sigma_2 - \sigma_4)$
	$p_z$	$\frac{1}{\sqrt{2}} (\sigma_5 - \sigma_6)$
<i>(ii) For pi bonds</i>		
$t_{1u}$	$p_x$	$\frac{1}{2} (\pi_{y_2} + \pi_{x_5} - \pi_{x_4} - \pi_{y_6})$
	$p_y$	$\frac{1}{2} (\pi_{x_1} + \pi_{y_5} - \pi_{y_3} - \pi_{x_6})$
	$p_z$	$\frac{1}{2} (\pi_{y_1} + \pi_{x_5} - \pi_{x_3} - \pi_{y_4})$
$t_{2g}$	$d_{xz}$	$\frac{1}{2} (\pi_{y_1} + \pi_{x_5} + \pi_{x_3} + \pi_{y_6})$
	$d_{yz}$	$\frac{1}{2} (\pi_{x_2} + \pi_{y_5} + \pi_{y_4} + \pi_{x_6})$
	$d_{xy}$	$\frac{1}{2} (\pi_{x_1} + \pi_{y_2} + \pi_{y_3} + \pi_{x_4})$

*The third step.* This final step is to place the molecular orbitals in order of energy. Reasonable approximations for the coulombic and exchange energies may be obtained by following the three rules:

- (i) The order of coulombic energies is taken to be

$$\sigma_{\text{ligand}} < \pi_{\text{ligand}} < 3d < 4s < 4p$$

The values are lower for ligand orbitals because the ligand is more electronegative than the metal.

- (ii) The extent of mixing of metal AO's and ligand orbitals in the MO's is proportional to the overlap of the AO's with ligand orbitals and inversely proportional to their coulombic energy differences.
- (iii) Bonding  $\sigma$  MO's are more stable than bonding  $\pi$  MO's and anti-bonding  $\sigma^*$  are less stable than antibonding  $\pi^*$ .

The relative energies of molecular orbitals for an octahedral complex are illustrated in Fig. 113.

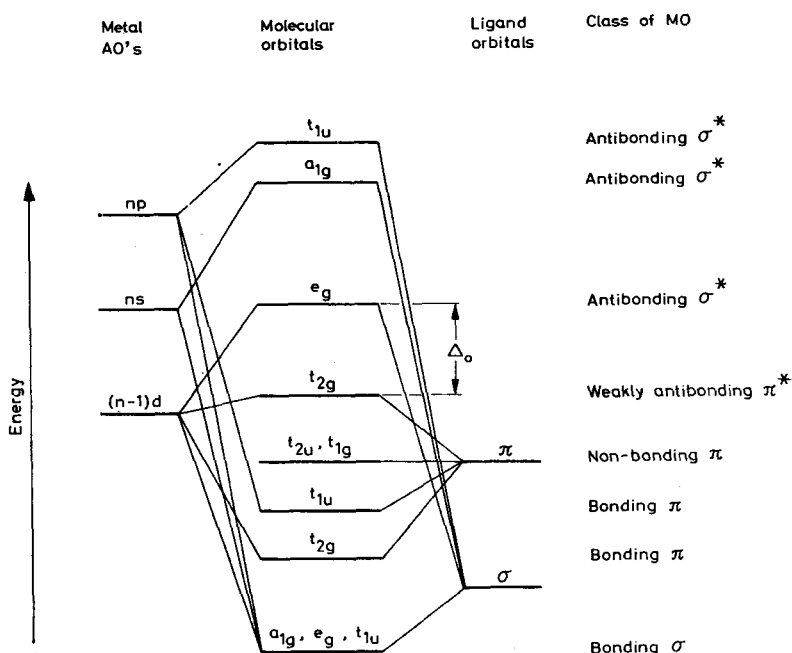


Fig. 113. Energies of orbitals involved in the formation of an octahedral complex.

Points to note about Fig. 113 are:

- (i) A bonding MO has a lower energy and an antibonding MO a higher energy than either of the orbital types contributing to it; a non-bonding MO has the same energy as the orbital type from which it is formed.
- (ii) The energies of bonding orbitals generally lie near those of the ligand orbitals, and the energies of antibonding orbitals near those of the metal orbitals.
- (iii) There is accommodation for 12 electrons in  $\sigma$ -bonding orbitals, for 12 electrons in  $\pi$ -bonding orbitals and for 12 electrons in non-bonding  $\pi$ -orbitals.

The advantage of the molecular orbital approach to metal-ligand bonding is that we can picture the filling of molecular orbitals with electrons in the order of their energy, irrespective of the origin of the electrons. By dis-



pending with an ionic model, which is no longer necessary, the various energy levels can be represented much more realistically.

Consider for instance an octahedral complex formed by  $\text{Cl}^-$  ions with a metal ion having three d electrons. Disregarding those electron pairs of the chlorine ions which are directed away from the metal, we have  $(6 \times 6) + 3$  valence electrons available, 39 in all. Of these 12 are needed to fill the sigma bonding orbitals, and 24 for the bonding and non-bonding  $\pi$  orbitals  $t_{2g}$ ,  $t_{1u}$ ,  $t_{2u}$  and  $t_{1g}$ . The last three of the 39 electrons are accommodated in the weakly antibonding  $t_{2g}$  orbitals. The form of the energy level diagram shows that these  $t_{2g}$  orbitals, although formed largely from metal d orbitals, also contain a contribution from ligand  $\pi$  orbitals (Rule (ii) p. 180). In the present instance the ligands have sufficient electrons to fill their  $\pi$  orbitals; and the  $t_{2g}$  level remains high above the ligand  $\pi$  level. But when there are empty  $\pi$  orbitals on the original ligands the  $t_{2g}$  electrons tend to escape towards them. The result is to bring the energy of the  $t_{2g}$  orbitals closer to that of the ligand  $\pi$  orbitals.

The cyanide ion, although it is without empty  $\pi$  orbitals of low energy, does have empty  $\pi^*$  orbitals of only slightly higher energy (Fig. 114)

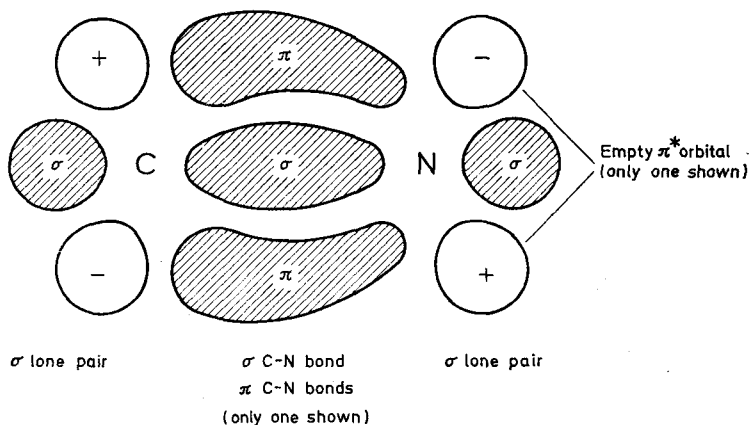


Fig. 114. MO's in  $\text{CN}^-$  ion ( $\text{KK } z\sigma^2 y\sigma^2 x\sigma w\pi^4$ ).

The  $\pi^*$  orbitals are of suitable symmetry to combine with the  $t_{2g}(\pi^*)$  of the metal; electrons in the  $t_{2g}$  which are released towards them are said to undergo  $\pi$ -back-donation to the ligand. The ligand itself is known as a  $\pi$ -acceptor ligand. The resultant fall in the energy of the orbital increases the gap between its energy and that of the  $e_g(\sigma^*)$  orbital (*i.e.* the value of  $\Delta_0$  increases). Thus the MO theory is able to explain why the  $\text{CN}^-$  ion lies so far towards the high-energy end of the spectrochemical series.

Clearly the effect of  $\pi$  back-donation is to increase the covalent character of the bond between the metal and the co-ordinating atom, whereby the bond is also strengthened. In the present example the creation of  $\pi$  bonding between metal and carbon increases the strength of the M-C bond; at the same time however the C-N bond is weakened a little because of the partial filling of an orbital which is antibonding with respect to C-N. Manifestly, the strength of the C-N bond in cyanocomplexes of different metals must be different and this can be demonstrated by infrared spectroscopy (p. 140).

### Tetrahedral complexes

In the building-up of the molecular orbitals in a tetrahedral complex, the only  $\sigma$  orbital that is entirely of the metal is the  $ns$  ( $a_1$ ). The  $(n-1)$   $d_{xy}$ ,  $d_{xz}$  and  $d_{yz}$  ( $t_2$ ) and the  $np_x$ ,  $p_y$  and  $p_z$  ( $t_2$ ) orbitals may be used in both  $\sigma$  and  $\pi$  bonding. The  $(n-1)$   $d_{x^2-y^2}$  and  $d_z$  are pure  $\pi$  orbitals (Fig. 115). There is maximum  $\pi$ -bonding in a tetrahedral complex when all  $\pi$ -bonding  $e$  and  $t_2$  orbitals (five altogether) are filled and all the  $\pi^*$  are empty. For example, the permanganate ion,  $MnO_4^-$  has six electrons in the

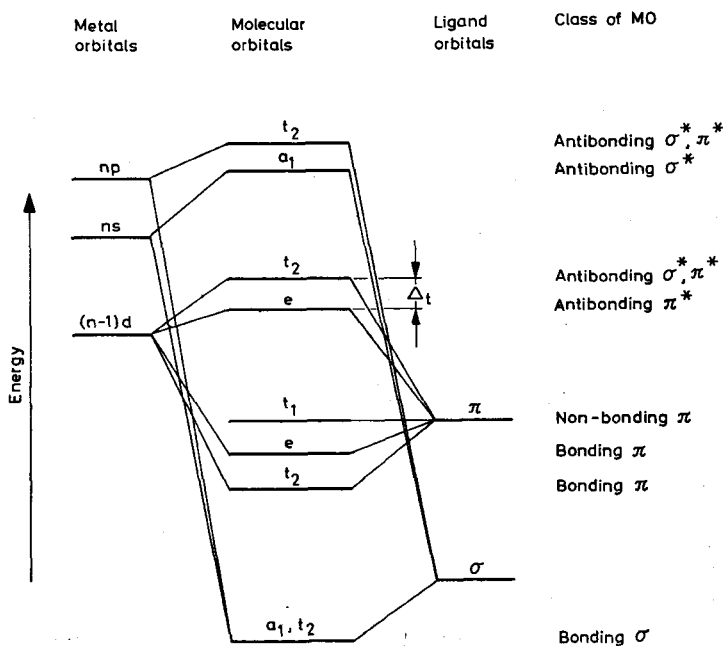


Fig. 115. Energy levels of orbitals involved in the formation of a tetrahedral complex.

$\pi$ -bonding  $t_2$  and four in the slightly higher  $e$  orbitals, making five  $\pi$ -bonds.

### Charge-transfer spectra

A solution of iodine in carbon tetrachloride has the same violet colour as iodine vapour; this is due in both instances to an absorption of light characteristic of  $I_2$  molecules. But in a basic solvent, such as alcohol or pyridine, iodine gives a brown solution, although appreciable reaction has not occurred between the  $I_2$  and the solvent molecules. The difference is because in such solvents every energy quantum absorbed transfers an electron from a molecule of the base to a high-energy, empty orbital of the  $I_2$  molecule. This can be considered as an intermolecular electron transfer. The charge-transfer absorption gives rise to charge-transfer spectra.

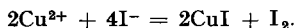
There are also intramolecular transitions, particularly in complex ions. Electronic transitions from an orbital localised mainly on one atom to an orbital localised mainly on another atom usually occur at much higher energies than  $d-d$  transitions. The resulting charge-transfer spectrum consists of strong absorption, usually in the ultraviolet region (p. 171). Such charge-transfer processes are of two types: ligand to metal, abbreviated  $L \rightarrow M$ , in which an electron is transferred from an orbital localised mainly on the ligand to one localised mainly on the metal, and metal to ligand in which the electron is transferred in the reverse direction, abbreviated  $M \rightarrow L$ .

The  $L \rightarrow M$  charge transfer is shown by complexes of  $O^{2-}$ ,  $Cl^-$ ,  $Br^-$  and of  $I^-$  particularly. For  $d^0$  complexes, where a  $d-d$  transition is not possible,  $\Delta$  can be estimated only from charge-transfer absorption frequencies. An example is  $MnO_4^-$ , the purple colour of which is due to a low-energy  $O^{2-} \rightarrow Mn^{7+}$  charge transfer in the tetrahedral complex. The bands at 1.85, 3.22 and  $4.44 \times 10^4 \text{ cm}^{-1}$  in this absorption spectrum have been assigned to transitions  $t_1(\pi) \rightarrow e(\pi^*)$ ,  $t_2(\pi) \rightarrow e(\pi^*)$  and  $t_1(\pi) \rightarrow t_2(\sigma^*, \pi^*)$  respectively (Fig. 115). Thus  $\Delta$  is found to be  $2.59 \times 10^4 \text{ cm}^{-1}$  by difference  $e(\pi^*) \rightarrow t_2(\sigma^*, \pi^*)$ .

The  $M \rightarrow L$  charge transfer occurs in complexes containing ligands which have stable but empty orbitals. Complexes of  $\pi$ -acceptor ligands such as  $NO$ ,  $CO$  and  $CN^-$  often have such absorption bands.

Charge-transfer transitions, unlike  $d-d$  transitions, are often neither multiplicity-forbidden nor Laporte-forbidden; consequently they give strong absorption bands with extinction coefficients in the range 500–2000. This fact enables charge-transfer absorption to be distinguished from  $d-d$  transitions for which  $\epsilon_{\text{Max}}$  is usually below 100.

A charge-transfer process is obviously closely related to an oxidation-reduction process. In fact, with ligands of low electronegativity a charge-transfer process can become a redox reaction. Thus the dark colour of a solution containing  $\text{Cu}^{2+}$  and  $\text{Cl}^-$  ions is attributed to strong charge-transfer ( $\text{L} \rightarrow \text{M}$ ) absorption in a  $\text{Cu}^{\text{II}}$  chloro-complex. Bromide ions cause an even stronger colour than  $\text{Cl}^-$ . But  $\text{I}^-$  ions lose electrons to orbitals centred entirely on the copper; as a result the  $\text{Cu}^{2+}$  cations are reduced to  $\text{Cu}^+$  and the iodide anions are oxidised to iodine:



### Factors influencing structure in transition-metal complexes

The shape of a complex ion or molecule is governed largely by two types of interaction:

- (i) The ligands themselves exert a mutual coulombic repulsion, greatest for large, monatomic anions such as  $\text{Br}^-$  and  $\text{I}^-$ , smallest for small, uncharged ligands like  $\text{NH}_3$  and  $\text{H}_2\text{O}$ .
- (ii) The electrons in the  $\pi^*$  and  $\sigma^*$  orbitals, by their number and distribution, stabilise some arrangements of ligands but not others; stabilisation happens particularly when the ligands themselves create strong fields.

Most transition-metal complexes have one of the three structures; octahedral, square or tetrahedral. The octahedral structure, which utilises all six of the strong  $\sigma$  orbitals ( $n-1$ ) $d_{x^2-y^2}$ , ( $n-1$ ) $d_{z^2}$ ,  $ns$ ,  $np_x$ ,  $np_y$ , and  $np_z$ , is the preferred arrangement unless interactions (i) and (ii) above make this an unstable structure.

Weak-field ligands with large mutual repulsions (*e.g.*  $\text{I}^-$ ,  $\text{Br}^-$  and very large molecules) tend to form tetrahedral complexes because the coulombic repulsions are reduced when there are few ligands and they are not crowded together.

In complexes with strong-field ligands the number of d electrons contributed by the metal ion is of great importance. A  $d^6$  ion with strong-field ligands forms low-spin, undistorted octahedral complexes in which six electrons are accommodated in the weakly antibonding  $\pi^*t_{2g}$  orbitals. But in a  $d^7$  complex one electron must enter the strongly antibonding  $\sigma^*e_g$  orbital. The usual result is that one ligand is lost and an  $\text{ML}_5$  complex, with one unpaired electron in a potentially  $\sigma$ -bonding orbital like the  $d_{z^2}$ , is formed; this  $\text{ML}_5$  monomeric complex then dimerises to  $\text{M}_2\text{L}_{10}$ . Thus  $d^7$  ions with strong-field ligands such as  $\text{CO}$  and  $\text{CN}^-$  often form dimeric complexes with metal-metal bonds; examples are the compound  $\text{Mn}_2(\text{CO})_{10}$  and the anion  $[\text{Co}_2(\text{CN})_{10}]^{6-}$ .

The  $d^8$  complexes have already been discussed under crystal-field theory (p. 164). For them the molecular-orbital picture is effectively the same, a square arrangement of strong-field ligands enables eight electrons to be accommodated in relatively stable orbitals. In instances where the metal is in a low oxidation state, however, a trigonal bipyramidal structure is possible (e.g.  $\text{Fe}(\text{CO})_5$ ), because back-donation both strengthens the  $\pi$ -bonding, which is favoured in the trigonal-bipyramidal arrangement, and relieves the concentration of negative charge at the metal.

For  $d^9$  metal ions, both octahedral and square arrangements of ligands have electrons in strongly antibonding  $\sigma^*$  orbitals. Tetragonal arrangements are often more stable, but dimeric complexes with metal-metal bonds are also possible. Complexes of  $d^{10}$  metal ions are tetrahedral. The arrangement enables all the electrons to occupy low-energy orbitals (p. 183).

For complexes of weak-field ligands with small mutual repulsions, there is usually no reason for the structure to be other than octahedral unless the metal ion is either a  $d^9$  or a  $d^{10}$  one. The  $d^9$  complexes are usually tetragonal, the  $d^{10}$  almost always tetrahedral.

In the complexes of Period 5 and Period 6 transition metals, the higher values of  $\Delta$  make the occupancy of antibonding orbitals a more important factor in determining structure. At the same time the greater distances between the ligands, owing to longer metal-ligand bonds, reduce their mutual repulsion. Thus  $\text{PdBr}_4^{2-}$  and  $\text{PtBr}_4^{2-}$  are planar, which is the preferred symmetry for  $d^8$  strong-field, weak-repulsion ligands; whereas  $\text{NiBr}_4^{2-}$  is tetrahedral, which is the preferred symmetry for  $d^8$  weak-field, strong-repulsion ligands.

#### FURTHER READING

- J. S. GRIFFITH AND L. E. ORGEL, *Ligand Field Theory*, Quarterly Reviews, 11 (1957) 381.
- T. M. DUNN, *The Visible and Ultraviolet Spectra of Complex Compounds* in J. LEWIS AND R. G. WILKINS, *Modern Coordination Chemistry*, New York, Interscience, 1960.
- C. K. JØRGENSEN, *Absorption Spectra and Chemical Bonding in Complexes*, London, Pergamon, 1961.
- J. S. GRIFFITH, *The Theory of Transition Metal Ions*, London, Cambridge Univ. Press., 1961.
- L. E. ORGEL, *Spectra of Transition-Metal Complexes*, J. Chem. Phys., 23 (1955) 1004.
- C. K. JØRGENSEN, *The Nephelauxetic Series* in F. A. COTTON, *Progress in Inorganic Chemistry*, New York, Interscience, Vol. 4 (1962) 73.
- C. J. BALLHAUSEN, *Intensities of Spectral Bands in Transition-metal Complexes* in F. A. COTTON, *Progress in Inorganic Chemistry*, New York, Interscience, Vol. 2 (1960) 251.

## Chapter 9

# The Solid State

### EXPERIMENTAL EVIDENCE ON STRUCTURE

The term *structure* when applied to solids refers to the arrangement of the atoms, ions or molecules which compose them. This arrangement in a solid may be the ordered one of the crystal or the random one of amorphous material. In fact crystals are probably never perfectly ordered nor amorphous material completely random, but this does not detract from the practical usefulness of the distinction. Evidence on which our current knowledge of the structure of solids is based has been obtained from a study of their diffraction of X-rays, electrons or neutrons. These methods are very briefly outlined below.

#### X-ray diffraction

Friedrich (1912), at the suggestion of von Laue, demonstrated that X-rays produce diffraction patterns when passed through crystals. W. L. Bragg (1912) determined the structures of NaCl, KCl and ZnS by directing a beam of monochromatic X-rays on a crystal of the respective compound. If the beam is deflected through an angle  $2\theta$ , the angles of incidence and reflection for a layer of atoms will be  $\theta$  and the spacing  $d$  between the successive layers is given by

$$n\lambda = 2d \sin \theta.$$

in which  $\lambda$  is the wave length of the X-rays and  $n$  a small whole number.

#### *Powder method*

The atoms in crystals form a diffraction grating for X-ray and other short-wave radiation. Because it is a three-dimensional grating, diffraction occurs only at certain orientations of the grating (that is of the crystal) with respect to the direction of an incident beam. Debye and Scherrer (1917) used the diffraction pattern recorded for a monochromatic beam of X-rays falling on a powder of small crystals, or crystal fragments, to deduce Bragg angles and hence structure. The *powder method*, in which finely divided material, compressed or held in the form of a rod, is rotated

in a beam of near-monochromatic X-rays and the diffractions from it are recorded on a photographic film mounted in a circular camera of known dimensions, has been developed to provide diffraction angles and intensities with great precision.

The method is much used in chemical investigation because of its applicability to powders and to material of poor crystallinity. It readily shows the presence of crystalline components in mixtures and hence has been an instrument for both qualitative and quantitative analysis. For these purposes the diffraction pattern of the sample is compared with the patterns of known materials. But the method has much more fundamental applications of which the following are listed: determination of crystal structure, measurement of transition temperatures and coefficients of thermal expansion, the investigation of phase equilibria and of reactions between solid or semi-solid materials.

#### *Single crystal method*

Schiebold (1919) showed that a single crystal rocked in a narrow beam of monochromatic X-rays gives diffractions which may be recorded as dark spots on a photographic plate. Provided the geometry of the system is known the Bragg angles may be found and the structure deduced. The *single crystal method* has also been much developed and, where a good crystal is available, it now provides the most powerful means of determining structure, particularly elaborate structure.

### **Electron diffraction**

An electron, in a beam of electrons, exhibits wave properties (p. 51), the wave length being dependent on the excitation voltage. These wave properties are employed to measure bond lengths and bond angles in gas molecules. Electrons of about  $5 \times 10^4$  volts ( $\lambda \sim 0.05 \text{ \AA}$ ) are passed through the gas or vapour at low pressure. The atoms in the molecules scatter the electron beam in much the same way as they diffract a beam of X-rays.

Electron diffraction is applied to solids too, the principles being again similar to those for X-rays. That the electrons do not penetrate so deeply is in some ways an advantage because it enables the nature of the surface and the surface film on a solid to be ascertained. For this purpose a pencil of electrons almost parallel to the surface is used. However, neither X-rays nor electrons are diffracted sufficiently by hydrogen to enable the positions of its atoms to be ascertained with much certainty.

### Neutron diffraction

The diffraction of X-rays and electrons is due to interaction with the orbital electrons of the atoms they encounter. The diffraction of neutrons (p. 5) springs from different causes.

- (i) *Nuclear scattering* is brought about by interaction with protons or neutrons in the nucleus and depends upon (a) nuclear *size* (which increases only slowly with atomic weight) and (b) nuclear *structure* (a dependence which appears to vary arbitrarily from one element to the next). Thus the hydrogen atom scatters neutrons as well as the potassium and better than the cobalt. This is in marked contrast to X-rays where the scattering increases smoothly with the number of extra-nuclear electrons in the atom.
- (ii) *Magnetic scattering* arises from interaction between the magnetic moment of the neutron and that of the atom or ion in question. Thus the  $\text{Fe}^{3+}$  ion, with its unpaired electrons, gives additional scattering superimposed upon the nuclear scattering. Magnetic scattering is used to investigate the magnetic properties of alloys.

Neutrons emerging from an atomic reactor have a range of energies. They are collimated and monochromated to give a narrow pencil of neutrons with an energy corresponding to a wave length of about  $1 \text{ \AA}$ . After scattering by the specimen, usually a single crystal, the diffraction pattern is obtained by means of a counter, filled with  $^{10}\text{BF}_3$ , connected to a pen-recorder.

The diffraction of neutrons provides a way of locating hydrogen atoms in compounds and is used to complement X-ray study of crystals especially by locating and characterising water molecules in hydrates.

### STRUCTURE AND PROPERTIES

The properties of a solid depend not only on the number and kind of atoms composing it but also on their arrangement. The empirical formula reveals nothing of this, for a compound  $\text{AB}_2$  can exist in the solid:

- (i) as separate molecules (B–A–B in solid carbon dioxide);
- (ii) as an infinite layer (Fig. 116) (cadmium iodide,  $\text{CdI}_2$ , is like this, though the atoms are not quite co-planar);
- (iii) in various three-dimensional structures (Fig. 117) (fluorite,  $\text{CaF}_2$ , has cubic crystals with one of these arrangements).

In (i) every carbon atom is connected to two oxygen atoms, in (ii) every cadmium atom has six iodine atoms as nearest neighbours, and in (iii) every calcium atom has eight fluorine atoms as nearest neighbours. The chemical formula of a solid should therefore be considered in relation to



its crystal structure. Even two solids as similar in formulation as  $\text{PCl}_5$  and  $\text{PBr}_5$  differ structurally; the former consists of equal numbers of  $\text{PCl}_4^+$  ions and  $\text{PCl}_6^-$  ions, the latter of equal numbers of  $\text{PBr}_4^+$  and  $\text{Br}^-$  ions.

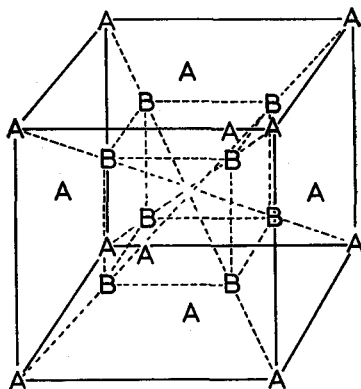
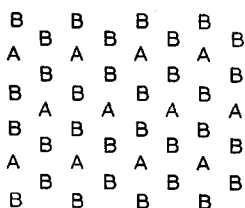


Fig. 116. Infinite layer of formula  $\text{AB}_2$ .

Fig. 117. Cubic structure of formula  $\text{AB}_2$ .

### The unit cell

A crystalline solid consists of atoms (or ions) packed regularly in a three-dimensional arrangement. For any point in the pattern it is possible to find other points possessing exactly the same environment. Such points then define a regular *lattice*: one lattice point can be reached from another by taking a suitable number of primitive translations (steps) along each of three suitable directions. Clearly the whole pattern can be built up by translating a block of essentially different points lying in a certain *unit cell*. The nature of the solid is determined by the size, shape and content of its unit cell.

The size and shape of a unit cell is defined by the lengths ( $a$ ,  $b$ ,  $c$ ) of three intersecting edges and the angles ( $\alpha$ ,  $\beta$ ,  $\gamma$ ) between them (Fig. 118).

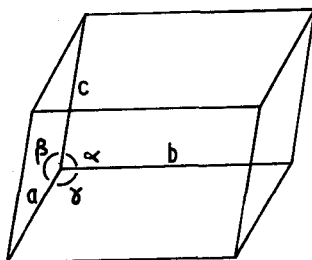


Fig. 118. Unit cell.

There are seven types of unit cell (Table 17) and therefore seven *simple* or *primitive* lattices with one unit of pattern at each cell corner.

TABLE 17

THE SEVEN TYPES OF UNIT CELL

System	Cell edges	Cell angles	Example
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	Rock salt
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	White tin
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	Mercuric chloride
Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ \beta \neq 90^\circ$	Potassium chlorate
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	Potassium dichromate
Hexagonal	$a \neq b \neq c$	$\alpha = \beta = 90^\circ \gamma = 120^\circ$	Silica
Rhombohedral	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$	Calcite

### Bravais lattices

If the *contents* of a unit cell containing a number of units of pattern (atoms, molecules) have symmetry, the number of distinct types of space lattice, as Bravais noted in 1848, becomes *fourteen* (Fig. 119). And when other symmetry operations are recognised (*e.g.* rotation of the lattice) there are found to be 230 distinct varieties of crystal symmetry.

A compound lattice that contains body-, face-, or end-centred points can always be regarded as a *simple* lattice with a smaller unit cell. Thus, the body-centred tetragonal lattice is a special case of the triclinic lattice (Fig. 120). The centred lattices describe most readily the higher symmetry.

### Cohesive forces in crystals

Although the sub-division of valency bonds into types is not rigid, four main types are distinguishable in solids. When all the bonds are of the same type the solid is *homodesmic*.

TABLE 18

HOMODESMIC SOLIDS

Type of binding	Examples
(i) Ionic	Rock salt, fluorite
(ii) Homopolar	Diamond, zinc blende
(iii) Metallic	Copper, manganese
(iv) Van der Waals	Argon

Should the bonds be all of equal strength the solid is *isodesmic*, otherwise it is *anisodesmic*.

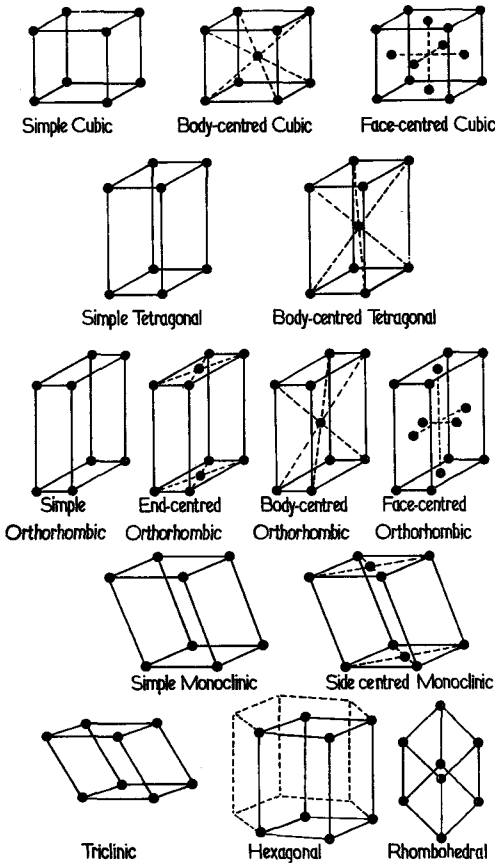


Fig. 119. Bravais lattices.

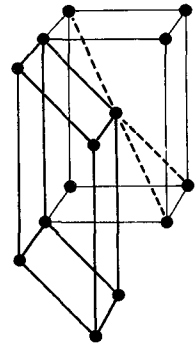


Fig. 120. Relation of body-centred tetragonal to triclinic.

*Heterodesmic* solids contain more than one type of bond; two examples are given:

- (i) Solid carbon dioxide has homopolar bonds in the individual molecules; but the molecules are held to one another by Van der Waals' forces.
- (ii) Antimony consists of puckered sheets of covalently bound atoms with metallic binding holding the sheets together.

### Ionic binding

Monatomic ions may be considered as incompressible spheres which are usually only slightly polarised by the ions of opposite charge around them.

There are two conditions for an arrangement of ions in space to have minimum potential energy:

- (i) The larger ions (usually the anions) round a smaller ion of opposite sign must all 'touch' it.
- (ii) The co-ordination number of an ion, that is the number of nearest neighbours of opposite sign, must be as large as possible, subject to condition (i) being observed.

The co-ordination numbers 5, 7, 9, 10 and 11 are excluded by geometry if the ionic arrangement is to form a regular spatial pattern; in addition, the co-ordination number 12 is excluded by the requirement that positive and negative charges balance one another. Only 6  $\text{Cl}^-$  ions (1.81 Å) can be accommodated round a  $\text{K}^+$  ion (1.33 Å) so that they all 'touch' the cation; very many more  $\text{K}^+$  ions could be accommodated round the  $\text{Cl}^-$  ion. But electrical neutrality must be achieved, and as the system is stable only when the cation touches all the anions surrounding it, the co-ordination in potassium chloride is 6 : 6. Any single  $\text{K}^+$  ion has as its nearest neighbours 6  $\text{Cl}^-$  ions arranged octahedrally; similarly any  $\text{Cl}^-$  has a corresponding arrangement of  $\text{K}^+$  ions around it (Fig. 121).

The  $\text{Cs}^+$  ion (1.69 Å) can accommodate about it 8  $\text{Cl}^-$  ions and the co-ordination in caesium chloride is 8 : 8 (Fig. 122).

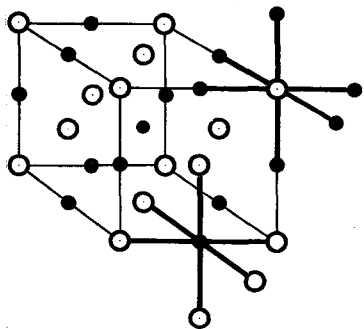


Fig. 121.

KCl lattice showing 6:6 co-ordination.

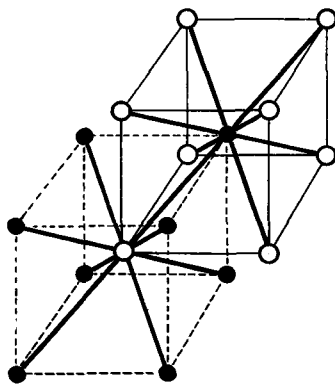


Fig. 122.

CsCl lattice, showing 8:8 co-ordination.

### Radius ratios

The number of anions surrounding the cation in the crystal, the *crystallographic co-ordination number* of the cation, depends on the ratio  $r_c/r_a$ , of

the cationic and anionic radii. The limiting values of  $r_c/r_a$  for various co-ordination numbers are given in Table 19.

TABLE 19  
CORRESPONDENCE BETWEEN  $r_c/r_a$  VALUES, CO-ORDINATION  
NUMBER OF CATION, AND THE ARRANGEMENT OF IONS

$r_c/r_a$	Co-ordination number of cation	Arrangement
1	12	Close packing
1 → 0.73	8	At cube corners
0.73 → 0.41	6	Octahedral
0.41 → 0.22	4	Tetrahedral
In anisodesmic crystals square, triangular and linear arrangements are possible:		
0.73 → 0.41	4	Square
0.22 → 0.16	3	Triangular
0.16	2	Linear

In crystals of a compound  $AB_2$  the co-ordination number of A is twice that of B and the structure is determined by the co-ordination number of the smaller ion. The *radius ratio rule* is clear-cut only with simple ions. Dimorphism is much commoner where complex ions are involved. Even the relatively simple  $CO_3^{2-}$  ion can co-ordinate in different ways without causing any change in the empirical formula of the compound; thus  $CaCO_3$  exists as both the minerals calcite and aragonite. In general, the rule is most likely to break down where large, easily polarised anions are present.

### Strength of ionic binding

As the energy required to separate a pair of ions is approximately proportional to

$$\frac{z_1 z_2}{r_c + r_a}$$

where  $z_1$  and  $z_2$  are the respective charges, the hardness (Table 20) and melting point (Table 21) of crystals with similarly charged ions should vary inversely as the inter-ionic distance. Where the inter-ionic distance is about the same, the relative hardness and melting point become dependent on the ionic charges (Table 22).

TABLE 20  
( $r_c + r_a$ )-VALUES AND HARDNESS OF SOME OXIDES

	MgO	CaO	SrO	BaO
$r_c + r_a$ (Å)	2.05	2.40	2.53	2.75
Hardness (Mohs' scale)	6.5	4.5	3.5	3.2

TABLE 21

 $(r_c + r_a)$ -VALUES AND MELTING POINTS OF THE SODIUM HALIDES

	<i>NaF</i>	<i>NaCl</i>	<i>NaBr</i>	<i>NaI</i>
$r_c + r_a$ (Å)	2.29	2.76	2.90	3.14
M.p. (°C)	988	801	740	660

TABLE 22

INFLUENCE OF IONIC CHARGE ON STRENGTH OF IONIC BINDING

	<i>NaF</i>	<i>CaO</i>
$r_c + r_a$ (Å)	2.29	2.40
$z_1 \times z_2$	1	4
Hardness (Mohs' scale)	3.2	4.5
M.p. (°C)	988	2570

Crystals with strong ionic bonds always have low coefficients of thermal expansion. Though the solids are non-conducting because the electrons are all firmly bound in atomic orbitals, conductance by migration of ions occurs in the fused state. Moreover, ionic bonds are often broken by media of high dielectric constant such as water ( $\epsilon = 78$ ). Binary simple salts, exemplified by NaCl, are generally more easily dissociated in aqueous solution than such compounds as MgO where the interionic attraction is large.

Certain principles are evident in the building up of ionic crystals. These, known as Pauling's rules, are useful even when the ionic picture is not strictly valid and considerable covalent character must be conceded:

- (i) A co-ordinated polyhedron of anions is formed about each cation, the cation-anion distance being determined by the radius sum, and the co-ordination number by the radius ratio.
- (ii) In a stable co-ordination structure, the total number of the valency bonds which reach an anion from all the neighbouring cations is equal to the charge of the anion.
- (iii) The existence of edges, and particularly faces, common to two anion polyhedra decreases the stability of the structure.
- (iv) Cations with a high charge number and a small co-ordination number tend not to share polyhedron elements with one another.
- (v) The environments of all chemically similar anions in a structure tend to be similar.

These rules are particularly valuable in their application to more complicated structures.

### The Jahn-Teller effect in crystals

So far it has been assumed that the field due to a monatomic ion is spherically symmetrical, but for cations which have certain d-electron configurations this is untrue. For instance a regular octahedral arrangement of anions is not possible around the  $\text{Cu}^{2+}$  ( $t_{2g}^6, e_g^3$ ) ion which has a degenerate ground state, with either the  $d_x$  or the  $d_{x^2-y^2}$  orbital containing only one electron. If it is the  $d_{x^2-y^2}$ , then the charge on the Cu nucleus is more shielded along the  $z$ -axis than in the  $x$ - and  $y$ -axial directions. As a result the equilibrium positions of anions in the  $xy$ -plane will be closer to the metal than those on the  $z$ -axis. Consequently, the arrangement of anions round the cation is distorted from the octahedral, even when the radius ratio is favourable for 6 : 6 co-ordination.

Thus CuO has a tetragonal unit cell (p. 192) unlike the monoxides of other transition metals of Period 4 such as MnO and NiO, which have cubic NaCl structures. The lack of distortion in NiO suggests that the  $\text{Ni}^{2+}$  ion exists in the symmetrical high-spin form of the  $t_{2g}^6 e_g^2$  state. The magnetic properties of NiO are in accordance with this electronic configuration (p. 175). But on the other hand PdO has a tetragonal unit cell; the crystal field exerted by the oxygen ions is evidently sufficient to cause spin-pairing of the electrons in the  $e_g$  level of the Period 5 ion. There is actually a square arrangement of oxygen atoms around the Pd (p. 716) as expected for a low-spin  $d^8$  cation (p. 164).

### Homopolar crystals

Unlike ionic structures, where crystallographic co-ordination numbers are determined by the radius ratio rule and the bonds are not directed, homopolar structures have directed bonds. An element in the  $N^{\text{th}}$  group of the Periodic Table can form  $8-N$  bonds per atom and co-ordination numbers are small, usually four or less.

Few crystals are perfectly homopolar. An example is diamond which is homopolar though not purely covalent (*cf.*  $\text{H}_2$  where  $\text{H}^+ - \text{H}^-$  and  $\text{H}^- - \text{H}^+$  both contribute to the bond). In diamond the individual carbon atoms are held tetrahedrally to 4 others by bonds similar to those between the carbon atoms in aliphatic compounds; accordingly the crystal is a truly homopolar, homodesmic solid. Silicon and germanium are similar. Zinc blende, ZnS, has a like character, but the 4 bonds about the individual atoms are formed from 2 electrons derived from the zinc and 6 from the sulphur atoms. The valency electrons tend to be drawn towards the sulphur atoms, conferring some polarity on the bonds. This illustrates the fact that there is no sharp demarc-

ation between homopolar and ionic crystals. Zinc blende would normally be considered covalently bonded—a low co-ordination number usually implies directed bonds—but in this, and indeed in many other instances, it is convenient to regard the structure formally as being composed of  $Zn^{2+}$  and  $S^{2-}$  ions, the latter distorted, or polarised, in the field of the former (p. 106). Such an approach is possible because in solids the exigencies of packing and electrical neutrality are determining factors. Of course, the greater the divergence from ionic character the greater is the departure from Pauling's first rule; bond lengths are shortened and co-ordination numbers reduced below those required by the radius rule.

### Metals

The true metals comprise those of Gps. IA and IIA, the transitional elements and the coinage metals: they are designated by T (p. 132). Atoms of a T metal are closely packed and without directional bonds. The metals are relatively soft and malleable since the atoms glide easily over one another.

B sub-group metals are rather more covalent in character, those of Gps IIB and IIIB being nearer true metals than Se, Te, As, Sb and Bi. Zinc and cadmium, for example, have distorted, close-packed hexagonal arrangements of atoms in which the axial ratios are about 1.87 instead of the ideal 1.63 (p. 745). Aluminium and indium have approximately face-centred cubic lattices, and thallium has a close-packed hexagonal one. In Gp. IVB, white tin possesses a structural character between that of lead and silicon; its co-ordination number is 6. Grey tin has the diamond structure and a co-ordination number of 4. Lead is face-centred cubic and behaves as a true metal. The atoms present in the solid may contain the  $6s^2$  inert pairs, which gives it the character of a Gp. IIA metal.

### Substitutional alloys

These are obtained by starting with metal X and gradually replacing its atoms with those of metal Y. Two true metals yield a TT alloy. But TB and BB alloys are also possible.

A typical TT combination is formed by silver and gold, both of which have a face-centred cubic lattice and atoms of very nearly the same size (Au, 1.442 Å; Ag, 1.432 Å). They give a continuous series of solid solutions with random distribution of gold and silver atoms. An alloy of this type is possible when the radius ratio of the atoms does not exceed 1.14 and their charge numbers are alike.



Copper has a radius of 1.288 Å. At a high temperature, gold forms a continuous solid solution with it. Rapid quenching retains this condition, but slow annealing allows the atoms to segregate. At a composition Au:Cu = 1:1, alternate sheets of gold and copper appear and the symmetry is converted from cubic to tetragonal. With Au:Cu = 1:3, the ordered form is cubic, Au being at the cube corners and Cu at the face centres (Fig. 123).

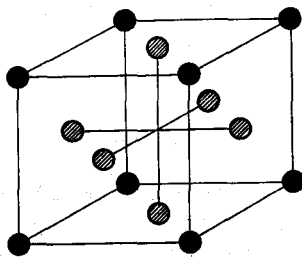


Fig. 123. Alloy with Au:Cu ratio 1:3.

The disordered form of this alloy of gold and copper is brittle; the ordered form is more malleable, more ductile, and a better conductor. At the *order-disorder transition temperature* the specific heat increases markedly, thermal energy being necessary to disorder the atoms and increase the entropy.

#### *Electron compounds*

An example of a TB alloy is found in the system silver-cadmium. Silver has a face-centred cubic structure, cadmium an elongated close-packed hexagonal one like zinc (p. 197). Five phases occur. The random  $\alpha$ -phase contains less than 42% Cd. At about this composition a  $\beta$ -phase begins to be formed, and at 50% Cd the structure is ordered body-centred cubic. At 57% Cd a complicated  $\gamma$ -phase appears, and from 70–82% Cd a close-packed hexagonal  $\epsilon$ -phase. Finally, at high Cd concentrations a  $\eta$ -phase is formed which is a solid solution of silver in cadmium in close-packed hexagonal arrangement. Many other TB systems show a similar sequence of intermediate phases. In the zinc, aluminium and tin alloys of copper,  $\beta$ -,  $\gamma$ - and  $\epsilon$ -phases appear at certain compositions (Table 23). Hume-Rothery (1926) pointed out that the appearance of a particular phase depended on the ratio of valency electrons to atoms (Table 24). For a  $\beta$ -phase it is  $3/2$ .

For a  $\gamma$ -phase the ratio is  $21/13$  and for an  $\epsilon$ -phase  $7/4$ . The fractions are most easily remembered as  $\beta$   $21/14$ ,  $\gamma$   $21/13$  and  $\epsilon$   $21/12$ . The phases themselves are sometimes referred to as *electron compounds*.

TABLE 23  
COMPOSITION AND PHASE OF SOME ALLOYS

$\beta$	$\gamma$	$\epsilon$
CuZn	$\text{Cu}_5\text{Zn}_8$	$\text{CuZn}_3$
$\text{Cu}_3\text{Al}$	$\text{Cu}_9\text{Al}_4$	$\text{Cu}_5\text{Al}_2$
$\text{Cu}_5\text{Sn}$	$\text{Cu}_{31}\text{Sn}_8$	$\text{Cu}_5\text{Sn}$

TABLE 24  
RATIO OF VALENCY ELECTRONS TO ATOMS FOR SOME ALLOYS

Cu (1) + Zn (2)	3/2
3Cu (1) + Al (3)	6/4
5Cu (1) + Sn (4)	9/6

An alloy of a T metal with a B element of Gps. VB and VIB often has intermediate phases quite different from those of the constituent elements. They frequently have structures like NiAs (p. 202); examples are the arsenides, antimonides, bismuthides, sulphides, selenides and tellurides of many T metals. The binding in these is partly covalent and partly ionic.

### Interstitial alloys

The hydrides, borides, carbides and nitrides of the transitional elements have metallic properties. Only atoms with small covalent radii are capable of occupying the interstices in relatively close-packed arrangements:

H	B	C	N
0.37	0.82	0.77	0.75 Å

These interstitial alloys are of great technical importance; for instance all steels are interstitial alloys of carbon and iron.

When the radius ratio is less than 0.59 the alloy is 'normal' and the *metal—interstitial atom* arrangement is face-centred cubic, close-packed hexagonal or body-centred cubic. The 'complex' interstitial alloys have a radius ratio greater than 0.59 and are less stable. Carbon and nitrogen always occupy octahedral holes in interstitial alloys; hydrogen always occupies the smaller tetrahedral interstices. In face-centred cubic and close-packed

hexagonal lattices there are as many octahedral holes as there are metal atoms and twice as many tetrahedral holes.

*Austenite*, an iron-carbon phase in steel, has a face-centred cubic arrangement of iron atoms and a maximum carbon content corresponding to the filling, quite at random, of one twelfth of the octahedral interstices. Rapid quenching of austenitic steel, which is stable at high temperature, causes the iron atom arrangement to change to body-centred, but the interstitial carbon atoms hold the metal atoms apart and allow them to assume a tetragonal, rather than a cubic, configuration. This supersaturated solid solution is *martensite*. Tempering precipitates the carbon as an  $\epsilon$ -iron carbide with a close-packed hexagonal structure at low temperatures, but at higher temperatures *cementite*,  $\text{Fe}_3\text{C}$ , is produced. During these last transformations the iron positions alter only slightly, the changes being due to the diffusion and re-arrangement of the carbon atoms.

The nature of the valency forces in interstitial alloys has been variously explained. It is clear that such alloys are restricted to metals with incompletely filled d orbitals. Electrons may be donated by the interstitial atoms, leaving these as positive ions and resulting in binding of a metallic nature.

### Clathrates

When quinol is crystallised from aqueous solution in the presence of argon at 40 atmospheres, the solid has the properties of quinol but contains argon which is set free when the quinol is melted or dissolved. The gas molecule is trapped inside a cage of hydrogen-bonded quinol molecules. Clathrates are formed by krypton, xenon and such gases as  $\text{HCl}$ ,  $\text{HBr}$ ,  $\text{SO}_2$  and  $\text{CO}_2$  with quinol, the general formula being  $[\text{C}_6\text{H}_4(\text{OH})_2]_3\text{X}$ , where X represents a molecule of the gas.

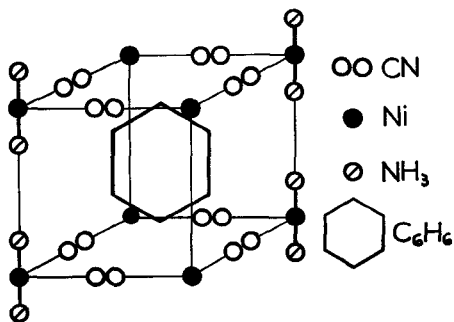


Fig. 124. Unit cell of benzene ammino-nickel cyanide clathrate.

An ammoniacal solution of nickel cyanide produces a pale mauve clathrate when shaken vigorously with benzene. The formula is  $\text{Ni}(\text{CN})_2 \cdot \text{NH}_3 \cdot \text{C}_6\text{H}_6$  and the structure as shown in Fig. 124.

### AB structures

There are three principal types among isodesmic crystals of this empirical formula:

- (i) 8:8 co-ordination as in caesium chloride (p. 193);  
e.g. CsBr, CsI, RbF, TlCl, TlBr, TlI,  $\text{NH}_4\text{Cl}$ ,  $\text{NH}_4\text{Br}$ , AgLi, AlFe.
- (ii) 6:6 co-ordination as in rock-salt (p. 104);  
e.g. Li, Na and K halides,  $\text{NH}_4\text{I}$ , RbCl, RbBr, RbI, the oxides MgO, CaO, SrO, BaO, CaO, MnO and NiO, and the compounds LaSb and CeBi.
- (iii) 4:4 co-ordination as in zinc blende (Z) and wurtzite (W) (p. 202);  
e.g. (Z) AgI, AlSb, BeS, BeSe, CSi, CdSe, CuBr, HgS;  
(W) AgI, BeO, CdS,  $\text{NH}_4\text{F}$ , ZnO, MgTe.

Zinc forms a bivalent ion with an 18-electron structure and a moderately small radius (0.74 Å). The large  $\text{S}^{2-}$  ion (1.84 Å) is considerably polarised by it and the two forms of ZnS are predominantly homopolar, since both atoms can adopt  $\text{sp}^3$  hybridisation and pool their valence electrons. Blende is cubic (Fig. 125), wurtzite hexagonal (Fig. 126), there being an average of 4 electrons per atom for bond formation as in diamond. Homopolar compounds of this type are formed by many pairs of elements whose valency electrons total 8. They are called *adamantine compounds* and have either a blende or wurtzite structure (see Table 25).

TABLE 25

EXAMPLES OF ADAMANTINE COMPOUNDS

Formulae	Valency electrons	Atomic numbers	Inter-atomic distances
CuBr (Z)	1 + 7 = 8	29 + 35 = 64	2.46 Å
ZnSe (Z)	2 + 6 = 8	30 + 34 = 64	2.45 Å
GaAs (Z)	3 + 5 = 8	31 + 33 = 64	2.44 Å
GeGe (Z)	4 + 4 = 8	32 + 32 = 64	2.46 Å

The *Grimm-Sommerfeld rule* states that if the sum of the atomic numbers is constant and the number of valency electrons is constant the inter-atomic distances are constant.

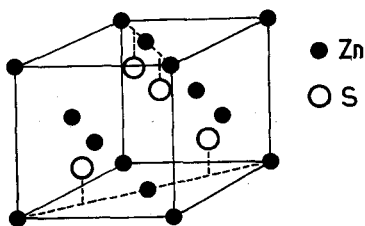


Fig. 125. Cubic lattice of zinc blende (ZnS).

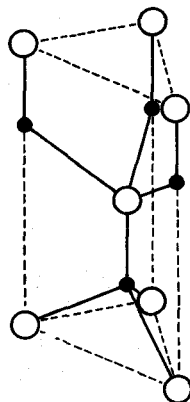


Fig. 126. Hexagonal lattice of wurtzite (ZnS).

The non-adamantine lattice of nickel arsenide, NiAs, is another common AB structure (Fig. 127); it is also displayed by FeS, FeSe, CoS, CoSe, CoTe, NiS, NiSe, NiTe, NiSb, MnSb, CoSb. Each metal atom is surrounded by a slightly distorted octahedron of six Gp. VB or Gp. VIB atoms, which themselves form nearly regular tetrahedra without metal atoms, the structure being anisodesmic.

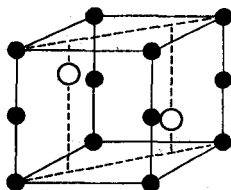


Fig. 127. Unit cell of nickel arsenide, black circles Ni (hexagonal system).

Symmetry in a crystal may be affected by some metal ions tending to form low-level excited states with asymmetrical electron distributions. Examples among AB compounds are HgO and PbO.

Thus the structure of HgO is quite different from that of ZnO and CaO. There are two short, collinear Hg-O bonds and two weaker bonds perpendicular to them. The lower symmetry can be explained in terms of electronic-promotion energies. For  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$  the promotion  $(n-1)d^{10} \rightarrow (n-1)d^9ns^1$  requires about 10 eV, but for  $\text{Hg}^{2+}$  only 5.3 eV is needed.

Linear complexes employing  $sd$  hybrid orbitals in bond formation are very common among  $Hg^{II}$  compounds, whereas  $Zn^{II}$  and  $Cd^{II}$  usually occur in highly symmetrical arrangements with metal ion co-ordination numbers 4 or 6.

Another type of metal ion which normally has a distorted co-ordination sphere in a crystal is the 'inert pair' type with  $ns^2$  ground state. In the  $Pb^{2+}$  ion, for example, there is a low-lying excited state,  $ns^1 np^1$ ; so that in  $PbO$ , the ion is best described as 3-co-ordinated, being based on a tetrahedral arrangement with one missing corner, and having a rather indefinite number of next nearest neighbours.

### $AB_2$ structures

Four types of  $AB_2$  structure are exemplified below.

(i) The fluorite structure shows 8 : 4 co-ordination; every  $Ca^{2+}$  ion being surrounded by eight  $F^-$  ions arranged at the corners of a cube and every  $F^-$  by four  $Ca^{2+}$  arranged tetrahedrally. It is effectively the  $CsCl$  structure with the alternate diagonal pairs missing (Fig. 128). Other compounds with the fluorite lattice are  $SrF_2$ ,  $BaF_2$ ,  $SrCl_2$ ,  $CdF_2$ ,  $PbF_2$ ,  $ThO_2$ ,  $Mg_2Sn$  and  $Al_2Cu$ .

The related antifluorite structure, exemplified by the monoxides and sulphides of  $Na$ ,  $K$  and  $Rb$  (but not  $Cs$ ), has every anion surrounded by eight cations in an arrangement which is the reverse of the  $CaF_2$  lattice which is shown in Fig. 128.

(ii) In rutile, a form of  $TiO_2$ , the co-ordination is 6 : 3, every  $Ti$  being surrounded by six  $O$  atoms, arranged roughly octahedrally, and each  $O$

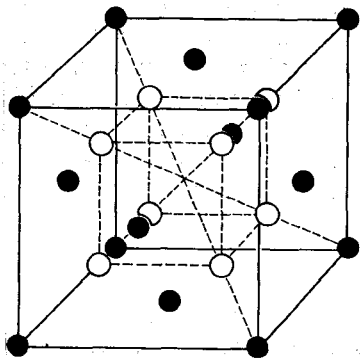


Fig. 128. Fluorite lattice, black circles  $Ca$ .

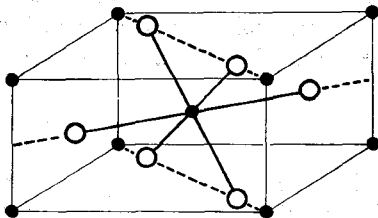


Fig. 129. Rutile structure, black circles  $Ti$ .

by three Ti atoms. The unit cell is tetragonal (Fig. 129). Other substances with this unit cell structure are  $\text{ZnF}_2$ ,  $\text{MnF}_2$ ,  $\text{CoF}_2$ ,  $\text{SnO}_2$ ,  $\text{TeO}_2$ ,  $\text{MnO}_2$ .

Copper(II) fluoride has a distorted rutile structure in which there are two  $\text{F}^-$  ions at 2.27 Å and four at 1.93 Å from the  $\text{Cu}^{2+}$  ion. This is typical of the Jahn-Teller distortion expected for a  $d^9$  ion. But when the metal ion has 5, 6, 7, 8 or 10 d electrons, its difluoride has an essentially undistorted structure.

(iii) Cristobalite, a form of  $\text{SiO}_2$ , shows 4 : 2 co-ordination (Fig. 130).

(iv) Cadmium iodide,  $\text{CdI}_2$ , has a typical layer lattice; the unit cell is hexagonal (Fig. 131).

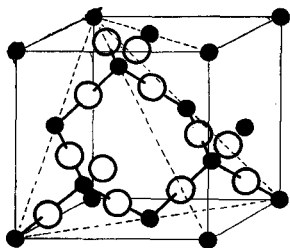


Fig. 130.  $\beta$ -Cristobalite, showing 4 : 2 co-ordination, black circles Si (incomplete unit cell).

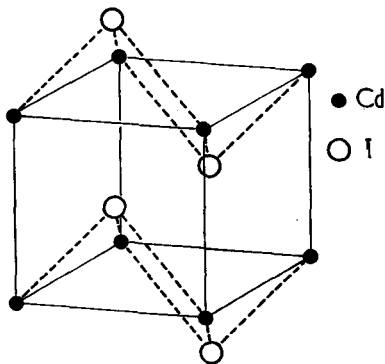


Fig. 131  
The layer lattice of cadmium iodide.

Unlike the truly ionic  $\text{CdF}_2$  (fluorite structure), the iodide forms electrically neutral layers of considerable extent. The force between the layers is small (Van der Waals) and the crystal easily cleaves into parallel sheets. Layer lattices are commonly formed by the iodides and bromides of bivalent metals and even by the chlorides of certain metals with very small cations. This results from polarisation of the anions. The same effect is exhibited by most hydroxides of the type  $\text{M}(\text{OH})_2$ , but in these the two-dimensional, giant molecules are held together by the rather stronger forces between  $\text{OH}^-$  ions of adjacent layers—the so-called hydroxyl bonds.

### $\text{AB}_3$ structures

The very simple  $\text{ReO}_3$  structure (p. 683) is rather uncommon. None of the trioxides of Gp. VI metals has quite such a simple structure, evidently because the  $\text{M}^{6+}$  cations are too small for perfect octahedral co-ordination

by oxygen ions. Of these trioxides,  $\text{WO}_3$  has an almost regular  $\text{ReO}_3$  structure but  $\text{MoO}_3$  is distorted; it has one oxygen further from the Mo than the other five thus making what is effectively a square pyramidal arrangement of oxygens round the molybdenum. In  $\text{CrO}_3$  there are chains  $-\text{CrO}_2-\text{O}-\text{CrO}_2-\text{O}-$ , with tetrahedral co-ordination around the chromium ions but with the oxygen ions in neighbouring chains completing very distorted octahedra. Many trifluorides, for instance  $\text{AlF}_3$ ,  $\text{ScF}_3$  and  $\text{FeF}_3$ , are similar to  $\text{ReO}_3$ , but the co-ordination in them is rarely perfectly octahedral; the terpositive cations are often just too small to fill the octahedral space completely.

Manganese(III) fluoride is an interesting example of Jahn-Teller distortion: in it there are three different Mn-F distances (Fig. 132). The magnetic

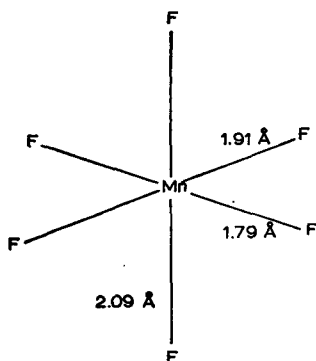


Fig. 132. Mn-F distances in  $\text{MnF}_3$  crystal.

moment of 4.9 Bohr magnetons implies that  $\text{MnF}_3$  has four unpaired d electrons in the  $\text{Mn}^{3+}$ ; three of these are in  $t_{2g}$  orbitals and the fourth is possibly in the  $d_{z^2}$ . This arrangement accounts for the long bonds on the z-axis (vertical) but not for the unequal Mn-F distances along x- and y-axes. However, neighbouring  $\text{MnF}_6$  arrangements are oriented in the crystal so that a fluoride ion, common to both, is at either 1.91 Å from each  $\text{Mn}^{3+}$  ion or at 2.09 Å from one and 1.79 Å from the next  $\text{Mn}^{3+}$  ion, thus allowing close-packing of distorted octahedra. It is the packing of the anions in the crystal, in addition to Jahn-Teller distortion, that determines the symmetry.

Trichlorides, tribromides and triiodides usually have layer lattices (p. 204).

### Complex ions in crystals

Solids containing complex ions often have quite simple structures: for



example  $K_2PtCl_6$  consists of  $K^+$  ions and octahedral  $PtCl_6^{2-}$  ions in which the chlorine atoms are bound covalently to the platinum. The structure is that of fluorite (Fig. 128) with the complex ions occupying places in the cubic lattice corresponding to those of the  $Ca^{2+}$  ions, and the  $K^+$  ions places corresponding to the  $F^-$  ions (Fig. 133).

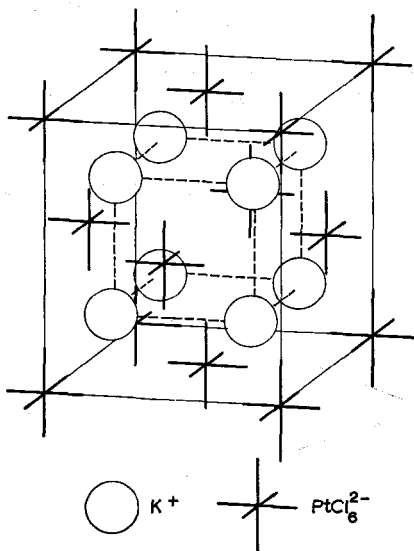


Fig. 133. Potassium chloroplatinate lattice.

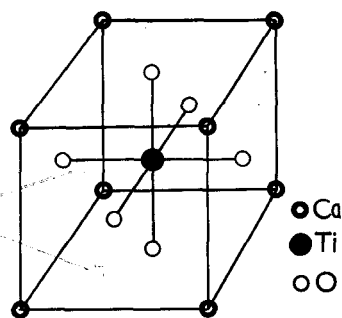


Fig. 134. Perovskite structure.

### Perovskites

Not all ternary compounds contain complex ions. Many with the empirical formula  $ABC_3$  have the cubic perovskite ( $CaTiO_3$ ) structure (Fig. 134). Examples are  $CaZrO_3$ ,  $LaAlO_3$ , and  $KMgF_3$ . The charges on the ions are not important provided the packing is close and the electrical neutrality is maintained. The larger cation occupies the  $Ca^{2+}$  position in all compounds of this structure:



Particularly interesting perovskite structures are the tungsten bronzes. The ideal composition is  $NaWO_3$  (Fig. 135), the charge-type being  $(1 + 5)^+ 6^-$ , as shown above. However, the compound can be crystallised with varying deficiencies of  $Na^+$ , provided that, for every missing  $Na^+$  ion, a 5-positive

tungsten ion becomes 6-positive. These sodium-deficient materials are known as *incomplete lattice* defect structures. When the deficiency is complete the limiting formula of  $WO_3$  is reached.

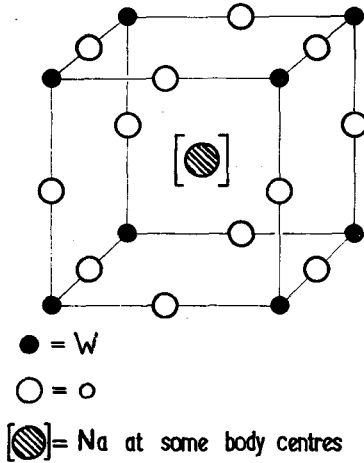


Fig. 135. Tungsten bronze structure.

### Spinel

The spinels are minerals with the empirical formula  $AB_2O_4$ . There are 2 : 3 spinels containing  $A^{2+}$  and  $B^{3+}$  ions, and 4 : 2 spinels containing  $A^{4+}$  and  $B^{2+}$  ions. All spinel structures have a face-centred cubic array of anions.

In a *normal* spinel the  $A^{2+}$  cations occupy one-eighth of the tetrahedral interstices (positions where a cation can be surrounded by four anions) and  $B^{3+}$  cations occupy half the octahedral spaces. In an *inversed* spinel such as  $NiFe_2O_4$  all the  $A^{2+}$  and half of the  $B^{3+}$  cations are in octahedral

TABLE 26

SPINEL STRUCTURES

	2 : 3 spinels	4 : 2 spinels
Normal	$MgAl_2O_4$ $MgMn_2O_4$ $Co^{II}(Co^{III})_2O_4$	
Inversed	$Fe^{III}(Fe^{II}Fe^{III})O_4$ $Fe(NiFe)O_4$	$Zn(TiZn)O_4$ $Co(SnCo)O_4$

holes, the other half of the  $B^{3+}$  cations are in tetrahedral holes. These inversed spinels are therefore best represented as  $B(AB)O_4$ ; for instance the above example is  $Fe^{III}(Ni^{II}Fe^{III})O_4$ .

The 4 : 2 spinels all have inversed structures.

The spinels are of great structural interest because they provide an example of co-ordination numbers which have been determined by a factor other than the radius ratio. For instance, the  $Ni^{2+}$  ion ( $d^8$ ) always displaces other ions from octahedral positions; and thus spinels containing it are always inversed. The  $Mn^{3+}$  ion ( $d^3$ ) displaces all other ions except  $Ni^{2+}$  from octahedral positions; hence all its spinels, except  $Mn(NiMn)O_4$ , are normal.

This tendency of  $d^3$  and  $d^8$  ions to occupy octahedral holes has been explained in terms of crystal field theory in the following way. Let us consider a  $d^3$  ion (Fig. 136). In an octahedral crystal field its five degenerate d orbitals are split into three  $t_{2g}$  and two  $e_g$  orbitals (p. 156). The potential

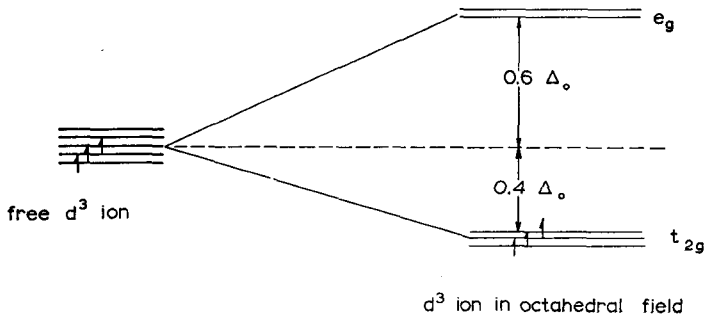


Fig. 136. Crystal field stabilisation of  $d^3$  ion in an octahedral space.

energy is thus  $3 \times 0.4 \Delta_0 (= 1.2 \Delta_0)$  less than it would have been without d-orbital splitting in the field. This fall in potential energy is called the crystal field stabilisation energy. For a  $d^3$  ion in a tetrahedral field the

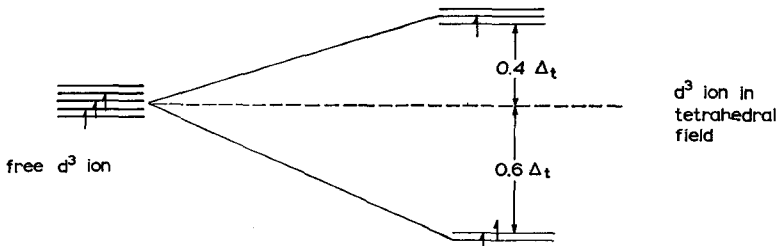


Fig. 137. Crystal field stabilisation of  $d^3$  ion in a tetrahedral space.

crystal field stabilisation energy is only  $0.8 \Delta_t$  (Fig. 137). Two electrons are stabilised ( $1.2 \Delta_t$  energy released) and one raised in energy level ( $0.4 \Delta_t$  energy absorbed). Examples of crystal field stabilisation energies for other  $d^n$  ions are shown in Table 27.

TABLE 27

CRYSTAL FIELD STABILISATION ENERGIES FOR TRANSITION METAL IONS

	<i>Octahedral field</i>	<i>Tetrahedral field</i>
$d^1$ and $d^6$	$0.4\Delta_o$	$0.6\Delta_t$
$d^2$ and $d^7$	$0.8\Delta_o$	$1.2\Delta_t$
$d^3$ and $d^8$	$1.2\Delta_o$	$0.8\Delta_t$
$d^4$ and $d^9$ **	$0.6\Delta_o$	$0.4\Delta_t$
$d^5$ and $d^{10}$	0	0

\* These ions have substantial additional stabilisation because of Jahn-Teller distortion.

As  $\Delta_o$  is about twice  $\Delta_t$ , the crystal field stabilisation is always greater in an octahedral field than in a tetrahedral field; but for  $d^3$  and  $d^8$  ions the effect is particularly large and the ions have a strong tendency to displace others from octahedral interstices.

### Silicates

In silica and the silicates oxygen atoms are arranged tetrahedrally round silicon atoms. These tetrahedra may be

- (i) separate,
- (ii) linked in chains or rings of 2, 3, 4 or 6 units,
- (iii) linked in long single or double chains,
- (iv) linked in sheets,
- (v) joined in 3-dimensional frameworks.

The tetrahedra always share corners, never edges or faces (Pauling's rules p. 195).

Silicates usually contain other oxygen ions besides those forming the tetrahedra. These  $O^{2-}$  anions can be replaced by  $OH^-$  and  $F^-$  provided electrical neutrality is maintained by the replacement of some of the cations by other cations of lower charge. Similarly cations are replaceable, without changing the structure of the silicate, by others of about equivalent size and the same charge, or by different numbers of other cations providing the same net charge; for instance  $Ca^{2+}$  may be replaced by  $2Na^+$ . The cation  $Al^{3+}$  is particularly important, since the ratio  $r_{Al^{3+}}/r_{O^{2-}} \sim 0.43$  is

close to the transition ratio from 4 co-ordination to 6 co-ordination arrangement. Aluminium thus fits into either a tetrahedral group,  $\text{AlO}_4^{5-}$ , or an octahedral group,  $\text{AlO}_6^{9-}$ . The  $\text{AlO}_4^{5-}$  group is roughly the same size as the  $\text{SiO}_4^{4-}$  tetrahedron and can replace it provided electrical neutrality is maintained by an adjustment of positive charge elsewhere in the structure.

In the orthosilicates, separate  $\text{SiO}_4^{4-}$  tetrahedra are linked only by cations. An example is olivine,  $\text{Mg}_2\text{SiO}_4$ , essentially a packing of  $\text{SiO}_4$  tetrahedra and  $\text{MgO}_6$  octahedra. The oxygen-silicon ratio higher than 4 found in some orthosilicates arises from oxygen atoms which are co-ordinated only to the metal atoms; thus, for instance,  $\text{Al}_2\text{SiO}_5$  consists of  $\text{Al}_2\text{O}^{4+}$  ions and  $\text{SiO}_4^{4-}$  tetrahedra (Fig. 138).

Two  $\text{SiO}_4$  tetrahedra may be linked by sharing one corner (Fig. 139), giving a separate  $\text{Si}_2\text{O}_7$  unit. Thorveitite,  $\text{Sc}_2\text{Si}_2\text{O}_7$ , is an example.

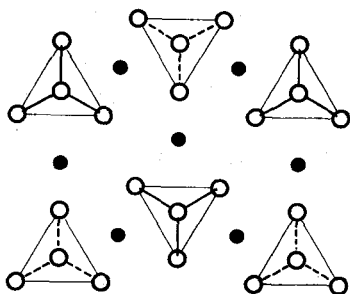


Fig. 138. Arrangement of  $\text{Al}_2\text{O}^{4+}$  ions and  $\text{SiO}_4^{4-}$  tetrahedra in  $\text{Al}_2\text{SiO}_5$ .

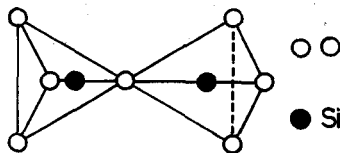


Fig. 139. Two  $\text{SiO}_4$  tetrahedra with one shared corner.

Closed rings of  $\text{SiO}_4$  tetrahedra give an O:Si ratio of 3; found, for example, in beryl,  $\text{Be}_3\text{Al}_2(\text{Si}_6\text{O}_{18})$ . Each Be is co-ordinated by 4 oxygens from 4 different six-membered rings, and each Al by 6 oxygens from 6 different rings. Relatively wide, empty channels pass through the structure (Fig. 140).

Pyroxenes are silicates in which the  $\text{SiO}_4$  tetrahedra share two corners to form long chains. The O:Si ratio again is 3, and diopside,  $\text{CaMg}(\text{SiO}_3)_2$ , is an example (Fig. 141).

Amphiboles consist of double chains, exemplified by tremolite,  $(\text{F},\text{OH})_2\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}$ . The additional  $\text{OH}^-$  and  $\text{F}^-$  anions cannot be linked to Si atoms; they are co-ordinated round the cations. Up to a quarter of the  $\text{SiO}_4$  tetrahedra can be replaced by  $\text{AlO}_4^{5-}$ , electrical neutrality being maintained by the replacement of  $\text{Mg}^{2+}$  by  $\text{Al}^{3+}$ , or the addition of  $\text{Na}^+$  or  $\text{Ca}^{2+}$  cations (Fig. 142).

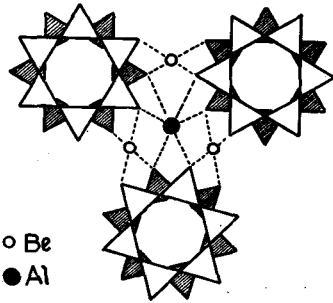


Fig. 140. Structure of beryl, showing channels running through superimposed rings of  $\text{SiO}_4$  tetrahedra.

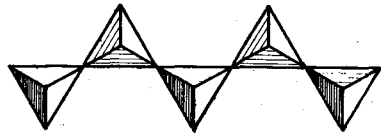


Fig. 141. Arrangement of  $\text{SiO}_4$  tetrahedra in a pyroxene.

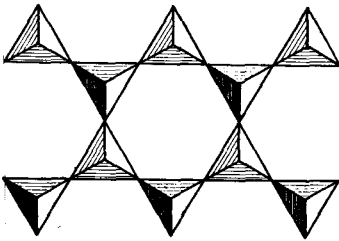


Fig. 142. Double-chain arrangement of  $\text{SiO}_4$  tetrahedra in an amphibole.

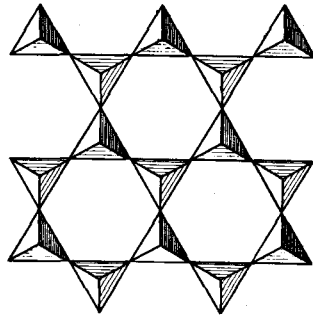


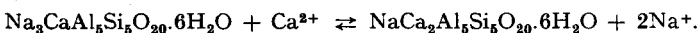
Fig. 143. Part of the sheet of  $\text{SiO}_4$  tetrahedra in a mica.

Micas are made up of sheets of  $\text{SiO}_4$  tetrahedra (Fig. 143), usually with  $\text{AlO}_4$  tetrahedra replacing some of the  $\text{SiO}_4$  units. In muscovite the sheet-composition is  $(\text{Si}_3\text{AlO}_{10})^{5-}$ , one quarter of the Si atoms being replaced by Al atoms. Two such sheets, with their tetrahedral vertices inwards, are linked by  $\text{Al}^{3+}$  ions whose octahedral co-ordination is completed by  $\text{OH}^-$  ions. The double sheets which have in consequence the composition  $[\text{Al}_2\text{AlSi}_3\text{O}_{10}(\text{OH})_2]^-$  are stacked one upon another with sufficient  $\text{K}^+$  ions between them to maintain electrical neutrality. The cleavage of the mica is due to weakness along these layers of  $\text{K}^+$  ions. A wide variety of replacement is possible; thus the 'binding' aluminium may be replaced by magnesium and the 'sandwich' potassium by sodium. The structure of talc is somewhat similar, except that the sheets are electrically neutral. In clays, the sheets are held together by hydroxyl bonds.

Silica, in its various crystalline forms, is a three-dimensional framework of  $\text{SiO}_4$  tetrahedral units which share all their corners. Cristobalite for instance has  $\text{SiO}_4$  tetrahedra arranged as are the atoms in zinc blende; tridymite as are those in wurtzite.

The feldspars have very open structures, shown in Fig. 144 for simplicity two-dimensionally. The cations are accommodated in holes running through the structure. Orthoclase,  $\text{KAlSi}_3\text{O}_8$ , has one quarter of the  $\text{SiO}_4$  tetrahedra replaced by  $\text{AlO}_4$  tetrahedra and, to preserve neutrality, requires one  $\text{K}^+$  ion for every  $\text{Al}^{3+}$  ion present.

Zeolites have an even more open framework. They contain water molecules which can be removed without the framework collapsing. Because cations are easily exchanged, the materials have been used extensively as 'base exchangers' for water-softening:



The solid reverts to the sodium form when treated with brine.

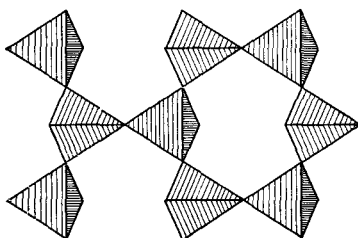


Fig. 144. Linking of  $\text{SiO}_4$  tetrahedra in a feldspar, showing very open structure.

### Water of crystallisation

Salt hydrates hold water molecules as

- (i) co-ordinated water,
- (ii) anion water,
- (iii) lattice water, or
- (iv) zeolite water.

The term water of constitution is a misnomer often applied to the compounds wrongly formulated as  $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$  and  $\text{MgO} \cdot \text{H}_2\text{O}$ . These are actually the true hydroxides  $\text{FeO}(\text{OH})$  and  $\text{MgO}(\text{OH})_2$ , and most of this class of compound have a layer lattice consisting of sheets of  $\text{OH}^-$  and  $\text{O}^{2-}$  ions with cations between them.

*Co-ordinated water.* Many cations form complex ions with four or six molecules of water co-ordinated to the metal:



The metal ion has usually charge number +2 or +3 and, being small, has a high complexing power. Small ions such as  $\text{Be}^{2+}$  (0.31 Å) and  $\text{Mg}^{2+}$  (0.65 Å) give hydrated ions of much greater size.  $\text{Be}(\text{H}_2\text{O})_4^{2+}$  has about the same dimensions as the  $\text{SO}_4^{2-}$  ion and beryllium sulphate tetrahydrate displays, in consequence, a caesium chloride structure. The magnesium compound  $[\text{Mg}(\text{H}_2\text{O})_6]\text{Cl}_2$  has a very slightly distorted fluorite lattice. The great majority of these aquo-complexes are of the high-spin type (p. 161). Cations are frequently, but not always, hydrated to the same extent in solution as in the crystal.

*Anion water.* This is not common, but certainly occurs in  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  and probably in  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ . When copper sulphate pentahydrate is heated the water of the complex ion is lost in two stages giving first  $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$  and then  $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ ; the anion water (Fig. 146) however remains tenaciously held up to 250°.

In  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  the copper atoms have the environment shown in Fig. 145. The fifth water molecule is hydrogen-bonded to oxygen atoms of neighbouring tetrahedral  $\text{SO}_4^{2-}$  ions (Fig. 146).

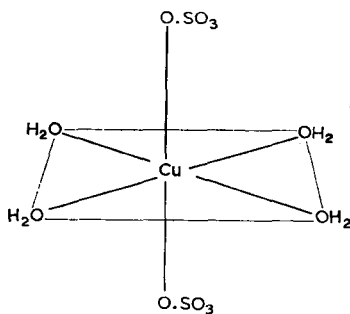


Fig. 145. Immediate environment of  $\text{Cu}^{2+}$  ion in crystal of copper sulphate pentahydrate.

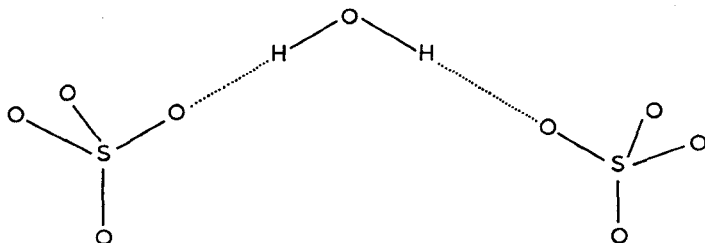


Fig. 146. Hydrogen-bonding of  $\text{SO}_4^{2-}$  tetrahedra by water molecule in  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ .



The water molecule appears to behave in some crystals very much as it does in ice (p. 289), attaching itself to other molecules by approximately tetrahedrally disposed hydrogen bonds provided atoms of sufficiently high electronegativity are present (Fig. 147). It is attached to F or O atoms in various ways; Fig. 148(b) shows the one employed in crystalline  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ . In some instances the water molecule is attached directly to both anion and cation (Fig. 149).

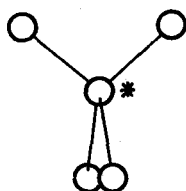
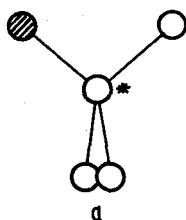
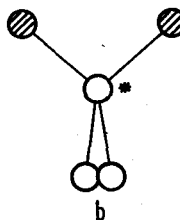


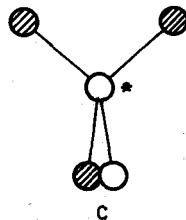
Fig. 147.



d



b



c

Fig. 148.

Fig. 147. Environment of a water molecule (\*) in ice.

Fig. 148. Environment of water molecule (\*) attached to oxygen atoms of anions (Shaded circles) and also to other water molecules.

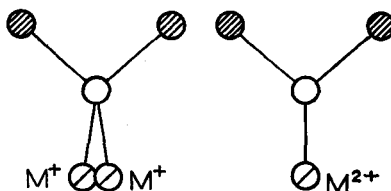


Fig. 149. Water molecules attached to both anions (shaded circles) and cations (circles with bar).

*Lattice water.* In some crystals, water molecules occupy definite lattice positions but are not associated directly with either anion or cation. In the alums six of the water molecules are co-ordinated round the  $3+$  cation and the other six are arranged at a much greater distance about the unipositive cation.

*Zeolite water.* This is the water found between the layers of a crystal lattice and in the interstices. It cannot be removed stepwise as can the water from  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ . Moreover, the lattice is only slightly affected by its removal.

### Defect structures: Non-stoichiometric compounds

Imperfections in crystal lattices are very often present; this is because the state of minimum potential is realised only at very low temperatures. Above these temperatures equilibrium in the structure is attained only with the displacement of atoms (or ions) from lattice sites. In stoichiometric ionic crystals two types of defect arise from thermal causes. A *Schottky defect* is due to the displacement of a cation and an anion. By leaving their respective sites unoccupied this produces two defects, but because the displacement involves a pair of ions the stoichiometry and electric neutrality are maintained. A *Frenkel defect* is due to the displacement of a cation or an anion to an interstitial position, thereby leaving a vacant lattice site. But the stoichiometry and electric neutrality are maintained as before. Both Schottky and Frenkel defects are also thermally produced in non-stoichiometric compounds.

However, non-stoichiometric compounds have in addition other kinds of lattice defects. These take the form of either cations or anions which are present in the crystal in a proportion over the stoichiometric ratio. When the proportion of cations is too high, electric neutrality is maintained by electrons trapped in the lattice and, when the proportion of anions is too high, by the loss of electrons from neighbouring cations whereby their positive charge is raised. Examples of compounds with extra cations are sodium chloride with  $\text{Na}^+$  ions and zinc oxide with  $\text{Zn}^{2+}$  ions above the stoichiometric proportion, and examples of compounds with extra anions are uranium dioxide with  $\text{O}^{2-}$  ions and iron(II) sulphide with  $\text{S}^{2-}$  ions above those required by the respective formulae.

Non-stoichiometry is very common in oxides and sulphides but it is also found in many other compounds. Silver bromide has a perfect face-centred cubic arrangement of  $\text{Br}^-$  ions but the  $\text{Ag}^+$  ions are partly in interstitial positions. The effect is even more marked in silver iodide. In addition to a  $\gamma$ -(blende) form and a  $\beta$ -(wurtzite) form it has an  $\alpha$ -form stable between  $146^\circ$  and  $552^\circ$  (the m.p.). In this the iodide ions are arranged in a body-centred cubic lattice but the  $\text{Ag}^+$  ions form what may be called an interstitial fluid, being apparently free to move through the rigid network of  $\text{I}^-$  ions. The variation of conductance with temperature in silver iodide is particularly interesting. As Table 28 shows there is a very large increase in conductance at the transition point,  $146^\circ$ , and a slight decrease when the fusion temperature is exceeded. Evidently  $\text{Ag}^+$  ions can move slightly more easily through the lattice of  $\text{I}^-$  ions than through the melt.

Solids in which different kinds of atoms occupy structurally equivalent sites have also defect structures. Thus mixed crystals, say of sodium and

TABLE 28

TEMPERATURE DEPENDENCE OF SP. CONDUCTANCE OF AgI ( $\text{ohm}^{-1} \text{cm}^{-1}$ )

Temp. ( $^{\circ}\text{C}$ )	143	146	540	560
Sp. conductance	0.00035	1.3	2.6	2.4

potassium chlorides (Fig. 150), are examples of defect lattices of this kind. Lithium titanate,  $\text{Li}_2\text{TiO}_3$ , has a rock-salt structure in which cation sites are occupied at random by  $\text{Li}^+$  and  $\text{Ti}^{4+}$ . It forms a continuous series of solid solutions with magnesium oxide— $\text{Li}^+$  (0.60 Å),  $\text{Ti}^{4+}$  (0.68 Å) and  $\text{Mg}^{2+}$  (0.65 Å) are ions of about the same size. Substitutional alloys (p. 198) are other examples of this sort of defect structure.

Non-stoichiometry in solids is a very general phenomenon—indeed, stoichiometry is exceptional—and it has been shown thermodynamically that a condensed phase, even at equilibrium, is not of unique composition except at its singular points (m.p., etc.), and at a temperature near absolute zero. A typical Daltonide, *i.e.* stoichiometric, compound like sodium chloride when in equilibrium with sodium is deep blue, but when in equilibrium with chlorine is colourless. And, although the material remains homogeneous throughout these changes, the alteration in composition is great enough to be detected analytically.

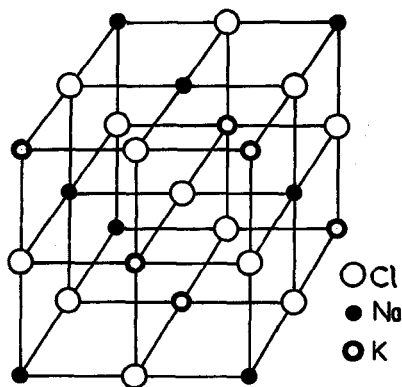


Fig. 150. Defect lattice in mixed crystal of sodium and potassium chlorides.

As regards nomenclature, it is usual to designate a non-stoichiometrical phase by a formula; for instance, the NaCl phase region, the FeO phase region, or the  $\text{UO}_2$  phase region. And this is to be taken as indicating

compositions near the values implied by these formulae. Indeed, stoichiometric FeO does not exist in an equilibrium system, and an attempt to produce it results in disproportionation to iron and an oxide richer in oxygen. Properties in a non-stoichiometric phase may change remarkably; thus for a series of cerium sulphides for which the lattice constants and structure are the same, the colour varies from black to red. The first material is almost a metallic conductor, which can be heated rapidly without fracture, and which is a reducing agent. The second has the properties of a ceramic and readily fractures on rapid heating or cooling; it is an insulator and can act as an oxidising agent.

Non-stoichiometric solids are now extensively used in industry as transistor and maser materials, and great developments in their use are taking place in science and technology. The manufacture of these remarkable phases frequently calls for inorganic substances of the highest purity and strictly controlled methods of production.

## CRYSTAL GROWTH

### Natural and Induced Atomic Displacements

An increased precision in the location of atoms in the crystal lattice has shown that some irregularity in their position is very common. This in turn has contributed an understanding of the way in which a crystal grows and of the changes brought about in a crystal lattice when it is bombarded by particles from without or when some of its atoms suffer radioactive disintegration within. It will be seen below that these may be matters of very practical concern.

#### Crystal growth through natural atomic displacements

First to recall the nomenclature used in naming the faces of, or planes within, crystals. This is done by *Miller indices* (1839) which are the reciprocals of the intercepts the plane makes with suitably chosen axes. The idea is most easily understood for the cubic system. The plane shaded in Fig. 151 is a 100 plane, the intercepts made on the OA, OB and OC axes by the plane being 1,  $\infty$  and  $\infty$  respectively so that the Miller indices are

$$\frac{1}{1}, \frac{1}{\infty}, \frac{1}{\infty} \text{ which are represented by the figures } 100.$$

The plane shaded in Fig. 152 is a 110 plane, the intercepts on the OA, OB

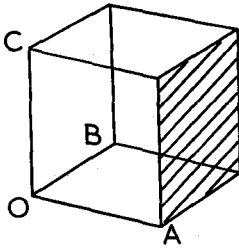


Fig. 151.

100 plane in cubic system.

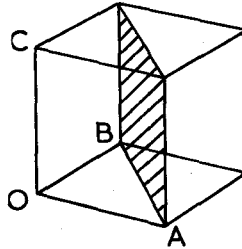


Fig. 152.

110 plane in cubic system.

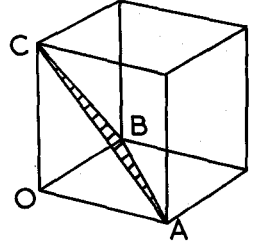


Fig. 153.

111 plane in cubic system.

and OC axes being 1,1 and  $\infty$ ; and that shaded in Fig. 153 is a 111 plane.

Crystal growth from vapour, as in sublimation for example, makes the simplest approach to the subject, and the principles involved apply to the more complicated situation in solutions. Consider the flat 001 surface of a cubic crystal in contact with its vapour and partly covered by an incomplete layer (Fig. 154).

When the vapour pressure is raised by an amount  $\Delta p$  above the vapour-solid equilibrium vapour pressure, the layer grows with a speed proportional to  $\Delta p$  until the surface is covered. But in order to start a new layer a two-dimensional nucleus must be formed (Fig. 155) for which the rate of nucleation has been found to be proportional to  $e^{-A/\Delta p}$ ,  $A$  being a constant.

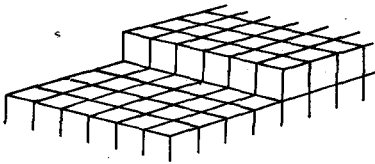


Fig. 154. 001 crystal surface partly covered with another layer.

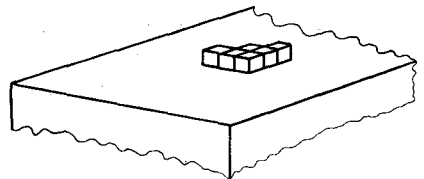


Fig. 155. Nucleus for the start of a new layer.

Clearly the stepwise character of a 110, 101, 011 or 111 surface makes nucleation easy to occur, but these surfaces disappear in the course of their growth leaving 100, 010 and 001 surfaces only (Fig. 116).

For surfaces of low indices such as the 100, the rate of nucleation predicted by the  $e^{-A/\Delta p}$  formula is smaller than the experimental rate by a factor of about  $e^{3,600}$  for low values of  $\Delta p$ . But iodine crystals grow at a measurable rate in iodine vapour when the vapour pressure is only 1.01 times the equilibrium vapour pressure. This great discrepancy between theory and

practice is best explained by assuming the growing crystal surface always to have random imperfections and, indeed, never to have been covered at any time by an unbroken, perfect layer.

Unit displacement of a *dislocation* need not be normal to the dislocation lines and can be parallel to it, giving rise to *screw dislocations* as shown in Fig. 157. When a screw dislocation terminates in the exposed face of a crystal, there is a permanently exposed 'cliff' of atoms; the addition of a further layer to the surface simply perpetuates the conditions and the need for two-dimensional nucleation disappears. The crystal grows up a series of spiral stairways.

At low supersaturations, crystals do not grow unless they contain dislocations, but these must not be too close to one another or growth is inhibited because the surface then approaches a perfect form. Perfection is, of course, impossible according to this theory, and is very unlikely to be realised in practice. This explanation of crystal growth is supported by study of the markings present on crystal faces and by the great discrepancy between the strength deduced theoretically for perfect crystals and the measured strengths of actual crystals; imperfections often make the actual crystals weaker by a factor of 100.

The growth of a crystal in solution probably proceeds similarly to the growth in vapour. In all instances a very high supersaturation (1.5 times) is normally needed to initiate growth.

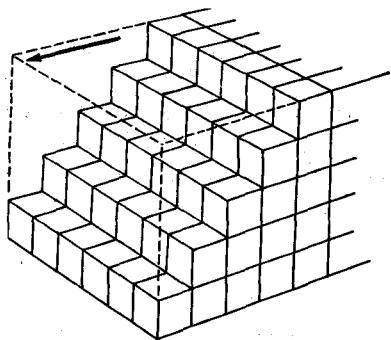


Fig. 156.

Growth of 001 surface from 101 plane.

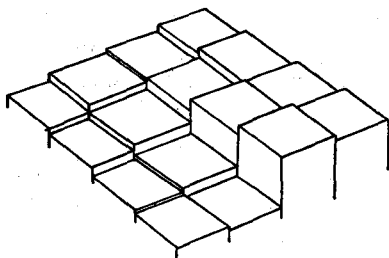


Fig. 157.

Screw dislocation in crystal.

### Artificial displacement of atoms

It is convenient to designate as artificial the atomic displacements brought about in a crystal by internal or external bombardment after its formation.

The displacement of an atom from its normal site creates at the same time a *vacancy* and an *interstitial* atom, individually termed *point defects*. They are caused by collision between the atom and another particle (electron, proton, neutron,  $\alpha$ -particle or recoil nucleus). An electron must have an energy of about 1MeV and an atom must receive 25eV for the impact to be effective. The reception of less energy simply puts the atom into an excited state from which it recovers by losing heat. The displacement of atoms has two results: first, the crystal lattice is strained and distorted, which may change its mechanical properties and even cause its disruption; secondly, energy is stored in the structure and will be released when interstitial atoms return to vacancies.

The effect of the first result is marked in metals, that of the second in graphite. In both instances, a return of the interstitial atoms to vacancies, the interstitial-vacancy pair combination as it is termed, can be achieved by heating the material to the *annealing temperature*.

Damage by external radiation is well illustrated by copper which, on exposure to neutrons, develops point defects on its *dislocation lines*. These are thereby 'locked' so that there is not the normal extension along them under stress, but rather a sudden yielding when the stress reaches the critical value. Briefly, the metal loses ductility. Other examples are provided by mild steel and uranium. The change from ductile to brittle in mild steel is at  $-30^\circ$ , but the transition temperature can be raised by irradiation to  $+40^\circ$ , making mechanical failure of the steel possible at ordinary atmospheric temperatures. Under bombardment, uranium crystals which are anisotropic grow more in the *c* axial direction than any other, with a consequent deterioration in the shape and strength of the piece of metal.

Graphite is another anisotropic material and irradiation causes carbon atoms to vacate the layer planes and lodge between them. As a result the graphite grows in the *c* direction, just as it does when lamellar compounds (p. 380) are formed. In addition much energy is stored in the lattice. When the irradiated graphite is raised to the annealing temperature interstitial-vacancy pair combination takes place; the potential energy is released as heat, and the damage repaired. Indeed, if the irradiation is carried out near the annealing temperature the damage is made good as it is sustained. This means that the graphite in nuclear reactors working at low temperatures accumulates more *Wigner energy* than its counterpart in reactors operated at higher temperatures. Hence a periodic annealing, or releasing of the energy, *Wigner release*, is necessary in the former, but may be unnecessary or infrequently required in the latter. The Windscale incident (1957) drew attention to the need to control the release of Wigner energy if dangerously high temperatures which will cause damage in the reactor and other troubles

are to be avoided. The rate of energy release depends on the temperature; accordingly this must be under control at all stages of the operation.

The displacement of atoms just discussed is due to causes outside the affected crystal. But in the early days of radioactivity the destruction of radium salts by self-irradiation was recognised. Indeed the process occurs more or less in all minerals and compounds containing radioactive atoms. It has been calculated that in 1 mg of a polonium compound  $2 \times 10^{19}$  atoms are knocked off their sites, mainly by recoil nuclei, in a day. As there are only about  $10^{19}$  atoms in this weight of the compound, every atom suffered, on the average, one displacement a day. By X-ray powder photography, with the special precautions necessitated by the polonium activity it is possible to follow the progressive destruction of the crystal structure thus predicted. Films taken of the freshly made compound are good, but when it has been kept a few days they are poor, and after it has been kept a few weeks they show no lines at all. The destruction of the crystal structure by self-radiation is then complete and the material is amorphous.

#### FURTHER READING

- R. W. M. D'EYE AND E. WAIT, *X-Ray Powder Photography in Inorganic Chemistry*, London, Butterworths, 1960.
- A. F. WELLS, *Structural Inorganic Chemistry*, 3rd Ed, Oxford, University Press, 1962.
- J. S. ANDERSON, *Some Basic Problems of Solid-state Chemistry*, Proc. Chem. Soc., (1964) 166.
- K. H. STERN AND E. S. AMIS, *Ionic Size*, Chem. Rev., 59 (1959) 1.
- J. D. DUNITZ AND L. E. ORGEL, *Stereochemistry of Ionic Solids*, in H. J. EMELÉUS AND A. G. SHARPE, *Advances in Inorganic Chemistry and Radiochemistry*, New York, Academic Press, 2 (1960) 1.
- R. E. RICHARDS, *The Location of Hydrogen Atoms in Crystals*, Quart. Rev., 10 (1956) 480.
- A. F. WELLS, *The Crystal Structures of Salt Hydrates and Complex Halides*, Quart. Rev., 8 (1954) 380.
- G. H. NANCOLLAS AND N. PURDIE, *The Kinetics of Crystal Growth*, Quart. Rev., 18 (1964) 1.
- B. K. VAINSHTEIN, *Application of Electron Diffraction to the Study of the Chemical Bond in Crystals*. Quart. Rev., 14 (1960) 105.

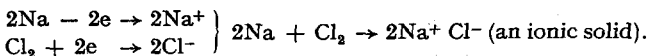


## Chapter 10

# Oxidation-Reduction : Redox Reactions

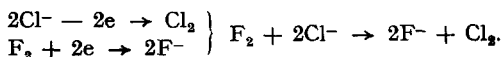
### Definitions

A great many chemical reactions can be broadly classified in terms of oxidation and reduction. Such reactions involve basically a transfer of electrons. Thus when sodium burns in chlorine the overall reaction can be regarded as the result of two processes:



The sodium atom loses an electron easily and is said to be *oxidised* by the chlorine to a sodium ion; and the chlorine atom, which accepts an electron readily is an *oxidising agent*. By accepting an electron the chlorine atom is *reduced* to a chloride ion and the sodium behaves towards the chlorine as a *reducing agent*. Normally the processes occur simultaneously, but in electrolysis they take place at different electrodes. One electrode puts electrons into, the other takes them out of the electrolyte.

Generally speaking the metallic elements are reducing agents and the non-metallic elements, with the exception of the noble gases, oxidising agents. But the terms are relative. Two oxidising agents may compete for electrons as happens when fluorine is bubbled through molten sodium chloride in which are the ions  $\text{Na}^+$  and  $\text{Cl}^-$ ,



Here fluorine, the stronger oxidising agent, takes the electrons and oxidises the chloride ion, which is just the reverse of the conversion of molecular chlorine to the ion by sodium described above. In the second instance the chloride ion acts as the reducing agent and is oxidised to the normal molecule. The  $\text{Cl}$  atom and the  $\text{Cl}^-$  ion are said to form an *oxidation-reduction couple*. The relative strengths of oxidising and reducing agents clearly depend on the free energy changes in the processes. These can be studied under controlled conditions in electric cells.

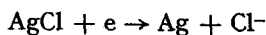
### Electrodes

Although every electrode process is one of either oxidation or reduction, it is convenient to recognise three main types of electrode:

(i) *The Cation Electrode* very readily liberates cations into the solution and is usually a metal, M. The reaction is  $M \rightarrow M^{z+} + ze$ ; the electrons flow away through the external circuit and the cations migrate into solution, the metal being oxidised by the solution. But the direction of the reaction can be reversed by driving electrons in at the electrode (electrolysis), under these conditions the cations approach the electrode, the *cathode*, and there receive electrons and are reduced to metal.

One electrode of this kind is the *hydrogen electrode*, in which pure hydrogen passes over platinised platinum. Such a surface is thermodynamically equivalent to one of gaseous hydrogen, cations being produced according to  $\frac{1}{2}H_2 \rightarrow H^+ + e$ .

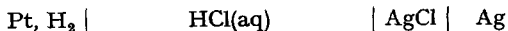
(ii) *The Anion Electrode* very readily liberates anions and is commonly a metal coated with one of its insoluble salts. Silver coated with silver chloride, for example, accepts electrons from the external circuit and produces chlorine anions which migrate into the solution,



Silver ions,  $Ag^+$ , in the solid chloride are reduced to the metal. When the reaction is made to proceed in reverse, electrons are extracted from the electrode to give silver ions,  $Ag - e \rightarrow Ag^+$ . These silver ions combine with chloride ions from the solution to form silver chloride on the surface of the electrode.

(iii) *The Oxidation-Reduction Electrode* is one in which the electrode itself is inert (e.g. pure platinum) and the solution contains ions of variable charge, say iron(II) and iron(III) ions. Supply of electrons to this system causes reduction of the higher charged ion to the lower,  $Fe^{3+} + e \rightarrow Fe^{2+}$ , and removal of electrons causes oxidation of the lower charged ion to the higher,  $Fe^{2+} - e \rightarrow Fe^{3+}$ .

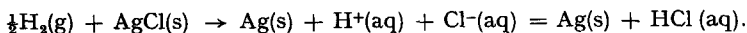
The free energy changes which accompany the flow of electrons always depend on the chemical potentials of the ions taking part in the reactions and hence on the *ionic activities*. The nature of the electrolyte is irrelevant except in so far as it determines these activities. Each electrode in its ambient solution constitutes a *half-cell*. By putting two half-cells together, preventing mixing if the two solutions differ, a complete cell is formed, with a natural direction of operation determined by the free energy changes. It is customary to represent such an arrangement (here the hydrogen electrode on the left and the silver-silver chloride electrode on the right) thus:



The phase boundaries are indicated by vertical lines, the solution is common. (The junction or 'bridge', used when the solutions at each electrode are different, is indicated by a double line). In the above cell the reactions are



and the cell reaction is



The free energy change per Faraday is thus

$$\Delta G_r = \Delta G^\circ + RT \ln Q_a,$$

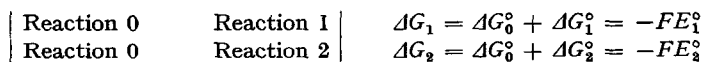
$$\text{and } Q_a = \frac{\{\text{HCl}\} \{\text{Ag}\}}{\{\text{H}_2\}^{\frac{1}{2}} \{\text{AgCl}\}}$$

$\Delta G_r^\circ$  refers to standard conditions and the braces,  $\{\text{HCl}\}$  etc., indicate mean activities. At 25°C and 1 at. pressure, the solids and the gas are in their standard states, irrespective of the HCl concentration, and their activities are therefore both unity. Since  $\Delta G_r = -FE$ , where  $E$  is the cell electromotive force

$$E - E^\circ = -(RT/F) \ln \{\text{HCl}_{(\text{aq})}\},$$

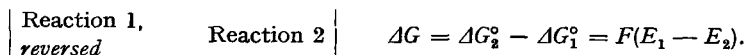
where  $E^\circ$  is the electromotive force with standard concentration and  $\{\text{HCl}_{(\text{aq})}\}$  is the mean ionic activity of  $\text{H}^+$  and  $\text{Cl}^-$  in solution, referred to this standard. For strong electrolytes at extreme dilution the activity would be measured by the molality (unity for a normal solution), but this is not true for working solutions and the concentration of HCl must be increased to 1.18  $M$  to produce a mean ionic activity of unity at 25°.  $E^\circ$  is called the standard electrode potential of the AgCl/Ag electrode relative to the standard hydrogen electrode, usually written  $E^\circ$ .

Now consider any two half-cells, with electrode reactions 1 and 2, combined in turn with a hydrogen half-cell (reaction 0) thus:



Then the difference in standard free energies of the two processes is  $\Delta G_2^\circ - \Delta G_1^\circ$ , and this is seen to be  $F(E_1^\circ - E_2^\circ)$ . Standard free energies of reactions involving ions and electrons, into which many reactions may be conventionally

separated, are therefore measured by their standard electrode potentials. Moreover, when reaction 1 is reversible, a third cell can be set up:



This cell will have a standard electromotive force  $E_{12}$ , say; and, since  $\Delta G^\circ = -FE_{12}$ , it follows that  $E_{12}^\circ = E_2^\circ - E_1^\circ$ . Hence the electromotive force of any cell may therefore be predicted when the standard electrode potentials of the constituent half cells are known.

### Redox potentials

The standard electrode potential for an oxidation-reduction process is called the *standard redox potential* of the pair of ions involved. A table of redox potentials finds immediate application in inorganic chemistry.

TABLE 29  
STANDARD REDOX POTENTIALS (pH 0)

<i>Electrode Reaction</i>	<i>Couple</i>	$E^\circ$ (V)
$F_2 + 2e = 2F^-$	$F_2/F^-$	+2.87
$O_3 + 2H^+ + 2e = H_2O + O_2$	$O_3/O_2$	+2.07
$S_2O_8^{2-} + 2e = 2SO_4^{2-}$	$S_2O_8^{2-}/SO_4^{2-}$	+2.01
$Ag^{2+} + e = Ag^+$	$Ag^{2+}/Ag^+$	+1.98
$Co^{3+} + e = Co^{2+}$	$Co^{3+}/Co^{2+}$	+1.82
$H_2O_2 + 2H^+ + 2e = 2H_2O$	$H_2O_2/H_2O$	+1.77
$MnO_4^- + 4H^+ + 3e = MnO_2 + 2H_2O$	$MnO_4^-/MnO_2$	+1.69
$2HClO + 2H^+ + 2e = Cl_2 + 2H_2O$	$HClO/Cl_2$	+1.63
$Ce^{4+} + e = Ce^{3+}$	$Ce^{4+}/Ce^{3+}$	+1.61
$2HBrO + 2H^+ + 2e = Br_2 + 2H_2O$	$HBrO/Br_2$	+1.59
$MnO_4^- + 8H^+ + 5e = Mn^{2+} + 4H_2O$	$MnO_4^-/Mn^{2+}$	+1.51
$PbO_2 + 4H^+ + 2e = Pb^{2+} + 2H_2O$	$PbO_2/Pb^{2+}$	+1.45
$2HIO + 2H^+ + 2e = I_2 + 2H_2O$	$HIO/I_2$	+1.45
$Cl_2 + 2e = 2Cl^-$	$Cl_2/Cl^-$	+1.36
$Cr_2O_7 + 14H^+ + 6e = 2Cr^{3+} + 7H_2O$	$Cr_2O_7^{2-}/Cr^{3+}$	+1.33
$2HNO_2 + 4H^+ + 4e = N_2O + 3H_2O$	$HNO_2/N_2O$	+1.29
$ClO_2 + H^+ + e = HClO_2$	$ClO_2/HClO_2$	+1.28
$N_2H_5^+ + 3H^+ + 2e = 2NH_4^+$	$N_2H_5^+/NH_4^+$	+1.275
$Tl^{3+} + 2e = Tl^+$	$Tl^{3+}/Tl$	+1.25
$MnO_2 + 4H^+ + 2e = Mn^{2+} + 2H_2O$	$MnO_2/Mn^{2+}$	+1.23
$O_2 + 4H^+ + 4e = 2H_2O$	$O_2/H_2O$	+1.21
$2IO_3^- + 12H^+ + 10e = I_2 + 6H_2O$	$IO_3^-/I_2$	+1.195
$ClO_4^- + 2H^+ + 2e = ClO_2^- + H_2O$	$ClO_4^-/ClO_2^-$	+1.19
$Cu^{2+} + 2CN^- + e = Cu(CN)_2^-$	$Cu^{2+}:CN^-/Cu(CN)_2^-$	+1.12

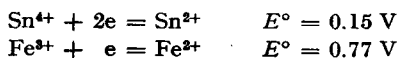
TABLE 29 (continued)

Electrode Reaction	Couple	$E^\circ$ (V)
$\text{N}_2\text{O}_4 + 2\text{H}^+ + 2e = 2\text{HNO}_2$	$\text{N}_2\text{O}_4/\text{HNO}_2$	+1.07
$\text{Br}_2 + 2e = 2\text{Br}^-$	$\text{Br}_2/\text{Br}^-$	+1.065
$\text{HNO}_2 + \text{H}^+ + e = \text{NO} + \text{H}_2\text{O}$	$\text{HNO}_2/\text{NO}$	+1.00
$\text{Pd}^{2+} + 2e = \text{Pd}$	$\text{Pd}^{2+}/\text{Pd}$	+0.99
$\text{NO}_3^- + 3\text{H}^+ + 2e = \text{HNO}_2 + \text{H}_2\text{O}$	$\text{NO}_3^-/\text{HNO}_2$	+0.94
$2\text{Hg}^{2+} + 2e = \text{Hg}_2^{2+}$	$\text{Hg}^{2+}/\text{Hg}_2^{2+}$	+0.92
$\text{Cu}^{2+} + \text{I}^- + e = \text{CuI}$	$\text{Cu}^{2+}:\text{I}/\text{CuI}$	+0.86
$\text{Rh}^{3+} + 3e = \text{Rh}$	$\text{Rh}^{3+}/\text{Rh}$	+0.8
$\text{Ag}^+ + e = \text{Ag}$	$\text{Ag}^+/\text{Ag}$	+0.799
$\text{Hg}_2^{2+} + 2e = 2\text{Hg}$	$\text{Hg}_2^{2+}/\text{Hg}$	+0.79
$\text{Fe}^{3+} + e = \text{Fe}^{2+}$	$\text{Fe}^{3+}/\text{Fe}^{2+}$	+0.77
$\text{O}_2 + 2\text{H}^+ + 2e = \text{H}_2\text{O}_2$	$\text{O}_2/\text{H}_2\text{O}_2$	+0.68
$\text{MnO}_4^- + e = \text{MnO}_4^{2-}$	$\text{MnO}_4^-/\text{MnO}_4^{2-}$	+0.57
$\text{I}_2 + 2e = 2\text{I}^-$	$\text{I}_2/\text{I}^-$	+0.54
$\text{Cu}^+ + e = \text{Cu}$	$\text{Cu}^+/\text{Cu}$	+0.52
$\text{VO}^{2+} + 2\text{H}^+ + e = \text{V}^{3+} + \text{H}_2\text{O}$	$\text{VO}^{2+}/\text{V}^{3+}$	+0.36
$\text{Fe}(\text{CN})_6^{3-} + e = \text{Fe}(\text{CN})_6^{4-}$	$\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$	+0.36
$\text{Cu}^{2+} + 2e = \text{Cu}$	$\text{Cu}^{2+}/\text{Cu}$	+0.34
$\text{SO}_4^{2-} + 4\text{H}^+ + 2e = \text{H}_2\text{SO}_3 + \text{H}_2\text{O}$	$\text{SO}_4^{2-}/\text{H}_2\text{SO}_3$	+0.17
$\text{Cu}^{2+} + e = \text{Cu}^+$	$\text{Cu}^{2+}/\text{Cu}^+$	+0.15
$\text{Sn}^{4+} + 2e = \text{Sn}^{2+}$	$\text{Sn}^{4+}/\text{Sn}^{2+}$	+0.15
$\text{S} + 2\text{H}^+ + 2e = \text{H}_2\text{S}$	$\text{S}/\text{H}_2\text{S}$	+0.14
$\text{TiO}^{2+} + 2\text{H}^+ + e = \text{Ti}^{3+} + \text{H}_2\text{O}$	$\text{TiO}^{2+}, \text{Ti}^{3+}$	+0.1
$\text{P} + 3\text{H}^+ + 3e = \text{PH}_3$	$\text{P}/\text{PH}_3$	+0.06
$\text{UO}_2^{2+} + e = \text{UO}_2^+$	$\text{UO}_2^{2+}/\text{UO}_2^+$	+0.05
$2\text{H}^+ + 2e = \text{H}_2$	$\text{H}^+/\text{H}_2$	0.00
$\text{Pb}^{2+} + 2e = \text{Pb}$	$\text{Pb}^{2+}/\text{Pb}$	-0.126
$\text{Sn}^{2+} + 2e = \text{Sn}$	$\text{Sn}^{2+}/\text{Sn}$	-0.136
$\text{Mo}^{3+} + 3e = \text{Mo}$	$\text{Mo}^{3+}/\text{Mo}$	-0.2
$\text{N}_2 + 5\text{H}^+ + 4e = \text{N}_2\text{H}_5^+$	$\text{N}_2/\text{N}_2\text{H}_5^+$	-0.23
$\text{Ni}^{2+} + 2e = \text{Ni}$	$\text{Ni}^{2+}/\text{Ni}$	-0.25
$\text{V}^{3+} + e = \text{V}^{2+}$	$\text{V}^{3+}/\text{V}^{2+}$	-0.255
$\text{H}_3\text{PO}_4 + 2\text{H}^+ + 2e = \text{H}_3\text{PO}_3 + \text{H}_2\text{O}$	$\text{H}_3\text{PO}_4/\text{H}_3\text{PO}_3$	-0.276
$\text{Co}^{2+} + 2e = \text{Co}$	$\text{Co}^{2+}/\text{Co}$	-0.28
$\text{Tl}^+ + e = \text{Tl}$	$\text{Tl}^+/\text{Tl}$	-0.34
$\text{In}^{3+} + 3e = \text{In}$	$\text{In}^{3+}/\text{In}$	-0.34
$\text{Cd}^{2+} + 2e = \text{Cd}$	$\text{Cd}^{2+}/\text{Cd}$	-0.40
$\text{Cr}^{3+} + e = \text{Cr}^{2+}$	$\text{Cr}^{3+}/\text{Cr}^{2+}$	-0.41
$\text{Fe}^{2+} + 2e = \text{Fe}$	$\text{Fe}^{2+}/\text{Fe}$	-0.44
$\text{Sb} + 3\text{H}^+ + 3e = \text{SbH}_3$	$\text{Sb}/\text{SbH}_3$	-0.51
$\text{Ga}^{3+} + 3e = \text{Ga}$	$\text{Ga}^{3+}/\text{Ga}$	-0.53

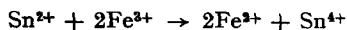
TABLE 29 (continued)

Electrode Reaction		Couple	$E^\circ$ (V)
As + 3H <sup>+</sup> + 3e	= AsH <sub>3</sub>	As/AsH <sub>3</sub>	-0.60
U <sup>4+</sup> + e	= U <sup>3+</sup>	U <sup>4+</sup> /U <sup>3+</sup>	-0.61
Te + 2H <sup>+</sup> + 2e	= H <sub>2</sub> Te	Te/H <sub>2</sub> Te	-0.72
Cr <sup>3+</sup> + 3e	= Cr	Cr <sup>3+</sup> /Cr	-0.74
Zn <sup>2+</sup> + 2e	= Zn	Zn <sup>2+</sup> /Zn	-0.763
TiO <sup>2+</sup> + 2H <sup>+</sup> + 4e	= Ti + H <sub>2</sub> O	TiO <sup>2+</sup> /Ti	-0.89
Nb <sup>3+</sup> + 3e	= Nb	Nb <sup>3+</sup> /Nb	-1.1
Mn <sup>2+</sup> + 2e	= Mn	Mn <sup>2+</sup> /Mn	-1.18
Ti <sup>2+</sup> + 2e	= Ti	Ti <sup>2+</sup> /Ti	-1.63
Al <sup>3+</sup> + 3e	= Al	Al <sup>3+</sup> /Al	-1.66
U <sup>3+</sup> + 3e	= U	U <sup>3+</sup> /U	-1.80
Be <sup>2+</sup> + 2e	= Be	Be <sup>2+</sup> /Be	-1.85
Np <sup>3+</sup> + 3e	= Np	Np <sup>3+</sup> /Np	-1.86
Sc <sup>3+</sup> + 3e	= Sc	Sc <sup>3+</sup> /Sc	-2.08
H <sub>2</sub> + 2e	= 2H <sup>-</sup>	H <sub>2</sub> /H <sup>-</sup>	-2.25
Lu <sup>3+</sup> + 3e	= Lu	Lu <sup>3+</sup> /Lu	-2.25
Am <sup>3+</sup> + 3e	= Am	Am <sup>3+</sup> /Am	-2.32
Mg <sup>2+</sup> + 2e	= Mg	Mg <sup>2+</sup> /Mg	-2.37
Gd <sup>3+</sup> + 3e	= Gd	Gd <sup>3+</sup> /Gd	-2.40
La <sup>3+</sup> + 3e	= La	La <sup>3+</sup> /La	-2.52
Na <sup>+</sup> + e	= Na	Na <sup>+</sup> /Na	-2.71
Ca <sup>2+</sup> + 2e	= Ca	Ca <sup>2+</sup> /Ca	-2.87
Sr <sup>2+</sup> + 2e	= Sr	Sr <sup>2+</sup> /Sr	-2.89
Ba <sup>2+</sup> + 2e	= Ba	Ba <sup>2+</sup> /Ba	-2.90
Ra <sup>2+</sup> + 2e	= Ra	Ra <sup>2+</sup> /Ra	-2.92
Rb <sup>+</sup> + e	= Rb	Rb <sup>+</sup> /Rb	-2.925
K <sup>+</sup> + e	= K	K <sup>+</sup> /K	-2.925
Li <sup>+</sup> + e	= Li	Li <sup>+</sup> /Li	-3.04

Suppose, for instance, we wish to know what happens when a solution containing tin(II) and tin(IV) ions is mixed with one containing iron(II) and iron(III) ions. From Table 29,



The standard free energy of the reaction



would thus be

$$\Delta G^\circ = -2FE^\circ, \quad \text{with} \quad E^\circ = 0.62 \text{ V};$$

and this allows us to write down immediately the equilibrium constant since  $\Delta G_r^\circ = -RT \ln K_a$ . For this reaction  $K_a$  is found to be  $\sim 10^{21}$ . Introducing activities (very roughly molalities),

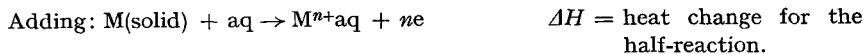
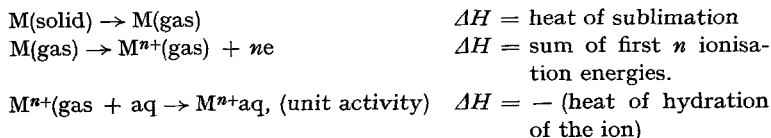
$$\frac{\{\text{Sn}^{4+}\} \{\text{Fe}^{2+}\}^2}{\{\text{Sn}^{2+}\} \{\text{Fe}^{3+}\}^2} \sim 10^{21}.$$

Reduction of the iron(III) and oxidation of the tin(II) ions therefore proceeds virtually to completion, leaving in solution iron(II) and tin(IV) ions.

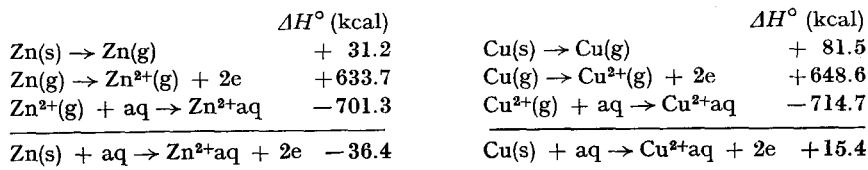
Quite generally, a couple of higher potential will oxidise a couple of lower potential. When the redox potentials are similar, the equilibrium constant is small and the oxidation may be incomplete; but, when one of the products separates through insolubility, its concentration in the denominator of the quotient  $Q_a$  will be almost zero, and the oxidation will continue.

### Factors governing the size of redox potentials

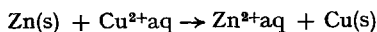
The redox potential of a metal ion/metal couple depends on the free-energy change of the process whereby one mole of the metal at 25° C is converted into ions at unit activity in aqueous solution. To calculate this energy the process is separated into three stages. In the worked examples heats of reaction are used in place of free energies because the entropy changes are not all known.



Applied to zinc and copper we have:



Thus the heat of reaction for the process



is given by

$$\Delta H = -36.4 - 15.4 = -51.8 \text{ kcal.}$$

As the entropy of the products is probably not greatly different from that of the reactants

$$\Delta G \sim -51.8 \text{ kcal or } \frac{-51.8}{23} \equiv -2.24 \text{ eV.}$$

Thus for the two-electron transfer:

$$E^\circ, \text{Cu}^{2+}/\text{Cu} - E^\circ, \text{Zn}^{2+}/\text{Zn} = \frac{+2.24}{2} \text{ Volts} = 1.12 \text{ V.},$$

in near agreement with the difference between the two experimental values

$$+0.34 - (-0.76) = +1.10 \text{ V.}$$

There are two major causes of 'noble' character (that is high  $E^\circ, \text{M}^{n+}/\text{M}$  value) in a metal:

- High sublimation energy, usually associated with high b.p. (*cf.* Zn, b.p.  $907^\circ$  and Cu, b.p.  $2310^\circ$ ).
- High ionization energy, associated particularly with transition metals which form cations of high charge.

The effect of (b) is usually partly reduced in small, highly-charged ions by their larger heats of hydration.

For non-metals such as the halogens, the value of  $E^\circ, \text{X}_2/\text{X}^-$  depends to a great extent on the hydration energy of the  $\text{X}^-$  ion. For instance with fluorine and iodine we have:

	$\Delta H^\circ(\text{kcal})$		$\Delta H^\circ(\text{kcal})$
$\frac{1}{2}\text{F}_2(\text{g}) \rightarrow \text{F}(\text{g})$	19	$\frac{1}{2}\text{I}_2(\text{s}) \rightarrow \text{I}(\text{g})$	26
$\text{F}(\text{g}) + \text{e} \rightarrow \text{F}^-(\text{g})$	-92	$\text{I}(\text{g}) + \text{e} \rightarrow \text{I}^-(\text{g})$	-75
$\text{F}^-(\text{g}) + \text{aq} \rightarrow \text{F}^-\text{aq}$	-123	$\text{I}^-(\text{g}) + \text{aq} \rightarrow \text{I}^-\text{aq}$	-72
$\frac{1}{2}\text{F}_2 + \text{aq} + \text{e} \rightarrow \text{F}^-\text{aq}$	-196	$\frac{1}{2}\text{I}_2(\text{s}) + \text{aq} + \text{e} \rightarrow \text{I}^-\text{aq}$	-121

Thus the calculated heat of reaction for the process



is given by

$$\Delta H = -75 \text{ kcal} \equiv -3.2 \text{ eV.}$$

The difference in the redox potentials is not in good agreement here ( $0.53 - 2.87 = -2.34\text{V}$ ), presumably because there is a particularly large negative entropy in the hydration of the small  $\text{F}^-$  ion. Nevertheless, the free energy of hydration of  $\text{F}^-$  is probably large enough to be the main reason for the very high value of  $E^\circ, \text{F}_2/\text{F}^-$ .

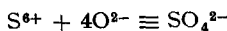


The relative importance of the factors which determine the redox potentials of couples which include oxoanions (*e.g.*  $\text{MnO}_4^-/\text{Mn}^{2+}$ ) are difficult to assess. The oxidations which they bring about involve a number of steps for which the energies cannot be evaluated accurately.

### Oxidation states

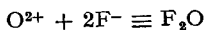
A convenient, formal concept used to characterise the state of oxidation of an element in a compound, and also in nomenclature (p. 580), is that of *oxidation number*. Atoms in a free element have zero oxidation number. In a molecule or ion, the oxidation number is equal to the charge the atom might be expected to have if the molecule were made entirely of ions, the anions among these being assumed to have noble gas structures. It follows that the sum of the oxidation numbers of the atoms forming a species (molecule or ion) is equal to the charge on that species.

Thus in  $\text{SO}_2$ , oxygen, the more electronegative element, is imagined to exist as  $\text{O}^{2-}$  (neon structure) ions, and the sulphur as an  $\text{S}^{4+}$  ion. The sulphur is in an oxidation state +4, designated  $\text{S}^{\text{IV}}$ . In  $\text{SO}_3$ , the sulphur has the oxidation state  $\text{S}^{\text{VI}}$ , as it also has in the  $\text{SO}_4^{2-}$  ion:



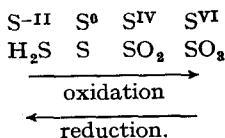
Oxygen in most classes of compounds is in the  $-2$  state but there are two notable exceptions to this general rule:

- (i) Peroxides in which oxygen is conventionally in the  $-1$  state, as is illustrated by  $2\text{H}^+ + \text{O}_2^{2-} \equiv \text{H}_2\text{O}_2$
- (ii) Oxygen fluoride in which fluorine is the more electronegative element and oxygen is in a  $+2$  state.



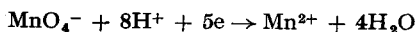
But these exceptions should not be allowed to confuse the general rule that the oxygen atom assumes the  $-2$  state in molecules and ions.

Oxidation or reduction of a compound always involves a change in the oxidation state of at least one atom in the compound:

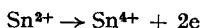


In these sulphur compounds, the oxidation state of the sulphur is raised by oxidation, lowered by reduction.

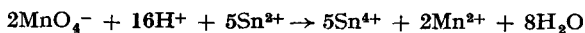
The number of electrons which must be transferred to effect a certain redox process is apparent when the change in oxidation number is known. A familiar example is oxidation by the permanganate ion  $\text{MnO}_4^- (\equiv \text{Mn}^{7+} + 4\text{O}^{2-})$  which contains  $\text{Mn}^{\text{VII}}$ . The reduction of  $\text{MnO}_4^-$  to  $\text{Mn}^{2+}$  ( $\text{Mn}^{\text{II}}$ ) clearly requires the addition of 5 electrons:



The oxidation of  $\text{Sn}^{2+}$  to  $\text{Sn}^{4+}$  requires the removal of 2 electrons.



When this oxidation is effected by  $\text{MnO}_4^-$  in acid solution the balanced equation is obtained by imagining a ten-electron transfer:



It must be remembered that this transfer is done not in one but in many steps.

### Elements with several oxidation states

Most of the non-metals and the 'd-block' metals (p. 81) can exist in several oxidation states. It is useful to be able to summarise the relationships between the states in a redox potential diagram. One method, due to W. T. Latimer, but given here with the I.U.P.A.C. sign convention, is illustrated for the common oxidation states of manganese.

### Manganese redox reactions in acid solution

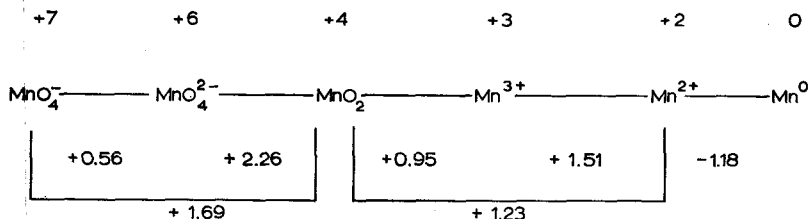


Fig. 158. Latimer diagram of redox potentials of manganese (Volts) at pH 0.

The figures indicate, for example, that

- (a)  $E^\circ, \text{MnO}_4^- / \text{MnO}_4^{2-} = +0.56\text{V}$  (1-electron transfer)
- (b)  $E^\circ, \text{MnO}_4^{2-} / \text{MnO}_2 = +2.26\text{V}$  (2-electron transfer)
- (c)  $E^\circ, \text{MnO}_4^- / \text{MnO}_2 = +1.69\text{V}$  (3-electron transfer)

Notice that the redox potential for the three-electron transfer (c) is equal

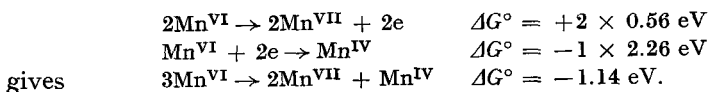
to  $\frac{2(b) + a}{3}$ . This result is to be expected because the free-energy change for the half-reaction  $\text{MnO}_4^- \rightarrow \text{MnO}_2$  (pH 0) is the same regardless of the path of reaction:

$$\Delta G = -3 \times 1.69 \text{ eV} = -(1 \times 0.56) - (2 \times 2.26) \text{ eV.}$$

The figures also provide information about the possible disproportionation reaction in which manganate would be converted to a mixture of permanganate and manganese dioxide:



Addition of the half-reactions,



Since  $\Delta G^\circ = -RT \ln K$ ,

$$\text{and } \log_{10} K = \frac{1.14 \times 2.3 \times 10^4}{1.987 \times 298 \times 2.303} \sim 18,$$

$$K = \frac{\{\text{Mn}^{\text{IV}}\} \{\text{Mn}^{\text{VII}}\}^2}{\{\text{Mn}^{\text{VI}}\}^3} \sim 10^{18} \text{ at } 298^\circ \text{ K.}$$

Hence the manganate(VI) ions disproportionate almost completely into permanganate ions and  $\text{MnO}_2$  in aqueous solution at pH 0 (p. 235).

A graphical method of illustrating redox relationships between the oxidation states of an element has been suggested by E. A. V. Ebsworth. Instead of redox potentials, the free energies of the various processes



are plotted against the oxidation state ( $Z$ ). The ordinates represent the free energies of the various oxidation states, relative to the metal, at pH 0. Fig. 159 for manganese may be compared with the Latimer diagram above.

The free-energy change for the process



is  $-2 \times +1.18$  electron volts, since  $E^\circ$ ,  $\text{Mn}^{2+}/\text{Mn} = -1.18\text{V}$ . Thus the  $\Delta G$  value for  $\text{Mn}^{2+}$  lies 2.36eV below that for  $\text{Mn}^\circ$ , taken as zero. The slope

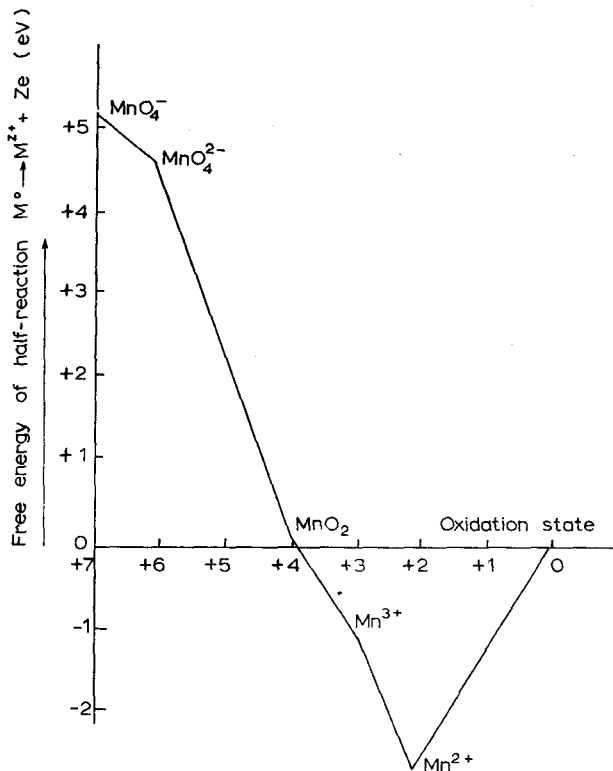
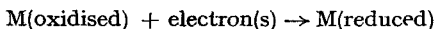


Fig. 159. Free energies of the oxidation states of manganese relative to the metal in aqueous solution at pH 0.

of the line drawn between this point and 0.0 is  $+\frac{2.36}{2}$ , that is  $-E^\circ, \text{Mn}^{2+}/\text{Mn}$ .

Other points are plotted similarly from the data given on the Latimer diagram for manganese. Thus the point for  $\text{Mn}^{\text{III}}$  is 1.51eV above that for  $\text{Mn}^{\text{II}}$ , and so on. The points are plotted from right to left to give an order of oxidation states which follows the I.U.P.A.C. convention:



This graphical method provides a clear picture of the redox-solution chemistry of an element. For the case illustrated, the minimum at  $\text{Mn}^{2+}$  indicates that this state is thermodynamically stable with respect to  $\text{Mn}^0$  and to all the oxidation states of manganese from  $\text{Mn}^{\text{III}}$  to  $\text{Mn}^{\text{VII}}$ . The fact that  $\text{Mn}^{\text{VI}}$  lies higher than a straight line drawn from  $\text{Mn}^{\text{VII}}$  to  $\text{Mn}^{\text{IV}}$

indicates that  $\text{Mn}^{\text{VI}}$  will disproportionate largely into the  $\text{Mn}^{\text{VII}}$  and  $\text{Mn}^{\text{IV}}$  states. But for the equilibrium



$K$  will be very small indeed since the  $\text{Mn}^{\text{IV}}$  point lies well below the straight line from  $\text{Mn}^{\text{VI}}$  to  $\text{Mn}^{\text{III}}$ . However, for



$K$  will be large, as  $\text{Mn}^{\text{III}}$  lies at a 'convex' point.

### Manganese redox reactions in alkaline solution

The diagrams given above refer to the reactions of manganese compounds at pH 0 (normal acidity). For alkaline solutions (pH 14) the reactions are different, and the Latimer diagram and Ebsworth graph are also different.

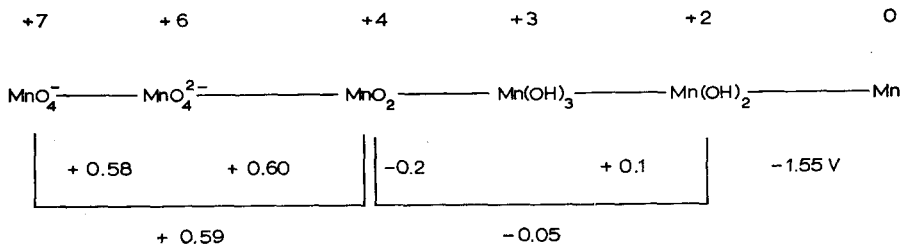


Fig. 160. The Latimer diagram for manganese at pH 14.

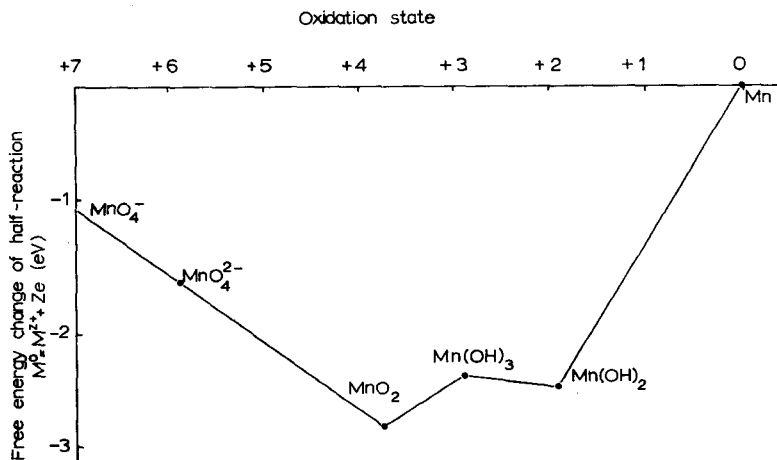


Fig. 161. Free energies of the oxidation states of manganese relative to the metal in aqueous solution at pH 14.

For the free energies of half-reaction the graph has the form shown in Fig. 161. Under alkaline conditions,  $\text{Mn}(\text{OH})_3$  disproportionates almost completely into  $\text{Mn}(\text{OH})_2$  and  $\text{MnO}_2$ :

$$K = \frac{\{\text{Mn}(\text{OH})_2\} \{\text{MnO}_2\}}{\{\text{Mn}(\text{OH})_3\}} \sim 10^5$$

Both  $\text{Mn}(\text{OH})_2$  and  $\text{MnO}_2$  are thermodynamically stable species (there are minima at both the +2 and +4 states). The manganate(VI) ion has less tendency to disproportionate in alkaline than in acid solution; the line through the +7, +6 and +4 states is almost straight, meaning that

$$K \text{ for } \frac{\{\text{Mn}^{\text{VII}}\}^2 \{\text{Mn}^{\text{IV}}\}}{\{\text{Mn}^{\text{VI}}\}^3} \sim 1$$

A green manganate(VI) can be made by oxidising  $\text{MnO}_2$  in strongly alkaline solution, but the addition of even such a weak acid as  $\text{CO}_2$  causes manganate(VI) to disproportionate into permanganate and  $\text{MnO}_2$ .

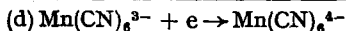
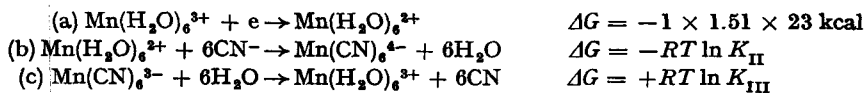


### Redox potentials of complex couples

The redox potential for the  $\text{Mn}^{\text{III}}/\text{Mn}^{\text{II}}$  couple has been shown above to depend on the pH of the solution. For  $\text{Mn}(\text{H}_2\text{O})_6^{3+}/\text{Mn}(\text{H}_2\text{O})_6^{2+}$  at pH 0  $E^\circ = +1.51\text{V}$  but for  $\text{Mn}(\text{OH})_3/\text{Mn}(\text{OH})_2$  at pH 14  $E^\circ = +0.10\text{V}$ . Another way in which the strong oxidising action of  $\text{Mn}^{\text{III}}$  can be reduced is by the addition of an excess of cyanide ions to the solution:



An energy cycle explains this change in  $E^\circ$ . For



For (d)  $\Delta G^\circ = -1.51 \times 23 \text{ kcal} + RT (\ln K_{\text{III}} - \ln K_{\text{II}})$ ,

where  $K_{\text{III}}$  = the stability constant for  $\text{Mn}(\text{CN})_6^{3-}$

$$= \frac{\{\text{Mn}(\text{CN})_6^{3-}\}}{\{\text{Mn}(\text{H}_2\text{O})_6^{3+}\} \{\text{CN}^-\}^6} \text{ at equilibrium,}$$

and  $K_{\text{II}}$  = the stability constant for  $\text{Mn}(\text{CN})_6^{4-}$ .

The constant  $K_{\text{III}}$  is much larger than  $K_{\text{II}}$ ; this is because the absence of one antibonding electron from  $\text{Mn}(\text{CN}_6)^{3-}$  very greatly strengthens the bonding in the complex. Thus  $\Delta G^\circ$  is far more positive for reaction (d) than for reaction (a), and  $E^\circ$  is consequently greatly reduced.

This effect of strong-field ligands on the redox potential of an  $\text{M}^{\text{III}}/\text{Mn}^{\text{II}}$  transition-metal couple is a fairly general one but there are important exceptions where  $K_{\text{II}} > K_{\text{III}}$  (p. 700).

### General use of free-energy diagrams

Free-energy diagrams will be used throughout the book to illustrate the relative thermodynamic stabilities of oxidation states for those elements which have several. Unless there is special interest in the case for alkaline solution, only the diagram for pH 0 will be given.

### FURTHER READING

- W. L. LATIMER, *The Oxidation States of the Elements and their Potentials in Aqueous Solutions*, 2nd Ed., Englewood Cliffs, N.Y., Prentice-Hall, 1952.
- A. G. SHARPE, *The Principles of Oxidation and Reduction*, London, The Royal Institute of Chemistry, 1959. Monographs for Teachers Series, No 2.
- E. A. V. EBSWORTH, *A Graphical Method of representing the Free Energies of Oxidation-Reduction Systems*, Education in Chemistry, 1 (1964) 123.
- G. KORTUM, *Treatise on Electrochemistry*, Amsterdam, Elsevier, 2nd Ed., 1965.

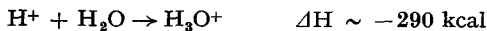
## Chapter 11

# Acids and Bases

### Introduction

Early studies of acids and bases were restricted to aqueous solutions and were made with an inadequate understanding of the peculiarities of water. The compounds were defined as substances which dissociated in water, the acids to give hydrogen ions and the bases hydroxide ions (Arrhenius, Ostwald, 1887). This definition does not express present views about aqueous solutions and cannot be applied to solutions in other solvents.

Thermodynamics shows that free  $H^+$  ions cannot exist in appreciable concentration in water itself, and spectroscopy that the hydration of the proton is a strongly exothermic reaction. Accordingly the dissociation of an acid in water leads to the hydrated proton  $H^+$  aq., often represented by  $H_3O^+$  and referred to as the hydroxonium ion:



The hydrogen ion in aqueous solutions is almost certainly associated with more than one water molecule (for the structure of water see p. 289). However  $H_3O^+$  itself exists in some ionic lattices, for instance in  $H_3O^+ClO_4^-$  which is isomorphous with  $NH_4^+ClO_4^-$ .

On the other hand, an acid dissociates in anhydrous ethyl alcohol to give the cation  $C_2H_5OH_2^+$  and in liquid ammonia to give the cation  $NH_4^+$ .

Turning to bases, we find something similar. For instance, sodium hydroxide is a strong base in water, giving the hydroxide ion  $OH^-$ . But it is less ionised in anhydrous alcohol than in sodium ethoxide,  $C_2H_5ONa$ , which gives the anion  $C_2H_5O^-$ . This anion also appears in solutions of amines in ethyl alcohol. In liquid ammonia the anion present is  $NH_2^-$ . The liquids exemplify solvents in which the anion is not the hydroxide ion.

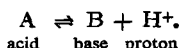
Clearly acids and bases cannot be defined simply as substances respectively producing by dissociation the ions  $H^+$  and  $OH^-$ .

### Lowry-Brönsted theory of acids and bases

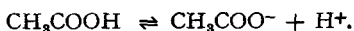
Lowry and Brönsted (1923) independently defined an acid as a compound or ion with a tendency to lose a proton, and a base as a compound or ion



with a tendency to gain a proton. The proton will be associated with a solvent molecule but may for convenience be represented formally by  $H^+$ . An acid A by losing a proton becomes a base B. The base B will tend to regain the proton and revert to the acid A. There will be an equilibrium:



Thus for acetic acid:

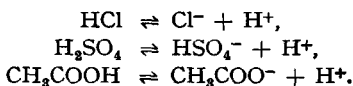


Clearly the acetate ion is by definition a base. Moreover, the acetic acid and the acetate ion are together known as a *conjugate acid-base pair*. The term is applied generally to any two species related to each other as A is to B in the general equation.

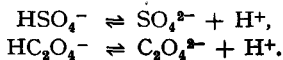
### Acids

The definition allows for the existence of three types of acid:

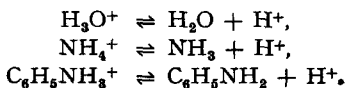
- (i) *Molecular acids*, such as hydrochloric, sulphuric and acetic acids, which lose protons to give, as conjugate bases, the chloride, bisulphate and acetate ions respectively:



- (ii) *Anion acids*, such as the bisulphate  $HSO_4^-$  and bi-oxalate  $C_2O_4H^-$  ions, which lose protons to give, as conjugate bases, the sulphate  $SO_4^{2-}$  and oxalate  $C_2O_4^{2-}$  ions respectively:



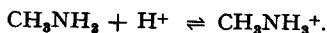
- (iii) *Cation acids*, such as the hydroxonium  $H_3O^+$ , ammonium  $NH_4^+$ , and the anilinium  $C_6H_5NH_3^+$  ions, which lose protons to give water, ammonia and aniline, respectively, as conjugate bases:



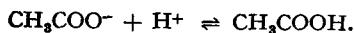
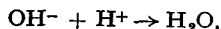
### Bases

Two types of base are possible:

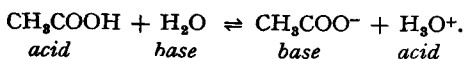
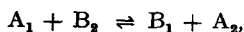
- (i) *Molecular bases*, such as ammonia and ethylamine, which combine with protons to give cations:



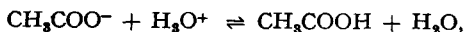
(ii) *Anion bases*, such as the hydroxide and acetate ions, which combine with protons to give uncharged molecules:



The equilibrium  $\text{A} \rightleftharpoons \text{B} + \text{H}^+$  is purely formal because of the non-existence of the proton in water and other solvents. When an acid loses its proton it does so to a base. The acid is thereby converted to its conjugate base and the base to its conjugate acid, as exemplified in the general and particular expressions:



The latter represents the transfer of a proton from an acetic acid molecule to a water molecule and the consequent formation of two ions. Written in the opposite sense,



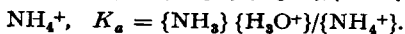
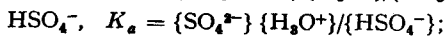
the equilibrium is seen to depend upon the transfer of a proton from a hydroxonium ion to an acetate ion. This process is responsible for the 'buffer action' (p. 241) of an acetate when a strong acid is added to the solution.

### Acid-base equilibria in water

Reactions which transfer a proton are known as *protolytic reactions*. The equilibrium constants of *protolyses* allow a comparison to be made of acid and base strengths. The conjugate pair,  $\text{H}_3\text{O}^+$ ,  $\text{H}_2\text{O}$ , is used as a standard,

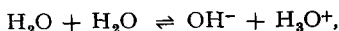


and the equilibrium constant of the reaction is the *acidity constant*,  $K_a = \frac{\{\text{B}\} \{\text{H}_3\text{O}^+\}}{\{\text{A}\} \{\text{H}_2\text{O}\}}$ . For dilute solutions  $\{\text{H}_2\text{O}\}$  is independent of concentration and tends to unity, and the dissociation constant is  $K_a \sim \frac{\{\text{B}\} \{\text{H}_3\text{O}^+\}}{\{\text{A}\}}$  in terms of activities. Equations of this type may be used to compare strengths of molecular, anion and cation acids. Thus for



The strengths of bases are inversely related to the strengths of the

conjugate acids, and it is necessary to use only one constant, the strength of a base being expressed as the reciprocal of the strength of its conjugate acid. Thus for  $\text{NH}_3$ ,  $K_b = \{\text{NH}_4^+\} / \{\text{NH}_3\} \{\text{H}_3\text{O}^+\}$ . Now if  $K_w$  is the acidity constant for  $\text{H}_2\text{O}$ , *i.e.* the equilibrium constant for



$$K_w = \frac{\{\text{OH}^-\} \{\text{H}_3\text{O}^+\}}{\{\text{H}_2\text{O}\}^2} \sim \{\text{OH}^-\} \{\text{H}_3\text{O}^+\} \text{ (the autoprotolysis constant)}$$

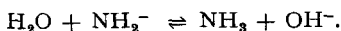
and therefore

$$K_b = \frac{\{\text{NH}_4^+\} \{\text{OH}^-\}}{\{\text{NH}_3\}} \frac{1}{K_w} = \frac{K_b \text{ (classical)}}{K_w}$$

The exponent  $\text{p}K_a (= -\log_{10}K_a)$ , *cf.*  $\text{pH}$ , is also a convenient measure of acid strength.

No acid species much stronger than  $\text{H}_3\text{O}^+$  ( $K_a = 55 \text{ mole kg}^{-1}$ ) can appear in appreciable quantity in water. Hydrogen chloride which is stronger is almost entirely converted to  $\text{H}_3\text{O}^+$  and  $\text{Cl}^-$  and, similarly,  $\text{H}_2\text{SO}_4$  to  $\text{H}_3\text{O}^+$  and  $\text{HSO}_4^-$ . Since, however,  $K_a$  for  $\text{HSO}_4^-$  is  $10^{-2} \text{ mole kg}^{-1}$ , that anion can exist in appreciable concentrations in water.

On the same grounds, a base much stronger than  $\text{OH}^-$  cannot exist in appreciable quantity because such a base would be hydrolysed by water to its conjugate acid and  $\text{OH}^-$ :



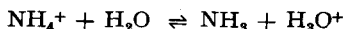
The above are examples of *strong electrolytes* in water. A *weak electrolyte* in water is one with a neutral molecule which is not an electrolyte but which is partly changed into ions in aqueous solution.

TABLE 30  
STRENGTHS OF SOME ACIDS

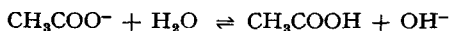
				$K_a$	$\text{p}K_a$
Hydrochloric acid	$\text{HCl}$	$+$	$\text{H}_2\text{O} \rightleftharpoons \text{Cl}^- + \text{H}_3\text{O}^+$	$\sim 10^7$	-7
Iodic acid	$\text{HIO}_3$	$+$	$\text{H}_2\text{O} \rightleftharpoons \text{IO}_3^- + \text{H}_3\text{O}^+$	$2.0 \times 10^{-1}$	0.7
Phosphoric acid	$\text{H}_3\text{PO}_4$	$+$	$\text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{PO}_4^- + \text{H}_3\text{O}^+$	$5.0 \times 10^{-2}$	1.3
Carbonic acid	$\text{H}_2\text{CO}_3$	$+$	$\text{H}_2\text{O} \rightleftharpoons \text{HCO}_3^- + \text{H}_3\text{O}^+$	$4.5 \times 10^{-7}$	6.4
Hydrocyanic acid	$\text{HCN}$	$+$	$\text{H}_2\text{O} \rightleftharpoons \text{CN}^- + \text{H}_3\text{O}^+$	$7.2 \times 10^{-10}$	9.1
Ammonium ion	$\text{NH}_4^+$	$+$	$\text{H}_2\text{O} \rightleftharpoons \text{NH}_3 + \text{H}_3\text{O}^+$	$5.6 \times 10^{-10}$	9.3
Bicarbonate ion	$\text{HCO}_3^-$	$+$	$\text{H}_2\text{O} \rightleftharpoons \text{CO}_3^{2-} + \text{H}_3\text{O}^+$	$5.6 \times 10^{-11}$	10.3
Ethane	$\text{C}_2\text{H}_6$	$+$	$\text{H}_2\text{O} \rightleftharpoons \text{C}_2\text{H}_5^- + \text{H}_3\text{O}^+$	$\sim 10^{-34}$	34

### Hydrolysis and buffer action

As the equilibrium

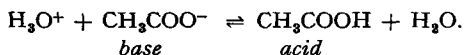


represents the hydrolysis of the ammonium salt of a strong acid,  $K_a$  for the ammonium ion is also the hydrolysis constant. The equation



represents the hydrolysis of the acetate of a strong base. Here the hydrolysis constant,  $K_h = \{\text{CH}_3\text{COOH}\} \{\text{OH}^-\} / \{\text{CH}_3\text{COO}^-\}$ , is related to the dissociation of the acid by the expression  $K_h = K_w / K_a$ .

Hydroxonium ions added to a solution of acetate ions are largely converted into undissociated acetic acid molecules:



Since  $K_a$  for the acid =  $\{\text{base}\} \{\text{H}_3\text{O}^+\} / \{\text{acid}\}$ ,

therefore  $\{\text{H}_3\text{O}^+\} = K_a \{\text{acid}\} / \{\text{base}\}$ ,

and  $-\log_{10} \text{H}^+ = -\log_{10} K_a - \log_{10} \{\text{acid}\} / \{\text{base}\}$ ,

or  $\text{pH} = \text{p}K_a - \log_{10} \{\text{acid}\} / \{\text{base}\}$ .

The ratio  $\{\text{acid}\} / \{\text{base}\}$  is the *buffer ratio*. Because the buffer ratio is not altered by dilution, neither is the pH in any except strong solutions. In strong solutions the attraction between ions becomes sufficiently great to interfere with the simple equilibria. Small additions of acid and alkali alter the buffer ratio and pH very little. Obviously, buffering is most efficient when  $\{\text{acid}\} \sim \{\text{base}\}$ , *i.e.* when  $\text{pH} \sim \text{p}K_a$ .

Thus a solution containing equimolar concentrations of acetic acid molecules and acetate ions has a pH given by

$$\begin{aligned} \text{pH} &= \text{p}K_{\text{acetic acid}} - \log_{10} \frac{\{\text{HAc}\}}{\{\text{Ac}^-\}} \\ &= 4.75 - \log 1.0 = 4.75. \end{aligned}$$

When the acid concentration is 10 times that of the acetate ion,

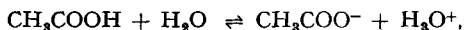
$$\text{pH} = 4.75 - \log 10 = 3.75;$$

but when the acetate ion is 10 times more concentrated,

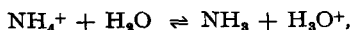
$$\text{pH} = 4.75 - \log 0.1 = 5.75.$$

### Methods of studying acid-base equilibria in water

For an equilibrium such as



in which ions appear on one side of the equation only, the equilibrium constant is conveniently obtained from the electrical conductance. For equilibria such as



where conductance changes are small, the concentration of  $\text{H}_3\text{O}^+$  ions may be obtained from potential measurements. The concentration of hydroxonium and hydroxide can also be inferred from their respective catalytic effect in specific reactions. Sometimes the equilibrium may be investigated colorimetrically. The concentration of an uncharged species such as ammonia may, on occasion, be determined from partition coefficients with another phase, say chloroform.

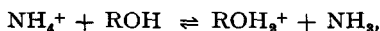
### Acids and bases in non-aqueous protonic solvents

A protonic solvent is one which contains hydrogen in the molecule and which is thus capable of acting, under certain conditions, as a proton donor. The behaviour of a solute in a solution depends on whether the solvent (i) tends to gain or lose a proton, (ii) admits recombination of ions.

Water, being both a proton donor and a proton acceptor, is said to be *amphiprotic*. It has a considerable dipole moment and a very high dielectric constant so that solvation of the ions, together with the dielectric effect (p. 107), discourages their recombination. These characteristics are responsible for the simple form taken by the ionic theory before the study of non-aqueous solvents revealed the more complex relationship between concentration and degree of ionisation.

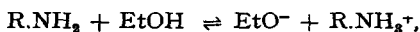
### Amphiprotic solvents resembling water

Alcohols resemble water as solvents but have much smaller dielectric constants, these are 32 for methyl and 25 for ethyl alcohol against 78 for water. For equilibria such as



where ions are involved on both sides, the dielectric effect is small;  $\{\text{NH}_3\} \{\text{EtOH}_2^+\} / \{\text{NH}_4^+\} \{\text{EtOH}\}$  is only about six times greater than  $\{\text{NH}_3\} \{\text{H}_3\text{O}^+\} / \{\text{NH}_4^+\} \{\text{H}_2\text{O}\}$ , indicating that ethyl alcohol is a stronger base than water.

For equilibria such as



where both ions are on one side, differences in dielectric constant cause the equilibrium constants to be much less than for aqueous solutions. Amines

have dissociation constants in ethyl alcohol less by a factor of about  $10^{-4}$  than in water; the fatty acids less by a factor which is usually about  $10^{-5}$ .

The electrical free energy of a pair of ions of charges  $+e$  and  $-e$  at a distance  $r$  in a medium of dielectric constant  $\epsilon$  is given by  $G = e^2/\epsilon r$ . The difference in value between the electrical free energy in water and that in ethyl alcohol as solvent is given by

$$\Delta G = \frac{e^2}{r} \left( \frac{1}{\epsilon_1} - \frac{1}{\epsilon_2} \right) \text{ (The Born equation)}$$

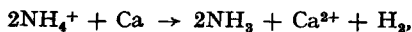
If  $\epsilon_1 = 78$ ,  $\epsilon_2 = 25$  and  $r \sim 2 \times 10^{-8}$  cm,  $\Delta G \sim -5600$  cal/mole. The ratio of the equilibrium constants is given by

$$\frac{-\Delta G}{e RT} \sim 2 \times 10^4.$$

This is about the observed figure, suggesting the difference in behaviour to be due largely to differences in inter-ionic attraction.

### Basic or protophilic solvents

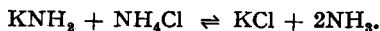
Ammonia (b.p.  $-33^\circ$ ,  $\epsilon$  22) is, like water, an unsymmetrical molecule (p. 118) with a lone pair and a fairly high dipole moment. The autoprotolysis reaction is slight;  $[\text{NH}_4^+][\text{NH}_2^-] \sim 10^{-32}$  at the boiling point ( $-33^\circ$ ). The protonic acid,  $\text{NH}_4^+$ , formed by ammonium salts in solution in ammonia, liberates hydrogen with such metals as calcium:



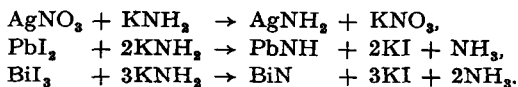
and decomposes salts of weaker acids:



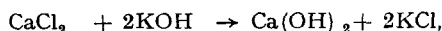
Metallic amides, imides and nitrides behave as bases in the solvent. Thus potassium amide turns phenolphthalein red and can be titrated conductometrically with an ammonium salt:



Heavy metal amides, imides or nitrides are precipitated by potassium amide:



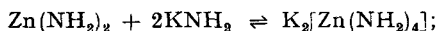
These correspond with the precipitation, sometimes of the hydroxide:



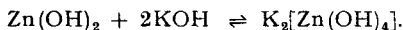
and sometimes of the oxide:



by caustic potash in aqueous solution. Furthermore, zinc amide reacts with potassium amide in liquid ammonia to give potassium ammonozincate;



a reaction formally similar to that between zinc hydroxide and aqueous potash in water:



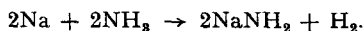
Ammonia, a strongly basic solvent and therefore a strong proton acceptor, encourages the dissociation of acids:



Acids of  $pK_a \sim 5$  in water dissociate almost completely in liquid ammonia. But the acids which dissociate extensively in water do not stand out so markedly in this respect in ammonia because the ionisation of acids weak in water, such as the carboxylic acids, is so much greater in liquid ammonia. This basic solvent is said to have a 'levelling' effect on the strength of the acids. However, as the acidic properties (proton donating powers) of ammonia are very weak, strong bases dissociate in it only slightly and weak bases scarcely at all.

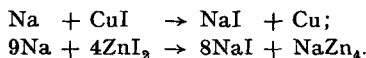
The solubilities of salts in liquid ammonia are markedly different from their solubilities in water. Ammonium salts are generally very soluble, as are also metal nitrates and iodides, including silver iodide, but fluorides and chlorides have low solubilities. Ammonia is not, in general, a good solvent for highly ionic compounds, possibly largely because of its low dielectric constant. But it is a better solvent than water for non-polar compounds, and for those with highly polarisable anions such as iodides. Non-metals like iodine, sulphur, selenium and phosphorus show a moderate solubility.

The alkali metals dissolve in ammonia, without the evolution of hydrogen, giving blue, strongly conducting solutions. In dilute solutions the cation appears to be  $\text{Na}^+$ , probably solvated as  $\text{Na(NH}_3)_m^+$ , and the anion  $\text{NH}_3^-$  or  $(\text{NH}_3)_n^-$ , which also contributes the colour. Metals such as platinum and iron catalyse the decomposition of the solution with the formation of sodium amide and the liberation of hydrogen:



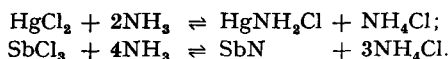
A solution of sodium in liquid ammonia furnishes a useful reducing agent,

converting halides of the more noble metals to the element or an inter-metallic compound:



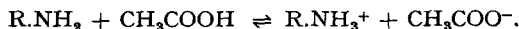
With phosphine, a solution of sodium in liquid ammonia gives  $\text{NaPH}_2$  and hydrogen. Compounds, formulated  $\text{NaNNO}$ ,  $\text{KNO}$  and  $\text{Ba}(\text{NO})_2$ , are formed when nitric oxide is brought into an ammonia solution of the respective metal. These have structures different from the hyponitrites (p. 442).

Ammonolysis, the equivalent of hydrolysis in aqueous solution, is rather less extensive than the latter because of the slight autoprotolysis ( $2\text{NH}_3 \rightarrow \text{NH}_4^+ + \text{NH}_2^-$ ) of ammonia itself:

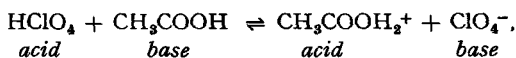


### Acidic or protogenic solvents

(i) Acetic acid has a strong levelling effect (p. 244) on the strength of bases, such as aliphatic amines and alkylanilines, which do not ionise greatly in water:



Inorganic acids which are strong acids in water ionise less readily in acetic acid, and differences between their strengths become more obvious in that medium; for instance the dissociation constants of nitric, hydrochloric, sulphuric, hydrobromic and perchloric acids are spread in the ratios 1:9:30:160:400. Because the dissociation of perchloric acid in acetic acid:

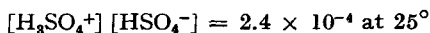


is so considerable it may be used to titrate, potentiometrically, such compounds as amides and oximes which ionise fairly strongly as bases in the solvent.

(ii) As a solvent, formic acid might be expected to behave as does acetic acid; but, having a dielectric constant (62) almost 10 times greater than that of acetic acid (probably through hydrogen bonding in the liquid), it shows a particularly high autoprotolysis constant:

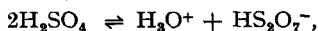


(iii) Sulphuric acid also displays a high degree of autoprotolysis



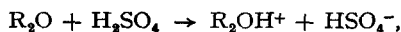


As however, the other dissociation of sulphuric acid:

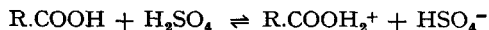


occurs to only a slightly less extent, the interpretation of conductance and e.m.f. measurements is difficult. The dielectric constant is not known, but it is probably high, and interionic forces should be correspondingly small. The low volatility and the high viscosity are also consistent with a high dielectric constant.

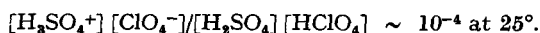
Sulphuric acid is so strongly protogenic that most compounds of oxygen and nitrogen accept protons from it to some extent. Not only amines, but ethers and ketones, give twice the normal freezing point depression, suggesting that such reactions as



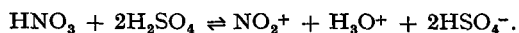
go virtually to completion. Many carboxylic acids dissociate as bases in sulphuric acid:



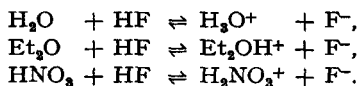
And even perchloric acid ionises like a weak acid in sulphuric acid:



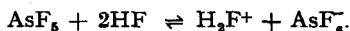
Certain substances, however, undergo reactions more complicated than proton transfer when dissolved in sulphuric acid. Nitric acid, for instance, gives the nitronium ion which is the active agent in aromatic nitration:



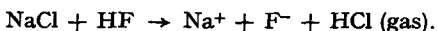
(iv) Hydrofluoric acid has a surprisingly low conductance in the anhydrous liquid condition; but it has a very high dielectric constant (84), a high dipole moment (1.9 D) and a strong tendency to associate. For simplicity, it is treated here as a monobasic acid, rather than the dibasic acid,  $\text{H}_2\text{F}_2$ , which it really is. It is similar to sulphuric acid in its effects on acids and bases, the only acids showing measurable dissociation in it being perchloric and per-iodic acids. If dissolves water, ethers, ketones, aliphatic acids and even nitric acid, all of them functioning as bases:



Some non-metal fluorides dissolve to give acid solutions:



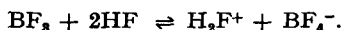
Alkali-metal chlorides, bromides, iodides and cyanides dissolve in hydrogen fluoride to give the free acids:



Many solutes react with anhydrous hydrogen fluoride, an example being sulphuric acid which produces fluorosulphuric acid;



Mixtures of hydrogen fluoride and boron trifluoride are very powerful proton donors: the substances react as shown.



In this liquid mixture even aromatic hydrocarbons behave as bases; for instance hexamethylbenzene is largely converted into  $\text{C}_6\text{HMe}_6^+\cdot\text{BF}_4^-$  and forms a strongly conducting solution.

### Aprotic solvents

Hydrocarbons and their halogen derivatives have no tendency to gain or lose protons; they are inert and exhibit no levelling effect. The dielectric constants are very low (2 to 6) and the ions associate, rendering conductance measurements of no value for determining the extent of protolysis. Protolytic equilibria are also complicated by association of the uncharged molecules themselves; carboxylic acids, for example, exist as dimers in benzene. The same factors reduce greatly the solubilities of acids and bases in these solvents.

### Comparison of acid strengths in various solvents

Because the dissociation of an acid depends in a complex way on the chemical properties, molecular dipole and dielectric constant of the solvent in which it is dissolved, attempts to define absolute acid strength independently of the solvent have been unavailing. Nevertheless, relative strengths are independent, within a power of 10, of the nature of the solvent provided the acids belong to the same charge type, whether that be molecular, anionic or cationic. The independence of the nature of the solvent shown by acids of the same chemical character is even more marked.

### Acid strength and molecular structure

(i) Simple hydrides of Gps. V to VII show the approximate  $\text{p}K_a$  values given in Table 31.

Where there are several acids of a similar type the  $\text{p}K_a$  values vary regularly down the series. The changes in value are an expression of the overall effect of the energies of (a) dissociation of the hydrides to atoms, (b) ionisation of the hydrogen atom, (c) hydration of the hydrogen ion, (d) electron affinity of the other atom or radical, and (e) the solvation of the

TABLE 31  
 $pK_a$  VALUES OF HYDRIDES OF GFS. V, VI, VII

Group V	Group VI	Group VII
NH <sub>3</sub> 23	H <sub>2</sub> O 15	HF 4
	H <sub>2</sub> S 7	HCl -7
	H <sub>2</sub> Se 4	HBr -9
	H <sub>2</sub> Te 3	HI -11

anion. These stages are set out below and give by addition the heat of dissociation of a binary acid into ions in aqueous solution.

Stage		Heat required
(a)	HX(gas) → H(g) + X(g)	$D$
(b)	H(g) → H <sup>+</sup> (g) + e	$I_H$
(c)	H <sup>+</sup> (g) + aq → H <sub>aq</sub> <sup>+</sup>	$\Delta H_{aqH^+}$
(d)	X(g) + e → X <sup>-</sup> (g)	$-A_x$
(e)	X <sup>-</sup> (g) + aq → X <sub>aq</sub> <sup>-</sup>	$\Delta H_{aqX^-}$
Adding:	HX(g) + aq → H <sub>aq</sub> <sup>+</sup> + X <sub>aq</sub> <sup>-</sup>	$\Delta H_{(acid\ dissociation)}$

Thus for acid dissociation

$$\Delta H = D - A_x + \Delta H_{aqX^-} + I_H + \Delta H_{aqH^+}$$

As the last two terms ( $I_H$  and  $\Delta H_{aqH^+}$ ) are constants for all binary acids, the change of heat of acid dissociation from one acid to another must depend on the first three terms. The dissociation constants depend on  $\Delta G$ , not  $\Delta H$ , of course, but for most of the cases which have been thoroughly studied the entropy differences are not large enough to affect the trends in the change of acid strength through a series of binary acids.

In the series NH<sub>3</sub>, H<sub>2</sub>O and HF, increasing electron affinity ( $A$ , p. 81) is the likeliest cause of increasing acid strength; but in the group HF to HI the determining factor is probably the decreasing dissociation energy ( $D$ ).

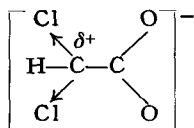
(ii) Oxoacids of the general formula H<sub>n</sub>XO<sub>m</sub> fall into four fairly well-defined classes depending on the ratio of oxygen to hydrogen atoms in the molecule:

- Where  $m = n$ , as in HOCl, HOBr, H<sub>3</sub>BO<sub>3</sub> and H<sub>6</sub>TeO<sub>6</sub>, the  $pK$  value for the first ionisation is between 7 and 11.
- Where  $m = n + 1$ , as in HClO<sub>2</sub>, HNO<sub>2</sub>, H<sub>2</sub>SO<sub>3</sub> and H<sub>3</sub>PO<sub>4</sub>, the  $pK$  value is approximately 2.
- Where  $m = n + 2$ , as in HNO<sub>3</sub>, HClO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub>, the  $pK$  value is between -1 and -3.

(d) Where  $m = n + 3$ , as in  $\text{HClO}_4$  and  $\text{HIO}_4$ , the  $\text{p}K$  value is approximately  $-8$ .

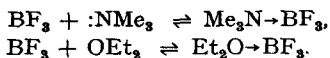
Clearly, telluric acid, about which there was doubt, fits into this scheme as  $\text{H}_6\text{TeO}_6$ , not as  $\text{H}_2\text{TeO}_4 \cdot 2\text{H}_2\text{O}$ . However, phosphorous and hypophosphorous acids, with  $\text{p}K$  2 and 1 respectively, behave as  $\text{HPO}(\text{OH})_2$  and  $\text{H}_2\text{PO}(\text{OH})$ , in accordance with their known basicities. Increase in acid strength appears to be associated with the stabilisation of the anion. The greater the charge number of the central atom, the greater its electronegativity, and the lower the energy of the MO's which can accommodate the electron to which the anion owes its charge.

(iii) Aliphatic acids have a  $\text{p}K$  of about 5. The substitution of hydrogen in alkyl groups by elements with high electronegativity (F, Cl) increases acid strength, particularly when more than one hydrogen atom is replaced, and when substitution is made at the carbon atom nearest the carboxylic group. In the dichloroacetate ion, for example, stability is conferred through the chlorine increasing the electronegativity of the alkyl C and thereby lowering the energy of the whole ion by attracting away some of the negative charge conferred on the other C by the oxygen atoms.

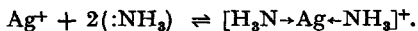


### Lewis acids

For an acid to be a proton donor, it must contain hydrogen. This led G. N. Lewis (1938) to develop a more general concept of an acid as a substance which is an electron acceptor. This substance accepts the unshared electron pair of the base with which it forms a covalent link. Thus described, boron trifluoride is an acid:



The silver ion is also an acid:



And so, indeed, is any species with an outer electron structure capable of expansion. Most proton acids conform to the Lewis definition if the reaction between base and acid is considered to start with a hydrogen bond,  $\text{XH} \cdots \text{B}$ . In this way an electron may be said to be accepted by the acid  $\text{HX}$ . Experi-

mentally, Lewis classes as acids substances exhibiting the typical acidic properties: (a) catalytic action, (b) ability to neutralise bases, (c) effect on indicators, (d) displacement by a stronger acid.

Although boron trifluoride, sulphur trioxide and the like may be titrated against bases in inert solvents, there is no unequivocal instance of a Lewis acid causing catalysis in the absence of protons. Thus the concept is rather formal and has the weakness that it fails to lead, as does the Lowry-Brönsted theory, to a simple comparison of acid strengths. An importance of Lewis's definition lies in the attention it has drawn to electron-accepting species, whether they be called acids or not, for their behaviour is fundamental to reactions in non-protonic solvents.

The Lewis treatment of bases is not significantly different from that of Lowry and Brönsted.

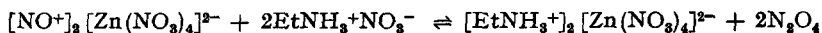
### Non-protonic solvents

#### (i) Dinitrogen tetroxide

Liquid dinitrogen tetroxide (b.p. 21°), has a very low conductance and small dielectric constant (2.4). Its self-ionisation is thus:



There is no proton. The cation,  $\text{NO}^+$ , must be counted the acid, and the anion,  $\text{NO}_3^-$ , the base characteristic of the system. Zinc dissolves in liquid  $\text{N}_2\text{O}_4$  evolving nitric oxide and forming  $[\text{NO}^+]_2[\text{Zn}(\text{NO}_3)_4]^{2-}$ . This compound is an acid in dinitrogen tetroxide and reacts with ethylammonium nitrate, which behaves as a base in the solvent:



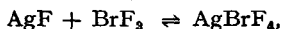
Liquid dinitrogen tetroxide forms addition compounds with ethers,  $\text{N}_2\text{O}_4 \cdot 2\text{Et}_2\text{O}$  (m.p. -75°) with diethyl ether, and  $\text{N}_2\text{O}_4 \cdot (\text{C}_2\text{H}_4)_2\text{O}$  (m.p. +45°) with dioxan, the latter having a high melting point possibly because the use of both oxygen atoms allows an indefinitely extended aggregation.

#### (ii) Bromine trifluoride

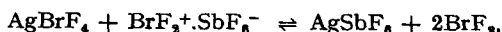
Bromine trifluoride, a pale yellow liquid (b.p. 128°), shows some conductance and is ionised thus:



Potassium and silver fluorides give strongly conducting solutions of tetrafluorobromites when dissolved in bromine trifluoride:



and antimony pentafluoride and tin(IV) fluoride form compounds which appear to be  $\text{BrF}_2^+ \cdot \text{SbF}_6^-$  and  $(\text{BrF}_2^+)_2 \text{SnF}_6^{2-}$ . The fluoroantimonate is a good conductor in bromine trifluoride and the reaction,

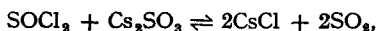


has been followed conductometrically. Substances giving rise to  $\text{BrF}_2^+$  ions are considered as acids in this solvent and those producing  $\text{BrF}_4^-$  ions as bases.

### (iii) Sulphur dioxide

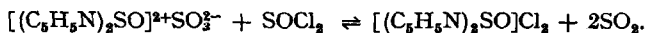
Liquid sulphur dioxide (b.p.  $-10^\circ$ ), which has a dielectric constant of 14 and a dipole moment of 1.61 D, is a good solvent. There does not appear to be any self-ionisation of the type displayed by dinitrogen tetroxide (p. 250). Isotope exchange shows that sulphite sulphur exchanges with sulphur dioxide and that thionyl halide sulphur does not. On the other hand,  $\text{SO}_3$  exchanges oxygen but not sulphur with solvent  $\text{SO}_2$ .

Both sulphites and thionyl halides dissolve in liquid  $\text{SO}_2$  and increase the conductance. The latter probably form  $\text{SOX}^+$  ions. Reactions, such as

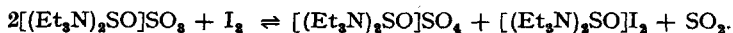


have been followed conductometrically. Some inorganic salts form addition compounds with  $\text{SO}_2$  corresponding to the hydrates and ammoniates; instances are  $\text{NaI} \cdot 2\text{SO}_2$ ,  $\text{BaI}_2 \cdot 4\text{SO}_2$  and  $\text{KSCN} \cdot \text{SO}_2$ . Of the halides the iodides are the most soluble.

Many amines give conducting solutions. Molecular weight and conductance measurements suggest that the ions  $\text{R}_3\text{N}^{2+}$  and  $\text{SO}_2^{2-}$  are present in the solution of a tertiary amine, but another explanation is that the base  $[(\text{R}_3\text{N})_2\text{SO}]^{2+} \cdot \text{SO}_3^{2-}$  is formed. Pyridine has been titrated conductometrically in the solvent with thionyl chloride, possibly by the reaction



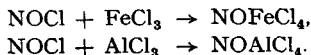
Iodine is reduced to iodide by triethylamine, probably as indicated:



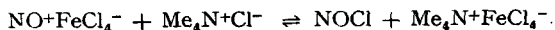
The oxidation accompanying the reduction of iodine is difficult to explain unless sulphite ions are assumed to be present.

### (iv) Nitrosyl chloride

Liquid nitrosyl chloride (b.p.  $-6^\circ$ ), has the comparatively high dielectric constant of 18.2 at the b.p. and a strong tendency to complex with metallic halides:



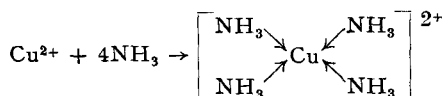
The first of these complexes has been titrated conductometrically with tetramethyl ammonium chloride:



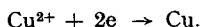
The idea that  $\text{NO}^+$  is the acid and  $\text{Cl}^-$  the base in liquid nitrosyl chloride is supported by the observation that when the iron(III) complex,  $\text{NOFeCl}_4$ , is electrolysed, nitric oxide appears at the cathode and chlorine at the anode.

### Relation between acid-base and oxidation-reduction behaviour

In Lewis's terms, an acid accepts electrons with the formation of a covalent bond:



An oxidising agent accepts complete transfer of electrons:



Thus the difference between acidity and oxidising character should be considered as one of degree; complete electron capture and electron sharing are just different aspect of electrophilic behaviour.

Similarly, a reducing agent transfers electrons completely:



whereas a base donates electrons to form a covalent link:



Both reducing action and basic behaviour are thus forms of electron donation.

### FURTHER READING

- R. P. BELL, *The Use of the terms 'Acid' and 'Base'*, *Quart. Rev.*, 1 (1947) 113.  
 R. P. BELL, *The Proton in Chemistry*, London, Methuen, 1959.  
 L. F. AUDRIETH AND J. KLEINBERG, *Non-aqueous Solvents*, London, Wiley, 1953.  
 H. S. BRITTON, *Hydrogen Ions*, 4th Ed., London, Chapman Hall, 1955.  
 V. GUTMANN, *Reactions in some Non-aqueous Ionising Solvents*, *Quart. Rev.*, 10 (1956) 451.

- R. S. DRAGO AND K. F. PURCELL, *The Co-ordination Model for Non-aqueous Solvent Behaviour*, in F. A. COTTON (Ed.), *Progress in Inorganic Chemistry*, New York, Interscience, 6 (1964) 271.
- G. H. NANCOLLAS, *Interactions in Electrolyte Solutions*, Amsterdam, Elsevier, 1966.



## Hydrogen

### Occurrence and physical properties

Terrestrially, except in the upper atmosphere, hydrogen occurs almost entirely in compounds; of these water and the hydrocarbons are the most abundant. Its importance is, however greatly beyond what might be suggested by its terrestrial abundance (0.81%) because it combines with nearly every other element and is, moreover, an essential constituent of all living matter. It is a colourless, odourless gas which is less dense than any other gas and is almost insoluble in water.

TABLE 32

PHYSICAL PROPERTIES OF HYDROGEN

<i>B.p.</i> (°C)	<i>M.p.</i> (°C)	<i>Critical temp.</i> (°C)
-252.8	-259.1	-239.9

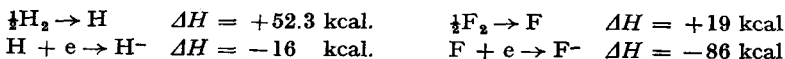
#### *Isotopes*

Hydrogen has three isotopes. The atom of deuterium,  ${}^2_1\text{H}$ , is about twice as heavy as that of ordinary hydrogen; tritium,  ${}^3_1\text{H}$ , three times as heavy. These uniquely large mass ratios are responsible for a difference in chemical properties between the isotopes of hydrogen far greater than that shown by the isotopes of any other element. However, so little deuterium and tritium are present in natural hydrogen ( $1.6 \times 10^{-4}$  and  $10^{-18}$  by weight respectively) that its properties are substantially those of  ${}^1_1\text{H}$  itself.

#### *The hydrogen ions $\text{H}^+$ and $\text{H}^-$*

With electron configuration  $1s^1$ , hydrogen nearly always forms covalent bonds; but positive and negative singly charged ions have been recognised. Loss of the electron leaves the proton  $\text{H}^+$ , the ionisation energy of the hydrogen atom being 13.6 eV. The proton exerts so strong a positive field that it is unable to exist alone in the presence of polarisable species. Thus the 'hydrogen ion' in water becomes  $\text{H}_3\text{O}^+$ , in ammonia  $\text{NH}_4^+$ , the proton being bonded to the molecule by a lone pair of electrons (p. 237).

The addition of an electron to the hydrogen atom produces the hydride ion,  $H^-$ , the electron affinity being 0.7 eV ( $\Delta H = -16$  kcal mole<sup>-1</sup>). This quantity and the dissociation energy of the hydrogen molecule,  $H_2 \rightarrow 2H$ , namely  $\Delta H = +104.5$  kcal, are of importance in a consideration of the heat of formation of metal hydrides. The figures can be compared with those for fluorine:



As the  $H^-$  ion is comparable in size with the  $F^-$  ion, the lattice energies of ionic hydrides and fluorides of the same structural type must be similar. Applying the Born-Haber cycle (p. 102) we can see that the formation of an ionic fluoride will release far more energy than will the formation of an ionic hydride. Nevertheless,  $H^-$  ions exist in alkali-metal hydrides. The hydride ion is large because of the mutual repulsion of the electrons, which offsets the nuclear attraction, but variable (from 1.26 Å in LiH to 1.54 Å in CsH) because the rather diffuse electron cloud is easily polarised.

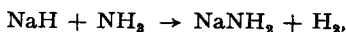
The  $H^-$  ion is an extremely strong base; the reaction



when represented



indicates that  $H^-$  is a stronger base than  $OH^-$  in aqueous solution. Similarly,



or



shows  $H^-$  to be a stronger base than  $NH_2^-$  in liquid ammonia.

### Ortho and para hydrogen

#### *Reason for the two forms*

Two hydrogen atoms combine to form the very stable hydrogen molecule (p. 97),  $2H(1s^1) \rightarrow H_2(\sigma 1s^2)$  with an energy drop of 104.5 kcal per mole. Heisenberg showed, however, that when nuclear spins are taken into account there are, in effect, two observable 'isomers'. These result from parallel coupling of the nuclear spins, with three possible quantum states; and antiparallel coupling, with only one (*cf.* p. 18). At room temperature, the different quantum states are about equally probable, but spontaneous transitions between them have a very low probability and can be ignored. Consequently, ordinary hydrogen behaves as though it were a mixture of 3 vol. *ortho* hydrogen (spins parallel) and 1 vol. *para* hydrogen (spins anti-

parallel). But, owing to symmetry, the allowed states of rotation of the molecule as a whole differ in the two instances, the lowest state being somewhat lower for the p- than for the o-form. Thus at very low temperatures, where the molecules tend to go into their lowest quantum states, the proportion of p-hydrogen tends towards 100%, when there would be true thermodynamic equilibrium. However, transition from one nuclear spin state to another is so slow (the collision 'half-life' at room temperature is several years) that the 3:1 proportion persists in metastable equilibrium during cooling. These conclusions are confirmed by measurements of conductance and specific heat, which are distinctly greater for the p- than the o-form (in contrast with the b.p. and m.p. which are slightly less). True equilibrium at any temperature is achieved in the presence of a catalyst: (i) activated charcoal at low temperature, or a transition metal at room temperature; (ii) atomic hydrogen; (iii) a paramagnetic substance such as  $O_2$  or NO. And it is also attained in the discharge tube or by heating to 800 °C or above. Thus, at 20 °K in the presence of active charcoal, 99.7% pure p-hydrogen results. On the other hand, concentration of o-hydrogen beyond 75% is impossible and its tabulated properties are those inferred from the mixture.

#### *Conversion of forms and its application*

The mechanism of conversion, which is exothermal in the direction o  $\rightarrow$  p, involves dissociation of the molecule and recombination of the atoms, during which the nuclear spins re-couple, parallel or anti-parallel, in equilibrium proportions. This occurs, for example, on collision (the high temperature mechanism); and probably in chemisorption, when the atoms are separated by going into different lattice sites and subsequently recombine with nuclear spins oppositely coupled.

Knowledge of the two forms of molecular hydrogen has found industrial application. As stated, the change o- $H_2 \rightarrow$  p- $H_2$  is exothermal, but so slow that it takes about a month for normal 25% p-liquid to be converted to 90% p-liquid. The energy released by the change is sufficient to evaporate 64% of the original liquid. Hence to keep liquid hydrogen without loss constant refrigeration is necessary. However a rapid and effective catalyst, a hydrous iron(III) oxide, has been developed which enables normal hydrogen to be converted to 99% p-hydrogen during liquefaction. The change greatly facilitates the storage of liquid by making it unnecessary to refrigerate to prevent loss by boiling.

#### *Ortho and para deuterium*

Deuterium also exists in ortho and para forms, but the ortho form is the

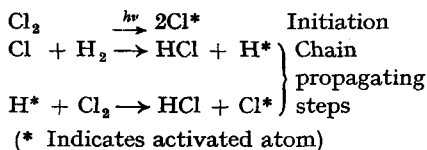
more stable at low temperatures. The equilibrium mixture at elevated temperatures contains 33.3% of para deuterium.

The ortho forms of both hydrogen and deuterium have a small magnetic moment due to the nuclear spins of the two being of the same sense; the para forms have none. Nonetheless, hydrogen is essentially diamagnetic as it is without unpaired electrons, and the magnetic moment of a nucleus is very much less than that of an electron.

Strictly, hydrogen and deuterium are not unique, and nuclear spins should be recognised in discussing other molecules. But only with a low moment of inertia is the separation of rotational energy states large enough to give one form an appreciable preference, and then only at low temperatures. Ortho and para forms of  $F_2$ ,  $Cl_2$  and  $N_2$  have been distinguished at very low temperatures; but generally the 'high temperature' mixture is the equilibrium form for all readily accessible temperatures and accordingly the nuclear spins may be disregarded.

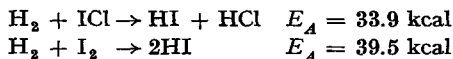
### Reactions of hydrogen

Hydrogen is relatively unreactive at ordinary temperatures. Apart from fluorine, which spontaneously explodes with hydrogen in the dark, the other strongly electronegative elements react with hydrogen only on heating or on irradiation. Combination with chlorine, which is started by light or heat, is a simple chain reaction:



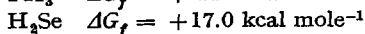
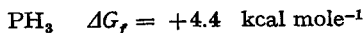
With bromine and with oxygen the chain reactions are more complex.

Combination with nitrogen (p. 263) and the hydrogenation of gaseous hydrocarbons occur on surface-catalysts. Only a few reactions of hydrogen are known to involve  $H_2$  molecules:



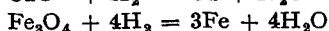
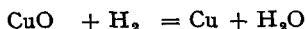
For these the activation energies ( $E_A$ ) amount to about 25–30% of the sum of the bond energies, the usual value for reactions of this type.

The comparatively unreactive character of hydrogen in the absence of catalysts arises largely from the strength of the H–H bond (104.5 kcal); which also accounts for the low thermal stabilities of many hydrides, for instance:



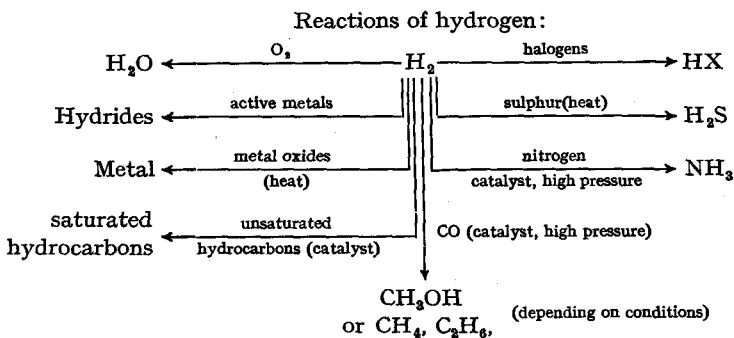
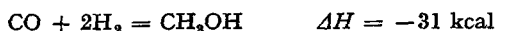
Of the metals, most of those in Gps. IA, IIA, IIIA, IVA and VA and also the lanthanides and actinides combine exothermally with hydrogen under suitable conditions.

Hydrogen reduces many metal oxides to metal at moderate temperatures:



But it is not as effective a reducing agent as carbon at high temperatures (p. 373).

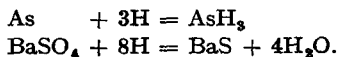
Hydrogen reacts with carbon monoxide to give a variety of products, depending on the conditions; the most important of these reactions is that used for the production of methanol:



### Atomic hydrogen

The hydrogen molecules are dissociated into atoms by heat, by radiation of a specific wave length, and by an electric discharge at low pressure. The atoms do not combine on collision because the energy set free, 104.5 kcal per mole, causes immediate redissociation when converted into vibrational energy. For recombination to take place a third body must be present to absorb the excess of energy. The lifetime of a hydrogen atom at room temperature, even at low pressures, is short on account of the catalytic combination of atoms on the walls of the vessel.

Atomic hydrogen is a stronger reducing agent than  $\text{H}_2$ : unlike the latter it combines directly with Ge, Sn, As, Sb, Te:



It does not form a hydride with either lead or bismuth.

#### *Atomic hydrogen torch*

Langmuir showed that a considerable proportion of the hydrogen passed through an arc between tungsten electrodes is split into atoms even with the gas at one atmosphere pressure. If this stream of partly atomised gas is directed on to a metal surface, the heat of combination is sufficient to produce a high temperature. This is the principle of the hydrogen torch, used in welding metals, which in action surrounds the weld with an atmosphere of the molecular hydrogen and thus prevents surface oxidation. It is especially applicable to such metals as aluminium which are readily oxidised but which do not easily absorb hydrogen.

### Deuterium

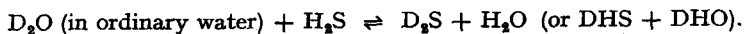
The isotope  ${}^2_1\text{H}$  was observed spectroscopically in 1931 and the preparation of nearly pure  $\text{D}_2\text{O}$  was achieved two years later by prolonged electrolysis of an 0.5 M NaOH solution between nickel electrodes. Three factors favour the liberation of  $\text{H}_2$  at the cathode rather than  $\text{D}_2$ :

- (i)  $\text{H}_2\text{O}$  is more readily reduced than  $\text{D}_2\text{O}$ :  $\text{H}_2\text{O} + e \rightarrow \text{OH}^- + \text{H}$ ;
- (ii) the activation energy for  $\text{H} + \text{H} \rightarrow \text{H}_2$  is less than for  $\text{D} + \text{D} \rightarrow \text{D}_2$ ;
- (iii) HD exchanges with the  $\text{H}_2$  of water:  $\text{HD} + \text{H}_2\text{O} \rightarrow \text{HDO} + \text{H}_2$ .

Differences in overvoltage (the potential arising from the non-reversible nature of the electrode processes) are probably not of major importance since the material of the cathode does not affect the separation factor.

The concentration of  $\text{D}_2$  in ordinary water was attained by successively reducing the original volume to about one seventh by electrolysis. As the electrolysis proceeds the proportion of  $\text{D}_2$  in the evolved gas rises. When it reaches 0.02%, the gas is burnt in oxygen and the  $\text{H}_2\text{O}/\text{D}_2\text{O}$  mixture added to the electrolyte of an earlier stage. Such an electrolytic separation has produced most of the considerable quantities of  $\text{D}_2\text{O}$  already in use for 'moderating' fast neutrons in heavy-water atomic reactors.

Heavy water is also produced by the Spevack method which uses the exchange reaction:



A temperature of  $100^\circ$  favours the forward reaction. The equilibrium mixture of sulphides is passed into water at  $25^\circ$ , when the reverse reaction is favoured.

Continued cycles lead to a liquid containing  $\sim 2\%$   $D_2O$  which is concentrated to 90% by fractional distillation and to 99.8% by electrolysis.

The physical properties of  $D_2O$  differ slightly from those of  $H_2O$  (Table 33).

TABLE 33  
PHYSICAL PROPERTIES OF  $H_2O$  AND  $D_2O$

	<i>B.p.</i> ( $^{\circ}C$ )	<i>M.p.</i> ( $^{\circ}C$ )	<i>S.g.</i> ( $20^{\circ}C$ )
$H_2O$	100	0	0.998
$D_2O$	101.4	3.8	1.106

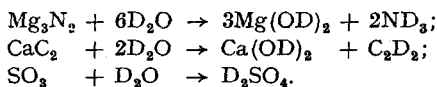
Its dielectric constant is about 2% below that of  $H_2O$ , making the liquid a slightly poorer ionising solvent; the autoprotolysis constant (p. 240)  $[D_3O^+][OD^-]$ , is  $3 \times 10^{-15}$  at  $25^{\circ}$ , and the solubilities of electrolytes are correspondingly less than in water. For instance, the solubility of NaCl at  $25^{\circ}$  in  $H_2O$  is 35.9 g/100 g, in  $D_2O$ , 30.9 g/100 g.

Deuterium gas is made by the electrolysis of  $D_2O$  containing some  $P_2O_5$ . The b.p., m.p., latent heats of fusion and evaporation, and heat of dissociation of  $D_2$  are all higher than those of  $H_2$  (Table 34).

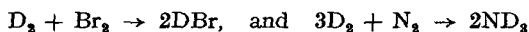
TABLE 34  
PHYSICAL PROPERTIES OF  $H_2$  AND  $D_2$

	<i>B.p.</i> ( $^{\circ}K$ )	<i>M.p.</i> ( $^{\circ}K$ )	<i>Latent heat of fusion</i> ( <i>cal/mole</i> )	<i>Heat of dissociation</i> ( <i>kcal/mole</i> )
$H_2$	20.4	13.95	28	104.5
$D_2$	23.5	18.65	52	104.9

Deuterium compounds are exactly analogous to those of hydrogen, and are often obtained directly from  $D_2O$ :



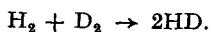
Deuterium is somewhat less reactive than hydrogen. Activation energies for reactions such as



are greater than for those with  $H_2$ . In keeping with this, the adsorption of deuterium on an active surface is slower than that of hydrogen.

### Exchange reactions

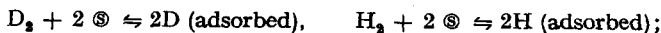
When  $H_2$  and  $D_2$  are mixed at a sufficiently high temperature, exchange occurs:



Many such exchange reactions are known; the one above is almost certainly an atomic reaction with a chain mechanism:

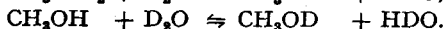
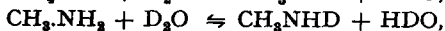
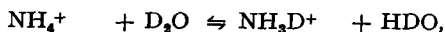


Exchange on a catalytic surface is also common. Deuterium replaces hydrogen in water, ammonia, methane and other simple hydrides on the surface of metals such as platinum and nickel which are good catalysts for hydrogenation. The exchange of adsorbed deuterium with gaseous hydrogen on finely divided nickel is almost certainly an adsorption-desorption process:

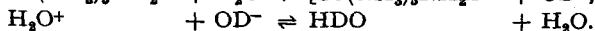
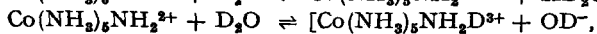
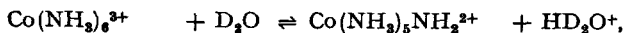


Ⓢ represents an empty site.

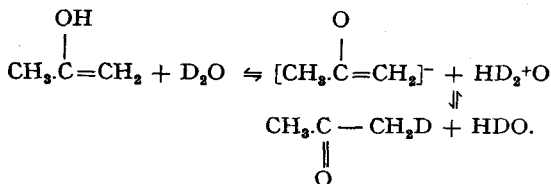
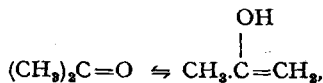
Heavy water exchanges deuterium with compounds containing labile hydrogens:



The suggested mechanism of exchange between  $D_2O$  and the hexa-ammine-cobalt(III) ion is



But the hydrogen atoms of alkyl groups do not exchange readily unless enol-keto tautomerism occurs:



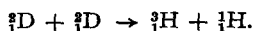
The rate of this reaction is measured by isolating some of the reaction



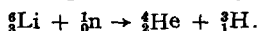
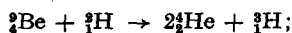
product in the pure state, burning it to produce  $\text{H}_2\text{O}$  and  $\text{HDO}$ , and determining the deuterium present by density or with the mass spectrometer. Here deuterium is, in fact, being used as a non-radioactive tracer.

### Tritium

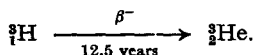
The heaviest isotope of hydrogen, tritium, was first made (1934) by bombarding deuterium compounds with deuterons:



Certain other nuclear reactions lead to tritium formation:



The second of these, the bombardment of lithium-6 with neutrons in an atomic reactor, has been extensively used in its production; the tritium is adsorbed by uranium metal and released by heating. The nuclide is a low-energy  $\beta$ -emitter (0.018 MeV) with a half-life of 12.5 years:



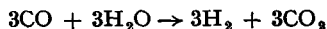
Tritium has proved a useful tracer, since the amount of it in a compound can be deduced from its  $\beta$ -activity. For the measurement of such low-energy radiation either gas-counting or liquid-scintillation counting is used.

### Industrial production and uses of hydrogen

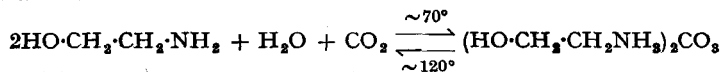
Hydrogen is manufactured principally by the steam-hydrocarbon process, based on the mixture of hydrocarbons discarded in the 'cracking' of crude petroleum. This material is freed from sulphur by passing it over bauxite at  $400^\circ$  to convert sulphur compounds to  $\text{H}_2\text{S}$  which is removed by a caustic scrubbing. The vapour along with steam then goes over a nickel catalyst at  $800^\circ$  and reactions occur exemplified by:



To the hot gases leaving the furnace, steam is added in order to reduce the temperature to  $400^\circ$ , when a second reaction occurs:



The hydrogen is freed from  $\text{CO}_2$  by scrubbing the gases with aqueous ethanolamine



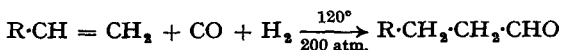
From this the  $\text{CO}_2$  is subsequently recovered by heating the solution to  $120^\circ$ . In industrial practice, further  $\text{CO} \rightarrow \text{CO}_2$  stages are necessary to complete the removal of  $\text{CO}$ .

Vast quantities of hydrogen are produced in refining processes associated with the petroleum industry and designed to increase the octane number of the product. Typical reactions are the dehydrogenation of naphthalenes and paraffins to aromatic hydrocarbons:

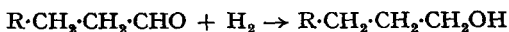


Industrial hydrogen is used mainly in catalytic hydrogenation processes:

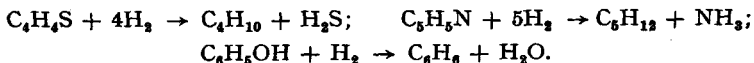
- (i)  $\text{N}_2 \rightarrow \text{NH}_3$  (Haber process);
- (ii)  $\text{CO} \rightarrow \text{CH}_3\text{OH}$  (Methanol process);
- (iii) Unsaturated vegetable oils  $\rightarrow$  saturated fats (particularly for margarine).
- (iv) The 'oxo' process: the hydroformylation of alkenes to aldehydes and to alcohols. In this a mixture of  $\text{H}_2$  and  $\text{CO}$  is added to the alkene in the presence of cobalt catalyst:



If the temperature is increased to  $185^\circ$  the main product is the alcohol:



The active catalyst in the reaction is probably  $\text{Co}_2(\text{CO})_8$  (p. 406). Besides other synthetic purposes, hydrogen finds use in the removal of sulphur, nitrogen and oxygen from petroleum feed stocks by the catalytically promoted reactions:



#### FURTHER READING

- A. FARKAS, *Orthohydrogen, Parahydrogen and Heavy Hydrogen*, Cambridge, University Press, 1935.
- J. HALPERN, *Homogeneous Reactions of Molecular Hydrogen in Solution*, *Quart. Rev.*, 10 (1956) 463.
- G. C. PIMENTEL AND A. L. MCCLELLAN, *The Hydrogen Bond*, San Francisco, Freeman, 1960.
- D. D. ELEY, *Mechanisms of Hydrogen Catalysis*, *Quart. Rev.*, 3 (1949) 209.
- B. SIEGEL, *Hydride Formation by Atomic Hydrogen Reactions*, *J. Chem. Ed.*, 38 (1961) 496.

## Chapter 13

# The Hydrides

### GENERAL

#### The four types of hydride

Hydrides are broadly of four types, *saline*, *metallic*, *molecular* and *polymeric* (Table 35).

TABLE 35  
TYPES OF HYDRIDES

Type	Physical character	Bonding	Examples
Saline	Salt-like, Resemble chlorides	Largely ionic	NaH, CaH <sub>2</sub>
Metallic	Metallic appearance. Brittle. Conductors or semiconductors	Partly ionic, with residual metallic bonds	TiH <sub>1.73</sub> PrH <sub>2.7</sub>
Polymeric	Solids, Non-conductors	Covalent, hydrogen-bridged	(AlH <sub>3</sub> ) <sub>x</sub>
Molecular	Gases or volatile liquids	Covalent	NH <sub>3</sub> , H <sub>2</sub> O.

Saline hydrides are formed by elements with electronegativities in the range 0.9 to 1.2: such are the alkali metals, the alkaline earth metals and the lanthanides. They have ionic lattices, high melting points and, when fused, are electrolytes.

Metallic hydrides, characteristic of some of the transition metals with electronegativities in the range 1.2 to 1.4, are in effect alloys and are non-stoichiometric.

Most of the saline and metallic hydrides can be made by heating the metal in hydrogen or by electrodeposition of hydrogen on a metal cathode, when the hydrogen atoms produced by the discharge of the ions penetrate the metal lattice. With the exception of palladium, which has a low electronegativity for its place in the Periodic Table, transition metals of Gps. VI, VII and VIII do not combine with hydrogen.

Molecular hydrides are formed by most elements of the B groups from

IIIB to VIIB. They are covalent compounds and usually gases at room temperature.

Polymeric hydrides are formed by some elements with electronegativities in the range 1.4 to 2.0. They are solids containing molecules linked together in 2- and 3-dimensional patterns by hydrogen-bridge bonds.

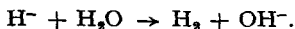
### THE SALINE HYDRIDES

These are crystalline compounds made by heating the metal in hydrogen; calcium, for instance, reacts at 150°. Those of the alkali metals, XH, have the sodium chloride type lattice (p. 104); those of the Gp. IIA metals are less regular. All have stoichiometric compositions and the crystals are ionic, being somewhat denser than the metal from which they are made owing to the strong polar bonds in the ionic lattice.

Those stable in the fused state (LiH), or when dissolved in a suitable melt (CaH<sub>2</sub>), yield hydrogen at the anode on electrolysis in accordance with Faraday's laws, the ionisation being:



The hydrides of lithium, calcium and strontium are the most stable of this class; others undergo thermal decomposition above 400°. All are oxidised by air and some ignite spontaneously at room temperature; all react vigorously with water. The reaction is essentially:



Lithium, alone of the Group IA hydrides, has a heat of formation comparable with those of the Group IIA compounds.

Lithium hydride and sodium hydride are used in making the valuable reducing agents lithium aluminium hydride, LiAlH<sub>4</sub>, and sodium borohydride, NaBH<sub>4</sub>.

TABLE 36  
HEATS OF FORMATION OF THE SALINE HYDRIDES  
(kcal/mole hydrogen)

LiH	NaH	KH	RbH	CsH	CaH <sub>2</sub>	SrH <sub>2</sub>	BaH <sub>2</sub>
21.6	13.9	14.1	13.5	13.0	45.1	42.3	40.9

It is doubtful whether the hydrides of the lanthanides are truly ionic. The heats of formation of some are high, that of the cerium compound

$\text{CeH}_{2.8}$  being 42.3 kcal/mole. However, most of them resemble the metallic hydrides in being non-stoichiometric. But as regards composition much depends on mode of preparation; a titanium hydride, precisely  $\text{TiH}_2$ , has been made from the carefully purified elements.

A similar uptake of hydrogen occurs in the actinide series; uranium absorbs it rapidly at  $250^\circ$  to give a black powder  $\text{UH}_3$ , which decomposes at  $450^\circ$ , leaving the metal as a highly reactive powder. This hydride has a cubic lattice. It is a strong reducing agent, converting silver nitrate, copper sulphate and mercury(II) chloride to the respective metals. Its specific gravity is about 11, compared with 18.7 for uranium itself.

### THE METALLIC HYDRIDES

Reversible adsorption or occlusion of hydrogen by metals is common, particularly in those belonging to the transition series. Palladium is the most striking example; during electrolysis a cathode of the metal absorbs about 800 times its volume of hydrogen. The hydrogen thus taken up can usually be removed by heating in a vacuum but traces are often tenaciously retained. Iron, palladium and platinum are permeable to hydrogen at high temperatures. The properties of the metallic hydrides are not very different from those of the parent metals. Their compositions are not stoichiometric.



The metal lattices are expanded but otherwise little distorted by the introduction of hydrogen; the densities are below those of the parent metal. Many are interstitial compounds but with lanthanide and actinide hydrides the high heats of formation suggest that the bonding is to a certain degree ionic. They are probably best considered as lanthanide metals containing ionic  $\text{LnH}_3$  phases.

Palladium hydride has a long history. Gillespie and Hall (1926) obtained pressure-composition curves (Fig. 162) suggesting the formation of two solid solutions; one at  $250^\circ$ , stoichiometrically  $\text{Pd}_2\text{H}$ , a second at  $180^\circ$  with a composition approaching  $\text{PdH}_{0.6}$ . Metallic palladium is face-centred cubic, and the absorption of hydrogen increases the lattice parameter from 3.883 Å to 3.894 Å without a change of phase, but further absorption so strains the metallic lattice as to cause a sudden increase to 4.018 Å with the appearance of a  $\beta$ -phase.

Iron behaves similarly; there is a sudden increase in the uptake of hydrogen at about  $900^\circ$ , just the transition temperature of the  $\alpha$ - $\gamma$  phase change, followed by an equally sudden release of hydrogen at about  $1400^\circ$ ,

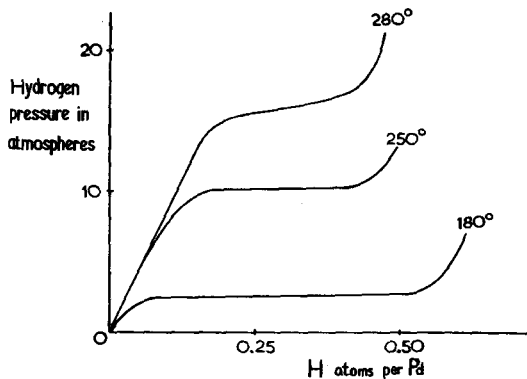


Fig. 162. Pressure-composition curves for hydrogen-palladium system.

the  $\gamma$ - $\delta$  transition temperature. Both the  $\alpha$  and  $\delta$  phases are body-centred cubic. The  $\gamma$  phase is face-centred; so presumably there is greater interstitial space in that phase.

In many metallic hydrides, the hydrogen nuclei are more tightly packed than in solid hydrogen itself. The hydrogen is, in effect, compressed at many hundred atmospheres pressure, and the materials can be used as sources of pure hydrogen.

There are many 'borderline' hydrides of metals which are difficult to classify. A good example is copper hydride,  $\sim \text{CuH}$ , made by mixing lithium aluminium hydride, dissolved in pyridine and ether with copper(I) iodide in pyridine:



The blood-red solution formed yields a bright-red, crystalline solid when more ether is added. The solid, stable below  $50^\circ$ , decomposes rapidly above  $100^\circ$ . It is copper(I) hydride, which is stoichiometrically deficient in hydrogen,  $\text{CuH}_{0.96}$ , and has a low heat of formation ( $\Delta H_f = -5.1$  kcal/mole). The compound does not resemble the saline hydrides.

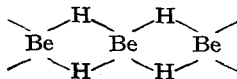
## THE COVALENT HYDRIDES

In many instances one element forms both molecular and polymeric hydrides, which makes it convenient to treat both types under the heading of covalent hydrides. We shall deal with them by Periodic Groups.

### Polymeric hydrides of beryllium and magnesium

Beryllium hydride, empirically  $\text{BeH}_2$ , cannot be made by the action of hydrogen on the metal, but tert-butylberyllium,  $((\text{CH}_3)_3\text{C})_2\text{Be}$ , formed when  $\text{BeCl}_2$  reacts with  $(\text{CH}_3)_3\text{CMgCl}$ , decomposes at  $100^\circ$  to give the white solid  $\text{BeH}_2$  and isobutene. The hydride is stable to  $240^\circ$  and is hydrolysed only slowly by water, though faster by acids. Magnesium hydride,  $\text{MgH}_2$ , also a white solid of moderate thermal stability, is best made by the decomposition of magnesium dialkyls.

The structure of  $\text{BeH}_2$  and  $\text{MgH}_2$  are not known but the compounds are most probably polymers, with hydrogen-bridged chains:



The structure should be compared with that of diborane  $\text{B}_2\text{H}_6$  (p. 271).

### Hydrides of boron (boranes)

The structures and reactions of the hydrides of boron are of great interest. They have been the object of much research, and several new hydrides have been made relatively recently. Six of them were discovered by Stock (1914-20) whose starting material was the gaseous product of the reaction between magnesium boride and dilute hydrochloric acid. They were  $\text{B}_2\text{H}_6$ ,  $\text{B}_4\text{H}_{10}$ ,  $\text{B}_5\text{H}_9$ ,  $\text{B}_5\text{H}_{11}$ ,  $\text{B}_6\text{H}_{10}$  and  $\text{B}_{10}\text{H}_{14}$ . Stock's remarkable success was due to a vacuum technique which he developed for handling compounds sensitive to oxygen and moisture. Monomeric  $\text{BH}_3$  was not found; there would be insufficient electrons in such a molecule to stabilise the bonding in the way it is stabilised in the monomeric boron halides (p. 341).

Most of the boranes which have been fully characterised belong to either the  $\text{B}_n\text{H}_{n+4}$  or the  $\text{B}_n\text{H}_{n+6}$  series:

(i)  $\text{B}_n\text{H}_{n+4}$  series:

$\text{B}_2\text{H}_6$  (gas)  $\text{B}_5\text{H}_9$ ,  $\text{B}_6\text{H}_{10}$ ,  $\text{B}_8\text{H}_{12}$  (liquids)  $\text{B}_{10}\text{H}_{14}$ ,  $\text{B}_{18}\text{H}_{22}$  and iso- $\text{B}_{18}\text{H}_{22}$  (solids)

(ii)  $\text{B}_n\text{H}_{n+6}$  series:

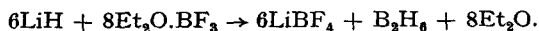
$\text{B}_4\text{H}_{10}$ ,  $\text{B}_5\text{H}_{11}$ ,  $\text{B}_6\text{H}_{12}$ ,  $\text{B}_9\text{H}_{15}$  (liquids)  $\text{B}_{10}\text{H}_{16}$ ,  $\text{B}_{20}\text{H}_{26}$  (solids)

In addition to the above, the structure of the solid,  $\text{B}_{20}\text{H}_{16}$ , has been determined.

The usual terminology is di-, tetra-, penta- (etc.) borane to signify the number of boron atoms, followed by a numeral to show the number of hydrogen atoms: thus  $\text{B}_{10}\text{H}_{14}$  is written decaborane-14.

Generally speaking, the stabilities of the hydrides increase with their molar mass. However, members of the  $B_nH_{n+4}$  series are more stable than those of the  $B_nH_{n+6}$  series which have about the same mass. Thus pentaborane-9 decomposes slowly even at  $150^\circ$ , and is hydrolysed by water only on prolonged heating, whereas pentaborane-11 decomposes rapidly at  $25^\circ$  and is hydrolysed immediately by cold water.

The boranes, with the exception of  $B_6H_{10}$ , are no longer made by Stock's method. The starting material for them is diborane,  $B_2H_6$ , for which the best method of large scale preparation is to add the boron trifluoride-ether complex slowly to a suspension of lithium hydride in ether and gently reflux the mixture:



Ethane, usually present as an impurity, is removed by passing the products into dimethyl ether at  $-80^\circ$ , to form a solid complex,  $BH_3 \cdot Me_2O$ , from which the ethane may be pumped. The complex is decomposed by warming and the diborane purified by fractional distillation.

The higher boranes listed above, with the exception of the two  $B_{18}H_{22}$  isomers, are made by heating diborane alone or with hydrogen. Thus when passed through a tube at  $115^\circ$ , diborane is largely converted to pentaborane-11. This, warmed with hydrogen at  $100^\circ$ , gives tetraborane with some diborane:

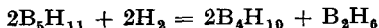


TABLE 37

## REACTIONS OF DIBORANE

$B_2H_6$	$\xrightarrow{H_2 + \text{heat}}$	higher boranes
	$\xrightarrow{H_2O}$	$H_3BO_3 + H_2$
	$\xrightarrow{NaH}$	$Na^+BH_4^-$
	$\xrightarrow{BMe_2}$	$B_2H_2Me_4$
	$\xrightarrow[120^\circ]{NH_3}$	$(NH_3)_2BH_2 + BH_4^-$
	$\xrightarrow{NMe_3}$	$Me_3N + BH_3^-$
	$\xrightarrow{BX_3}$	$B_2H_5X$ (X = Cl and Br)
	$\xrightarrow{\text{alkenes}}$	alkyl borons
	$\xrightarrow[100^\circ \text{ 20 atm.}]{CO}$	$H_3BCO$

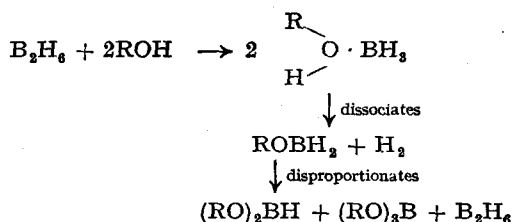


When, however, diborane and hydrogen are passed through a tube at 200°, pentaborane-9 is obtained. Kinetic studies suggest the changes involve a radical mechanism with perhaps borine,  $\text{BH}_3$ , as an intermediate, though direct evidence of this entity is wanting. At higher temperatures the boranes give non-volatile products of variable composition,  $(\text{BH}_x)_n$ . At 700°, the breakdown of these materials to boron and hydrogen is complete.

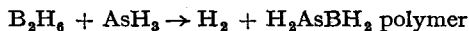
When kept dry at room temperature, diborane suffers about a 10% decomposition per year, but with water it hydrolyses rapidly to boric acid and hydrogen. Like the two pentaboranes it burns spontaneously in air.

In general, the reactions of boranes fall into two classes:

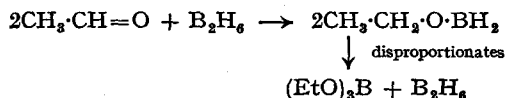
- (i) Those in which a  $\text{BH}_3$  group is removed from the borane, often by a nucleophile to give first an adduct, which then dissociates or decomposes.



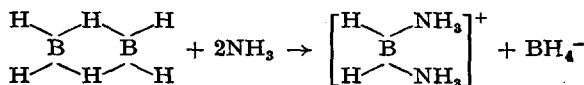
Related reactions occur with molecules whose donor power is insufficient to allow stable adducts to be formed:



With unsaturated ligands, irreversible decomposition of the adduct often occurs by the transfer of hydrogen from a boron atom to the ligand:



- (ii) Those in which hydrogen-bridge bonds are cleaved unsymmetrically. This probably occurs in the ammonia-diborane reaction



### Structures

Considerable interest has centred on the structures of the boranes. They are all electron-deficient compounds; that is they have too few valency electrons to permit every one of the adjacent atoms to be held together by electron-pair bonds. Diborane has been the most studied and much

evidence has accumulated for a double hydrogen-bridge at right angles to the plane of the other four hydrogen atoms (Fig. 163).

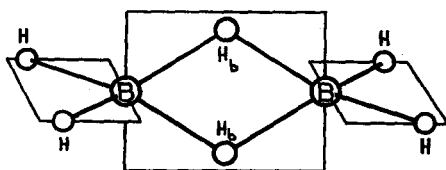


Fig. 163. Hydrogen-bridged structure of diborane.

The presence of two kinds of boron-hydrogen bond is indicated both by the Raman spectrum and by the chemical evidence that four only of the hydrogen atoms in the molecule are replaceable by methyl groups. Electron diffraction leads to the parameters: B-H 1.19 Å, B-H<sub>b</sub> 1.33 Å, B-B 1.77 Å, ∠HBH 121.5° and ∠H<sub>b</sub>BH<sub>b</sub> 100°. Raman and infrared spectra of the tetramethyl compound suggest an absence of terminal hydrogen atoms, and electron diffraction shows the four carbon atoms and two boron atoms to be coplanar. Although a double hydrogen bridge is certain, the precise

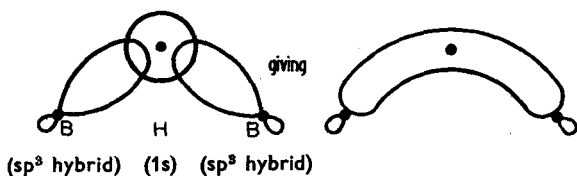


Fig. 164. Contributions to molecular orbitals in diborane.

nature of the bonds involved is still uncertain. Clearly they are abnormal and a suggestion is that they are formed by an overlap of the sp<sup>3</sup> tetrahedral hybrids and hydrogen 1s orbitals. Each electron pair is then less localised than usual, extending over three centres (Fig. 164). This accounts for the symmetry and absence of free rotation between the boron atoms.

The boron skeletons of the higher boranes can be considered as fragments of octahedra (B<sub>5</sub>H<sub>9</sub> and B<sub>10</sub>H<sub>16</sub>) or of icosahedra. The B<sub>12</sub>H<sub>12</sub><sup>2-</sup> ion present in K<sub>2</sub>B<sub>12</sub>H<sub>12</sub> (p. 279) is almost perfectly icosahedral (Fig. 165). The structural relation of B<sub>10</sub>H<sub>14</sub> and B<sub>6</sub>H<sub>10</sub> to the B<sub>12</sub>H<sub>12</sub><sup>2-</sup> ion are shown in the diagram (Fig. 166). At each corner of the figures is a boron atom which is attached to a hydrogen atom 1.20–1.30 Å away; the hydrogen-bridge bonds are shown as curves. The actual structures are somewhat less regular than in the simplified illustrations. In B<sub>10</sub>H<sub>14</sub>, for example, the B-B distances vary from 1.71 Å for the 1–3 distance to 2.01 Å for the 5–10 and 7–8 distances.

The straight lines do not represent bonds; the nature and disposition of the bonds are discussed below.

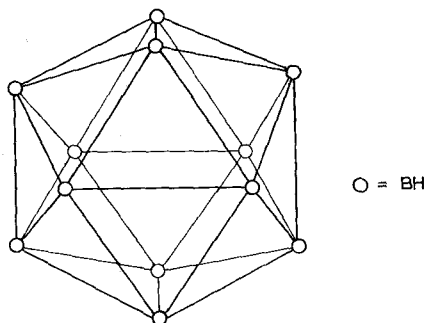
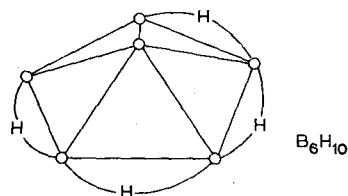


Fig. 165. The  $B_{12}H_{12}^{2-}$  ion.



BH at every apex

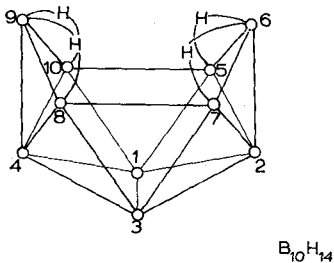
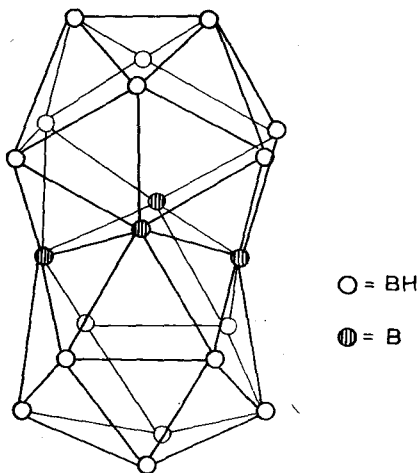
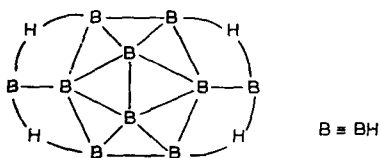
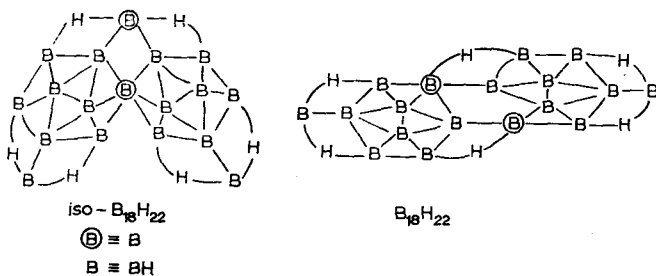


Fig. 166. Structures of  $B_6H_{10}$  and  $B_{10}H_{14}$  in which the circles indicate BH and  $\curvearrowright$  a hydrogen bridge bond (Cf.  $B_{12}H_{12}^{2-}$  in Fig. 165).

The structure of  $B_{20}H_{16}$ , the only borane yet characterised which has fewer hydrogen atoms than boron atoms in the molecule, consists of two large isocahedral fragments fused together (Fig. 167).

There are two isomeric boranes of formula  $B_{18}H_{22}$ . The relation of their structures to that of  $B_{10}H_{14}$  is shown in the form of planar projections (Fig. 169) of the molecules, which can be considered as  $B_{10}H_{14}$  molecules (Fig. 168) joined at two boron atoms originally hydrogen-bridged.

Fig. 167. Structure of B<sub>20</sub>H<sub>18</sub>.Fig. 168. Planar projection of B<sub>10</sub>H<sub>14</sub> molecule (B indicates BH).Fig. 169. Planar projections of B<sub>18</sub>H<sub>22</sub> and iso-B<sub>18</sub>H<sub>22</sub>  
(B in circle indicates B, and B indicates BH).*Some other borane structures*

The structure of B<sub>4</sub>H<sub>10</sub> is shown in Fig. 170.

B<sub>10</sub>H<sub>16</sub> consists of two square pyramids like those in Fig. 171 joined by a B-B bond at their apices.

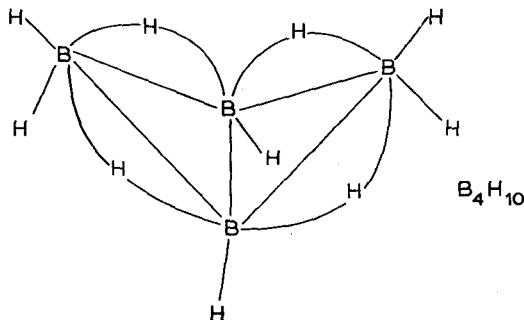


Fig. 170. The structure of  $B_4H_{10}$ . The bond angles are such that the boron skeleton can be considered to be either an octahedral or an icosahedral fragment.

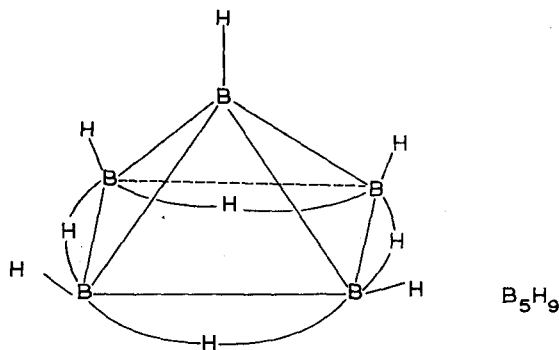
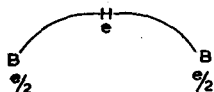


Fig. 171. The structure of  $B_5H_9$ .

Many of the atoms in borane molecules are obviously joined by bonds quite different in type from the sigma- and pi-bonds used in describing carbon compounds. The 'end' B-H bonds can be considered as normal, two-centre bonds in which two electrons are used to make a bonding MO. But to describe hydrogen-bridge bonding and also the boron-boron bonds, the concept of three-centre bonds is useful. In these bonds three atoms are bound together by two electrons. The three-centre bonds are considered to be of three types:

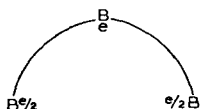
(a) The hydrogen-bridge bonds described above in which a hydrogen s-orbital overlaps hybrid orbitals of two boron atoms, each of which contributes the equivalent of one-half electron:



(b) Closed three-centre bonds formed by the overlap of boron hybrid orbitals containing both s and p contributions:



(c) Open three-centre bonds formed by the overlap of hybrid orbitals on two of the boron atoms with a p orbital on the third atom:



The structure of  $B_{10}H_{14}$ , described in bonds of these types, is shown in Fig. 172.

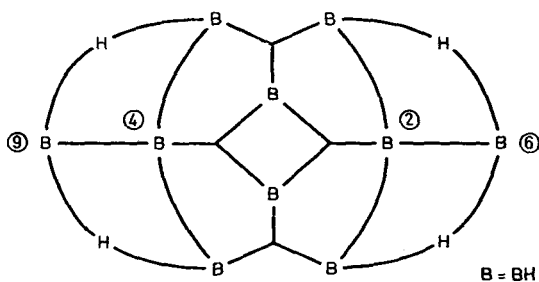


Fig. 172. Topological drawing of  $B_{10}H_{14}$  (B indicates BH).

This topological diagram is something of an oversimplification. A more realistic approach would be to imagine the boron atoms in such large icosahedral fragments as being bound by 'multicentre' bonds. Nevertheless the three-centre bond approach does predict correctly that atoms 6 and 9 should constitute the most positive positions in  $B_{10}H_{14}$ —these are the points at which nucleophiles attack the molecule—and that 2 and 4 should be the most negative, again in agreement with experiment.

### Compounds derived from boranes

#### Carboranes

These are compounds in which boron atoms of boranes are replaced by carbon atoms without loss of the structure based on the icosahedron or an icosahedral fragment.

Decaborane-14 reacts with acetonitrile to give  $(\text{MeCN})_2\text{B}_{10}\text{H}_{12}$  (Fig. 173).

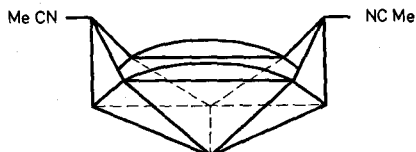
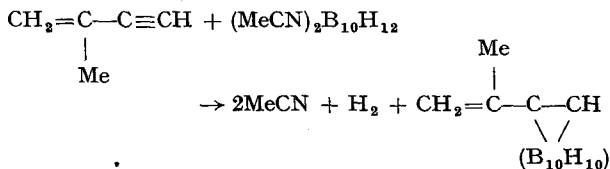


Fig. 173. Structure of  $(\text{MeCN})_2\text{B}_{10}\text{H}_{12}$  (BH at every apex).

due to a nucleophilic attack at boron atoms 6 and 9.

This compound reacted with isopropenylacetylene in benzene in a sealed vessel at  $80^\circ$  to give a product without either a triple bond or a bridge hydrogen.



It was the first example of a series of compounds called the carboranes. The parent substance, of this series, carborane-10, made by the action of acetylene on  $(\text{MeCN})_2\text{B}_{10}\text{H}_{12}$ , has a distorted icosahedral structure (Fig. 174).

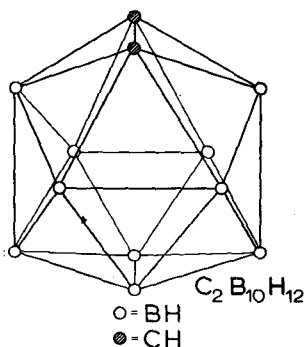


Fig. 174. The structure of 1,2-dicarboclovedecaborane.

The diagram (Fig. 174) represents the 'ortho' isomer, for which the name 1,2 dicarbaclovodecaborane has been proposed. Two other isomers, the 'meta', or 1,7 compound, and the 'para' or 1,12, can be obtained by heating the 'ortho' carborane. Other series of carboranes have been made in which the skeleton comprises only a fragment of an icosahedron.

### Nitrogen derivatives

The reaction between ammonia and diborane depends upon the conditions. Excess of ammonia at low temperatures produces the salt-like diammoniate,  $[(\text{NH}_3)_2\text{BH}_2]^+\text{BH}_4^-$ , because with  $\text{NH}_3$  there is an unsymmetrical cleavage ( $\text{BH}_2^+ + \text{BH}_4^-$ ) in contrast to the symmetrical one ( $\text{BH}_3 + \text{BH}_3$ ) resulting from reactions with amines. The monomer  $\text{BH}_3\cdot\text{NH}_3$  has indeed been made by the action of an ammonium halide on a borohydride:



At higher temperatures excess of ammonia gives boron nitride, BN. When, however, the proportions are two molecules of ammonia to one of diborane, the volatile cyclic borazine is produced in yields up to 45%. In this compound the boron and nitrogen atoms are all in trigonal ( $\text{sp}^2$ ) valence states, the 2p lone pairs on the three nitrogens providing  $6\pi$  electrons as in benzene. The boron-nitrogen and carbon-carbon analogues are isoelectronic and compounds of this kind show certain similarities, but because the boron-nitrogen

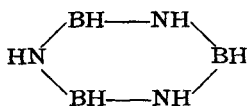


Fig. 175. Borazine.

bond is between atoms of different electronegativity and has an unsymmetrical charge cloud it is decidedly weaker. This is true even in borazine, although the bonds in it are non-localised. Consequently borazine is considerably more reactive than benzene, forming addition compounds with hydrogen halides, methanol, water and methyl iodide.

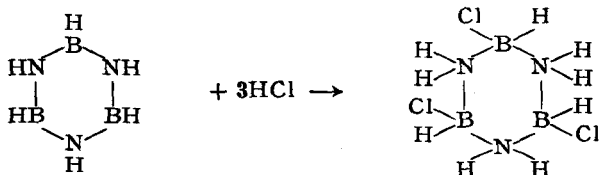


Fig. 176. Addition compound of borazine with HCl.



The hydrochloride loses hydrogen at 50° giving the symmetrical trichloroborazine:

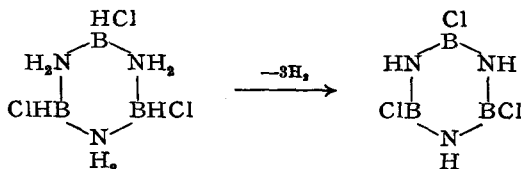


Fig. 177. Dehydrogenation of the hydrochloride of borazine.

### *Phosphorus and arsenic derivatives*

Development from aminoboron chemistry led to phosphino- and arsino-boron compounds. Diborane and phosphine react at  $-110^\circ$  to give  $B_2H_6 \cdot 2PH_3$ , which is much less stable than the diammoniate. Trimethylamine displaces phosphine from it quantitatively at  $-40^\circ$ , suggesting the ionic structure  $H_3P^+ \cdot BH_3^-$ :



At ordinary temperatures diborane reacts slowly with phosphine to form hydrogen and a non-volatile white polymer of the approximate composition  $(H_2P \cdot BH_2)_x$ . It behaves similarly with arsine. Methyl substituted phosphine and arsine yield more stable compounds than the hydrides, some being recrystallisable from organic solvents even when they are exposed to air.

### *Oxygen and sulphur derivatives*

A number of oxygen and sulphur compounds are sufficiently powerful electron-pair donors to form borine adducts by reaction with diborane. Of these the unstable solid dimethyl ether borine,  $Me_2O^+ \cdot BH_3^-$ , used in the purification of diborane, is well known.

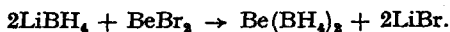
## Borohydrides

Sodium borohydride results from the reaction



which proceeds rapidly at  $250^\circ$ , and is extracted from the products with isopropylamine. Lithium borohydride is best made by passing diborane into an ethereal solution of lithium hydride. These borohydrides are salt-like; the sodium compound has a face-centred cubic lattice of discrete  $Na^+$  and tetrahedral  $BH_4^-$  ions, and the lithium compound is only a little less

regular. They are involatile and unaffected by dry air. Lithium borohydride is particularly useful for making other borohydrides:



Beryllium, aluminium and some transition metals such as thorium differ from the alkali metals in forming volatile borohydrides which constitute the most volatile compounds of these elements. On pyrolysis they decompose giving hydrogen and non-volatile residues. Electron diffraction and infra-red studies suggest they possess bridge structures.

In addition to the  $\text{BH}_4^-$  ion there are other borohydride ions such as  $\text{B}_{10}\text{H}_{10}^{2-}$ ,  $\text{B}_{12}\text{H}_{12}^{2-}$  and  $\text{B}_{20}\text{H}_{18}^{2-}$  derived from the higher boranes. The compound  $(\text{Et}_3\text{NH}^+)_2\text{B}_{10}\text{H}_{10}^{2-}$  is made by treating  $\text{B}_{10}\text{H}_{12}(\text{CNMe})_2$  (p. 276) with an excess of  $\text{Et}_3\text{N}$  in refluxing benzene for several hours. The n.m.r. spectrum of the boron-11 compound was so simple that the structure of the ion was realised to be highly symmetrical. An X-ray analysis of the copper salt  $\text{Cu}_2\text{B}_{10}\text{H}_{10}$  showed the ions to be capped antiprisms with a BH at every apex (Fig. 178).

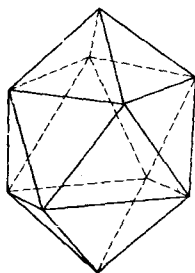


Fig. 178. Structure of the  $\text{B}_{10}\text{H}_{10}^{2-}$  ion (BH at every apex).

The compound  $\text{Na}_2\text{B}_{12}\text{H}_{12}$ , made by adding  $\text{B}_2\text{H}_6$  to a solution of  $\text{NaBH}_4$  in 1,2-dimethoxyethane at  $-80^\circ$  and then heating the mixture to  $120^\circ$  for 10 hours in an autoclave, contains the regular icosahedral  $\text{B}_{12}\text{H}_{12}^{2-}$  ion, whose structure (p. 272) provides the clue to the structural chemistry of the boranes.

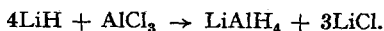
### Hydrides of aluminium and indium

When lithium hydride in limited amounts is added to ethereal aluminium chloride a white solid,  $(\text{AlH}_3)_x$ , of unknown structure, separates slowly:

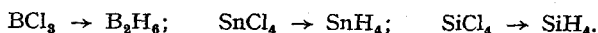


It remains stable up to 100°, but beyond, decomposes into aluminium and hydrogen. With diborane it reacts to form aluminium borohydride.

Lithium hydride, added in larger amounts to ethereal aluminium chloride, produces the ether-soluble lithium aluminium hydride, a valuable, strong reducing agent:



Not only aldehydes and ketones, but even carboxylic acids are reduced to alcohols by it; nitriles go to primary amines and halides to hydrides:



Although adducts such as trimethylaminegallane,  $\text{Me}_3\text{NGaH}_3$ , have been prepared, attempts to make digallane by treating them with  $\text{BF}_3$  have proved unsuccessful. However, trialkylgallanes,  $\text{R}_3\text{Ga}$ , can be made by treating gallium trihalides with aluminium alkyls, and salts of the  $\text{GaH}_4^-$  ion have also been prepared.

Hydrides of indium can be made, however. Indium halides are reduced by LiH in ether at  $-30^\circ$  to give the solid  $\text{LiInH}_4 \cdot 3\text{Et}_2\text{O}$ , which decomposes above  $0^\circ$  into LiH and the polymeric  $(\text{InH}_3)_x$ . Indium trichloride is reduced by  $\text{LiInH}_4$  to a dimeric  $\text{In}_2\text{H}_6$  which polymerises rapidly to  $(\text{InH}_3)_x$  at room temperature. When the polymer is warmed at low pressure it loses hydrogen and gives a white, polymeric monohydride,  $(\text{InH})_x$ .

### Hydrides of carbon and silicon

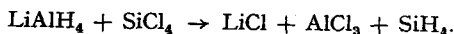
No element forms such a variety of hydrides as carbon. In addition to the numerous known alkanes,  $\text{C}_n\text{H}_{2n+2}$ , structural isomerism predicts many more not yet isolated. For example, over thirty six million isomeric forms of  $\text{C}_{25}\text{H}_{52}$  can be formulated. To these an even larger number of possible unsaturated hydrocarbons may be added.

Silicon, for reasons given below, presents a very different picture, the highest hydride having a chain of only six silicon atoms. The series corresponds to the simplest saturated hydrocarbons, the paraffins.

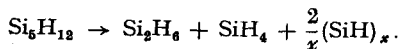
TABLE 31  
MELTING AND BOILING POINTS OF THE SILANES

	$\text{SiH}_4$ <i>Silane</i>	$\text{Si}_2\text{H}_6$ <i>Disilane</i>	$\text{Si}_3\text{H}_8$ <i>Trisilane</i>	$\text{Si}_4\text{H}_{10}$ <i>n-Tetrasilane</i>	$\text{Si}_5\text{H}_{12}$ <i>Pentasilane</i>	$\text{Si}_6\text{H}_{14}$ <i>Hexasilane</i>
M.p.	$-185^\circ$	$-132^\circ$	$-117^\circ$	$-84^\circ$	Isomers not yet separated	
B.p.	$-112^\circ$	$-14^\circ$	$53^\circ$	$107^\circ$	$> 100^\circ$	$> 100^\circ$

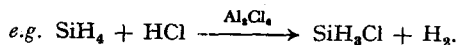
A mixture containing all the silanes is obtained when magnesium silicide is dropped into dilute hydrochloric acid in an enclosed, low-pressure system. Fairly pure monosilane itself is made in good yield by adding magnesium silicide to ammonium bromide in liquid ammonia, in which the ammonium salt behaves as a strong acid. The pure gas results from the action of lithium aluminium hydride on silicon tetrachloride:



The thermal stabilities of the silanes are much lower than those of the corresponding alkanes. The higher silanes decompose on moderate heating to give lower silanes and solid unsaturated hydrides:



Above 500°, decomposition to the elements is complete. The silanes are spontaneously inflammable and explosive in air; they are not hydrolysed at a pH of less than 7, but in water containing a trace of alkali hydrolysis is rapid and complete. They have strong reducing properties; permanganates are reduced to manganese dioxide, and mercury(II) to mercury(I) ions and mercury. Unlike the alkanes, the silanes enter into substitution reactions with halogen acids (other than hydrofluoric) on warming in the presence of the corresponding aluminium halide:



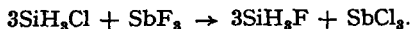
Although bonds between silicon and other elements are usually stronger than the corresponding ones involving carbon, this is not true for the silicon-hydrogen bond (76.0 kcal/mole) which is weaker than the carbon-hydrogen bond (99.3 kcal/mole).

#### *Silyl radical and silyl compounds*

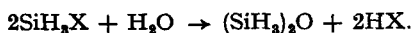
As the electronegativity of silicon (1.8) is less than that of carbon (2.5), the silyl radical  $\text{SiH}_3$  should be a less powerful electron acceptor than the methyl group. This would be so were it not for the vacant d orbitals of the silicon atom which enable  $\pi$ -bonding to take place. Theory, supported by experimental evidence, indicates that there would be overlap between a vacant silicon  $d_{\pi}$  orbital and a  $p_{\pi}$  orbital on an atom of a Group V, VI or VII element already attached to the silicon atom by a  $\sigma$  bond. The  $\pi$  bond is generally stronger the more electronegative the acceptor atom, but silicon attracts electrons more strongly than its accepted electronegativity would suggest. This kind of bonding cannot occur with carbon because its d orbitals (3d) are too high in energy to contribute appreciably. The

fact also accounts nicely for the strength of the C—H bond and the weakness of the Si—H bond.

This point is illustrated by the silyl halides, whose properties are greatly affected by the presence of a silicon-silicon bond. The preparation of the chloride, bromide and iodide of monosilane is described above; the fluoride is made by the action of the chloride on antimony fluoride:



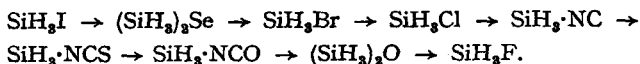
The iodide is liquid at room temperature, the rest are gaseous. Surprisingly only the bromide is spontaneously inflammable in air. The reaction of the fluoride with water is not recorded; the others are hydrolysed immediately to disilyl ether, a colourless gas:



On the other hand, hydrolysis with aqueous alkalis is complete, producing hydrogen and silicates. Silyl iodide gives a Wurtz-type reaction with sodium, which affords a useful path to disilane:



Silyl chloride and ammonia give amines, the most stable being the liquid trisilylamine; this is spontaneously inflammable in air and vigorously decomposed by water into silica, ammonia and hydrogen. Silyl iodide may be converted into several other silyl compounds by means of a silver salt.



The sequence implies that a compound may be converted into one coming later in the series by means of the appropriate silver salt, although all the changes have not been tested.

In general, silyl compounds present a contrast to their methyl analogues in that they more readily enter into reactions in which the identity of the radical is maintained. This is exemplified in the instantaneous conversion of the silyl halides by water into disilyl ether, and in their rapid reaction with silver salts. The principal causes of this reactivity are

- (i) the ease with which the co-ordination number of the silicon atom rises from four to six;
- (ii) the larger size, and consequently greater vulnerability to attack, of the silicon atom;
- (iii) the appreciable polarity of the  $\text{Si}^+\text{—H}^-$  bond (polarity is almost absent in the C—H bond) which renders it more reactive towards nucleophilic reagents.

These three factors also favour the formation of complexes.

### Hydrides of germanium and tin

Germanium hydrides are made in ways similar to those used for making boranes and silanes. A mixture of mono-, di- and trigermanes results from the action of dilute hydrochloric acid on magnesium germanide. Monogermane itself is conveniently made by reducing germanium tetrachloride with ethereal lithium aluminium hydride. Germanes from  $\text{Ge}_2\text{H}_6$  to  $\text{Ge}_8\text{H}_{18}$  have been made by circulating monogermane at 0.5 atm. pressure through an ozoniser electric discharge tube at  $-78^\circ$ .

TABLE 39  
MELTING AND BOILING POINTS OF THE GERMANES

		<i>M.p.</i>	<i>B.p.</i>
Monogermane	$\text{GeH}_4$	$-165^\circ$	$-90^\circ$
Digermane	$\text{Ge}_2\text{H}_6$	$-109^\circ$	$29^\circ$
Trigermane	$\text{Ge}_3\text{H}_8$	$-106^\circ$	$110^\circ$

The germanes decompose at lower temperatures than the silanes, but are less inflammable and much less easily hydrolysed; monogermane is not attacked even by 30% caustic soda. Halogenation may be effected as with the silanes. An amorphous, yellow polymer  $(\text{GeH}_2)_x$  is obtained when calcium germanide,  $\text{Ca}_2\text{Ge}$ , is treated with acid. Between  $120$ – $220^\circ$  it decomposes, the three volatile germanes being among the products.

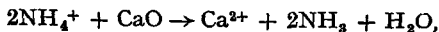
Tin forms the gaseous hydride  $\text{SnH}_4$ . It is best made by reducing tin(IV) chloride with ethereal lithium aluminium hydride. Stannane decomposes, at room temperature, into tin and hydrogen, but it is not hydrolysed by 15% caustic soda. This hydride is formed by the action of atomic hydrogen on metallic tin.

There is considerable doubt about the existence of a lead hydride; certainly no trace of it appears when metallic lead is treated with atomic hydrogen.

### Group VB hydrides

#### *Ammonia*

Ammonia is made in the laboratory by heating an ammonium salt with a base:



or by treating a nitride with water:

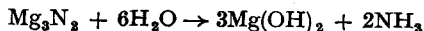


TABLE 40  
MELTING AND BOILING POINTS OF GROUP VB HYDRIDES

		<i>M.p.</i>	<i>B.p.</i>
Ammonia	NH <sub>3</sub>	-78°	-33°
Phosphine	PH <sub>3</sub>	-132°	-87°
Arsine	AsH <sub>3</sub>	-116°	-62°
Stibine	SbH <sub>3</sub>	-88°	-17°
Hydrazine	N <sub>2</sub> H <sub>4</sub>	+2°	+113°
Phosphorus dihydride	P <sub>2</sub> H <sub>4</sub>	-99°	+52° (extrapolated)

(For hydrazoic acid see p. 453.)

It is manufactured industrially by passing nitrogen and hydrogen over an iron catalyst at  $\sim 500^\circ$  and 200–1000 atmospheres pressure:



Because the reaction is exothermic, the higher the temperature the more unfavourable the equilibrium; below  $500^\circ$  however the rate is inconveniently low. A conversion of 10–14% in the Haber process operating at 300 atm, and 40% in the Claude process operating at 900 atm is usual. The ammonia is removed from the mixed gases and the residual mixture of nitrogen and hydrogen is recycled through the converter.

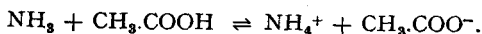
The ammonia molecule has been shown by infrared and microwave studies to be pyramidal with the H—N—H angle  $\sim 107^\circ$ . This is because the valency electrons round the nitrogen atom can be roughly described as using  $sp^3$  hybrid orbitals, one containing two electrons (the lone pair) and the other three being singly occupied. Overlap of these with the 1s orbitals of the three hydrogen atoms should give three molecular orbitals (at the tetrahedral angle  $109.5^\circ$ ) but the hybridisation is not strictly  $sp^3$ . The lone-pair orbital is more electron-repellant than the others, thus forcing the bonds together and reducing the angle between them to  $107^\circ$  (see p. 118).

The ammonia crystal has an approximately face-centred cubic lattice, the lone pair of electrons being used in hydrogen bonding to three other molecules. The free inversion displayed by the gaseous molecule thus does not occur in the solid as infrared spectroscopic evidence shows.

Ammonia, like water and hydrogen fluoride, is associated in the liquid state, as is evident from its melting point, boiling point, latent heats and surface tension considered in relation to those of phosphine and arsine. The association is due to hydrogen bonding which occurs in liquid ammonia but not in liquid phosphine and arsine.

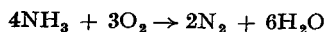
Liquid ammonia has a significant dielectric constant (1.49 D) and is an

ionising solvent (p. 243). Through its lone pair, the molecule is a strong proton acceptor, and the liquid facilitates the extensive dissociation of weak acids; thus acetic acid is almost as completely dissociated in liquid ammonia as a mineral acid is in water:

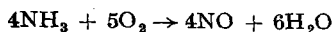


Liquid ammonia dissolves many of the active metals (Na, Ca) to give blue solutions in which there are solvated metal ions and solvated electrons (p. 311). The solutions are fairly stable but have strong reducing properties.

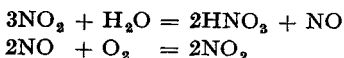
Gaseous ammonia burns in oxygen with a low-temperature flame to produce nitrogen and water:



At about 800°, on a platinum catalyst, ammonia and air readily react to give nitric oxide and water



When ammonia and air are passed through a hot platinum gauze, the reaction provides the first step in the manufacture of nitric acid. The NO produced is oxidised to NO<sub>2</sub>, as it cools, by the excess of air which is present. Finally successive reactions with water and oxygen from the air give a solution of nitric acid:

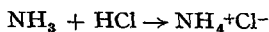


Ammonia is very soluble in water; there the molecule is partly hydrated and partly converted to ammonium ion:

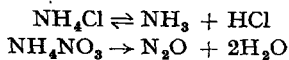


The formation of an ammonium hydroxide is very improbable in these aqueous solutions.

The gas reacts with acids to give ammonium salts containing the tetrahedral NH<sub>4</sub><sup>+</sup> ion:



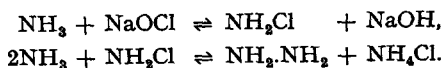
Ammonium halides dissociate on heating; salts of some of the oxo-acids decompose:



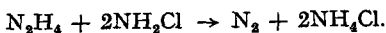
### *Hydrazine*

Hydrazine is still manufactured (Raschig, 1907) by oxidising aqueous ammonia, present in a large excess, with sodium hypochlorite. Two reactions occur:





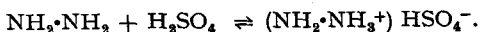
The reactants are mixed at a low temperature and rapidly heated to promote reaction of the chloramine with ammonia. Glue or gelatine is used to promote the slow reaction and to inhibit the secondary reaction:



This the glue does by chelating such metal ions as  $\text{Cu}^{2+}$  which catalyse the secondary reaction.

Commercially the hydrazine is recovered as the hydrate.

To prepare anhydrous hydrazine, sulphuric acid and alcohol are added to the hot solution of the hydrate. From this crystals of hydrazine sulphate separate on cooling:



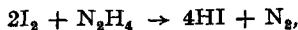
Distillation with concentrated caustic potash gives anhydrous hydrazine, b.p.  $113.5^\circ$ , which is thermally stable but is very reactive and burns in air.

It forms a monohydrate,  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ , and is a weak base. The existence of the hydrazinium cation  $\text{N}_2\text{H}_6^{2+}$  has been confirmed in the compounds  $\text{N}_2\text{H}_6(\text{SbCl}_6)_2$  and  $\text{N}_2\text{H}_6(\text{BF}_4)_2$ . Both the base and its salts are strong reducing agents, converting iodates to iodides, iron(III) salts to iron(II) salts, and gold(III) salts to colloidal gold.

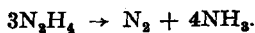
Hydrazine bears the same relation to ammonia as hydrogen peroxide to water. That the molecule is similar to hydrogen peroxide is shown by the Raman spectrum and high dipole moment (1.83 D) of the monomeric vapour. Like the hydroxyl groups in hydrogen peroxide, (p. 504) the  $\text{NH}_2$ -groups in hydrazine are without free rotation.

In the solid (m.p.  $2^\circ$ ) the molecules, apparently hydrogen-bonded to one another, are arranged in zig-zag chains.

Anhydrous hydrazine burns spontaneously in dry oxygen and reacts readily with halogens:



It sets free ammonia from ammonium chloride and decomposes when heated:

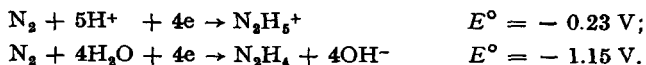


The anhydrous liquid is a good solvent for sulphur, selenium, phosphorus, and arsenic.

Aqueous solutions of hydrazine, like those of hydrogen peroxide, show both oxidising and reducing properties. In acids the redox potential is high (p. 225), and suggests that hydrazine should be a strong oxidising agent:



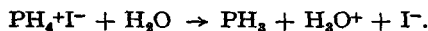
The reaction is slow, however, with all but the strongest reducing agents such as  $\text{Ti}^{3+}$ . Hydrazine is easily oxidised in either acids or alkalis; the reactions are complicated, nitrogen being the commonest product:



The four-electron change necessary for the quantitative conversion to nitrogen occurs only within certain limits of pH, concentration and temperature. Chlorine, bromine, iodine and iodates bring about this reaction quantitatively at  $\sim$  pH 7. Dissolved molecular oxygen oxidises aqueous hydrazine to nitrogen in a series of stages, so that hydrazine is an effective deoxidant for boiler-water. Several metal ions, particularly copper, catalyse the reaction.

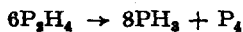
### Phosphines

Phosphine, like ammonia, is pyramidal with the H—P—H angle  $93^\circ$  (cf.  $\text{NH}_3$ ,  $107^\circ$ ). It is much less soluble and a much weaker base than ammonia, but a much stronger reducing agent. Phosphonium salts are decidedly less stable than those of ammonium. They dissociate as do ammonium salts on heating;  $\text{PH}_4\text{Cl}$  is stable at  $-75^\circ$  and completely decomposed at  $\sim -50^\circ$ , the corresponding temperatures for  $\text{PH}_4\text{Br}$  and  $\text{PH}_4\text{I}$  being  $\sim -50^\circ$ ,  $\sim 0^\circ$  and  $0^\circ$ ,  $62^\circ$ , respectively. The same order is found for the ammonium salts, but with temperatures in the range  $250\text{--}400^\circ$ . The difference in behaviour is ascribable to the lower electronegativity of phosphorus (2.06 against 3.07 for nitrogen) as also is the ready disruption of the phosphonium ion by water:



Alkyl and aryl substituted phosphines are similar to the amines in structure but highly inflammable. The quaternary phosphonium bases are, like the corresponding nitrogen compounds, very strongly ionised.

The unstable, colourless, liquid diphosphine,  $\text{P}_2\text{H}_4$ , (m.p.  $-99^\circ$ , b.p.  $51.7^\circ$ ) is a minor by-product of the hydrolysis of phosphides ( $\text{Ca}_3\text{P}_2$ ) which give mainly phosphine; it is separated from the latter by freezing it out. Unlike hydrazine it is without basic properties. But like hydrazine it is readily oxidised and is a strong reducing agent; it has the same structure. There the similarity ends because its lone pairs are quite ineffective, so that it is insoluble in water and without trace of basic character. It is photo- and heat-sensitive giving phosphine and phosphorus:



The liberated phosphorus adsorbs some of the phosphine to form a complex,  $(P_2H)_x$ . The yellow solid, usually termed a hydride, is odourless, insoluble in cold dilute hydrochloric acid, but decomposed by water giving hydrogen and a phosphorous acid.

#### *Other Gp. V hydrides*

Like phosphine, the trihydrides of arsenic and antimony are not formed by direct combination with molecular hydrogen. They are usually prepared by reducing arsenic or antimony compounds with atomic hydrogen produced at a zinc surface dissolving in dilute hydrochloric acid:



Both are strong reducing agents, without basic properties and easily decomposed by heat; the decomposition of arsine begins at 230°.

Phosphorus, arsenic and antimony are all readily attacked by atomic hydrogen to yield their respective trihydrides. There is evidence that a hydride of bismuth is not formed in this way.

### Hydrides of Group VIB

The bond angles in water vapour, hydrogen sulphide and hydrogen selenide are respectively 104.5°, 92.3° and 90°. Roughly speaking the 'prepared' oxygen atom is well described as using tetrahedral hybrid  $sp^3$  orbitals (p. 118), two doubly occupied and two singly, and the water molecule results from the overlap of each of the latter with an  $s$  orbital of hydrogen. Less hybridisation occurs with sulphur and the other elements, which have a much lower electronegativity than oxygen (O, 3.50; S, 2.44; Se, 2.48), and the final form is determined by various factors. Oxygen probably adopts the symmetrical (tetrahedral) configuration because in this way it is better able to 'draw in' the hydrogen electrons and approach the condition of having two electrons in each hybrid.

The Group VI hydrides exhibit an appreciable increase in acid strength with increasing molecular weight, the  $pK_a$  (p. 240) values of aqueous solutions being approximately as given in Table 41.

TABLE 41  
 $pK_a$  VALUES OF GROUP VI HYDRIDES

$H_2O$	$H_2S$	$H_2Se$	$H_2Te$
15	7	4	3

This is mainly due to a fall in dissociation energies; solvation energies and electron affinities increase in the reverse direction. There is no connection between acid strength and electronegativity, for the dipole moments decrease from water to hydrogen telluride.

### Water

Upon the singular properties of water all biochemistry, much of geochemistry and a great deal of general chemistry depends. Ice at  $-183^{\circ}$  has a rigid arrangement of atoms in which oxygen is tetrahedrally co-ordinated by  $sp^3$  orbitals with four hydrogens, two closely ( $1.00 \text{ \AA}$ ) and two more remotely ( $1.76 \text{ \AA}$ ). This leads to the very open wurtzite structure with the oxygen atoms  $2.76 \text{ \AA}$  apart, and the hydrogen atoms at points one third along this distance. It accounts for ice being less dense than water.

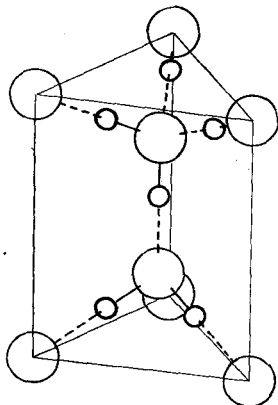
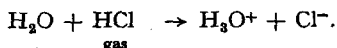
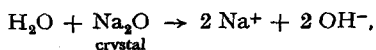


Fig 179. Wurtzite-like structure of ice.

The hydrogen bonding in ice suffers a progressive break-down as the temperature rises and there is increasing freedom of movement of the  $H_2O$  units, but the structure remains sufficiently open for the density of melting ice at  $0^{\circ}$  to be less than that of water at  $0^{\circ}$ , when the liquid still retains some of the open character of the solid. As the liquid warms, the density is affected by (a) the breaking of hydrogen bonds leading to a closer packed structure, and (b) the thermal expansion. At  $4^{\circ}$  these just balance one another, and water is at its maximum density. Above  $4^{\circ}$  thermal expansion takes charge and the density continues to fall to the boiling point, but at  $50^{\circ}$  about half the hydrogen bonding still remains and even boiling water retains some.

Water is the most remarkable of all solvents (p. 106). It has a very high dielectric constant (78 at  $25^{\circ}$ ), has a considerable dipole moment ( $1.85 \text{ D}$ ),

and is amphoteric. As an ionising medium it acts, upon occasion, as either a donor or an acceptor of protons: thus it facilitates the dissociation of both bases and acids (p. 239):



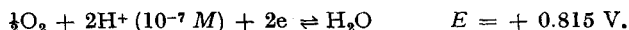
Because water molecules are dipolar they cluster round both positive and negative ions; these hydrate sheaths greatly reduce the ionic attraction between the oppositely charged ions and hence their tendency to recombine.

The chemical versatility of water is further increased by its ability either to oxidise or reduce. For the equilibrium in pure water at 25°,



Water gives hydrogen with reducing agents possessing redox potentials (p. 225) more negative than this, but the process is very slow when the hydrogen overvoltage (p. 259) is high. Thus zinc ( $E^\circ, \text{Zn}^{2+}/\text{Zn} = -0.763 \text{ V}$ ) is passive in pure water, though it sets free hydrogen from dilute acids where  $E, \text{H}^+/\text{H}_2$  is much nearer zero.

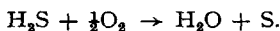
The reducing action of the water is summarised in the equation



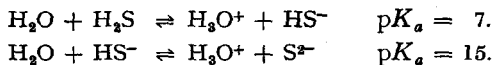
In consequence of this, oxygen is liberated only by strong oxidising agents. The redox potential decreases as the  $\text{OH}^-$  ion concentration increases, and alkaline solutions are more easily oxidised than pure water.

### *Hydrogen sulphides*

By contrast, hydrogen sulphide is without hydrogen bonding; the solid is close-packed, and the liquid density has a normal temperature dependence. The gas burns in air; there is considerable decomposition within the flame, which consequently deposits sulphur on a cold surface, and complete combustion at its outer edge. The catalysed oxidation by air on an iron(III) oxide surface can be made to release the whole of the sulphur:

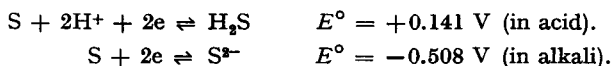


Hydrogen sulphide is moderately soluble in water in which it is a weak dibasic acid:

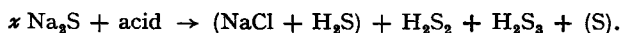


Like carbon dioxide, sulphur dioxide and ammonia it is completely expelled

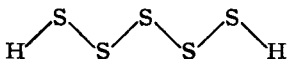
from boiling water. It acts as a reducing agent with, generally, the liberation of sulphur, but in strong oxidising agents, such as concentrated nitric acid, the sulphur may be converted into  $\text{SO}_2$  or  $\text{SO}_3$ , or their derivatives:



Sulphur forms at least three liquid hydrides; hydrogen persulphide,  $\text{H}_2\text{S}_2$ , and the polysulphides  $\text{H}_2\text{S}_3$  and  $\text{H}_2\text{S}_5$ . The first two are made by dissolving sulphur in aqueous sodium sulphide, pouring the solution of polysulphides, which certainly contains  $\text{Na}_2\text{S}_5$ , into concentrated hydrochloric acid at  $-10^\circ$ , and fractionating the yellow oil which separates

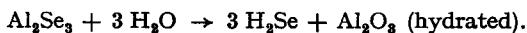


Pure anhydrous ammonium pentasulphide when treated with anhydrous formic acid gives  $\text{H}_2\text{S}_5$ . All the liquids readily decompose into  $\text{H}_2\text{S}$  and sulphur. They dissolve in solvents like benzene and chloroform. Their structures involve chains of sulphur atoms.



#### *Hydrogen selenide and hydrogen telluride*

Hydrogen selenide, made by decomposing aluminium selenide with water, is much less thermally stable than its sulphur analogue:



It is slowly oxidised to selenium by moist oxygen. The corresponding compound of tellurium decomposes rapidly at room temperature and is even more easily oxidised. Both have strong reducing properties; thus  $\text{H}_2\text{Se}$  gives free selenium in addition to the selenide when passed into a solution of a heavy metal cation. There are no hydrogen polyselenides or polytellurides, nor would these be expected in view of the weakness of the Se—Se and Te—Te bonds and of the bonds between these elements and hydrogen. The last point is exemplified by a marked increase in  $\Delta H_f^\circ$  of the simple hydrides in passing down Group VI (Table 42). This increase is also observed in the covalent hydrides of Groups IV, V and VII.

The hydrides of selenium and tellurium, like those of tin and antimony, are strongly endothermic, probably owing to the high dissociation energy of the hydrogen molecule and the small electronegativity of the hydrogen atom.

TABLE 42  
HEATS OF FORMATION OF HYDRIDES OF GROUP VI  
(in kcal/mole)

	H <sub>2</sub> O	H <sub>2</sub> S	H <sub>2</sub> Se	H <sub>2</sub> Te
$-\Delta H_f^\circ$	68.3	4.8	-20.5	-36.9

### Hydrides of Group VIIB

TABLE 43  
PROPERTIES OF HYDRIDES OF GROUP VIIB

	HF	HCl	HBr	HI
B.p. (°C)	19.4	-85	-67	-35
$\Delta H_f^\circ$ (kcal/mole)	-65	-22	-12	+6
Bond energy (kcal/mole)	134	102	86	70
$pK_a$	4	-7	-9	-11

As was found in the two previous groups, the boiling point of the first member of Group VII is again notably high because of association.

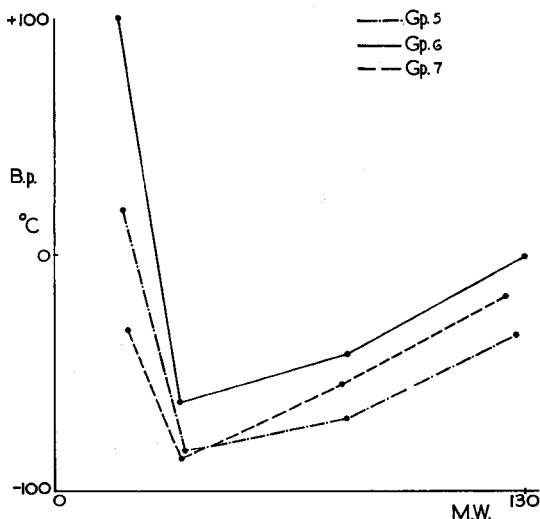


Fig. 180. Relation between boiling point and molecular weight in the volatile hydrides of Groups V, VI and VII.

Hydrogen chloride shows a considerable fall from the value for hydrogen fluoride; thence the rise in boiling point is very nearly proportional to the molecular weight (Fig. 180).

Hydrogen fluoride is very strongly hydrogen-bonded; its entropy of vaporisation at the boiling point is high (24.9 cal deg<sup>-1</sup> per mole), but not as high as that of water (26.0 cal deg<sup>-1</sup> per mole). Solid hydrogen fluoride probably consists of cyclic (HF)<sub>6</sub> molecules; some zig-zag chains (Fig. 181) are present in the liquid. The hydrogen bonding with fluorine, though the strongest known, is considerably less than the 70 kcal/mole typical of a  $\sigma$  covalent bond.

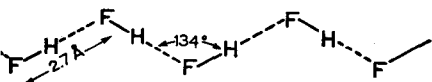


Fig. 181. Chain of hydrogen fluoride.

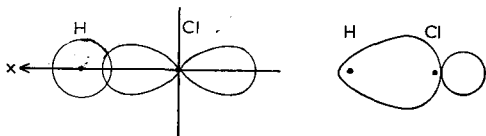


Fig. 182. Contributions to bonding MO in HCl molecule.

The decrease in ionic character from hydrogen fluoride to hydrogen iodide is marked and due to increasing symmetry in the distribution of the bonding electrons. At first sight, the bond is a simple one, compounded of the  $1s$  and the  $p_x$  atomic orbitals of hydrogen and halogen respectively.

$$\psi = a\psi(\text{H} : 1s) + b\psi(\text{Cl} : 3p_x)$$

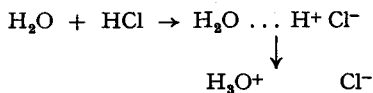
In a molecular orbital of this kind,  $b/a$  always exceeds unity, but the ratio is much larger for fluorine than for iodine, indicating that the charge cloud 'leans' more heavily towards the fluorine than towards the iodine atom (*cf.* Fig. 182) in the respective hydrides.

This simple picture is inadequate because some  $sp$  hybridisation occurs on the halogen atom, one hybrid being engaged in the bond and the other pointing out behind the halogen and containing a lone pair; the lone pair plays a large part in determining the dipole moment (p. 142) of the halogen halides.

Disparity between the MO coefficients,  $a$  and  $b$ , indicates ionic character in every instance; the dipole moment of hydrogen chloride is 1.03 D. Its infrared absorption spectrum gives a bond length of 1.26 Å, so that, were the molecule completely ionic (*i.e.* H<sup>+</sup>Cl<sup>-</sup>), the value of  $\mu$  would be  $1.26 \times 4.80 = 6.05$  D. In fact, the bonding is mainly covalent in the free molecule. If the degree of polarity is measured by  $1.03/6.05 = 0.169$ , it could be said that the bond in HCl is about 83% covalent. On this basis hydrogen iodide would be 95% covalent, the corresponding polarity being 0.05.



Dissociation of the halogen halides in polar solvents is due to the breaking of the hydrogen-halogen bond through the approach of a lone pair on the water molecule to a hydrogen atom in the hydrogen halide causing a retraction of the molecular orbital towards the halogen and thereby allowing the water molecule to capture the liberated proton.



The necessary energy for the process is provided by the heat of formation of the aquated  $\text{H}^+$  and halide ions. The increase in acidity from hydrogen fluoride to hydrogen iodide arises almost entirely from the decreasing strength of the hydrogen-halogen bond, since the other heat and entropy terms are largely self-cancelling.

The monohydrate formed by  $\text{HCl}$  at low temperatures has been shown by X-ray diffraction at  $-35^\circ$  to be  $\text{H}_3\text{O}^+\text{Cl}^-$ , every hydrogen atom being bonded by hydrogen bonds to the nearest chlorine atom. The hydrogen bonds  $\text{OH}\dots\text{Cl}$  are 2.95 Å in length.

#### FURTHER READING

- T. R. P. GIBB, *Primary Solid Hydrides* in F. A. COTTON (Ed.), *Progress in Inorganic Chemistry*, New York, Interscience, 3 (1961) 315.
- W. N. LIPSCOMB, *Boron Hydrides*, New York, Benjamin, 1963.
- F. G. A. STONE, *Chemistry of the Boron Hydrides*, *Quart. Rev.*, 49 (1955) 174.
- J. C. SHELDON AND B. C. SMITH, *The Borazoles*, *Quart. Rev.*, 14 (1960) 200.
- H. C. LONGUET-HIGGINS, *The Structures of Electron-deficient Molecules*, *Quart. Rev.*, 11 (1957) 121.
- A. G. MACDIARMID, *Silanes and their Derivatives*, in H. J. EMELÉUS AND A. G. SHARPE (Eds.), *Advances in Inorganic Chemistry and Radiochemistry*, New York, Academic Press, 3 (1961) 207.
- R. A. REED, *Hydrazine and its Derivatives*, London, Royal Institute of Chemistry Lectures, Monographs and Reports Series, 1957, No. 5.
- P. G. OUSTON, *The Structure of Ice*, *Quart. Rev.*, 5 (1951) 344.
- W. L. JOLLY, *Metal-Ammonia Solutions*, in F. A. COTTON (Ed.), *Progress in Inorganic Chemistry*, New York, Interscience, 1 (1959) 235.
- G. G. LIBOWITZ, *The Solid-State Chemistry of Binary Metal Hydrides*, New York, Benjamin, 1965.
- M. F. HAWTHORNE, *Decaborane-14 and its Derivatives*, in H. J. EMELÉUS AND A. G. SHARPE (Eds.), *Advances in Inorganic Chemistry and Radiochemistry*, New York, Academic Press, 5 (1963) 307.

## Chapter 14

# The Noble Gases

### GROUP 0

The gases helium, neon, argon, krypton, xenon and radon, the first five isolated by Ramsay and his associates (1894–98), constitute Group 0 of the Periodic Table. All are monatomic and, with the exception of helium, their atoms have electronic structures completed by a closed subshell of three doubly-occupied p orbitals. The resulting  $^1S$  ground state leads to the atoms of the elements being without tendency to covalent bonding and the formation of an uncharged diatomic molecule, because the two atoms possess between them sufficient electrons to fill both the bonding and anti-bonding molecular orbitals (p. 98). Although  $\text{He}_2^+$ , with only one electron in the  $\sigma^*$  1s orbital, does occur in the discharge tube. Moreover, the first ionisation energies of the closed shell structure are very large (p. 83) and ionic bonding of these elements is thereby rendered difficult. Up to 1962 (p. 299) the elements were called the 'inert gases'—'noble' is now a more appropriate description.

TABLE 44  
ATOMIC PROPERTIES OF THE NOBLE GASES

	<i>He</i>	<i>Ne</i>	<i>Ar</i>	<i>Kr</i>	<i>Xe</i>	<i>Rn</i>
Atomic number	2	10	18	36	54	86
Electron configuration	$1s^2$	$2s^22p^6$	$3s^23p^6$	$4s^24p^6$	$5s^25p^6$	$6s^26p^6$
Ionisation energy (eV)	24.6	21.6	15.8	14.0	12.1	10.8
Van der Waals radius (Å)	1.2	1.6	1.9	2.0	2.2	—

Interaction between the atoms of a noble gas is slight, the Van der Waals forces being due entirely to dispersion interaction. Liquefaction is therefore difficult and the elements have much lower b.p. than compounds of a similar molecular weight but with less symmetrical electron distributions and correspondingly larger electrostatic and polarisation interactions (Table 45)

TABLE 45

BOILING POINTS OF THE NOBLE GASES AND OF ELEMENTS AND COMPOUNDS WITH A SIMILAR MOLECULAR MASS

	<i>Mass</i>	<i>B.p.</i> (°K)		<i>Mass</i>	<i>B.p.</i> (°K)
He	4	4.2	H <sub>2</sub>	2	20
Ne	20	27	CH <sub>4</sub>	16	92

The liquefaction of helium by a controlled expansion process necessitates preliminary cooling because its Joule-Thomson coefficient is negative (this means that spontaneous expansion heats the gas) down to an 'inversion temperature' of 40° K. All the gases have  $C_p/C_v$  ratios very close to 5/3, the theoretical value for an ideal monatomic gas. The elements are liquid over very small temperature ranges. Helium can be solidified only when compressed; under 26 atmospheres pressure it solidifies at 0.9° K.

TABLE 46

PHYSICAL PROPERTIES OF THE NOBLE GASES

	<i>He</i>	<i>Ne</i>	<i>Ar</i>	<i>Kr</i>	<i>Xe</i>	<i>Rn</i>
M.p. (°K)		24	84	116	161	202
B.p. (°K)	4.2	27	87	120	166	208
Heat of vaporisation (kcal/mole)	0.02	0.44	1.50	2.31	3.27	4.30

### *Helium II*

When helium-4 is cooled to 2.18° K at 1 atmosphere pressure (the  $\lambda$ -point) a remarkable liquid, helium II, is obtained. It has

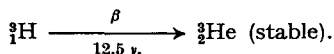
- (i) very high heat conductance—600 times that of copper at room temperature;
- (ii) very low viscosity—about one thousandth that of hydrogen gas;
- (iii) ability to flow up the surface of the containing vessel.

The liquid is produced only from  $\frac{4}{3}\text{He}$ , not from  $\frac{3}{2}\text{He}$ .

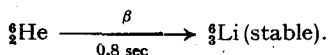
### Helium

The  $\alpha$ -particles set free in radioactive disintegration take up electrons to form atoms of helium-4. The gas is therefore to be found associated with minerals containing  $\alpha$ -emitters; pitchblende, which contains uranium, and monazite, which contains thorium, are examples. Helium-3, though a stable

nuclide, comprises only  $1.4 \times 10^{-3}\%$  of terrestrial helium; it is a product of the radioactivity of tritium, itself a result of the action of cosmic rays on deuterium (p. 262):



If a helium isotope of mass 5 should exist, it must have a very short life indeed. Incidentally, there is no other nuclide of this mass and there is no mass number, other than 5, which is not represented by at least one nuclide. Helium-6 is a  $\beta$ -emitter of short half-life.



Helium is much less common on earth than on larger planets or stars (p. 32). Its high molecular velocity, and the large mean free path available, enable it to escape readily from the upper atmosphere, where it is relatively abundant, because of the weakness of the gravitational field at that height. The principal source of the element is natural gas (up to 8% He) found in the south of the U.S.A., the other gases, mainly hydrocarbons, being separated from it by liquefaction. Attempts have been made to obtain it from the atmosphere by making use of its ability to diffuse through heated, thin-walled silica capillaries and in other ways.

### Separation of noble gases from air

The non-radioactive noble gases are all present in the atmosphere. Their volume percentages at sea level are: argon 0.93%, neon  $1.8 \times 10^{-3}\%$ , helium  $5.2 \times 10^{-4}\%$ , krypton  $1.1 \times 10^{-4}\%$ , xenon  $9 \times 10^{-6}\%$ .

Liquid air is, to a first approximation, a ternary mixture of nitrogen (b.p. 77° K), argon (b.p. 87° K) and oxygen (b.p. 90° K). In the fractional distillation of liquid air there is a point on the column where the mid-boiling fraction reaches a maximum concentration, and from which a side-cut may be taken to give a liquid containing mainly oxygen and argon. This cut is fractionated separately into crude argon and oxygen; the oxygen is returned to the column. The crude argon, which has up to 20% oxygen, is mixed with hydrogen and sparked to convert the oxygen into water; the unused hydrogen is later oxidised by hot CuO.

Neon is not condensed during the main distillation of liquid air; it accumulates on the nitrogen side and is withdrawn. The nitrogen in the extracted gas is removed, first by low-temperature liquefaction and, finally, by charcoal adsorption.

Krypton and xenon remain dissolved in the liquid oxygen; they can be separated by selective low-temperature adsorption.

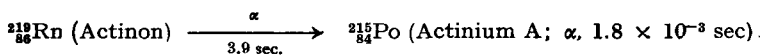
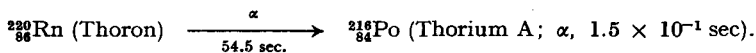
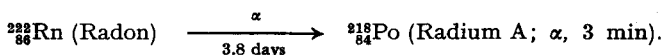
### Uses

Helium, formerly used for airships, is now employed, like argon, to provide an inert gaseous shield during the welding of Mg, Al, Ti and stainless steel. It probably has a future in gas-cooled atomic reactors as a material for transferring heat, since it is inert and does not become active under irradiation. An oxygen-helium mixture is used in the treatment of asthma as it diffuses more rapidly than air through constricted lung passages. A similar mixture is supplied to deep-sea divers because helium, being less soluble than nitrogen, does not cause caisson sickness or 'bends' by bubbling out of the blood when the pressure is released. Helium is a suitable gas for low-temperature gas thermometry, because of its low boiling point and also its near-ideal behaviour.

Argon is chiefly employed in welding and other operations which require both a non-oxidising atmosphere and the absence of nitrogen. Since about 1920, it has been used in gas-filled electric bulbs to reduce the rate of evaporation from the tungsten filament, and also more recently in thermionic tubes (thyratons) and fluorescent lamps. Krypton replaces argon in high-efficiency filament lamps, such as miners' cap lamps. Xenon is employed in some electronic flash tubes for high-speed photography. The first four members of the group, particularly neon, but krypton increasingly, are used in the low-pressure discharge tubes for coloured signs.

### Element 86: radon, thoron, actinon

These isotopes of element 86 result from the  $\alpha$ -particle activity of the radium isotopes which belong respectively to the uranium-238, the thorium-232, and the uranium-235 natural radioactive series. Radon, thoron and actinon are all  $\alpha$ -particle emitters of short half-life. They have in common the symbol Rn.



Element 86 is a noble gas and has physical and chemical properties appropriate to its position as the last member of Group 0.

### Compounds of the noble gases

#### *Pre-1962*

Recognition of the stable electronic structure of the noble gases (p. 77), although contributing enormously to the interpretation of valency, probably restricted attempts to prepare chemical compounds of the elements. Pauling in 1933 predicted their formation, but up to Bartlett's work in 1962 there were only the compounds observed in discharge tubes, some unstable hydrates and the clathrates.

Hydrates and deuterates have been made by compressing the gases with water and  $D_2O$ . Those formed by the heavier elements are the most stable and contain six  $H_2O$  or  $D_2O$  molecules to one inert gas atom; as for example in  $Xe \cdot 6H_2O$  where the xenon atom is evidently polarised by the strong dipole of the water molecule. In keeping with this, the water-solubility of the gases increases down Group 0.

TABLE 47

ABSORPTION COEFFICIENTS OF NOBLE GASES IN WATER AT 20° C

<i>He</i>	<i>Ne</i>	<i>Ar</i>	<i>Kr</i>	<i>Xe</i>	<i>Rn</i>
0.0097	0.014	0.05	0.11	0.24	0.51

Quinol forms clathrates (p. 200) with argon, krypton and xenon when crystallised from benzene or water under a considerable pressure of the noble gas. The noble gas atoms are caged inside groups of quinol molecules which are joined together by hydrogen bonds. The argon clathrate contains about 9% by weight, corresponding to about one argon atom to three quinol molecules. The molecular ratios for the krypton and xenon clathrates are nearly the same as for clathrates holding molecules such as  $CO$ ,  $CO_2$  and  $SO_2$ , which are about the same size as  $Kr$  and  $Xe$ .

#### *Post-1962*

The history of the discovery that the noble gases actually do form stable, conventional compounds is an interesting and exciting one. Neil Bartlett had found that platinum hexafluoride was a strong enough oxidising agent to convert molecular oxygen to the oxygenyl compound  $O_2^+PtF_6^-$ . From this he reasoned that xenon should be similarly converted by  $PtF_6$  to a cation, since the first ionisation energy of xenon, 12.2 eV, is about the same as that of the oxygen molecule (*i.e.*  $O_2 \rightarrow O_2^+ + e$ ). When he mixed

the deep-red vapour of  $\text{PtF}_6$  with an excess of xenon at room temperature, they reacted immediately to give a yellow solid which he identified as  $\text{Xe}^+\text{PtF}_6^-$ . In this way a wide new field of investigation was opened up; some of the results from this will now be described.

It is now clear that when Xe reacts with  $\text{PtF}_6$  the compound  $\text{XePtF}_6$  is not the only product. The adduct can contain more platinum, and then has the composition  $\text{Xe}(\text{PtF}_6)_x$  where  $x$  is between 1 and 2. Similar adducts,  $\text{Xe}(\text{RuF}_6)_x$  and  $\text{Xe}(\text{RhF}_6)_x$ , are also formed when xenon reacts with the appropriate hexafluoride at room temperature.

## Fluorides

### *Xenon tetrafluoride*

The first fluoride of xenon,  $\text{XeF}_4$ , was prepared in 1962 by Claassen, Selig and Malm who heated 1 vol. of fluorine with 5 vols. of xenon in a metal vessel which they afterwards cooled rapidly. It has since been synthesised by simply passing the two gases through a heated nickel tube and condensing out the product. The tetrafluoride is a colourless, crystalline solid which readily sublimes, the vapour being also colourless. It can be stored in Pyrex, is soluble without reaction in hydrogen fluoride, and in iodine pentafluoride. It reacts with hydrogen to form HF and liberate xenon, and with water to give  $\text{XeO}_3$  in solution.

The yellow solid  $\text{Xe}(\text{SbF}_6)_2$ , m.p.  $60^\circ$ , is made by dissolving  $\text{XeF}_2$ , or  $\text{XeF}_4$ , in  $\text{SbF}_5$ . The straw-coloured  $\text{Xe}(\text{TaF}_6)_2$  is formed by the action of  $\text{XeF}_4$  on molten  $\text{TaF}_5$ .

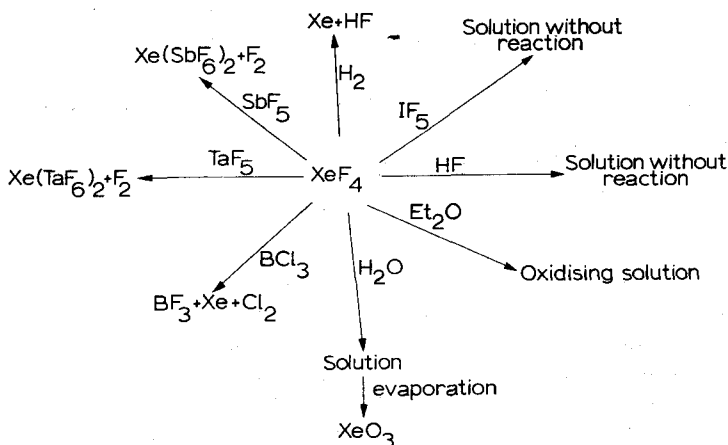


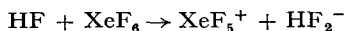
Fig. 183. Reactions of  $\text{XeF}_4$ .

*Xenon difluoride*

This is produced by heating the streaming elements in a short nickel tube (short to reduce the formation of  $\text{XeF}_4$ ), by subjecting them to an electrical discharge, by heating a mixture of xenon, oxygen and fluorine and in many other ways. Like the tetrafluoride the difluoride is a colourless crystalline solid; it is the least volatile fluoride of xenon and melts about  $140^\circ$ . The liquid and vapour are also colourless. It dissolves in hydrogen fluoride without reaction, is reduced by hydrogen to Xe and HF, and reacts with  $\text{SbF}_5$  to give  $\text{Xe}(\text{SbF}_6)_2$ .

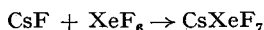
*Xenon hexafluoride*

This is prepared by heating xenon and fluorine under pressure. As would be expected, it is the most volatile of the three fluorides; the crystals are white below  $42^\circ$ , when they become pale yellow. They melt at  $46^\circ$ . The hexafluoride also dissolves in hydrogen fluoride, but differs from  $\text{XeF}_2$  and  $\text{XeF}_4$  by giving a conducting solute:

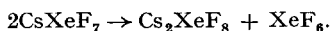


It is reduced by hydrogen to Xe and HF and, under a controlled hydrolysis, yields the oxofluoride  $\text{XeOF}_4$  or  $\text{XeO}_3$  according to conditions.

Liquid  $\text{XeF}_6$  dissolves CsF to give the salt  $\text{CsXeF}_7$ .

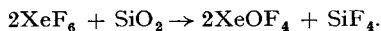


This can be separated as a yellow solid which is stable up to  $50^\circ$ . Above that temperature it loses  $\text{XeF}_6$  to give colourless  $\text{Cs}_2\text{XeF}_8$ , stable up to  $400^\circ$ .



Although RbF is only slightly soluble in  $\text{XeF}_6$ , it reacts with it to give colourless  $\text{RbXeF}_7$ , stable below  $20^\circ$ , and  $\text{Rb}_2\text{XeF}_8$ , also colourless, stable up to  $400^\circ$ . KF and NaF form only the octafluoroxenates  $\text{K}_2\text{XeF}_8$  and  $\text{Na}_2\text{XeF}_8$ , and these are less thermally stable than those of Rb and Cs.

Xenon hexafluoride attacks silica to produce xenon oxofluoride and hydrogen fluoride:

*Other fluorides*

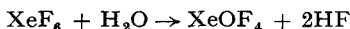
The radical  $\text{XeF}$  was detected by its e.s.r. spectrum in crystals of  $\text{XeF}_4$  irradiated with  $\gamma$ -rays. This species, which is stable only at low temperatures, is paramagnetic, and renders the host lattice bright blue. There is evidence



of the presence of  $\text{XeF}_8$  in the products of the high-pressure reaction of xenon and fluorine.

*Xenon oxofluoride,  $\text{XeOF}_4$*

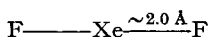
This is prepared by the reaction of the hexafluoride with water:



It is a colourless liquid which solidifies about  $35^\circ$  and can be kept in a nickel vessel.

### Fluoride structures

*Xenon difluoride* has a linear molecule in both gaseous and solid phases (cf. the  $\text{ICl}_2^-$  ion, p. 148):



In the solid these are packed parallel to one another (Fig. 184).

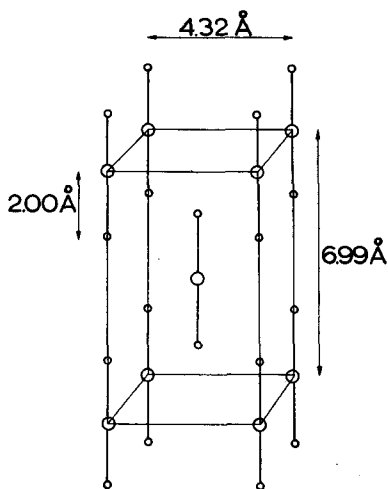


Fig. 184. Crystal structure of  $\text{XeF}_2$ .

The bonding may involve only one  $5p\sigma$  AO of the Xe and the  $2p\sigma$  AO's of the fluorines leaving three lone-pairs symmetrically placed in a plane through the Xe atom and at right angles to the F—Xe—F line.

If we consider three atomic orbitals, the  $5p_z$  on the xenon atom and the  $2p_z$  on each of the fluorine atoms, we see that these can be combined

to give three molecular orbitals, of which one is bonding, one is non-bonding and one is anti-bonding. The symmetry and overlap of the AO's is represented in Fig. 185.

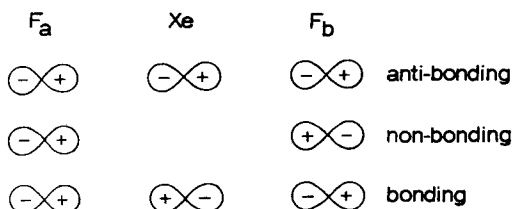


Fig. 185. AO's available for MO formation in  $XeF_2$ .

The non-bonding MO receives no contribution from the xenon  $5p_z$  AO because this orbital has the wrong symmetry for combination, as indicated by the algebraic signs of the  $\psi$  values.

The energies and occupancies of the MO's are represented in Fig. 186:

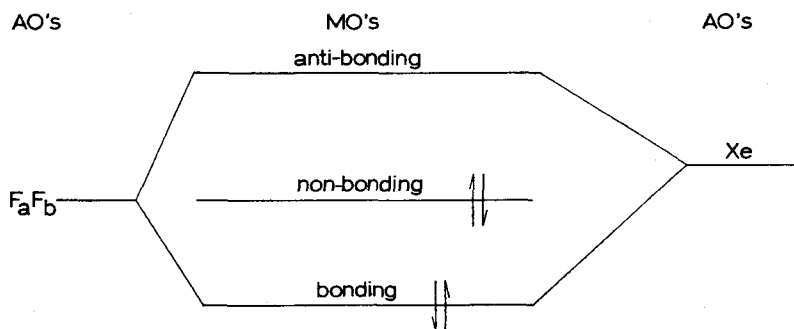


Fig. 186. Energies of MO's in  $XeF_2$ .

$XeF_2$ , in common with the other xenon compounds, is an electron-excess compound, in contrast with the electron-deficient compounds such as the boranes (p. 270).

The molecular orbital theory predicts that stability is enhanced by high electronegativity of the outer atoms and lower ionisation energy of the central atom, in agreement with the known stabilities of noble gas compounds. The theory also predicts that a compound like  $XeF_2$  will have considerable ionic character, with a charge of about  $+e$  on the xenon and about  $-\frac{1}{2}e$  on each fluorine, consistent with the remarkably high heat of dissociation of the difluoride, 12.3 kcal mole<sup>-1</sup>.

*Xenon tetrafluoride* has a square structure (*cf.*  $ICl_4^-$ , p. 150) which is

considered to be due to the use of two  $5p$  AO's of the xenon, and to have two lone pairs above and below the xenon atom (Fig. 187).

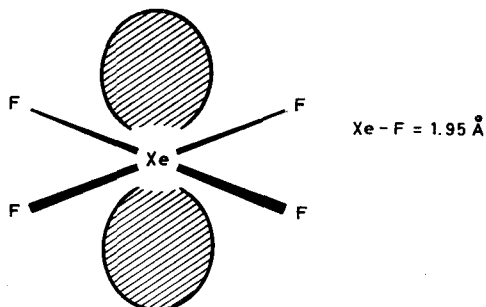


Fig. 187. Bonds and lone pairs in  $\text{XeF}_4$  molecule.

*Xenon hexafluoride* has slightly distorted octahedral molecules. If the MO's are considered to be formed from the three  $5p\sigma$  AO's of the xenon and the  $2p\sigma$  AO's of the fluorines, there then remains one lone pair of electrons on the Xe which accounts for the asymmetry of the molecule. On this description of the bonding there should be the possibility of a compound with 8-co-ordination; indeed there is some evidence for a higher fluoride, possible  $\text{XeF}_8$ .

*Xenon oxo fluoride* has been shown by infrared and Raman spectra to have a square pyramidal structure (Fig. 188):

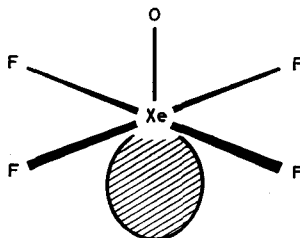


Fig. 188. Structure of  $\text{XeOF}_4$  molecule; it has one  $\sigma$  lone pair.

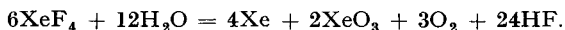
The Xe-O bond has appreciable double bond character; the Xe and the fluorine atoms are almost coplanar. There is a lone pair of electrons opposite the oxygen atom.

### Oxides

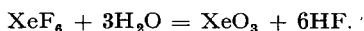
#### *Xenon trioxide*

Xenon tetrafluoride does not react with dry silica, but it undergoes a

succession of reactions with water of which the approximate results may be represented thus:



The trioxide, a non-volatile, highly explosive solid ( $\Delta H_f = +96$  kcal mole<sup>-1</sup>), can be separated from this mixture. It can be made more directly by the slow hydrolysis of  $\text{XeF}_6$ :



Xenon trioxide, as X-ray analysis shows, has a trigonal pyramidal structure shown in Fig. 189:

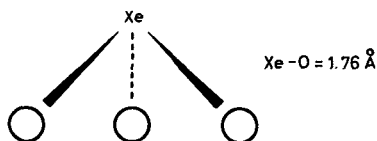


Fig. 189. Pyramidal structure of  $\text{XeO}_3$  molecule.

similar to the isoelectronic  $\text{IO}_3^-$  ion, with a lone pair of electrons directly above the Xe atom.

#### *Xenon tetroxide*

This oxide,  $\text{XeO}_4$ , which is an unstable gas at room temperature, is made by treating  $\text{Na}_4\text{XeO}_6$  with  $\text{H}_2\text{SO}_4$ . Infrared examination shows the molecule present in the vapour to be tetrahedral. At low temperature it is a yellow solid.

### Acids

An acid,  $\text{H}_6\text{XeO}_6$ , has also been made by acid hydrolysis of  $\text{XeF}_6$ . However, alkaline hydrolysis with aqueous  $\text{NaOH}$  gives sodium perxenate hexahydrate,  $\text{Na}_4\text{XeO}_6 \cdot 6\text{H}_2\text{O}$  in which xenon has the oxidation number +8. The perxenate ion,  $\text{XeO}_6^{4-}$ , has a regular octahedral structure, with the  $\text{Xe-O}$  distance = 1.8 Å.

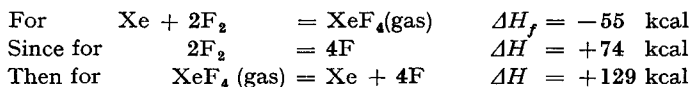
### Compounds of krypton and radon

Compounds of other noble gases include  $\text{KrF}_2$ , made by the photolysis of fluorine and krypton in an argon matrix at 20° K (that is in frozen argon) and  $\text{KrF}_4$ , a colourless liquid made by passing an electric discharge through a krypton-fluorine mixture at the temperature of liquid nitrogen.

A radon fluoride has been made; oxides and chlorides of this element are probably capable of synthesis, but the  $\alpha$ -activity of radon may render the compounds too short-lived to be isolated.

### Thermochemistry of noble gas compounds

The standard heat of formation of  $\text{XeF}_4$  has been measured by reducing the compound with hydrogen in an isothermal calorimeter.

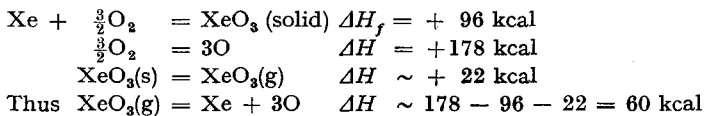


Thus the mean bond energy for the Xe-F bond is about

$$129/4 \sim 32 \text{ kcal mole}^{-1}.$$

The bond energy in  $\text{XeF}_6$ , obtained by similar methods, is about the same, and in  $\text{XeF}_2$ , obtained from vibrational spectra, only slightly less,  $\sim 28$  kcal mole<sup>-1</sup>.

Oxygen compounds of xenon are less thermodynamically stable. From the heat of explosion of  $\text{XeO}_3$  in a bomb calorimeter,  $\Delta H_f$  for  $\text{XeO}_3$  solid has been found to be about +96 kcal. The Xe-O bond energy cannot be calculated unless the heat of sublimation of  $\text{XeO}_3$  can be measured, and this is not possible, as the solid explodes on heating. If a value of about 22 kcal mole<sup>-1</sup> is assumed for the heat of sublimation, the mean bond energy  $E(\text{Xe-O})$  in  $\text{XeO}_3$  is probably not more than 20 kcal (*cf.* 118 kcal for O-O in  $\text{O}_2$ ).



$$E(\text{Xe-O}) \sim 60/3 \sim 20 \text{ kcal mole}^{-1}$$

Calculations based on the known value of the heat of dissociation of  $\text{Cl}_2$  (58 kcal), and on extrapolation for the Xe-Cl bond energy made from comparisons of chlorides with fluorides for other elements, suggest that xenon chlorides should all be markedly endothermic compounds.

## FURTHER READING

- N. BARTLETT, *The Chemistry of the Noble Gases*, Endeavour, 23 (1964) 3.
- G. J. MOODY AND J. D. R. THOMAS, *Compounds of the Noble Gases*, J. Royal Inst. Chem., 88 (1964) 31.
- N. N. GREENWOOD, *Chemistry of the Noble Gases*, Education in Chemistry, 1 (1964) 176.
- C. A. COULSON, *The Nature of the Bonding in Xenon Fluorides and Related Molecules*, J. Chem. Soc., (1964) 1442.
- J. H. HOLLOWAY, *Reactions of the Noble Gases*, in F. A. COTTON (Ed.), *Progress in Inorganic Chemistry*, New York, Interscience, 6 (1964) 241.

Chapter 15

## The Alkali Metals

### GROUP IA

The atoms of the metals lithium, sodium, potassium, rubidium, caesium and francium, have a singly occupied s orbital outside one or more closed shells of noble-gas structure. Owing to the screening of the nucleus which these shells provide, the valence electron is very weakly held, the first ionisation energy is low and, because the second ionisation energy is very high, they give only the unipositive,  $M^+$  ion. Their chemistry is accordingly essentially ionic: in combination with strongly electronegative elements they tend to form ionic solids such as NaCl, and their simple salts are soluble in water and give the solvated  $M^+aq$  cation.

But the elements also show covalent bonding. Their vapours contain some  $M_2$  molecules (p. 107) and they form organometallic compounds (p. 316); in both of these covalent bonding occurs.

TABLE 48  
ATOMIC PROPERTIES OF THE ALKALI METALS

	<i>Li</i>	<i>Na</i>	<i>K</i>	<i>Rb</i>	<i>Cs</i>	<i>Fr</i>
Atomic number	3	11	19	37	55	87
Electron configuration	$1s^2 2s^1$	$2s^2 2p^6 3s^1$	$3s^2 3p^6 4s^1$	$4s^2 4p^6 5s^1$	$5s^2 5p^6 6s^1$	$6s^2 6p^6 7s^1$
Covalent radius (Å)	1.34	1.54	1.96	2.11	2.25	—
Ionic radius, $M^+$ (Å)	0.60	0.95	1.33	1.48	1.69	—
Metallic radius (Å)	1.55	1.90	2.35	2.48	2.67	—

Such differences as there are between the ionic chemistry of the elements are due, as will be seen later, to differences in ionic radius, ionisation energy and electrode potential. For instance the ionisation energies decrease down the sub-group. But lithium, with the highest ionisation energy, has a relatively low electrode potential owing to the high heat of hydration of the ion, which, in turn, is due to its small size and less effectively screened nuclear charge. As a result, lithium in contact with water is as strong a

reducing agent as caesium, but when dry it is less easily oxidised than other metals of the sub-group.

TABLE 49

IONISATION ENERGIES AND ELECTRODE POTENTIALS OF THE ALKALI METALS

	<i>Li</i>	<i>Na</i>	<i>K</i>	<i>Rb</i>	<i>Cs</i>
Ionisation energy <i>I</i> (eV)	5.39	5.14	4.34	4.18	3.90
Electrode potential $E^\circ$ , M <sup>+</sup> /M (V)	-3.02	-2.71	-2.92	-2.99	-3.02

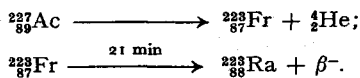
## Elements: occurrence and properties

TABLE 50

PROPERTIES OF THE ALKALI METALS

	<i>Li</i>	<i>Na</i>	<i>K</i>	<i>Rb</i>	<i>Cs</i>
Density (g/cc)	0.53	0.97	0.86	1.53	1.90
Atomic volume	12.9	23.7	45.5	56.1	69.8
M.p. (°C)	180	98	63.5	39	28.5
B.p. (°C)	1336	883	759	700	670

Sodium (2.63% of lithosphere) and potassium (2.40% of lithosphere) are high in abundance among the elements in the earth's crust; their amounts in sea water are respectively 1.14% and 0.04%. Sodium and its compounds are chiefly derived from sodium chloride; the principal source of potassium is carnallite,  $\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$ . The other elements of the family are much less common. Lithium (0.0065% of lithosphere), mainly in aluminosilicates such as petalite,  $(\text{Li, Na})\text{AlSi}_4\text{O}_{10}$ , and spodumene,  $\text{LiAl}(\text{SiO}_3)_2$ , has an abundance less than rubidium (0.031% of lithosphere) and about ten times greater than caesium. Francium occurs naturally only in minute amounts and, of its four known isotopes—all radioactive—the longest lived is  $^{223}\text{Fr}$  (half-life 21 min). Its progenitor is actinium-227, and the nuclide is itself a  $\beta$ -emitter:



It is co-precipitated with Rb and Cs perchlorates or chloroplatinates.

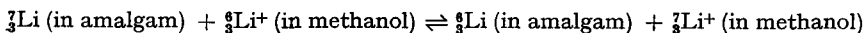
Both potassium and rubidium have natural active isotopes. Potassium-40 is a feeble  $\beta$ -emitter with a half-life of  $1.3 \times 10^9$  years; it makes up about 0.012% of the natural element. Of the two natural isotopes of rubidium,



one,  $^{87}\text{Rb}$ , which accounts for nearly 28%, is a weak  $\beta$ -emitter, half-life  $6 \times 10^{10}$  years.

### Separation of the isotopes of lithium

Lithium occurs as  $^6\text{Li}$  (7.3%) and  $^7\text{Li}$  (92.7%) with one isotope nearly 17% greater in mass than the other. The isotopes show a slight difference in chemical behaviour, and when lithium amalgam falls through a methanol solution of lithium chloride an equilibrium is established:



Lithium-6 has a slightly less negative electrode potential; and as a result the proportion of  $^6\text{Li}$  in the amalgam increases.

Lithium-6 ions are preferentially adsorbed by a zeolite in its sodium form and some separation of  $^6\text{Li}^+$  from  $^7\text{Li}^+$  can be attained by means of very tall cation-exchange columns. The separation of lithium-6 is important because of its use in the preparation of tritium in nuclear reactors (p. 262).

### The metals

#### *General*

Reduction of alkali-metal cations is difficult so that the only practicable methods of preparing the metals are electrolytic; and, currently, electrolyses of the fused chlorides are employed. In most compounds the elements appear as an extremely ionic type, nevertheless covalent diatomic molecules exist in vapour of the metals though the proportion is small, not more than 1% even in lithium vapour, for the dissociation energies are low, Li-Li 27.2, Na-Na 17.5, K-K 11.8, Rb-Rb 11.3, Cs-Cs 10.4 kcal. The  $\sigma$  bonds in the molecules are covalencies formed by the overlap of s orbitals, possibly with some p-orbital contribution. Although the overlap is considerable, the resultant charge cloud is diffuse, owing to an efficient screening of the nuclear attraction, and the bonds are weak.

The metals are highly active, increasingly so with atomic number. When freshly cut they are silvery, but they rapidly tarnish in air, the rate of tarnishing increasing down the group. Lithium, with its high ionisation potential, reacts rather slowly with water and with liquid bromine, and not at all with oxygen below  $100^\circ$ . But with non-metals possessing small anions, the metal is more active and forms compounds more stable than those of any of the other metals. Its hydride, carbide and nitride may all be made by direct combination, whereas sodium gives only hydride in this way. The combination of two elements, both with small ions, confers

a high lattice energy on the crystal, and these reactions of lithium are highly exothermic and lithium hydride is far more stable to heat than the other alkali metal hydrides. When lithium burns in air or oxygen the only oxide formed is  $\text{Li}_2\text{O}$ ; in this respect the metal differs from its congeners, which form peroxides  $\text{M}_2\text{O}_2$ , and superoxides,  $\text{MO}_2$  (p. 508). A remarkable property of metallic lithium, undoubtedly related to the size and reactivity of its ion, is its ability to attack glass; the other alkali metals can be manipulated in glass vessels, but molten lithium rapidly cuts a way through.

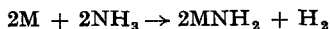
#### *Behaviour with liquid ammonia*

The metals dissolve in liquid ammonia to form metastable, coloured solutions; and the solubilities can be as high as  $5M$ . With Li, Na and K it is possible, above a certain concentration, to have two immiscible solutions in equilibrium, a heavier, blue, dilute metal phase and a lighter, bronze, concentrated metal phase. This is because dissolving the metal causes a considerable increase in liquid volume. The blue solutions have approximately the same absorption spectra, irrespective of the particular metal present.

The constitution of the solutions changes with concentration:

- (i) In extremely dilute solutions the metal atoms form  $\text{M}^+$  ions surrounded by  $\text{NH}_3$  molecules with their N atoms directed towards the metal. The electrons which are set free by the ionisation form centres in the liquid around which  $\text{NH}_3$  molecules are arranged with hydrogens directed towards the electron. The presence of these electrons has been shown by paramagnetic resonance (p. 88).
- (ii) In moderately concentrated solutions ( $M/20$  to  $M$ ) ammoniated metal ions are bound by paired electrons into small clusters of two, three or four ions.
- (iii) In more concentrated solutions ( $> M$ ) ammoniated metal ions are bound together by unpaired electrons in much the same way as are the metal ions in a molten metal.

These systems are remarkably stable and the solutions liberate hydrogen only very slowly:



But traces of transition metal ions catalyse the reaction. The solutions have strong reducing properties and are used in preparative chemistry.

#### *Uses*

The metals are employed in a variety of alloys. Lithium generally hardens and strengthens, but also causes embrittlement; from 0.05 to 0.1% is used in

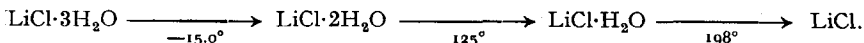
Al, Zn and Mg alloys. Sodium is an important additive to lead; such an alloy is the basis of the manufacture of lead tetraethyl, and another, containing 0.6% Na, 0.6% Ca and 0.05% Li, is a bearing metal. Ternary alloys of caesium with aluminium and either barium or strontium are used in photoelectric cells. Liquid sodium or sodium-potassium alloy is employed to transfer heat from the core of certain atomic reactors, *e.g.* Dounreay fast breeder.

### Halides

All the alkali-metal halides, except caesium chloride, bromide and iodide, form cubic crystals with the rock salt lattice and show a co-ordination number of 6. The exceptions are also cubic, but they have the caesium chloride structure (p. 193) characterised by a co-ordination number of 8. The radius ratio for CsCl,  $Cs^+/Cl^- = 0.93$ , allows 8 co-ordination, but is so near the ratio for 6 co-ordination (p. 194) that caesium chloride is dimorphous, changing, at  $445^\circ$ , from the caesium chloride structure to the rock salt structure. The crystalline halides are generally markedly ionic, though, as expected, lithium iodide is somewhat covalent, for iodide is the largest and most easily polarised simple anion and lithium, the smallest alkali-metal cation, possesses the strongest polarising power.

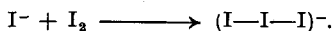
Lithium iodide forms a solid complex with ammonia,  $Li(NH_3)_4I$ , but the related hydrate, alcoholate and amine complexes are less stable. These complexes presumably involve ion-dipole bonds (p. 134), the nitrogen lone pairs surrounding the  $Li^+$ ; some covalent character is also permissible if *s* and *p* orbitals on the Li are invoked. The chloride, bromide and iodide of lithium are much more soluble in alcohol and ether than those of the other alkali metals, but this is not always a reliable indication of covalent character. The property is employed in separating lithium from sodium.

Lithium chloride is particularly deliquescent and forms hydrates:



### Polyhalides

Many polyhalides of alkali metals are known, the most important being the tri-iodides and the very stable mixed halides of the type  $MICl_4$ . Lithium and sodium do not form tri-iodides. The potassium compound exists as a monohydrate stable below  $25^\circ$ , but dehydration is accompanied by loss of iodine. The rubidium and caesium compounds are anhydrous and crystalline. The stronger positive fields round the lithium and sodium ions curtail the spread of negative charge from the iodide ion to an iodine molecule.



Rubidium and caesium also form tribromides, and mixed trihalides, particularly of the  $MICl_2$  type, are known; in these the  $(Cl-I-Cl)^-$  ion is linear. The compounds  $KIBrCl$  and  $CsIBrF$  have also been isolated. All the alkali metals form stable orange-red polyhalides of the type  $MICl_4$ , containing a square complex ion (p. 150).

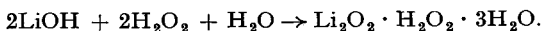
In passing it may be noted that potassium, rubidium and caesium form sparingly soluble chloroplatinates by which they can be readily separated from the soluble lithium and sodium compounds:

	$K_2PtCl_6$	$Rb_2PtCl_6$	$Cs_2PtCl_6$
Solubility at 20° (g/100 g)	1.12	0.141	0.07

### Oxides

The metals burn in oxygen to yield (i) lithium monoxide,  $Li_2O$ , (ii) sodium peroxide,  $Na_2O_2$ , and (iii) potassium, rubidium and caesium superoxides,  $MO_2$ , respectively. The anions formed in the oxide ( $O^{2-}$ ), the peroxide ( $O_2^{2-}$ ) and the superoxide ( $O_2^-$ ) are shown in parenthesis.

The lithium ion, because it is so small, has a much stronger positive field around it than the sodium ion. A strong positive field near one oxygen anion restricts the spread of negative charge towards another oxygen atom, making the formation of higher oxides difficult. Thus lithium peroxide is only readily made by precipitation from alcoholic lithium hydroxide with hydrogen peroxide:



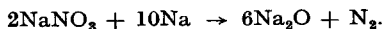
The precipitate when dried over phosphorus pentoxide in a vacuum becomes the white, anhydrous peroxide; this reverts to the monoxide when heated.

The positive field round the sodium ion is too weak to prevent the conversion of the  $O^{2-}$  anion into a peroxide ion, but is strong enough to prevent further oxidation to a superoxide.

The weaker fields round the larger unipositive ions of potassium, rubidium and caesium allow the superoxide ion  $O_2^-$  to be formed.

The superoxides have the tetragonal lattice of calcium carbide, in which the anion has an unpaired electron, its structure (*cf.* the oxygen molecule p. 108) being  $KK(z\sigma)^2(y\sigma)^2(x\sigma)^2(w\pi)^4(v\pi)^3$ . It confers paramagnetism on the compounds, the only ones, among those of Gp. IA, known to be paramagnetic.

The normal oxides of the alkali metals, other than lithium, are usually made by reducing the nitrate or nitrite with the metal itself:



Lithium oxide dissolves quietly in water; the others more energetically.

Lithium hydroxide monohydrate crystallises from the solution. Structurally every lithium ion is surrounded tetrahedrally by two hydroxide ions and two water molecules. Every tetrahedral group has an edge and two corners to produce double chains held laterally by hydrogen bonds (shown by broken lines) between the hydroxide ions and the water molecules. Every water molecule has four near neighbours, two lithium ions of the same chain and two hydroxide ions, one from each of two other chains (Fig. 190).

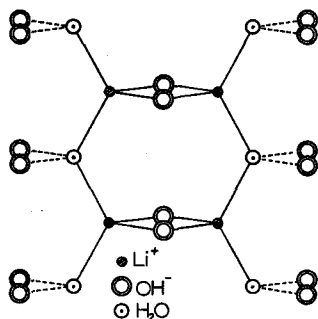


Fig. 190. Structure of  $\text{LiOH}\cdot\text{H}_2\text{O}$ .

Phase rule studies show that both sodium and potassium hydroxides form several hydrates.

### Sulphides

All the alkali metals form hydrosulphides  $\text{MHS}$ , monosulphides  $\text{M}_2\text{S}$ , and a series of polysulphides  $\text{M}_2\text{S}_x$ , where  $x$  has values from 2 to 6.

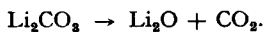
The hydrosulphides are prepared by saturating an aqueous or aqueous alcoholic solution of the appropriate hydroxide with hydrogen sulphide, and may be crystallised as hydrates therefrom, *e.g.*  $\text{NaHS}\cdot 3\text{H}_2\text{O}$  and  $\text{KHS}\cdot \frac{1}{2}\text{H}_2\text{O}$ . With the exception of  $\text{LiSH}$  which is thermally unstable, these may be dehydrated or even fused without extensive decomposition.

The monosulphide and polysulphides are formed by burning the metals in sulphur vapour, by the action of sulphur on the metals dissolved in liquid ammonia, and by the action of the molten metals on sulphur dissolved in toluene. Hydrates or alcoholates and, in some cases, the anhydrous compounds may be prepared by dissolving sulphur in hot solutions of the hydrosulphides or monosulphides. Potassium, rubidium and caesium give all the sulphides where  $x = 1, 2, 3, 4, 5,$  or  $6$ ; sodium only up to the pentasulphide, and lithium only those for which  $x = 1, 2$  and  $4$ . All the metals form two polysulphides of relatively outstanding stability; one is invariably the

disulphide, and the other is the tetrasulphide in the case of lithium and sodium, and the pentasulphide in the case of potassium, rubidium or caesium. The amount of water of crystallisation and the solubility decrease with increase in atomic number of the metal, the gradation being most marked between sodium and potassium.

### Oxoacid salts

Lithium carbonate decomposes to the oxide when heated in a stream of hydrogen at 800°:



The strong polarising action of the small cation on the large complex anion,  $\text{CO}_3^{2-}$ , presumably assists the reaction. Lithium oxide has the antiferroelectric structure (p. 203), and the reaction proceeds because (i) the highly polarisable carbonate ion readily loses an oxygen ion and (ii) the gain in lattice energy resulting from the substitution of a smaller oxide ion for the larger carbonate ion enables the centres of charge to approach more closely.

Lithium carbonate is so sparingly soluble as to be precipitated from solutions of lithium salts by sodium carbonate. It dissolves in water containing carbon dioxide but there is no direct evidence that a solid bicarbonate can be formed. The bicarbonates of the other alkali metals may all be obtained in solid form. Those of rubidium and caesium are more soluble and thermally stable than the sodium and potassium salts.

Lithium nitrate decomposes on heating in a similar way to calcium nitrate to give the oxide:



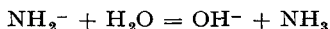
The other alkali metal nitrates yield the nitrites and oxygen. Only the lithium and sodium nitrates are deliquescent and hydrated, the rest are anhydrous.

Lithium orthophosphate,  $\text{Li}_3\text{PO}_4$ , is precipitated when sodium phosphate is added to an alkaline solution of a lithium salt. Phosphates of the other metals are soluble.

The sulphates of potassium, rubidium and caesium are isomorphous and anhydrous. The solubility of sodium sulphate depends upon the composition of the solid phase. It increases rapidly with temperature up to 32.38°, and within this range crystallisation gives the decahydrate. Above 32.38° the solubility falls slightly with temperature and the anhydrous salt separates as fine crystals. Lithium sulphate crystallises as the monohydrate,  $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ . It is doubtful whether  $\text{Li}_2\text{SO}_4$  forms an alum, although such compounds are formed by the elements from sodium to caesium (*e.g.*  $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ ).

### Nitrogen compounds.

All the alkali metals react when heated in ammonia to form white, crystalline amides,  $MNH_2$ , insoluble in organic solvents, and decomposed immediately by cold water:



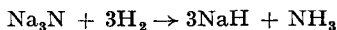
Only lithium forms an imide; it is made by heating the amide,  $LiNH_2$ , to near its m.p. under reduced pressure:



Dark-red lithium nitride,  $Li_3N$ , is made by heating the metal in nitrogen, but for nitrides of the other alkali metals indirect methods must be used.  $Na_3N$  can be made by dissolving sodium and sodium azide in liquid ammonia, allowing the  $NH_3$  to evaporate, and then warming:



The red solid decomposes at  $150^\circ$  to the metal and  $N_2$ , and reacts with hydrogen at  $120^\circ$  to give sodium hydride and ammonia:



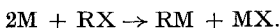
It is evident that lithium forms more stable nitrogen compounds than do the other Group I metals.

### Organometallic compounds

An organometallic compound is one in which there is direct bonding between carbon and a metal, or, in more general usage, between carbon and an element of lower electronegativity. The organometallic compounds of the alkali metals belong to three classes:

- (i) Colourless alkyls and aryls, of largely covalent character.
- (ii) Coloured ionic compounds such as  $(C_6H_5)_3C^- Na^+$  and  $C_6H_5CH_2^- Na^+$ .
- (iii) Colourless ionic compounds of hydrocarbons, like acetylene and cyclopentadiene, which have acidic character (p. 394).

The alkyls and aryls can be made by adding the metal to the alkyl or aryl halides in benzene or ether:



The lithium compounds, except for  $CH_3Li$ ,  $C_2H_5Li$ , and  $C_6H_5Li$  which are solids, are liquid at room temperature. In solution in hydrocarbons,  $C_2H_5Li$  is hexameric and  $t-BuLi$  is tetrameric, with Li and C atoms oc-

cupying the vertices of interpenetrating tetrahedra. Mass spectroscopy shows ethyl-lithium vapour to contain mainly the hexamer and tetramer; the bonding is probably of the multicentre type (p. 273).

An X-ray analysis of the structure of  $\text{CH}_3\text{Li}$  has recently been completed. The solid contains  $(\text{CH}_3\text{Li})_4$  units as shown in Fig. 191.

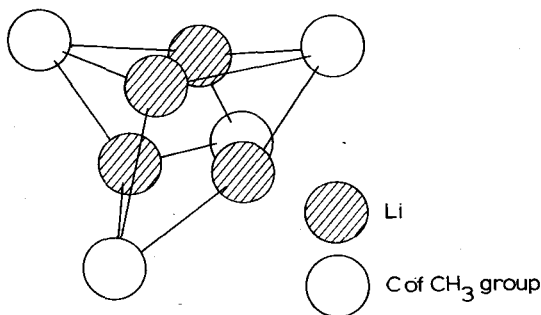
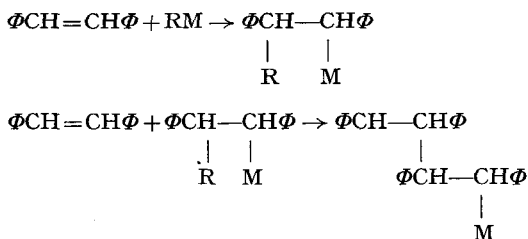


Fig. 191. Tetrameric methyl-lithium.

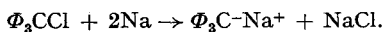
The lithium atoms are arranged in a regular tetrahedron, the carbon atoms in an interpenetrating tetrahedron which has its vertices opposite to the face-centres of the first. The C-Li distance is 2.28 Å. Every carbon atom can be considered to form a four-centre bond with three lithium atoms.

The alkyls and aryls of the other alkali metals are colourless, amorphous solids, insoluble in organic solvents. Like the lithium compounds, they are thermally unstable, strongly hydrolysed by water, and most of them are spontaneously inflammable in air. The compounds initiate polymerisation in styrene and similar substances, probably by the mechanism:



and so on.

The coloured ionic compounds such as  $\phi_3\text{C}^-\text{Na}^+$  can be made by treating the halide with the metal:

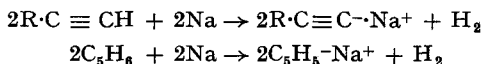


They usually give conducting solutions when dissolved in ether. The anion



is almost certainly stabilised by a delocalisation of the negative charge over the aromatic system.

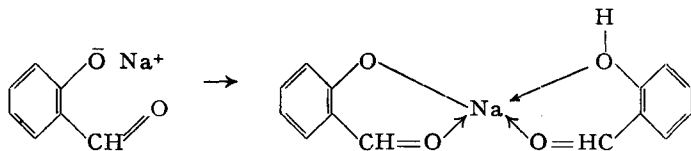
The metals react with acidic hydrocarbons in solvents such as liquid ammonia or dimethylformamide:



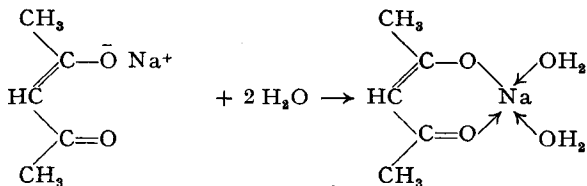
The products are colourless solids.

### Complex compounds

Though the sizes and electronic configurations of the alkali-metal cations are not conducive to co-ordination with ligands, chelating groups do impose some acceptor properties on them. Thus when sodium hydroxide is added to salicylaldehyde the salt produced takes up a further molecule of salicylaldehyde to form a compound which is covalent.



A similar result is sometimes achieved by hydration. The anhydrous sodium derivative of acetylacetonate is salt-like but the dihydrate shows covalency, being soluble in non-polar solvents like toluene.



Potassium, rubidium and caesium form both 4- and 6-covalent compounds with salicylaldehyde; a 6-covalent one is shown in Fig. 192.

Increasing atomic number of the alkali metal influences the stability of these covalent compounds because it is accompanied by (i) an increased ease of ionisation which weakens the tendency to accept electrons, (ii) an increased size of the atom which raises the maximum co-ordination number. This accords well with the known stability of the 4-covalent compounds of sodium and of the 6-covalent compounds of rubidium.

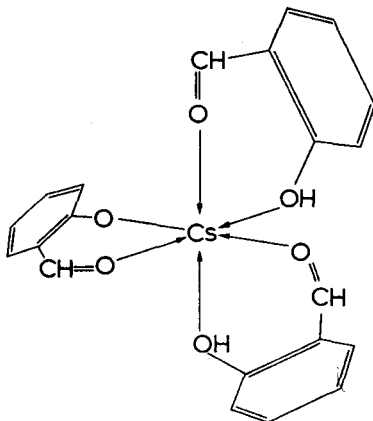
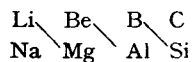


Fig. 192. Tris(salicylaldehydato)caesium.

### Similarities of lithium and magnesium

A feature of the second period of the Periodic Table is the similarity the chemistry of an individual element shows to that of the element a group higher in the third period: *diagonal similarities* as they are often termed:



In general the polarising powers of cations increase across a period because of the increasing charge, but diminish down a group because of the increasing ionic radius. When both movements are made simultaneously, one effect, in part at least, compensates for the other and there may be no marked change in properties. In illustration of this the similarity between lithium and magnesium may be cited; this is exemplified by:

- (i) the formation of normal oxides, not peroxides, when the metal is burnt;
- (ii) the instability of the carbonates and nitrates;
- (iii) the formation of the carbides and nitrides by direct combination of the elements;
- (iv) the insolubility of the carbonates and phosphates;
- (v) the strong hydration of the ions;
- (vi) the solubility of salts such as chlorides in organic solvents;
- (vii) the high solubility of the alkyls in organic solvents.

## FURTHER READING

- D. S. LAIDLER, *Lithium and its Compounds*, London, Royal Institute of Chemistry. Monograph, 1957, No. 6.
- E. A. BRAUDE, *Organic Compounds of Lithium*, in J. W. COOK (Ed.), *Progress in Organic Chemistry*, London, Butterworths, Vol. 3 (1955) 172.
- M. C. R. SYMONS, *Nature of Metal Solutions*, Quart. Rev., XIII (1959) 99.
- M. C. R. SYMONS AND W. T. DOYLE, *Colour Centres in Alkali Halide Crystals*, Quart. Rev., XIV (1960) 62.
- L. BREWER AND E. BRACKETT, *The Dissociation Energies of Gaseous Alkali Halides*, Chem. Rev., 61 (1961) 425.

## Chapter 16

# Beryllium, Magnesium and the Alkaline Earth Metals

### GROUP IIA

In the physical properties of the metals and also in their chemistry, beryllium and magnesium stand somewhat apart from the remaining elements of Group IIA. The separation is recognised by designating calcium, strontium, barium and radium the *alkaline earth elements*. Beryllium and magnesium are sufficiently unreactive towards air to allow their mechanical use either alone or as major constituents of alloys, but the rest of the metals are readily and progressively attacked by air of ordinary humidity. Chemically beryllium and magnesium are distinguished by having covalent compounds, particularly the former element, whereas the chemistry of the rest of the group is essentially ionic. Amongst themselves, the alkaline earth elements show considerable similarity in properties and there is a regular change in these properties with increasing atomic number. The electropositive character and thermal stability of salts increase down the group and the solubilities of most of their salts decrease in the same direction, along with their ability to form hydrates.

This said, the trend of properties throughout this group is similar to that in Group IA, but the greater nuclear charges make the corresponding atoms smaller. The bivalent ions of the alkaline earth metals, formed by the loss of two electrons from the atoms, are much smaller than the univalent ions of the alkali metals. The extreme smallness of  $\text{Be}^{2+}$  makes that element even more exceptional in Group IIA than is lithium in Group IA. For instance the promotion  $\text{Be}[1s^2 2s^2] \rightarrow \text{Be}[1s^2 2s^1 2p^1]$  occurs easily, giving rise (through sp hybridisation) to two largely covalent bonds. Provided electron-rich ligands are available the number of valencies can be increased to four by donation and the use of  $sp^3$  hybrid bonds. In these circumstances it is usual to associate the valence electrons formally with the more electronegative groups, beryllium being shown as  $\text{Be}^{2+}$ , thus recognising the availability of the s and p orbitals for the introduction of covalent character.

The first ionisation energies decrease considerably from beryllium to calcium. Despite the second ionisation energies often being large, the few

TABLE 51  
ATOMIC PROPERTIES OF GROUP IIA ELEMENTS

	<i>Be</i>	<i>Mg</i>	<i>Ca</i>	<i>Sr</i>	<i>Ba</i>	<i>Ra</i>
Atomic number	4	12	20	38	56	88
Electronic configuration	1s <sup>2</sup> 2s <sup>2</sup>	2p <sup>6</sup> 3s <sup>2</sup>	3p <sup>6</sup> 4s <sup>2</sup>	4p <sup>6</sup> 5s <sup>2</sup>	5p <sup>6</sup> 6s <sup>2</sup>	6p <sup>6</sup> 7s <sup>2</sup>
Covalent radius (Å)	0.90	1.30	1.74	1.92	1.98	—
Ionic radius M <sup>2+</sup> (Å)	0.31	0.65	0.99	1.13	1.35	1.40
Metallic radius (Å)	1.12	1.60	1.97	2.16	2.22	—

compounds with unipositive ions such as CaCl and CaI are easily converted to dihalides.

Beryllium has a standard electrode potential less negative than that of magnesium; the anomalous behaviour of lithium in relation to sodium is not repeated by beryllium, even though Be<sup>2+</sup> is very readily hydrated.

TABLE 52  
IONISATION ENERGIES AND ELECTRODE POTENTIALS OF GROUP IIA ELEMENTS

	<i>Be</i>	<i>Mg</i>	<i>Ca</i>	<i>Sr</i>	<i>Ba</i>	<i>Ra</i>
<i>I</i> 1 (eV)	9.32	7.64	6.11	5.69	5.21	5.27
<i>I</i> 2 (eV)	18.21	15.03	11.87	10.98	9.95	10.1
<i>E</i> <sup>o</sup> , M <sup>2+</sup> /M (V)	-1.70	-2.34	-2.87	-2.89	-2.90	—

The smaller atomic diameters of these elements result in higher densities, much higher m.p. and b.p., and greater hardness than are shown by the Group IA elements. Beryllium has a particularly high melting point.

TABLE 53  
PROPERTIES OF GROUP IIA ELEMENTS

	<i>Be</i>	<i>Mg</i>	<i>Ca</i>	<i>Sr</i>	<i>Ba</i>	<i>Ra</i>
Density (g/cc)	1.86	1.75	1.55	2.6	3.6	5.0
Atomic volume	4.85	14.00	26.1	34.0	38.3	45.2
M.p. (°C)	1280	651	851	800	850	960
B.p. (°C)	2770	1107	1437	1366	1637	—

Beryllium (6 × 10<sup>-4</sup>% of lithosphere) has its only commercial source in beryl, Be<sub>3</sub>Al<sub>2</sub>Si<sub>6</sub>O<sub>18</sub>. This when fused and quenched in water becomes soluble

in concentrated  $\text{H}_2\text{SO}_4$ , giving a solution containing the sulphates of beryllium, aluminium and the alkali metals. The addition of  $(\text{NH}_4)_2\text{SO}_4$  allows the aluminium to be removed as the sparingly soluble ammonium alum. The  $\text{BeSO}_4$  is then crystallised from the solution and converted to  $\text{BeO}$  (Fig. 193).

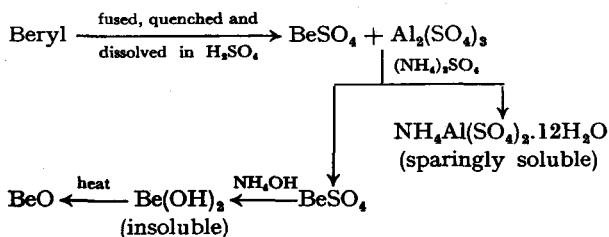


Fig. 193. BeO from beryl by sulphate route.

Alternatively compacts of beryl powder and  $\text{Na}_2\text{SiF}_6$  are heated at  $750^\circ$ . From the sinter sodium fluoroberyllate,  $\text{Na}_2\text{BeF}_4$ , is extracted with water, most of the Al and Si remaining in insoluble compounds. Crude  $\text{Be}(\text{OH})_2$  is precipitated from the solution by raising the pH and purified by converting it to  $\text{Na}_2\text{BeO}_2$  with NaOH, filtering and reprecipitating the  $\text{Be}(\text{OH})_2$  by hydrolysis.

Other beryllium compounds and the metal are obtainable from the hydroxide (Fig. 194).

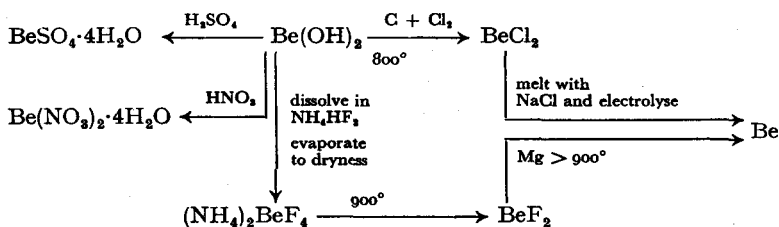


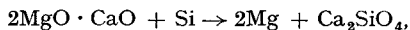
Fig. 194. Formation of beryllium and some of its compounds from  $\text{Be}(\text{OH})_2$ .

The metal is purified by melting in a vacuum and is cast under argon. Of h.c.p. structure, it has a high tensile strength, but is brittle even in the purest form yet obtained. Its mechanical properties are greatly improved by sintering it as a compressed powder ( $1150^\circ\text{C}$ ). Its transparency to X-rays makes Be a useful window material, and its high m.p. and low neutron cross-section allow its use in the nuclear-energy industry, especially as it remains protected by an oxide film when heated in air up to at least  $600^\circ$ . Increasingly, it is being used in alloys; beryllium copper, containing 2–2.25% Be and 0.25–0.5% Ni, is particularly hard and has a high elas-

ticity. BeO has ceramic properties of possible use in atomic reactors.

Magnesium (1.93% of earth's crust) occurs in magnesite,  $\text{MgCO}_3$ , dolomite,  $\text{MgCa}(\text{CO}_3)_2$ , kieselite,  $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ , carnallite,  $\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$ , and many silicates. Dolomite is not isomorphous with  $\text{CaCO}_3$  or  $\text{MgCO}_3$ ; its composition is always very close to  $\text{MgCa}(\text{CO}_3)_2$  and it appears to be a distinct compound. The chlorophyll of green plants is a compound containing magnesium. Magnesium chloride is obtained from carnallite, from which it separates as a solid phase when the mineral is fused.

Magnesium is now made by the reduction of calcined dolomite with ferrosilicon in retorts of nickel-chromium steel, at  $1160^\circ$  and  $10^{-3}$  atm. The reaction, effectively



is of considerable thermodynamic interest. The chemical potentials of the products are kept low

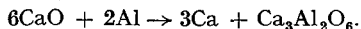
- (a) by working at extremely low pressure so that the partial pressure of magnesium vapour is small;
- (b) by using calcined dolomite instead of MgO as starting material, which gives calcium silicate as product instead of silica.

A favourable free energy of reaction is thus achieved at the comparatively low temperature of  $1160^\circ$ .

The magnesium vapour is condensed in steel-tube condensers. A much purer metal (99.98% Mg) is produced in this way than by electrolysis.

The metal, like beryllium, has a h.c.p. structure and is used in light alloys, particularly with aluminium, but also with Zn, Mn, Sn, Zr and Ce. Mg is a good reducing agent; turnings are heated with  $\text{UF}_4$  in graphite-lined, closed, steel reactors to produce billets of uranium metal.

Calcium (3.4% of lithosphere) occurs as carbonate in the minerals aragonite and calcite and the rocks limestone, chalk and marble, and as sulphate in anhydrite,  $\text{CaSO}_4$ , and gypsum,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ . All are plentiful and widely distributed. The metal, which has both h.c.p. and c.c.p. forms, is made either by electrolyzing the fused chloride,  $\text{CaCl}_2$ , a by-product of the Solvay process, or by reducing calcined limestone with aluminium at  $1200^\circ$  and  $10^{-3}$  atm in a retort of nickel-chromium steel. The reaction is effectively



The calcium which distils over is about 99% pure, the principal impurity being magnesium.

The high free energies of formation of CaO and  $\text{CaF}_2$  make calcium a powerful reducing agent. It has been used in the preparation of a number of metals which have oxides particularly resistant to reduction (*e.g.* chromium from  $\text{Cr}_2\text{O}_3$ ).

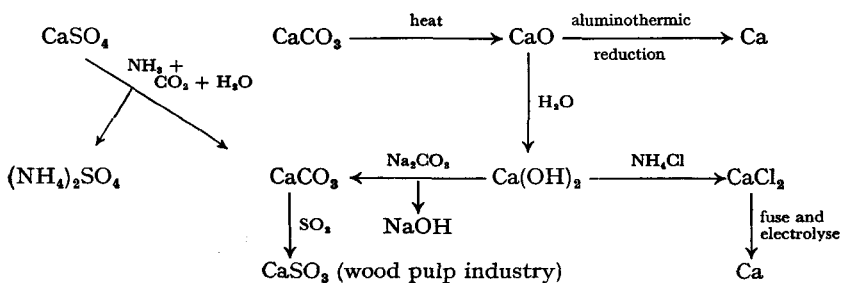


Fig. 195. Manufacture of calcium metal and calcium sulphite.

Strontium (0.02% of lithosphere) occurs as strontianite,  $\text{SrCO}_3$ , and celestite,  $\text{SrSO}_4$ . The metal which has the c.c.p. structure is without economic importance except in pyrotechnics. The radioactive strontium-90 is long-lived and, being easily assimilated and incorporated in bone, is a dangerous product of uranium fission.

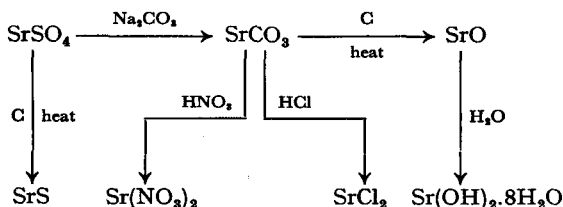


Fig. 196. The chemistry of some strontium compounds.

Barium (0.04% of lithosphere) occurs widely in veins as barytes,  $\text{BaSO}_4$ , which is sometimes converted to witherite,  $\text{BaCO}_3$ , by atmospheric agency. The reactions used in the production of barium compounds from sulphate and carbonate are shown in Fig. 197.

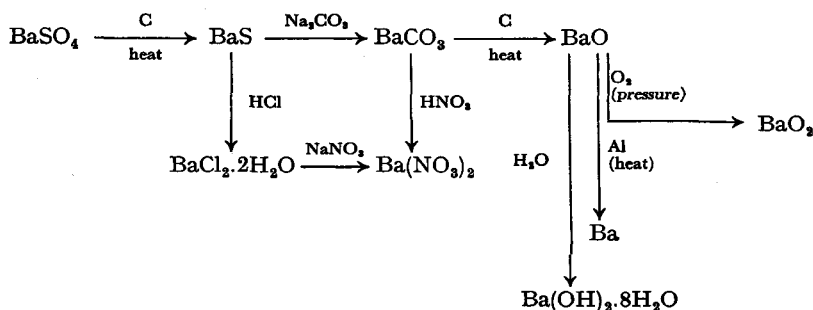


Fig. 197. Manufacture of barium and some of its compounds from barytes.



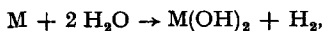
Radium is obtained from pitchblende,  $U_3O_8$ , in which it is formed by the disintegration of  $^{238}U$  (p. 22), the equilibrium ratio being  $3.4 \times 10^{-7}$ . The sulphate is co-precipitated with  $BaSO_4$  when  $BaCl_2$  is added to a sulphuric acid extract of the ore. After boiling with  $NaOH$  to remove lead, the sulphates are converted to carbonates by sodium carbonate fusion and dissolved in  $HCl$  to the chlorides. Fractional crystallisation of these removes much of the barium; the final separation of the rest is effected by the same means after conversion of the chlorides to bromides.

### Chemical properties of the metals

The metals combine directly, at an appropriate temperature, with all the halogens, oxygen, sulphur and nitrogen. Ca, Sr and Ba also combine directly with hydrogen at normal pressure but Mg does so only at 200 atm.



Ca, Sr and Ba decompose cold water,



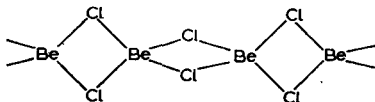
but Mg does so only when amalgamation prevents the formation of a protective layer of oxide. Mg burns in steam but Be fails to react at red heat. Except for Be, which is rendered passive by nitric acid, the metals dissolve readily in dilute mineral acids. Like Al but unlike the other metals of Group IIA, beryllium is soluble in caustic alkalis.

### Halides

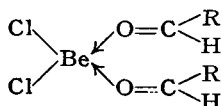
Unlike the Group IA halides, some of these are only feebly ionic, particularly those of beryllium.  $BeF_2$  appears to be one of very few metal fluorides which are not completely ionised in solution. The solid often occurs in a glassy modification of random structure rather than as crystals. It is hygroscopic and very soluble in water, the very great solvation energy of  $Be^{2+}$  outweighing the effect of a high lattice energy. The complex tetrafluoroberyllate ion,  $BeF_4^{2-}$ , is stable in solution as well as in crystals; its compounds resemble sulphates in structure and solubility. Several compounds are known of the type  $M_2^I M^{II}(BeF_4)_2 \cdot 6H_2O$ , analogous with schönite,  $K_2Mg(SO_4)_2 \cdot 6H_2O$ .

The fluorides of magnesium and the alkaline earth metals are sparingly soluble;  $MgF_2$  and  $KF$  form  $K_2MgF_4$ , but the  $MgF_4^{2-}$  ion does not exist in solution. Magnesium forms many double salts but few true complexes.

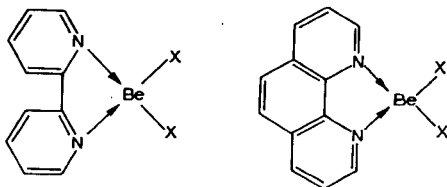
Beryllium chloride exists as a polymeric solid containing chains of the form:



Co-ordination about the beryllium is irregular tetrahedral, the adjacent  $\text{Be} \begin{smallmatrix} \text{Cl} \\ \diagup \\ \text{Cl} \end{smallmatrix} \text{Be}$  planes being at  $90^\circ$  to each other but the angle  $\text{ClBeCl}$  being  $98^\circ$  instead of the  $109\frac{1}{2}^\circ$  of a regular tetrahedron. In the vapour (b.p.  $488^\circ$ ) beryllium chloride is without dipole moment, its molecule being linear, corresponding to Be in the  $sp$  valence state. In the fused state (at  $405^\circ$ ),  $\text{BeCl}_2$  is one of the few halides with an electrical conductance intermediate between that of a characteristically ionic halide ( $\text{NaCl}$ ) and a covalent one ( $\text{CCl}_4$ ). The compound is soluble in organic solvents and, like  $\text{AlCl}_3$ , catalyses the Friedel-Crafts reaction; it thus behaves as a Lewis acid (p. 249). Aldehydes, ketones and ethers co-ordinate readily to anhydrous  $\text{BeCl}_2$ ,  $\text{BeBr}_2$  and  $\text{BeI}_2$ .



The complexes of  $\text{BeX}_2$  ( $X = \text{Cl}, \text{Br}$  or  $\text{I}$ ) with bipyridyl and *o*-phenanthraline:

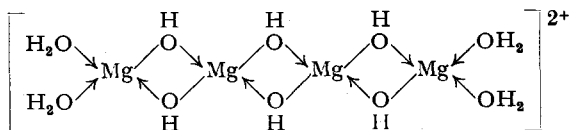


owe their colour to charge transfer (p. 184). These complexes involve the use of  $sp^3$  hybrid orbitals giving a tetrahedral disposition of the four bonds about the Be atom.

Beryllium chloride forms many double salts such as  $\text{Na}_2\text{BeCl}_4$ , but the  $\text{BeCl}_4^{2-}$  ion does not exist in solution as does  $\text{BeF}_4^{2-}$ . The chloride has a hydrate  $\text{BeCl}_2 \cdot 4\text{H}_2\text{O}$ , an unusually stable tetra-ammine  $\text{Be}(\text{NH}_3)_4\text{Cl}_2$  and a chelate ethylenediamine complex,  $\text{Be}(\text{en})_2\text{Cl}_2$ . The formation of 4-coordinate complexes by  $\text{Be}^{2+}$  is very common; nearly all its inorganic salts have tetrahydrates containing the ion  $[\text{Be}(\text{H}_2\text{O})_4]^{2+}$ . The water of hydration is tightly held;  $\text{Be}(\text{H}_2\text{O})_4\text{Cl}_2$ , for instance, loses very little  $\text{H}_2\text{O}$  even when kept for several months in a vessel containing  $\text{P}_2\text{O}_5$ . The ionic mobility

of the aquated beryllium ion in water is low; the solutions have high viscosities and abnormal osmotic pressures. The large ions of the group, such as  $\text{Ba}^{2+}$ , do not form co-ordinate links with water molecules, the solvation forces being of ion-dipole type (p. 134), and the hydration numbers in aqueous solution are smaller.

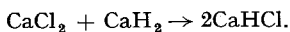
Magnesium chloride forms complexes with ethers, aldehydes and ketones similar to those of  $\text{BeCl}_2$ . It has several hydrates. A strong aqueous solution of  $\text{MgCl}_2$  dissolves  $\text{MgO}$  giving a compound  $\text{MgCl}_2 \cdot 3\text{Mg}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ . The suggested structure for the ion is



The 'beryllated' ions formed when aqueous beryllium salts dissolve  $\text{Be}(\text{OH})_2$  may be similar.

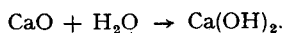
$\text{MgBr}_2$  and  $\text{MgCl}_2$  are soluble in many organic solvents and the halides (other than the fluorides) of even strontium and barium are moderately soluble in alcohol, resembling lithium in this respect.

The halides of calcium, strontium and barium react with their hydrides at  $900^\circ$  in hydrogen to give mica-like solids which have the  $\text{PbClF}$  structure.

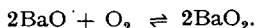


### Oxides

All the normal oxides have the sodium chloride structure (6:6 co-ordination), except  $\text{BeO}$  which has a wurtzite lattice (4:4 co-ordination). The heats of formation are very large (135–150 kcal/mole).  $\text{BeO}$  is unreactive to water; even the large heat of hydration of  $\text{Be}^{2+}$  is evidently insufficient to overcome the stabilising effect of the high lattice energy.  $\text{MgO}$  reacts with water only when prepared at a low temperature, but all the alkaline earth oxides slake readily:



The hydroxides increase in solubility with molecular weight. The monoxides,  $\text{SrO}$  and  $\text{BaO}$  are converted to peroxides when heated with oxygen under pressure.

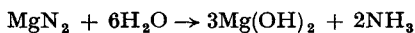


The stability of the  $[\text{—O—O—}]^{2-}$  ion is evidently due to the low polarising power of these cations compared with those of earlier elements in the

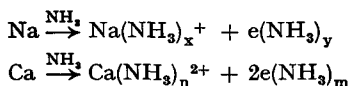
group. Peroxide hydrates of the form  $\text{MO}_2 \cdot 8\text{H}_2\text{O}$  are formed by Ca, Sr and Ba when  $\text{H}_2\text{O}_2$  is added to cold saturated solutions of the hydroxides; dehydration is possible without decomposition. All three anhydrous peroxides contain  $[\text{—O—O—}]^{2-}$  ions in the tetragonal calcium carbide lattice.

### Compounds with nitrogen

The metals combine with nitrogen on heating to give solid nitrides,  $\text{M}_3\text{N}_2$ . Reaction occurs at  $900^\circ$  in the case of beryllium but at much lower temperatures for the other metals.  $\text{Be}_3\text{N}_2$  is hydrolysed slowly by water but quite quickly by aqueous acids and alkalis. The other nitrides react rapidly, however:



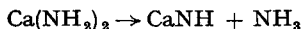
Magnesium and the alkaline earth metals dissolve in liquid ammonia. The solutions of calcium have been shown to have molar extinction coefficients (p. 166) twice those of solutions of any Group I metal in ammonia (p. 311), probably because the calcium solutions contain twice as great a concentration of solvated electrons:



Amides can be obtained by evaporating solutions of the metals in ammonia, but  $\text{Mg}(\text{NH}_2)_2$  is best made by passing  $\text{NH}_3$  into a solution of  $\text{MgEt}_2$  in ether. Magnesium amide decomposes at red heat to the nitride:



but calcium amide resembles lithium amide in giving an imide as the first product:

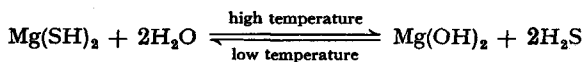


### Sulphides

Beryllium burns in sulphur vapour forming BeS. This cannot be made in the wet way, though, like BeO, it is unreactive to water. Magnesium sulphide, similarly made from the metal and sulphur, hydrolyses rapidly:



The hydrosulphide is soluble and the reversible reaction



provides a means of purifying hydrogen sulphide. The sulphides of Ca, Sr and Ba are made by reducing the sulphates with carbon. They hydrolyse in the same way as MgS.

The structures of the sulphides, selenides and tellurides of the Gp. IIA metals illustrate the effect of the cation/anion size ratio on co-ordination number (Table 54).

TABLE 54  
STRUCTURES AND CO-ORDINATION OF SULPHIDES ETC.  
OF GROUP IIA ELEMENTS

	<i>Be</i>	<i>Mg</i>	<i>Ca</i>	<i>Sr</i>	<i>Ba</i>
Sulphide	B	R	R	R	R
Selenide	B & W	R	R	R	R
Telluride	W	B	R	R	R
Structures:	B = zinc blende.		W = wurtzite.		R = rocksalt.
Co-ordination:	4:4		4:4		6:6

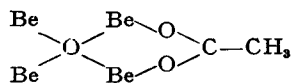
*Polysulphides.* Studies on barium sulphide—sulphur mixtures indicate the existence of  $\text{BaS}_2$  and  $\text{BaS}_3$ , both unstable at their respective m.p. When sulphur is added to boiling aqueous  $\text{Ba}(\text{SH})_2$  it dissolves, and orange-red crystals of  $\text{BaS}_4 \cdot \text{H}_2\text{O}$  together with a little yellow  $\text{BaS}_3 \cdot 3\text{H}_2\text{O}$  separate on cooling. No individual polysulphide of the other members of the group has been made.

### Oxoacid salts

The carbonates exhibit the increase in stability with molecular weight expected to accompany increase in cationic size. Addition of a soluble carbonate to a solution of a beryllium salt gives hydroxide carbonates of indeterminate composition. Magnesium salts, similarly treated, yield the carbonates  $\text{Mg}(\text{OH})_2(\text{MgCO}_3)_x \cdot \text{H}_2\text{O}$ , where  $x = 4$  or  $5$  depending on the temperature of precipitation. Passage of  $\text{CO}_2$  into the suspension gives a solution, probably not the hydrogen carbonate; this deposits  $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$  on warming to  $50^\circ$ . The same rhombic hydrate is obtained from solutions of  $\text{MgSO}_4$  and sodium hydrogen carbonate when they stand. Sodium carbonate precipitates the anhydrous carbonates of Ca, Sr and Ba from solution. Their thermal stability is indicated by their dissociation pressures at  $800^\circ$ :  $\text{CaCO}_3$  168 mm,  $\text{SrCO}_3$  0.70 mm,  $\text{BaCO}_3$  0.03 mm. A figure for  $\text{MgCO}_3$  is not available but its thermal stability is certainly less than that of  $\text{CaCO}_3$ . The trend is similar to that in the Group IA carbonates, and for similar reasons (p. 315).

Carbonates of bivalent cations crystallise in hexagonal form when their radii lie between 0.78 and 1.00 Å, and in rhombic form when between  $\sim 1.00$  and 1.43 Å. The radius of  $\text{Ca}^{2+}$  being 0.99 Å, both a hexagonal (calcite) and a rhombic (aragonite) form occur.

Beryllium chloride dissolved in an ethyl acetate–dinitrogen tetroxide mixture gives straw-coloured crystals of  $\text{Be}(\text{NO}_3)_2 \cdot 2\text{N}_2\text{O}_4$ . These decompose on heating in a vacuum, first to the involatile anhydrous nitrate,  $\text{Be}(\text{NO}_3)_2$  then to the volatile oxide nitrate,  $\text{Be}_4\text{O}(\text{NO}_3)_6$ . The structure of this closely resembles that of the well known oxide acetate,  $\text{Be}_4\text{O}(\text{CH}_3\text{CO}_2)_6$ , in which an oxygen atom is at the centre of a tetrahedron of beryllium atoms, and the acetate groups form six chelate rings along the edges of the tetrahedron, of which only one is shown in the partial formula.



In  $\text{Be}_4\text{O}(\text{NO}_3)_6$ , the nitrate groups form the bridges between the beryllium atoms:

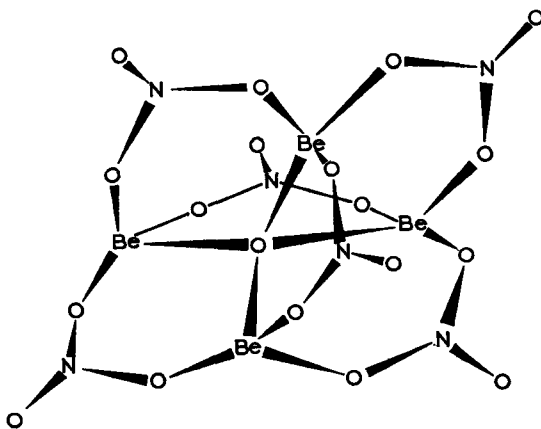
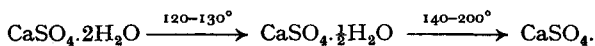


Fig. 198. Beryllium oxide nitrate (basic beryllium nitrate).

Like the oxide acetate and similar compounds, the oxide nitrate is volatile; however, it differs from them in being insoluble in non-polar liquids such as  $\text{CCl}_4$  and  $\text{C}_6\text{H}_6$ .

The hydration and solubilities of the sulphates are of interest. In the  $\text{BeSO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$  system  $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$  is the stable crystalline form below  $89.0^\circ$  and  $\text{BeSO}_4 \cdot 2\text{H}_2\text{O}$  above; there is no evidence of a monohydrate.

$\text{MgSO}_4$  has many hydrates. Both  $\text{BeSO}_4$  and  $\text{MgSO}_4$  are freely soluble in water.  $\text{CaSO}_4$  has a low but appreciable solubility. Its dihydrate, gypsum, is readily dehydrated:



The easy cleavage of gypsum crystals arises from its layer lattice structure; the  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  together make up the individual layers which are linked by hydrogen bonds between the water molecules and oxygen atoms of the sulphate ions. Every water molecule has as its nearest neighbours one  $\text{Ca}^{2+}$  and two oxygen atoms. By contrast strontium and barium sulphates are anhydrous and very sparingly soluble:  $\text{CaSO}_4$  2.0 g/l,  $\text{SrSO}_4$  0.1 g/l,  $\text{BaSO}_4$  0.0024 g/l at  $15^\circ$ .

### Solubilities

The solubilities of calcium, strontium and barium salts may be summarised:

Very soluble:  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{NO}_2^-$ ,  $\text{ClO}_3^-$ ,  $\text{ClO}_4^-$ ,  $\text{CH}_3\text{CO}_2^-$

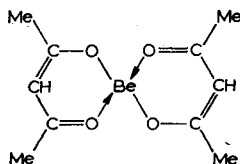
Moderately soluble:  $\text{OH}^-$ ,  $\text{F}^-$ ,  $\text{BrO}_3^-$ ,  $\text{NO}_3^-$  (except  $\text{CaF}_2$  which is insoluble)

Sparingly soluble or insoluble:  $\text{CO}_3^{2-}$ ,  $\text{SO}_3^{2-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{IO}_3^-$ ,  $\text{C}_2\text{O}_4^{2-}$

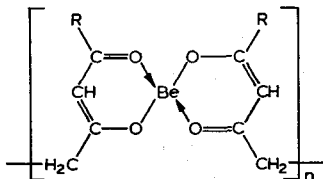
With the exception of the hydroxides, fluorides, carbonates and oxalates the order of solubility of the salts indicated above is  $\text{Ca}^{2+} > \text{Sr}^{2+} > \text{Ba}^{2+}$

### Complexes

Beryllium forms neutral chelate complexes with oxygen ligands. An example is bis(acetylacetonyl)beryllium:



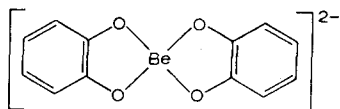
made by dissolving  $\text{Be}(\text{OH})_2$  in dilute acetic acid and treating the solution with acetylacetone. Linear chelate polymers such as



can be made.

There is also an interesting series of basic beryllium complexes with the carboxylic acids which are covalent compounds of remarkable stability. Basic beryllium acetate,  $\text{Be}_4\text{O}(\text{OOC}\cdot\text{CH}_3)_6$ , melts at  $283^\circ$ , boils at  $330^\circ$  without decomposition and dissolves in  $\text{CHCl}_3$  as the monomer; it lacks ionic properties. Its structure has a central O atom surrounded tetrahedrally by four Be atoms, and with six  $\text{CH}_3\cdot\text{C}\begin{smallmatrix} \text{O} \\ \diagup \\ \text{O} \end{smallmatrix}$  groups spanning the edges of the tetrahedron.

Beryllium also forms anionic complexes with chelating oxygen ligands. An alkaline solution of catechol dissolves  $\text{Be}(\text{OH})_2$  to give a salt of



Magnesium compounds hydrate readily, and anhydrous magnesium halides form addition compounds with aldehydes, ketones and ethers, which are structurally similar to those of Be. Otherwise its complexes are few and unstable.

Calcium, strontium and barium form some poorly characterised  $\beta$ -diketone complexes and rather unstable amines; the tendency to covalence, even as indicated by hydration of the ions, has decreased with cation size. The determination of magnesium and calcium with sodium ethylenediamine tetra-acetate, E.D.T.A., probably involves the formation of a chelate complex whose stability is enhanced by the presence of 5-membered rings.

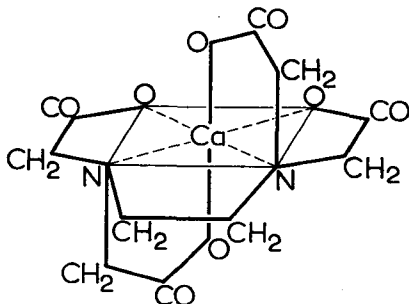


Fig. 199. Calcium E.D.T.A. complex (binate ion).

### Organometallic compounds

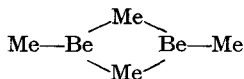
#### *Beryllium*

Beryllium alkyls and aryls are liquids or low-melting solids made by treating beryllium halides (say  $\text{BeCl}_2$ ) with lithium alkyls or aryls. They



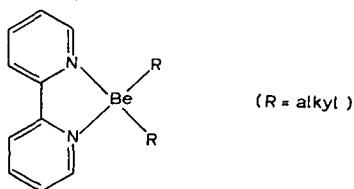
are spontaneously inflammable in air and are violently hydrolysed by water.

Dimethylberyllium is a solid polymer but its vapour contains the dimer



The methyl bridges can be explained in terms of three-centre bonds (p. 275). Di-isopropylberyllium is a dimer in benzene. On heating it is converted to the polymer  $[(\text{CH}_3)_2\text{CHBeH}]_n$ . But pyrolysis of di-tertiarybutylberyllium at about  $100^\circ$  gives  $\text{BeH}_2$  and  $(\text{CH}_3)_2\text{C}=\text{CH}_2$ .

Beryllium alkyls react with nitrogen ligands such as dipyrindyl and orthophenanthroline to give highly coloured compounds:



They probably owe their colour to electron transfer from the Be-R bond to the lowest-energy unoccupied orbital of the nitrogen ligand.

### *Magnesium*

The best-known organomagnesium compounds are the Grignard reagents usually formulated  $\text{RMgX}$  ( $\text{R} = \text{alkyl or aryl}$ ,  $\text{X} = \text{Cl, Br or I}$ ). They are made by dissolving magnesium in a carefully dried mixture of the alkyl or aryl halide in ether. The solution probably contains solvated  $\text{R}_2\text{Mg}$  and  $\text{MgX}_2$  molecules. Unsolvated solids cannot be made from the ether solutions. However, there is evidence that in hydrocarbon solvents Grignard reagents have the approximate formula  $\text{R}_3\text{Mg}_2\text{X}$  and contain both alkyl-bridge and hydrogen-bridge bonds.

Dialkyl and diaryl magnesium compounds resemble the corresponding beryllium compounds.

Magnesium reacts with cyclopentadiene to give the colourless, ionic  $(\text{C}_5\text{H}_5)_2\text{Mg}$  which has the same type of sandwich structure as ferrocene (p. 395).

### *Calcium, strontium and barium*

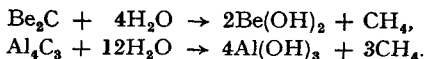
Organometallic compounds of these elements are of little importance, but the cyclopentadienyls are interesting. These can be made by the action

of cyclopentadiene on the hydrides at  $\sim 300^\circ$ , or on the metals Ca and Sr in dimethylformamide.

### Similarities between beryllium and aluminium

Though considerably larger than  $\text{Be}^{2+}$ , the greater charge of the  $\text{Al}^{3+}$  ion renders its polarising power of the same order; for the ions the charge/(radius)<sup>2</sup> ratio is  $\text{Al}^{3+}$  12.0 and  $\text{Be}^{2+}$  19.2. The similarities between the two elements led to an early belief that beryllium was a member of Group III. Its low atomic heat supported this idea, and not until 1871 did Mendeleev correctly place the element in Group II—an early triumph for the periodic classification. The diagonal similarity between beryllium and aluminium (p. 319) remains:

- (i) The standard electrode potentials of the metals are of the same order ( $\text{Be}^{2+}/\text{Be} - 1.70 \text{ V}$ ;  $\text{Al}^{3+}/\text{Al} - 1.67 \text{ V}$ ).
- (ii) Both metals are rendered passive by nitric acid.
- (iii) Both metals dissolve in caustic alkalis with hydrogen evolution.
- (iv) The halides are similar in their solubilities in organic solvents and their behaviour as Lewis acids.
- (v) Beryllium carbide,  $\text{Be}_2\text{C}$ , and aluminium carbide,  $\text{Al}_4\text{C}_3$ , both yield methane on hydrolysis:



### FURTHER READING

- D. A. EVEREST, *The Chemistry of Beryllium*, Amsterdam, Elsevier, 1964.  
 F. E. DARWIN AND J. H. BUDDERY, *Beryllium*, London, Butterworths, 1960.  
 G. A. BALUEVA AND S. T. IOFFE, *Organic Compounds of Beryllium, Calcium, Strontium and Barium*, Russian Chemical Reviews, 31 (1962) 439.  
 R. W. MURRAY AND M. A. AIA, *Alkaline Earth Phosphates*, Chem. Rev., 61 (1961) 433.

## Boron and Aluminium

Boron is a non-metal and its chemistry is dominated by covalent compounds, whereas aluminium is a metal although it too has many covalent compounds. These first two elements of Group III, despite the electron configuration  $ns^2np^1$ , are effectively trivalent since promotion to  $ns^1np^2$  occurs very readily. They form cations with an inert-gas structure much less readily than the elements of Group II which precede them, and their bonding is predominantly covalent. The covalent and  $M^{3+}$  ionic radii are given in Table 55.

TABLE 55  
ATOMIC PROPERTIES OF BORON AND ALUMINIUM

	B	Al
Atomic number	5	13
Electron configuration	$2s^2 2p^1$	$3s^2 3p^1$
Covalent radius (Å)	0.82	1.18
Ionic radius $M^{3+}$ (Å)	0.20	0.50
Metallic radius (Å)	0.98	1.43

Many compounds of boron and aluminium are electron-deficient since an octet (p. 119) is not normally present. There are only three electron pairs in the valence shell, instead of the four characteristic of Groups IV to VII, and electron-pair repulsions are, accordingly, smaller than usual, so that the atoms tend to be electron 'acceptors'. Their simple molecules, with an incomplete octet around the element, invariably contain  $sp^2$  hybrid bonds lying in a plane with the electron pairs as far apart as possible (p. 147). But the tendency to complete an octet is shown by the existence of tetrahedral compounds, such as  $BH_3CO$ , in which  $sp^3$  hybridisation may be invoked, the fourth hybrid sharing the carbon lone pair which it overlaps. Such compounds could, very artificially, be formulated as complexes containing the  $B^{3+}$  ion (the approach of ligand field theory, p. 177) but there is no doubt that the use of electron-pair bonds gives a more realistic description. At the same time, the ionic formulation is useful in discussing

more elaborate complexes and forms a convenient bridge with classical chemistry provided it is understood that the bonding is largely covalent.

Though the first ionisation energy of boron and aluminium is fairly low, the second is high, the p electron being removed much more easily than one of the s pair. In spite of the large total ionisation energies, the standard redox potentials for  $M^{3+}/M$  are negative because of the high heats of hydration.

TABLE 56

IONISATION ENERGIES AND ELECTRODE POTENTIALS OF BORON AND ALUMINIUM

		<i>B</i>	<i>Al</i>
Ionisation energy	<i>I</i> 1 (eV)	8.30	5.95
"	" 2 "	25.15	18.82
"	" 3 "	37.92	28.44
$E^\circ$ , $M^{3+}/M$ (V)		-0.73	-1.67

### The elements: preparation and properties

The densities and atomic volumes of boron and aluminium are normal for the places they occupy in the Periodic Table. Boron's extremely high m.p. indicates very strong binding forces. The structure of several crystalline forms of pure boron have been clearly established; of these the simplest is the rhombohedral form, which contains units of nearly regular icosahedra (*cf.* p. 272) in a slightly deformed close packing. Crystals of the purest material are very hard, 9-10 on Mohs' scale. The specific conductance increases about 100 times between 20° and 600°.

Aluminium has a low m.p. compared with neighbouring elements; its face-centred cubic lattice is characteristic of a true metal; it is soft, and its conductance is high.

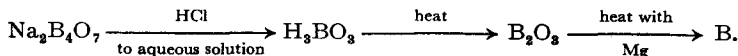
TABLE 57

PHYSICAL PROPERTIES OF BORON AND ALUMINIUM

	<i>B</i>	<i>Al</i>
Density (g/cc)	2.4	2.7
Atomic volume	4.4	10.0
M.p. (°C)	2300	660
B.p. (°C)	2550	2500

Boron ( $5 \times 10^{-3}$  % of the lithosphere) probably owes its scarcity to the readiness with which it suffers transmutation. It occurs principally as borates in hot springs and lakes in volcanic regions: the minerals are borax,  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ , kernite,  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$ , and colemanite,  $\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5\text{H}_2\text{O}$ .

An amorphous form of the element can be made by reducing the oxide with magnesium:



The brown product always contains some boron suboxide in solid solution. It is used in the manufacture of impact-resistant steels and, because of its high neutron cross-section, of alloys for atomic reactor control rods. Aluminothermic reduction of  $\text{B}_2\text{O}_3$  yields crystalline material once thought to be pure boron but now known to contain the aluminium borides,  $\text{AlB}_{12}$  and  $\text{AlB}_2$ . Black crystalline boron has been made by reducing  $\text{BBr}_3$  vapour with hydrogen on a tantalum filament at  $1300^\circ$ . Probably because of the larger particle size and more nearly perfect lattice, this solid is much less reactive than amorphous boron. Electrolysis of  $\text{KBF}_4$  also yields boron of high purity.

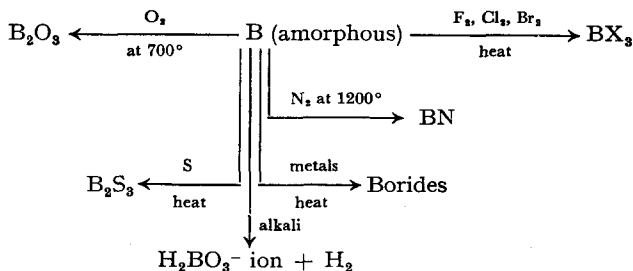
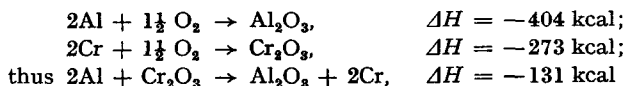


Fig. 200. The reactions of boron.

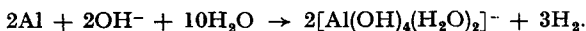
Aluminium (7.45% of the lithosphere) is widely distributed in igneous rocks, but the only workable ore is bauxite (p. 343). A solution of sodium aluminate results when bauxite is digested under pressure with caustic soda;  $\text{Fe}_2\text{O}_3$  and other solid impurities may be removed by allowing them to settle. The clear solution is stirred, at  $25\text{--}50^\circ$ , with a little crystalline  $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ , when much of the aluminium is thrown down as the trihydrate of alumina. This, on heating to  $1200^\circ$ , becomes  $\alpha\text{-Al}_2\text{O}_3$ ; it is dissolved in a fused mixture of cryolite,  $\text{Na}_3\text{AlF}_6$ , with a little fluorspar and electrolysed for the technical production of the metal.

The metal appears unreactive because of the rapid formation, in air, of a tenacious oxide layer. Though its standard electrode potential is  $-1.67$  V, it does not dissolve in water and, even with dilute HCl, reacts slowly until

the oxide layer has been removed, after which the reaction is rapid. Amalgamation dislodges the oxide layer, causes the metal to oxidise rapidly in air, and also makes it a good reducing agent even in neutral solution. The metal reacts in a similar way to boron with oxygen, sulphur, nitrogen and the halogens. The very great heat of formation of alumina enables aluminium to be used for the reduction of metal oxides, such as  $\text{MnO}_2$  and  $\text{Cr}_2\text{O}_3$ , by the *thermit process*:



Aluminium dissolves readily in caustic alkali solutions to give the aluminate ion (Fig. 202, p. 344):



Nitric acid renders the metal passive.

Aluminium furnishes light, strong alloys: Al-Si alloys ( $\sim 12\%$  Si) can be cast; Duralumin (4% Cu, 0.5% Mn and 0.5 Mg) and Y-alloy (4% Cu, 2% Ni and 1% Mg) can be both wrought and cast.

### Halides

Boron and aluminium give trihalides.  $\text{BF}_3$  is most conveniently made by heating  $\text{B}_2\text{O}_3$  with concentrated  $\text{H}_2\text{SO}_4$  and a fluoride. It reacts with aluminium chloride and bromide to produce involatile  $\text{AlF}_3$  and volatile  $\text{BCl}_3$ . The volatility of the boron trihalides decreases with molecular weight (Table 58).

TABLE 58

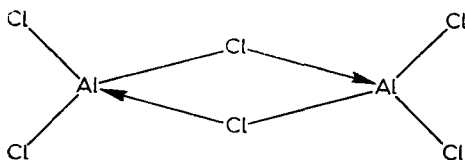
MELTING AND BOILING POINTS OF BORON AND ALUMINIUM TRIHALIDES

	B		Al	
	M.p.	B.p.	M.p.	B.p.
Fluoride	$-127^\circ$	$-101^\circ$	†	$1291^\circ$ (subl.)
Chloride	$-107^\circ$	$12^\circ$	$192^\circ$ *	$180^\circ$ (subl.)
Bromide	$-46^\circ$	$91^\circ$	$97^\circ$	$255^\circ$
Iodide	$43^\circ$	$210^\circ$	$180^\circ$	$381^\circ$

† Sublimes at 1 atm.

\* Material in a sealed tube.

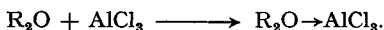
The boron compounds are covalent and monomeric in the vapour phase, as is  $\text{BCl}_3$  in benzene solution. By contrast,  $\text{AlF}_3$  is an ionic, crystalline solid of high m.p.; but the more volatile chloride and bromide exist as dimers, both in the vapour phase and in non-polar solvents, in which the halogen atoms

Fig. 201. Dimer of  $\text{AlCl}_3$ .

are tetrahedrally arranged about each aluminium atom (Fig. 201). The arrows indicate donations of chlorine lone pairs, imagined to be in tetrahedral hybrids, to bonds formed with vacant  $sp^3$  hybrids on the Al atoms. This results in a 'bridge' structure, typically formed by electron-deficient atoms.

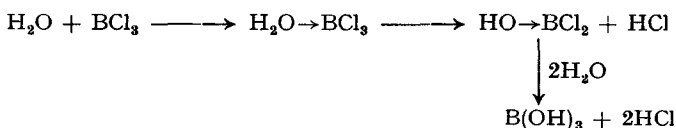
Hydrides with this type of bridge bonding are specially important and are discussed elsewhere (p. 271).

In co-ordinating solvents such as ether, however,  $\text{Al}_2\text{Cl}_6$  gives place to a tetrahedral, mononuclear complex:

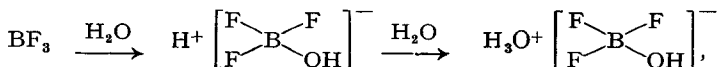


Electron diffraction shows that the boron trihalides are planar molecules with the angle  $\text{X}-\text{B}-\text{X}$  equal to  $120^\circ$ ; the bonds are somewhat shorter than the normal single bonds, there being fewer bond-pair repulsions.

Hydrolysis of the chloride, bromide and iodide of boron is rapid and complete. The reaction presumably begins with the donation of an oxygen lone pair to the boron:



The trifluoride, however, forms 1:1 and 1:2 adducts with water:



the latter being stable enough to be distilled without decomposition.

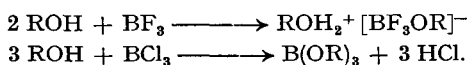
The relative acceptor strengths of  $\text{BF}_3$ ,  $\text{BCl}_3$  and  $\text{BBr}_3$  have been found by measuring the heats of formation and dipole moments of such compounds as their 1:1 adducts with pyridine. The results, together with those from infrared studies, indicate that the electron-acceptor power increases in the order



This is opposite to the order suggested by the relative electronegativities of the halogens. The inductive effect in these molecules is evidently out-

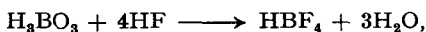
weighed by another, which is a tendency for electrons from the smaller halogen atoms to be partly back-donated to the boron, to give some double-bond character to the B—X bonds and to reduce the electron deficiency on the boron.

The fact that  $\text{BF}_3$  forms a wider range of complexes than the other trihalides is probably due to a greater difficulty of heterolysis with the B—F bond than with the B—Cl and B—Br bonds. Thus molecules of the alcohols, aldehydes and ketones, which form addition compounds with  $\text{BF}_3$ , break the boron-halogen bonds in the other halides:



The tendency of donor groups containing O, N, S and P to co-ordinate with  $\text{BF}_3$  makes the compound an extremely useful catalyst in organic chemistry.

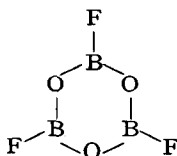
Boric acid dissolves in 50% HF to give tetrafluoroboric acid:



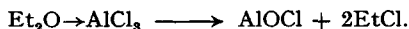
The compound has not been isolated in the pure state. The  $\text{BF}_4^-$  ion in crystalline fluoroborates is shown, by X-ray analysis, to be tetrahedral,  $\text{KBF}_4$  being isomorphous with  $\text{KClO}_4$ . Tetrafluoroborates also resemble perchlorates in solubility. Other tetrahalogenoborates have been made recently:  $\text{C}_5\text{H}_5\text{NHBCl}_4$  and  $\text{C}_5\text{H}_5\text{NHBBr}_4$ , and the corresponding iodo-complexes.

Anhydrous  $\text{AlCl}_3$  resembles  $\text{BF}_3$  in its acidity and catalytic power (p. 249). Anhydrous  $\text{AlF}_3$  is insoluble in water, though soluble stable hydrates may be prepared; the other halides dissolve with considerable hydrolysis. Their solutions in organic solvents have low conductance.

Unstable oxide halides of both boron and aluminium are known. When  $\text{B}_2\text{O}_3$  and  $\text{BF}_3$  are heated together a cyclic compound is formed:



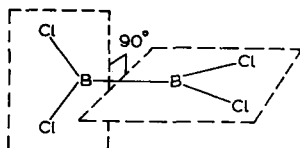
$\text{AlOCl}$  and  $\text{AlOBr}$  result from heating compounds of the trihalides with ether:



A liquid subchloride of boron,  $\text{B}_2\text{Cl}_4$ , is made by passing  $\text{BCl}_3$  vapour at 1–2 mm through a glow discharge between mercury electrodes. Its



structure is of interest. In the vapour and liquid phase the two  $\text{BCl}_2$  groups are in planes perpendicular to one another:



In the solid, however, the arrangement is coplanar. The compound is reduced by  $\text{LiBH}_4$  (p. 278) to diborane. It decomposes slowly at room temperature to  $\text{B}$  and  $\text{BCl}_3$ , and reacts with water to give boric acid and hydrogen. The molecule is converted to an ion by some donor molecules:  $\text{Me}_3\text{N}$  reacts with it to give  $[(\text{Me}_3\text{N})_2\text{B}_2\text{Cl}_4]^{2-}$ . Gaseous  $\text{B}_2\text{F}_4$  has been obtained by fluorinating  $\text{B}_2\text{Cl}_4$  with  $\text{SbF}_3$ . The thermally unstable liquid  $\text{B}_2\text{Br}_4$  is made by treating  $\text{B}_2\text{Cl}_4$  with  $\text{BBr}_3$  and the yellow solid  $\text{B}_2\text{I}_4$  by passing a radiofrequency discharge through  $\text{BI}_3$  vapour.

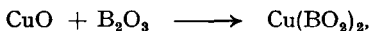
The yellow solid  $\text{B}_4\text{Cl}_4$  and the red solid  $\text{B}_8\text{Cl}_8$ , formed by the spontaneous decomposition of  $\text{B}_2\text{Cl}_4$ , have interesting structures. The molecule of  $\text{B}_4\text{Cl}_4$ , consists of a tetrahedron of boron atoms surrounded by four chlorine atoms, each bound to one boron. In  $\text{B}_8\text{Cl}_8$ , the molecule has a dodecahedron of boron atoms with a chlorine atom bound to every one of them.

### Oxides

A glassy form of boric oxide,  $\text{B}_2\text{O}_3$ , results from dehydrating  $\text{H}_3\text{BO}_3$  at red heat:



A crystalline form (p. 345), m.p.  $450^\circ$ , appears after dehydrating  $\text{HBO}_2$  by keeping it under reduced pressure and slowly raising the temperature to  $400^\circ$  over a period of some weeks. Boric oxide, though more acidic than  $\text{Al}_2\text{O}_3$ , is amphoteric; it combines with metal oxides to give metaborates as in the borax-bead test:



and with phosphorus pentoxide to give a phosphate:



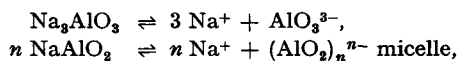
Boron phosphate is slightly soluble when freshly prepared, but crystallises and becomes insoluble on heating, when it is stable enough to be sublimed ( $1450^\circ$ ). In the crystal lattice both the boron and phosphorus atoms are surrounded, tetrahedrally, by oxygen atoms. There is also an arsenate,  $\text{BAAsO}_4$ .

An oxide with the empirical formula BO is obtained by heating boric oxide with boron at about 1350° and collecting the sublimate. The white solid turns brown on prolonged heating. It exists mainly as B<sub>2</sub>O<sub>2</sub> in the vapour, but is highly polymeric in the solid. With water it gives white crystals of hypoboric acid, H<sub>4</sub>B<sub>2</sub>O<sub>4</sub>, as well as boric acid and hydrogen.

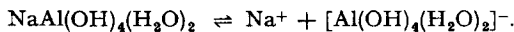
Alumina, Al<sub>2</sub>O<sub>3</sub>, just as boric oxide, may be prepared by dehydrating one of the hydrous oxides. These exist in four well defined forms: the monohydrate AlO(OH), as boehmite ( $\gamma$ -monohydrate) and diaspore ( $\alpha$ -monohydrate), and the trihydrate Al(OH)<sub>3</sub>, as gibbsite ( $\gamma$ -trihydrate) and bayerite ( $\alpha$ -trihydrate). Of these, all but bayerite occur naturally in bauxite. On dehydration diaspore passes directly to corundum ( $\alpha$ -alumina); the others yield a series of anhydrous aluminas, e.g.  $\gamma$ -alumina, which pass into  $\alpha$ -alumina only at higher temperatures (about 850°C).  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> has a well-defined, close-packed O<sup>2-</sup> structure with Al<sup>3+</sup> in the tetrahedral holes, whereas  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> has a distorted, badly organised, microcrystalline structure of the spinel type. In consequence,  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> is dense, hard, and resistant to chemical attack and can be brought into solution only after fusion with a flux such as KHSO<sub>4</sub>, whereas  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> is less dense, is soft, and has a high surface area, so that it is relatively soluble in aqueous alkalis and acids and an excellent and selective absorbent used in dehydration, decolorisation and chromatography.

Ruby, sapphire, amethyst and emerald are  $\alpha$ -alumina with traces of specific impurities. Artificial forms are made by fusing finely powdered alumina with a trace of the colouring oxide (Cr<sub>2</sub>O<sub>3</sub> for ruby) in an oxy-hydrogen flame.

Aluminium hydroxide acts primarily as a base, but it also ionises weakly as an acid ( $pK_a = 12.2$ ). The osmotic properties of sodium aluminate solutions are identical with those of NaOH; thus both must have the same number of ions. Dissociations such as



are ruled out. Furthermore, conductance and pH measurements indicate that hydrolysis to NaOH and colloidal alumina is slight. Sodium aluminate appears to ionise as a 1 : 1 electrolyte:



The high viscosity can be explained by the linking of hydrated aluminate ions (Fig. 202) with each other and with water molecules by hydrogen bonding.

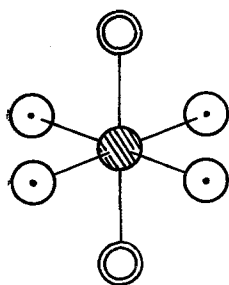


Fig. 202. Aluminate ion present in sodium aluminate.

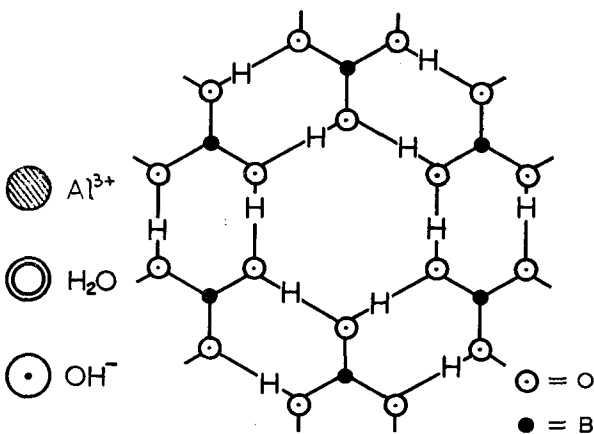
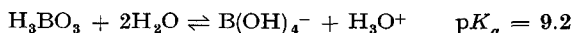


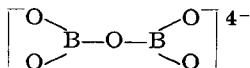
Fig. 203. Hydrogen-bonded structure of boric acid.

### Boric acid and the borates

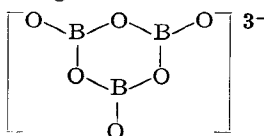
Phase studies of the system  $B_2O_3-H_2O$  show that  $HBO_2$  and  $H_3BO_3$  are the only stable boric acids, though salts of greater complexity exist such as  $Na_2B_4O_7$ ,  $Ca_2B_6O_{11}$  and  $NaCaB_5O_9$ . The flaky crystals of orthoboric acid have a layer structure formed by triangular  $BO_3$  groups joined by hydrogen bonds (Fig. 203). The compound is volatile in steam. It is a very weak acid, which behaves in solution as an electron-acceptor (*i.e.* a Lewis acid) rather than as a proton-donor:



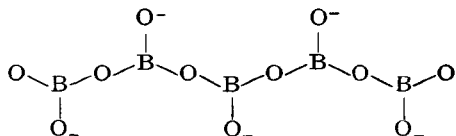
Crystal analysis of borates shows they bear some similarity to the silicates (p. 209), the unit being the triangular  $BO_3$  in place of the tetrahedral  $SiO_4$ . The rather uncommon orthoborates, *e.g.*  $Mg_3(BO_3)_2$ , possess discrete  $BO_3^{3-}$  ions. The pyroborates such as  $Co_2B_2O_5$  contain ions of the form:



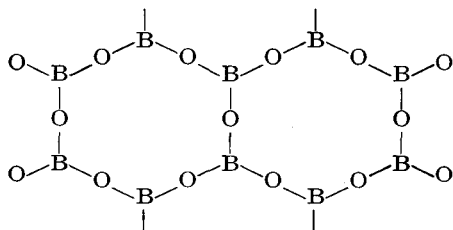
Of the borates much the most common are the metaborates; these have chain and ring forms. Sodium metaborate, correctly formulated  $Na_3B_3O_6$ , contains the six-membered ring ions:



Calcium metaborate, typical of the bipoisitive metal borates, has negatively charged chains held together by  $\text{Ca}^{2+}$  ions between them:



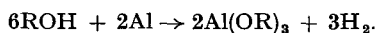
The crystalline form of  $\text{B}_2\text{O}_3$  (p. 342) has two-dimensional sheets made by linking these chains together:



#### *Boric and aluminic esters*

Esters of orthoboric acid can be made by treating boric acid with  $\text{H}_2\text{SO}_4$  and the alcohol. The esters are monomeric liquids with normal Trouton constants. They hydrolyse rapidly in water.

Aluminium powder dissolves in certain thoroughly dried alcohols:



The triethyl ester, m.p.  $139^\circ$ , is almost insoluble in alcohol but very soluble in benzene. It is easily hydrolysed by water. The aluminic esters have much less tendency to form co-ordination compounds than have the boric esters.

#### **Nitrogen compounds**

White, insoluble, refractory boron nitride, BN, is simply made by fusing together  $\text{B}_2\text{O}_3$  and  $\text{NH}_4\text{Cl}$ , by strongly heating compounds such as borazine (p. 277) and  $\text{BF}_3 \cdot \text{NH}_3$ , and by burning boron in nitrogen. It has a graphite-like structure (Fig. 204) in which the bonding within the layers is by  $\text{sp}^2$

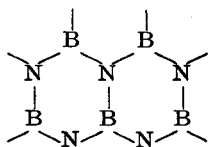
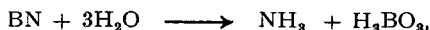
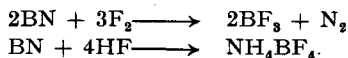


Fig. 204. Graphite-like structure of boron nitride.

hybrids of both B and N, the remaining electrons being in delocalised  $\pi$  orbitals above and below the plane. The separation of the layers is considerable and the bonding is essentially of the Van der Waals type (p. 136). The structure differs from that of graphite in having the hexagons directly under one another (B under N). Boron nitride is very stable and unreactive. It is, however, decomposed by steam at red heat:

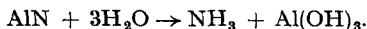


and by fluorine and HF at lower temperatures:



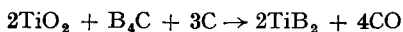
Under pressures of about 70,000 atmospheres, boron nitride at 3000° changes into the adamantine form (p. 201), borazon, claimed to be harder than diamond. The conversion is similar to that of graphite into diamond.

When heated aluminium combines directly with nitrogen to give AlN with a wurtzite structure. It is much more reactive than BN, being hydrolysed by cold water:



### Borides

Metal borides can be made by direct combination of the elements in a vacuum at high temperature ( $\sim 2000^\circ$ ), by reduction of a metal oxide with  $\text{B}_4\text{C}$  and carbon,



or by electrolysis of a fused borate. In the last method, the liberated metal reduces borate to boron and combination then occurs. The borides are hard, have high m.p. and are good conductors; they resemble the interstitial carbides and nitrides of metals (p. 199). They are usually fairly stable and resistant to attack but basic oxidising agents such as  $\text{Na}_2\text{O}_2$  decompose them on heating. The structures, like those of intermetallic compounds, are determined more by the requirements of the metal and boron lattices than by valency relationships.

Metal borides have arrangements based on:

- (i) isolated boron atoms ( $\text{M}_2\text{B}$ ),
- (ii) zig-zag chains ( $\text{MB}$ ),
- (iii) double chains ( $\text{M}_3\text{B}_4$ ),
- (iv) hexagonal layers ( $\text{MB}_2$ ),
- (v) three-dimensional frameworks ( $\text{MB}_6$ ).

The iron boride  $\text{FeB}$  (Fig. 205) is an example of (ii); the Fe atoms are at the corners of trigonal prisms and the B atoms at their centres, the latter being covalently bound in zig-zag chains. Aluminium boride,  $\text{AlB}_2$ , is an example of (iv); the borons are joined in hexagons to form infinite layers with the aluminiums in layers between them (Fig. 206). The borides of alkaline earth metals,  $\text{CaB}_6$ ,  $\text{SrB}_6$ ,  $\text{BaB}_6$ , and several isomorphous borides of the lanthanides have cubic  $\text{CsCl}$ -type structures with an octahedron of boron atoms occupying the centre of the unit cell (Fig. 207).

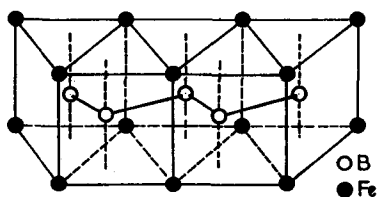


Fig. 205. Structure of  $\text{FeB}$ .

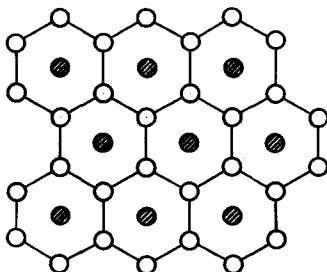


Fig. 206. Structure of  $\text{AlB}_2$ , with separate layers of aluminium atoms and boron atoms.

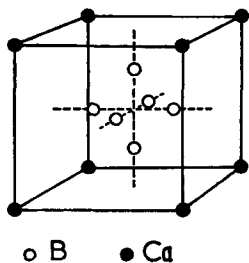


Fig. 207. Cubic structure of  $\text{CaB}_6$ .

### Alums

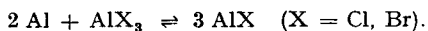
Potash alum,  $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ , contains  $\text{K}^+$ ,  $\text{Al}^{3+}$  and tetrahedral  $\text{SO}_4^{2-}$  ions. Six of the water molecules are octahedrally co-ordinated to the  $\text{Al}^{3+}$  and six are used to link these  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$  ions to neighbouring sulphate ions. It is thus a lattice compound rather than a complex. A unipositive ion which is smaller than  $\text{K}^+$  does not form a very stable alum, and the still smaller  $\text{Li}^+$  ion does not form one at all. Moreover, for alum formation the radius of the  $\text{M}^{3+}$  ion must be small; the large lanthanide  $\text{M}^{3+}$  ions do not form alums.

### Oxo-compounds of aluminium

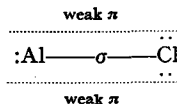
The  $\text{Al}^{3+}$  ion (radius 0.50 Å) is near enough in size to  $\text{Si}^{4+}$  ion (radius 0.43 Å) to replace it in the  $\text{SiO}_4$  tetrahedra of silicate structures (p. 209). The deficiency of positive charge created by the change is made up by incorporating positive ions (p. 211). Such compounds as  $\text{AlPO}_4$  and  $\text{AlAsO}_4$  have quartz structures; these are made possible because the deficiency of positive charge in the  $\text{AlO}_4$  tetrahedron is balanced by the excess of positive charge in the adjacent  $\text{PO}_4$  tetrahedron. The corresponding compounds of boron,  $\text{BPO}_4$  and  $\text{BAsO}_4$ , have distorted cristobalite structures.

### Compounds of unipositive aluminium

When the vapour of either  $\text{AlCl}_3$  or  $\text{AlBr}_3$  is passed over Al metal at  $1000^\circ$  under reduced pressure, the aluminium evaporates quickly and can be condensed in a state of high purity, apparently because of the reversible reaction:



This allows the aluminium to be removed as  $\text{AlX}$  which then disproportionates, and the procedure has been proposed as a method of purifying the metal. In  $\text{AlX}$ , the Al may be regarded as in an sp valence state with a lone pair on the side remote from the X. The electron deficiency would then encourage slight sharing of two halogen lone pairs to give two weak  $\pi$  bonds. In this situation the aluminium would be described as formally unipositive.



Supporting this picture, band spectra show the strength of the bond in  $\text{AlCl}$  to be greater than the strengths of the  $\text{Al—Cl}$  bonds in  $\text{AlCl}_3$ .

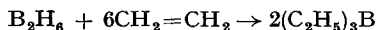
Evaporation of  $\text{Al}_2\text{O}$  occurs when  $\text{Al}_2\text{O}_3$  and Al are heated together under reduced pressure at a very high temperature. A similar observation has been made when Be is heated in contact with  $\text{BeO}$ ; some volatile suboxide is again formed.

### Organometallic compounds

#### Boron

The trialkyls of boron can be made by

- (i) treating  $\text{BF}_3$  with an appropriate Grignard reagent,
- (ii) treating  $\text{B}_2\text{H}_6$  or  $\text{Al}(\text{BH}_4)_3$  with an olefin,



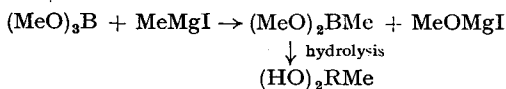
(iii) 'hydroboration', by the addition of an olefin to a mixture of  $\text{NaBH}_4$  and  $\text{AlCl}_3$  in diglyme.

Trimethylboron is a gas, and  $\text{Et}_3\text{B}$  and  $\text{Pr}_3\text{B}$  are liquids. Both the latter compounds are monomeric in the vapour state; their molecules are planar. The lower alkyls of boron inflame spontaneously in air or chlorine gas and form amines with  $\text{NH}_3$ , but do not react with water. By contrast, the aryls are stable in air. The trialkyls of boron are oxidised, for example by aqueous  $\text{HBr}$ , to dialkyl boric acids,  $\text{R}_2\text{BOH}$ , also called boronic acids. Their esters can also be made by the action of trialkyls on aldehydes:

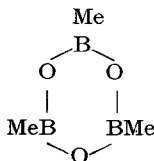


Corresponding aromatic derivatives are known.

The monoalkyl boric acids, or boronous acids,  $\text{RB(OH)}_2$  can be made by hydrolysis of their esters; these esters are obtained by treating methyl or ethyl borates with a Grignard reagent.

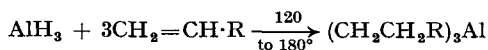


Anhydrides of these acids can be made by treating them with  $\text{P}_2\text{O}_5$ . The methyl compound  $(\text{CH}_3\text{BO})_3$  has a cyclic structure:



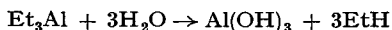
### Aluminium

Magnesium-aluminium alloy reacts with an alkyl halide in ether to give an etherate of the trialkyl,  $\text{R}_3\text{Al} \cdot \text{OEt}_2$ . Trialkyls are also made by the action of  $\alpha$ -olefins on  $\text{AlH}_3$ :



This reaction does not give a good yield when ethylene itself is used.

Trimethylaluminium, a solid, m.p.  $15^\circ$ , is a dimer; the molecule has bridging methyl groups. Triethylaluminium, however, is a liquid. The lower trialkyls are spontaneously inflammable. All react strongly with water:



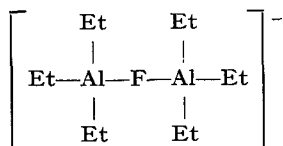


Triphenylaluminium,  $(C_6H_5)_3Al$ , is best made from aluminium and diphenylmercury,  $(C_6H_5)_2Hg$ .

Some of the trialkyls form adducts with alkali-metal halides:



Salts of the  $Al_2Et_6F^-$  ion are much stronger electrolytes than those of the  $AlEt_3F^-$  ion because the unipositive ion cannot approach close enough to the halogen in the complex



ion to form a dipole.

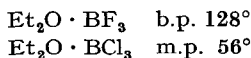
Both the trialkyls and triaryls of aluminium act as Lewis acids and form a variety of compounds with electron-donating reactants. The trialkyls, for example, form 1:1 adducts with amines which, on pyrolysis, give alkanes and organometallic Al—N polymers. Triphenylaluminium reacts with aliphatic amines in toluene to give polymers such as  $[Me_2N \cdot Al(C_6H_5)_2]_n$  and  $[MeN \cdot Al(C_6H_5)]_n$ ; but with non-orthosubstituted aromatic amines like *p*-toluidine it gives crystalline tetramers  $(C_6H_5Al \cdot NAr)_4$ .

A variety of compounds of the type  $Alk_2AlX$  are known, where  $X = CN$ , halogen,  $NMe_2$ , or  $SMe$ .

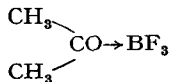
## Complexes

### Boron

Boron's strong tendency to 4-covalence is shown in its complexes. The  $BF_4^-$  ion, like the isoelectronic  $BeF_4^{2-}$  ion and  $CF_4$  molecule, is tetrahedral. The borohydride ion is also tetrahedral, the boron atom again being in the  $sp^3$  valence state. The trihalides co-ordinate readily with ethers:

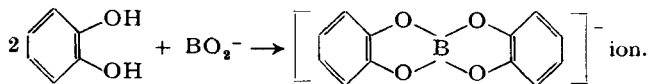


The trifluoride also forms co-ordination compounds with esters, aldehydes and ketones; the compound shown is a stable solid:

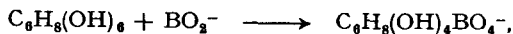


Chelate oxo-anions containing 4-covalent boron are formed by the borate ion with some cis-diols.

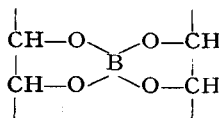
With catechol:



With mannitol:

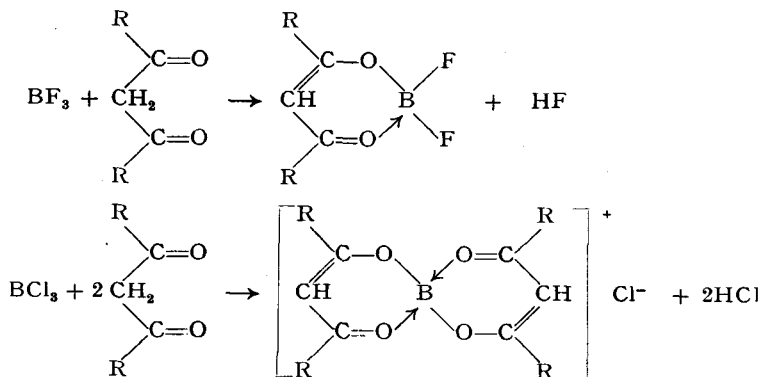


an ion in which boron has the environment



The ion does not form a bond with a proton since the boron atom is already exerting its maximum covalence of four, but it does bind  $\text{H}_3\text{O}^+$  electrostatically. For this reason, boric acid can be titrated against  $\text{NaOH}$  to a definite end-point in the presence of mannitol or glycerol.

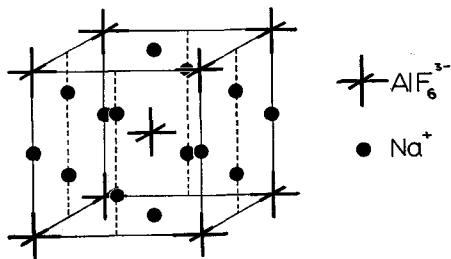
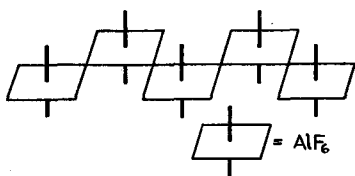
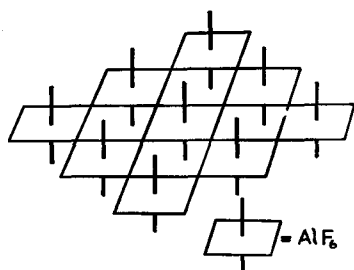
$\text{BF}_3$  and  $\text{BCl}_3$  differ from one another in their reactions with  $\beta$ -diketones in benzene solution:



The second complex is a positive boronium ion. Another example of a boronium compound is the  $[\text{C}_6\text{H}_5)_2\text{B}(\text{dipyridyl})]^+\text{ClO}_4^-$ .

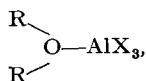
### Aluminium

Aluminium forms fluoro-, chloro- and bromo-complexes, containing tetrahedral  $\text{AlX}_4^-$  ions and, in the case of fluorine, octahedral  $\text{AlF}_6^{3-}$  ions. In the cubic cell of cryolite,  $\text{Na}_3\text{AlF}_6$ , the corners and centre are occupied by distorted  $\text{AlF}_6^{3-}$  octahedra, and the  $\text{Na}^+$  ions are arranged as in Fig. 208. In  $\text{Tl}_2\text{AlF}_5$ , infinite chain ions  $(\text{AlF}_5)_n^{2n-}$  are formed by the sharing of corners of

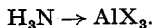
Fig. 208. Structure of  $\text{Na}_3\text{AlF}_6$ .Fig. 209. Infinite chain ions in  $\text{Tl}_2\text{AlF}_6$ .Fig. 210. Infinite planar ions joined at corners in  $\text{NaAlF}_4$ .

$\text{AlF}_6$  octahedra (Fig. 209), whereas in  $\text{NaAlF}_4$ , the planar  $(\text{AlF}_4)_n^{n-}$  ions are formed by sharing corners with four other octahedra (Fig. 210).

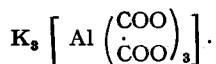
The trihalides of aluminium form complexes with  $\nabla$ ethers, aldehydes, ketones and alcohols, such as:



With ammonia they give solid, covalent monoammines:



Octahedral 6-co-ordinate chelate oxo-complexes are common. They may be described in terms of  $\text{sp}^3\text{d}^2$  hybridisation (p. 120), the 3d orbitals being energetically only slightly higher than the 3p. Such orbitals are not available in boron and octahedral complexes do not occur. This is also true of the  $\beta$ -diketone complexes and the trioxalato-aluminates such as



## FURTHER READING

- Borax to Boranes*, Advances in Chemistry Series, No. 32, Easton, Pa., American Chemical Society, 1961.
- N. N. GREENWOOD AND R. L. MARTIN, *Boron Trifluoride Co-ordination Compounds*, Quart. Rev., VIII (1954) 1.
- W. GERRARD AND M. F. LAPPERT, *Reactions of Boron Trichloride with Organic Compounds*, Chem. Rev., 58 (1958) 1081.
- H. G. HEAL, *Recent Advances in Boron Chemistry*, London, Royal Institute of Chemistry Monograph, (1960) No. 1.
- A. K. HOLLIDAY AND A. G. MASSEY, *Boron Subhalides and Related Compounds with Boron-Boron Bonds*, Chem. Rev., 62 (1962) 303.
- T. G. PEARSON, *The Chemical Background of the Aluminium Industry*, London, Royal Institute of Chemistry Monograph (1955) No. 3.
- N. N. GREENWOOD, R. V. PARISH AND P. THORNTON, *Metal Borides*, Quart. Rev., XX (1966) 441.
- R. THOMPSON, *Borides: Their Chemistry and Applications*, London, Royal Institute of Chemistry Monograph (1965) No. 5.

Chapter 18

## Gallium, Indium and Thallium

### GROUP IIIB

The metals gallium, indium and thallium all have the  $ns^2 np^1$  configuration and  $^2P$  ground state, met with in boron and aluminium. The atomic and ionic radii of the elements begin with values close to those of aluminium (p. 336) and increase somewhat with increasing atomic number.

TABLE 59  
ATOMIC PROPERTIES OF THE GROUP IIIB ELEMENTS

	<i>Ga</i>	<i>In</i>	<i>Tl</i>
Atomic number	31	49	81
Electron configuration	$4s^2 4p^1$	$5s^2 5p^1$	$6s^2 6p^1$
Covalent radius (Å)	1.26	1.44	1.48
Ionic radius, $M^{3+}$ (Å)	0.62	0.81	0.95
Metallic radius (Å)	1.41	1.66	1.71

Moreover, the ionisation energies do not differ greatly from those of aluminium but owing to the reduced 'polarising power' of the larger  $M^{3+}$  ions (p. 106) the heats of hydration become smaller and the standard electrode potentials less negative.

TABLE 60  
IONISATION ENERGIES AND ELECTRODE POTENTIALS OF GROUP IIIB ELEMENTS

		<i>Ga</i>	<i>In</i>	<i>Tl</i>
Ionisation energy <i>I</i>	1 (eV)	6.0	5.8	6.1
"	2 "	20.4	18.8	20.3
"	3 "	30.6	27.9	29.7
$E^\circ$ , ( $M^{3+}/M$ ) (V)		-0.52	-0.34	0.72
$E^\circ$ , ( $M^+/M$ ) "			-0.25	-0.34

The chemistry of gallium is very similar to that of aluminium in that there is little tendency to form unipositive compounds. A tendency to

retain the  $5s^2$  shell appears in indium with the compound  $\text{InCl}$ . This contains unipositive indium, although as the redox potential data indicate, it disproportionates in water to give the trichloride. With thallium the  $6s^2$  shell is very stable and the  $\text{Tl}^+$  ion (radius 1.40 Å) appears in many well-characterised salts (see below).

The  $\text{M}^{\text{I}}$  state increases in stability in going down the sub-group, but the  $\text{M}^{\text{III}}$  state decreases in stability. The chlorides  $\text{MCl}_3$  are essentially covalent. Whereas  $\text{GaCl}_3$  and  $\text{InCl}_3$  are stable,  $\text{TlCl}_3$  begins to lose chlorine above  $70^\circ$ .

### Preparation and properties of the elements

The metals are remarkable for the difference between their melting and boiling points. The extreme example, gallium, is liquid at ordinary pressure over a range of two thousand degrees and has been employed for high-temperature ( $1000^\circ$ ) thermometry, in a quartz envelope. It has a strong tendency to superfusion and will remain liquid at room temperature for a considerable period.

TABLE 61

PROPERTIES OF THE GROUP IIIB ELEMENTS

	<i>Ga</i>	<i>In</i>	<i>Tl</i>
Density (g/cc)	5.93	7.29	11.85
Atomic volume	11.76	15.74	17.25
Melting point	$29.8^\circ$	$156^\circ$	$449^\circ$
Boiling point	$2070^\circ$	$2100^\circ$	$1390^\circ$

Gallium ( $10^{-4}\%$  of the earth's crust) is present in zinc blende,  $\text{ZnS}$ , which may contain up to 0.5%, and also in certain (*e.g.* British) coal ash. The metal, which is deposited by electrolysis from alkaline solutions of its salts, is silvery-white, hard and brittle. High-purity gallium has been made by the hydrogen reduction in a quartz vessel, of zone-refined gallium trichloride. The orthorhombic crystal has a complex lattice. The co-ordination is strictly one-fold, a given gallium atom having one atom situated 2.43 Å from it and six others at distances varying from 2.70 to 2.79 Å. This co-ordination is denoted by  $1 + \bar{6}$ ; the notation applies only when the six atoms are separated from the reference atom by a distance not greater than 1.2 times that of the nearest one. The metal is stable in dry air and does not decompose water. It dissolves in caustic alkalis and in mineral acids, other than nitric which renders it passive. Its chemistry (Fig. 211) is, in fact, very similar to that of aluminium.

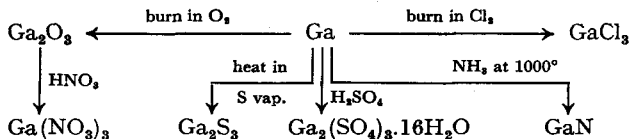


Fig. 211. Outline chemistry of gallium.

Indium ( $10^{-5}\%$  of the earth's crust) is also present in zinc blende, but rarely above 0.1%. It can be precipitated from solution by zinc and purified electrolytically. Its tetragonal unit cell is a very slightly distorted version of the f.c.c. of a true metal (Fig. 212). The metal is soft. It differs from aluminium and gallium in its insolubility in boiling caustic alkalis; otherwise its reactions are similar.

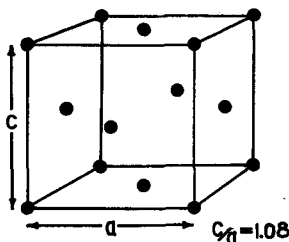


Fig. 212. Structure of indium.

Thallium ( $10^{-5}\%$  of earth's crust) is recovered principally from the flue dust of pyrites burners. The soft, grey metal, which has a hexagonal close-packed structure, is rather more reactive than gallium and indium because of the ease with which it forms a unipositive ion. It oxidises in moist air,

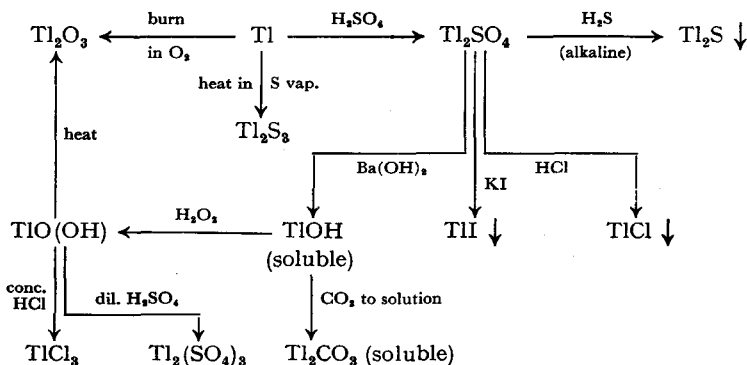


Fig. 213. Outline chemistry of thallium.

decomposes steam at red heat and dissolves readily to form thallium(I) compounds in dilute mineral acids other than HCl, because of the insolubility of TlCl.

### Halides

The trifluorides are ionic solids of high m.p. and low solubility similar to  $\text{AlF}_3$ . The other trihalides are soluble, though strongly hydrolysed, and largely covalent when anhydrous. The trichloride of gallium is a white solid, m.p.  $78^\circ$ . The vapour at  $500^\circ$  consists largely of the dimeric molecules  $\text{Ga}_2\text{Cl}_6$ ; the liquid, on the evidence of its Raman spectrum, appears to be dimeric also. The dichloride,  $\text{GaCl}_2$ , can be made by heating  $\text{GaCl}_3$  with the metal to a limited temperature. At a higher temperature  $\text{GaCl}_2$  disproportionates:



However, the corresponding iodide disproportionates into the triiodide and monoiodide:



Although the empirical formula  $\text{GaCl}_2$  appears to indicate bivalent gallium, the material is not paramagnetic, as it would be with a  $\text{GaCl}_2$  unit containing an odd electron. Its structure is ionic, containing the tetrahedral  $\text{GaCl}_4^-$  anion (which is well known) and the  $\text{Ga}^+$  cation. The crystals are isomorphous with those of  $\text{GaAlCl}_4$ .

The monochlorides of both gallium and indium have been made by heating the metals in argon containing 1%  $\text{Cl}_2$ .

Indium trichloride,  $\text{InCl}_3$ , has a much higher m.p. ( $568^\circ$ ) than the other trichlorides of the group. There is no evidence of dimerisation and the fused material is a fairly good conductor. The tribromide, too, is far more ionic in character than the tribromides of Ga and Tl.

Thallium(III) chloride hydrate,  $\text{TlCl}_3 \cdot 4\text{H}_2\text{O}$ , can be made by passing  $\text{Cl}_2$  into an aqueous suspension of TlCl and evaporating at  $60^\circ$ . The anhydrous chloride melts at  $60-70^\circ$ ; it is unstable, and further heating converts it to TlCl. It resembles  $\text{BCl}_3$  in giving stable addition compounds with  $\text{NH}_3$  and  $\text{Et}_2\text{O}$  and in not forming a dimer. Material of the composition  $\text{TlI}_3$ , made by treating TlI with iodine, is not thallium(III) iodide but a polyiodide containing the  $\text{Tl}^+$  ion, and is isomorphous with  $\text{RbI}_3$  and  $\text{CsI}_3$ . On heating it decomposes in two stages:





Thallium(I) chloride, bromide and iodide are made by precipitation with the appropriate halide ion from a thallium(I) sulphate solution. TlCl resembles AgCl in solubility, structure and sensitivity to light but is insoluble in ammonia; the  $Tl^+$  ion is evidently too large to form stable ammonia complexes. TlF is yellow and resembles AgF in colour, structure and solubility.

#### Halogen complexes

Halogen complexes are formed by the three metals. The fluorogallates have the octahedral  $GaF_6^{3-}$  ion but the solids are hydrates and differ in structure from cryolite. Hexafluorogallic acid,  $H_3GaF_6$ , has been made by the action of HF on  $Ga[GaCl_4]$ . Complexes of the general formula  $[GaL_4]^+[GaX_4]^-$  ( $X = Cl$  or  $Br$ ), with such ligands (L) as ethers and thioethers, are formed by allowing these volatile compounds to diffuse into  $Ga[GaX_4]$  dissolved in benzene. Chelating ligands also form complexes of gallium(I) tetrachlorogallate(III) such as  $[Ga(acac)_2]^+[GaCl_4]^-$  and  $[Ga(dipy)_2]^+[GaCl_4]^-$ .

Indium gives hydrated 6-co-ordinate complexes,  $M_3[InCl_6]H_2O$ .

Thallium has four types of chlorocomplexes:



The  $[Tl_2Cl_9]^{3-}$  ion is composed of two octahedra fused together by sharing three corners and a common face (Fig. 214). Bromocomplexes are generally similar to the chlorocomplexes. Iodocomplexes are known for thallium but not for the others.

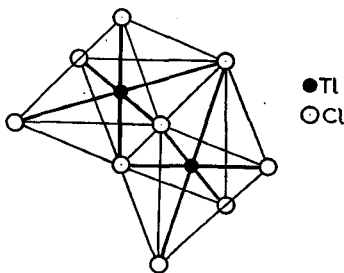


Fig. 214. Structure of the  $Tl_2Cl_9^{3-}$  ion.

The luminescence of solutions of thallium(I) chloride with alkali metal chlorides is due to the absorption of light by the  $[TlCl_2]^-$  ion.

### Oxides

The oxides,  $M_2O_3$ , can all be made by heating the metals in oxygen. The heats of formation, though high, are much lower than that of  $Al_2O_3$ , and the oxides are easily reduced.

TABLE 62  
HEATS OF FORMATION OF  $Al_2O_3$ ,  $Ga_2O_3$  AND  $In_2O_3$

	$Al_2O_3$	$Ga_2O_3$	$In_2O_3$
$\Delta H_f$	-404	-258	-223 kcal

Black  $Ga_2O$  results from heating  $Ga_2O_3$  with Ga to  $500^\circ$  in a vacuum. Black, easily fusible  $Tl_2O$  is formed when  $TlOH$  is heated to  $100^\circ$  in the absence of air. Thallium(I) hydroxide, made by adding baryta water to thallium(I) sulphate solution and evaporating, is a yellow crystalline solid which dissolves to give an alkaline solution. The addition of  $H_2O_2$  to this precipitates brown thallium(III) metahydroxide,  $TlO(OH)$ . Ga also forms a metahydroxide  $GaO(OH)$ . The hydroxides of gallium and indium are amphoteric and very similar to  $Al(OH)_3$ , but thallium hydroxide is entirely basic.

### Thallium(I) salts

The single charge and large size of the  $Tl^+$  ion endows its compounds with many properties reminiscent of those of the alkali metals. For instance, alkaline  $TlOH$  absorbs  $CO_2$  to form a solution of  $Tl_2CO_3$ , which hydrolyses similarly to  $K_2CO_3$ . The hydroxide is evidently a strong base. Thallium(I) sulphate,  $Tl_2SO_4$ , the orthophosphates,  $Tl_3PO_4$ ,  $Tl_2HPO_4$  and  $TlH_2PO_4$ , the chlorate and the perchlorate are all isomorphous with the corresponding potassium salts ( $K^+$  radius = 1.33 Å,  $Tl^+$  radius = 1.40 Å). The sulphate gives an alum  $TlAl(SO_4)_2 \cdot 12H_2O$ . It forms a continuous series of solid solutions with  $(NH_4)_2SO_4$  and  $K_2SO_4$  and a double salt with  $CuSO_4$  which is isomorphous with  $(NH_4)_2SO_4 \cdot CuSO_4 \cdot 6H_2O$ .

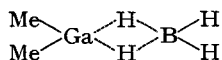
In its halides and sulphide, unipositive thallium bears some resemblance to silver ( $Ag^+$  radius = 1.26 Å);  $Tl_2S$  is precipitated by  $H_2S$  only from slightly alkaline solutions. The variable charge number of thallium, according as its 6s<sup>2</sup> shell is disturbed or not, is largely responsible for the diversity of its properties.

### Other compounds

The sulphides  $M_2S_3$  are all made by direct combination of the elements. But GaS is also known and has an unusual layer lattice containing  $Ga_2^{4+}$  ions. The nitride GaN, unreactive to water and acids, is made by heating gallium in ammonia at  $1000^\circ$  or  $Ga_2O_3$  in ammonia at  $480^\circ$ . The corresponding indium compound is best made by heating  $(NH_4)_3InF_6$ . Both nitrides have the wurtzite lattice.

Gallium resembles aluminium in not forming a carbonate, but a basic carbonate of indium can be precipitated from solution. Gallium(III) sulphate,  $Ga_2(SO_4)_3 \cdot 16H_2O$ , and indium(III) sulphate,  $In_2(SO_4)_3$ , both form alums, but thallium(III) sulphate,  $Tl_2(SO_4)_3 \cdot 7H_2O$ , obtained by dissolving  $Tl_2O_3$  in dilute sulphuric acid, does not. The  $Tl^{3+}$  ion (radius  $0.95 \text{ \AA}$ ) is evidently too large for the lattice, resembling those of the lanthanides in this respect.

Bridge bonds (p. 271), of the kind formed by boron (the first member of Group III), are also formed by both aluminium and gallium, though less frequently. An example is



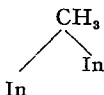
### Organometallic compounds

Trialkylgalliums,  $R_3Ga$ , have been made from gallium trihalides and aluminium alkyls in the presence of KCl, or by a prolonged heating of gallium metal with mercury dialkyls. They are spontaneously inflammable liquids or solids, and are hydrolysed by water:



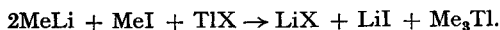
But they form very stable complexes with ethers and amines. Triethylgallium (b.p.  $143^\circ$ ) is monomeric in the vapour but dimeric in benzene.

Trimethylindium (m.p.  $88^\circ$ ) is a polymeric solid made from indium and  $Me_2Hg$  at  $100^\circ$ . The structure of the solid is an unusual one; it contains unsymmetrical bridges:



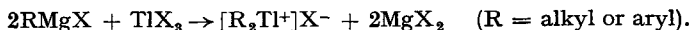
In the vapour and in benzene, however, the compound is monomeric. It is hydrolysed by water to  $MeIn(OH)_2$ , but dilute mineral acids, HX, give  $InX_3$ . The other known trialkyls of indium are monomeric, as is also  $(C_6H_5)_3In$ , made from diphenylmercury and indium.

The trialkyls and triaryls of thallium are thermally unstable. The solid  $\text{Me}_3\text{Tl}$  is made on treating a thallium(I) halide with methyl-lithium and methyl iodide:



It is spontaneously inflammable, but hydrolyses in water only as far as  $\text{Me}_2\text{TlOH}$ . It dissolves in ether and benzene in which it behaves as a monomer.

When a thallium trihalide is treated with a Grignard reagent, peculiarly stable salts are formed:



These salts are not hydrolysed by water. The  $\text{Me}_2\text{Tl}^+$  ion in aqueous solution has been shown by Raman spectroscopy to have a linear arrangement  $\text{C}-\text{Tl}-\text{C}$ , as in the isoelectronic  $\text{Me}_2\text{Hg}$  molecule.

### Complexes

In their terpositive states the Group IIIB metals figure in a number of complexes. The trihalides of gallium and indium form many amines,  $\text{MX}_3(\text{NH}_3)_n$  in which  $n$  can be as large as seven. The corresponding thallium(III) amines hydrolyse rapidly in water, but the ethylenediamine-complexes  $\text{Tl}n_n\text{X}_3$  ( $n = 1, 2$  or  $3$ ), are hydrolysed only slowly. The indium trihalides form 1, 2 complexes with some sulphur-containing ligands such as  $\text{Me}_2\text{S}$ ,  $\text{MeSH}$  and tetrahydrothiophen.

The most stable oxo-complexes are chelate compounds. Gallium and indium form tris- $\beta$ -diketone complexes, soluble in alcohol and benzene, and structurally similar to those of aluminium (Fig. 215). Gallium and thallium form trioxalato compounds like the oxalato-aluminates:  $\text{M}_3^+[\text{Ga}(\text{C}_2\text{O}_4)_3]\text{H}_2\text{O}$ . All the metals form tris-complexes with oxine (Fig. 216).

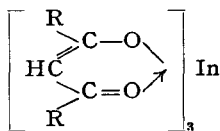


Fig. 215.

Tris- $\beta$ -diketone complex of indium.

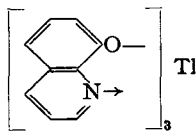


Fig. 216.

Tris-complex of thallium with oxine.

## FURTHER READING

- I. A. SHEKA, I. S. CHAUS AND T. T. MITYUREVA, *The Chemistry of Gallium*, Amsterdam, Elsevier, 1966.
- R. J. CLARK, E. GRISWOLD AND J. KLEINBERG, *Some Observations on Lower Halides of Indium*, J. Am. Chem. Soc., 80 (1958) 4764.
- N. N. GREENWOOD, *The Ionic Properties and Thermochemistry of Addition Compounds of Gallium Trichloride and Tribromide*, J. Inorg. Nucl. Chem., 8 (1958) 234.
- N. N. GREENWOOD, *The Chemistry of Gallium*, in H. J. EMELÉUS AND A. G. SHARPE (Eds.) *Advances in Inorganic Chemistry and Radiochemistry*, New York, Interscience, Vol. 5 (1963) 91.

## Carbon and Silicon

The electronic structure of the carbon atom gives the element a remarkable diversity of chemical properties. The four valence electrons occupy the configuration  $2s^2 2p^2$  in the  $^3P$  ground state but promotion and hybridisation (p. 113) to  $2s 2p^3$  occurs very freely and accounts for the characteristic valency of four which is never exceeded.

Silicon differs from carbon in that 3d orbitals are accessible, giving a greater variety and an increased number of valency states (p. 113). It can thus exhibit a covalency greater than 4, as in the  $\text{SiF}_6^{2-}$  ion.

TABLE 63  
ATOMIC PROPERTIES OF CARBON AND SILICON

	C	Si
Atomic number	6	14
Electron configuration	$2s^2 2p^2$	$3s^2 3p^2$
Covalent radius (Å)	0.77	1.17
Ionic radius $M^{4+}$ (Å)	—	0.39

The covalent radius of carbon is small, and the radius of the  $C^{4+}$  ion should be remarkably small. The element forms covalent bonds except with metals of insignificant electronegativity; thus, for instance,  $\text{NaCH}_3$  ionises to  $\text{Na}^+$  and  $\text{CH}_3^-$ . Even with the most strongly electronegative element, fluorine, carbon forms bonds which are predominantly covalent.

The ionisation energies (Table 64) indicate that silicon is capable of forming positive ions more easily than carbon, but it too forms mainly covalent compounds.

TABLE 64  
IONISATION ENERGIES OF CARBON AND SILICON

	1st	2nd	3rd	4th
Carbon (eV)	11.3	24.4	47.9	64.5
Silicon (eV)	8.15	16.3	33.5	45.1

### Bond strengths in carbon and silicon compounds

A striking feature of the chemistry of carbon is the ease with which its atoms combine with one another. The strength of the C—C single bond is exceptionally high for a homopolar bond. The Si—Si single bond is very much weaker than the bond between silicon and either chlorine or oxygen, both elements which are much more electronegative than silicon. In consequence silicon atoms form only short chains and the links between the atoms are easily broken.

TABLE 65  
BOND ENERGIES (kcal) OF CARBON AND SILICON

<i>Carbon</i>		<i>Silicon</i>	
C—C	85	Si—Si	53
C—Cl	81	Si—Cl	91
C—O	86	Si—O	108
C—H	99	Si—H	76

The C—H bond is particularly strong and this accounts for the great stability of saturated hydrocarbons and the enormous number of compounds with carbon-hydrogen bonds. In contrast the Si—H bond although fairly strong does not lead to many hydrides because silicon atoms form only short chains. The silicon hydrides are very reactive.

### The elements

Elementary carbon occurs in two crystalline forms. In diamond the C atoms are arranged tetrahedrally and equidistant (Fig. 217), C—C = 1.54 Å. They are bound covalently by electron pairs which occupy localised MO's formed by an overlapping of the  $sp^3$  hybrids. This structure confers great hardness on the crystal but permits of four well-defined cleavages.

In a graphite crystal the layers of carbon atoms are in a regular hexagonal network with a C—C bond length of 1.42 Å, the different layers being 3.40 Å apart (Fig. 218). Every carbon atom is bound to three others in the layer by covalent bonds which can be described by localised molecular orbitals, built up by overlapping  $sp^2$  hybrids, holding two electrons in each orbital. The electrons in the unhybridised p orbitals form a mobile system of metallic type (p. 134). In single crystals the material is soft and the cleavage well developed, one layer of atoms sliding easily over another. Carbon has particularly high m.p. and b.p.

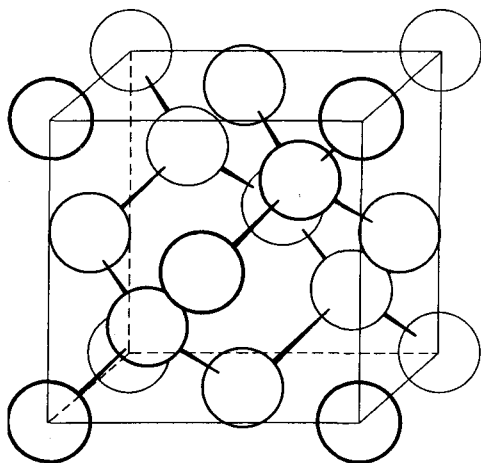


Fig. 217. Diamond structure.

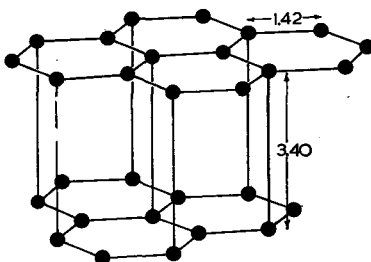


Fig. 218. Graphite structure.

TABLE 66

PROPERTIES OF CARBON AND SILICON

	C		Si
	<i>Diamond</i>	<i>Graphite</i>	
Density (g/cc)	3.52	2.25	2.49
Atomic volume	3.4	5.3	11.4
Melting point (°C)		3500	1420
Boiling point (°C)		4800	2700

*Carbon* (0.08% of the earth's crust) occurs in the elementary state as diamond, graphite and other, less ordered, forms of the element; in solid, liquid and gaseous hydrocarbons, and in mineral carbonates such as limestone, magnesite and dolomite. The atmosphere contains 0.03% of  $\text{CO}_2$  by volume, from which source a great variety of compounds of biological generation are derived.

Clear diamonds, occasionally in coloured form, are used as gems because the high index of refraction ( $\sim 2.42$ ) enhances internal reflexion and brilliance in the cut stone. Diamonds are of great industrial importance: larger, opaque, natural diamonds are mounted in tools for cutting metal and rock, and diamond powder is a widely used abrasive for arming grinding and cutting wheels. Some of the smaller sized material is manufactured by heating graphite to temperatures of  $\sim 3000^\circ$  under pressures exceeding  $10^5$  atm, in the presence of a little metal (*e.g.* Mn, Fe or Co) a film of which



is presumed to dissolve carbon as graphite and allow it to crystallise as diamond.

Graphite, of which the natural supply is limited, is manufactured in various ways depending upon the purpose for which it is intended. Finely divided material, pure and soft for lubrication, is produced in the Acheson process. In this, powdered coke is heated for about a day to temperatures reaching  $\sim 2500^\circ$ , by letting it serve as the resistance in an electric furnace. The conversion to graphite is probably catalysed by the presence of a little silicon derived from the coke or the furnace walls.

Massive graphite required for electrodes and other refractory purposes is made by mixing powdered coke (see below for varieties) with pitch, moulding, pressing, or extruding the plastic material to shape, heating to  $\sim 1250^\circ$  in order to drive off volatiles, and finally graphitising at  $\sim 2500^\circ$  by making the pieces resistance elements in an electric furnace. The purity depends on the raw materials used and the precautions taken during the processing; it must be high when the products are intended for electrodes or for building into atomic reactors. The graphite blocks for the latter purpose are formed by an extrusion process which orients the crystallites and renders the finished material anisotropic (for irradiation damage and Wigner energy see p. 220).

Graphite is singular in being the only known material the mechanical properties of which improve with rising temperature; accordingly it is used for the dies and plungers in high-temperature ( $> 1500^\circ$ ) hot pressing of metal powders such as those of beryllium and of the refractory 'hard metals' such as TiC.

Other artificial carbons are:

- (i) Charcoal, made by carburising wood, cellulose or sugar. The ash in the product depends on the starting material and can be very low.
- (ii) Coke, made by carburising coal, varies widely in composition and mechanical properties; that made by carburising residues from the distillation of pitch and natural oil is a more uniform product.
- (iii) Gas carbon, found in the upper part of retorts used for gas manufacture.
- (iv) Animal charcoal, made by charring treated bones, consists of finely divided carbon supported on calcium phosphate. The carbon has a high surface area and is used to decolorise solutions by adsorbing the colouring matter.
- (v) Carbon black, made by burning natural gas in a deficiency of air and collecting the soot on cooled metal plates, is low in ash, but contains tars and liquid and gaseous hydrocarbons. It also has a large surface area and is added as a catalyst in rubber vulcanisation and also as a filler in rubber manufacture.

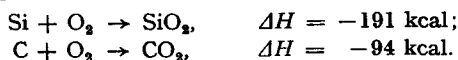
These artificial carbons are usually described as amorphous but most of them show some crystallinity, the more so the higher the temperature of preparation.

Diamond does not ignite in oxygen below  $\sim 800^\circ$  and is only slowly attacked by sulphur vapour at  $1000^\circ$ . Graphite reacts a little more readily, igniting in oxygen at  $690^\circ$ . Both burn with a bright, flameless glow to carbon dioxide. The structure of diamond renders it chemically unreactive but that of graphite allows penetration between the layer planes of carbon atoms. Thus, though not attacked by dilute acids, it is converted to graphite oxide (p. 381) by a mixture of concentrated  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  to which a little  $\text{KClO}_3$  has been added. Other lamellar compounds (p. 380) are formed when alkali metals penetrate between the planes in graphite.

*Silicon* (25.7% of the earth's crust) though only about half as plentiful as oxygen is the second most abundant element. It occurs extensively in many forms of  $\text{SiO}_2$ , silicates and aluminosilicates. The element, hard, grey and crystalline, is made commercially by heating silica with carbon or  $\text{CaC}_2$  in an electric furnace. Crystalline silicon has the diamond structure with an interatomic distance of  $2.34 \text{ \AA}$  (*cf.* diamond  $1.54 \text{ \AA}$ ). It can be purified by zone refining (p. 410) until the impurity content is less than  $10^{-7}\%$ , when it may be employed in semiconductor devices such as transistors.

Silicon dissolves, generally with the formation of a silicide, in most metals, exceptions being Bi, Pb and Tl. It is used as a deoxidiser and an alloying constituent in steel making, and in massive proportions in the manufacture of acid-resistant iron. For these purposes the silicon is usually added as ferrosilicon prepared by the electrochemical reduction of  $\text{SiO}_2$  and  $\text{Fe}_2\text{O}_3$  with carbon.

Silicon is chemically more reactive than carbon. It burns in oxygen at  $400^\circ$ , the reaction being strongly exothermic:



It combines directly with all the halogens at temperatures ranging from  $300^\circ$  upwards, with sulphur vapour at  $600^\circ$ , with nitrogen at  $1300^\circ$  and with carbon at  $2000^\circ$ . Though acid resistant (except to HF) it is attacked by hot alkalis:



and by steam at red heat:



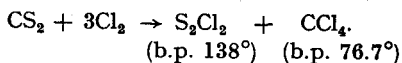
#### Halides

The halides of carbon are very numerous because of the tendency of

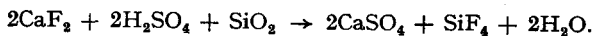
carbon atoms to form chains. A limited number of halides containing Si chains have been made, one with every halogen in compounds of the formula  $\text{Si}_2\text{X}_6$ , additional chlorides up to  $\text{Si}_6\text{Cl}_{14}$  and bromides up to  $\text{Si}_3\text{Br}_8$ .

Of the simple tetrahalides,  $\text{CF}_4$  and  $\text{SiF}_4$  are gases;  $\text{CCl}_4$ ,  $\text{SiCl}_4$  and  $\text{SiBr}_4$  liquids;  $\text{CBr}_4$ ,  $\text{Cl}_4$  and  $\text{SiI}_4$  solids.

Carbon tetrachloride is made on a large scale by passing  $\text{Cl}_2$  into  $\text{CS}_2$  in the presence of a little iodine:



Silicon tetrafluoride is conveniently made by treating a mixture of fluorite and silica with concentrated  $\text{H}_2\text{SO}_4$ :

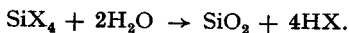


The water is retained by the sulphuric acid, and the  $\text{SiF}_4$  is freed from HF by passing it over dry NaF, whereby solid  $\text{NaHF}_2$  is formed. The other silicon tetrahalides are generally made by direct combination with the halogen. Mixed tetrahalides such as  $\text{SiF}_3\text{Cl}$  and  $\text{SiCl}_2\text{Br}_2$  have also been obtained.

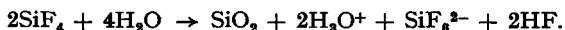
The fluorides of carbon are interesting. Fluorine enters the graphite lattice at  $200^\circ$  to form the interstitial compound  $(\text{CF})_n$ . At higher temperatures the elements give a mixture of  $\text{CF}_4$ ,  $\text{C}_2\text{F}_4$ ,  $\text{C}_2\text{F}_6$  and  $\text{C}_3\text{F}_8$ . Fluorocarbons are conveniently made by passing hydrocarbons over cobalt(III) fluoride at  $150$ – $200^\circ$  or chlorocompounds over  $\text{SbF}_3$  (Swarts' Reaction). Under these conditions when  $\text{CCl}_4$  replaces the hydrocarbon a mixture of  $\text{CCl}_3\text{F}$ ,  $\text{CCl}_2\text{F}_2$ ,  $\text{CCl}_3\text{F}$  and  $\text{CF}_4$  is obtained. The mixed fluorochloro-carbons, known as freons, are useful refrigerants, being volatile, non-toxic and non-corrosive. Higher boiling fluorocarbons form important lubricants which are less reactive and less sensitive to heat than corresponding hydrocarbons.

The fluorocarbons are inert and their derivatives often have very different properties from those of the hydrocarbons because of the high electronegativity of fluorine. For instance,  $(\text{CF}_3)_3\text{N}$  is not basic; the attraction of electrons by the fluorine atoms prevents the nitrogen acting as a donor.

Carbon halides resist hydrolysis because only s and p orbitals are available for bond formation. This restricts the maximum covalency to four and precludes the donation of electrons by the oxygen atom in a water molecule to a carbon atom. But silicon halides do hydrolyse, since the unoccupied silicon 3d orbitals lie not far above the 3s and 3p.



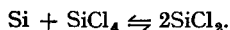
However, with silicon tetrafluoride, the HF formed reacts with some of the tetrafluoride to form fluorosilicic acid:



The octahedral  $\text{SiF}_6^{2-}$  ion is the only halogeno-complex of silicon; the bonding involves  $sp^3d^2$  hybrids and accordingly carbon does not form such a compound. Fluorosilicic acid,  $\text{H}_2\text{SiF}_6$ , known only in solution, is a strong acid. Its heavy-metal salts are soluble, and those of Na, K, Ba and the lanthanides sparingly soluble.

Silicon forms a limited number of halides containing Si chains; there is one of these with every halogen element in compounds of the general formula  $\text{Si}_2\text{X}_6$ , additional chlorides up to  $\text{Si}_6\text{Cl}_{14}$ , and bromides up to  $\text{Si}_3\text{Br}_8$ . The chloride  $\text{Si}_5\text{Cl}_{12}$  made by the action of trimethylamine on  $\text{Si}_2\text{Cl}_6$  is probably  $\text{Si}(\text{SiCl}_3)_4$ , with a neopentane structure.

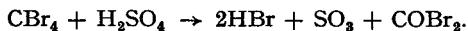
Differing from carbon, silicon resembles Ge, Sn and Pb in forming a dichloride. The relation between pressure and temperature in the Si/SiCl<sub>4</sub> system at high temperatures shows an equilibrium to exist:



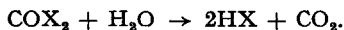
But the dichloride is present in appreciable quantities only above 1100°.

#### *Oxohalides*

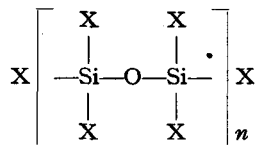
Carbon forms oxohalides:  $\text{COF}_2$  and  $\text{COCl}_2$  are colourless gases made by union of carbon monoxide and the halogen. The molecules are planar, a form which suggests  $sp^2$  hybridisation. In  $\text{COCl}_2$  the small angle of 112° between the C—Cl bonds is due to a strong repulsion exerted on each by the spin-paired electrons of the C—O bond. Carbonyl bromide,  $\text{COBr}_2$ , is a colourless liquid best made by dropping concentrated  $\text{H}_2\text{SO}_4$  on to  $\text{CBr}_4$ :



All three compounds are easily hydrolysed:



Silicon oxohalides of structure,



can be obtained either by treating  $\text{SiO}_2$  with a mixture of oxygen and chlorine or bromine, or by partially hydrolysing the silicon tetrahalide with moist

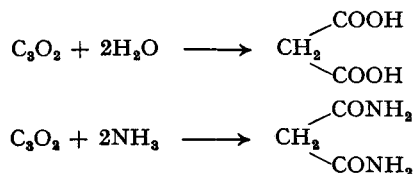
ether. The fluoride  $\text{Si}_2\text{OF}_6$  is made by fluorinating the corresponding chloride:



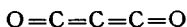
### Oxides of carbon

#### *Carbon suboxide*

Carbon suboxide,  $\text{C}_3\text{O}_2$ , is a gas formed when malonic acid, or one of its esters, is heated with  $\text{P}_2\text{O}_5$ . When dry, it is fairly stable at room temperature but polymerises readily on warming; the liquid (b.p.  $6^\circ$ ) so produced further polymerises to a dark red, water-soluble solid.  $\text{C}_3\text{O}_2$  behaves as the anhydride of malonic acid:



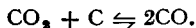
A mixture with oxygen explodes when sparked. The molecule is linear, but the structure



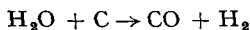
is an over-simplification; the bonds are all somewhat shorter than normal double bonds, the carbon-carbon distance being  $1.28 \text{ \AA}$  (*cf.*  $1.33 \text{ \AA}$ ) and the carbon-oxygen,  $1.16 \text{ \AA}$  (*cf.*  $1.22 \text{ \AA}$ ). There are two  $\pi$ -bond systems (*cf.*  $\text{N}_2$  triple bond, p. 108) but these are non-localised, and contribute only *fractional*  $\pi$  bonds (p. 130).

#### *Carbon monoxide*

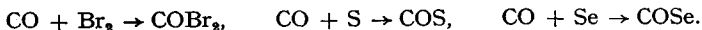
Carbon monoxide, CO, can be made by the dehydration of formic acid, but is too insoluble to be considered as the acid anhydride. The gas is produced industrially in large quantities by the 'producer-gas' reaction between carbon and  $\text{CO}_2$  at high temperatures:



Carbon monoxide is also one of the products of the 'water-gas' reaction:



It reacts with chlorine and bromine in sunlight, and with molten sulphur and heated selenium in the dark:

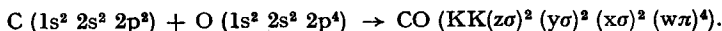


Several transition metals give carbonyls (p. 383) and some salts and complexes of these metals also combine with carbon monoxide:



The reaction of hydrogen with CO provides the basis of an industrial process for making methanol; it is carried out at high pressure over a mixed copper-zinc catalyst. Though CO is insoluble in, and unreactive with, water at ordinary pressures, formic acid is produced at high pressures. Under similar conditions CO and aqueous NaOH combine to give sodium formate.

The CO molecule is isoelectronic with  $\text{N}_2$  and its MO's are formally the same:



However the  $\text{CO}^+$  ion has a shorter carbon-oxygen bond than the neutral molecule, indicating that the highest occupied orbital is non-bonding, whereas the  $\text{N}_2^+$  ion has a longer nitrogen-nitrogen bond than the neutral molecule. It is likely that in carbon monoxide the oxygen 2s electrons form a lone pair ( $z\sigma$ ) and that one carbon sp hybrid holds a second lone pair ( $y\sigma$ ). The bonding orbital  $x\sigma$  would then be formed by overlap of a carbon sp hybrid and an oxygen p orbital. Lateral overlap of the remaining (singly occupied) 2p orbitals results in two  $\pi$ -type MO's, leaning somewhat towards the oxygen (Fig. 219). Ionisation is probably from the carbon lone pair and not from a  $\pi$ -bond orbital. The dipole moment of the  $\pi$  electrons is

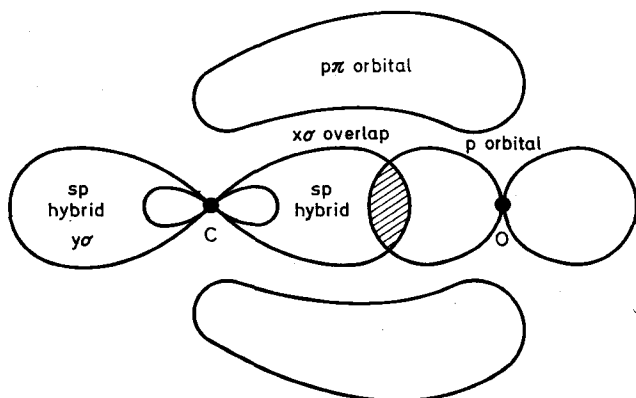
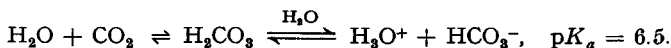


Fig. 219. Bonds in the CO molecule. There is another  $p\pi$  orbital in the plane perpendicular to the paper through C—O.

strongly offset by the carbon lone pair; this lone pair is also responsible for the co-ordinating power displayed in the carbonyls (p. 386).

### Carbon dioxide

Carbon dioxide is the most stable oxide of carbon at room temperature. Industrially it is recovered from flue gases and lime kilns, the  $\text{SO}_2$  and  $\text{H}_2\text{S}$  present being removed from the gases by scrubbing with aqueous  $\text{KMnO}_4$  and  $\text{Na}_2\text{CO}_3$ . Carbon dioxide dissolves in water giving, at N.T.P., a 0.04 molar solution in which the carbonic acid is only slightly ionised:



The equilibrium moves to the left as the temperature is raised and the gas can be completely expelled from the water. The pH of a saturated solution of the gas at 1 atmosphere is 3.7. Commercially the gas is solidified as *dry ice*, added to oxygen as a respiratory stimulant, and to flavoured water for carbonated drinks.

The molecule is linear with carbon-oxygen distances of 1.15 Å, which is considerably shorter than that calculated for a double bond (1.22 Å). Two  $\pi$ -bond systems are expected, in perpendicular planes, but each would extend over all centres (*cf.* carbon suboxide) contributing slightly more than half a  $\pi$  bond in each link.

### Thermodynamics of the oxidation of carbon

The standard molal entropies of C, CO,  $\text{CO}_2$  and  $\text{O}_2$  in cal deg<sup>-1</sup> mole<sup>-1</sup> are:

$$\begin{array}{ll} \text{C}, S^\circ = 1.36 & \text{CO}_2, S^\circ = 51.06 \\ \text{CO}, S^\circ = 47.30 & \text{O}_2, S^\circ = 49.00 \end{array}$$

The standard entropy changes for the following reactions at 25° are

$$\begin{array}{ll} \text{(a) } 2\text{CO}(\text{g}) + \text{O}_2(\text{g}) = 2\text{CO}_2(\text{g}) \cdot \Delta S^\circ = (2 \times 51.06) - (2 \times 47.30) - 49.00 \\ & = -41.48 \\ \text{(b) } \text{C}(\text{s}) + \text{O}_2(\text{g}) = \text{CO}_2(\text{g}) \cdot \Delta S^\circ = 51.06 - (49.00 + 1.36) \\ & = +0.70 \\ \text{(c) } 2\text{C}(\text{s}) + \text{O}_2(\text{g}) = 2\text{CO}(\text{g}) \cdot \Delta S^\circ = (2 \times 47.30) - 49.00 - (2 \times 1.36) \\ & = +42.88 \end{array}$$

Although these values relate to 25°, they are a guide to the thermodynamics of reactions in the carbon-oxygen system at higher temperatures. For any reaction

$$-\Delta S = \left( \frac{\partial \Delta G}{\partial T} \right)_p,$$

the gradient of the free energy–temperature graph. The slope is very nearly linear so long as there is no change in the physical states of the reactants or products (states shown in brackets in the equations) such as the melting of a solid or the condensation of a gas.

Fig. 220 shows the free energy–temperature plots of the three oxidation reactions. This composite graph, in which the number of moles of the common reactant (here oxygen) is the same for every reaction, is known as an Ellingham diagram.

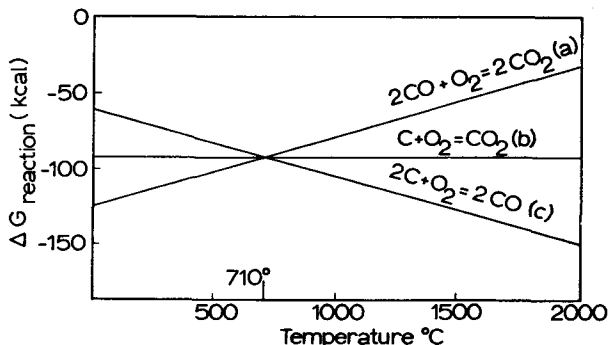
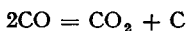


Fig. 220. Ellingham diagram showing the variation of the free energy of reaction with temperature for the three reactions which are formulated.

For reaction (a)  $\Delta S$  is negative and  $\Delta G$  increases with temperature; for (b)  $\Delta S$  is almost zero and  $\Delta G$  hardly changes; and for (c)  $\Delta S$  is positive and  $\Delta G$  decreases.

The free-energy change for the reaction



is given by  $\Delta G(c) - \Delta G(b)$ . For this reaction  $\Delta G$  is positive above  $710^\circ$ , but negative below that temperature. Thus higher temperatures favour the formation of CO and lower temperatures that of  $\text{CO}_2$ .

By adding to Fig. 220 lines representing the free-energy changes for the oxidation of metals, a diagram is produced (Fig. 221) from which the effect of temperature on the reduction of the respective oxides to metal by carbon or by carbon monoxide may be deduced.

The first thing to note on the diagram is that all the lines relating to the oxidation of metals are either straight (when they refer to the metal in one phase—solid for manganese) or made up of straight sections in which direction changes at phase-change points (the melting and sublimation points for zinc and magnesium). Secondly, it is observed that all the slopes are positive, that is  $\Delta G$  increases with temperature.



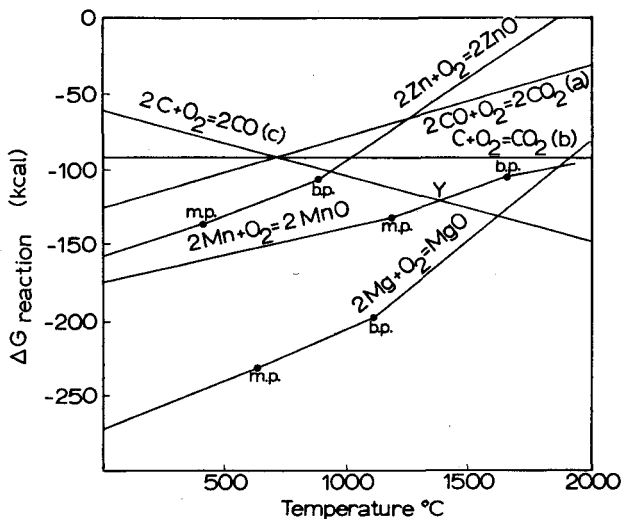
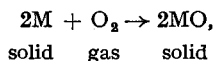


Fig. 221. Free energy-temperature plots illustrating the reduction of metallic oxides.

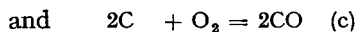
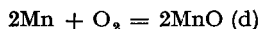
Normally metal oxides have their atoms in a highly-ordered crystal lattice and therefore the oxides have low entropies. But the entropy of gaseous oxygen is high; thus in the oxidation:



$\Delta S_{\text{reaction}}$  is negative. When, at a higher temperature, oxidation of liquid metal by oxygen occurs,  $\Delta S_{\text{reaction}}$  becomes more negative in this reaction above the melting point. Again, it becomes even more negative above the boiling point because disorder in the vapour is greater than in the liquid.

#### Reduction of manganese oxide (MnO)

Let us consider particularly the point Y (Fig. 221) at which  $\Delta G$  has the same values for



Moreover, for reaction (e)  $2MnO + 2C = 2CO + 2Mn$ ,  $\Delta G = 0$ . Above this temperature  $\Delta G(d) > \Delta G(c)$ , and  $\Delta G(e)$  is therefore negative. At equilibrium the active mass of Mn exceeds that of MnO and reduction of the metal oxide is favoured. But line (d) (Fig. 221) reaches line (b) at a much higher temperature. Thus the existence of the stable monoxide of carbon, with

its positive entropy of formation, allows many transition-metal oxides, of which MnO is typical, to be reduced by carbon at moderate temperatures. Clearly, if CO<sub>2</sub> were the only oxide of carbon which could be formed, the reduction of these metal oxides by carbon would need higher temperatures. Most metal ores are either oxides or compounds easily converted into oxides, and carbon, in the form of coke, is a cheap, readily-available, reducing agent, hence these thermodynamic facts are of considerable importance.

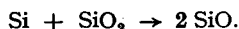
#### *Reduction of magnesium and other oxides*

It can be seen from Fig. 221 that magnesium oxide becomes reducible by coke at about 1600°. The free energies of formation of oxides like CaO and Al<sub>2</sub>O<sub>3</sub> are much lower, however, and reduction with coke would require heating the reactants to very high temperatures which would be uneconomic.

Carbon, although thermodynamically easily able to reduce a particular metal oxide, may be unsuitable for that purpose for other reasons, such as the formation of metallic carbides.

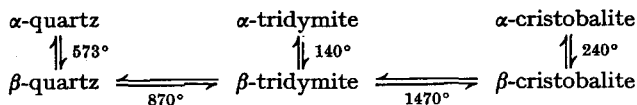
### Oxides of silicon

Silicon monoxide is believed to be formed by the reduction of SiO<sub>2</sub> by Si at a high temperature:



Its existence at room temperature has been questioned; the X-ray diffraction pattern formerly attributed to SiO may arise from a mixture of  $\beta$  cristobalite and  $\beta$  silicon carbide; the carbon being derived from the reaction vessel.

In contrast to the discrete molecules of carbon dioxide, silicon dioxide forms condensed, three-dimensional systems of indefinite extension which are high-melting solids. Silica has three crystalline forms, quartz, tridymite and cristobalite, all have a low-temperature ( $\alpha$ ) and a high-temperature ( $\beta$ ) modification.



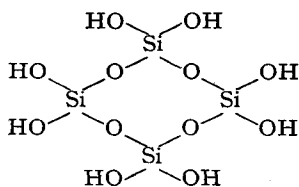
In cristobalite the Si atoms are arranged as are the C atoms in diamond, (p. 365), except that they have O atoms midway between them. In quartz and tridymite the regular structure is replaced by a screw-like arrangement of the atoms. Transitions between the forms take place slowly, and all

three are found in nature. However, the transitions between their respective  $\alpha$  and  $\beta$  modifications are rapid.

Silica melts at  $1710^\circ$ . Even when slowly cooled the molten material sets to a vitreous, non-crystalline solid. Its plastic range allows large masses to be forged and hollow ware to be blown; its low coefficient of expansion renders it immune to thermal shock; its transparency especially to u.v. makes it suitable for lenses and prisms. Specially pure synthetic silica is now made for laboratory ware used in preparing the pure materials required by the electrical industry (*e.g.* transistors), and for optical parts calling for minimum absorption.

Silica gel is a hard, granular, translucent material containing about 4%  $\text{H}_2\text{O}$ . It results from the removal of salts and water from the continuous gel formed by acidifying the solution of an alkali-metal silicate, and has a large surface area. Silica gel is employed as a drying agent, as a catalyst in the hydrolysis of aryl halides to phenols, and as a support for other catalysts, such as for example the  $\text{V}_2\text{O}_5$  used in the oxidation of naphthalene to phthalic acid or of  $\text{SO}_2$  to  $\text{SO}_3$ . A silica-alumina gel with 10 to 13% of  $\text{Al}_2\text{O}_3$  is made by the cogelation of silicate and aluminate solutions with a mineral acid; it is a catalyst for the cracking of petroleum.

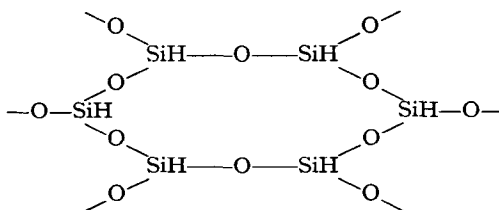
The monosilicic acid,  $\text{Si}(\text{OH})_4$ , is probably the only silicic acid species to be found in dilute solutions. However, the isothermal dehydration of silicic acid, prepared by the action of damp air on  $\text{SiS}_2$ , leads to an acid  $\text{H}_8\text{Si}_4\text{O}_{12}$  for which has been suggested the structure:



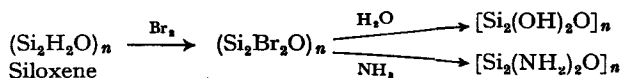
Further dehydration by dioxan or  $\text{SO}_2\text{Cl}_2$  provides less definite evidence for other silicic acids.

### Other silicon-oxygen compounds

When silicochloroform is hydrolysed with steam at  $450^\circ$ , a compound  $[(\text{HSiO})_2\text{O}]_n$ , with strong reducing properties is formed. Its structure resembles that of mica, having large sheets of connected hexagons with Si atoms at the corners and O atoms midway along the sides (Fig. 222). When heated to  $507^\circ$ , the compound is converted to  $\text{Si}_2\text{O}_3$  with a loss of the hydrogen which presumably had provided hydrogen bonds between the sheets; bonds which are now replaced by Si—Si interplanal links.

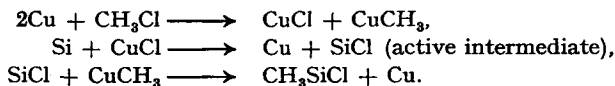
Fig. 222. Structure of  $[(\text{HSiO})_2\text{O}]_n$ .

Siloxene, a similar compound in the form of a flaky, white solid, is made by the action of HCl gas and ethyl alcohol on  $\text{CaSi}_2$ . It is spontaneously inflammable in air and a strong reducing agent. The H atoms can be replaced partly or wholly by halogens:

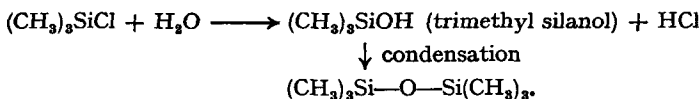


### Silicones

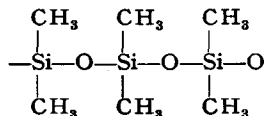
Hydrolysis of the alkyl and aryl substituted silicon halides produces silicones. The halogen derivatives themselves are made by passing an alkyl or aryl halide over a copper-silicon alloy at about  $300^\circ$ . Evidence has been found for the mechanism:



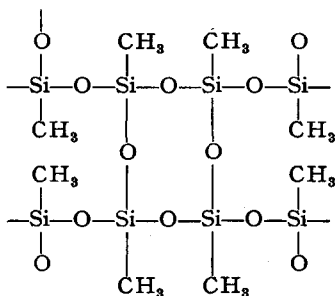
And so on, through  $(\text{CH}_3)_2\text{SiCl}$  and  $(\text{CH}_3)\text{SiCl}_2$  etc., until the four valencies of silicon are saturated. Hydrolysis of  $(\text{CH}_3)_3\text{SiCl}$  gives a disiloxane:



Hydrolysis of  $(\text{CH}_3)_2\text{SiCl}_2$  gives a chain compound:

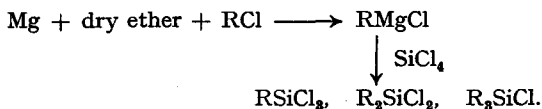


Hydrolysis of  $\text{CH}_3\text{SiCl}_3$  gives a cross-linked chain system:



The extent of the cross-linking and the nature of the alkyl or aryl substituent determines the nature of the polymers. They range from oily liquids to rubbery solids. All are water-repellant, thermally and electrically insulating and chemically inert. These properties render them widely useful in industry; they appear as lubricants, antifoams, low-temperature hydraulic fluids, and in cosmetics.

Though the copper silicide method is preferred for the production of methyl-substituted compounds, a Grignard-type synthesis is commonly used for other alkyl and aryl substituted substances:

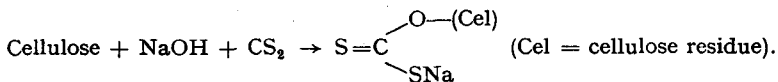


## Sulphides

### *Sulphides of carbon*

Carbon disulphide,  $\text{CS}_2$ , is a volatile liquid (b.p.  $46^\circ$ ), highly refractive, insoluble in water but soluble in ethyl alcohol and ether. The molecule is linear, with C—S distances of  $1.55 \text{ \AA}$ , indicating that the bonds are effectively double bonds. The single-bond distance for the same pair of atoms is  $1.79 \text{ \AA}$ .

It is made by the action of sulphur vapour on electrically heated coke. Its main uses are as a solvent and in the manufacture of  $\text{CCl}_4$  (p. 368), viscose rayon and thiocarbanilide. Alkali celluloses combine with  $\text{CS}_2$  to give cellulose xanthate:

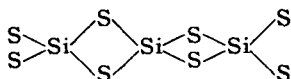


This when extruded through a jet into an acid bath gives rayon. Thiocarbanilide,  $\text{S}=\text{C}(\text{NH}\cdot\text{C}_6\text{H}_5)_2$ , results when  $\text{CS}_2$  is passed into boiling aniline. It is used in the manufacture of dyes and pharmaceuticals, and in the vulcanisation of rubber.

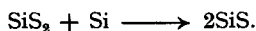
A brown polymer,  $(CS)_n$ , is formed when  $CS_2$  is exposed to light and a subsulphide,  $C_3S_2$ , when an arc is struck between carbon poles beneath the liquid. If the arc is between a carbon cathode and a selenium or tellurium anode then the liquids  $CSSe$  or  $CSTe$  are formed.

#### *Sulphides of silicon*

Silicon disulphide forms fibrous crystalline macromolecules with a structure intermediate between that of  $CO_2$ , with its individual molecules, and the three-dimensional  $SiO_2$ . In it the sulphur atoms are arranged tetrahedrally round the Si atoms:

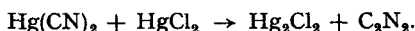


Though solid  $SiO$  cannot be obtained from  $SiO_2$  (p. 375), the monosulphide,  $SiS$ , can be made by heating  $SiS_2$  with silicon:



#### Compounds with nitrogen

Cyanogen,  $C_2N_2$ , is readily evolved when mercury(II) cyanide is heated with mercury(II) chloride:



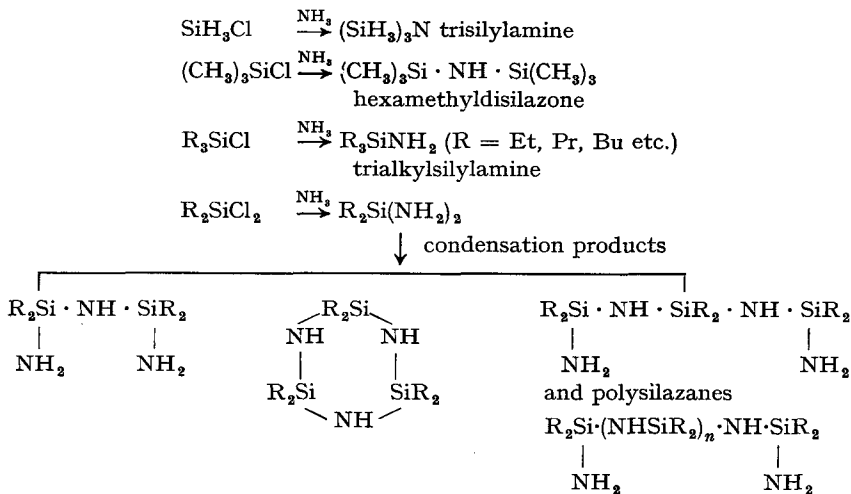
The colourless, very poisonous, gas (b.p.  $-21^\circ$ ) reacts with alkaline solutions to give a mixture of cyanide and cyanate:



The molecule is linear and without dipole moment, the intermolecular distances being  $C-N$ , 1.16 Å and  $C-C$ , 1.37 Å. Since the lengths are 1.15 Å for the  $C\equiv N$  bond and 1.54 Å for the  $C-C$  single bond, it suggests that the  $\pi$  bonds of the  $C\equiv N$  groups are sufficiently delocalised to reduce the electron density between carbon and nitrogen and increase it between carbon and carbon.

Silicon nitride,  $Si_3N_4$ , is a refractory material made by direct combination of the elements above  $1300^\circ$ . Another method is to allow the hydrides or halides of silicon to react with ammonia and to heat the amino- and imino-silanes produced. These give the polymer  $[Si(NH_2)_2]_n$  which yields  $Si_3N_4$ .

Organosilicon compounds containing  $Si-N$  bonds are numerous. Examples are formulated as follows:



When R is a small group (H, Me, Et) the principal products are polysilazanes, but when R is butyl or aryl, the 6-membered ring compounds predominate.

Trihalogenosilanes react with ammonia to give, almost entirely, polysilazanes. Alkyl silanes require much more nucleophilic reagents than do the halogen compounds to convert them to silicon-nitrogen compounds. A solution of lithium in liquid ammonia converts  $\text{Et}_3\text{SiH}$  into a mixture of  $\text{Et}_3\text{SiNH}_2$ , triethylsilylamine, and  $(\text{Et}_3\text{Si})_2\text{NH}$ , hexaethylidisilazone.

### Graphite compounds

Graphite absorbs liquid potassium and at the same time swells in a direction perpendicular to the cleavage. When the excess of potassium is evaporated, there remains a copper-coloured material with the composition  $\text{KC}_8$  which is converted, on further heating, to  $\text{KC}_{24}$ . X-ray examination shows  $\text{KC}_8$  to have potassium atoms inserted between every layer of carbon atoms in the graphite structure and  $\text{KC}_{24}$  to have potassium atoms between alternate layers only. The diamagnetism of the original graphite is absent from  $\text{KC}_8$  which is, in fact, a better electrical conductor than solid potassium. Equilibrium pressure measurements have also disclosed the entity  $\text{KC}_{24}$ . Lamellar compounds  $\text{MC}_8$  and  $\text{MC}_{24}$  (where M represents Rb or Cs) have also been made, their stability increasing with the size of the metal atom. The bonding in these compounds is essentially ionic.

*Graphite oxide*

Graphite also swells when heated for a period in a solution of  $\text{KClO}_3$  in  $\text{HNO}_3$ , with the formation of graphite oxide, the normal interplanar distance of 3.4 Å in graphite being increased. Graphite oxide absorbs water. The interplanar distance is  $\sim 6$  Å when the material is dried over  $\text{P}_2\text{O}_5$ ,  $\sim 9$  Å when kept in air, and  $\sim 11$  Å when soaked in water. A rapid method of preparation is to heat graphite with an anhydrous mixture of  $\text{H}_2\text{SO}_4$ ,  $\text{NaNO}_3$  and  $\text{KMnO}_4$  at below  $45^\circ$  for less than 45 min. Thus prepared, the 'dry' oxide is said to have the composition  $\text{C}_7\text{O}_4\text{H}_2$ , whatever the graphite used. The C : O ratio has been variously reported, but always as less than 2 : 1. Preparations have ranged from yellow to dark brown. The oxide is unstable, decomposing at  $\sim 200^\circ$  to  $\text{CO}_2$ , CO and carbon.

The constitution and structure of graphite oxide has been much investigated and finality has not been reached. But it is probable that the planar aromatic rings of the graphite (p. 365) are puckered and partly broken to allow both C—OH and C=O bonds to be formed. Although the oxide shows some acidic character ( $\text{C—OH} \rightarrow \text{C—O}^- + \text{H}^+$ ) the bonding of the interplanar species, in contrast to that in the alkali-metal compounds, is predominantly covalent.

'Graphitic salts' can also be made. For instance sulphuric acid in the presence of strong oxidising agents forms the compound  $\text{C}_{24}\text{HSO}_4 \cdot 2\text{H}_2\text{SO}_4$ . Phosphoric, selenic and perchloric acids behave somewhat similarly. Lamellar compounds are also formed by  $\text{CrO}_2\text{Cl}_2$  and  $\text{CrO}_2\text{F}_2$ ; the product of reaction between graphite and fluorine at  $200^\circ$ ,  $(\text{CF})_n$ , is of the same type, with an inter-layer distance of 8.17 Å.

**Carbides**

The carbides can be divided into four groups: (1) salt-like, (2) interstitial, (3) iron-type, and (4) covalent.

*(1) Salt-like carbides*

Members of this class can usually be made by heating the metal, its oxide or hydride with carbon, carbon monoxide or a hydrocarbon. The salt-like carbides are easily hydrolysed by water and are classified according to the aliphatic hydrocarbon they give.

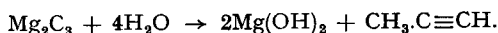
(a) The acetylides, such as  $\text{CaC}_2$ ,  $\text{CrC}_2$ ,  $\text{BaC}_2$  and  $\text{MgC}_2$ , give acetylene when treated with water. They are made by heating the oxide and carbon and have tetragonal crystals containing  $\text{M}^{2+}$  and  $\text{C}_2^{2-}$  ions arranged as are the  $\text{Na}^+$  and  $\text{Cl}^-$  ions in rock salt but with the c axis parallel to the C—C bonds lengthened ( $c/a \sim 1.2$ ). In contrast, the compounds  $\text{Cu}_2\text{C}_2$ ,  $\text{Ag}_2\text{C}_2$



and  $\text{Au}_2\text{C}_2$  are precipitated from aqueous solution, the first by passing acetylene into ammoniacal copper(I) chloride, and the last by passing acetylene into gold(I) thiosulphate. They are formally acetylides, but are not hydrolysed by water.

(b) The methanides, such as  $\text{Al}_4\text{C}_3$  and  $\text{Be}_2\text{C}$ , yield methane on hydrolysis. Both are made by combination of the elements at about  $1500^\circ$ , and are much harder materials than the acetylides.

(c) Magnesium carbide,  $\text{Mg}_2\text{C}_3$ , which is formed when  $\text{MgC}_2$  is heated, and is believed to contain  $\text{C}_3^{2-}$  ions, yields allylene on hydrolysis:



Thorium and the lanthanides also form carbides,  $\text{MC}_2$ , when their oxides are heated with carbon in an electric furnace. They have been reported as giving a mixture of acetylene, olefines and hydrogen on hydrolysis. But later work suggests that pure  $\text{ThC}_2$  yields only acetylene, making it an acetylide.

### (2) *Interstitial carbides*

These are made by the direct union of metal and carbon or the reduction of the oxide with carbon at about  $2000^\circ$ . They are very high-melting materials (particularly  $\text{TaC}$ , m.p.  $3900^\circ$ ), good electrical conductors, very hard but brittle, and inert chemically except under oxidising conditions. Cemented carbides, based on  $\text{WC}$ , are used as hard facings for tools and dies, the metallic binder, usually cobalt, permits fabrication by sintering at  $1200^\circ$  and gives increased strength. Additions of  $\text{TiC}$  and  $\text{TaC}$  serve to vary the properties. Self-bonded carbides are made by hot-pressing the powder without the addition of binder metal at  $2000^\circ$ .

### (3) *Carbides of the iron type*

These carbides are formed by metals which have a metallic radius below  $1.3 \text{ \AA}$ . Iron ( $1.26 \text{ \AA}$ ), chromium ( $1.27 \text{ \AA}$ ) and manganese ( $1.27 \text{ \AA}$ ) form carbides with properties intermediate between the salt-like and the interstitial. Structurally  $\text{Fe}_3\text{C}$ ,  $\text{Mn}_3\text{C}$  and  $\text{Ni}_3\text{C}$  have C atoms inside the trigonal prisms formed by the metal atoms. They are easily decomposed by acids and water. In  $\text{Cr}_3\text{C}_2$  the carbon atoms form chains in the solid.

### (4) *Covalent carbides*

The binary compounds of carbon with elements of higher electronegativity, e.g. hydrogen, sulphur, chlorine, are gases or volatile liquids, e.g.  $\text{CH}_4$ ,  $\text{CS}_2$ ,  $\text{CCl}_4$ ; they are formally classified as hydrides, sulphides, halides etc., not as carbides. The carbides of silicon and boron are quite different,

being thermally stable, hard, chemically-inert solids. Silicon carbide, SiC, exists in three forms related structurally to one another as are diamond, zinc blende and wurtzite. It is made by reducing SiO<sub>2</sub> with carbon in an electric furnace. Boron carbide, B<sub>4</sub>C, also made by reducing the oxide with carbon, has a complicated structure in which icosahedra of 12 boron atoms alternate with C<sub>3</sub> chains.

Silicon carbide, widely employed as an abrasive (carborundum), is finding increasing use as a refractory. It has a better thermal conductivity at high temperatures than any other ceramic and is very resistant to abrasion and corrosion especially when bonded with silicon nitride. Hot-pressed, self-bonded SiC may be suitable as a container for the fuel elements in high-temperature, gas-cooled atomic reactors and also for the structural parts of the reactors. Boron carbide, which is even harder than silicon carbide, becomes now readily available commercially because of its value as a radiation shield, and is being increasingly used as an abrasive.

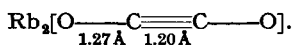
## METAL CARBONYLS

### Simple carbonyls

Many of the transition metals of Groups VI, VII and VIII form volatile, diamagnetic carbonyls in which the charge number of the metal atom is zero. These are listed with significant properties in Table 67 (p. 385).

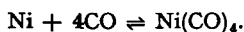
Palladium and platinum do not form simple carbonyls.

Compounds with the empirical formulae M<sup>0</sup>CO and M<sup>II</sup>(CO)<sub>2</sub> formed by alkali and alkaline earth metals, are not true carbonyls. The compound Rb<sub>2</sub>(CO)<sub>2</sub> has been shown recently to have an acetylenediolate structure at low temperatures:



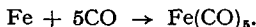
#### *Preparation of carbonyls*

Nickel when freshly reduced combines with carbon monoxide at room temperature and ordinary pressures:

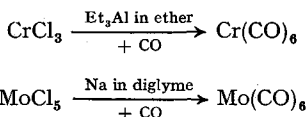


Retention of the carbonyl by adsorption on the surface of the finely divided metal with consequent fall in yield is largely avoided by passing the CO over nickel pellets, freezing out the carbonyl, and recycling the stripped gas.

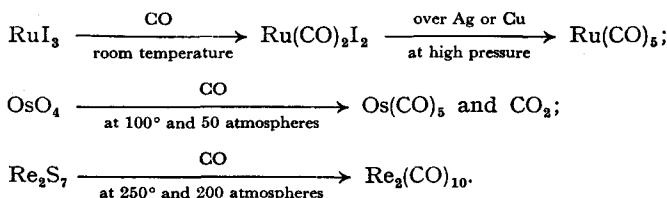
Finely divided iron reacts less easily, CO at 200° and 100 atmospheres pressure being necessary to effect combination:



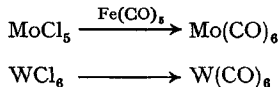
Other metal carbonyls are made by reducing suitable salts or complexes in the presence of carbon monoxide under pressure. Among the reducing agents which have been used are triethylaluminium in ether, zinc or magnesium powder in pyridine, and sodium in diglyme:



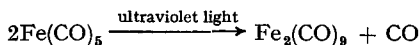
Carbonyls of some of the metals near osmium in the Periodic Table can be made by the reaction of CO under pressure with some of their compounds:



In place of carbon monoxide,  $\text{Fe}(\text{CO})_5$  can be used to convert certain metal salts to carbonyls:



The secondary carbonyls such as  $\text{Fe}_2(\text{CO})_9$  are often obtainable by photo-decomposition or thermal decomposition of primary ones:



Recently, mixed metal carbonyls such as that containing cobalt and manganese,  $(\text{CO})_4\text{CoMn}(\text{CO})_5$ , have been made by treating a sodium carbonylate (p. 389) with a carbonyl halide (p. 390) of another metal.

#### *Properties of the simple carbonyls*

The simple carbonyls of the  $\text{M}(\text{CO})_n$  type are colourless liquids or low-melting solids, except  $\text{V}(\text{CO})_6$  which is a black solid and  $\text{Fe}(\text{CO})_5$  which is a yellow liquid. Carbonyls with more than one metal atom per molecule are usually coloured solids, but  $\text{Re}_2(\text{CO})_{10}$  forms colourless, monoclinic crystals. The melting and boiling points of the simple carbonyls will be found in Table 67.

TABLE 67  
THE BINARY METAL CARBONYLS  
(formulae and physical character)

V	VI	VII	VIIIA	VIIIB	VIIIC
V(CO) <sub>6</sub> Black crystals d. 70°	Cr(CO) <sub>6</sub> Colourless crystals sublime in vacuo	Mn <sub>2</sub> (CO) <sub>10</sub> Golden crystals m.p. 154°	Fe(CO) <sub>5</sub> Yellow liquid b.p. 103°	Co <sub>2</sub> (CO) <sub>8</sub> Orange crystals m.p. 51°	Ni(CO) <sub>4</sub> Colourless liquid b.p. 43°
			Fe <sub>2</sub> (CO) <sub>9</sub> Bronze platelets d. 100°	Co <sub>4</sub> (CO) <sub>12</sub> Black crystals d. 60°	
			Fe <sub>3</sub> (CO) <sub>12</sub> Dark-green crystals d. 140°		
	Mo(CO) <sub>6</sub> Colourless crystals sublime in vacuo d. 180°	Tc <sub>2</sub> (CO) <sub>10</sub> Colourless crystals sublime in vacuo	Ru(CO) <sub>5</sub> Colourless liquid f.p. -22°	Rh <sub>2</sub> (CO) <sub>8</sub> Orange- yellow crystals m.p. 76°	
			Ru <sub>3</sub> (CO) <sub>12</sub> Green crystals d. 150°	Rh <sub>6</sub> (CO) <sub>16</sub> Black crystals	
	W(CO) <sub>6</sub> Colourless crystals sublime in vacuo d. ~ 180°	Re <sub>2</sub> (CO) <sub>10</sub> Colourless crystals m.p. 177°	Os(CO) <sub>5</sub> Colourless liquid f.p. -15°	Ir <sub>2</sub> (CO) <sub>8</sub> Greenish- yellow crystals	
			Os <sub>3</sub> (CO) <sub>12</sub> Yellow crystals m.p. 224°		

Of these only Vanadium carbonyl, V(CO)<sub>6</sub>, is paramagnetic.

The carbonyls are readily combustible;  $V(CO)_6$  and the cobalt carbonyls are sensitive to air. Some, such as  $Fe(CO)_5$  and  $Ni(CO)_4$  are also very toxic, and must be treated with caution.

#### *Structure of the simple carbonyls*

In simple carbonyls of the  $M(CO)_n$  type, the  $M-C-O$  bonds are collinear or nearly so. The carbon-oxygen distances are but slightly greater than the 1.13 Å observed in carbon monoxide, and the carbon-metal distances are somewhat less than that for a single bond. The  $C-O$  stretching frequencies of the simple carbonyls account for infrared absorption in the range 1900–2050  $cm^{-1}$  which is less than that for the absorption of carbon monoxide itself, namely 2146  $cm^{-1}$ . The donor power of the lone pair on the carbon atom in carbon monoxide is slight, for CO forms only very weak complexes with a few Lewis acids; one of these complexes is borine carbonyl,  $BH_3CO$ . In contrast, the electrons accepted from the carbon of CO by transition-metal ions create a ligand field which lowers the energies of just those d orbitals whose symmetry properties enable them to form bonding MO's with the vacant antibonding  $\pi$  orbitals of the CO molecule. The resulting 'back-donation' effect which produces some double-bond character in the  $M-C$  bond is analogous to that described for the isoelectronic  $CN^-$  ion on p. 182. The explanation accounts for the strength of the  $M-C$  bond and also for the weakness of the  $C-O$  bond in carbonyls relative to that bond in carbon monoxide. Except for vanadium ( $Z = 23$ ), the metals in the  $M(CO)_n$  type of carbonyls have even atomic numbers and the lone pairs of the ligands would, if completely donated, give the metal in the carbonyl the configuration of the next higher noble gas. Complete donation does not actually happen, but the 'noble-gas rule' correctly indicates the number of ligands, as may be seen in Table 68.

TABLE 68

<i>Simple carbonyl</i>	<i>Electrons</i>				<i>Noble gas for comparison</i>	<i>Z</i>
	<i>from CO's</i>	<i>from metals</i>	<i>total</i>			
$Ni(CO)_4$	8	+	28	= 36	Kr	36
$Fe(CO)_5$	10	+	26	= 36	Kr	36
$Cr(CO)_6$	12	+	24	= 36	Kr	36
$Mo(CO)_6$	12	+	42	= 54	Xe	54

Carbon monoxide behaves differently from other ligands in almost always adhering to this rule. Even the isoelectronic  $CN^-$  and  $NO^+$  ions do not conform to it.

This suggests that simple carbonyls are invariably spin-paired complexes (p. 161). Except for vanadium, metals with  $Z$  odd do not form simple mononuclear carbonyls. In the mononuclear carbonyl nitrosyls and carbonyl hydrides, however, a metal with an odd atomic number can similarly complete its  $d$  shell. Thus in  $\text{Co}(\text{CO})_3\text{NO}$  the  $\text{NO}$  group can be considered to contribute the single electron necessary to complete the  $3d$  shell of the metal atom. The three  $\text{CO}$  molecules and the isoelectronic  $\text{NO}^+$  are co-ordinated tetrahedrally, just as are the four  $\text{CO}$  molecules in  $\text{Ni}(\text{CO})_4$ .

Also isoelectronic with  $\text{Ni}(\text{CO})_4$  is  $\text{Fe}(\text{CO})_2(\text{NO})_2$  which has bonds of the same length. Iron pentacarbonyl,  $\text{Fe}(\text{CO})_5$ , has the trigonal bipyramidal structure associated with  $dsp^3$  hybridisation. But the hexacarbonyls of  $\text{Cr}$ ,  $\text{Mo}$  and  $\text{W}$  have the octahedral structure consistent with  $d^2sp^3$  hybridisation.

### Polynuclear carbonyls

#### *Bridging CO groups*

In addition to linear  $\text{M}-\text{C}-\text{O}$  groups, some binuclear and polynuclear carbonyls of transition metals in Period 4 also contain bridging  $\text{CO}$  groups bonded to two metal atoms. Such a bridging group contributes one electron to orbitals on each of the metal atoms to form a  $\sigma$  bond with each of them. But in addition to the  $\sigma$  bonds some  $\pi$  bonding also occurs, as is evident from the low values of the  $\text{C}-\text{O}$  stretching frequencies. These are usually about  $1850\text{ cm}^{-1}$ , which is only a little larger than the  $1828\text{ cm}^{-1}$  of the  $>\text{C}=\text{O}$  group in  $\text{COCl}_2$ . For example iron enneacarbonyl,  $\text{Fe}_2(\text{CO})_9$ , has a strong absorption band at  $1830\text{ cm}^{-1}$  due to the bridging  $\text{CO}$  groups and another at about  $2000\text{ cm}^{-1}$  due to the terminal  $\text{CO}$  groups (Fig. 223).

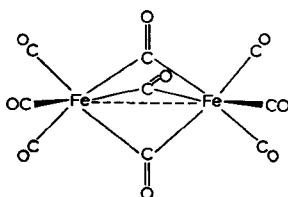


Fig. 223. Structure of di-iron enneacarbonyl,  $\text{Fe}_2(\text{CO})_9$ .

There is also a weak interaction between the metal atoms; that is there is a weak metal-metal bond. The  $\text{Fe}-\text{Fe}$  distance in the molecule is  $2.49\text{ \AA}$ .

Carbon monoxide bound to three metal atoms occurs in the carbonyl derivative  $(\pi\text{-C}_5\text{H}_5\text{Ni})_3\text{CO}$  (Fig. 224).

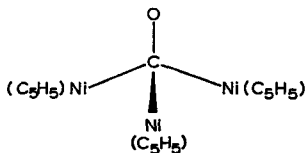


Fig. 224. Carbonyl group attached to three metal atoms.

For this compound the absorption band due to C—O stretching is at  $1724\text{ cm}^{-1}$ , which is about the same as that for the  $\text{>C=O}$  group in acetaldehyde.

#### *Metal-metal bonds*

Metal-metal bonds occur in carbonyls either in conjunction with bridging CO groups, as in the iron enneacarbonyl, or as the sole bond between two metal atoms in a binuclear carbonyl such as  $\text{Mn}_2(\text{CO})_{10}$  and the corresponding Te and Re carbonyls. In the structure of manganese decacarbonyl four of the carbonyl groups about each manganese atom are in planes lying at  $90^\circ$  to the axis of the molecule and relatively disposed (staggered) as shown in Fig. 225. The Mn—Mn distance is  $2.93\text{ \AA}$ ; this is longer than the Fe—Fe distance in  $\text{Fe}_2(\text{CO})_9$ , where there is also carbonyl bridging in addition to metal-metal bonding between the metal atoms.

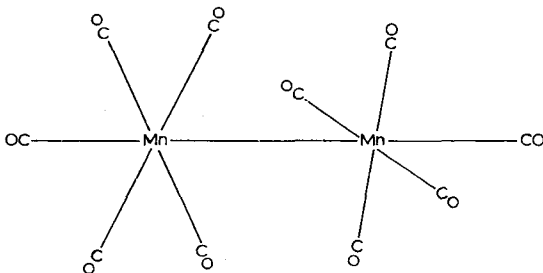


Fig. 225. Structure of  $\text{Mn}_2(\text{CO})_{10}$  molecule.

In osmium dodecacarbonyl,  $\text{Os}_3(\text{CO})_{12}$ , the osmium atoms are arranged at the corners of an equilateral triangle and there are six CO groups in the plane of the triangle and three others above and three below that plane (Fig. 226).

#### *The noble gas rule applied to polynuclear carbonyls*

By considering every carbonyl bridging bond and every metal-metal bond to represent the donation of one electron to the atom to which it is

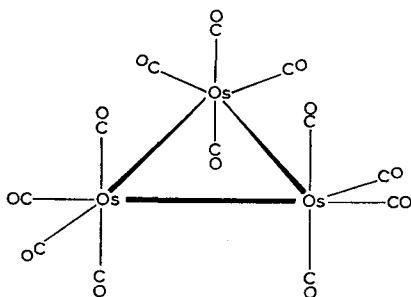


Fig. 226. Structure of  $\text{Os}_3(\text{CO})_{12}$  molecule.

attached, the rule can be extended to polynuclear carbonyls. Thus either of the iron atoms in  $\text{Fe}_2(\text{CO})_9$  has

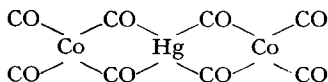
26	'iron' electrons.
6	'terminal CO' electrons.
3	'bridging CO' electrons.
1	'metal-metal bond' electron.
36	(the atomic number of Krypton).

There appear to be only a few exceptions to the rule.

### Derivatives of the metal carbonyls

#### *Salts of carbonylate anions*

Iron pentacarbonyl dissolves in aqueous alkali to give a yellow solution of sodium hydrogen iron carbonylate,  $\text{NaHFe}(\text{CO})_4$ . Other carbonylates can be made from metal carbonyls by treating them with aqueous or alcoholic alkalis, with amines, or with Lewis bases such as sulphoxides. The anions of these salts are usually oxidised by air. The sodium and potassium salts are water-soluble. Addition to their aqueous solutions of  $\text{Hg}^{2+}$  and  $\text{Cd}^{2+}$  ions precipitates the monomeric  $\text{Hg}[\text{Co}(\text{CO})_4]_2$  and  $\text{Cd}[\text{Co}(\text{CO})_4]_2$ . These compounds are soluble in organic solvents, are covalent in character, and have the structure:



It is of interest to note that in an isoelectronic, isostructural series made up of carbonylate and carbonyl ions, the C—O stretching frequencies rise by about  $100 \text{ cm}^{-1}$  for every unit increase of positive charge:



Species	$\text{Fe}(\text{CO})_4^{2-}$	$\text{Co}(\text{CO})_4^-$	$\text{Ni}(\text{CO})_4$
C—O frequency ( $\text{cm}^{-1}$ )	1786	1886	2057

This shows that back-donation from metal to carbon in these ions is strengthened as the species becomes more negative.

Polynuclear carbonylates have also been made from polynuclear carbonyls by the action of bases. The structures of these compounds are not necessarily related to those of the parent carbonyls. The  $\text{Fe}_2(\text{CO})_8^{2-}$  ion, for example, which is derived from an enneacarbonyl with bridging CO groups, has only terminal CO groups and there is a metal-metal bond. The six CO groups out of the axis of the molecule, which are staggered in relation to one another (Fig. 227), are in planes at  $90^\circ$  to the Fe—Fe bond.

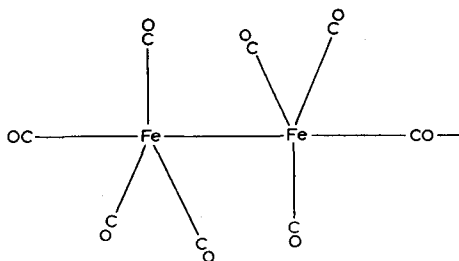


Fig. 227. Structure of  $\text{Fe}_2(\text{CO})_8^{2-}$  ion.

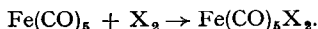
### *Carbonyl hydrides*

Acidification of aqueous or alcoholic  $\text{NaCo}(\text{CO})_4$  and  $\text{NaHFe}(\text{CO})_4$  in the absence of air gives, respectively, the thermally unstable yellow liquids  $\text{HCo}(\text{CO})_4$  and  $\text{H}_2\text{Fe}(\text{CO})_4$ . The colourless liquid  $\text{HMn}(\text{CO})_5$  can be made from  $\text{Mn}_2(\text{CO})_{10}$  and hydrogen under 200 atm. pressure. Electron diffraction shows the  $\text{Fe}(\text{CO})_4$  and  $\text{Co}(\text{CO})_4$  skeletons in these compounds to be slightly distorted from tetrahedral, but it has been established by means of n.m.r. spectra that the hydrogen atoms are not attached to the oxygen atoms and are only about 1.1–1.2 Å from the iron nucleus. The nature of the bonding is uncertain. In  $\text{HRe}(\text{CO})_5$  there is absorption in the infrared at  $1832 \text{ cm}^{-1}$ , a figure consistent with stretching frequencies found in known metal hydrides.

$\text{HCo}(\text{CO})_4$  is probably the principal catalytic agent in the oxo reaction mentioned on p. 263.

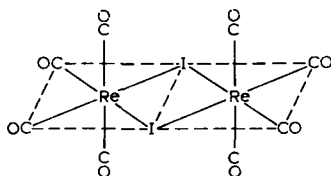
### *Carbonyl halides*

Iron pentacarbonyl forms unstable addition compounds with the halogens:



These lose carbon monoxide to give more stable substances of the formula  $\text{Fe}(\text{CO})_4\text{X}_2$ . The iodide,  $\text{Fe}(\text{CO})_4\text{I}_2$ , can even be sublimed in a vacuum without decomposition. Reduction of the iodide by hydrogen produces  $\text{Fe}(\text{CO})_2\text{I}_2$ ; this can also be made by the reaction between  $\text{Fe}(\text{CO})_5$  and  $\text{I}_2$  in boiling benzene. Both  $\text{Ni}(\text{CO})_4$  and  $\text{Co}_2(\text{CO})_8$  are decomposed by halogens and do not form carbonyl halides. There are carbonyl halides of ruthenium, rhodium, rhenium, osmium and iridium, and also of elements which do not form a simple carbonyl; examples are  $[\text{Pd}(\text{CO})\text{Cl}_2]_n$ ,  $[\text{Pt}(\text{CO})\text{X}_2]_n$  and  $\text{Cu}(\text{CO})\text{X}$  ( $\text{X} = \text{Cl}, \text{Br}$  or  $\text{I}$ ).

All the polynuclear carbonyl halides of which the structures are known are bridged not through carbonyl groups but through halogen atoms:



### Nitrosyl carbonyls

When CO is passed into a suspension of  $\text{Co}(\text{CN})_2$  in aqueous potassium hydroxide at  $0^\circ$ , a solution of  $\text{KCo}(\text{CO})_4$  results. Passing NO into this solution produces  $\text{Co}(\text{CO})_3\text{NO}$ , a volatile liquid with physical properties very similar to  $\text{Ni}(\text{CO})_4$ . Dry nitric oxide reacts with  $\text{Fe}_3(\text{CO})_{12}$  to give a mixture of  $\text{Fe}(\text{CO})_2(\text{NO})_2$  and  $\text{Fe}(\text{CO})_5$ .

The compounds  $\text{Mn}(\text{CO})(\text{NO})_3$ ,  $\text{Fe}(\text{CO})_2(\text{NO})_2$ ,  $\text{Co}(\text{CO})_3\text{NO}$  and  $\text{Ni}(\text{CO})_4$  are isoelectronic, since the NO molecule contains one more electron than CO. If the extra electron is imagined to be located in an MO which is close to the metal d-orbitals in energy, the structures approximate to the formal oxidation states  $\text{Mn}^{-\text{III}}(\text{CO})(\text{NO}^+)_3$ ,  $\text{Fe}^{-\text{II}}(\text{CO})_2(\text{NO}^+)_2$  and  $\text{Co}^{-\text{I}}(\text{CO})_3(\text{NO}^+)$ . This is, however, a highly artificial representation. There is undoubtedly strong back-donation to the  $\pi^*$  orbitals of the  $\text{NO}^+$ ; in evidence of this, the N—O stretching frequencies are in the range  $1600\text{--}1900\text{ cm}^{-1}$  compared with about  $2250\text{ cm}^{-1}$  for the  $\text{NO}^+$  in nitrosonium salts. Nevertheless, the four isoelectronic compounds above can all be considered to obey the noble-gas rule in a formal sense.

### Other derivatives

Electron-donor molecules can replace the CO groups in carbonyls. In this way neutral compounds and ions in great variety are obtainable: examples are  $\text{Fe}_2(\text{CO})_4\text{en}_3$ ,  $\text{Fe}(\text{CO})_3(\text{PPh}_3)_2$ ,  $\text{Mo}(\text{CO})_3(\text{AsCl}_3)_3$ ,  $[\text{HFe}(\text{CO})_3$

$(\text{PPh}_3)_2]^+$ ,  $[\text{Co}(\text{CO})_3\text{PPh}_3]^-$ . Complexes with  $\pi$ -bonding ligands such as cyclopentadiene are also common (p. 396).

#### FURTHER READING

- G. R. HENNIG, *Interstitial Compounds of Graphite* in F. A. COTTON (Ed.), *Progress in Inorganic Chemistry*, New York, Interscience Publishers, Vol. 1 (1959) 125.
- M. M. DUBININ, *The Porous Structure of Active Carbons*, Quart. Rev., IX (1955) 101.
- R. C. CROFT, *Lamellar Compounds of Graphite*, Quart. Rev., XIV (1960) 1.
- E. W. ABEL, *The Metal Carbonyls*, Quart. Rev., XVII (1963) 133.
- D. J. G. IVES, *Principles of the Extraction of Metals*, London, Royal Institute of Chemistry, Monograph for Teachers, No. 3 (1960).
- E. G. ROCHOW, *An Introduction to the Chemistry of the Silicones*, New York, 2nd Edn., Wiley, 1951.
- A. G. MACDIARMID, *Silanes and their Derivatives* in H. J. EMELÉUS AND A. G. SHARPE (Eds.), *Advances in Inorganic Chemistry and Radiochemistry*, New York, Academic Press, Vol. 3 (1961) 207.
- R. FESSENDEN AND J. S. FESSENDEN, *The Chemistry of Silicon-Nitrogen Compounds*, Chem. Rev., 61 (1961) 361.
- F. G. A. STONE AND D. SEYFERTH, *The Chemistry of Silicon involving probable use of d-type Orbitals*, J. Inorg. Nuclear Chem., 1 (1955) 112.
- T. K. BROTHERTON AND J. W. LYNN, *The Synthesis and Chemistry of Cyanogen*, Chem. Rev., 59 (1959) 841.
- U. WANNAGAT, *The Chemistry of Silicon-Nitrogen Compounds*, in H. J. EMELÉUS AND A. G. SHARPE (Eds.), *Advances in Inorganic Chemistry and Radiochemistry*, New York, Academic Press, Vol. 6 (1964) 225.
- J. J. ZUCKERMAN, *The Direct Synthesis of Organosilicon Compounds*, *ibid.*, 383.

## Organometallic Compounds

### Definition of 'organometallic'

The term organometallic is usually restricted to compounds in which a metal atom is bonded directly to a carbon atom of a hydrocarbon radical or molecule. In this context, however, the term metal is conventionally extended to include elements less electronegative than carbon, such as boron, arsenic and silicon. Thus trimethylboron,  $(\text{CH}_3)_3\text{B}$ , is classified as an organometallic compound. However, trimethyl orthoborate,  $\text{B}(\text{OCH}_3)_3$ , is not so classified because it does not contain a boron-carbon bond. Thus although a compound contains many hydrocarbon radicals it is not classified as organometallic when all the carbon atoms are linked to the metal through atoms such as oxygen, nitrogen and sulphur. But when even one of the carbon atoms is directly linked to metal, as in  $\text{CH}_3 \cdot \text{B}(\text{OCH}_3)_2$ , the compound is termed organometallic.

Moreover such compounds as carbides, cyanide complexes and carbonyls which of course contain metal-carbon bonds, are not generally considered as organometallic compounds. Many organometallic compounds of the transition metals can however be most easily prepared from carbonyls.

It is sometimes convenient to divide organometallic compounds into simple and mixed. A simple organometallic compound is one, such as  $(\text{C}_2\text{H}_5)_4\text{Pb}$  or  $(\text{CH}_3)_3\text{SnH}$ , which has only hydrocarbon radicals or hydrogen atoms attached to the metal. Simple organometallic compounds can be subdivided into the symmetrical, like  $(\text{C}_2\text{H}_5)_2\text{Hg}$ , and the unsymmetrical, like  $\text{C}_2\text{H}_5\text{HgC}_4\text{H}_9$ . A mixed organometallic compound, such as  $\text{C}_6\text{H}_5\text{MgBr}$ ,  $(\text{C}_4\text{H}_9)_2\text{SnCl}_2$  or  $\text{C}_6\text{H}_5\text{SbO}(\text{OH})_2$ , has groups other than hydrocarbon radicals and hydrogen atoms attached directly to the metal.

### Types of metal-carbon bonds

In dealing with their structure and reactivity, organometallic compounds are best considered in relation to the character of the metal-carbon bond. Of these there are three types: ionic, covalent  $\sigma$ -bond and covalent  $\pi$ -bond.

*(i) Ionic organometallic compounds*

In these compounds the hydrocarbon residue exists as a carbanion which, being negatively charged, is attracted to the metal cation by non-directional, electrostatic forces. The organosodium compounds are typical of the ionic class; most of them are colourless, salt-like solids, which are electrolytes when fused and are insoluble in non-polar solvents. Extra thermal stability is conferred on these compounds when the carbanion contains either an acetylenic triple bond, as in  $R \cdot C \equiv C^-$ , in which the  $sp$ -hybridised carbon atom is strongly electronegative, or a conjugated system, as in  $CH_2=CH-CH_2^-$ , in which a non-localised  $\pi$ -bond can stabilise the ion.

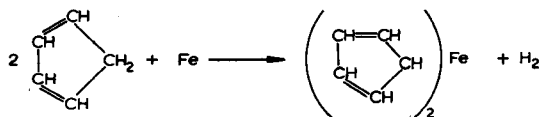
Organometallic compounds show a gradual transition from ionic to  $\sigma$ -bonded covalent forms. Thus the alkyls of sodium are more ionic and less covalent in character than those of lithium. Methyl-lithium and ethyl-lithium are colourless solids and propyl-lithium and butyl-lithium are liquids; dimethylberyllium is a solid and diethylberyllium a liquid. In straight-chain alkyl compounds of metals the carbon-metal bond becomes increasingly covalent as the carbon chain is lengthened.

*(ii)  $\sigma$ -bonded covalent organometallic compounds*

The majority of organometallic compounds of non-transition elements are covalent compounds with  $M-C$   $\sigma$ -bonds. The polarity of the bond depends not only on the difference in electronegativity between  $M$  and  $C$ , as expressed in the electronegativity scale (p. 127), but also on the metal orbitals which are available, the steric requirements, and the polarisability of the electron cloud.

*(iii)  $\pi$ -bonded organometallic compounds of transition metals*

Until 1951, it appeared that organic derivatives of transition metals were generally inaccessible, but in that year two groups of workers made an entirely new type of organometallic compound; it was bis(cyclopentadienyl) iron,  $(C_5H_5)_2Fe$ . This compound was produced either by the action of cyclopentadienylmagnesium bromide on  $FeCl_3$  in ether, or by passing cyclopentadiene vapour over finely-divided iron at  $300^\circ$ :



It has a 'sandwich' structure in which the iron atom lies between two  $C_5H_5$  rings (Fig. 228).

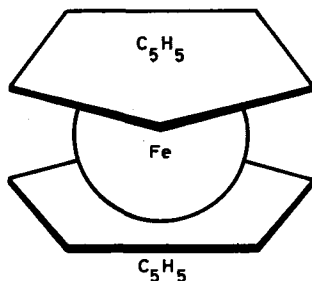


Fig. 228. 'Sandwich' structure of the ferrocene molecule.

Bonding results from the overlap of  $\pi$ -electrons of the cyclopentadienyl rings with unfilled d-orbitals of the metal, and can therefore be called  $\pi$ -bonding.

A large number of  $\pi$ -bonded organometallic compounds have now been made. 'Sandwich' compounds have been described with benzene, thiophene, indene and other similar systems in addition to those with cyclopentadiene. In a compound such as dibenzenechromium (Fig. 229).

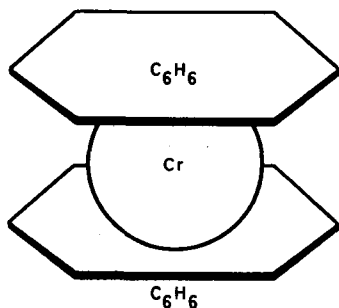


Fig. 229. Dibenzenechromium 'sandwich' molecule.

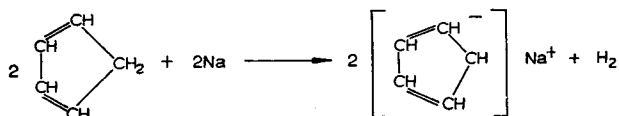
it should be noted that the metal is  $\pi$ -bonded to benzene molecules, themselves, not to phenyl radicals. The formation of compounds by the coordination of transition metals by means of the  $\pi$ -electrons of olefins such as ethylene in Zeise's salt (p. 402), of dienes such as butadiene in butadiene-iron tricarbonyl, and of aromatic molecules, is now known to be very common.

### Influence of the metal on bonding

The effect of the metal itself on the nature of the bonding in organo-

metallic compounds may be brought into rational order by considering some different types of cyclopentadienyl derivatives.

(i) To consider first the ionic type which is exemplified by cyclopentadienylsodium. This is made by the reaction of cyclopentadiene with the metal in a solvent such as benzene or liquid ammonia:



It is an essentially ionic compound, insoluble in non-polar solvents, and hydrolysed by water. The solid contains  $\text{Na}^+$  ions equidistant from the five C atoms of the  $\text{C}_5\text{H}_5^-$  ion (Fig. 230).

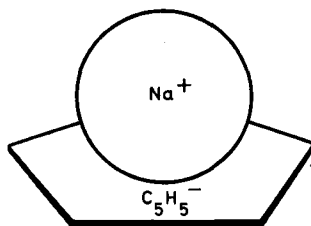


Fig. 230. Arrangement of sodium ion and cyclopentadienide ion in solid sodium cyclopentadienide.

Cyclopentadiene compounds of this type, in which the ring-to-metal bonding is effectively ionic, are formed by other alkali and alkaline-earth metals. They are often called cyclopentadienides to stress the anionic character of the  $\text{C}_5\text{H}_5^-$  ring.

(ii) A second distinct type of cyclopentadienyl compound is formed by non-transition elements such as silicon. In these compounds the bonding consists of localised carbon-metal  $\sigma$ -bonding formed by sharing of an electron-pair (Fig. 231).

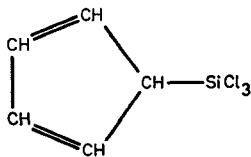


Fig. 231. Sigma-bonded structure of trichlorocyclopentadienylsilicon.

In such compounds the diene character of the cyclopentadiene is preserved; thus they undergo the Diels–Alder reaction with maleic anhydride to give stable adducts.

Among the cyclopentadienyl compounds of the congeners of silicon are  $(C_5H_5)_2Sn$  and  $(C_5H_5)_2Pb$ . These diamagnetic compounds are monomeric in benzene and have rather large dipole moments. Their infrared and n.m.r. spectra suggest that they have 'sandwich' structures in which the planes of the rings are not parallel but inclined towards each other. The bonding is therefore neither completely localised as in the silicon compounds nor completely delocalised as in  $(C_5H_5)_2Fe$ .

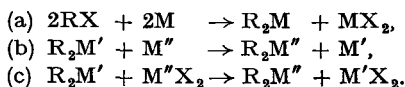
(iii) The third distinct type of bonding in cyclopentadienyl derivatives is the completely delocalised  $\pi$ -bonding already described. Nearly all the cyclopentadienyl derivatives of transition metals are of this type, but there are some exceptions. For example,  $(C_5H_5)_2Mn$  is shown by its infrared spectrum and its magnetic properties to be essentially ionic,  $[C_5H_5^-]_2Mn^{2+}$ . This anomaly may be due to the extra stability conferred by the half-filled d-shell in  $Mn^{2+}$  which is a ( $d^5$ ) ion.

#### ORGANOMETALLIC COMPOUNDS OF NON-TRANSITION ELEMENTS

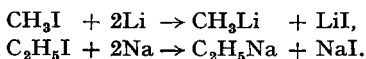
The differences between the  $\sigma$ -bonded compounds of the non-transitional elements and the generally  $\pi$ -bonded organometallic derivatives of transition elements are considerable. For this reason we shall consider the two types separately.

#### Methods of preparation

(I) There are three preparative methods of wide application. These can be formulated (for metals in the +2 state) as

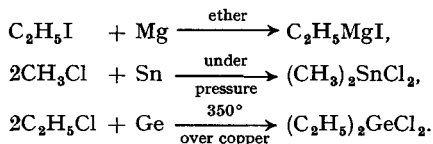


(i) Examples of (a), which is usually carried out in inert solvents such as ether, are

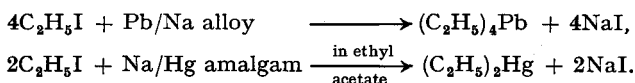


A slight variation of the same reaction gives rise to compounds such as the Grignard reagents and the dialkyltin dihalides:

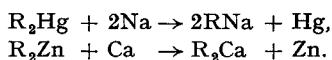




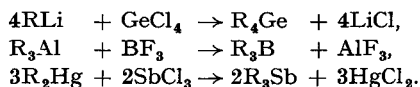
The metal is sometimes more reactive when in the form of an alloy or an amalgam.



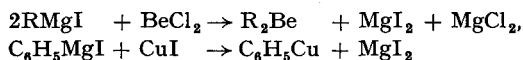
(ii) Examples of the metal-exchange reactions (b) are



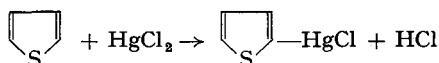
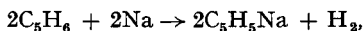
(iii) Examples of alkyl-halogen exchange reactions (c) are



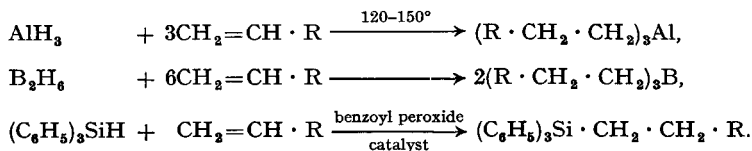
The Grignard reagents form an important group of reagents suitable for similar exchange processes:



(II) An interesting type of preparative reaction, of less general application, is called *metallation*; it consists of a hydrogen-metal exchange:

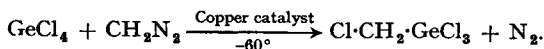


(III) The use of  $\alpha$ -olefins as synthetic reagents forms the basis of a newer method of making covalent organometallic compounds, particularly of aluminium, boron and silicon.



A similar sort of reaction, termed *hydroboration*, is effected by adding an olefin to a mixture of  $\text{NaBH}_4$  and  $\text{AlCl}_3$  in diglyme; this gives good yields

of trialkylboranes. *Methylenation* by diazomethane is yet another way of inserting carbon atoms next to the metal:



(IV) Electrolytic methods of preparation are gaining in importance. Industrially the most widely-used of all organometallic compounds,  $\text{Et}_4\text{Pb}$ , can be made by the electrolysis of  $\text{NaAlF}_6$  between an aluminium cathode and a lead anode.

### Relative reactivity of metal-carbon bonds

The reactivity of a compound refers to the rate at which it reacts with another substance. In general the metal is more important than the organic moiety in determining the reactivity of organometallic compounds; the lower the ionisation energy of the metal the more reactive the compound. The reactivity in which we are interested is not necessarily related to thermal stability or a tendency to inflame in air. Thus trimethylboron is very inflammable, that is very readily oxidised, but not otherwise very reactive; conversely, an alkyl of gold is thermally extremely unstable but not particularly reactive.

#### Orders of reactivity

The reactivity of organometallic compounds is determined by their rates of addition to unsaturated bonds such as  $\text{>C=C<}$ ,  $\text{>C=O}$  and  $\text{-C}\equiv\text{N}$ . For metals of the first three A sub-groups, this reactivity increases down the group:



But for the B sub-groups reactivity decreases in the same direction:



Across the first three groups of a period reactivity decreases:



The least reactive compound of an A sub-group is more reactive than the most reactive compound of the corresponding B sub-group:

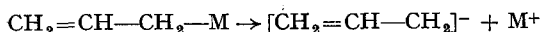


In Groups V, VI and VIII the reactivities decrease down the A sub-groups and increase down the B sub-groups. Across a period there is an increase in reactivity



This regularity is not found in Group IV, where the order of reactivity is rather variable.

It is difficult to generalise on the effect of the organic group on reactivity for a given metal, but a radical or anion which can be stabilised by  $\pi$ -electron delocalisation is particularly easily formed in a bond-cleavage process:



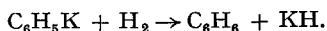
For compounds of the same metal, an unsymmetrical compound  $RMR'$  is usually more reactive than a symmetrical compound  $R_2M$ .

Solvents are often of importance in determining reactivity, because solvated species are frequently formed and it is their reactivities which are displayed.

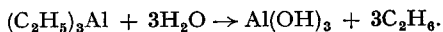
### Typical reactions of organometallic compounds of the non-transition elements

#### (I) With inorganic reagents

- (i) Many ionic and  $\sigma$ -bonded organometallic compounds are oxidised spontaneously by oxygen or air.
- (ii) Cleavage by hydrogenation often occurs even at room temperature and in the absence of a catalyst:

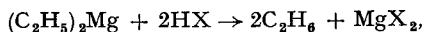


- (iii) Many are quickly hydrolysed by water:

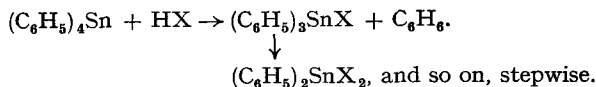


But some, such as tetra-alkylsilicons, hydrolyse slowly.

- (iv) Acids, such as hydrogen halides in benzene, react to give hydrocarbons and metals salts:



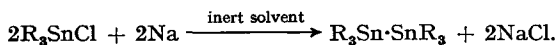
But sometimes the reactions are slow:



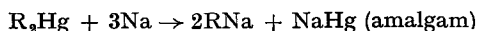
- (v) Halogens such as iodine usually cleave the  $M-C$  bonds:



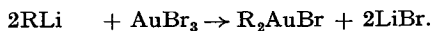
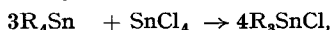
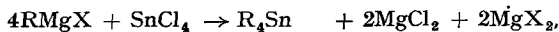
- (vi) Active metals usually extract halogens:



Or they may replace less active metals:

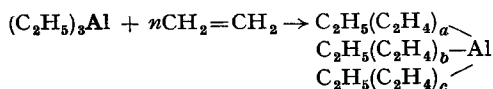
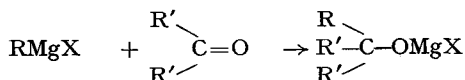


(vii) Metal halides react in the various ways shown:



(II) *With organic reagents*

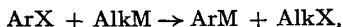
(i) Most  $\sigma$ -bonded organometallic compounds form addition compounds with unsaturated organic compounds:



$$[a + b + c = n]$$

The last reaction is used to produce polyethylenes which can have molecular weights up to three million. Transition metal halides such as  $TiCl_4$  catalyse the process (p. 405).

(ii) Alkyls of metals usually react with aryl halides:



the halogen being more cationic in the aryl halide than in the alkyl halide.

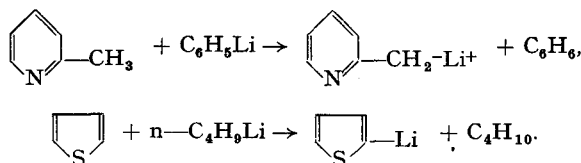
(iii) Many organometallic compounds behave as Lewis acids and form adducts with amines. The Lewis acid strengths, based on the strengths of the metal-nitrogen bonds, increase along the series:



But they first rise and then fall again down a group:



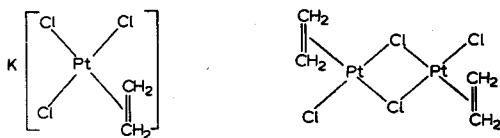
(iv) Organic compounds containing a labile hydrogen atom which is bound directly to a carbon atom are metallated by some organometallic compounds:



## ORGANOMETALLIC COMPOUNDS OF THE TRANSITION ELEMENTS

(i)  $\pi$ -Bonded olefin and diene compounds of metals

Two compounds made by Zeise in 1827 from ethylene and a chloroplatinate have been shown to have the structures:



There is a planar, approximately square, bond arrangement round the platinum atoms, but it is the bonding from the metal atom to the perpendicular carbon-carbon bond which is of greatest interest. The highest-energy electrons of ethylene lie in the  $\pi$ -bond; MO's of only slightly higher energy are the unfilled, antibonding  $\pi^*$  (Fig. 232a). Bonding with the metal can be described as due to combination of a  $\pi$  orbital with a hybrid AO on the metal atom, the system being stabilised by back-donation from a metal d orbital of correct symmetry (Fig. 232b).

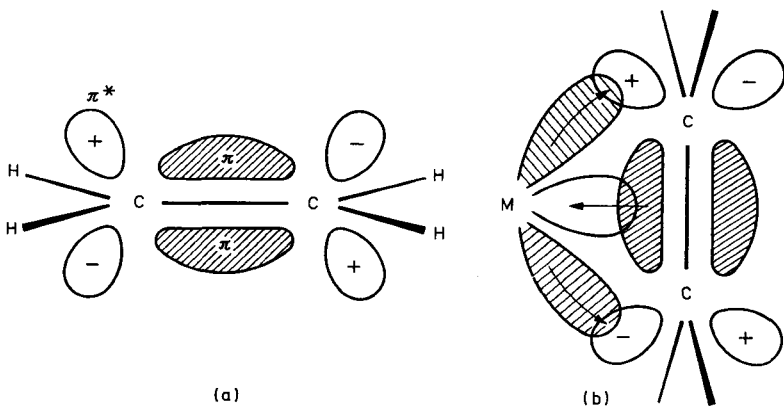
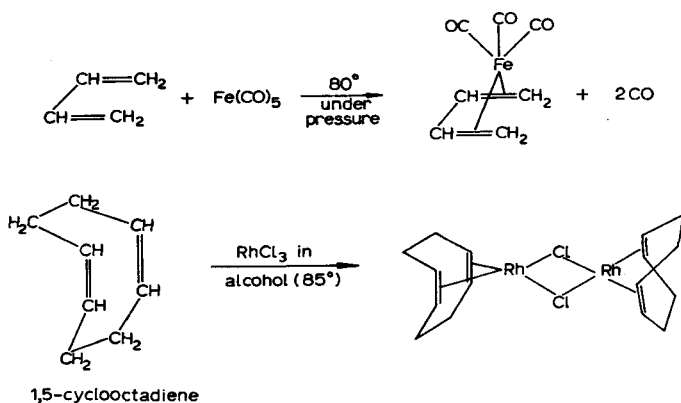


Fig. 232 (a). Ethylene molecule, with filled  $\pi$  orbitals and unfilled  $\pi^*$  orbitals. (b) Bonding of ethylene to a transition-metal ion by overlap of filled  $\pi$  orbital with metal d orbital and by back-donation from the metal to the unfilled  $\pi^*$  orbital.

Transition-metal organometallic compounds containing similar  $\pi$ -bonds can be made from a variety of olefins and dienes, usually by their direct action on a metal halide or a complex such as a carbonyl:



It is of interest that 1,3 cyclooctadiene gives the same compound. The 1,3 diene is isomerised to the 1,5 in about 99% yield. Iron pentacarbonyl, however, converts the 1,5 diene to the 1,3 without there being any evidence of the formation of an organometallic intermediate.

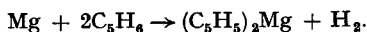
#### (ii) $\pi$ -Bonded aromatic compounds of metals

Interest in  $\pi$ -cyclopentadienyls following the preparation of ferrocene in 1951 has resulted in an extensive study of them and their derivatives. As a result, cyclopentadiene derivatives of more than fifty metals have been made; in the majority of them the metal is bound to the ring by  $\pi$ -bonding.

### Methods of preparing $\pi$ -cyclopentadienyls and similar compounds

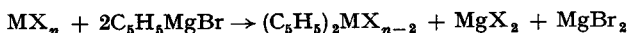
#### *Pentadienyls*

(i) In a few instances cyclopentadiene vapour reacts directly with the finely divided metal:

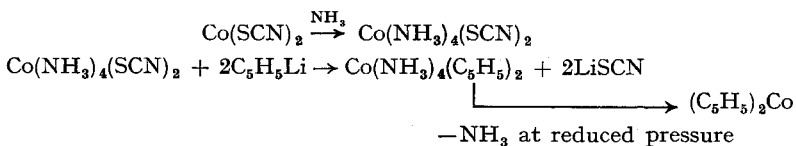


Similarly prepared are  $\text{C}_5\text{H}_5\text{Tl}$ ,  $\text{C}_5\text{H}_5\text{In}$  and ferrocene.

(ii) A widely applicable method is the treatment of a salt of the metal with  $\text{C}_5\text{H}_5\text{MgBr}$ :



(iii) Alkali-metal cyclopentadienides react with salts in solvents such as liquid ammonia:

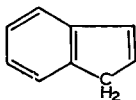


(iv) Metal carbonyls often react with a cyclopentadiene to give either  $\pi$ -cyclopentadienyls or  $\pi$ -cyclopentadienyl carbonyls. Examples of the latter are  $\text{C}_5\text{H}_5\text{V}(\text{CO})_4$ ,  $[\text{C}_5\text{H}_5\text{Cr}(\text{CO})_3]_2$ ,  $\text{C}_5\text{H}_5\text{Co}(\text{CO})_2$  and  $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$ . In these compounds the noble-gas rule is nearly always obeyed. If the metal is assumed to be bonded to a  $\text{C}_5\text{H}_5$  by all five  $\pi$ -electrons, to each carbonyl group by two electrons and to the other metal when the compound is a dimer by an electron-pair, then the total number of electrons surrounding the metal atom is that possessed by the next noble gas.

(v)  $\pi$ -Pentadienyl carbonyls such as  $[\text{C}_5\text{H}_5\text{Os}(\text{CO})_2]_2$  and  $[\text{C}_5\text{H}_5\text{Ru}(\text{CO})_2]_2$  have been prepared by treating an appropriate carbonyl halide with  $\text{C}_5\text{H}_5\text{Na}$  in ether.

### Indenyls

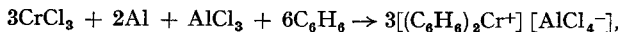
Success in the preparation of  $\pi$ -cyclopentadienyls prompted a search for similar compounds. Indene:



which contains the same type of five-membered ring as cyclopentadiene, forms sandwich compounds. There are  $(\text{C}_9\text{H}_7)_2\text{Co}$ , made from  $\text{Co}(\text{SCN})_2$  and  $\text{C}_9\text{H}_7\text{K}$  in liquid ammonia, and  $(\text{C}_9\text{H}_7)_2\text{Fe}$ , made from  $\text{FeCl}_3$  and  $\text{C}_9\text{H}_7\text{Li}$ .

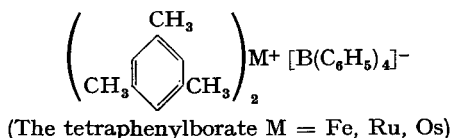
### $\pi$ -Compounds of benzene and their derivatives

Dibenzenechromium,  $(\text{C}_6\text{H}_6)_2\text{Cr}$ , is a dark-brown, crystalline solid, m.p.  $285^\circ$ , made by first refluxing  $\text{CrCl}_3$  with benzene, aluminium powder and aluminium chloride in the presence of a little mesitylene:



then converting the chloroaluminate to the perchlorate, and, finally,

reducing the  $(C_6H_6)_2Cr^+$  ion to  $(C_6H_6)_2Cr$  with a dithionate. This, and other dibenzene sandwich compounds, such as  $(C_6H_6)_2Mo$  and  $(C_6H_6)_2W$ , are much less thermally stable than the  $\pi$ -cyclopentadienyls. Iron and its congeners form moderately stable  $\pi$ -bonded compounds with mesitylene:



A new synthetic method for bisarene- $\pi$ -compounds uses a mixture of  $Et_3Al$  with a halide of the transition metal and the aromatic compound in n-heptane at about  $130^\circ$ . The mixture is digested with methanol, hydrolysed with water, and the cation is isolated as the tetraphenylborate. By this method *trans*-stilbene and  $CrCl_3$  have given the first bridged bisarene- $\pi$ -compound (Fig. 233).

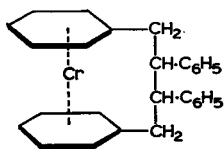


Fig. 233. Bridged  $\pi$  compound formed from *trans*-stilbene and  $CrCl_3$ .

### Chemistry of organometallic compounds

The chemistry of the  $\pi$ -organometallic compounds is very extensive. Not only are they capable of forming many inorganic derivatives and salts, but the more stable compounds like ferrocene have a considerable organic chemistry of their own; this is because the rings are capable of aromatic substitution.

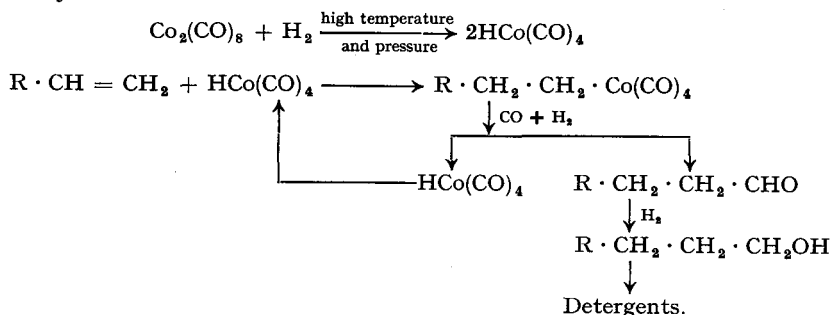
### Uses of organometallic compounds

The most important compound industrially is tetraethyl lead; more than 30 thousand tons are made every year in Britain alone as an additive for motor spirit. Several organometallic compounds are used as polymerisation catalysts; butylsodium for the conversion of butadiene to buna rubber, alkyls of lithium for the production of elastomers from alkenes and dienes. Triethylaluminium, with  $TiCl_4$ , acts as a Ziegler-Natta catalyst for the polymerisation of ethylene.



A  $\pi$ -complex of ethylene with  $\text{PdCl}_2$  is hydrolysed by water to acetaldehyde, palladium metal and  $\text{HCl}$ . However, in the presence of  $\text{CuCl}_2$  the palladium remains as palladium chloride and the copper is precipitated as  $\text{CuCl}$ . This is afterwards converted back again to  $\text{CuCl}_2$ . This reaction forms the basis of a method for converting ethylene to acetaldehyde and hence to vinyl acetate.

The conversion of alkenes into alcohols in the oxo- or hydroformylation reaction, by the action of hydrogen and carbon monoxide in the presence of  $\text{Co}_2(\text{CO})_8$ , probably proceeds through the formation of an alkylcobalt carbonyl:



#### FURTHER READING

- G. E. COATES, *Organometallic Compounds*, 3rd. Edn., London, Methuen, 1965.
- M. D. RAUSCH, *Cyclopentadienyl Compounds of Metals and Metalloids*, J. Chem. Education, 37 (1960) 568.
- H. GILMAN, *Organometallic Compounds*, in *Organic Chemistry*, Vol. I, 2nd. Edn., 1943.
- G. WILKINSON AND F. A. COTTON, *Cyclopentadienyl and Arene Metal Compounds* in F. A. COTTON (Ed.), *Progress in Inorganic Chemistry*, Vol. I, (1959) 1.
- E. O. FISCHER, *Co-ordination Compounds of Unsaturated Hydrocarbons with Metals* in *The International Conference on Co-ordination Chemistry*, Chemical Society Special Publication, No. 13, 1959.
- P. L. PAUSON, *Ferrocene and Related Compounds*, *Quart. Rev.*, 9 (1955) 391.
- E. G. ROCHOW, *Organometallic Chemistry*, London, Chapman and Hall, 1964.
- E. O. FISCHER AND H. WERNER, *Metal  $\pi$ -Complexes: Vol. 1, Complexes with Di- and Oligo-olefinic Ligands*, Amsterdam, Elsevier, 1966; Vol. 2, *Complexes with Mono-olefinic Ligands*, in preparation.
- D. SEYFERTH AND R. B. KING, *Annual Surveys of Organometallic Chemistry*, Amsterdam, Elsevier (Vol. 1 covering the year 1964; Vol. 2 covering the year 1965, etc.).
- D. SEYFERTH (Co-ordinating Editor) *et al.*, *Organometallic Chemistry Reviews*, Amsterdam, Elsevier, Vol. 1 (1966), Vol. 2 (1967), etc.

Chapter 21

## Germanium, Tin and Lead

### GROUP IVB

The atoms of the Gp. IVB elements resemble those of carbon and silicon in having the  $ns^2np^2$  electron configuration and  $^3P$  ground state, and in forming the tetrahedral bonds associated with  $sp^3$  hybridisation. But downwards there is an increasing tendency to form instead an 'inert-pair' ion; and, in its most stable salts, lead preserves an  $ns^2$  'core', appearing as  $Pb^{2+}$ . Since the atoms have rather low electronegativities, the bonds in many of their compounds are fairly strongly ionic. The usual practice is to regard the metals formally as ions, with charge number +4 or (for Pb) +2, and to assign ionic radii (as distinct from the atomic or 'metallic' radii) on this basis.

TABLE 69  
ATOMIC PROPERTIES OF GROUP IVB ELEMENTS

	<i>Ge</i>	<i>Sn</i>	<i>Pb</i>
Atomic number	32	50	82
Electron configuration	$4s^2 4p^2$	$5s^2 5p^2$	$6s^2 6p^2$
Covalent radius (Å)	1.22	1.41	1.47
Ionic radius, $M^{2+}$ (Å)			1.20
Ionic radius, $M^{4+}$ (Å)	0.53	0.71	0.84
Metallic radius (Å)	1.37	1.62	1.75

The  $Pb^{2+}$  ion is recognisable in  $PbS$ , which has the typical rock salt structure, and in the solid  $PbF_2$  (m.p.  $818^\circ$ ). But  $Sn^{2+}$  is not an apt description of tin in its bivalent compounds, these being predominantly covalent. The ionisation energies, the electrode potentials  $M^{2+}/M$ , and the electronegativities of the elements are shown in Table 70.

The first ionisation energies of Sn and Pb may be contrasted with those of Cd (8.88) and Hg (10.43), atoms which have comparable radii ( $\sim 1.48$ ) but also have the closed shell structure  $ns^2$ . Their similar electrode potentials indicate similar free energies (and hence, roughly, heats) of hydration for

TABLE 70  
IONISATION ENERGIES, ELECTRODE POTENTIALS AND  
ELECTRONEGATIVITIES OF GROUP IVB ELEMENTS

	<i>Ge</i>	<i>Sn</i>	<i>Pb</i>
Ionisation energy 1 (eV)	8.13	7.32	7.41
"    "    2 (eV)	15.86	14.5	14.96
$E^\circ, M^{2+}/M$ (V)	0.0	-0.136	-0.126
Electronegativity (Allred-Rochow scale)	2.02	1.72	1.55

the  $M^{2+}$  ions. The electrode potentials for  $M^{4+}/M^{2+}$  are, however, very different:

$$E^\circ, Pb^{4+}/Pb^{2+} = 1.5 \text{ V.} \quad E^\circ, Sn^{4+}/Sn^{2+} = 0.15 \text{ V.}$$

Consequently, lead(IV) compounds in acid solution are much stronger oxidising agents than tin(IV) compounds.

The free energies, relative to the element, of the common oxidation states in solution at  $pH = 0$  are shown graphically in Fig. 234.

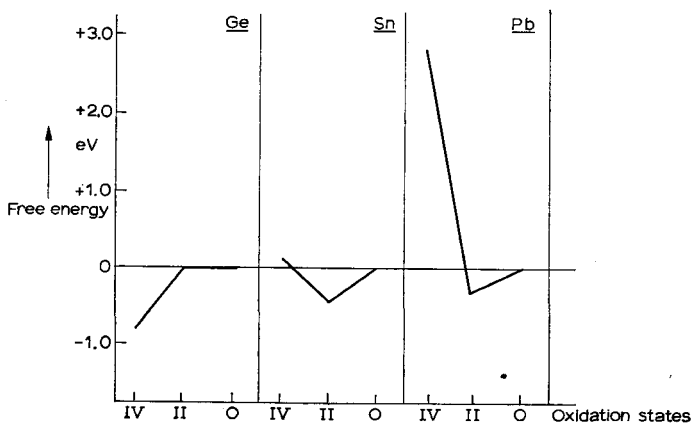


Fig. 234. Free energies of oxidation states of Ge, Sn and Pb relative to the element at  $pH = 0$ .

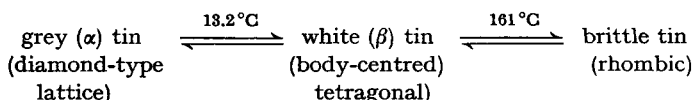
The bipoisitive state of germanium is unstable, tending to disproportionation:



But the bipoisitive  $Sn^{II}$  and  $Pb^{II}$  are both quite stable in this respect.

### Properties of the elements

The elements themselves show a marked transition from the rather non-metallic germanium to the distinctly metallic lead. Germanium has a diamond-type lattice and a m.p. intermediate between the very high values of carbon and silicon and the low ones of tin and lead. Tin exists in three solid forms:



Lead, however, has only the characteristically metallic c.c.p. form. Both tin and lead resemble gallium and indium in their long temperature ranges of liquidity, respectively 2128 and 1428 degrees.

TABLE 71  
PROPERTIES OF GROUP IVB ELEMENTS

	<i>Ge</i>	<i>Sn</i>	<i>Pb</i>
Density (g/cc)	5.36	5.77 ( $\alpha$ ) 7.29 ( $\beta$ )	11.34
Atomic volume	13.55	16.23 ( $\beta$ )	18.27
M.p. ( $^\circ\text{C}$ )	959	232	327
B.p. ( $^\circ\text{C}$ )	2700	2360	1755

Germanium has remarkable electrical properties. In the purest form it has a specific resistance, at room temperature, of about 50 ohm  $\text{cm}^{-1}$ . But when the temperature is raised increasing numbers of electrons are excited and pass from a filled energy band, over a narrow energy gap, into an empty 'conduction band' and the resistance falls. The metal is an 'intrinsic semiconductor'. It also forms 'impurity' semiconductors. One part per million of a Group III or Group V metal can reduce the specific resistance by a factor of 50 or more. Antimony, for instance, with its 5 valence electrons, when incorporated in the lattice with 4 co-ordination, *donates* an electron to the germanium conduction band and provides *negative* current carriers. The addition produces an 'N type' semiconductor. A Group III impurity such as Al produces a 'P type' semiconductor, the more electronegative atoms *accepting* electrons from the filled band and leaving 'holes' which behave as *positive* current carriers.

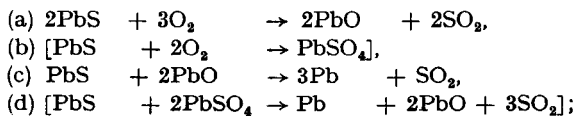
### Preparation of the elements

In Britain, germanium is recovered principally from flue dusts and coal ash. The only ore used commercially is germanite, (Cu, Ge, Fe, Zn, Ga) (S, As), containing about 6% Ge. When these substances are strongly heated with HCl the chloride,  $\text{GeCl}_4$ , distils off. It is hydrolysed to  $\text{GeO}_2$ , which is dried and reduced by hydrogen, carbon or a mixture of C and KCN under a molten salt flux. The element is silvery-white, hard, brittle and without allotropes.

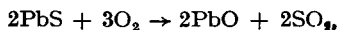
Very pure germanium is made by zone refining, usually achieved by slowly traversing a rod of the solid element with a molten zone by means of a moving radio-frequency heater. Impurities are thus concentrated in a short section at one end of the bar, which is discarded. The success of the process depends on the difference between the solid and liquid solubilities of the impurity elements present in the germanium at the point of solidification.

Tin ( $4 \times 10^{-3}\%$  of the earth's crust) is remarkable for its three allotropes and its numerous stable isotopes; of these there are ten, ranging in mass from 112 to 124 (p. 12). The only important ore is cassiterite,  $\text{SnO}_2$ . When the ore is roasted, the impurities sulphur and arsenic are oxidised to  $\text{SO}_2$  and  $\text{As}_2\text{O}_3$  respectively; the latter sublimes into cooled chambers and is a source of arsenic. The residual  $\text{SnO}_2$  is reduced with carbon (p. 372) in a blast or reverberatory furnace, and the metal is tapped off. Its principal use is in the manufacture of tinfoil, but the alloys with copper (bronzes), with lead (solders) and with lead and antimony (type metals) are important. The metal, ordinarily in its tetragonal form, is silvery, with a slight blue tinge, soft and malleable. Grey or  $\alpha$ -tin, stable below  $13.2^\circ$ , has a diamond-like structure and is brittle. The change from white to grey, which is accompanied by a fall in density, is slow above  $-50^\circ$  unless some grey tin is present to catalyse the change. Above  $161^\circ$ ,  $\gamma$ -tin, a more brittle metallic modification, is stable.

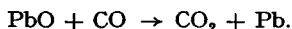
Lead ( $2 \times 10^{-4}\%$  of the earth's crust) occurs principally as galena,  $\text{PbS}$ , and cerussite,  $\text{PbCO}_3$ . The metal is obtained by ore-hearth smelting in which furnace conditions are controlled so that (a) in which about 2/3 of the sulphide reacts is followed by (c). Reactions (b) and (d) play a minor part.



Alternatively an oxidising roast may be used:



followed by blast furnace smelting (p. 693):



A later method of extraction is by the electrolysis of PbS dissolved in molten  $\text{PbCl}_2$ ; Pb and S are liberated at cathode and anode respectively.

Lead is without allotropes and the pure metal is very soft; the hardness is increased by the presence of Sb, Cu and the other elements. The resistance of lead to atmospheric corrosion and to attack by acids leads to its employment in chemical plant and for pipes and cable sheathing. The presence of 0.050–0.065% of tellurium improves the properties desirable for these purposes, such as the grain-size, hardness, tensile strength and corrosion resistance. Alloyed with a little Sb, it is used in large quantities for the electrode grids in lead-acid storage batteries.

Silver occurs in lead ores and appears in the metal from the smelter; its removal and recovery from crude lead is usually commercially worthwhile. Parkes' process, used for this purpose, is based on the low solubility of zinc in molten lead and the very high distribution coefficient for silver between the zinc and lead layers. After stirring zinc into the molten lead, the Zn–Ag alloy which freezes and floats to the top when the molten metal cools is skimmed off and processed for the recovery of silver.

### Reactions of the metals

The principal reactions of germanium and tin are shown in Fig. 235 and involve the elements in their quadrivalent states.

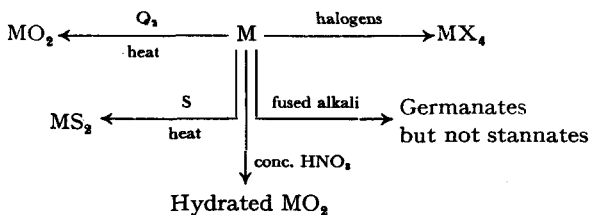


Fig. 235. Outline chemistry of Ge and Sn (M).

There are compounds of bivalent germanium such as  $\text{GeCl}_2$ ; they suffer disproportionation when heated and are readily oxidised to the quadrivalent state.

However, lead behaves differently from germanium and tin because its 6s electrons have little tendency to participate in  $\text{sp}^3$  hybridisation and the quadrivalent state is thermally unstable except with ligands of very high electronegativity. Hence the element usually features in its +2 oxidation state (Fig. 236).

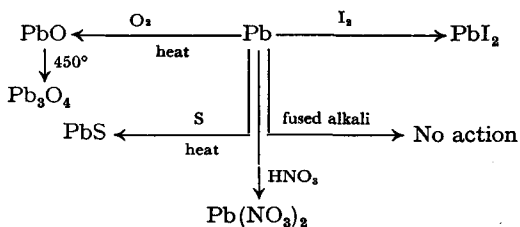
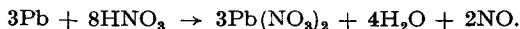


Fig. 236. Outline chemistry of Pb.

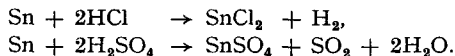
The three elements are rather unreactive towards acids. Germanium is not attacked by HCl or HF. Both Ge and Sn are oxidised by concentrated  $HNO_3$  to the hydrated dioxides:



In contrast, lead is dissolved, forming the nitrate:



The high hydrogen overvoltage at tin is responsible for the metal's lack of reactivity towards cold dilute acids. However, on heating, concentrated HCl and  $H_2SO_4$  both react:



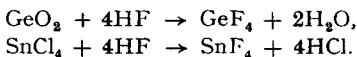
The action of these acids on lead is limited by the low solubilities of  $PbCl_2$  and  $PbSO_4$  which form coatings on the metal; but on heating both acids penetrate the coatings and dissolve the metal. Some  $H_2$  is obtained, as well as  $SO_2$ , from concentrated  $H_2SO_4$ .

## Halides

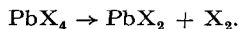
### Tetrahalides

The physical properties of the tetrahalides, except those of  $SnF_4$  and  $PbF_4$ , correspond to those of the covalent halides of carbon and silicon.  $GeF_4$  is a gas similar to  $SiF_4$ , the tetrachlorides of the three elements and the bromides of germanium and tin are liquids, and  $GeI_4$  and  $SnI_4$  solids of low m.p. The compounds  $SnF_4$ , which sublimes at  $705^\circ$ , and  $PbF_4$ , which melts at  $600^\circ$ , are both more ionic in character than the other tetrahalides.

The tetrahalides of Ge and Sn are usually made by the action of the halogen itself on the heated element; the fluorides are obtained by the reactions:



The tetrahalides  $\text{PbF}_4$  and  $\text{PbCl}_4$  result from oxidising the dihalide with the corresponding halogen, the latter at a moderate temperature because of the instability of  $\text{PbCl}_4$ . Neither bromine nor iodine is sufficiently strongly electron-accepting to withdraw electrons from the  $6s^2$  shell of  $\text{Pb}^{2+}$ ; hence the absence of these tetrahalides. And  $\text{PbF}_4$  and  $\text{PbCl}_4$  dissociate on warming:



Lead tetrafluoride is consequently a good fluorinating agent.

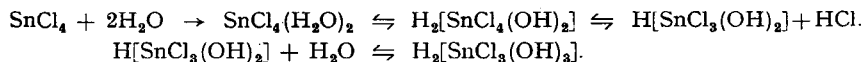
The known tetrahalides with their physical characteristics are set out in Table 72.

TABLE 72  
TETRAHALIDES OF GERMANIUM, TIN AND LEAD

<i>Halides</i>	<i>Ge</i>	<i>Sn</i>	<i>Pb</i>
Tetrafluorides	Colourless gas subl. p. $-37^\circ$	Colourless solid subl. p. $705^\circ$	Pale-yellow crystals m.p. $600^\circ$
Tetrachlorides	Colourless liquid b.p. $83^\circ$	Colourless liquid b.p. $114^\circ$	Yellow, oily liquid Thermally unstable
Tetrabromides	Pale-grey crystals m.p. $26^\circ$	White crystals m.p. $33^\circ$	
Tetraiodides	Red crystals m.p. $146^\circ$	Orange crystals m.p. $144^\circ$	

The n.m.r. spectrum of a mixture of  $\text{SnCl}_4$ ,  $\text{SnBr}_4$  and  $\text{SnI}_4$  indicates that mixed halides with all the possible halogen combinations are present.

The tetrahalides are hydrolysed irreversibly by water, complexes often being produced. Thus  $\text{SnCl}_4$ , hydrolysed in the presence of cineol, produces a salt of the ion  $[\text{SnCl}_3(\text{OH})_3]^{2-}$ , indicating that hydrolysis is initiated by the co-ordination of water molecules to the metal atom:

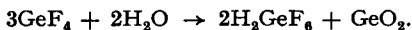


A crystalline hydrate,  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ , is obtained when a limited amount of water is added to tin(IV) chloride. The ionic character of this solid, as com-

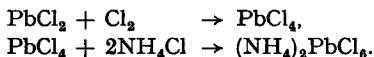


pared with  $\text{SnCl}_4$ , is probably due to the presence of the complex ion  $[\text{Sn}(\text{H}_2\text{O})_4]^{4+}$ .

$\text{GeF}_4$  hydrolyses similarly to  $\text{SiF}_4$  which gives fluorosilicic acid,  $\text{H}_2\text{SiF}_6$  (p. 369):

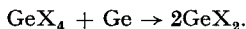


Octahedral complex ions,  $\text{MX}_6^{2-}$ , are generally very stable;  $\text{GeF}_6^{2-}$ , like  $\text{SiF}_6^{2-}$ , is particularly so. Ammonium hexachloroplumbate(IV) is precipitated when  $\text{NH}_4\text{Cl}$  is added to the solution produced by passing  $\text{Cl}_2$  into a suspension of  $\text{PbCl}_2$  in  $\text{HCl}$ :



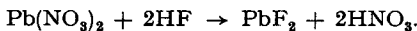
### *Dihalides*

The dihalides are rather more ionic in character. Those of germanium are colourless-to-yellow solids made by passing the tetrahalide vapour over the heated metal:



At higher temperatures this reaction is reversed and there is disproportionation. Germanium di-iodide has the layer-lattice structure of  $\text{CdI}_2$  (p. 204). The germanium dihalides are all strong reducing agents. Germanochloroform,  $\text{GeHCl}_3$ , is formed when  $\text{GeCl}_2$  reacts with  $\text{HCl}$  gas at  $40^\circ$ ; it is a colourless fuming liquid.

The dihalides of tin and lead are monomeric in the vapour; the molecules are angular (p. 147). In  $\text{PbBr}_2$  the  $\text{Br-Pb-Br}$  angle is  $86^\circ$ . These anhydrous compounds cannot strictly be considered ionic, but tetratin(II) hydroxide dichloride,  $\text{Sn}_4(\text{OH})_6\text{Cl}_2$ , the only definite compound crystallising from aqueous solutions, is the salt  $[\text{Sn}_3(\text{OH})_4]^{2+}[\text{Sn}(\text{OH})_2\text{Cl}_2]^{2-}$ . The lead dihalides are all sparingly soluble in cold water and can be precipitated:



The difluoride,  $\text{PbF}_2$ , crystallises with the rutile structure (p. 203). Yellow  $\text{PbI}_2$  dissolves in hot water to give a colourless solution containing hydrated  $\text{Pb}^{2+}$  ions.

Complex halides such as  $\text{KSnCl}_3$ ,  $\text{K}_2\text{SnCl}_4$ ,  $\text{K}_2\text{PbCl}_4$  and  $(\text{NH}_4)_2\text{PbCl}_4$  can be made from tin(II) and lead(II) chlorides. The formulae of the alkali metal fluoroplumbates(II) depend on the ionic radius of the Group I metal. Potassium fluoride gives  $\text{K}_4\text{PbF}_6$  with  $\text{PbF}_2$ , but rubidium and caesium fluorides give the perovskite-type compounds  $\text{MPbF}_3$ . Potassium and rubidium also form non-stoichiometric compounds  $\text{M}_n\text{Pb}_{1-n}\text{F}_{2-n}$  where

$n = 0.2$  to  $0.3$ . These have an anti- $\alpha$ AgI structure (p. 215) with additional  $F^-$  ions fitting into the lattice.

### Oxides

The dioxides,  $GeO_2$  and  $SnO_2$ , are the ultimate oxidation products of the metals and are stable at high temperatures. Lead dioxide,  $PbO_2$ , is much less thermally stable and is made by the oxidation of  $Pb^{2+}$  in alkaline solution. All three dioxides have structures of the rutile type (p. 203) but  $GeO_2$  has also a cristobalite structure stable above  $1033^\circ$ .

Though freshly precipitated germanium dioxide was formerly referred to as germanic acid there is no X-ray evidence for a definite hydrate. However,  $GeO_2$  reacts with basic oxides to form germanates usually isomorphous with the silicates. Sodium metagermanate,  $Na_2GeO_3$ , is soluble in water. Tetraethyl germanate,  $Ge(OEt)_4$ , b.p.  $185^\circ$ , made by refluxing  $GeCl_4$  with  $NaOEt$  in alcohol, is converted into a gel of hydrated  $GeO_2$  on the addition of water to the alcoholic solution. Removal of the alcohol under reduced pressure leaves a hard material with adsorbent characteristics similar to silica gel.

The alkali-metal stannates and plumbates form trihydrates containing octahedral anions, *e.g.*  $Sn(OH)_6^{2-}$ . These are isomorphous with one another and with the platinates. The dioxides dissolve in acids only in the presence of  $F^-$  and  $Cl^-$  ions.

X-ray examination of the products of the thermal decomposition of  $PbO_2$  discloses two intermediate, non-stoichiometric phases between  $PbO_2$  and  $Pb_3O_4$ . The  $\alpha$ -phase is close to  $Pb_7O_{11}$  and the  $\beta$ -phase to  $Pb_2O_3$ . Red lead itself,  $Pb_3O_4$ , formed by heating either litharge,  $PbO$ , or lead dioxide,  $PbO_2$ , in air, consists of chains of  $PbO_6$  octahedra sharing opposite edges linked by Pb atoms each co-ordinated to three oxygens (Fig. 237).

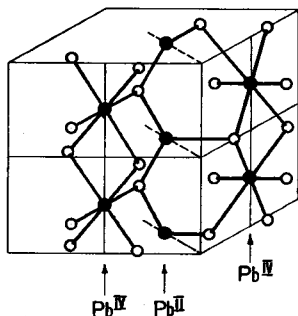
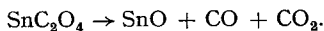


Fig. 237. Structure of  $Pb_3O_4$ .

The monoxides, though amphoteric, are only weakly so on the acidic side, particularly SnO and PbO. Black GeO can be made by heating in an inert atmosphere the yellow precipitate of hydrated GeO obtained when a solution of  $\text{GeCl}_4$  is warmed with hypophosphorous acid. Tin(II) oxide results when the oxalate  $\text{SnC}_2\text{O}_4$  is heated in the absence of oxygen:

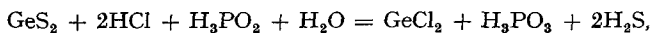


Crystalline black SnO and yellow PbO are both tetragonal with layer lattices in which the metal atom is bonded to four oxygen atoms arranged in a square on one side of it. The adjacent layers are held together by metal-metal bonds (Fig. 279, p. 499).

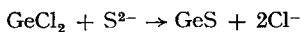
### Sulphides

The sulphides,  $\text{GeS}_2$  and  $\text{SnS}_2$ , unlike  $\text{SiS}_2$ , are not hydrolysed by water.  $\text{GeS}_2$  is made by direct combination of the elements, but the reaction between Sn and S goes as far as  $\text{SnS}_2$  only in the presence of  $\text{NH}_4\text{Cl}$ .  $\text{GeS}_2$  has a quartz-like structure,  $\text{SnS}_2$  a layer lattice of the cadmium iodide type (p. 204). The compounds are precipitated in a somewhat impure condition by adding  $\text{H}_2\text{S}$  to acidified germanate and stannate solutions. The precipitates dissolve in alkali sulphide solutions to give thiogermanates and thio-stannates:  $\text{Na}_2\text{SnS}_3 \cdot 8\text{H}_2\text{O}$  and  $\text{Na}_4\text{SnS}_4 \cdot 18\text{H}_2\text{O}$  have been isolated but a thiogermanate has not been obtained from solution.

Black GeS is the most thermally stable of the  $\text{Ge}^{\text{II}}$  compounds. It is best made by reducing a suspension of  $\text{GeS}_2$  in 6*M* HCl with hypophosphorous acid:



neutralising the solution produced and treating it with  $\text{H}_2\text{S}$ :



$\text{SnS}$  is obtained as a grey solid by heating the metal with sulphur at  $900^\circ$ , or as a brown precipitate when  $\text{H}_2\text{S}$  is passed into a tin(II) salt solution. It does not dissolve in alkali sulphides; but in polysulphides, such as yellow ammonium sulphide, it gives solutions of thio-stannates from which the higher sulphide is precipitated on acidification.

The structure of  $\text{PbS}$  is of particular interest as the compound crystallises with the typically ionic NaCl lattice in marked contrast to the layer lattice of PbO. It may well be the least ionic compound to do so.

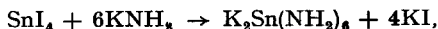
### Nitrogen compounds

When germanium tetraiodide is treated with  $\text{NH}_3$  the compound  $\text{Ge}(\text{NH})_2$  is obtained (*cf.* cyanamide  $\text{NCNH}_2$ ). Heating to  $150^\circ$  converts this to germanam, the germanium analogue of silicam,  $(\text{SiN})_2\text{NH}$ :

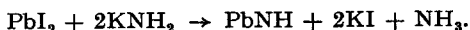


Further heating yields the nitride  $\text{Ge}_3\text{N}_4$ . Germanium di-iodide reacts with liquid ammonia to give the imide  $\text{Ge}:\text{NH}$ .

Tin(IV) iodide reacts with potassium amide to give potassium ammonostannate and not an amide or imide,



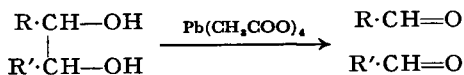
and metallic tin reacts with  $\text{KNH}_2$  in liquid  $\text{NH}_3$  to give  $\text{KSn}(\text{NH}_2)_3$ . This is easily oxidised, in the presence of an excess of  $\text{KNH}_2$ , to the ammonostannate shown above. Lead iodide reacts with potassium amide in liquid ammonia to give an imide:



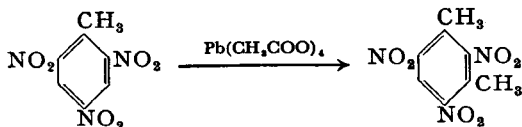
### Oxoacid salts

The only Group IVB oxoacid salts of importance are those of lead. Most of the lead(II) salts are sparingly soluble. The solubilities of  $\text{PbSO}_4$ ,  $\text{PbCrO}_4$  and  $\text{PbC}_2\text{O}_4$  resemble those of the corresponding barium salts; the  $\text{Pb}^{2+}$  ion (1.20 Å) and the  $\text{Ba}^{2+}$  ion (1.35 Å) are similar in size. Lead acetate  $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$  is easily soluble in water but ionises very slightly.

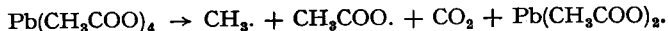
Lead tetra-acetate, the only stable lead(IV) oxoacid salt, is deposited in white needles on cooling solutions of red lead,  $\text{Pb}_3\text{O}_4$ , in hot acetic acid ( $\text{PbO}_2$  is insoluble). It is used as an oxidising agent:



and is also employed as a methylating agent:



This is probably a free-radical reaction in which the  $\text{CH}_3$  radical, derived from the pyrolysis of the tetra-acetate, takes part:



### Organometallic compounds

The alkyl and aryl compounds of germanium and tin are numerous. They are generally rather stable, thermally and hydrolytically, as might be expected for organic derivatives of the congeners of carbon. Lead alkyls are less thermally stable, and fewer are known, but they include the most commercially important of all organometallic compounds, lead tetraethyl  $\text{Et}_4\text{Pb}$  (p. 398).

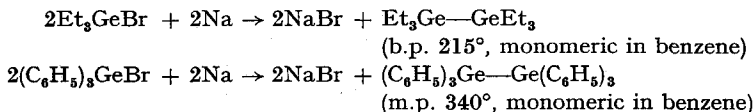
#### *Organogermanium compounds*

Germanium alkyls are best made from germanium tetrahalides and zinc alkyls:

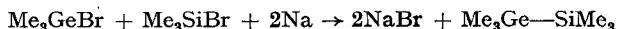


Tetraethylgermanium is monomeric in the vapour and in benzene solution; it is not oxidised by hot nitric acid. The simplest tetra-aryl germanium,  $(\text{C}_6\text{H}_5)_4\text{Ge}$ , is made from  $\text{GeCl}_4$ ,  $\text{C}_6\text{H}_5\text{Br}$  and sodium. The solid, m.p.  $233^\circ$ , volatilises without decomposition and is not attacked by boiling aqueous alkalis. Like the alkyls, the aryls are soluble in organic solvents.

Organogermanium compounds containing Ge-Ge bonds are common; they can be made by a reaction analogous to the Würtz reaction:



Polygermane derivatives are also known, and it is of interest that a mixed silicon-germanium alkyl has been made, also by Würtz coupling:

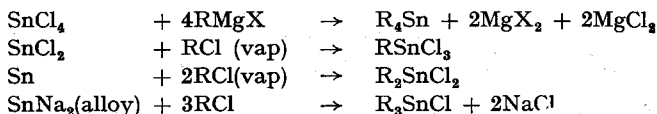


Germanium forms many organo-compounds analogous to carbon compounds by reactions similar to those of organic chemistry. An example is the conversion of a monohalide to an oxide, corresponding to an ether:



#### *Organotin compounds*

The tetraalkyls of tin and their halogen derivatives are formed in reactions such as:



The tetraalkyls are colourless liquids, insoluble in water but soluble in organic solvents. They neither polymerise nor co-ordinate.

Derivatives of distannane and the polystannanes up to  $\text{Sn}_5$  are known.  $\text{Et}_3\text{SnBr}$  reacts with sodium in liquid ammonia to give hexaethyldistannane:



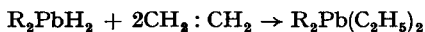
The halogen compounds are usually halogen-bridged polymers, but  $\text{Me}_3\text{SnF}$  has an ionic lattice containing planar  $\text{Me}_3\text{Sn}^+$  ions and  $\text{F}^-$  ions.

### *Organolead compounds*

The alkyls of lead are much less thermally stable than those of germanium and tin. A few organolead compounds containing Pb–Pb bonds have been obtained, but they are unstable. Although plumbane itself cannot be made, dialkyl plumbanes are produced by the reduction of the corresponding halide by  $\text{KBH}_4$  in ether:



These compounds undergo addition reactions with alkenes:



### FURTHER READING

- O. H. JOHNSON, *Germanium and its Inorganic Compounds*, Chem. Rev., 51 (1952) 431.
- E. C. BAUGHAN, *Comments on the Thermochemistry of the Elements of Groups IV and IVB*, Quart. Rev., 1 (1953) 103.
- D. QUANE AND R. S. BOTTEI, *Organogermanium Chemistry*, Chem. Rev., 63 (1963) 403.
- R. K. INGHAM, S. D. ROSENBERG AND H. GILMAN, *Organotin Compounds*, Chem. Rev., 60 (1960) 459.
- R. W. LEEPER, L. SUMMERS AND H. GILMAN, *Organolead Compounds*, Chem. Rev., 54 (1954) 101.
- N. L. PARR, *Zone Refining*, Royal Institute of Chemistry, Monograph No. 3, 1957.
- F. GLOCKLING, *Organogermanium Chemistry*, Quart. Rev., 20 (1966) 45.

## Nitrogen and Phosphorus

These elements, with five valence electrons, form bonds which are almost exclusively covalent in character. For this reason, it is not generally profitable to invoke an ionic description, however formal, and the definition of an ionic radius is usually of little value. An exception might be made in certain phosphorus complexes where an empirical  $P^{5+}$  radius may be defined and used in the usual way.

TABLE 73

ATOMIC PROPERTIES OF NITROGEN AND PHOSPHORUS		
	<i>N</i>	<i>P</i>
Atomic number	7	15
Electron configuration	$2s^2 2p^3$	$3s^2 3p^3$
Covalent radius (Å)	0.75	1.06
Ionic radius, $M^{5+}$ (Å)		0.34

The chief differences between nitrogen and phosphorus arise from the availability of d orbitals in the shell with principal quantum number 3. These d orbitals give phosphorus valence properties not shared by nitrogen; for example, a capacity for 6-co-ordination associated with octahedral hybridisation (p. 120).

In the ground state, both atoms have three singly occupied p orbitals. With this configuration, which gives a  $^4S$  state, is associated a spherically symmetrical distribution of electrons and a high ionisation energy. Since the compounds are essentially covalent, however, ionisation energies are less important than electronegativities.

TABLE 74

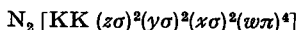
IONISATION ENERGY AND ELECTRONEGATIVITY  
OF NITROGEN AND PHOSPHORUS

	<i>N</i>	<i>P</i>
Ionisation energy (eV)	14.48	10.9
Electronegativity (Allred-Rochow scale)	3.07	2.06

Owing to the readiness with which both nitrogen and phosphorus form covalent bonds, the simple ions do not exist in solution; but compounds like  $\text{NH}_3$  are proton acceptors, and complex ions such as  $\text{NH}_4^+$  are therefore common.

### *Stereochemistry of nitrogen compounds*

The chemistry of nitrogen and phosphorus is dominated by a tendency of the atoms to complete their octets, an end which may be achieved in a number of ways. The electron configuration of the nitrogen molecule may be described in molecular orbitals terms as



where it is evident (p. 108) that the  $\sigma$  bond results from occupation of  $x\sigma$ , which may be roughly a  $\sigma 2p$  orbital, while  $(w\pi)^4$  represents two filled  $\pi 2p$  orbitals and describes two  $\pi$  bonds. The result is a triple bond, of length 1.09 Å, giving a heat of dissociation for  $\text{N}_2$  of 225 kcal per mole (*cf.*  $\text{H}_2$ , 104 and  $\text{O}_2$ , 117). The character of this bond is largely responsible for the inert nature of the gas and the low thermal stabilities of the oxides (Table 75). It is probable that the  $\sigma$  bond in  $\text{N}_2$  is better described by invoking sp

TABLE 75

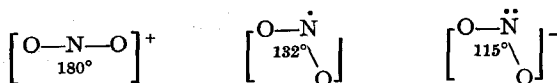
HEATS OF FORMATION OF OXIDES OF NITROGEN (KCAL/MOLE)

$\text{N}_2\text{O}$	-17	$\text{NO}_2$	-2
$\text{NO}$	-21.5	$\text{N}_2\text{O}_5$	+5
		( <i>cf.</i> $\text{P}_4\text{O}_{10}$ )	+365)

hybridisation; in this case  $(z\sigma)^2$  and  $(y\sigma)^2$  are replaced by the lone pairs (one on each nitrogen) which point away from the bond (*cf.* p. 108). It then becomes more obvious that there are four electron pairs (lone pairs or bond pairs) in the vicinity of each nitrogen atom. The tendency to form compact electron pairs becomes more marked in compounds where the hybridisation is dictated by molecular geometry; as, for example, in tetrahedral  $\text{NH}_4^+$  (p. 134). Examples of the principal types and of the situations in which they are appropriate are given in Table 76.

Bond angles in  $\text{NH}_3$ ,  $\text{NMe}_3$  and  $\text{NF}_3$  decrease as the electronegativity of the atom or group attached to the nitrogen increases (p. 423). In such angular species as  $\text{NOCl}$  and  $\text{NO}_2^-$ , the bond angles, here of  $116^\circ$  and  $115^\circ$ , are consistent with strong lone-pair-bond-pair repulsion. The bond angles in the series  $\text{NO}_2^+$ ,  $\text{NO}_2$ ,  $\text{NO}_2^-$  are interesting:





The nitronium ion, being without non-bonding electrons, is linear, the others are angular; the repulsion exerted by the single non-bonding electron in  $\text{NO}_2$  is less than that exerted by the non-bonding pair in  $\text{NO}_2^-$ .

TABLE 76  
HYBRIDISATION OF NITROGEN ATOM

Hybrid	Bonding pairs	Lone pairs	Molecular shape	Examples
$\text{sp}^3$	$4\sigma$	0	Tetrahedral	$\text{NH}_4^+$ , $\text{NEt}_4^+$ , $\text{Me}_3\text{N}-\text{O}$
	$3\sigma$	1	Pyramidal	$:\text{NH}_3$ , $:\text{NMe}_3$ , $:\text{NF}_3$
$\text{sp}^2$	$3\sigma$ $1\pi$	0	Triangular	$\text{Cl}-\text{N} \begin{array}{l} \diagup \text{O} \\ \diagdown \text{O} \end{array}$ $\text{O}-\text{N} \begin{array}{l} \diagup \text{O} \\ \diagdown \text{O} \end{array}$
	$2\sigma$ $1\pi$	1	Angular	$\text{Cl}-\overset{\cdot\cdot}{\text{N}}-\text{O}$ $\text{O}-\overset{\cdot\cdot}{\text{N}}-\text{O}$
$\text{sp}$	$2\sigma$ $2\pi$	0	Linear	$\text{O}=\overset{+}{\text{N}}-\text{O}$

#### Stereochemistry of phosphorus compounds

In the gas phase, phosphorus, unlike nitrogen, exists as a tetrahedral molecule  $\text{P}_4$  (Fig.238). The  $\sigma$  bonds, in spite of their being 'bent', are apparently preferred to the  $\pi$  bonds of a nitrogen-like configuration. The dissociation energy of the phosphorus molecule is small and the element accordingly much more reactive than nitrogen.

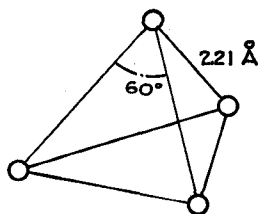


Fig. 238. Structure of  $\text{P}_4$  molecule.

Phosphorus, like nitrogen, can complete an octet of four tetrahedrally arranged electron pairs either by forming three covalent bonds, which thus have pyramidal arrangement, or by forming four covalent bonds in ions

such as  $\text{PH}_4^+$ , which is akin to  $\text{NH}_4^+$ . But because 3d orbitals are also available in phosphorus all the valency electrons can be used to form five bonds with trigonal-bipyramidal arrangement as in  $\text{PCl}_5$ . Octahedral complexes also occur in anions such as  $\text{PCl}_6^-$  (Table 77).

TABLE 77  
HYBRIDISATION OF PHOSPHORUS ATOM

Hybrid	Bonding pairs	Lone pairs	Molecular shape	Examples
$\text{sp}^3$	$4\sigma$	0	Tetrahedral	$\text{PH}_4^+$ , $\text{PCl}_4^+$
	$3\sigma$	1	Trigonal pyramidal	$\text{PCl}_3$ , $\text{P}_4\text{O}_6$
	$4\sigma$ $1\pi$	0	Tetrahedral	$\text{POCl}_3$ , $\text{PO}_4^{3-}$
$\text{sp}^3\text{d}$	$5\sigma$	0	Trigonal bipyramidal	$\text{PCl}_5$ , $\text{PF}_5$
$\text{sp}^3\text{d}^2$	$6\sigma$	0	Octahedral	$\text{PCl}_6^-$

The bond angle in  $\text{PH}_3$ ,  $\sim 94^\circ$ , is much less than in  $\text{NH}_3$ ,  $\sim 107^\circ$ ; nitrogen, with its much greater electronegativity, forms stronger and shorter bonds with the hydrogen, whereby the repulsive effect of the lone pair is less than in the phosphorus compound.

In molecules of the type  $\text{POX}_3$ , the angle X-P-X is always less than the tetrahedral angle ( $\text{POF}_3$ ,  $102.5^\circ$  and  $\text{POCl}_3$ ,  $103.5^\circ$ ) because the double bond repels the single bonds more than the single bonds repel each other (p. 152).

### Thermodynamic stability of the oxidation states in nitrogen and phosphorus

The free energies, relative to the element, of the various oxidation states of nitrogen and phosphorus in solution at  $\text{pH} = 0$  are shown graphically in Fig. 239.

For nitrogen there is a pronounced minimum at the zero oxidation state, which emphasises the stability of the nitrogen molecule with respect to  $\text{NH}_2\text{OH}$  and  $\text{H}_2\text{N}_2\text{O}_2$ . The points for all its positive oxidation states between 0 and +5 lie above the straight line connecting  $G(\text{V})$  and  $G(\text{O})$ . These compounds are all thermodynamically unstable towards disproportionation. The only species represented in the graph which has a lower free energy than nitrogen itself is  $\text{NH}_4^+$ :



For phosphorus compounds at  $\text{pH} = 0$  the picture is entirely different.

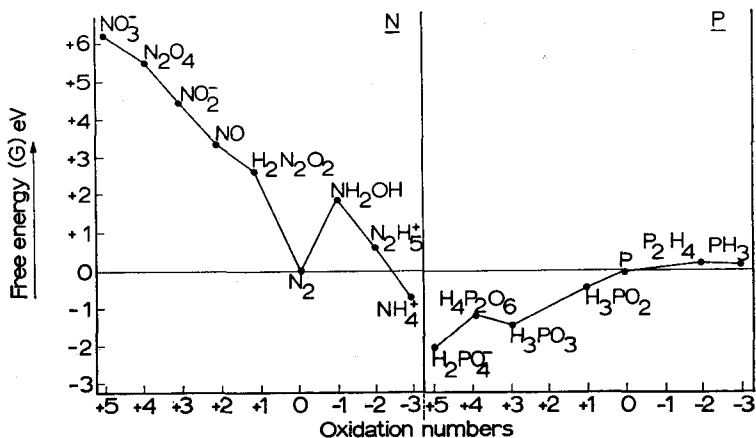


Fig. 239. Free energies of oxidation states of nitrogen and phosphorus, relative to the elements, at pH = 0.

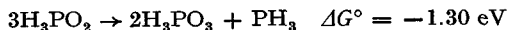
The phosphorus molecule itself is unstable with respect to disproportionation into the +1 and -3 states:



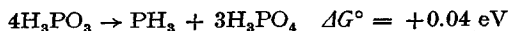
At pH = 14 the free energy release is even greater:



Hypophosphorous acid itself is unstable:



The decomposition of phosphorous acid into phosphine and phosphoric acid has a small positive free-energy change:



But in hot solutions, from which the  $\text{PH}_3$  volatilises, the decomposition proceeds to completion. Thus, through the various steps, phosphorus is unstable with respect to its hydrolysis to  $\text{H}_3\text{PO}_4$  and  $\text{PH}_3$ . The low free energies of the positive oxidation states of phosphorus indicate that even weak oxidising agents will oxidise the element all the way to  $\text{H}_3\text{PO}_4$ .

### The elements: preparation and properties

#### Nitrogen

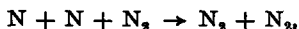
Nitrogen, the principal gas of the atmosphere (78 vol %), is separated

industrially from liquid air by fractional distillation. The gas is rather inert. Chemical separation from the air by means of the producer-gas reaction provides nitrogen for ammonia and cyanamide manufacture. Terrestrial nitrogen consists of nitrogen-14 and about 0.4% of nitrogen-15; the latter is used for isotopic labelling.

Nitrogen, in common with oxygen and hydrogen, gives a characteristic colour in the low-pressure electrical discharge. When the discharge is switched off there is no 'afterglow' in hydrogen, it is exceedingly brief in oxygen, but persists for several seconds in nitrogen. It seems reasonably certain that the discharge produces nitrogen atoms in the ground state and that the 'afterglow' accompanies a pre-association of atoms into unstable molecules from which they pass into stable molecules.



The process giving rise to the afterglow is of second order with respect to nitrogen atoms and first order with respect to nitrogen molecules, suggesting an overall reaction,



involving a three-body collision. It is not a simple process, however, because the nitrogen atom, having three unpaired electrons, can form a variety of nitrogen molecules, one of which is the pre-associated molecule. This may reach a stable form by one of three routes, giving rise to emission of energy belonging to three band systems.

The behaviour of active nitrogen at the temperature of liquid helium suggests that the solid contains atoms which, on reacting, emit a bright green glow accompanied by blue flashes on the surface of the vessel. The chemical reactions of active nitrogen are also consistent with the presence of atoms; thus hydrocarbons yield chiefly HCN, presumably by an attack on the C atoms rather than the abstraction of hydrogen, since neither  $\text{NH}_3$  nor  $\text{NH}_2 \cdot \text{NH}_2$  has been detected.

The chemically inert character of nitrogen is largely due to the high bonding energy of the molecule (p. 421). Combination occurs with both oxygen and hydrogen under suitable conditions; both reactions have been extensively studied and used commercially:



Of the metals, only lithium combines at moderate temperatures,  $6\text{Li} + \text{N}_2 \rightarrow 2\text{Li}_3\text{N}$ ; the Group IIA metals combine at about red heat,  $3\text{Ca} + \text{N}_2 \rightarrow \text{Ca}_3\text{N}_2$ ; and boron and aluminium at bright red heat,  $\text{B} + \text{N} \rightarrow \text{BN}$ . Silicon and some elements of higher groups (p. 452) react at tem-

peratures above 1200°. The nitrides of the Group I metals other than lithium cannot be made by direct combination (p. 316).

Active nitrogen is much more chemically reactive, forming a nitride with mercury in the cold, and combining directly with phosphorus, iodine, sulphur and arsenic. It has no action on molecular oxygen or hydrogen but it decomposes nitric oxide into its elements:

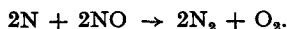


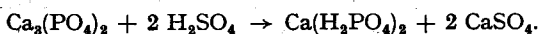
TABLE 78

PROPERTIES OF NITROGEN AND PHOSPHORUS

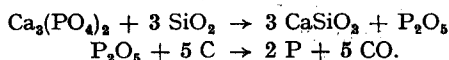
	<i>Nitrogen</i>	<i>Phosphorus (white)</i>
Density (g/cc)	1.027 (solid at -210°)	1.83
Atomic volume	13.65	16.96
Melting point (°C)	-210	44
Boiling point (°C)	-196	287

### *Phosphorus*

Phosphorus (0.11% of the lithosphere) is found mainly in minerals based on calcium phosphate, such as collophanite, the monohydrate,  $\text{Ca}_3(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ , and apatite,  $\text{Ca}_5\text{F}(\text{PO}_4)_3$ . About 90% of the phosphate rock mined is converted into fertilisers, the rest is used for making elementary phosphorus, phosphorus compounds and such alloys as phosphor bronze. For the manufacture of fertilisers, rock phosphate is finely ground and treated with sufficient concentrated sulphuric acid to convert it to the soluble dihydrogen phosphate:



Elementary phosphorus is extracted from the mineral by heating with sand and coke, generally electrically, and condensing the vapour to give the white variety of the element:



White phosphorus when pure melts to a colourless liquid which crystallises in the cubic system; the solid contains individual  $\text{P}_4$  tetrahedra held together by Van der Waals forces. It can be changed to a hexagonal form by high pressure, the transition temperature being  $-77^\circ$ .

The black allotrope, similar to graphite in appearance and conductance, first made only at very high pressures, was later made from white phos-

phorus at ordinary pressure in the presence of mercury and a 'seed' of the black variety. Transformation was complete after 8 days during which the temperature was gradually raised from 220° to 370°. The atoms in black phosphorus are covalently linked to form buckled sheets in an extended network of 3-co-ordinated atoms.

Red phosphorus is produced when either the white or the black allotrope of the element is heated. It is an intermediate form in which the structural order is incompletely organised. Its physical properties are those of a polymeric material: the  $P_4$  tetrahedra have been opened up and interlinked during its formation from white phosphorus, whereas the puckered layers of P atoms have been broken down during its formation from black phosphorus. The vapour pressure of red phosphorus is surprisingly high in view of its structure.

When phosphorus is cooled rapidly from 1000° to  $-196^\circ$  a dark brown solid is obtained, stable indefinitely at that temperature and probably containing  $P_2$  molecules. At  $-100^\circ$  the brown phosphorus changes irreversibly to a mixture of approximately 20% red and 80% white phosphorus; as the temperature is raised the rate of conversion increases but the ratio of the allotropes alters little.

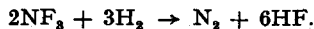
A vitreous form of phosphorus has been prepared by heating the white form with mercury. It is stable in moist air and is harder than black phosphorus.

## Halides

### *Nitrogen halides*

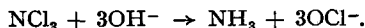
Trihalides of nitrogen with fluorine and chlorine have been isolated, but for bromine and iodine only the ammonia complexes,  $NBr_3(NH_3)_6$  and  $NI_3(NH_3)_6$ , are known.

Nitrogen trifluoride is a colourless gas (b.p.  $-119^\circ$ ) of normal vapour density, made by electrolysis of fused  $NH_4HF_2$  in a copper vessel. The crude gas which contains HF,  $N_2$ ,  $H_2$ ,  $N_2O$ ,  $O_2$ ,  $O_3$ ,  $NH_2F$  and  $NHF_2$  is passed over KF to remove HF,  $MnO_2$  to remove  $O_3$ , is frozen, distilled and then washed with NaOH to remove  $NH_2F$  and  $NHF_2$ . An exothermic compound ( $\Delta H_f = -26$  kcal),  $NF_3$  is much more thermally stable and chemically inert than the other nitrogen halides. It is not hydrolysed by water or alkali and is non-explosive, though it reacts violently with hydrogen on sparking:



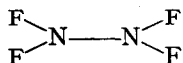
Nitrogen trichloride is a yellow, oily liquid made by the action of chlorine on  $NH_4Cl$  in concentrated aqueous solution. An endothermic compound,

( $\Delta H_f = +55$  kcal), it explodes above its boiling point or on impact, and is easily hydrolysed:

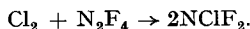


Difluorodiazine,  $\text{N}_2\text{F}_2$ , a minor product of the electrolysis of  $\text{NH}_4\text{HF}_2$ , has well defined isomers (*cis* m.p.  $\sim -195^\circ$ , b.p.  $-105.7^\circ$ ; *trans* m.p.  $-172^\circ$ , b.p.  $-114^\circ$ ). The *trans* isomer is converted to the *cis* on heating; it is appreciably less reactive than the *cis* with glass and mercury.

Tetrafluorohydrazine,  $\text{N}_2\text{F}_4$ , is produced when  $\text{NF}_3$  is passed over hot copper and other metals which abstract fluorine. The compound boils at  $-73^\circ$ , has a critical temperature of  $36^\circ$ , and has the structure

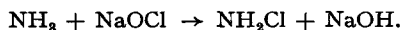


Its vapour contains  $\text{NF}_2$  free radicals as well as  $\text{N}_2\text{F}_4$  molecules (*cf.*  $\text{N}_2\text{O}_4$ , p. 436). With chlorine under ultraviolet irradiation it gives the monochlorofluoride:



#### *Derivatives of nitrogen halides*

Monochloramine,  $\text{NH}_2\text{Cl}$ , is formed when  $\text{NH}_3$  and  $\text{NaOCl}$  react in aqueous solution in equimolar quantities:



Distillation of the mixture at low pressure, followed by drying and condensing the vapour, gives colourless crystals m.p.  $-66^\circ$ , unstable at higher temperatures when dry. Dichloramine,  $\text{NHCl}_2$ , is formed when chlorine is passed into ammonium sulphate solution buffered to pH  $5 \pm 0.5$ , but has not been isolated.  $\text{NH}_2\text{F}$  can be made pure. It is more reactive than  $\text{NF}_3$ , being hydrolysed by alkalis;  $\text{NH}_2\text{Cl}$ , on the contrary, is less reactive than  $\text{NCl}_3$ .

Purple  $\text{NBr}_3(\text{NH}_3)_6$ , resulting from the action of bromine vapour on an excess of ammonia, and black  $\text{NI}_3(\text{NH}_3)_6$ , made by treating iodine with strong aqueous ammonia, are both highly explosive solids.

#### *Phosphorus halides*

The halides of phosphorus are, with the exceptions indicated in Table 79, colourless.

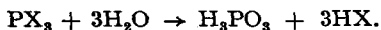
The trihalides are usually prepared by direct combination under controlled conditions, but  $\text{PF}_3$  is best made by the action of  $\text{AsF}_3$  or  $\text{CaF}_2$  on  $\text{PCl}_3$ :



TABLE 79  
PHOSPHORUS HALIDES

	<i>Trihalides</i>	<i>Pentahalides</i>	<i>Others</i>
Fluorides	PF <sub>3</sub> b.p. -95°	PF <sub>5</sub> b.p. -75°	
Chlorides	PCl <sub>3</sub> b.p. 76°	PCl <sub>5</sub> sublimes 163°	P <sub>2</sub> Cl <sub>4</sub> b.p. 180°
Bromides	PBr <sub>3</sub> b.p. 173°	PBr <sub>5</sub> m.p. 100° (yellow)	
Iodides	PI <sub>3</sub> m.p. 61° (dark red)		P <sub>2</sub> I <sub>4</sub> m.p. 124° (orange)

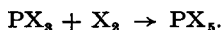
Hydrolysis gives phosphorous acid and the halogen hydracid; the ease of hydrolysis increases with the atomic weight of the halogen:



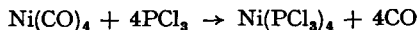
They all react with oxygen and sulphur:



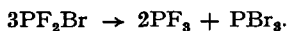
and with halogens except when X = I:



By using their lone pairs, the molecules can act as ligands in complexes:



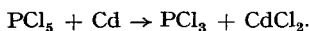
Mixed halides such as PF<sub>2</sub>Br have been made; they decompose on heating:



The pentahalides are produced by the addition of another molecule of halogen to the trihalide, one 3d orbital of the phosphorus atom being now occupied. Solid PCl<sub>5</sub> is made by dropping liquid PCl<sub>3</sub> into dry chlorine. The thermal stability of the pentahalides decreases as the molecular weight rises. PCl<sub>5</sub> dissociates on slight heating,

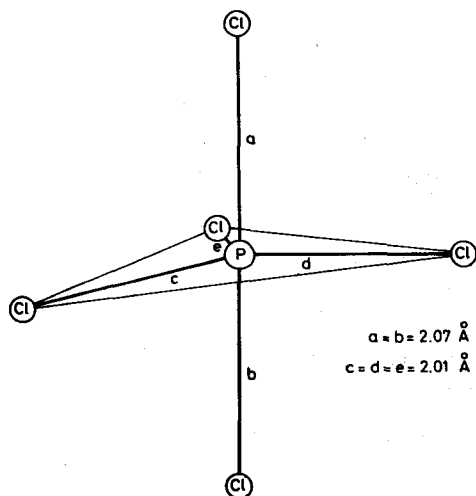


and is readily reduced by some metals on warming,



When the vapour from phosphorus pentachloride is passed over CaF<sub>2</sub> at 300–400° the pentafluoride is formed. In the vapour phase PF<sub>5</sub> (b.p. -75°) and PCl<sub>5</sub> (subl. 163°) have trigonal bipyramidal molecules. In PF<sub>5</sub> the bonds are all equal in length (1.57 Å), but in PCl<sub>5</sub> three are 2.01 Å and two 2.07 Å (Fig. 240).



Fig. 240. Bond lengths in the  $\text{PCl}_5$  molecule.

Solid  $\text{PCl}_5$  contains tetrahedral  $\text{PCl}_4^+$  and octahedral  $\text{PCl}_6^-$  ions arranged in a CsCl lattice, but  $\text{PBr}_5$  has  $\text{PBr}_4^+$  and  $\text{Br}^-$ . A solution of  $\text{PCl}_5$  in methyl nitrite conducts electricity, and  $\text{PBr}_5$  gives similar conducting solutions.

Hydrolysis of the pentahalides occurs in two stages:

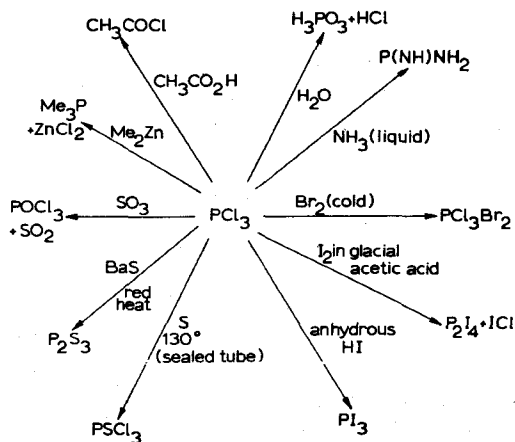


Fig. 241(a). Typical reactions of phosphorus trichloride.

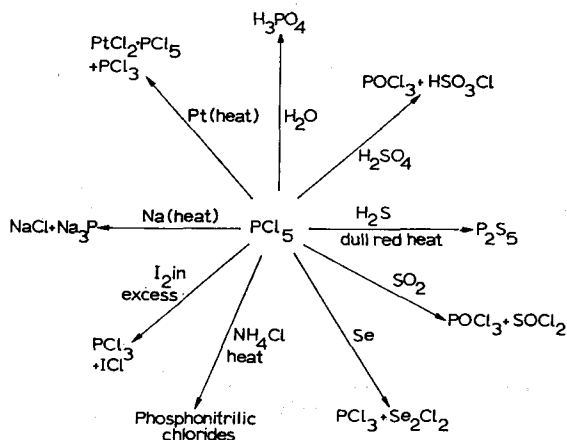


Fig. 241(b). Typical reactions of phosphorus pentachloride.

Diphosphorus tetrachloride,  $P_2Cl_4$ , is a colourless, oily, fuming liquid made by passing a silent discharge through a mixture of  $PCl_3$  and hydrogen. It decomposes at its b.p.,  $180^\circ$ , to P and  $PCl_3$ ; it is hydrolysed to HCl,  $H_3PO_3$  and P; and it is liable to inflame spontaneously in air. The corresponding iodide,  $P_2I_4$ , is deposited as orange crystals when solutions of phosphorus and iodine in  $CS_2$  are mixed. It decomposes to  $PI_3$  and P on heating and is hydrolysed to  $H_3PO_3$ ,  $H_3PO_2$  and HI.

### Oxides of nitrogen

It is convenient to classify the oxides of nitrogen and phosphorus in the traditional manner in terms of the formal charge on the nitrogen or phosphorus atoms, when electrons are regarded as being transferred to the oxygen atoms to give them formally a  $-2$  charge number. The charge numbers of nitrogen and phosphorus in the oxides are then:

+1	+2	+3	+4	+5
$N_2O$	NO	$N_2O_3$	$N_2O_4$	$N_2O_5$
		$P_4O_6$	$(PO_2)_n$	$P_4O_{10}$

The oxides of nitrogen, except  $N_2O_5$ , are gases at room temperature, whereas all those of phosphorus are solid.

TABLE 80  
PHYSICAL PROPERTIES OF THE OXIDES OF NITROGEN

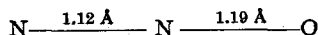
	$N_2O$	$NO$	$N_2O_3$	$N_2O_4$	$N_2O_5$
Molecular weight	44	30	76	92	108
Melting point ( $^{\circ}C$ )	-102.4	-163.6	-102.0	-9.3	+30*
Boiling point ( $^{\circ}C$ )	-88.5	-151.8	+3.5*	+21.3*	+47*
Colour of solid	Colourless	Colourless	Light blue	Colourless	Colourless

\* With decomposition

### Nitrous oxide

Nitrous oxide,  $N_2O$ , is made by heating  $NH_4NO_3$ . Colourless and unreactive at room temperature, the gas is, through decomposition, an oxidising agent above  $600^{\circ}$ :  $2N_2O \rightarrow 2N_2 + O_2$ . It is not the anhydride of hyponitrous acid and, though but slightly soluble, gives a neutral solution.

Bonds lengths in the  $N_2O$  linear molecule are respectively 1.12 and 1.19 Å:



If both the nitrogen and oxygen atoms are considered to use  $sp$  hybrid orbitals the structure can be explained in terms of two  $\sigma$  bonds and two pairs of non-localized  $\pi$  orbitals extending over all three centres. The lowest orbitals in each pair, which differ only by rotation through  $90^{\circ}$  about the axis, give two partial  $\pi$  bonds in the  $N-N$  and  $N-O$  bonding (Fig. 242(a)). The higher orbitals will be weakly bonding in one link,  $N-N$ , and weakly antibonding in the other,  $N-O$  (Fig. 242(b)). Both bonds in the molecule will have some triple-bond character, this being higher in the  $N-N$  link.

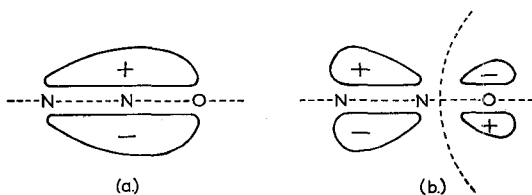
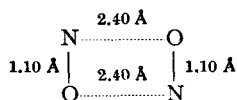


Fig. 242. Delocalised  $\pi$  orbitals (showing nodes) in  $N_2O$ :  
(a) bonding in both regions,  $N-N$  and  $N-O$ ;  
(b) weakly bonding in  $N-N$ , weakly anti-bonding in  $N-O$ .

The molecule is isoelectronic and isosteric with  $CO_2$  and the physical properties of the two compounds show similarities (crit. temp.,  $N_2O$ ,  $36.5^{\circ}$ ;  $CO_2$ ,  $31.1^{\circ}$ ). The chief commercial use of nitrous oxide is as an anaesthetic.

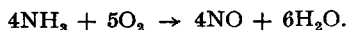
### Nitric oxide

Nitric oxide, NO, is a colourless gas which condenses to a dark-blue liquid. The molecule is paramagnetic, having one odd electron in an anti-bonding  $\pi$  orbital. This is consistent with the fact that the cation  $\text{NO}^+$  (that is NO with the odd electron removed) has a shorter and stronger bond. The solid contains rectangular dimers with the dimensions indicated, although the X-ray evidence does not distinguish between similar and opposite orientations of the N—O groups:

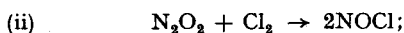
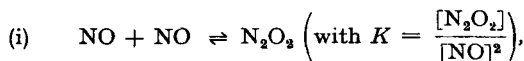


The liquid has a high Trouton constant and a low dielectric constant. The bond length in the monomer is 1.14 Å and the molecule is very stable, so that association to  $\text{N}_2\text{O}_2$  is endothermic at ordinary temperature. The gaseous molecule is monomeric and has a small dipole moment of 0.16 debye.

Nitric oxide is made on a large scale by oxidising ammonia with air on the surface of platinum above 500°:



The gas is oxidised to  $\text{N}_2\text{O}_4$  by oxygen and to nitrosyl halides, NOX, by  $\text{F}_2$ ,  $\text{Cl}_2$  and  $\text{Br}_2$ . The reactions have empirical third-order kinetics but are probably bimolecular, involving the dimer even though there is no direct evidence for its presence in the vapour. For instance, the formation of nitrosyl chloride may be represented thus:



The rate is proportional to the  $[\text{N}_2\text{O}_2][\text{Cl}_2]$ , *i.e.* to  $K[\text{NO}]^2[\text{Cl}_2]$ .

#### Paramagnetism of nitric oxide

The paramagnetic moment of NO increases up to 250° but above that temperature it remains almost constant; the variation is not in accordance with the Curie law (p. 87). The two lowest electronic energy levels of the NO molecule are separated by only 121  $\text{cm}^{-1}$ , which is comparable with  $kT$  (0.70T in  $\text{cm}^{-1}$ ) at normal laboratory temperature. The distribution

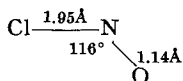
of the molecules between two states of similar energy but different  $J$  value is responsible for the anomalous variation of magnetic moment with temperature.

### Compounds from nitric oxide

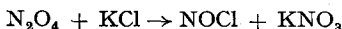
Nitric oxide forms compounds in three ways.

- (i) Electron sharing, to form highly coloured, covalent substances, typified by the volatile, easily hydrolysed nitrosyl halides (see below).
- (ii) Electron gain, to form  $\text{NO}^-$ , as found in sodium nitrosyl made by the action of nitric oxide on the metal in liquid ammonia:  $\text{Na} + \text{NO} \rightarrow \text{NaNO}$ .
- (iii) Electron loss, to form  $\text{NO}^+$ , the nitrosonium ion (see below).

The covalent, nitrosyl halides have bent molecules:



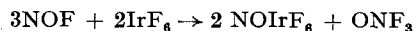
The  $\text{N}-\text{X}$  bonds are long, suggesting much polar character.  $\text{NOF}$  is made by mixing  $\text{F}_2$  with an excess of  $\text{NO}$  in a copper tube, and  $\text{NOCl}$  by passing  $\text{N}_2\text{O}_4$  over moist  $\text{KCl}$  at room temperature:



$\text{NOBr}$  is formed when  $\text{NO}$  is passed into bromine at  $-15^\circ$ . The iodide has not been made. Nitrosyl halides react with hydroxylic compounds to give nitrites:



$\text{NOF}$  and  $\text{IrF}_6$  mixed in a copper vessel at  $-196^\circ$  and warmed to room temperature produce  $\text{ONF}_3$ :



It is a colourless gas (m.p.  $\sim -100^\circ$ ) with infrared and n.m.r. spectra consistent with the structure  $\overset{-}{\text{O}}\overset{+}{\text{N}}\text{F}_3$ , one which renders the compound moderately stable.

The ionisation potential for the process  $\text{NO} \rightarrow \text{NO}^+ + e$  is 9.5 eV, much lower than that for  $\text{N}_2 \rightarrow \text{N}_2^+ + e$  ( $\sim 16$  eV) or  $\text{O}_2 \rightarrow \text{O}_2^+ + e$  ( $\sim 15$  eV). Just as happens with the odd electron in an atom, the odd electron in  $\text{NO}$  is more readily lost than one from a doubly occupied orbital since such an electron moves outside a closed shell and is more effectively screened from the nucleus (*cf.* p. 70). Nitrosonium compounds such as  $\text{NO}^+\text{ClO}_4^-$ ,  $\text{NO}^+\text{HSO}_4^-$  and  $\text{NO}^+\text{BF}_4^-$ , are prepared in non-hydroxylic solvents; they are usually isomorphous with the hydroxonium and ammonium salts  $\text{H}_3\text{O}^+\text{ClO}_4^-$  and  $\text{NH}_4^+\text{ClO}_4^-$ . The nitrosonium ion is intermediate in size between  $\text{H}_3\text{O}^+$  and  $\text{NH}_4^+$ .

Though stable in non-hydroxylic solvents, nitrosonium compounds react with hydroxylic solvents:



This equilibrium is displaced to the left in strongly acid media.

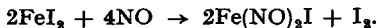
### Metal complexes containing the NO group

In these complexes, nitrogen is the donor atom and in most of them NO is bound as  $\text{NO}^+$ , an ion which is isoelectronic with  $\text{CN}^-$  and CO. The NO group can thus donate one extra electron to the metal; this accounts for the stability of tricarbonyl-nitrosylcobalt,  $\text{Co}(\text{NO})(\text{CO})_3$ , which has the same electronic pattern as  $\text{Ni}(\text{CO})_4$  (p. 387). Co-ordination complexes of this type do not usually contain more than one NO group.

### Nitrosyls

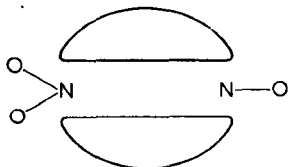
Unstable metal nitrosyls are formed by Fe, Ru and Ni. Black  $\text{Fe}(\text{NO})_4$ , made by heating iron carbonyl with NO under pressure at  $50^\circ$ , is the most stable. The structure is unknown, but the ionic formula  $\text{NO}^+[\text{Fe}(\text{NO})_3]^-$  has been suggested to explain its low volatility. Ruthenium tetranitrosyl,  $\text{Ru}(\text{NO})_4$ , is made as cubic, red crystals when NO is passed into  $\text{Ru}_3(\text{CO})_{12}$ . A compound of empirical formula  $\text{Ni}(\text{NO})_2$  is obtained as a blue powder when NO is passed into  $\text{Ni}(\text{CO})_4$  dissolved in  $\text{CHCl}_3$ .

The nitrosyl carbonyls such as  $\text{Co}(\text{NO})(\text{CO})_3$  are much more stable than the nitrosyls themselves. Nitrosyl halides,  $\text{Fe}(\text{NO})_2\text{X}$ ,  $\text{Co}(\text{NO})_2\text{X}$  and  $\text{Ni}(\text{NO})\text{X}$  are known; their stability falls from Fe to Ni and from I to Cl. Fluorides are unknown. The most stable nitrosyl halide,  $\text{Fe}(\text{NO})_2\text{I}$ , results from passing NO over  $\text{FeI}_2$  at  $100^\circ$ :



### Dinitrogen trioxide

This, the anhydride of nitrous acid, exists only in the solid state, m.p.  $-102^\circ$ ; the liquid of the composition  $\text{N}_2\text{O}_3$ , produced by the condensation of 2 vol. NO and 1 vol.  $\text{N}_2\text{O}_4$  at  $-20^\circ$ , is probably a mixture. For dinitrogen trioxide the structure  $\text{O}_2\text{N} \cdot \text{NO}$ , with a  $\pi$ -only N—N bond, has been suggested:



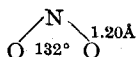
Molecular-orbital, spectroscopic and thermochemical evidence support the assignment of the band in the visible spectrum to an electronic transition between a lone pair on the nitroso nitrogen and an anti-bonding  $\pi^*$  orbital, and of the band in the near-ultraviolet spectrum to a  $\pi-\pi^*$  transition in a nitroso-nitro molecule with a  $\pi$ -only N—N bond. Incidentally, there is some evidence for an ONONO form of the dinitrogen trioxide molecule at the temperature of liquid helium.

In concentrated  $\text{H}_2\text{SO}_4$  the blue colour disappears as fully ionised nitrosonium hydrogen sulphate is formed:



### Dinitrogen tetroxide

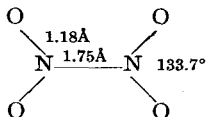
Dinitrogen tetroxide is best made by heating  $\text{Pb}(\text{NO}_3)_2$  and condensing the compound from the gases evolved. It is colourless and diamagnetic in the dimeric form,  $\text{N}_2\text{O}_4$ , which is found pure only in the solid state, m.p.  $-9.3^\circ$ . This melts to a pale yellow liquid, b.p.  $21.3^\circ$ , which contains about 1% of the brown, paramagnetic monomer,  $\text{NO}_2$ , with one unpaired electron. The vapour darkens progressively on heating and, at  $100^\circ$ , has about 90% of the monomer. The monomeric dioxide,  $\text{NO}_2$ , is angular:



Its bonding energy is less than that of nitric oxide, which accounts for the much greater tendency to dimerisation shown by the nitrogen dioxide molecule.

The monomer,  $\text{NO}_2$ , an odd-electron molecule, has many of the characteristics of a free radical since it (i) associates with other radicals, (ii) abstracts hydrogen from saturated hydrocarbons, (iii) adds to unsaturated hydrocarbons. Its photolysis, decomposition and oxidising action owe little, however, to its radical character.

There are two dimers of  $\text{NO}_2$ , each of which can exist in several conformations. The dimer  $\text{ONONO}_2$  is stable at the temperature of liquid helium; the  $\text{O}_2\text{N} \cdot \text{NO}_2$  dimer is stable at higher temperatures. There are five curious features about the latter's structure:



These are the following:

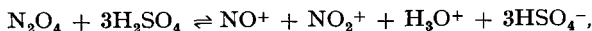
- (i) the very long N—N bond, almost 0.3 Å longer than that in hydrazine,
- (ii) the large ONO angles,
- (iii) the high barrier to internal rotation,
- (iv) the planarity of the molecule,
- (v) the stability of the molecule relative to the ONONO<sub>2</sub> and ONOONO conformations.

The N—N bond has been variously described as a  $\pi$ -only bond (Coulson, 1957) and a 'splayed' single bond (Bent, 1963) implying that the electron density is not so strongly concentrated in the line of the nuclei as in a  $\sigma$  bond. Vicinal interactions between the unshared electrons or the oxygen atoms and the N—N antibonding orbital are probably important factors in the stabilisation of the structure.

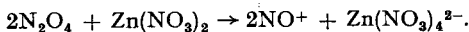
#### *General reactions of dinitrogen tetroxide*

The ionisation of N<sub>2</sub>O<sub>4</sub> is encouraged by

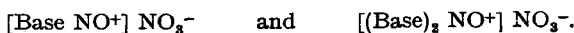
- (i) solvents of high dielectric constant such as HClO<sub>4</sub> and H<sub>2</sub>SO<sub>4</sub>; in concentrated sulphuric acid both nitrosonium and nitronium ions are produced:



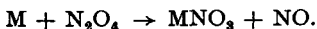
- (ii) the removal of NO<sup>+</sup> as complexes by Lewis bases,
- (iii) the removal of NO<sub>3</sub><sup>-</sup>, as, for example, when Zn(NO<sub>3</sub>)<sub>2</sub> dissolves to form a complex ion:



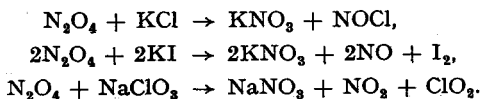
Very many electron donors, such as amines and ethers, combine with N<sub>2</sub>O<sub>4</sub> to produce compounds of the types



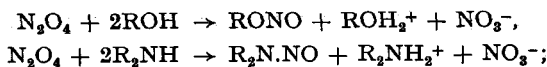
Metals which react with liquid N<sub>2</sub>O<sub>4</sub> (Na, K, Zn, Ag, Pb and Hg) all set free nitric oxide:



Salts react to produce nitrates:

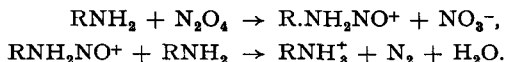


Hydroxylic and amino solvents are usually nitrosated by N<sub>2</sub>O<sub>4</sub>:

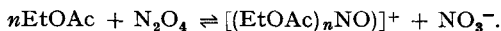




but with primary amines nitrogen is evolved in a two-stage reaction:

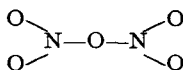


Mixtures of  $\text{N}_2\text{O}_4$  with organic solvents have proved particularly useful for the preparation of anhydrous nitrates. Copper does not dissolve in liquid  $\text{N}_2\text{O}_4$  but it reacts with an  $\text{N}_2\text{O}_4$ /ethyl acetate mixture to give the blue compound  $\text{Cu}(\text{NO}_3)_2 \cdot \text{N}_2\text{O}_4$  from which anhydrous  $\text{Cu}(\text{NO}_3)_2$  is obtained by heating to  $85^\circ$ . The ethyl acetate acts as an electron donor towards the  $\text{N}_2\text{O}_4$  molecule, the energy of interaction being about 2 kcal mole<sup>-1</sup>; so the ionisation of the  $\text{N}_2\text{O}_4$  is enhanced.



### Dinitrogen pentoxide

This is made by the dehydration of nitric acid with  $\text{P}_2\text{O}_5$ . The molecular structure of the compound in non-ionising solvents is



But in concentrated sulphuric acid it ionises to give the nitronium ion,  $\text{NO}_2^+$ :



The solid consists of  $\text{NO}_2^+$  and  $\text{NO}_3^-$  ions, the first being linear and the second planar. The colourless crystals are stable in diffused light below  $8^\circ$  but on warming, or exposing to sunlight, decomposition occurs. They dissolve in water with a hissing noise to give  $\text{HNO}_3$ . The oxide itself has a strong oxidising action, converting, for example,  $\text{I}_2$  to  $\text{I}_2\text{O}_5$ .

### Nitronium compounds

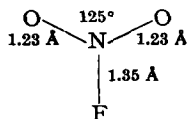
The  $\text{NO}_2^+$  ion, with a Raman displacement of  $1400 \text{ cm}^{-1}$ , is present in sulphuric, selenic and perchloric acid solutions of  $\text{HNO}_3$ . The same Raman line is given by solid nitronium perchlorate,  $\text{NO}_2^+\text{ClO}_4^-$ , which can be separated from a solution made by dissolving  $\text{HNO}_3$  and  $\text{HClO}_4$  in nitromethane. Compounds such as  $\text{NO}_2^+\text{BF}_4^-$  and  $\text{NO}_2^+\text{PF}_6^-$  have been made by dissolving the appropriate fluoride or oxide in bromine and treating the solution with  $\text{N}_2\text{O}_4$  followed by  $\text{BrF}_3$ .

### Nitryl halides

Nitryl fluoride,  $\text{NO}_2\text{F}$ , is made when fluorine reacts with a 2 : 1 excess of  $\text{NO}_2$ , or when fluorine is passed over heated  $\text{NaNO}_2$ :

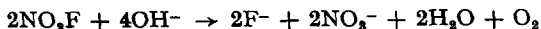


Nitryl chloride,  $\text{NO}_2\text{Cl}$ , is made by treating  $\text{NOCl}$  with ozone. Both the fluoride and chloride are colourless gases. They have planar molecules with the structure shown, which is consistent with their hydrolysis to  $\text{HNO}_3$  and  $\text{HX}$ .

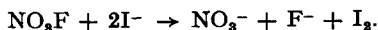


### Pernitryl fluoride

This compound,  $\text{NO}_3\text{F}$ , also known as fluorine nitrate, is formed as a colourless, explosive gas by the action of fluorine on concentrated nitric acid. It is purified by freezing with liquid air followed by fractional distillation at  $-42^\circ$ .  $\text{NO}_3\text{F}$  explodes to give  $\text{NOF}$  and  $\text{O}_2$  when sparked, but a first-order decomposition into the same products proceeds slowly at  $80-110^\circ$ . The gas hydrolyses slowly with water yielding oxygen, and fluoride and nitrate ions:



It oxidises iodides:

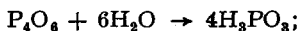


### Oxides of phosphorus

The three oxides of phosphorus are  $\text{P}_4\text{O}_6$ ,  $(\text{PO}_2)_n$  and  $\text{P}_4\text{O}_{10}$ . The first and last have structures based on the  $\text{P}_4$  tetrahedron (Fig. 238).

In the  $\text{P}_4\text{O}_6$  molecule (Fig. 243) oxygen atoms bridge the edges of the tetrahedron, the  $\text{P}-\text{O}$  distance is  $1.65 \text{ \AA}$  and the angles  $\text{POP}$  and  $\text{OPO}$  are  $127.5^\circ$  and  $99^\circ$  respectively. In the  $\text{P}_4\text{O}_{10}$  molecule (Fig. 244) an extra oxygen atom is attached to each  $\text{P}$  atom at a distance of  $1.39 \text{ \AA}$ . It is interesting that a compound  $\text{P}_4\text{O}_6\text{S}_4$ , made by heating  $\text{P}_4\text{O}_6$  with sulphur, has a similar structure.

Phosphorus trioxide,  $\text{P}_4\text{O}_6$ , is made by passing a mixture of oxygen and nitrogen, 3 : 1 by volume, over white phosphorus at  $45-50^\circ$ . The white solid melts at  $24^\circ$ . It is converted to phosphorous acid by cold water:



but hot water produces a mixture of phosphoric acid, phosphorus and phosphine.

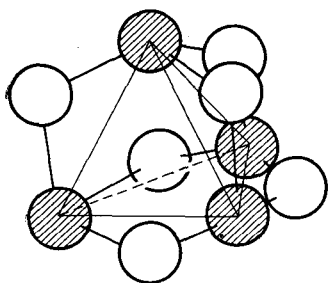


Fig. 243. Structure of  $\text{P}_4\text{O}_6$  molecule.

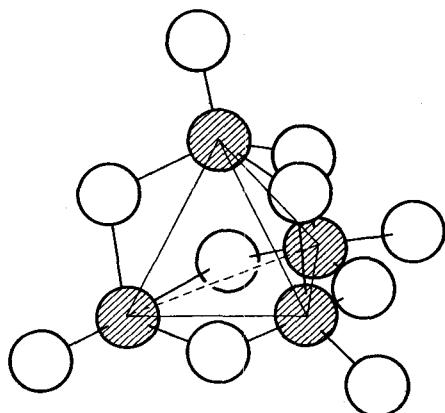
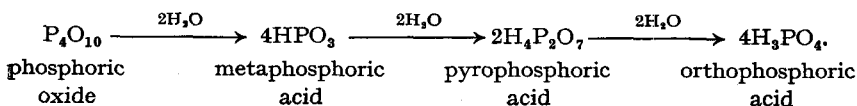


Fig. 244. Structure of  $\text{P}_4\text{O}_{10}$  molecule.

When  $\text{P}_4\text{O}_6$  is heated above  $210^\circ$  the polymeric oxide  $(\text{PO}_2)_n$  and red phosphorus are formed. Solid  $(\text{PO}_2)_n$  sublimates at about  $180^\circ$  and the density of the vapour indicates the molecular formula  $\text{P}_4\text{O}_8$ . The oxide is not the anhydride of hypophosphoric acid,  $\text{H}_4\text{P}_2\text{O}_6$ .

Phosphoric oxide,  $\text{P}_4\text{O}_{10}$ , produced when phosphorus burns in an excess of oxygen, has three crystalline forms of increasing structural complexity; they are hexagonal, orthorhombic and tetragonal. It is the anhydride of the phosphoric acids:



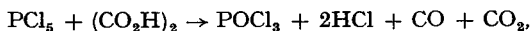
### Oxohalides of phosphorus

Compounds of the POX series have not been made but those of the  $\text{POX}_3$  series are represented by

	B. p.
$\text{POF}_3$	$-40^\circ$
$\text{POCl}_3$	$105^\circ$
$\text{POBr}_3$	$189^\circ$

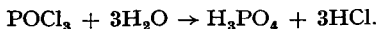
and by the 'mixed' halides  $\text{POF}_2\text{Cl}$ ,  $\text{POFCl}_2$ ,  $\text{POF}_2\text{Br}$  and  $\text{POFBr}_2$ .

Phosphoryl chloride is best made by heating  $\text{PCl}_5$  with anhydrous oxalic acid:



The bromide can be obtained similarly from  $\text{PBr}_5$ . Phosphoryl fluoride and the 'mixed' halides are made by treating the chloride or bromide with  $\text{SbF}_3$ .

$\text{POCl}_3$  hydrolyses rather slowly in cold water:



It is used in organic chemistry as a rather milder reagent than  $\text{PCl}_5$  for replacing  $-\text{OH}$  groups by  $-\text{Cl}$ .

The  $\text{POX}_3$  molecules are all tetrahedral:

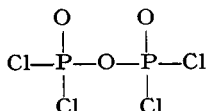


with  $\text{P}-\text{O} = 1.55 \text{ \AA}$ , very close to the double-bond distance. The  $\text{P}-\text{X}$  distances are almost the same as in the corresponding  $\text{PX}_3$  molecules. The compounds are monomeric when liquid; the liquids have normal Trouton constants, but there is slight self-ionisation in  $\text{POCl}_3$ :



which acts as an ionising solvent.

More complex oxohalides are known; pyrophosphoryl chloride:



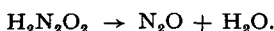
is made from  $\text{P}_2\text{O}_5$  and  $\text{PCl}_5$  (p. 42).

### Oxoacids of nitrogen

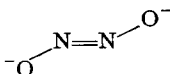
*Hyponitrous acid*,  $\text{H}_2\text{N}_2\text{O}_2$ , has been made from its salts. A solution of sodium hyponitrite is produced by reducing concentrated aqueous  $\text{NaNO}_2$  with sodium amalgam. The insoluble silver salt, precipitated from a neutral solution of sodium hyponitrite, when treated with anhydrous  $\text{HCl}$  in dry ether gives a solution of hyponitrous acid:



The white crystals of the acid obtained by evaporating the ether solution, after removing the silver chloride, decompose spontaneously:

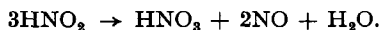


The silver salt has been shown by infrared spectroscopy to have anions with the *trans* configuration.

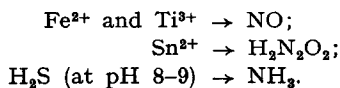


*Nitroxyl acid*,  $\text{H}_2\text{NO}_2$ , has not been made; but the yellow sodium salt  $\text{Na}_2\text{NO}_2$  is produced by the electrolysis of  $\text{NaNO}_2$  in liquid ammonia, or by the reduction of  $\text{NaNO}_2$  with sodium in the same solvent. The salt decomposes at  $100^\circ$ , giving  $\text{Na}_2\text{O}$ ,  $\text{NaNO}_2$ ,  $\text{NaNO}_3$  and nitrogen.

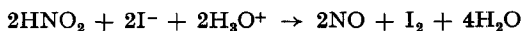
*Nitrous acid*,  $\text{HNO}_2$ , can be made in aqueous solution by dissolving a mixture of  $\text{NO}$  and  $\text{NO}_2$  in ice-cold water. Though the acid is known only in solution, its salts and esters are moderately stable. The Group IA and Group IIA nitrites are thermally stable, being made by heating the nitrate alone or with a reducing agent like carbon. Nitrous acid is a fairly strong acid ( $\text{p}K_a = 3.3$  at  $18^\circ$ ). The solution decomposes slowly:



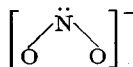
It is easily oxidised to nitric acid; but it is also easily reduced to  $\text{NO}$ ,  $\text{N}_2\text{O}$ ,  $\text{H}_2\text{N}_2\text{O}_2$ ,  $\text{NH}_2\text{OH}$ ,  $\text{N}_2$  or  $\text{NH}_3$ , depending on the reducing agent used:



The reaction



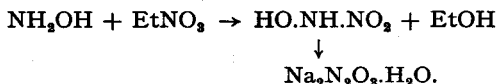
is quantitative and can be used for the determination of  $\text{NO}_2^-$  ion. The nitrite ion is angular: the nitrogen atom has three  $\text{sp}^2$  orbitals, one containing the lone-pair electrons:



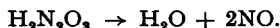
Nitrite esters can usually be made by treating the alcohols with acidified sodium nitrite at  $0^\circ$ .

*Hyponitric acid*,  $\text{H}_2\text{N}_2\text{O}_3$ , is very unstable, but its sodium salt can be made

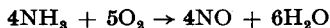
as the monohydrate by treating free hydroxylamine in methanol with ethyl nitrate in the presence of sodium methoxide:



On acidification decomposition occurs:



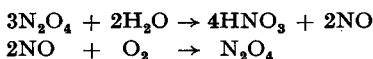
*Nitric acid*,  $\text{HNO}_3$ , is made industrially from synthetic ammonia. The ammonia is oxidised in a stream of air on the surface of a hot platinum gauze to nitric oxide:



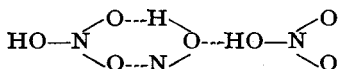
The nitric oxide air mixture is cooled, when the nitric oxide is oxidised to an equilibrium mixture of nitrogen dioxide and dinitrogen tetroxide:



The equilibrium mixture is dissolved in water in the presence of air, when consecutive reactions occur until all the oxides of nitrogen are converted to nitric acid:

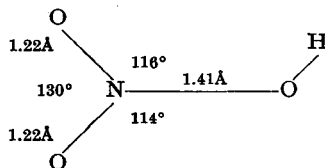


The pure acid exists as white crystals, m.p.  $-41^\circ$ . Melting these gives a faintly yellow liquid which shows weak Raman lines at  $1050 \text{ cm}^{-1}$  and  $1400 \text{ cm}^{-1}$ , indicating some dissociation to  $\text{NO}_2^+$  and  $\text{NO}_3^-$  has occurred. The liquid, which has a density of 1.54 at  $0^\circ$ , boils at  $83^\circ$ . Crystalline hydrates are formed, such as  $\text{HNO}_3 \cdot \text{H}_2\text{O}$ , m.p.  $-38^\circ$ , sometimes called the ortho-acid, and  $\text{HNO}_3 \cdot 3\text{H}_2\text{O}$ , m.p.  $-18.5^\circ$ . The acid is extracted from 6–16 *M* aqueous solution into benzene or toluene as the hemihydrate:



Nitric acid forms a constant-boiling mixture with water, of composition 68.4%  $\text{HNO}_3$  and b.p.  $121.9^\circ$ . Concentration can be effected by distillation with  $\text{H}_2\text{SO}_4$ .

The gaseous molecule is planar:



Bonding to the nitrogen atom is evidently through  $sp^2$  hybrid orbitals, the remaining p electrons being used in  $\pi$  bond formation in which all the oxygens participate. There is no satisfactory explanation of the fact that the O—N—O angle nearest the hydrogen atom is rather larger than that on the other side. Any intramolecular hydrogen-bonding would be expected to reduce the angle a little.

Liquid nitric acid and its strong aqueous solutions decompose, particularly on exposure to light, to give  $N_2O_4$ , oxygen and water. A solution of  $N_2O_4$  in anhydrous nitric acid constitutes fuming nitric acid. When  $HNO_3$  acts as an oxidising agent the usual products are NO from the dilute acid and  $N_2O_4$  from the concentrated acid, but other products, such as  $N_2O$ ,  $NH_2OH$  and  $NH_3$ , can be obtained under appropriate conditions. The oxidising action is catalysed by the presence of  $N_2O_4$ .

### Oxoacids of phosphorus

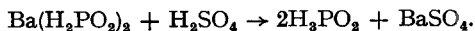
The acids can be classified according to the formal charge number of the phosphorus (Table 81). In them the phosphorus atoms always have four  $sp^3$  bonds.

TABLE 81  
OXOACIDS OF PHOSPHORUS

Charge number	Formula	Name
+1	$H_3PO_2$	Hypophosphorous acid
+3	$HPO_3$	Meta-
	$H_4P_2O_5$	Pyro-
	$H_3PO_3$	Ortho-
		} phosphorous acids
+4	$H_4P_2O_6$	Hypophosphoric acid
+5	$HPO_3$	Meta-
	$H_4P_2O_7$	Pyro-
	$H_3PO_4$	Ortho-
		} phosphoric acids

The peroxy-acids are dealt with elsewhere (p. 511).

*Hypophosphorous acid*,  $H_3PO_2$ , is made by acidifying, with dilute sulphuric acid, the barium hypophosphite solution obtained when white phosphorus is dissolved in hot baryta water:



It can be separated as deliquescent, colourless crystals, m.p.  $26.5^\circ$ . Raman spectra, X-ray analysis of its salts and a uniformly monobasic character

show it to have the structure represented in Fig. 245. In this the hydrogen atom of the OH is ionisable and the anion is  $\text{H}_2\text{PO}_2^-$ ; this is tetrahedral.

The acid ionises fairly strongly in water ( $\text{p}K_a = 2$ ). Both acid and salts are strong reducing agents:

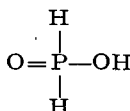
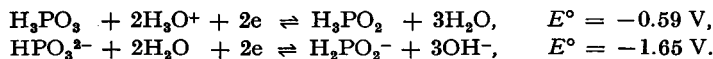


Fig. 245.

Structure of hypophosphorous acid.

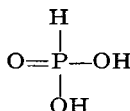
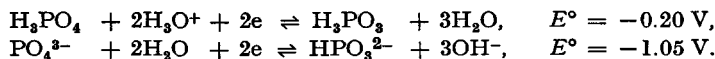


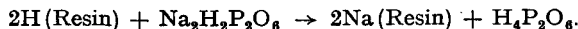
Fig. 246. Suggested structure of orthophosphorous acid.

*Orthophosphorous acid*,  $\text{H}_3\text{PO}_3$ , can be made by hydrolysing  $\text{PCl}_3$  with ice-cold water. The solid (m.p.  $70^\circ$ ) can be crystallised from solution. Nuclear magnetic resonance spectroscopy of the acid and of its salts and esters shows that there is one hydrogen atom directly linked to phosphorus (Fig. 246). This hydrogen, like the corresponding hydrogen atoms in hypophosphorous acid, is not ionised.

The first ionisation constant of  $\text{H}_3\text{PO}_3$  is higher than that of  $\text{H}_3\text{PO}_4$  ( $\text{p}K_a = 2$ ). Both orthophosphorous acid and its salts are strong reducing agents:

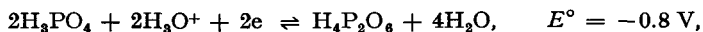


*Hypophosphoric acid*,  $\text{H}_4\text{P}_2\text{O}_6$ , can be prepared as a dihydrate from the solution obtained when  $\text{Na}_2\text{H}_2\text{P}_2\text{O}_6$  is poured through a column of cation-exchange resin in its hydrogen form:



The sodium salt is made by the action of alkaline, aqueous  $\text{NaOCl}$  on red phosphorus.

The acid is tetrabasic, but the commonest salts are those in which only two of the hydrogens are replaced. Both acid and salts are remarkably stable towards oxidising and reducing agents. For the reaction



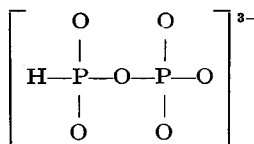
and for



Support for the formula  $\text{H}_4\text{P}_2\text{O}_6$  comes from cryoscopic and Raman evidence



and from the diamagnetism of the salts. The  $^{31}\text{P}$  n.m.r. spectrum shows the structure to contain one  $\text{H}-\text{P}$  bond and a  $\text{P}-\text{O}-\text{P}$  linkage. Accordingly, the structure



is proposed for the ternegative anion,  $\text{HP}_2\text{O}_6^{3-}$ .

### Phosphoric acids

The  $\text{P}_4\text{O}_{10}-\text{H}_2\text{O}$  system is complex. Analysis of mixtures containing more than 72.4%  $\text{P}_4\text{O}_{10}$  shows that the relative amounts of condensed acids, such as  $\text{H}_4\text{P}_2\text{O}_7$ ,  $\text{H}_5\text{P}_3\text{O}_{10}$  and  $\text{H}_6\text{P}_6\text{O}_{18}$ , vary considerably with composition. The mixtures are not composed simply of  $\text{H}_3\text{PO}_4$  and  $\text{P}_4\text{O}_{10}$ .

*Orthophosphoric acid*,  $\text{H}_3\text{PO}_4$ , a colourless solid, m.p.  $42.4^\circ$ , is made by removing water from syrupy phosphoric acid under reduced pressure. The arrangement of oxygen atoms round the phosphorus atom in this tribasic acid is only approximately tetrahedral (Fig. 247),

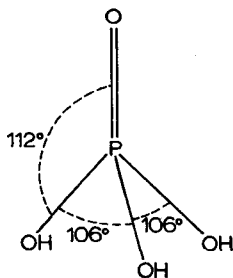


Fig. 247.

Structure of orthophosphoric acid.

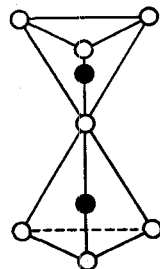


Fig. 248.

$\text{PO}_4$  tetrahedra in  $\text{P}_3\text{O}_7^{4-}$  ion.

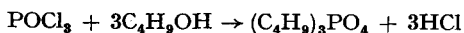
the  $\text{P}-\text{O}-\text{H}$  angles being  $106^\circ$  and the  $\text{P}=\text{O}$  angles,  $112^\circ$ . The 'keto' oxygen is attached to an adjacent 'hydroxo' oxygen by a hydrogen bond.

### Phosphates

These salts form the phosphorus minerals of which apatite,  $3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaF}_2$ , is the most important. It is the source of phosphorus, superphosphate (p. 426) and phosphoric acid. The last is made by treating apatite with concentrated sulphuric acid and filtering off the insoluble calcium sulphate.

Much sodium phosphate is used in water treatment. Most of the heavy metals give insoluble phosphates, and can be removed from water in that form.

There are many esters of orthophosphoric acid of which tri-*n*-butyl phosphate (TBP) is the best known because it has been extensively used in the solvent extraction of metal salts from aqueous solution. TBP is made by treating  $\text{POCl}_3$  with the alcohol:



It is used in a kerosene solution and extracts such nitrates as  $\text{UO}_2(\text{NO}_3)_2$  and  $\text{PuO}_2(\text{NO}_3)_2$  from dilute nitric acid as  $\text{MO}_2(\text{NO}_3)_2 \cdot 2\text{TBP}$ . By washing this loaded organic phase with 0.1 *M*  $\text{HNO}_3$  containing a reducing agent,  $\text{Pu}^{\text{VI}}$  is reduced to  $\text{Pu}^{\text{III}}$  and enters the aqueous phase, leaving the  $\text{U}^{\text{VI}}$  still unreduced as the TBP solvate in the kerosene. From this the uranium can be removed by washing the organic phase with water in which the salt  $\text{UO}_2(\text{NO}_3)_2$ , essential to the TBP solvate, is ionised and goes into solution.

*Pyrophosphoric acid*,  $\text{H}_4\text{P}_2\text{O}_7$ , is the colourless solid crystallised from an 80%  $\text{P}_4\text{O}_{10}$  solution which contains  $\text{H}_3\text{PO}_4$  and  $\text{H}_5\text{P}_3\text{O}_{10}$  in addition to  $\text{H}_4\text{P}_2\text{O}_7$ . The first dissociation constant of  $\text{H}_4\text{P}_2\text{O}_7$  is higher than that of the ortho acid ( $\text{p}K_a = 0.8$ , cf.  $\text{p}K_a = 2.1$  for  $\text{H}_3\text{PO}_4$ ). All the hydrogens are replaceable, but the commonest pyrophosphates are  $\text{M}^{\text{I}}\text{H}_2\text{P}_2\text{O}_7$  and  $\text{M}^{\text{II}}\text{P}_2\text{O}_7$ . These contain the anion  $\text{P}_2\text{O}_7^{4-}$  (Fig. 248).

*Metaphosphoric acids* of empirical formula  $\text{HPO}_3$  may be obtained on further dehydration of  $\text{H}_3\text{PO}_4$  by heating at  $316^\circ$ . Their nature is in doubt; the existence of a monomer is unlikely, for the vapour is believed to be dimeric even at white heat. The metaphosphates of sodium have been studied in some detail. The sparingly soluble Maddrell's salt, made by heating  $\text{NaH}_2\text{PO}_4$  at  $315^\circ$ , is thought to be a mixture of two salts of similar, but not identical, structures. A trimetaphosphate  $\text{Na}_3(\text{PO}_3)_3$  is obtained by heating  $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$ . The  $\text{P}_3\text{O}_9^{3-}$  anion consists of three  $\text{PO}_4^{3-}$  tetrahedra joined through common oxygen atoms (Fig. 249).

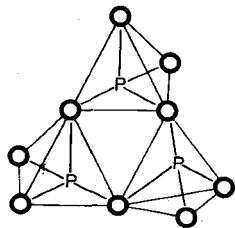


Fig. 249. Structure of  $\text{P}_3\text{O}_9^{3-}$  ion.

The compound known as sodium hexametaphosphate is made by rapidly cooling molten metaphosphate. It is best considered as a metaphosphate glass. The material is soluble and acts as a water softener, removing  $\text{Ca}^{2+}$  ion from solution by chelation to the colloidal polyanions:

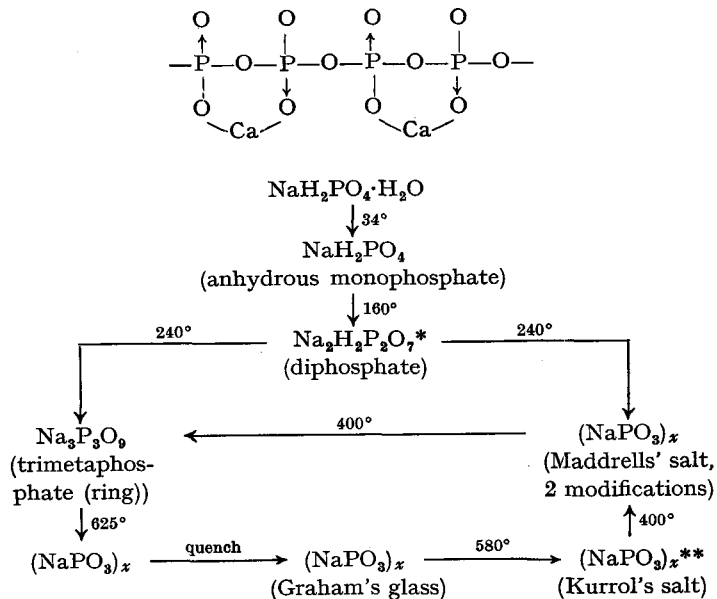


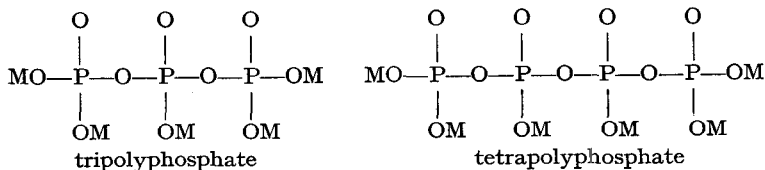
Fig. 250. Condensed phosphates obtained by heating  $\text{NaHPO}_4 \cdot \text{H}_2\text{O}$ .

\* Proportions depend on water vapour pressure.

\*\* Tempering just below the melting point and inducing crystallisation by local cooling.

### Polyphosphates

The term polyphosphate is usually applied to salts of the chain-like ions  $[\text{P}_n\text{O}_{3n+1}]^{-n-2}$ :



The  $^{31}\text{P}$  n.m.r. spectra have been of value in elucidating the structures of these ions.

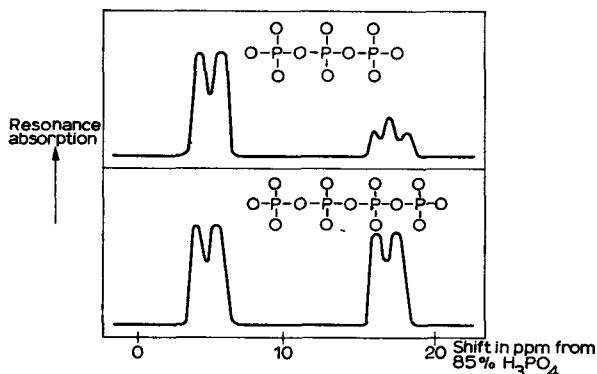


Fig. 251.  $^{31}\text{P}$  n.m.r. spectra of triphosphate and tetraphosphate ions.

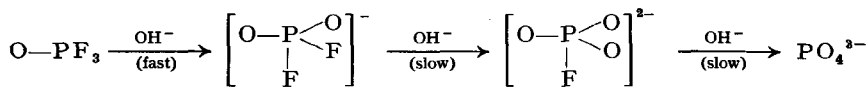
The absorption peaks on the left of Fig. 251 are due to  $^{31}\text{P}$  atoms in end groups of the tri- and tetraphosphate ions. They are doublets, indicating that each  $^{31}\text{P}$  atom is attached to one other  $^{31}\text{P}$  neighbour in an environment different from its own. The absorption peak at the top right encloses only half the area of the one below it and is a 1.2.1 triplet, indicating that one  $^{31}\text{P}$  atom is attached to two others which are in different chemical environments from itself.

The peak on the right of the tetraphosphate curve covers the same area as that on the left, indicating that there are as many middle  $^{31}\text{P}$  groups as end ones in this ion, namely two. The doublet form indicates that each is attached to only one other  $^{31}\text{P}$  atom which has an environment different from its own (p. 18).

Polyphosphates are added to detergents for the removal of surface dirt. They are strongly adsorbed on the dirt particles which they thus render hydrophilic.

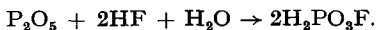
#### Fluorophosphoric acids

Phosphoryl fluoride,  $\text{POF}_3$ , hydrolyses in alkaline solutions in the following manner:



The last two stages of hydrolysis are so slow that salts of the fluorophosphoric acid,  $\text{HPO}_2\text{F}_2$ , can be separated from the solution, but the acid itself has not been made. The ammonium salt of the acid,  $\text{NH}_4\text{PO}_2\text{F}_2$ , can also be obtained by fusing together  $\text{NH}_4\text{F}$  and  $\text{P}_2\text{O}_5$ .

The acid  $\text{H}_2\text{PO}_3\text{F}$  is produced as an oily liquid from a mixture of  $\text{P}_2\text{O}_5$  and concentrated aqueous  $\text{HF}$ :



### Sulphur compounds of nitrogen and phosphorus

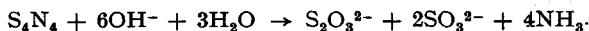
#### *Sulphur nitrides*

Sulphur lies between nitrogen and phosphorus in electronegativity. Thus binary sulphur–nitrogen compounds are correctly named sulphur nitrides. On the other hand, sulphur–phosphorus compounds are named phosphorus sulphides.

Tetrasulphur tetranitride,  $\text{S}_4\text{N}_4$ , is produced when dry  $\text{NH}_3$  is passed into a solution of  $\text{S}_2\text{Cl}_2$  in dry ether, separating as orange crystals, m.p.  $178^\circ$ .



The compound is diamagnetic and strongly endothermic. It explodes on heating, is soluble in many organic solvents, and is attacked slowly by water which does not wet it easily. Boiling alkalis cause hydrolysis:



Electron and X-ray diffraction show all the bonds to be equal in length and the interbond angles  $\text{NSN} = 104^\circ$  and  $\text{SNS} = 113^\circ$ . The probable form of the molecule is an eight-membered 'cradle' ring (Fig. 252). It is the

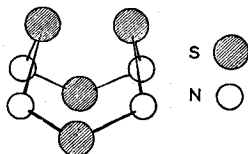
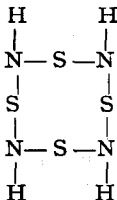
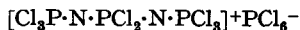


Fig. 252. Cradle-shaped structure of  $\text{S}_4\text{N}_4$  molecule.

parent substance of other sulphur nitrides and derivatives of sulphur nitrides. Thus the ring can be split by heating to give white disulphur dinitride,  $\text{S}_2\text{N}_2$ , also soluble in organic solvents, which is converted into the insoluble dark-blue polymer,  $(\text{SN})_n$ , at room temperature. Moreover,  $\text{S}_4\text{N}_4$  can be reduced by tin(II) chloride to tetrasulphur tetraimide:



An interesting reaction of  $S_4N_4$  is that with  $PCl_3$  to give the compound  $P_4N_2Cl_{14}$  which has a complex cation:



### Phosphorus sulphides

There are four sulphides of phosphorus,  $P_4S_3$ ,  $P_4S_5$ ,  $P_4S_7$  and  $P_4S_{10}$ . The last is the only sulphide with a structure similar to that of an oxide. The structural relationship of the sulphides to the  $P_4$  molecule and to one another is clearly shown in Fig. 253 where the dark circles stand for phosphorus atoms.

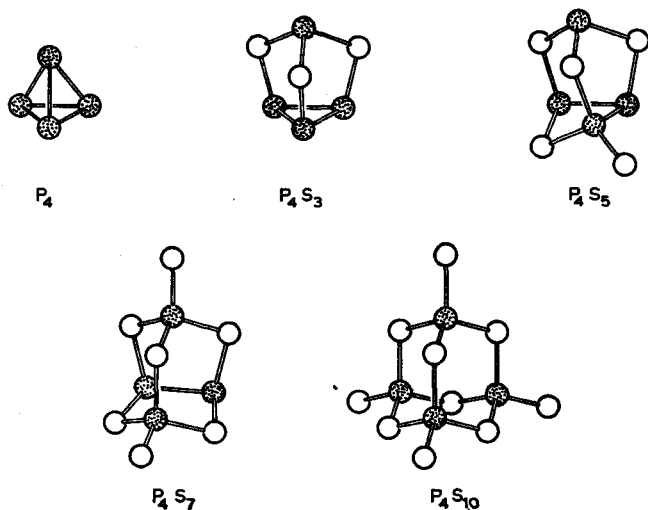


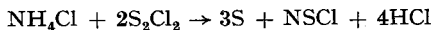
Fig. 253. Structures of phosphorus sulphides. (By courtesy of S. van Houten.)

The sulphide  $P_4S_3$ , made by heating red phosphorus with sulphur in an atmosphere of  $CO_2$ , is the yellow crystalline solid, m.p.  $174^\circ$ , used in 'strike-anywhere' matches. The other sulphides have a similar physical appearance, somewhat higher melting points and much lower stabilities.  $P_4S_3$  is attacked only very slowly by cold water and cold  $HCl$ , but decomposed by hot water to give  $H_2S$ ,  $PH_3$  and phosphorus oxo-acids. Cold  $HNO_3$  converts it to  $H_3PO_4$ ,  $H_2SO_4$  and sulphur; aqueous  $KOH$  produces  $PH_3$ , hydrogen, and the phosphite, hypophosphite and sulphide ions.

### Thiohalides

The compound thiazyl chloride,  $NSCl$ , the sulphur analogue of nitrosyl

chloride, NOCl, is made from a suspension of  $\text{NH}_4\text{Cl}$  in refluxing  $\text{S}_2\text{Cl}_2$ ; and by other methods.



Phosphorus does not form a corresponding compound, but the thiophosphoryl halides are known:

	B.p.
$\text{PSF}_3$	$-53^\circ$
$\text{PSCl}_3$	$+125^\circ$
$\text{PSBr}_3$	$+175^\circ$ (with decomposition)

Also there are 'mixed' halides corresponding to the phosphoryl halides such as  $\text{POF}_2\text{Cl}$  (p. 441).

$\text{PSCl}_3$  is made by heating  $\text{P}_2\text{S}_5$  with  $\text{PCl}_3$ , and  $\text{PSBr}_3$  by the action of bromine on a solution of sulphur and phosphorus in  $\text{CS}_2$ . Both can be converted to 'mixed' fluorides or to  $\text{PSF}_3$  by the action of  $\text{SbF}_3$ , according to the conditions. The molecules are similar to those of  $\text{POX}_3$  (p. 441) with P—S 1.94 Å, indicating a double bond, in  $\text{PSCl}_3$  and  $\text{PSBr}_3$ , but down to 1.85 Å in  $\text{PSF}_3$ , indicating some triple-bond character in the fluorine compound.

### Nitrides

The nitrides are of three types; these are the ionic, the covalent and the interstitial.

*Ionic nitrides.* These contain the  $\text{N}^{3-}$  ion, of radius 1.71 Å; this, incidentally, is the only simple ternegative ion known. Lithium nitride,  $\text{Li}_3\text{N}$ , made from the elements, with a heat of formation of 47.2 kcal, is the only exothermic and thermally stable nitride of Group I. The explosive  $\text{Na}_3\text{N}$ ,  $\text{K}_3\text{N}$  and  $\text{Rb}_3\text{N}$  are produced when an arc is struck between a Pt cathode and an alkali metal anode under liquid nitrogen. Beryllium, magnesium and other Group IIA elements form ionic nitrides, like lithium, when heated in nitrogen.  $\text{Be}_3\text{N}_2$  and  $\text{Ca}_3\text{N}_2$  have the highest heats of formation, 135.7 kcal and 103.2 kcal respectively. The ionic nitrides are hydrolysed to the hydroxides and ammonia.

*Covalent nitrides.* These include volatile compounds of nitrogen with hydrogen, the halogens and carbon respectively and also involatile, high-melting, adamantine compounds formed by nitrogen with Group III elements, as typified by aluminium nitride, AlN. Boron nitride, BN, has an adamantine form, borazon, produced at high pressure, as well as the usual form which is similar in structure to graphite. The latter is used as an anti-sticking

compound in glass-makers' moulds and also for coating crucible linings, since it is not wetted by molten iron. Boron nitride is readily made by heating  $B_2O_3$  and  $NH_4Cl$  together, the product being a white powder. Silicon nitride,  $Si_3N_4$  ( $\Delta H_f^\circ = -179$  kcal), is a commercial product manufactured by converting silicon tetrachloride to the amide with ammonia and then decomposing the amide by heat:



*Interstitial nitrides.* The transition metals, including those of Group IIIA, form true interstitial compounds (p. 199), many with the composition MN and the NaCl structure. Other interstitial nitrides,  $Mo_2N$ ,  $W_2N$ ,  $Fe_4N$  and  $Mn_4N$ , are hard, high-melting, good conductors of metallic appearance, commonly made by heating the powdered metal in nitrogen or ammonia at about  $1200^\circ$ . They vary considerably in thermal stability, reactivity and ease of hydrolysis, and are less thermally stable than the corresponding metal oxides. For some elements the nitride, oxide and carbide are isomorphous, an example being TiN, TiO and TiC. Heats of formation are often high in spite of the high dissociation energy of molecular nitrogen. Some interstitial nitrides are conveniently made by ammonolysis of halides in liquid ammonia, the amides first formed being converted to nitrides on heating. Another method is to effect simultaneous reduction and nitriding by heating the oxide, for instance iron oxide, in ammonia.

### Phosphides

A mixture of sodium phosphides is made by direct combination between the elements. It appears to contain  $Na_3P$  and  $Na_5P_2$  and is used for sea flares, since with water it produces a mixture of hydrogen phosphides which is spontaneously inflammable in air. Also used for the same purpose are  $Mg_3P_2$  and  $Zn_3P_2$ , made by warming intimate mixtures of the elements, and  $Ca_3P_2$ , made by heating CaO in phosphorus vapour. Thus prepared, calcium phosphide always contains some phosphate.

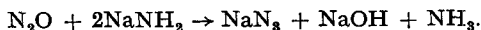
Ferrophosphorus contains the phosphides  $Fe_2P$  and  $FeP$ . These phosphides and those of the other transition metals are dark-coloured, metal-like solids which are not attacked by water. They conduct electricity.

### Formal derivatives of ammonia

#### *Hydrazoic acid*

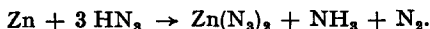
Hydrazoic acid,  $HN_3$ , is present in the aqueous distillate from the action of  $NaN_3$  on dilute  $H_2SO_4$ . Sodium azide for the purpose is made by passing  $N_2O$  over sodium amide at  $190^\circ$ :





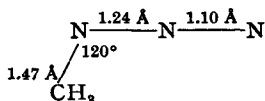
The pure liquid, b.p.  $37^\circ$ , is obtained by fractionating the distillate and drying the concentrated acid over  $\text{CaCl}_2$ . Hydrazoic acid is a colourless, mobile liquid, easily exploded by shock. The vapour is monomeric.

The acid dissociates only slightly in aqueous solution ( $\text{p}K_a = 4.7$ ). Metals dissolve with the evolution of  $\text{NH}_3$  and  $\text{N}_2$ :

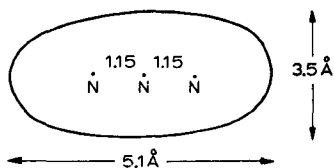


Crystalline salts are formed with ammonia,  $\text{NH}_4 \cdot \text{N}_3$  (empirically  $\text{N}_4\text{H}_4$ ), and with hydrazine,  $\text{NH}_2 \cdot \text{NH}_3 \cdot \text{N}_3$  (empirically  $\text{N}_5\text{H}_5$ ). Other azides are the explosive chloroazide  $\text{ClN}_3$  (gas), bromoazide  $\text{BrN}_3$  (orange liquid), and iodoazide  $\text{IN}_3$  (yellow solid). The first and second can be made from  $\text{NaN}_3$  by treating it with sodium hypochlorite and bromine respectively.

Fully ionised azides like those of the Group I metals and barium are non-explosive and yield nitrogen and the metal on heating. But  $\text{LiN}_3$  is an exception; it is converted to the nitride. The covalent azides, such as those of organic radicals and of Ag, Cu, Tl, Pb and Hg, are explosive. In these compounds the nitrogen atoms are arranged collinearly but the molecule is unsymmetrical:



In solid inorganic azides, the  $\text{N}_3^-$  ion is linear and symmetrical:

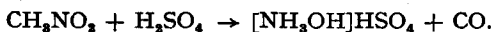


In shape it is approximately an ellipsoid of revolution with axes 5.1, 3.5 and  $3.5 \text{ \AA}$ ; the nitrogen nuclei embedded in this electron cloud are  $1.15 \text{ \AA}$  apart. The individual gaseous ion, which has been detected by mass spectrometry, probably has the same structure.

### *Hydroxylamine*

Hydroxylamine,  $\text{NH}_2\text{OH}$ , is a colourless solid, m.p.  $33^\circ$ , very soluble in water and the lower alcohols, less so in other organic liquids. The hydrogen

sulphate,  $[\text{NH}_3\text{OH}]\text{HSO}_4$ , is made industrially by adding concentrated  $\text{H}_2\text{SO}_4$  to refluxing nitromethane at  $110\text{--}120^\circ$ :



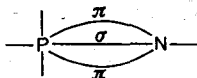
This hydrogen salt is converted to the normal sulphate  $[\text{NH}_3\text{OH}]_2\text{SO}_4$  by the action of 85% methanol, and the sulphate is converted to the chloride by dissolving it in hot, concentrated HCl and crystallising the chloride from the solution:



When the chloride is added to sodium methoxide in methanol and the precipitated NaCl is filtered off, a solution is obtained from which free  $\text{NH}_2\text{OH}$  can be crystallised at  $-10^\circ$  to  $-20^\circ$ . Before reaching its m.p., the compound decomposes into  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ ,  $\text{N}_2\text{O}$  and NO. It is a weak monoacid base without acidic properties. Like its aquo analogue,  $\text{H}_2\text{O}_2$ , and its ammono analogue hydrazine,  $\text{N}_2\text{H}_4$  (p. 286), hydroxylamine can act either as an oxidising or a reducing agent according to the circumstances.

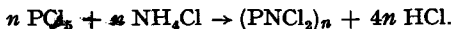
### Phosphonitrilic compounds

Compounds of phosphorus and nitrogen based on the  $\pi$ -bonded unit



have attracted attention because they form polymers with properties which might be useful at high temperatures. The materials range from fluids possibly useful for heat transfer and lubrication, to solids with some mechanical characteristics of organic polymers. They show similarities to aromatic compounds, although the  $\pi$ -bonding is somewhat different.

Phosphonitrilic chlorides were first prepared by the ammonolysis of phosphorus pentachloride; dry distillation gives a mixture of  $(\text{PNCl}_2)_3$  and  $(\text{PNCl}_2)_4$ :

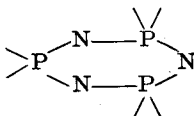


The method was improved by dissolving the  $\text{PCl}_5$  in tetrachloroethane; this increases the yield of higher polymers. The product is a liquid mixture of polymers from which the excess of  $\text{NH}_4\text{Cl}$  is removed by filtration. The filtrate is mainly  $(\text{PNCl}_2)_3$ , but other polymers, up to  $(\text{PNCl}_2)_6$ , are also present. Concentrating the liquid under reduced pressure gives a material, part of which is insoluble in petroleum ether and is believed to be a mixture

of linear polymers,  $\text{PCL}_4(\text{PNCl}_2)_n\text{Cl}$ , but most of which is soluble in that solvent and consists of cyclic  $(\text{PNCl}_2)_n$  polymers.

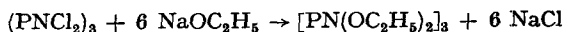
The preparative reaction is very versatile; the phenyls,  $(\text{PNPh}_2)_{3,4}$ , can be obtained from  $\text{Ph}_2\text{PCl}_3$  and the methyls,  $(\text{PNMe}_2)_{3,4}$ , from  $\text{Me}_2\text{PCl}_3$ . Bromides and mixed halides can also be made.

The trimeric compounds have a planar  $\text{P}_3\text{N}_3$  ring

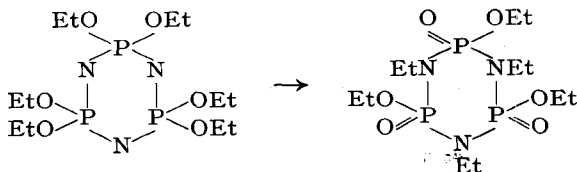


in which the hybrid P—N bonds are all equal in length (1.60 Å) and shorter than the P—N bond (1.78 Å) in the phosphoramidate ion,  $\text{NH}_2\text{PO}_3^{2-}$ . They are comparatively inert compounds, thermally stable and not readily hydrolysed; they can be steam-distilled without serious loss. The crystalline trimer (and also the tetramer) can be further condensed to rubber-like materials, of molecular weight  $> 20,000$ , by heating at  $\sim 300^\circ$ . Unfortunately, however, the elastic properties are lost on exposure to damp air.

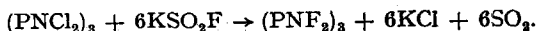
Although the chloro-compounds are much less reactive than is usual for phosphorus-chlorine compounds, they react smoothly with alcohols and alkoxides:



This product is a clear, viscous oil which changes to a gel on standing. Ammonia and amines produce compounds such as  $[\text{PN}(\text{NH}_2)_2]_3$  and  $[\text{PN}(\text{NH}\cdot\text{C}_6\text{H}_5)_2]_3$ , and some or all of the chlorine in  $(\text{PNCl}_2)_3$  can be replaced to give such compounds as  $[\text{PNCl}(\text{Me}_2\text{N})]_3$ ,  $\text{P}_3\text{N}_3\text{Cl}_4\text{Ph}_2$ , and  $[\text{PN}(\text{MeO})_2]_3$ . At  $200^\circ$   $[\text{PN}(\text{OC}_2\text{H}_5)_2]_3$  isomerises thus:



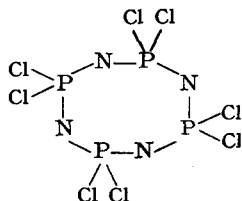
The bromo-compounds  $(\text{PNBr}_2)_3$  and  $(\text{PNBr}_2)_4$  are formed when  $\text{NH}_4\text{Br}$  replaces  $\text{NH}_4\text{Cl}$  in the preparative reaction; the fluoro-analogues are, however, made by the action of potassium fluorosulphite on  $(\text{PNCl}_2)_3$  at  $120^\circ$ :



The fluoro-trimer, m.p.  $\sim 18^\circ$ , b.p.  $51^\circ$ , is insoluble in polar liquids, even in

concentrated  $\text{H}_2\text{SO}_4$ . By contrast,  $(\text{PNMe}_2)_3$ , m.p.  $195^\circ$ , dissolves readily in water.

The tetramer formed in the preparative reaction with  $\text{NH}_4\text{Cl}$  is also cyclic, but the ring is puckered, not planar as with the trimer  $(\text{PNCl}_2)_3$ :



However, the compound  $(\text{PNF}_2)_4$ , made by treating  $(\text{PNCl}_2)_4$  with  $\text{KSO}_2\text{F}$ , is planar; this indicates that the substituents, as well as the ring size, are important in determining whether the ring is puckered or flat. A chlorofluoropolymer,  $(\text{PNFCl})_4$ , is made by heating the trimer  $(\text{PNCl}_2)_3$  with  $\text{PbF}_2$ . This is the only reaction yet reported by which a phosphonitrilic ring can be enlarged. All the possible trimeric and tetrameric phosphonitrilic fluoride chlorides have now been obtained. Chlorine in the tetramer  $(\text{PNCl}_2)_4$  can be substituted to give  $(\text{PNPhCl})_4$  by treatment with  $\text{PhMgBr}$ , and  $[\text{PN}(\text{NHPh})_2]_4$  by treatment with  $\text{PhNH}_2$ .

Bonding in the trimeric cyclic phosphonitrilic halides is interesting. Four electrons of the individual nitrogen atoms may be considered to occupy approximately  $\text{sp}^3$  hybrid orbitals, one in every P—N bond and two in a lone pair. The fifth electron, in a  $p_x$  orbital, is available for  $\pi$  bond formation. The individual phosphorus atoms have four electrons arranged approximately tetrahedrally in  $\sigma$  bonds, leaving the fifth electron, in a d orbital, available for  $\pi$  bonding. Overlap results in  $d\pi-p\pi$  bonding; this is unlike the  $\pi$  bonds in benzene which arise from an overlap of p orbitals only

#### FURTHER READING

- K. R. JENNINGS AND J. W. LINNETT, *Active Nitrogen*, *Quart. Rev.*, **12** (1958) 116.
- C. B. COLBURN (Ed.), *Developments in Inorganic Nitrogen Chemistry*, Amsterdam, Elsevier, Vol. 1 (1966), Vol. 2 (in preparation).
- I. R. BEATTIE, *Dinitrogen Trioxide* in F. A. COTTON (Ed.), *Progress in Inorganic Chemistry*, Vol. 5, London, Interscience, 1963, p. 1.
- P. GRAY, *The Chemistry of Dinitrogen Tetroxide*, Royal Institute of Chemistry Monograph, London, 1958, No. 4.
- C. C. ADDISON AND J. LEWIS, *The Chemistry of the Nitrosyl Group*, *Quart. Rev.*, **9** (1955) 115.

- B. O. FIELD AND C. J. HARDY, *Inorganic Nitrates and Nitrate-compounds*, Quart. Rev., 18 (1964) 361.
- P. GRAY, *Chemistry of the Inorganic Azides*, Quart. Rev., 17 (1963) 441.
- N. L. PADDOCK, *Structure and Reactions in Phosphorus Chemistry*, Royal Institute of Chemistry Monograph, London, 1962, No. 2.
- S. B. HARTLEY, W. S. HOLMES, J. K. JACQUES, M. F. MOLE AND J. C. MCCOUBREY COUBREY, *Thermochemical Properties of Phosphorus Compounds*, Quart. Rev., 17 (1963) 204.
- N. L. PADDOCK, *Phosphonitrilic Derivatives and Related Compounds*, Quart. Rev., 18 (1964) 211.
- C. C. ADDISON AND N. LOGAN, *Anhydrous Metal Nitrates*, in H. J. EMELÉUS AND A. G. SHARPE (Eds.), *Advances in Inorganic Chemistry and Radiochemistry*, New York, Academic Press, Vol. 6 (1964) 71.
- R. F. HUDSON, *The Structure and Reactivity of Organophosphorus Compounds*, *ibid.*, Vol. 5 (1963) 347.
- B. F. G. JOHNSON AND J. A. MCCLEVERTY, *Nitric Oxide Complexes of Transition Metals*, in F. A. COTTON (Ed.), *Progress in Inorganic Chemistry*, New York, Interscience, Vol. 7 (1966) 277.

Chapter 23

**Arsenic, Antimony and Bismuth**

GROUP VB

The elements of Group VB, like nitrogen and phosphorus, have the  $ns^2np^3$  electron configuration and the  $^4S$  ground state which indicates three singly-occupied orbitals. Arsenic, antimony and bismuth differ from nitrogen and phosphorus, however, in having a lower electronegativity, which decreases with increasing atomic number. They are dominantly trivalent elements and tend to form three electron-pair bonds roughly at right angles, leaving an  $ns^2$  lone pair; but some hybridisation occurs and results in distortion towards more nearly tetrahedral bonds (p. 118). All five valence electrons may, nevertheless, participate in bonding, d-hybridisation yielding bipyramidal, square pyramidal and octahedral sets of bonds. In many of these compounds the metal is described formally as having charge number +5 or +3, but the bonding is often mainly covalent; only in bismuth compounds is there any real approach to a simple cation. In solution the only ions which occur are  $M^{3+}$ , moreover they are hydrated.

TABLE 82  
ATOMIC PROPERTIES OF GROUP VB ELEMENTS

	<i>As</i>	<i>Sb</i>	<i>Bi</i>
Atomic number	33	51	83
Electron configuration	$4s^24p^3$	$5s^25p^3$	$6s^26p^3$
Covalent radius (Å)	1.19	1.38	1.46
Ionic radius, $M^{3+}$ (Å)	0.69	0.90	1.20
Metallic radius (Å)	1.39	1.59	1.70

The ionisation energies are high, as would be expected from the electron configuration, and the standard electrode potentials  $M^{3+}/M$  are all quite close together, diminishing ionisation energies apparently being offset by the increased ionic radii and reduced heats of hydration.

The 3rd, 4th and 5th ionisation energies of bismuth are larger than those of antimony. This, coupled with the greater size of the  $Bi^{3+}$ ,  $Bi^{4+}$  and  $Bi^{5+}$

ions, is the prime cause of the diminished stability of the +5 oxidation state of bismuth.

TABLE 83

IONISATION ENERGIES, ELECTRODE POTENTIALS AND  
ELECTRONEGATIVITIES OF GROUP VB ELEMENTS

	As	Sb	Bi
Ionisation energy $I$ (eV)	9.8	8.6	8.0
$E^\circ M^{3+}/M$ (V)	0.25	0.21	0.32
Electronegativity (Allred-Rochow)	2.20	1.82	1.67

### Thermodynamic stability of the oxidation states

The free energies, relative to the element, of the various oxidation states in solution at  $\text{pH} = 0$  are shown graphically in Fig. 254.

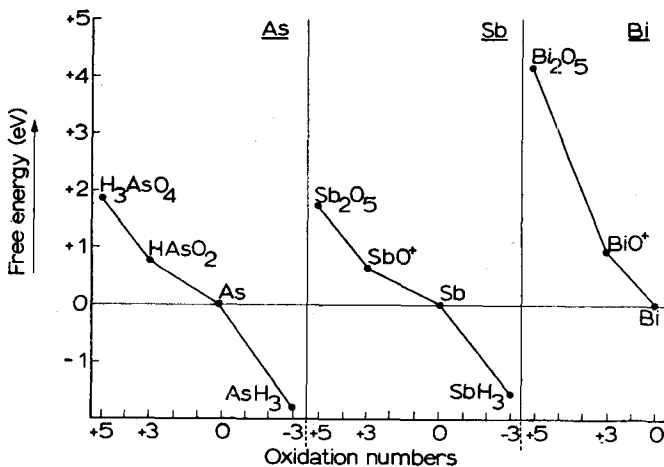
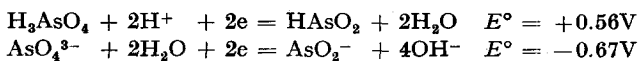


Fig. 254. Free energies, relative to the element, of the oxidation states of As, Sb and Bi at  $\text{pH} = 0$ .

For the three elements, the +3 state is stable with respect to disproportionation to the +5 state and the zero state. The redox potential for the  $\text{As}^{\text{V}}/\text{As}^{\text{III}}$  couple is strongly dependent on  $\text{pH}$ :



Thus in strongly acidic solution arsenic acid oxidises iodide to iodine ( $E^\circ \text{I}_2/\text{I}^- = 0.53\text{V}$ ) but in neutral and alkaline solutions iodine oxidises arsenite to arsenate.

Although the metals are most commonly depicted with charge numbers +5 or +3, their tendency towards non-metallic character is revealed in compounds with true metals. In such compounds as  $\text{Na}_3\text{As}$ ,  $\text{Mg}_3\text{Sb}_2$  and  $\text{K}_3\text{Bi}$ , many of which resemble the corresponding phosphides, the Gp.VB metal apparently accepts electrons to achieve a formal charge of -3.

### The elements

The elements well exemplify the trend towards a more metallic character with increasing atomic number; but even bismuth is not a true metal in the structural sense. The metallic allotropes of As, Sb and Bi consist of puckered sheets in which each atom is covalently bonded to three neighbouring atoms, the different sheets being held together by metallic binding. The 8-N rule (p. 134), which applies to most non-metallic solid elements, continues to operate. It is significant too that the elements are polyatomic in the vapour. Arsenic, for example, exists principally as tetrahedral  $\text{As}_4$  molecules at  $800^\circ$ ; at higher temperatures dissociation to  $\text{As}_2$  occurs but is incomplete even at  $1600^\circ$ . Antimony behaves similarly. Bismuth vapour is an equilibrium mixture of  $\text{Bi}_2$  and Bi, the former being in an appreciable proportion even at  $2000^\circ$ .

TABLE 84

PHYSICAL PROPERTIES OF GROUP VB METALS

	<i>As</i>	<i>Sb</i>	<i>Bi</i>
Density (g/cc)	5.7	6.6	9.8
Atomic volume	13.3	18.5	21.3
Melting point ( $^\circ\text{C}$ )	817 (36 atm.)	630	271
Boiling point ( $^\circ\text{C}$ )	616 (sublimes)	1440	1420

Both arsenic and antimony have yellow cubic  $\alpha$ -forms, soluble in  $\text{CS}_2$ . Yellow arsenic consists of tetrahedral  $\text{As}_4$  units (*cf.*  $\text{P}_4$ ); the  $\alpha$ -form of antimony is probably similar in structure but is unstable above  $-90^\circ$ . Black  $\beta$ -forms, analogous to amorphous phosphorus, result from rapid cooling of the vapours. They are metastable, changing rapidly at  $350\text{--}400^\circ$  into the  $\gamma$ -forms which are moderately good conductors of heat and electricity and exhibit metallic lustre, though brittle, easily fractured and of low ductility. Antimony and bismuth differ from normal metals in having



lower electrical conductivity as solids than as liquids; for Bi the conductance of the solid is only 0.48 of the liquid conductance. Bismuth also has the lowest thermal conductivity of any metal at the ordinary temperature.

The physical properties given in Table 84 are for the metallic forms. Arsenic sublimates at the ordinary pressure; the m.p. given is that for the element at 36 atm pressure.

### Occurrence, extraction and uses

The principal ore of arsenic ( $5 \times 10^{-4}$  % of earth's crust) is arsenical pyrites,  $\text{FeAsS}$ , but the element occurs commonly with nickel, copper and tin; The oxide,  $\text{As}_4\text{O}_6$ , is recovered from flue-dusts collected during the extraction of these metals. Sublimation of the crude material in the presence of galena, which prevents the formation of arsenites, purifies the oxide; this is then reduced to arsenic by carbon in a cast iron retort. The element itself has few uses; about 0.5% added to lead increases the surface tension of the molten metal and allows spherical lead-shot to be produced. The principal commercial form is the so-called white arsenic,  $\text{As}_4\text{O}_6$ . Arsenic compounds have been used mainly for their toxicity; arsenical insecticides were much used.

Antimony ( $5 \times 10^{-5}$  %) occurs as stibnite,  $\text{Sb}_2\text{S}_3$ , which is converted to the volatile oxide by roasting in air:



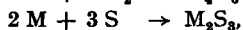
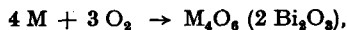
The sublimate can be reduced in a blast furnace similar to that used for smelting lead. The metal is alloyed with lead for electrical storage-battery plates and with tin in pewter, in both cases conferring greater hardness and mechanical strength. It is also used, with lead in corrosion-resistant piping, with lead and tin in type metals, and with tin, copper and lead in bearing metals. The oxide,  $\text{Sb}_4\text{O}_6$ , is employed in vitreous enamels and as a pigment.

Bismuth ( $10^{-5}$  %) occurs as  $\text{Bi}_2\text{S}_3$ , associated with the sulphide ores of lead and copper and also with  $\text{SnO}_2$ . The flue-dusts from the roasting of lead, copper and tin ores, and the anode sludge from copper refining, are worked-up for bismuth. The oxide can be reduced at  $\sim 500^\circ$  with iron and carbon in the presence of a flux. Electrolytic purification is possible from a solution of  $\text{BiCl}_3$  in  $\text{HCl}$ . The metal is used particularly in fusible alloys of which Wood's metal (Bi, Pb, Sn and Cd in the wt. ratio 4 : 2 : 1 : 1), m.p.  $71^\circ$ , and type metal are examples. Bismuth and many of its alloys expand on solidification and give sharp impressions. The salts are used in

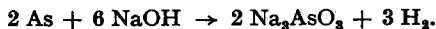
pharmaceutical preparations, showing a marked contrast in toxicity to those of arsenic.

### Reactions of the elements

The elements combine on heating with oxygen, sulphur and the halogens (X):



Antimony gives in addition to the trihalide some pentahalide with both  $F_2$  and  $Cl_2$ , but arsenic does this with fluorine only. The elements all dissolve in hot, concentrated  $H_2SO_4$  with the evolution of  $SO_2$ . Antimony and bismuth yield sulphates, arsenic forms  $As_4O_6$ . Bismuth dissolves readily in nitric acid to give  $Bi(NO_3)_3$ ; the other two elements are converted to mixtures of oxides. Hydrochloric acid has little action on any of the elements. Cold aqua regia dissolves antimony, producing a solution containing  $SbCl_6^-$  ions. Arsenic dissolves in fused  $NaOH$  but the others do not:



### Halides

TABLE 85

HALIDES OF GROUP VB ELEMENTS

	<i>F</i>	<i>Cl</i>	<i>Br</i>	<i>I</i>
As	AsF <sub>3</sub> AsF <sub>5</sub>	AsCl <sub>3</sub>	AsBr <sub>3</sub>	AsI <sub>3</sub>
Sb	SbF <sub>3</sub> SbF <sub>5</sub>	SbCl <sub>3</sub> SbCl <sub>5</sub>	SbBr <sub>3</sub>	SbI <sub>3</sub>
Bi	BiF <sub>3</sub>	BiCl <sub>3</sub>	BiBr <sub>3</sub>	BiI <sub>3</sub>

AsF<sub>3</sub> is a colourless, fuming liquid made by heating  $As_4O_6$  with  $CaF_2$  and  $H_2SO_4$  in a lead retort. The gaseous fluoride, AsF<sub>5</sub>, is the chief product of the treatment of arsenic with fluorine. In common with the structure of all the corresponding halides of this group, the trihalides are pyramidal (Fig. 255a) and the pentahalides are trigonal bipyramidal (Fig. 255b).

Pentahalides of arsenic, other than AsF<sub>5</sub>, are unknown. The trichloride, AsCl<sub>3</sub>, a colourless liquid, is formed by the chlorination of arsenic. White crystalline AsBr<sub>3</sub> and red crystalline AsI<sub>3</sub> are conveniently obtained by

treating the element with the halogen in a  $\text{CS}_2$  solution. The hygroscopic solid  $\text{AsCl}_2\text{F}_3$  is made by passing chlorine into ice-cold  $\text{AsF}_3$ . The conductance of the liquid rises with the addition of  $\text{Cl}_2$ , suggesting the formation of an ionic compound, possibly  $[\text{AsCl}_4][\text{AsF}_6]^-$ . Hydrolysis of the arsenic trihalides becomes more difficult with increasing atomic weight of the halogen. Unlike phosphorus and antimony, arsenic does not form a well-characterised oxohalide.

The white, solid  $\text{SbF}_3$  hydrolyses but slightly and can be made by the action of  $\text{HF}$  on  $\text{Sb}_2\text{O}_3$ . It forms complexes such as  $\text{K}_2\text{SbF}_5$ . The viscous  $\text{SbF}_5$ , made by refluxing  $\text{SbCl}_5$  with anhydrous  $\text{HF}$  followed by fractional distillation, freezes to a non-ionic solid. In this it differs from  $\text{PCl}_5$  which

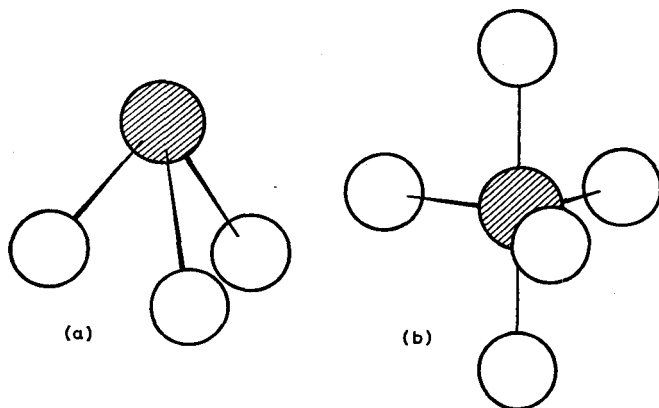
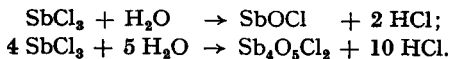
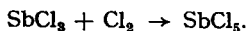


Fig. 255 (a) Pyramidal structure of  $\text{AsF}_3$  molecule.  
Fig. (b) Trigonal bipyramidal structure of  $\text{AsF}_5$  molecule.

contains  $\text{PCl}_4^+$  and  $\text{PCl}_6^-$  ions in the crystal (p. 542), it is composed of covalent trigonal bipyramidal molecules in both solid and vapour states. The white crystalline  $\text{SbCl}_3$ , made by heating antimony with mercury(II) chloride and recrystallising the product from  $\text{CS}_2$ , forms complexes such as  $\text{K}_2\text{SbCl}_5$ . The trichloride hydrolyses in two stages to well-characterised oxide chlorides:



Unlike arsenic, antimony forms a pentachloride,  $\text{SbCl}_5$ , which is made in a similar way to  $\text{PCl}_5$ :



An acid  $(\text{HSbCl}_4)_2 \cdot 9\text{H}_2\text{O}$  can be crystallised from an  $\text{HCl}$  solution of  $\text{SbCl}_3$

into which chlorine has been passed. The tribromide and tri-iodide of antimony are made from the elements.  $\text{SbI}_3$  hydrolyses to give  $\text{Sb}_4\text{O}_5\text{I}_2$ .

The white powder  $\text{BiF}_3$ , like  $\text{SbF}_3$ , is made from the oxide and  $\text{HF}$ ; with an excess of oxide, the oxide fluoride  $\text{BiOF}$  is formed. The trichloride, tribromide and tri-iodide of bismuth can all be made by direct combination of the elements:  $\text{BiBr}_3$  is yellow and  $\text{BiI}_3$ , black. The last is hydrolysed by hot water to bronze crystals of  $\text{BiOI}$ . Bismuth pentafluoride is a white solid made by treating molten bismuth with low-pressure fluorine. It is a very strong fluorinating agent.

### Oxides

The trioxides of arsenic, antimony and bismuth are of structural interest, because they show a transition from the molecular lattice characteristic of covalent compounds to an ionic lattice. Arsenic oxide contains  $\text{As}_4\text{O}_6$  molecules, similar in structure to  $\text{P}_4\text{O}_6$  molecules and based on the  $\text{As}_4$  tetrahedron. The cubic form of  $\text{Sb}_4\text{O}_6$  is similar, but above  $570^\circ$  this is converted to the macromolecular valentinite form containing infinite chains (Fig. 256).

Bismuth oxide has a number of forms of which two are important: the low-temperature  $\alpha$ -form with a complex structure; and a simple cubic form obtained after the oxide has been fused for a long time in a porcelain crucible and probably stabilised by traces of impurities. The latter has the same ionic structure as  $\text{Mn}_2\text{O}_3$ , the bismuth ions being octahedrally co-ordinated (Fig. 257). The trioxides thus range in structure from the molecular, through the macromolecular, to the ionic.

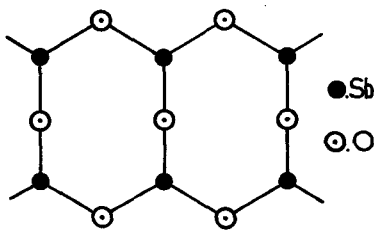


Fig. 256. Valentinite structure of  $\text{Sb}_4\text{O}_6$ .

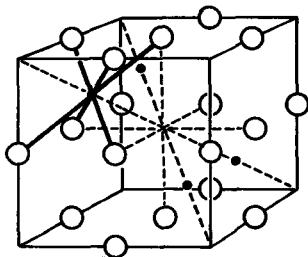


Fig. 257. Structure of  $\text{Bi}_2\text{O}_3$ .

Structural evidence on the pentoxides of arsenic and antimony is lacking. They are not formed from the elements but are produced when the elements are oxidised with nitric acid and the products are dehydrated. Prolonged dehydration of a hydrated oxide of  $\text{Sb}^{\text{V}}$  gives a compound,  $\text{Sb}_2\text{O}_4$ , which

is structurally analogous to  $\text{SbTaO}_4$ . Oxidation of  $\text{Bi}_2\text{O}_3$  by chlorine, bromine and persulphates takes place, but the nature of the products is unknown. A non-stoichiometric, buff powder, called sodium bismuthate, is made by fusing  $\text{Bi}_2\text{O}_3$  with  $\text{NaOH}$  and often formulated  $\text{NaBiO}_3$ . It is insoluble in water and moderately concentrated nitric acid, in which it will oxidise  $\text{Mn}^{2+}$  to  $\text{MnO}_4^-$  at room temperature.

Arsenic, like phosphorus and vanadium, forms finite oxo-anions. The condensed arsenates formed when  $\text{NaH}_2\text{AsO}_4 \cdot \text{H}_2\text{O}$  is heated are shown in Fig. 258.

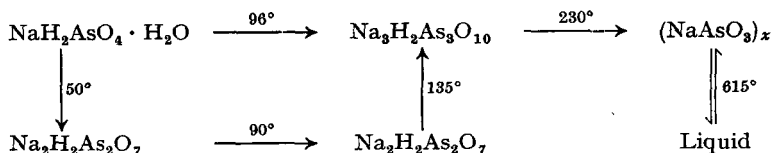
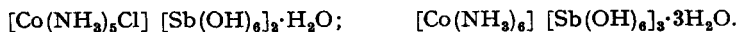


Fig. 258. Condensed arsenates obtained from  $\text{NaH}_2\text{AsO}_4 \cdot \text{H}_2\text{O}$  by heating.

There is not an arsenic analogue of sodium trimetaphosphate. The condensed ions are much less stable to hydrolysis than are the ions of the condensed phosphates; they change rapidly to  $\text{AsO}_4^{3-}$  ions.

The oxygen chemistry of  $\text{Sb}^{\text{V}}$  is quite different, being based not on the tetrahedral but the octahedral co-ordination of  $\text{Sb}^{\text{V}}$  by oxygen. There are two main groups of these oxo-complexes:

- (i) Salts containing  $\text{Sb}(\text{OH})_6^-$  ions. A well-known example is  $\text{Na}[\text{Sb}(\text{OH})_6]$ , formerly called sodium pyroantimonate. Hexahydroantimony amines can be made by replacing  $\text{K}^+$  from  $\text{K}[\text{Sb}(\text{OH})_6]$  with cobalt, chromium and copper amines:



- (ii) Mixed oxides based on  $\text{SbO}_6$  octahedra, such as  $\text{M}^{\text{I}}\text{SbO}_3$ ,  $\text{M}^{\text{II}}\text{Sb}_2\text{O}_6$ ,  $\text{M}^{\text{III}}\text{SbO}_4$  and  $\text{M}_2^{\text{II}}\text{Sb}_2\text{O}_7$ . Examples are  $\text{NaSbO}_3$ , structurally similar to ilmenite,  $\text{FeTiO}_3$ , and  $\text{FeSbO}_4$ , with a rutile structure. Obviously none of these compounds is an antimonate.

### Sulphides

As with the oxides, there is a transition from molecular to ionic structure in passing from arsenic sulphide to bismuth sulphide. Realgar gives a vapour containing  $\text{As}_4\text{S}_4$  molecules with a 'cradle' structure and  $\text{As}-\text{S} = 2.33 \text{ \AA}$ ,  $\text{As}-\text{As} = 2.49 \text{ \AA}$ ;  $\angle \text{As}-\text{S}-\text{As} = 101^\circ$ ,  $\angle \text{S}-\text{As}-\text{S} = 93^\circ$  (Fig. 259). The vapour of orpiment contains  $\text{As}_4\text{S}_6$  molecules with the  $\text{P}_4\text{O}_6$

structure and  $\text{As—S} = 2.25 \text{ \AA}$ ;  $\angle \text{As—S—As} = 100^\circ$ ,  $\angle \text{S—As—S} = 114^\circ$ . The compound is precipitated by passing  $\text{H}_2\text{S}$  into the acidified solution of an arsenite; it dissolves in aqueous alkali-metal sulphides to give a solution from which thioarsenites, for instance  $\text{Na}_3\text{AsS}_3$ , may be crystallised:

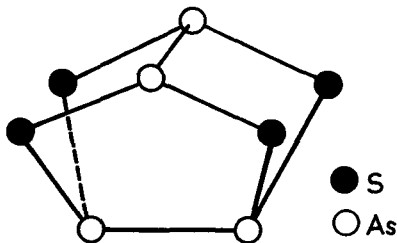
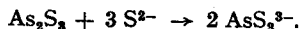


Fig. 259. Structure of  $\text{As}_4\text{S}_4$  molecule.

Thioarsenates, such as  $\text{Na}_3\text{AsS}_4 \cdot 8\text{H}_2\text{O}$  and  $(\text{NH}_4)_3\text{AsS}_4$ , are obtained from solutions made by the action of alkali-metal polysulphides on  $\text{As}_2\text{S}_3$ . Acidification of a thioarsenate solution gives a yellow precipitate containing a sulphide of arsenic, but there is no structural evidence that it is  $\text{As}_2\text{S}_5$ . A yellow solid of this composition is obtained by fusing As with S, extracting the cold mixture with aqueous  $\text{NH}_3$  and then precipitating with  $\text{HCl}$  at  $0^\circ$  or by passing  $\text{H}_2\text{S}$  quickly through a strongly acidified arsenate solution. Although these methods give material which analyses as  $\text{As}_2\text{S}_5$ , yet again there is no structural evidence for such a compound.

Antimony trisulphide occurs as the mineral stibnite. An orange form is precipitated when  $\text{H}_2\text{S}$  is passed into a solution of  $\text{SbCl}_3$  in hydrochloric acid. When heated at  $200^\circ$  in  $\text{CO}_2$ , this changes to a dark-grey, rhombic modification of greater density. Both forms dissolve in solutions containing sulphide ion to give thioantimonites; and, though they are soluble in polysulphide solutions, crystalline thioantimonates cannot be obtained from the solutions. The existence of an antimony pentasulphide is doubtful.

The commercial product used in rubber vulcanisation is made by boiling  $\text{Sb}_2\text{S}_3$  with S in aqueous  $\text{NaOH}$  and precipitating the solution with  $\text{HCl}$ . Its composition is variable, it always contains free sulphur and there is no structural evidence for a compound of the composition  $\text{Sb}_2\text{S}_5$ .

$\text{Bi}_2\text{S}_3$  is formed as grey, rhombic crystals when Bi is fused with sulphur, and as a dark brown precipitate when  $\text{H}_2\text{S}$  is passed into the solution of a bismuth salt. It is insoluble in solutions containing sulphide ion. The compounds  $\text{KBiS}_2$  and  $\text{NaBiS}_2$  are made by fusing  $\text{Bi}_2\text{S}_3$  with the appropriate Group IA sulphide; they oxidise rapidly in air.

### Oxoacid salts of bismuth

Bismuth, alone of the elements of the sub-group, forms stable salts with oxo-anions. The deliquescent nitrate,  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ , can be crystallised from a solution of the metal or  $\text{Bi}_2\text{O}_3$  in 20%  $\text{HNO}_3$ . It hydrolyses successively to  $\text{BiO}(\text{NO}_3)$  and  $\text{BiO}(\text{OH}) \cdot \text{BiO}(\text{NO}_3)$ , the latter being stable in boiling water. There is no evidence of a significant quantity of  $\text{Bi}(\text{OH})^{2+}$  ion in solutions of these basic nitrates in  $M/2$  to  $M$   $\text{HNO}_3$ .

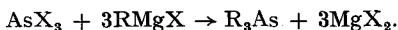
Bismuth sulphate,  $\text{Bi}_2(\text{SO}_4)_3$ , a white solid produced by evaporating a solution of the metal in concentrated  $\text{H}_2\text{SO}_4$ , gives on hydrolysis an insoluble hydroxide sulphate,  $\text{Bi}(\text{OH})_3 \cdot \text{Bi}(\text{OH})\text{SO}_4$ , which heating converts to the yellow bismuthyl sulphate  $(\text{BiO})_2\text{SO}_4$ .

The addition of an ammonium carbonate solution to a bismuth nitrate solution precipitates the oxide carbonate,  $[(\text{BiO})_2\text{CO}_3]_2 \cdot \text{H}_2\text{O}$ , which readily loses water and  $\text{CO}_2$  on heating.

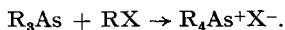
### Organometallic compounds

#### *Arsenic*

Organoarsenic compounds are numerous: research on them was stimulated by the early discovery that some of them were trypanocides. The trialkylarsines,  $\text{R}_3\text{As}$ , are colourless liquids made by treating arsenic trihalides with dialkyls of zinc or with Grignard reagents:

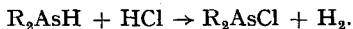


They oxidise rapidly in air and react with anhydrous hydrogen halides to form salts which are decomposed by water. But with alkyl halides they give tetra-alkylarsonium salts which dissolve in water to give neutral solutions:



The trialkylarsines act as electron donors in forming co-ordination compounds such as  $(\text{R}_3\text{As})_2\text{PdCl}_2$ . The triarylarines resemble the alkyl analogues.

Monoalkyl and dialkyl arsines are readily prepared. When sodium arsenite is treated with an alkyl halide a primary arsonic acid is formed,  $\text{R} \cdot \text{AsO}(\text{OH})_2$ , which can be reduced to  $\text{R} \cdot \text{AsH}_2$  by zinc and hydrochloric acid. Reduction of a secondary arsonic acid,  $\text{R}_2\text{AsO} \cdot \text{OH}$ , gives  $\text{R}_2\text{AsH}$ . These compounds liberate hydrogen from hydrogen halides:

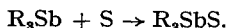


The products can react with the parent compounds to give diarsine derivatives:



*Antimony*

The trialkyls of antimony are colourless liquids, soluble in organic solvents but not in water. The lower ones are oxidised spontaneously in air. They are made by treating  $\text{SbCl}_3$  with zinc alkyls or Grignard reagents. They form adducts with halogens, sulphur and selenium:



There are also monoalkyl and dialkyl stibines and corresponding aryls.

*Bismuth*

Bismuth does not form monoalkyl or dialkyl derivatives, but rather unstable trialkyls can be made from the action of a Grignard reagent on bismuth trihalides. They are spontaneously inflammable and decompose above  $150^\circ$ , but they are stable to water, in which they are insoluble.

## FURTHER READING

- J. W. GEORGE, *Halides and Oxyhalides of the Elements of Groups Vb and VIb* in F. A. COTTON (Ed.), *Progress in Inorganic Chemistry*, Vol. II, London, Interscience, 1960, p. 33.
- E. THILO, *Condensed Phosphates and Arsenates* in H. J. EMELÉUS AND A. G. SHARPE (Ed.), *Advances in Inorganic Chemistry and Radiochemistry*, Vol. 4, New York, Academic Press, 1962, p. 1.
- D. S. PAYNE, *Halides of the Phosphorus Group Elements*. *Quart. Rev.*, 15 (1961) 173.
- G. BOOTH, *Complexes of the Transition Metals with Phosphines, Arsines and Stibines* in H. J. EMELÉUS AND A. G. SHARPE (Eds.), *Advances in Inorganic Chemistry and Radiochemistry*, Vol. 6, New York, Academic Press, 1964, p. 1.



## Oxygen, Sulphur, Selenium, Tellurium and Polonium

## GROUP VIB

As in the preceding group, Group VB, the elements of Group VIB show a gradual transition to more metallic character with increasing atomic number. Oxygen resembles nitrogen in being the only member of its group to be a gas at room temperature. The small atomic radius of oxygen probably plays a major part in determining its chemical behaviour, by contrast with fluorine where the chief factor is the low dissociation energy (37.7 kcal mole<sup>-1</sup>) of the molecule. For the oxygen molecule this is 117 kcal mole<sup>-1</sup>. The elements of Group VIB have six electrons in their  $ns^2np^4$  valence shells and all show bivalence in compounds in which they have two covalent links and two lone pairs. But in the elements below oxygen d hybridisation commonly occurs, giving complexes in which the atom is usually shown with the charge numbers +4 or +6.

TABLE 86  
ATOMIC PROPERTIES OF GROUP VIB ELEMENTS

	O	S	Se	Te	Po
Atomic number	8	16	34	52	84
Electron configuration	$2s^2 2p^4$	$3s^2 3p^4$	$4s^2 4p^4$	$5s^2 5p^4$	$6s^2 6p^4$
Covalent radius (Å)	0.74	1.02	1.16	1.35	1.64
Ionic radius, $M^{2-}$ (Å)	1.40	1.84	1.98	2.21	
„ „ „ $M^{4+}$ (Å)				0.89	1.02

The first ionisation energy of oxygen is high. The electron affinity  $O + 2e \rightarrow O^{2-}$ ,  $A = -7.28$  eV, has a surprisingly large negative value; in other words,  $O^-$  resists the introduction of the second electron needed to form the  $O^{2-}$  ion. Yet ionic oxides are common, owing to the large lattice energy of the crystals (p. 102). The electronegativity ascribed to oxygen is extremely high, being exceeded only by that of fluorine. This accords with oxides having a more ionic character than the corresponding sulphides (p. 501).

TABLE 87  
 IONISATION ENERGY, ELECTRON AFFINITY AND  
 ELECTRONEGATIVITY OF GROUP VIB ELEMENTS

	O	S	Se	Te
Ionisation energy $I$ (eV)	13.61	10.36	9.75	9.01
Electron affinity, $X \rightarrow X^{2-}$ (eV)	-7.28	-3.44	-4.21	
Electronegativity (Allred-Rochow scale)	3.50	2.44	2.48	2.01

### Properties of the elements

#### General

The gradation of physical properties follows a similar pattern to that of the preceding group and is similarly related to the atomic structure. Gaseous oxygen consists of diatomic molecules, sulphur of 'puckered' rings (p. 274) of 8 atoms in the rhombic, and probably also in the monoclinic crystalline form. The red allotrope of selenium also contains 8-membered rings but the usual grey form which is rather metallic-looking has zig-zag chains of atoms. Tellurium (Fig. 260) is rather similar to, but more metallic than, grey Se. It is monotropic in contrast to S, Se and Po. Polonium is dimorphic; the low-temperature  $\alpha$ -form has a simple cubic lattice and the high-temperature  $\beta$ -form a simple rhombohedral one, the transition temperature being  $75^\circ$ . The density is similar to that of bismuth. Polonium has a low m.p., resembling that of Bi, but its b.p. is more in accord with a Group VI element.

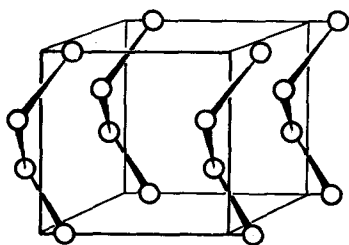


Fig. 260. Unit cell of tellurium, showing spiral arrangement of atoms.

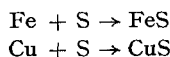
Chemically, the elements of Group VIB range from the very electronegative, non-metallic oxygen to the decidedly metallic polonium. Reactivity towards metals and hydrogen decreases down the group and becomes slight after selenium.

Otherwise the middle elements, sulphur, selenium and tellurium show

TABLE 88  
SOME PROPERTIES OF GROUP VIB ELEMENTS

	<i>O</i>	<i>S</i>	<i>Se</i>	<i>Te</i>	<i>Po</i>
Density of solid (g/cc)	1.27	2.06( $\alpha$ )	4.80(grey)	6.24(metal.)	9.51( $\beta$ )
Atomic volume	12.6	15.56	16.45	20.24	22.2
Melting point (°C)	-218.9	114.5	217.4	450	254
Boiling point (°C)	-183.0	444.6	684.8	1390	962

considerable chemical similarity. They burn in air to give  $\text{SO}_2$ ,  $\text{SeO}_2$  and  $\text{TeO}_2$ . They all react energetically with fluorine to give hexafluorides,  $\text{XF}_6$ , and with chlorine to give tetrachlorides,  $\text{XCl}_4$ . The three elements are attacked by hot nitric and sulphuric acids but not by non-oxidising acids such as  $\text{HCl}$  and  $\text{HF}$ . Sulphur and selenium dissolve in aqueous solutions of alkali sulphides and selenides to form the respective polysulphides and polyselenides. The elements react with most metals, on heating, to give binary compounds:

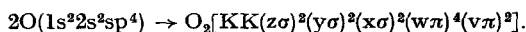


### Oxygen

The lithosphere contains about 47% oxygen by weight and the oceans about 89%. The atmosphere has 20.95% oxygen by volume. Taking hydrosphere and lithosphere together it constitutes nearly 50% by weight, almost twice the abundance of silicon and seven times that of aluminium. The element is a large-scale industrial product, stored and transported mainly as a liquid, and obtained by the fractional distillation of liquid air.

Ordinary oxygen contains, in addition to the most abundant isotope oxygen-16, about 0.2 vol. %  $^{18}\text{O}$  and 0.04 vol. %  $^{17}\text{O}$ . Water can be enriched in  $^{18}\text{O}$  by fractional distillation. This isotope has been used as a non-radioactive tracer to show, for example, that the oxygen liberated when  $\text{H}_2\text{O}_2$  is oxidised by  $\text{Ce}^{4+}$  or  $\text{MnO}_4^-$  ions comes wholly from the hydrogen peroxide.

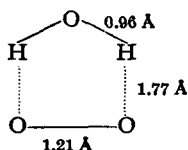
The oxygen molecule is paramagnetic. It contains two more electrons than  $\text{N}_2$ , and these, according to molecular orbital theory (p. 108), are in the antibonding orbitals:



As there are two such orbitals, they are singly occupied by these electrons which have parallel spin.

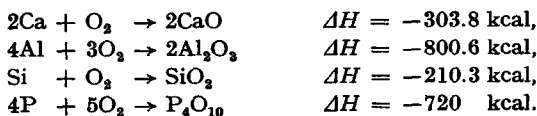
At room temperature and pressure, oxygen shows spectroscopic evidence of the diamagnetic species  $O_4$ ; the equilibrium concentration of  $O_4$  decreases as the temperature is raised. The bond between the two  $O_2$  molecules is weaker than an electron-pair bond but stronger than a Van der Waals attraction.

The solubility coefficient of oxygen in water is 0.029 at  $20^\circ$ . There is optical evidence for the hydrate  $O_2 \cdot H_2O$  which is believed to have the structure:



The hydrogen bonds differ from those between water molecules in that they have a proton sharing three electrons instead of four, one from an oxygen atom in the biradical form of the oxygen molecule and two from the O—H bond.

Oxygen is decidedly reactive, particularly at higher temperatures its combination with other elements being often strongly exothermal:



It does not react readily with nitrogen or directly with the halogens.

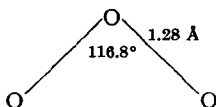
Atomic oxygen is produced by passing an electric discharge through the gas at 1 mm pressure, by radio-frequency excitation at higher pressures and by irradiating the gas with ultraviolet light of wave length less than 1900 Å. The atoms constitute a very strong oxidising agent:



### Ozone

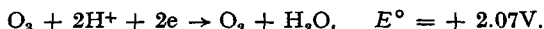
Ozone is made by passing a silent discharge through oxygen or by electrolysing a strong aqueous perchloric acid at  $-50^\circ$  between a lead cathode and a platinum anode, when anodic oxidation of the water occurs. Gaseous ozone is deeper blue than oxygen; it condenses at  $-112^\circ$  to a dark blue liquid which freezes at  $-193^\circ$  to a dark purple solid. Surprisingly, the liquid is not completely miscible with liquid oxygen.

Microwave and electron diffraction studies show the molecule to be angular:



It may be considered to have two  $\sigma$  bonds and a delocalised  $\pi$  orbital stretching over the three atoms. Every atom may be regarded as roughly  $sp^2$  hybridised, and the end atoms to have two lone pairs and the central atom one.

Ozone is one of the strongest oxidising agents. In acid solution:



Only fluorine, atomic oxygen, and  $\text{F}_2\text{O}$  have higher redox potentials. Ozone oxidises moist sulphur to  $\text{H}_2\text{SO}_4$ , raises silver(I) compounds to the +2 state, and converts olefinic compounds to ozonides. The reaction  $2\text{O}_3 \rightarrow 3\text{O}_2$ , which is catalysed by many metals and metal oxides, is exothermic and rapid above  $200^\circ$ .

Ozone is an important constituent of the upper atmosphere.

### Sulphur

Sulphur (0.052% of the lithosphere) occurs mainly as the element and in sulphides and sulphates.

The element has several allotropes. The form stable below  $98^\circ$  is  $\alpha$ -sulphur, whose rhombic crystals are built up from 8-membered, puckered rings of S atoms with S—S bond lengths of 2.12 Å and bond angles of  $105.4^\circ$  (Fig. 261). They are packed into 'crankshafts' stacked in crossed layers (Fig. 262).

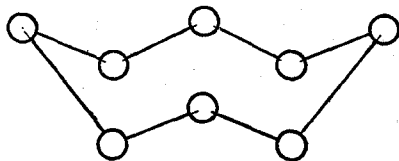


Fig. 261. 8-membered-ring of sulphur atoms.

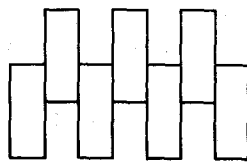
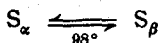


Fig. 262. Crankshaft stacking of 8-membered rings in  $\alpha$ -sulphur.

Between  $98$  and  $122^\circ$   $\beta$ -sulphur is stable. Its monoclinic crystals also contain 8-membered rings.

The two modifications (with a range of stability and a definite transition temperature) are the best-known example of enantiotropic allotropy:



Conversion from  $S_\alpha$  to  $S_\beta$  is accompanied by a small evolution of heat (0.1 kcal per g. atom) and a slight increase in volume. Although  $\beta$ -sulphur has a different crystal form, it is probably not very different in structure from  $\alpha$ -sulphur.

However, there is a second monoclinic form,  $\gamma$ -sulphur, which separates as needle-like crystals from certain solvents and also from melts cooled so as to avoid nucleation by  $\alpha$ -sulphur. This has also 8-membered rings stacked in 'sheared-penny rolls' which give a close-packed hexagonal arrangement in two dimensions (Fig. 263).

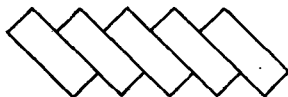


Fig. 263.  $\gamma$ -Monoclinic sulphur showing 'sheared-penny rolls' stacking of 8-membered rings.

Rhombohedral, or  $\rho$ -sulphur, like the  $\alpha$ -,  $\beta$ - and  $\gamma$ -forms, has properties typical of a solid composed of small, covalent molecules. It is made by pouring an aqueous solution of  $\text{Na}_2\text{S}_2\text{O}_3$  into concentrated HCl at  $0^\circ$  and extracting the mixture with toluene; from the toluene solution solid  $S_\rho$  can be crystallised. Although this form is metastable with respect to  $S_\alpha$ , the transformation is slow. X-ray analysis shows  $S_\rho$  to contain 6-membered puckered rings with the chair configuration (Fig. 264).



Fig. 264. Chair configuration of  $S_6$  rings in  $\rho$ -sulphur.

Ordinary sulphur,  $S_\alpha$ , melts at  $120^\circ$  to a pale yellow liquid,  $S_\lambda$ , of low viscosity; it consists of  $S_8$  rings, a structure which is maintained up to  $160^\circ$ . Above this temperature long spiral chains of  $\mu$ -sulphur are formed and increase in proportion up to the b.p. ( $444.5^\circ$ ). Above  $160^\circ$  there is also present a third form,  $\pi$ -sulphur, probably  $S_6$  and a precursor of  $S_\mu$ ; it increases to a maximum at about  $180^\circ$ . At this temperature the viscosity is also at a maximum and the liquid is almost unpourable, probably because of cross-linking between the chains.

When molten sulphur above  $160^\circ$  is poured into water, plastic sulphur is formed. Much of it consists of long spiral chains of  $S_\mu$ . On standing it

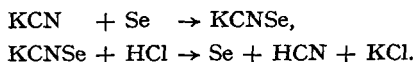
slowly hardens, becoming a mixture of  $S_{\mu}$  and solid  $S_{\alpha}$ , the latter, although amorphous, containing  $S_8$  groups.

Paramagnetic forms have been made (*cf.* oxygen above). When sulphur vapour at 500–700° and 1 mm, consisting mainly of  $S_2$  molecules, is passed over a surface at  $-196^\circ$ , a purple paramagnetic solid is obtained which may contain  $S_2$  molecules. At  $-80^\circ$  it reverts to  $S_{\alpha}$ .

Gaseous sulphur has been shown by vapour density measurements to contain  $S_8$ ,  $S_6$ ,  $S_4$  and  $S_2$ , the relative proportions depending on the temperature; the last is paramagnetic, like  $O_2$ .

### Selenium

This element ( $9 \times 10^{-6}\%$  of the earth's crust) occurs in small quantities in sulphide ores, particularly  $FeS_2$ . It is extracted from the flue-dusts produced in the roasting of sulphide ores and from the 'lead-chamber mud' formed in sulphuric acid manufacture, as a solution in aqueous KCN. From the filtered solution it is precipitated by the addition of HCl.



Selenium is used for decolorising glass and in photoelectric cells. Its electrical conductance in the metallic form is increased as much as 200 times by light. Another application is in the iron-selenium barrier-layer cell which generates a current when illuminated. This system is extensively used in rectifiers because current flows more readily from iron to selenium than in the opposite direction when an external alternating potential is applied.

The selenium precipitated from KCNSe by acid and from  $H_2SeO_3$  by  $SO_2$  is red and amorphous. It dissolves in  $CS_2$  and slow evaporation of the solution below  $72^\circ$  gives red,  $\alpha$ -monoclinic Se, whereas rapid evaporation gives red  $\beta$ -monoclinic Se.  $Se_x$  contains puckered  $Se_8$  rings with Se—Se—Se bonds of 2.34 Å and angles of  $105.5^\circ$ . Hexagonal crystals of grey 'metallic' Se, the stable allotrope at room temperature, are made by keeping the other forms at 200–220° for a time. Present evidence suggests that liquid Se has only one form. Several compounds, with the formula  $Se_nS_{8-n}$  and analogous to  $S_8$  and  $Se_8$ , have been isolated from fused sulphur-selenium mixtures, but only one,  $TeS_7$ , from fused sulphur-tellurium mixtures.

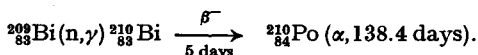
### Tellurium

The element ( $2 \times 10^{-7}\%$  of the lithosphere) occurs in sulphide ores, particularly those of copper, and as the tellurides of silver and gold. Its source is the anode sludge from the electrolytic refining of copper. The

sludge is treated with fuming sulphuric acid and the tellurium precipitated from the diluted solution with zinc. The element is added to lead to improve resistance to heat, mechanical shock and corrosion. The stable metallic form consists of hexagonal grey crystals with low electrical conductance little affected by light. Tellurium and grey selenium form a continuous range of solid solutions in which are chains of randomly arranged Se and Te atoms. A black, amorphous form is precipitated from telluric acid by  $\text{SO}_2$ .

### Polonium

The metal, known in trace quantities since 1898, is now made as the polonium-210 isotope in milligram quantities by the neutron irradiation of  $^{209}\text{Bi}$ .



The isotope is virtually a pure  $\alpha$ -emitter, but its high specific activity, 4.5 curies per mg, makes it a dangerous material, the maximum permissible body burden for ingested  $^{210}\text{Po}$  being only  $4 \times 10^{-12}\text{g}$ . (The 100-year polonium-209 would be preferred for chemical work but its production is expensive.) Polonium-210 is separated from the irradiated Bi by electrochemical replacement with Ag from solution in 0.5–2 M HCl at 70–80°:  $E^\circ$ ,  $\text{Po}^{4+}/\text{Po} = +0.75\text{V}$ . The elements Au, Hg, Pt and Te must first be removed by reduction with hydrazine. The polonium is sublimed from the surface of the silver in a vacuum; if the separation is delayed, sublimation becomes more difficult, possibly through compound formation. The metal is obtained from solution by precipitation as  $\text{PoS}$  followed by the decomposition of the sulphide in a vacuum at 500°, when the metal sublimes leaving a residue of decay lead sulphide. Polonium intimately mixed with beryllium forms a useful, weak source of neutrons.

### Oxidation states of sulphur, selenium and tellurium

The most common oxidation states in Group VI are  $-2$ ,  $+4$  and  $+6$ , represented respectively by the compounds  $\text{H}_2\text{Se}$ ,  $\text{H}_2\text{SeO}_3$  and  $\text{H}_2\text{SeO}_4$ . The free energies of some of the oxidation states, relative to the element, in aqueous solution at  $\text{pH} = 0$ , are illustrated in Fig. 265.

Features to be noted are (i) the extremely unstable character of  $\text{Se}^{\text{VI}}$ , and therefore the strong oxidising power of the element in this state, relative to its lower oxidation states, (ii) the stability of compounds of the  $+4$  state towards disproportionation for the three elements, (iii) the in-



stability of the hydrides of selenium and tellurium, and (iv) the instability of the  $S^V$  and  $S^{VI}$  states towards disproportionation.

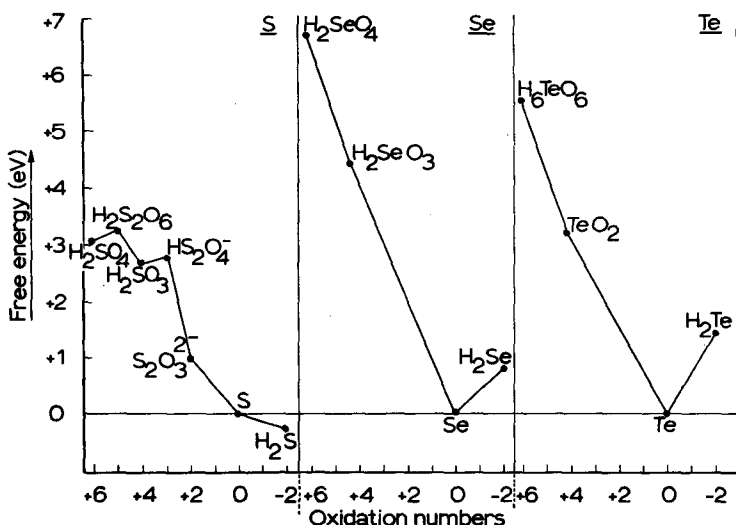
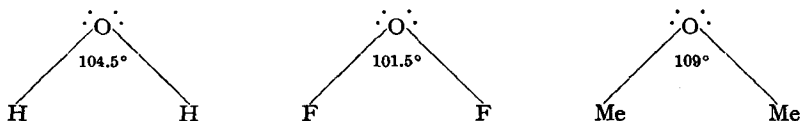


Fig. 265. Oxidation states of sulphur, selenium and tellurium. Free energies relative to the elements at  $pH = 0$ .

### Stereochemistry

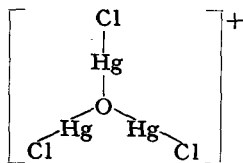
#### Oxygen

The oxygen atom, with a  $1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$  electronic configuration, forms two bonds in nearly all its compounds; the next orbital ( $3s$ ) lies too high in energy for the promotion of an electron to it and the consequent increase in valency to be feasible. Most of the simple inorganic covalent oxides and the aliphatic ethers seem to owe their structure to approximately  $sp^3$  hybrid orbitals, two of which are occupied by lone pairs. Examples are:



In ozone and in aromatic ethers, trigonal  $sp^2$  hybridisation is involved, the angle at the central oxygen being approximately  $120^\circ$ . The molecule  $(SiH_3)_2O$  is linear, however, suggesting that  $sp$  hybridisation can occur at the oxygen.

The ion  $O^+$  is isoelectronic with the atom N. It forms three covalent bonds in  $H_3O^+$ ; these are arranged similarly to the N—H bonds in ammonia and are due basically to  $sp^3$  hybridisation, with one position occupied by a lone pair. In the ion,



however, the O—Hg—Cl groups are nearly linear and the whole structure is approximately planar. There is no unambiguous example of 4-covalence in oxygen.

### Sulphur, selenium and tellurium

The stereochemistry of these elements is tabulated in Table 89. Sulphur, when it is two-bonded, differs from oxygen in having a valency angle less than the tetrahedral angle,  $109.5^\circ$ , except in  $SO_2$ . This lesser angle persists when aromatic groups are attached; for instance in  $(p\text{-CH}_3\text{-C}_6\text{H}_4)_2\text{S}$  the C—S—C angle is  $109^\circ$ . The small bond angle in  $H_2S$  ( $92.1^\circ$ ) suggests pure p orbitals, but nuclear quadrupole coupling constants indicate there are both s and d contributions to the bonding orbitals.

TABLE 89  
STEREOCHEMISTRY OF S, Se, Te

$\sigma$ pairs	$\pi$ pairs	Lone pairs	Hybrid	Shape	Examples
2	2	1	$sp^2$	V-shaped	* $SO_2$
3	3	0	$sp^2$	Triangular	* $SO_3$
4	2	0	$sp^3$	Tetrahedral	$SO_2Cl_2$ , $[SeO_4]^{2-}$
3	1	1	$sp^3$	Trigonal pyramidal	$SOCl_2$ , $SeOF_2$
2	0	2	$sp^3$	V-shaped	$H_2S$ , $Cl_2S$ , $S_8$
4	0	1	$sp^3d_{z^2}$	Distorted tetrahedral	$TeCl_4$
6	0	0	$sp^3d_{y^2}$	Octahedral	$SF_6$ , $SeF_6$ , $Te(OH)_6$ , $S_2F_{10}$
5	0	1	$sp^3d_{y^2}$	Square pyramidal	$[MeTeI_4]^-$
6	0	1	$sp^3d_{y^2}d_x$	Distorted octahedral	$Cl_4Te(NMe_2Ph)_2$

\*In  $SO_2$  and  $SO_3$  there are also  $\pi$  lone-pair and non-localised bonds.

### Polonium

The crystal structures of several polonium compounds have been determined. Both forms of  $PoO_2$  have ionic lattices;  $ZnPo$  has a zinc-blende, and  $PbPo$

a rock-salt structure. In  $\text{PoBr}_4$ , the Po is octahedrally co-ordinated with Br. Ammonium hexachloropolonate(IV),  $(\text{NH}_4)_2\text{PoCl}_6$ , is isomorphous with  $(\text{NH}_4)_2\text{PtCl}_6$ ; the Po-Cl distance, 2.38 Å, suggests a basically covalent bond.

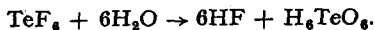
### Halides

TABLE 90  
HALIDES OF GROUP VIB ELEMENTS

	O	S	Se	Te	Po
F	$\text{F}_2\text{O}_2, \text{F}_2\text{O}$	$\text{S}_2\text{F}_2, \text{SF}_4,$ $\text{S}_2\text{F}_{10}, \text{SF}_6$	$\text{SeF}_4$ $\text{SeF}_6$	$\text{TeF}_4$ $\text{Te}_2\text{F}_{10}, \text{TeF}_6$	
Cl	$\text{Cl}_2\text{O}, \text{ClO}_2$ $\text{Cl}_2\text{O}_6, \text{Cl}_2\text{O}_7$	$\text{S}_x\text{Cl}_2, \text{S}_2\text{Cl}_2,$ $\text{SCL}_2, \text{SCL}_4$	$\text{Se}_2\text{Cl}_2,$ $\text{SeCl}_4$	$\text{TeCl}_2$ $\text{TeCl}_4$	$\text{PoCl}_2$ $\text{PoCl}_4$
Br	$\text{Br}_2\text{O}, \text{BrO}_2,$ $\text{BrO}_3$	$\text{S}_2\text{Br}_2.$	$\text{Se}_2\text{Br}_2,$ $\text{SeBr}_4$	$\text{TeBr}_2$ $\text{TeBr}_4$	$\text{PoBr}_2$ $\text{PoBr}_4$
I	$\text{I}_2\text{O}_4, \text{I}_4\text{O}_9,$ $\text{I}_2\text{O}_5$			$\text{TeI}_4$	$\text{PoI}_4$

### Hexahalides

Sulphur, selenium and tellurium all form the hexafluoride by direct combination; other hexahalides are unknown.  $\text{SF}_6$  and  $\text{SeF}_6$  are chemically inert, colourless gases. The former is non-toxic and at once the most inert sulphur compound and possibly the most inert non-ionic fluorine compound; it resists attack by fused KOH. The somewhat more reactive  $\text{SeF}_6$  is reduced by  $\text{NH}_3$  above  $200^\circ$ .  $\text{TeF}_6$ , also a colourless gas, is even more reactive, being hydrolysed by water:



This difference in reactivity arises from the higher maximum covalence possible with tellurium. The hexafluoride molecules are octahedral, with six  $\text{sp}^3\text{d}^2$  hybrid orbitals, and the low b.p. of the compounds are ascribable to the non-polarisable F atoms sheathing the molecules.

In addition to  $\text{SF}_6$ , some  $\text{S}_2\text{F}_{10}$  is obtained during the direct fluorination of sulphur. It is a liquid, b.p.  $29^\circ$ , and is like  $\text{SF}_6$  in being unreactive to alkalis. Unlike  $\text{SF}_6$ , however, it is highly toxic. It reacts with  $\text{Cl}_2$  at  $300^\circ$  to give  $\text{SClF}_5$ , a colourless gas which differs from  $\text{SF}_6$  and  $\text{S}_2\text{F}_{10}$  in being rapidly hydrolysed by alkalis. The S-S bond in  $\text{S}_2\text{F}_{10}$  is about 6% longer than the usual single-bond distance and the S-F distances are rather short.

### Tetrahalides

Sulphur tetrafluoride,  $\text{SF}_4$ , b.p.  $-40.5^\circ$ , which can be made by the direct fluorination of sulphur at  $-75^\circ$ , is more conveniently prepared by the action of sulphur dichloride on a suspension of sodium fluoride in acetonitrile or tetramethylene sulphone at  $70^\circ$ . A medium offering some chance of ionisation of the  $\text{NaF}$  is necessary.



The structure of  $\text{SF}_4$  has been deduced from its infrared, Raman, and  $^{19}\text{F}$  n.m.r. spectra. At  $-90^\circ$  the fluorine resonance spectrum has two resonance triplets of equal intensity (Fig. 266).

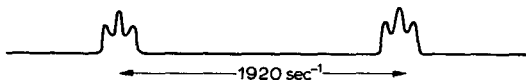


Fig. 266. Pair of resonance triplets in  $^{19}\text{F}$  n.m.r. spectrum of  $\text{SF}_4$  at  $-90^\circ$ .

Accordingly, the molecule must contain two pairs of equivalent fluorine nuclei. The spectrum could not arise from a regular tetrahedral structure (a), or a triangular pyramidal structure (b), but is consistent with the trigonal bipyramidal structure (c) with one equatorial position occupied by a lone pair (Fig. 267).

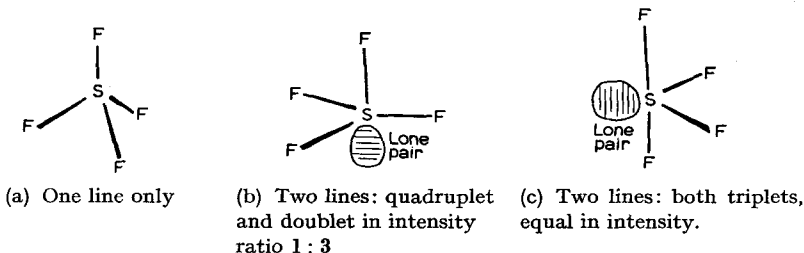
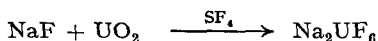
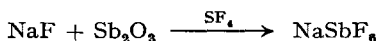
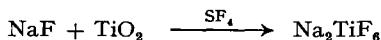


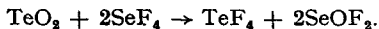
Fig. 267. Types of n.m.r. spectra consistent with three hypothetical structures.

This is just the structure predicted by the Sidgwick-Powell rule (p. 146).

Sulphur tetrafluoride is a useful fluorinating agent. It converts mixtures of alkali-metal fluorides and metal oxides into complex fluorides:



Selenium tetrafluoride is conveniently made by passing diluted fluorine over a selenium surface at 0°. The liquid, b.p. 106°, gives with NaF, KF, RbF and CsF the complex fluorides  $M^+SeF_5^-$ , unlike the other halogeno complexes of selenium which are  $M^+SeF_6^-$ . Both  $SF_4$  and  $SeF_4$  form solid 1 : 1 addition compounds with  $BF_3$ ,  $AsF_5$  and  $SbF_5$ . Pure, crystalline  $TeF_4$  is obtained by the reaction of  $TeO_2$  with  $SeF_4$  at 80° followed by evaporation of the excess of reagent and the  $SeOF_2$ .



Tetrachlorides of S, Se, Te and Po are formed by direct chlorination.  $SCl_4$  is a yellow liquid, stable only at low temperatures;  $SeCl_4$  is a colourless, crystalline solid subliming at 196°, and  $TeCl_4$  a white, hygroscopic solid, m.p. 224°. Fused  $TeCl_4$  is an even better conductor of electricity than  $BrF_3$  probably because

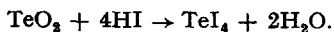


It gives with HCl the acid  $H_2TeCl_6$ ; the salt  $K_2TeCl_6$  is isomorphous with  $K_2SiF_6$  and  $K_2SnCl_6$ . The anion  $TeCl_6^{2-}$  is a regular octahedron. The tetrachlorides of selenium and tellurium have the same structure as that of  $SF_4$  shown in Fig. 267(c).

Yellow  $PoCl_4$  combines with  $NH_4Cl$  to give a compound which structural evidence suggests to be  $(NH_4)_2PoCl_6$ . A series of compounds  $M_2PoX_6$  where  $M = NH_4$  or Cs and  $X = Cl, Br$  or  $I$  have been made, and X-ray diffraction indicates that they are iso-structural with one another and with their tellurium analogues.

Selenium, tellurium and polonium form tetrabromides.  $SeBr_4$ , a yellow solid, loses  $Br_2$  to form  $Se_2Br_2$  even at room temperature, and hydrolyses to a clear solution of  $H_2SeO_3$  and  $HBr$ . Orange-red crystals of  $TeBr_4$ , along with green  $TeBr_2$ , result when tellurium reacts with bromine. Polonium forms carmine-red  $PoBr_4$  at 200°. A salmon-pink  $PoBr_2Cl_2$  is also known. The diffraction pattern of  $PoBr_4$  indicates a face-centred cubic cell of edge 5.6 Å; the intensities suggest this contains only one  $PoBr_4$  unit with the Po atom randomly distributed over the sites normally occupied by four cations. The Po atom is surrounded octahedrally by six Br atoms at a Po-Br distance of 2.8 Å; this lies between the covalent octahedral distance (2.6 Å) and the theoretical ionic distance (2.97 Å).

Neither sulphur nor selenium forms an iodide; Te and Po form only tetraiodides.  $TeI_4$  consists of iron-grey crystals, made either by direct union or by reaction in aqueous solution:



$PoI_4$  is a black solid.

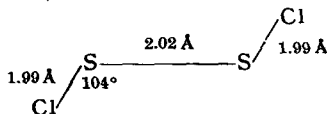
### Dihalides

The best-characterised dihalides are  $\text{SCl}_2$ , a red liquid made by saturating  $\text{S}_2\text{Cl}_2$  with chlorine at room temperature,  $\text{TeCl}_2$ , a black solid made by the action of  $\text{CCl}_2\text{F}_2$  on tellurium at  $500^\circ$  and  $\text{TeBr}_2$ , already mentioned. In  $\text{SCl}_2$  the bond angle is about  $103^\circ$ , in  $\text{TeBr}_2$   $98^\circ$ , suggesting considerable p-character in the bonding orbitals of the centre atom.  $\text{PoCl}_2$  has been made by reducing  $\text{PoCl}_4$  with  $\text{SO}_2$ .

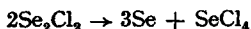
### Lower halides

Disulphur difluoride can be made by heating sulphur with a mixture of  $\text{HgF}$  and  $\text{CaF}_2$  or by passing a mixture of  $\text{SO}_2$  and  $\text{S}_2\text{Cl}_2$  over heated  $\text{KF}$ . There is evidence for two isomeric forms,  $\text{S}_2\text{SF}_2$  and  $\text{FS-SF}$ .

Sulphur and selenium form dimeric chlorides and bromides.  $\text{S}_2\text{Cl}_2$ , made by passing dry  $\text{Cl}_2$  over molten sulphur, is an amber liquid whose vapour dissociates a little and becomes red. Hydrolysis by water is slow;  $\text{HCl}$ , sulphur,  $\text{SO}_2$  and oxyacids, principally  $\text{H}_2\text{S}_5\text{O}_6$ , are formed. Electron diffraction by the vapour indicates a non-planar structure analogous to that of hydrogen peroxide (p. 504):



The S—S bond is appreciably shorter than in the  $\text{S}_8$  ring (2.08 Å).  $\text{Se}_2\text{Cl}_2$  has a similar structure. It is made by the reaction between  $\text{Se}$  and  $\text{SeCl}_4$ , into which it disproportionates on warming.



The brown, oily liquid hydrolyses readily to  $\text{H}_2\text{SeO}_3$ ,  $\text{Se}$  and  $\text{HCl}$ . The bromides  $\text{S}_2\text{Br}_2$  and  $\text{Se}_2\text{Br}_2$ , both red liquids, are products of direct combination of the elements.

Lower chlorides of sulphur,  $\text{S}_x\text{Cl}_2$ , have been made with chains of up to five S atoms by reducing  $\text{S}_2\text{Cl}_2$  vapour with hydrogen at a hot surface and passing the products over a cold surface.

## Oxides

### Monoxides

Disulphur monoxide,  $\text{S}_2\text{O}$ , is made by subjecting a mixture of  $\text{S}$  and  $\text{SO}_2$  at  $150\text{--}200^\circ$  to an electric discharge, or by heating certain heavy metal oxides with sulphur vapour at a low pressure. It has the structure  $\text{SSO}$  with S—S 1.88 Å, S—O 1.46 Å, and angle  $\text{SSO}$   $118^\circ$ . It has many

of the properties of a free radical, can exist for several days at 10 mm pressure, and reacts immediately with Hg, Fe, and Cu. Alcoholic KOH converts it to  $K_2S$ ,  $K_2S_2O_4$  and  $K_2SO_3$ .

Although SO and SeO are unknown, the black oxide, TeO, is obtained when  $TeSO_3$  is heated. When heated,  $PoSO_3$  also produces a black oxide believed to be PoO.

Powdered sulphur reacts vigorously with liquid  $SO_3$  forming a blue-green solid which decomposes slowly at room temperature, rapidly on warming, to give S,  $SO_2$  and  $SO_3$ . Se and Te also dissolve in  $SO_3$  producing solutions of green  $SeSO_3$  and red  $TeSO_3$ .

TABLE 91  
OXIDES OF GROUP VIB ELEMENTS

S	Se	Te	Po
$S_2O$			
		TeO	PoO
$S_2O_3$			
$SO_2$	$SeO_2$	$TeO_2$	$PoO_2$
$SO_3$	$SeO_3$	$TeO_3$	
$SO_4$			

### Dioxides

The four elements of the sulphur family form dioxides; these are structurally very different from one another. The  $SO_2$  molecule is angular ( $119.5^\circ$ ), owing its shape to  $sp^2$  hybrid orbitals about the sulphur, one occupied by a lone pair, but there is a little d-orbital contribution, too. The solid  $SeO_2$ , made by burning Se in air, is colourless and crystalline, sublimes at  $315^\circ$  and, under pressure, melts to an orange liquid; the colour is lost on cooling. X-ray analysis shows it to contain macromolecular chains with oxygen atoms projecting alternately on opposite sides and at  $90^\circ$  to the plane of the chain (Fig. 268).

The links to the shared oxygen and to the projecting oxygen both possess some double-bond character.  $SeO_2$  is used in organic chemistry to oxidise aldehydes and ketones containing the  $-CH_2-CO-$  system to  $-CO-CO-$ , the  $SeO_2$  being reduced to Se. The fact that only one  $-CH_2-$  group is affected suggests that a complex is formed, but none has been isolated.

$TeO_2$ , also made by combustion of the element, exists in two colourless forms, one having a rutile and the other a brookite type of structure, both indicating that the oxide has a dominantly ionic character.  $PoO_2$ , of which there are two forms, red tetragonal and yellow face-centred cubic, decomposes at  $500^\circ$  in a vacuum, surprisingly leaving the metal.

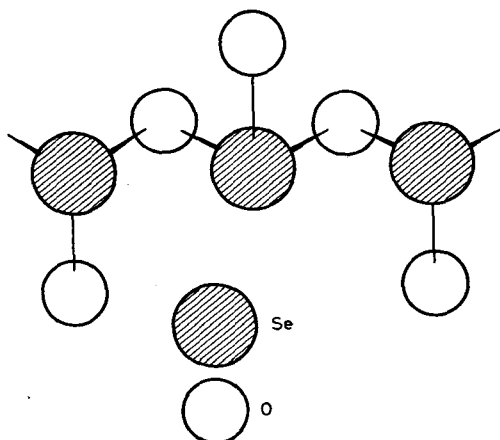


Fig. 268. Macromolecular chain structure of selenium dioxide.

The reactions of  $\text{SO}_2$ ,  $\text{SeO}_2$  and  $\text{TeO}_2$  with water are of interest. Gaseous  $\text{SO}_2$  dissolves, but the acid  $\text{H}_2\text{SO}_3$  cannot be isolated. Liquid  $\text{SO}_2$  has a limited miscibility with water but it is completely miscible with benzene.  $\text{SeO}_2$  gives an acidic aqueous solution from which colourless hexagonal  $\text{H}_2\text{SeO}_3$  can be crystallised.  $\text{TeO}_2$  is almost insoluble in water but dissolves not only in alkalis, but also in  $\text{H}_2\text{SO}_4$ ,  $\text{HCl}$  and  $\text{HNO}_3$ . The rhombic oxide hydroxide nitrate,  $\text{Te}_2\text{O}_3(\text{OH})\text{NO}_3$ , crystallises from a solution in nitric acid, an indication of the amphoteric character of  $\text{TeO}_2$ .

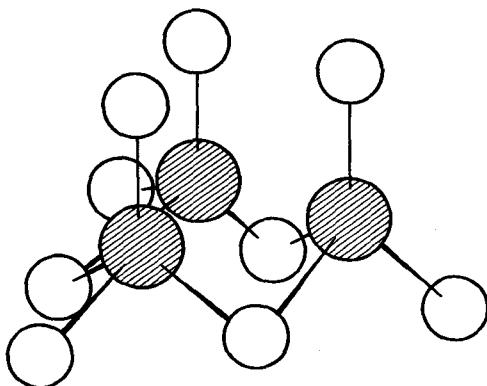


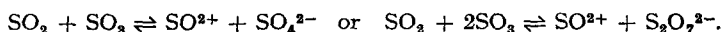
Fig. 269. Cyclic trimeric form of sulphur trioxide.



### Trioxides

Sulphur trioxide, made by the catalytic oxidation of  $\text{SO}_2$  with oxygen, is a colourless, readily volatile solid. The vapour consists of planar, monomeric molecules of zero dipole moment,  $\text{O—S—O}$  angle  $120^\circ$  and with bonds  $1.43 \text{ \AA}$ . The partly double-bond character is ascribable to a d-orbital contribution, stronger than that in  $\text{SO}_2$ . Solid  $\text{SO}_3$  exists in three forms; the two having asbestos-like structures with long chains of  $\text{SO}_2$  groups linked by oxygen atoms probably owe their existence to traces of moisture; the ice-like variety is a cyclic trimer (Fig. 269). Bond lengths indicate the oxygen atoms in the ring to be joined to the sulphur atoms by bonds which are essentially single. The projecting oxygen atoms are held by double bonds.

Sulphur trioxide dissolves in liquid  $\text{SO}_2$ . There is an exchange of oxygen but not of sulphur atoms between the two oxides, suggesting equilibria in the solution:



Though the means of comparing the strengths of Lewis acids is not entirely satisfactory,  $\text{SO}_3$  is clearly one of the strongest.

Sulphur trioxide, made industrially by the oxidation of  $\text{SO}_2$  (p. 487), is an intermediate in the manufacture of sulphuric acid and is itself an important sulphonating reagent in the detergent industry.

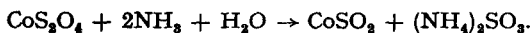
Selenium trioxide is formed, together with much  $\text{SeO}_2$ , when an electric discharge is passed through selenium vapour in oxygen at 4 mm pressure. The colourless, deliquescent solid is the anhydride of selenic acid.  $\text{TeO}_3$  is an orange solid made by heating telluric acid,  $\text{H}_6\text{TeO}_6$ , very strongly.

Sulphur is the only element in the group to form a tetroxide. This white solid is produced when dry  $\text{SO}_2$  and oxygen are passed through an ozoniser. There is cryoscopic evidence that it is monomeric. It decomposes at  $3^\circ$ , giving an orange liquid, empirically  $\text{S}_2\text{O}_7$ .  $\text{SO}_4$  is a very powerful oxidising agent, converting aniline to nitrobenzene. It does not form  $\text{H}_2\text{O}_8$  or a peroxyacid.

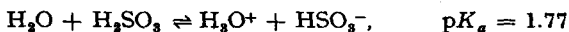
### Oxoacids of sulphur

Sulphoxylic acid	$\text{H}_2\text{SO}_2$	Exemplified only in its salts
Sulphurous acid	$\text{H}_2\text{SO}_3$	In aqueous solution and in salts
Disulphurous acid	$\text{H}_2\text{S}_2\text{O}_5$	Exemplified only in its salts
Dithionous acid	$\text{H}_2\text{S}_2\text{O}_4$	Exemplified only in its salts
Sulphuric acid	$\text{H}_2\text{SO}_4$	m.p. $10.5^\circ$
Disulphuric acid	$\text{H}_2\text{S}_2\text{O}_7$	m.p. $35^\circ$
Thiosulphuric acid	$\text{H}_2\text{S}_2\text{O}_3$	Isolated as solid stable at $\sim -78^\circ$
Thionic acids	$\text{H}_2\text{S}_x\text{O}_6$	( $x = 2-5$ ) In aqueous solution and in salts

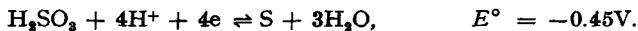
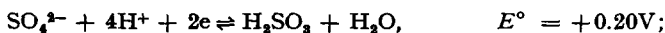
Sulphoxylic acid is known with certainty in its cobalt salt, made by the action of sodium dithionite on cobalt(II) acetate, followed by treatment with ammonia:



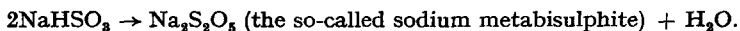
Sulphurous acid cannot be isolated from aqueous solutions of  $\text{SO}_2$ . However, the solution ionises fairly strongly:



Standard redox potentials are:



It has thus rather strong reducing properties, being itself reduced to sulphur only by very strong reducing agents. The dibasic acid forms two series of salts. The hydrogen sulphites,  $\text{MHSO}_3$ , yield disulphites of the type  $\text{M}_2\text{S}_2\text{O}_5$  on heating:

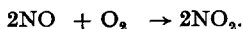
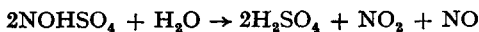


All of these compounds are reducing agents.

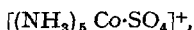
The sulphite ion in salts is pyramidal; the S—O distance (1.39 Å) is shorter than the S—O bonds in  $\text{SO}_2$  or  $\text{SOCl}_2$ .

Dithionites are made by reducing bisulphites, usually with zinc, or by shaking sodium or potassium amalgam with dry  $\text{SO}_2$  in the absence of oxygen. The salts reduce nitrocompounds to amines. An  $\text{Na}_2\text{S}_2\text{O}_4$  solution is used to reduce and dissolve vat dyes such as indigo. X-ray analysis shows the  $\text{S}_2\text{O}_4^{2-}$  ion in sodium dithionite to consist of two  $\text{SO}_2^-$  groups attached by a very long S—S bond (2.39 Å).

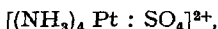
Sulphuric acid, commercially the most important acid of sulphur, is made by way of the catalytic oxidation of  $\text{SO}_2$  to  $\text{SO}_3$ ; this is done by air, either at a surface, such as  $\text{V}_2\text{O}_5$  or special mixtures of oxides, in the contact process, or with oxides of nitrogen as catalyst in the lead chamber process. The  $\text{SO}_3$  produced in the contact process is dissolved in sulphuric acid which is diluted as required. In the chamber process nitrosyl sulphuric acid is probably formed from sulphurous acid and nitrogen dioxide and is then hydrolysed by water thus:



Though a strong acid, the second ionisation of sulphuric acid is slight in any but the most dilute solutions. In the absence of water, the acid contains  $\text{HSO}_3^+$  ions, the active sulphonating agent (p. 246). X-ray analysis shows the  $\text{SO}_4^{2-}$  ion to be almost tetrahedral and the dimensions indicate considerable double bond character. The ion often holds 'anion water' in crystal structures, examples being  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  and  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ . In some complex compounds the  $\text{SO}_4$  group is bound covalently to the central atom. Examples are

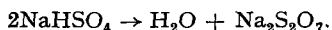


in which the  $\text{SO}_4$  group is attached by a single bond, and



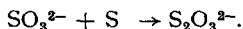
in which the group is bound by two covalent bonds.

Disulphuric (pyrosulphuric) acid,  $\text{H}_2\text{S}_2\text{O}_7$ , is formed when  $\text{SO}_3$  dissolves in  $\text{H}_2\text{SO}_4$ . It is an excellent sulphonating agent. Sodium disulphate (pyrosulphate),  $\text{Na}_2\text{S}_2\text{O}_7$ , can be made by heating sodium hydrogen sulphate strongly:

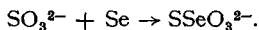


The salt is hydrolysed in water to give  $\text{HSO}_4^-$  ions. Evidence for higher isopolysulphates exists in the compound  $(\text{NO}_2)_2\text{S}_3\text{O}_{10}$ .

Anhydrous thiosulphuric acid, which is very unstable, has been obtained by the reaction of  $\text{H}_2\text{S}$  with  $\text{SO}_3$  at  $-78^\circ$ , either alone or in a liquid such as freon. It can also be made by the action of  $\text{H}_2\text{S}$  on chlorosulphuric acid,  $\text{HSO}_3\text{Cl}$ , at the same temperature. Thiosulphates are made by boiling alkali-metal sulphite solutions with sulphur:



Selenium also dissolves in sulphite solutions to give selenosulphates:



Thiosulphates are formed by many elements and radicals; some are fairly stable and soluble in water, those of the heavier metals are less soluble and less stable. The  $\text{S}_2\text{O}_3^{2-}$  ion is structurally analogous to  $\text{SO}_4^{2-}$  (Fig. 270).

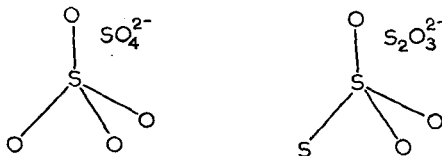
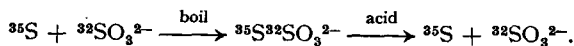
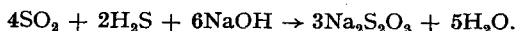


Fig. 270. Analogy between  $\text{S}_2\text{O}_3^{2-}$  and  $\text{SO}_4^{2-}$  ions.

$\text{Na}_2\text{S}_2\text{O}_3$ , made by boiling  $^{35}\text{S}$  with inactive  $\text{Na}_2\text{SO}_3$ , yields a precipitate of active sulphur on acidification but no activity remains in the  $\text{SO}_3^{2-}$  solution:



Hence there is no exchange between the two S atoms, and thus they cannot be equivalent in the molecule. When  $\text{H}_2^{35}\text{S}$  is used in the reaction:



similar evidence is obtained on acidifying the salt produced. All the central S atoms of the  $\text{S}_2\text{O}_3^{2-}$  ions come from  $\text{SO}_2$ , but the ligand atoms partly from  $\text{SO}_2$  and partly from  $\text{H}_2\text{S}$ .

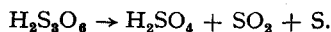
Addition of acid to a thiosulphate solution does not cause decomposition until a pH of 4.6 is reached. The  $\text{HS}_2\text{O}_3^-$  ion then formed, being much less stable than the  $\text{S}_2\text{O}_3^{2-}$  ion, decomposes quickly:



Thus thiosulphates exist only as neutral salts.

Dithionic acid appears in a solution of sulphurous acid which is being oxidised by finely divided  $\text{MnO}_2$ . From this solution, baryta precipitates all the sulphur-containing anions except dithionate, and, when the excess of  $\text{Ba}^{2+}$  has been precipitated by  $\text{H}_2\text{SO}_4$ , only  $\text{H}_2\text{S}_2\text{O}_6$  is left in the solution. Although conductance measurements show the acid to be dibasic, acid salts are unknown. Dithionates are soluble in water and, unlike salts of the higher thionic acids, are not decomposed by sulphites and sulphides.

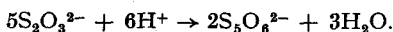
Potassium trithionate,  $\text{K}_2\text{S}_3\text{O}_6$ , can be made by passing  $\text{SO}_2$  into a solution of  $\text{K}_2\text{S}_2\text{O}_3$ . The salt crystallises on standing, leaving in solution  $\text{K}_2\text{S}_4\text{O}_6$  and  $\text{K}_2\text{S}_5\text{O}_6$  formed along with it. When aqueous  $\text{K}_2\text{S}_3\text{O}_6$  is acidified, decomposition occurs:



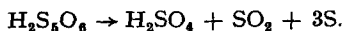
Sodium tetrathionate,  $\text{Na}_2\text{S}_4\text{O}_6$ , is formed when  $\text{Na}_2\text{S}_2\text{O}_3$  is oxidised with iodine. Although this, and other tetrathionates, can be isolated as solids, they are thermally unstable. Aqueous tetrathionic acid results from adding dilute  $\text{H}_2\text{SO}_4$  to a solution of  $\text{PbS}_4\text{O}_6$ ; attempts at concentration eventually cause decomposition:



Sodium pentathionate,  $\text{Na}_2\text{S}_5\text{O}_6$ , is made by treating a concentrated  $\text{Na}_2\text{S}_2\text{O}_3$  solution with very dilute hydrochloric acid in the presence of  $\text{As}_4\text{O}_6$  at  $-10^\circ$ :



The liquid deposits crystals of  $\text{Na}_2\text{S}_5\text{O}_8$  on standing. The acid itself is stable in fairly strong aqueous solution but eventually decomposes on concentration:



X-ray diffraction shows the dithionate ion to consist of two triangular pyramids joined at their apices (Fig. 271). In the trithionate ion the third sulphur atom lies between the other two with an S—S—S angle of  $103^\circ$  (Fig. 272). In the tetrathionate and pentathionate ions the additional sulphur atoms are attached to one another in zig-zag chains (Fig. 273).

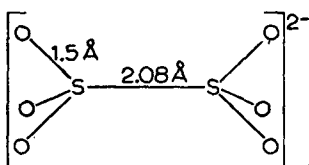


Fig. 271. Structure of dithionate ion.

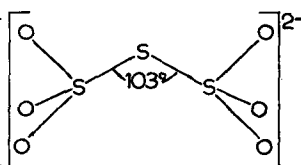


Fig. 272. Structure of trithionate ion.

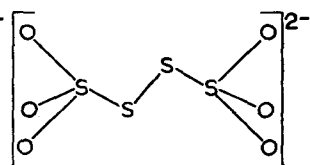


Fig. 273. Structure of tetrathionate ion.

### Oxoacids of selenium

Selenium, in contrast to sulphur, forms only the two oxoacids:

Selenious acid,  $\text{H}_2\text{SeO}_3$ , colourless solid.

Selenic acid,  $\text{H}_2\text{SeO}_4$ , colourless solid, m.p.  $59^\circ$ .

When a solution of  $\text{SeO}_2$  is evaporated the acid,  $\text{H}_2\text{SeO}_3$ , separates as hexagonal prisms. The Raman spectra of aqueous solutions of selenious acid show its dissociation to be very slight. There are normal and acid selenites, which ionise strongly in solution, and also superacid salts such as  $\text{KH}_3(\text{SeO}_3)_2$ . Heteropolyacids are formed with vanadic, molybdic and uranic acids.

Selenious acid is converted to selenic acid,  $\text{H}_2\text{SeO}_4$ , when refluxed with 30%  $\text{H}_2\text{O}_2$ . A 97.4% solution can be made by vacuum desiccation; the pure acid crystallises on cooling. This resembles sulphuric acid in (i) ionising strongly; (ii) forming selenates isomorphous with the sulphates; (iii) forming a nitroso-acid  $(\text{NO})\text{HSeO}_4$ . It differs from  $\text{H}_2\text{SO}_4$  by losing oxygen when heated above  $200^\circ$  and by oxidising chlorides to chlorine.



### Oxoacids of tellurium

Tellurous acid has not been prepared, the dioxide being insoluble in water. Tellurites may, however, be crystallised from solutions of  $\text{TeO}_2$  in aqueous alkali metal hydroxides.

Telluric acid,  $\text{H}_6\text{TeO}_6$ , can be made as colourless crystals by dissolving tellurium in aqua regia, adding a chlorate, evaporating in a vacuum, precipitating with  $\text{HNO}_3$  and, finally, recrystallising the product from water. The compound is a weak dibasic acid which gives the salts  $\text{NaTeO}(\text{OH})_5$  and  $\text{Na}_2\text{TeO}_2(\text{OH})_4$ . The molecule of telluric acid in the crystal has an octahedral  $\text{Te}(\text{OH})_6$  structure.

### Halogen derivatives of the oxoacids

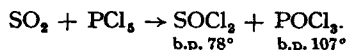
#### Sulphur

The principal oxohalides of sulphur are set out below:

<i>Sulphinyl (thionyl) halides</i>		<i>Sulphonyl (sulphuryl) halides</i>	
	b.p.		b.p.
$\text{SOF}_2$	$-30^\circ$	$\text{SO}_2\text{F}_2$	$-52^\circ$
$\text{SOCl}_2$	$78^\circ$	$\text{SO}_2\text{Cl}_2$	$69^\circ$
$\text{SOBr}_2$ (red)	$59^\circ/40 \text{ mm}$		

Other oxohalides such as  $\text{SOF}_4$ ,  $\text{SO}_3\text{F}_2$ ,  $\text{SOF}_6$  and  $\text{S}_2\text{O}_5\text{F}_2$  are known.

Sulphinyl chloride,  $\text{SOCl}_2$ , is made by the action of  $\text{SO}_2$  on  $\text{PCl}_5$ :



The colourless liquid is obtained by fractionating the mixture. The molecule is pyramidal (Fig. 274), and owes its shape to the use of  $\text{sp}^3$  hybrid orbitals round an S atom with one lone pair.

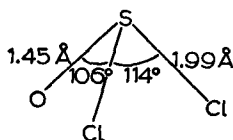


Fig. 274.

Structure of sulphinyl chloride.

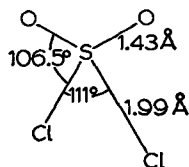
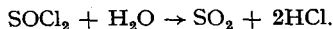


Fig. 275.

Structure of sulphonyl chloride.

Sulphinyl fluoride,  $\text{SOF}_2$ , a colourless gas which does not attack glass or mercury at room temperature, results from the action of  $\text{SbF}_3$  on  $\text{SOCl}_2$ . The red liquid  $\text{SOBr}_2$  is made by treating  $\text{SOCl}_2$  with  $\text{HBr}$ .  $\text{SOF}_2$  hydrolyses

slowly in water, in which it is sparingly soluble; the chloride hydrolyses violently:



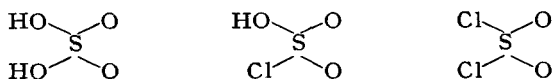
When  $\text{SO}_2$  and  $\text{Cl}_2$  are passed alternately over camphor they combine to give sulphonyl chloride,  $\text{SO}_2\text{Cl}_2$ , which can be distilled from the product. The liquid is rather slowly hydrolysed by water. The molecule forms a distorted tetrahedron (Fig. 275). Sulphonyl fluoride,  $\text{SO}_2\text{F}_2$ , made by heating  $\text{SO}_2$  and  $\text{F}_2$  together, is an inert gas, unaffected by water but decomposed by hot alkalis:



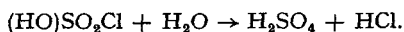
Important halogen-containing acids are:

chlorosulphuric	$\text{HSO}_3\text{Cl}$	b.p. $151^\circ$
fluorosulphuric	$\text{HSO}_3\text{F}$	b.p. $163^\circ$

When dry  $\text{HCl}$  is passed into fuming  $\text{H}_2\text{SO}_4$ , which contains  $\text{SO}_3$ , the compound  $\text{HOSO}_2\text{Cl}$ , chlorosulphuric acid, is formed. Its relation to  $\text{H}_2\text{SO}_4$  and  $\text{SO}_2\text{Cl}_2$  is shown; all the compounds have tetrahedral co-ordination:



It is hydrolysed violently by water:



Fluorosulphuric acid,  $(\text{HO})\text{SO}_2\text{F}$ , made by distilling fuming  $\text{H}_2\text{SO}_4$  with  $\text{CaF}_2$ , is a colourless liquid hydrolysed incompletely by water.

### Selenium

The seleninyl ( $\text{SeO}_2^{2+}$ ) compounds contain  $\text{Se}^{\text{IV}}$  and are thus related to  $\text{H}_2\text{SeO}_3$ .

$\text{SeOF}_2$ ,	colourless	b.p. $124^\circ$
$\text{SeOCl}_2$ ,	pale yellow	b.p. $176^\circ$ (decomposition)
$\text{SeOBr}_2$ ,	orange	m.p. $42^\circ$

$\text{SeOCl}_2$  is made by heating  $\text{SeO}_2$  and  $\text{SeCl}_4$  together in a sealed tube. It is converted to  $\text{SeOF}_2$  when passed over  $\text{AgF}$ , and to  $\text{SeOBr}_2$  when distilled from  $\text{NaBr}$ .

The selenonyl ( $\text{SeO}_2^{2+}$ ) derivatives of  $\text{H}_2\text{SeO}_4$  include  $\text{SeO}_2\text{F}_2$ , an easily hydrolysable gas made by heating  $\text{BaSeO}_4$  with  $\text{HSeO}_3\text{F}$ , itself obtained by the action of  $\text{HF}$  on  $\text{SeO}_3$ .

### Oxoacid salts of tellurium and polonium

Tellurium and polonium are the only elements of Group VIB which are sufficiently basic to form oxoacid salts. An oxide sulphate,  $\text{Te}_2\text{O}_3 \cdot \text{SO}_4$ , is obtained as white crystals when  $\text{TeO}$  is heated with concentrated  $\text{H}_2\text{SO}_4$ . A corresponding compound of polonium can be crystallised from a solution of  $\text{PoCl}_4$  in 0.02–0.025N  $\text{H}_2\text{SO}_4$ . With stronger  $\text{H}_2\text{SO}_4$ , however, a colourless hydrate of  $\text{Po}(\text{SO}_4)_2$  is formed. This loses water on standing or heating, becoming pink and finally purple. The purple anhydrous salt is stable up to 400°.

Tellurium dissolves in concentrated nitric acid. On evaporation colourless rhombic  $\text{Te}_2\text{O}_3(\text{OH})_3 \cdot \text{NO}_3$  crystallises. Polonium also forms a somewhat similar nitrate whose composition is as yet unknown.

### FURTHER READING

- S. C. ABRAHAM, *The Stereochemistry of Sub-Group VIB of the Periodic Table*, Quart. Rev., 10 (1956) 407.
- K. W. BAGNALL, *The Chemistry of Polonium*, Quart. Rev., 11 (1957) 30.
- H. L. ROBERTS, *The Chemistry of Compounds containing Sulphur-Fluorine Bonds*, Quart. Rev., 15 (1961) 30.
- G. H. CADY, *Fluorine-containing Sulphur Compounds*, in H. J. EMELÉUS AND A. G. SHARPE (Eds.), *Advances in Inorganic Chemistry and Radiochemistry*, Vol. 2, New York, Academic Press, 1960.
- J. W. GEORGE, *Halides and Oxyhalides of the Elements of Groups VB and VIB* in F. A. COTTON (Ed.), *Progress in Inorganic Chemistry*, Vol. II, London, Interscience, 1960.
- W. N. TALLER, (Ed.), *Sulphur Data Book*, London, McGraw-Hill, 1954.
- K. W. BAGNALL, *The Chemistry of Selenium, Tellurium and Polonium*, Amsterdam, Elsevier, 1966.
- S. M. WILLIAMSON, *Recent Advances in Sulphur-Fluorine Chemistry*, in F. A. COTTON (Ed.), *Progress in Inorganic Chemistry*, New York, Interscience, Vol. 7 (1966) 39.
- G. NICKLESS (Ed.), *Inorganic Sulphur Chemistry*, Amsterdam, Elsevier, in preparation.



## The Oxides

Of the known elements the lighter noble gases alone are without oxides.

In this chapter are considered only what we term the *normal* oxides, namely those with separate oxygen atoms or ions attached directly and only to the atom or ion of another element. Besides these there are the peroxides (p. 506) and superoxides (p. 508) in which the oxygen atoms are attached in pairs. In the hydrogen peroxide molecule (p. 504) they are connected to each other by a single bond,  $\text{H}-\text{O}-\text{O}-\text{H}$ ; in the lattice of ionic peroxides, such as  $\text{Na}_2\text{O}_2$ , they appear as  $\text{O}_2^{2-}$  ions; and in superoxides, such as  $\text{KO}_2$ , as  $\text{O}_2^-$  ions.

Normal oxides fall broadly into three classes according to their behaviour in water: (i) *basic* which are invariably ionic oxides of metals and which, when soluble, give alkaline solutions; (ii) *acidic*, essentially covalent compounds, which are roughly the soluble oxides of the non-metals and the higher oxides of the transition metals, and which give acidic solutions; (iii) *neutral* which include water and the relatively insoluble gases  $\text{CO}$  and  $\text{N}_2\text{O}$ .

The distribution through the Periodic Table of representative basic and acidic oxides is shown in Table 92; the oxides adjacent to the dividing line are commonly amphoteric; they show basic or acidic properties according to the conditions.

Oxygen, owing to its high electronegativity, readily forms ionic compounds, and most metallic oxides have simple ionic structures. Some metallic oxides, however, show considerable covalent character when the metal (*e.g.* a transition metal) can have a high charge number and a correspondingly greater electronegativity. The charge effect is well shown by manganese;  $\text{MnO}$  is an ionic solid with a rock-salt lattice, whereas  $\text{Mn}_2\text{O}_7$  is a covalent liquid.

Oxides of the non-metals range from the volatile monomers (*e.g.*  $\text{CO}_2$ ,  $\text{N}_2\text{O}$ ,  $\text{SO}_2$ ) to involatile macro-molecules (*e.g.*  $\text{B}_2\text{O}_3$ ,  $\text{SiO}_2$ ). Intermediately there are many oxides which, through association, are less volatile than might be expected (*e.g.*  $\text{H}_2\text{O}$ ,  $\text{SO}_3$ ,  $\text{P}_2\text{O}_5$ ).

The classification of oxides as acidic and basic is not rigid. Generally the molecular oxides of the non-metals are acidic, many being acid anhydrides,

and so too are the higher oxides of transition metals (*e.g.*  $\text{CrO}_3$ ,  $\text{Mn}_2\text{O}_7$ ). Such neutral oxides as  $\text{H}_2\text{O}$ ,  $\text{CO}$  and  $\text{N}_2\text{O}$  are exceptional. The more or less covalent  $\text{CuO}$  is without acid character and the similar  $\text{PbO}$  is weakly basic. Although the ionic metal oxides are usually basic,  $\text{ZnO}$  and  $\text{Al}_2\text{O}_3$  are amphoteric.

TABLE 92  
DISTRIBUTION OF OXIDES THROUGH THE PERIODIC TABLE

*Non-transition elements*

	<i>Basic</i>			<i>Acidic</i>		
$\text{Li}_2\text{O}$	$\text{BeO}$	$\text{B}_2\text{O}_3$	$\text{CO}_2$	$\text{N}_2\text{O}_5$		$\text{F}_2\text{O}$
$\text{Na}_2\text{O}$	$\text{MgO}$	$\text{Al}_2\text{O}_3$	$\text{SiO}_2$	$\text{P}_2\text{O}_5$	$\text{SO}_3$	$\text{Cl}_2\text{O}$
$\text{K}_2\text{O}$	$\text{CaO}$	$\text{Ga}_2\text{O}_3$	$\text{GeO}_2$	$\text{As}_2\text{O}_3$	$\text{SeO}_2$	$\text{Br}_2\text{O}$
$\text{Rb}_2\text{O}$	$\text{SrO}$	$\text{In}_2\text{O}_3$	$\text{SnO}$	$\text{Sb}_2\text{O}_3$	$\text{TeO}_2$	$\text{I}_2\text{O}_5$
$\text{Cs}_2\text{O}$	$\text{BaO}$	$\text{Tl}_2\text{O}$	$\text{PbO}$	$\text{Bi}_2\text{O}_3$	$\text{PoO}_2$	

*Transition elements and Gps. IB and IIB*

	<i>Basic</i>		<i>Acidic</i>				<i>Basic</i>		
$\text{Sc}_2\text{O}_3$	$\text{TiO}_2$	$\text{V}_2\text{O}_5$	$\text{CrO}_2$	$\text{Mn}_2\text{O}_7$	$\text{Fe}_2\text{O}_3$	$\text{CoO}$	$\text{NiO}$	$\text{Cu}_2\text{O}$	$\text{ZnO}$
$\text{Y}_2\text{O}_3$	$\text{ZrO}_2$	$\text{Nb}_2\text{O}_5$	$\text{MoO}_3$	$\text{Tc}_2\text{O}_7$	$\text{RuO}_4$	$\text{Rh}_2\text{O}_3$	$\text{PdO}$	$\text{Ag}_2\text{O}$	$\text{CdO}$
* $\text{Ln}_2\text{O}_3$	$\text{HfO}_2$	$\text{Ta}_2\text{O}_5$	$\text{WO}_3$	$\text{Re}_2\text{O}_7$	$\text{OsO}_4$	$\text{IrO}_2$	$\text{PtO}$	$\text{Au}_2\text{O}$	$\text{HgO}$
$\text{Ac}_2\text{O}_3$									

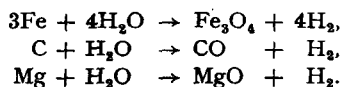
\* Ln = lanthanide atom.

### Methods of preparation

Many normal oxides are formed on burning the element in air or oxygen. This is true not only of the non-metals boron, carbon, sulphur and phosphorus, but also for the volatile metals zinc, cadmium, indium and thallium, the transition metals cobalt and iron, when in a finely divided condition, and the noble metals osmium, ruthenium and rhodium. With some elements, limiting the supply of oxygen produces the lower oxide (*e.g.*  $\text{P}_4\text{O}_6$  in place of  $\text{P}_4\text{O}_{10}$  (p. 439)).

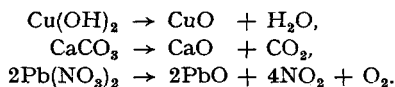
Lower oxides have been made by reducing a higher oxide with carbon or hydrogen (*e.g.*  $\text{MnO}_2$  to  $\text{MnO}$  and  $\text{V}_2\text{O}_5$  to  $\text{V}_2\text{O}_3$  by hydrogen).

A few elements are oxidised by steam at red heat:



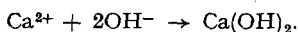
In the last reaction magnesium burns brilliantly.

Metal oxides are commonly prepared, and often manufactured, by the thermal decomposition of hydroxide, carbonate or nitrate:

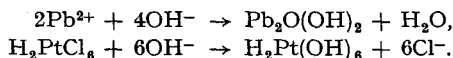


Certain precipitated hydroxides are easily converted to oxide,  $\text{Tl}(\text{OH})_3$  to  $\text{Tl}_2\text{O}_3$  even in boiling water, but others, for instance  $\text{Cu}(\text{OH})_2$ , which gives a hydrated black oxide, cannot be completely dehydrated without producing a non-stoichiometric oxide. Gold(III) hydroxide,  $\text{Au}(\text{OH})_3$ , is changed only to  $\text{AuO}(\text{OH})$  after prolonged standing over  $\text{P}_2\text{O}_5$ .

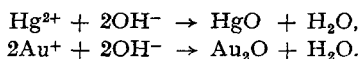
Precipitation by alkali from soluble salts usually gives a hydroxide:



Sometimes a complex hydrated oxide is formed:



But in other instances the oxide itself results:



Other oxidising agents, especially nitric acid and the oxides of nitrogen, convert some elements to oxides. Nitric acid, for example, oxidises sulphur to  $\text{SO}_2$  and  $\text{SO}_3$ , and germanium and tin to  $\text{GeO}_2$  and  $\text{SnO}_2$  respectively.

The preparation of pure, single-phase oxides of true stoichiometry is often difficult, sometimes impossible.  $\text{FeO}$  and  $\text{MnO}_2$  are examples, the former being always metal-deficient, the latter always oxygen-deficient (p. 697, 682).

## Oxide structures

### *Metallic oxides of predominantly ionic character*

#### *MO type*

Metal oxides of MO type are generally simple structurally, having  $\text{O}^{2-}$  and  $\text{M}^{2+}$  ions arranged in 4:4 or 6:6 co-ordination, depending on the ratio of the ionic sizes. The  $\text{Be}^{2+}$  ion (0.31 Å) has only four  $\text{O}^{2-}$  ions (1.40 Å) round it in  $\text{BeO}$ ; but most MO-type ionic oxides, with  $\text{M}^{2+}$  ranging from 0.5 Å to 1.0 Å, have the 6:6 co-ordination and rock-salt lattices. Examples are  $\text{MgO}$ ,  $\text{CaO}$ ,  $\text{SrO}$ ,  $\text{BaO}$ ,  $\text{CdO}$ ,  $\text{VO}$ ,  $\text{MnO}$  and  $\text{CoO}$ ; however  $\text{NiO}$  has a slightly distorted version of the lattice which gives it a rhombohedral structure. The normal oxides of the Group IA metals are ionic oxides of the  $\text{M}_2\text{O}$  type. They have the antifluorite crystal lattice arising from 4:8 co-ordination; a structure

so named because the position of anions and cations are the reverse of those in  $\text{CaF}_2$  (p. 203).

### $\text{MO}_2$ type

There are two main types of ionic oxides which are empirically formulated  $\text{MO}_2$ . Where the metal ion is large ( $\text{Th}^{4+}$ , 0.95 Å;  $\text{Ce}^{4+}$ , 1.01 Å;  $\text{U}^{4+}$ , 0.89 Å) the crystals are built up of fluorite-type unit cells with 8:4 co-ordination. But where the metal ion is smaller ( $\text{Sn}^{4+}$ , 0.71 Å;  $\text{Ti}^{4+}$ , 0.68 Å) the structure is based on the rutile lattice with 6:3 co-ordination. Other examples of this structure are  $\text{VO}_2$ ,  $\text{RuO}_2$ ,  $\text{PbO}_2$  and  $\text{TeO}_2$ . The rutile lattice is slightly deformed in  $\text{MoO}_2$  and  $\text{WO}_2$ .

### $\text{MO}_3$ type

The structurally simplest  $\text{MO}_3$  type oxide is rhenium oxide,  $\text{ReO}_3$  (Fig. 356, p. 683).  $\text{WO}_3$  and  $\text{CrO}_3$  are like it, but slightly deformed.

### $\text{M}_2\text{O}_3$ type

The usual lattices of the  $\text{M}_2\text{O}_3$  group of ionic oxides are those of corundum

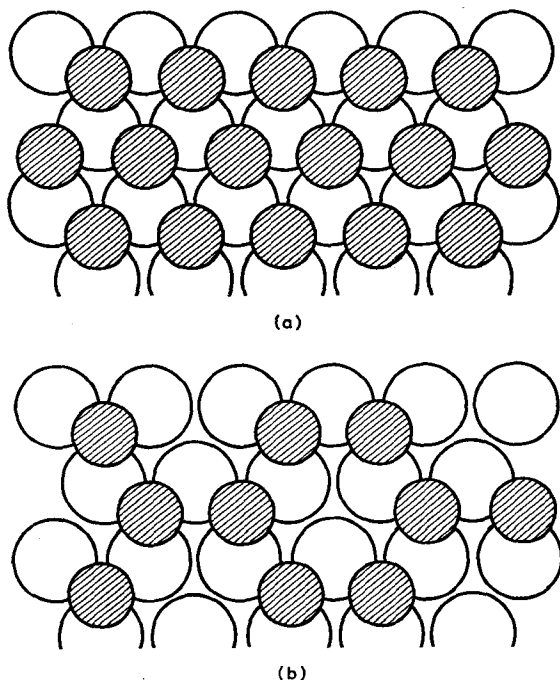


Fig. 276. Relation between structures of  $\text{MgO}$  and  $\alpha\text{-Al}_2\text{O}_3$ .  
(a)  $\text{MgO}$  structure; (b)  $\text{Al}_2\text{O}_3$  structure.

( $\text{Al}_2\text{O}_3$ ) and of the A- and C-type lanthanide sesquioxides. The relationship of the corundum lattice to that of  $\text{MgO}$  is shown in Fig. 276. In both structures  $\text{O}^{2-}$  ions are arranged octahedrally round the metal ions, but in  $\alpha\text{-Al}_2\text{O}_3$  one third of the metal ions are missing. The A-type lanthanide sesquioxides,  $\text{La}_2\text{O}_3$  is an example, have a hexagonal lattice (Fig. 277) and unusual co-ordination. Thus each  $\text{La}^{3+}$  ion has, as nearest neighbours, four  $\text{O}^{2-}$  at 2.42 Å and three  $\text{O}^{2-}$  at 2.69 Å.

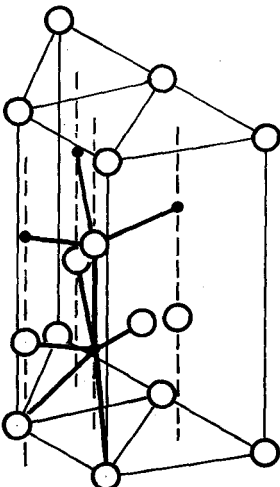


Fig. 277. Hexagonal lattice of A-type lanthanide oxide, e.g.  $\text{La}_2\text{O}_3$ .

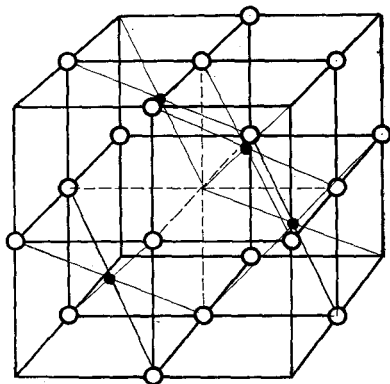


Fig. 278. Cubic lattice of C-type lanthanide oxide, e.g.  $\text{Sc}_2\text{O}_3$ .

The C-type oxide (Fig. 278),  $\text{Sc}_2\text{O}_3$  is an example, has the simpler symmetry of the cubic lattice and 6:4 co-ordination.

#### $M_3O_4$ type

In oxides with the empirical composition  $M_3O_4$ , the metal necessarily appears with two charge numbers. As a result, the compounds often resemble complex oxides (see below). Red lead,  $\text{Pb}_3\text{O}_4$ , which is isomorphous with  $\text{ZnSb}_2\text{O}_4$ , has a complicated structure. Octahedra of  $\text{Pb}^{\text{IV}}\text{O}_6$  share opposite edges to form chains; these are linked by  $\text{Pb}^{\text{II}}$  atoms each forming three bonds, pyramidally arranged, with its nearest oxygen neighbours (Fig. 237, p. 415).

#### *Metal oxides of more covalent character*

In these oxides the number of bonds round the metal is fewer than size considerations alone would suggest, and they are frequently arranged in

the same manner as the bonds present in complexes of the metal.

Silver(I) and copper(I) oxides are similar in structure (Fig. 382, p. 733), with the M—O bonds collinear and 2 : 4 co-ordination. But in PdO and PtO each metal atom has four coplanar bonds and each oxygen four tetrahedral ones in a tetragonal unit cell (Fig. 373, p. 716).

Layer lattices, when they occur in oxides, indicate a predominantly covalent character in the metal-oxygen bonds. The oxides SnO and PbO have layer lattices. Each metal atom is joined to four oxygens arranged in a square on one side of it (Fig. 279).

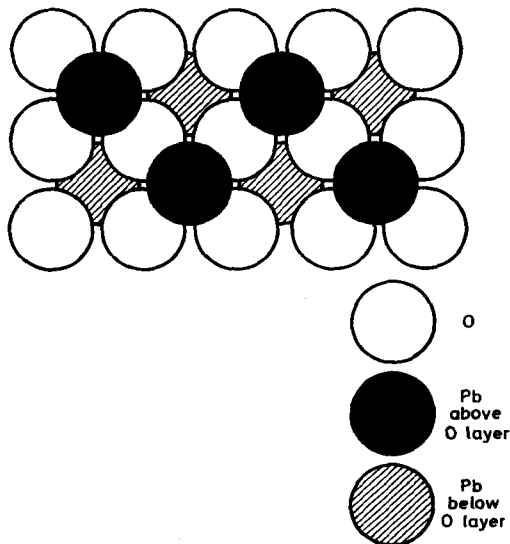


Fig. 279. Layer lattice of PbO (shown in plan in depth).

Molybdenum(VI) oxide,  $\text{MoO}_3$ , also has a layer structure; in it  $\text{MoO}_6$  octahedra share two edges and two corners with one another.

#### Complex oxides

Some complex oxides have complex ions (*e.g.*  $\text{CO}_3^{2-}$  and  $\text{NO}_3^-$ ) and others are without complex ions. Only the latter will be discussed here. They are of two main types. In the first, the lattice structures are the same as those of simple compounds, but in them random replacement of metal ions has occurred. Thus  $\text{Li}_2\text{TiO}_3$  has a random rock-salt structure with two thirds of the metal ion positions occupied by Li and one third by Ti. The lattice of  $\text{FeSbO}_4$  has a random rutile structure.

In the second type, the structures are not those of simple compounds. Three of these structures are of importance: they are respectively the *perovskite*,  $\text{CaTiO}_3$ ; the *ilmenite*,  $\text{FeTiO}_3$ ; and the *spinel*,  $\text{FeAl}_2\text{O}_4$ . In perovskite the large  $\text{Ca}^{2+}$  and  $\text{O}^{2-}$  ions form a close-packed structure with smaller  $\text{Ti}^{4+}$  ions uniformly arranged in some of the interstices (Fig. 280).

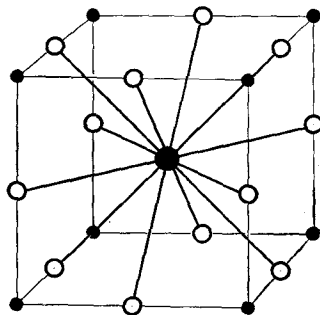


Fig. 280. Perovskite structure. Note relationship to  $\text{ReO}_3$  (p. 683).

Other complex oxides with a perovskite structure are  $\text{SrTiO}_3$ ,  $\text{CaZrO}_3$  and  $\text{LaAlO}_3$ .

In ilmenite, the oxygen ions are in close-packed hexagonal arrangement with both the  $\text{Fe}^{2+}$  and  $\text{Ti}^{4+}$  ions severally occupying one third of the octahedral holes. The compounds  $\text{MnTiO}_3$ ,  $\text{CoTiO}_3$  and  $\text{NiTiO}_3$  also have the ilmenite structure and there is no justification for calling them titanates. Ilmenite is isomorphous with  $\alpha\text{-Fe}_2\text{O}_3$  which has the corundum structure (Fig. 276 (b), p. 497). It differs from  $\alpha\text{-Fe}_2\text{O}_3$  only in having  $\text{Ti}^{4+}$  ions alternating with  $\text{Fe}^{2+}$  ions instead of ions of the same metal, namely  $\text{Fe}^{3+}$ .

A slightly more complicated arrangement is that in the spinels. The oxide ions in  $\text{FeAl}_2\text{O}_4$  are arranged in cubic close-packing with the  $\text{Fe}^{2+}$  ions in the tetrahedral, and the  $\text{Al}^{3+}$  ions in the octahedral interstices. Fig. 281 shows the arrangement of metal ions relative to two adjacent layers of oxygen ions.

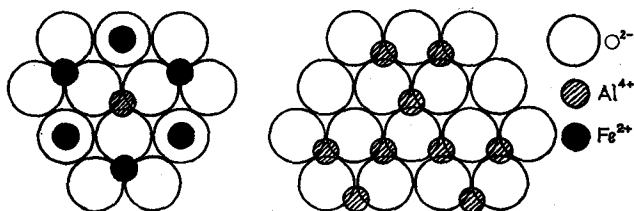
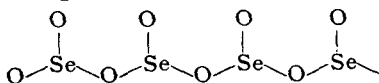


Fig. 281. Adjacent layers of  $\text{O}^{2-}$  ions with superimposed metal ions in  $\text{FeAl}_2\text{O}_4$ .

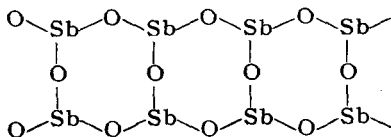
Other compounds with this structure include  $\text{CoAl}_2\text{O}_4$  and  $\text{MnAl}_2\text{O}_4$ ; these again have the  $\text{M}^{2+}$  ions in positions of tetrahedral, and the  $\text{M}^{3+}$  ions in positions of octahedral co-ordination. There is, however, a second rather more complicated type of spinel structure with a partly random arrangement of the metal ions. Examples are  $\text{Fe}(\text{MgFe})\text{O}_4$  and  $\text{Fe}(\text{TiFe})\text{O}_4$ , so formulated because one half of the Fe atoms are symmetrically arranged in octahedral positions and the other half randomly arranged, with the ions of the second metal, in tetrahedral positions. The effect of crystal-field stabilisation in determining spinel structure is discussed on p. 208.

#### *Oxides with chain structures*

Some elements of the B sub-group form oxides with chain-like structures which can be considered as intermediate in valency character between the infinite three dimensional metallic oxides and the molecular, non-metallic oxides. Examples are  $\text{SeO}_2$ :



and valentinite, which is a form of  $\text{Sb}_2\text{O}_3$ :



In this the Sb atoms form pyramidal bonds with bond angles about  $90^\circ$ .

#### *Solid oxides containing individual molecules*

The covalent oxides of non-metals form solids in which individual molecules are present, sometimes as the simple monomer, for instance  $\text{CO}_2$  and  $\text{SO}_2$ , and sometimes as a dimer or trimer. Dimeric forms include  $\text{P}_4\text{O}_6$  and  $\text{As}_4\text{O}_6$ . One of the forms of sulphur trioxide is trimeric (p. 485).

### **Comparison of oxides and sulphides**

Oxides are generally more ionic in character than the corresponding sulphides. The electronegativity assigned to oxygen is 3.50, that to sulphur only 2.44. Accordingly, elements of low electronegativity form markedly ionic bonds with oxygen but not necessarily with sulphur. This difference is clearly brought out when the structures of oxides and sulphides are compared. The only unequivocally ionic sulphides are those of the Group



IA and Group IIA metals and of a few of the transition metals, such as MnS. The existence of any truly ionic  $M_2S_3$  sulphide is doubtful, although the ready hydrolysis of  $Al_2S_3$  suggests that it may be one. No ionic  $MS_2$  sulphide is known. The  $S^{2-}$  ion is evidently too easily polarised to exist in the neighbourhood of a small quadripesitive cation. Instead, most of the solid disulphides have layer lattices, a type of structure very uncommon among the oxides:



Both the pyrites and marcasite forms of  $FeS_2$  contain covalently bound  $S_2$  units which are not ionic (Fig. 365, p. 698).

### Non-stoichiometry

The solid oxides and sulphides all show, to a greater or lesser extent, homogeneous phases which vary in composition from that represented by the stoichiometric formula of the named compound. These phases often retain the same structure but, nevertheless, show a certain range of differences in their other properties (p. 215).

### Thermochemistry of the oxides

In a series of oxides such as those of the metals of the third period,

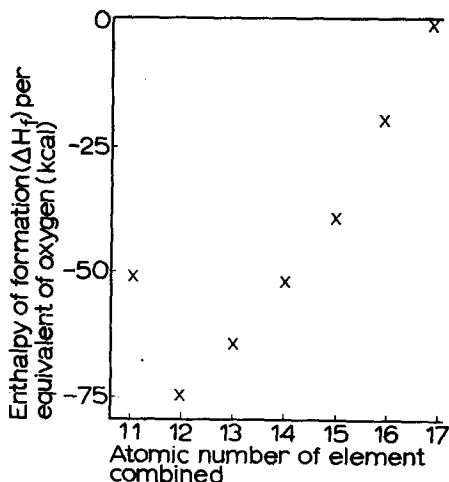


Fig. 282. Enthalpy of formation ( $\Delta H$ ) per equivalent of oxygen for  $Na_2O$ ,  $MgO$ ,  $Al_2O_3$ ,  $SiO_2$ ,  $P_4O_{10}$ ,  $SO_3$ ,  $Cl_2O_7$ .

differences between the enthalpies of formation of its members (Fig. 282) depend largely on the differences between the ionisation energies of the elements combining with oxygen and on the differences between the lattice energies of the oxides so formed. When a positive noble-gas type ion is replaced by one of higher charge but of the same structure, the enthalpy of formation is less negative, and consequently the stability decreases. The apparently anomalous fall in enthalpy of formation per oxygen equivalent from  $\text{Na}_2\text{O}$  to  $\text{MgO}$  is understandable when the lower crystal energy of  $\text{Na}_2\text{O}$ , caused by the mutual repulsion between unipositive metal ions, is taken into account. The effect is demonstrated more emphatically by the nitrides, where the stable  $\text{AlN}$  has a large crystal energy and the unstable  $\text{Na}_3\text{N}$  a small one. Nevertheless  $\text{Li}_3\text{N}$  is stable enough to be formed by direct combination of the elements, because the  $\text{Li}^+$  ion is much smaller than the  $\text{Na}^+$  ion and thus is smaller in relation to the size of the  $\text{N}^{3-}$  anion.

Enthalpies of formation of the oxides usually become more negative down a group in the Periodic Table:

	$\text{CO}_2$	$\text{SiO}_2$	$\text{TiO}_2$	$\text{ZrO}_2$	$\text{HfO}_2$
$\Delta H_f$ , per oxygen equivalent (kcal)	-23.5	-49.5	-54	-64	-83

Ionisation energies decrease with increase in size of the  $\text{M}^{4+}$  ions in passing from  $\text{Ti}^{4+}$  to  $\text{Hf}^{4+}$ . Lattice energies also decrease as the sum of the radii  $r_+$  and  $r_-$  increases, but the effect is overshadowed by the change in ionisation energy, particularly where the radius of the positive ion ( $r_+$ ) is small compared with that of the oxide ion ( $r_-$ ).

#### FURTHER READING

- R. WARD, *The Structure and Properties of Mixed Metal Oxides*, in F. A. COTTON (Ed.), *Progress in Inorganic Chemistry*, Vol. 1, London, Interscience, 1959, p. 465.
- L. BREWER, *Thermodynamic Properties of Oxides*, Chem. Rev., 52 (1952) 1.
- L. BREWER AND G. M. ROSENBLATT, *Dissociation Energies of Gaseous Oxides*,  $\text{MO}_2$ , Chem. Rev., 61 (1961) 257.

## Peroxides and Peroxo-Compounds

## Hydrogen peroxide

The geometry and probable electronic structure of  $\text{H}_2\text{O}_2$  are shown in Fig. 283.

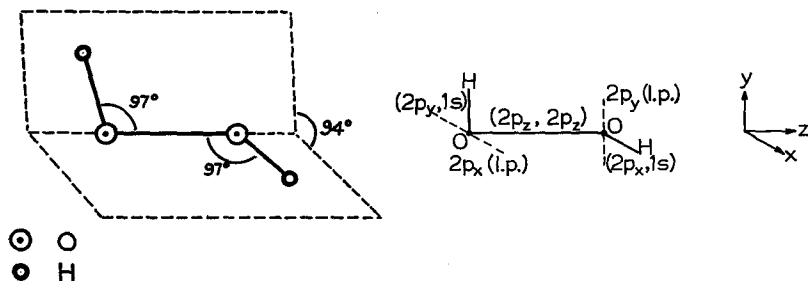


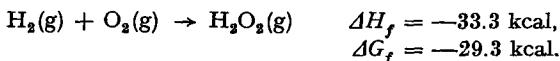
Fig. 283. Structure of  $\text{H}_2\text{O}_2$ .

The lengths of the O—O and O—H bonds are  $1.48 \pm 0.02 \text{ \AA}$  and  $1.01 \pm 0.03 \text{ \AA}$  respectively. The angles of  $97^\circ$  and  $94^\circ$  suggest only a slight distortion of the electronic structure shown; in which, for example,  $(2p_x, 1s)$  indicates a localised bond involving the oxygen  $2p_x$  orbital and the hydrogen  $1s$ . This configuration would (i) minimise lone-pair—lone-pair repulsions and (ii) maximise small contributions to bonding which can arise from slight delocalisation of the lone pairs. It would therefore account for the observed lack of free rotation about the O—O bond.

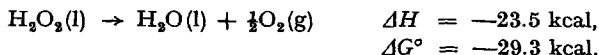
Liquid hydrogen peroxide is very pale-blue and is syrupy in consistency. It freezes at  $-0.46^\circ$  to tetragonal crystals, and is much denser than water ( $1.471 \text{ g/cc}$  at  $0^\circ$ ). The boiling point cannot be measured directly as the liquid decomposes explosively at a lower temperature, but extrapolation of vapour pressure data leads to a value of  $155.5^\circ$ . The entropy of vaporisation ( $27.3 \text{ cal/deg/mole}$ ) is high, indicating the destruction of a considerable 'local order' (p. 289) when the liquid vaporises, which is characteristic of polar liquids. The dipole moment is in fact high ( $2.01 \text{ Debyes}$ ); the dielectric constant is large ( $89$  at  $0^\circ$ ); and the autoprotolysis constant (p. 240),

$[H_3O_2^+][HO_2^-] = 1.55 \times 10^{-12}$ , indicates that the liquid is a good ionising solvent.

The enthalpy and free energy of formation are much less negative than those for water:

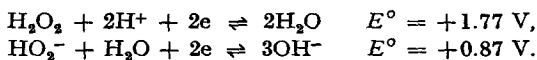


Liquid hydrogen peroxide is thermodynamically unstable:

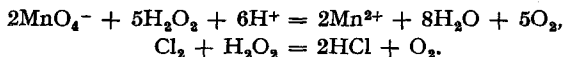


but its decomposition at 25° is not rapid in the absence of catalysts. Catalysts are silver, the platinum group metals, cobalt, iron, copper,  $MnO_2$  and several other oxides. As usual, the rate of reaction depends on their surface area.

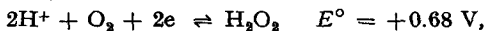
Hydrogen peroxide is a strong oxidising agent in both acid and alkaline solutions:



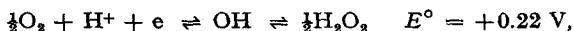
But with some strong oxidising agents, such as  $Cl_2$ , or  $MnO_4^-$  in acid solution, hydrogen peroxide is itself oxidised:



In acid solution:

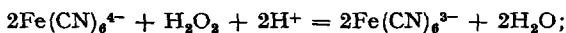


but in alkaline solution

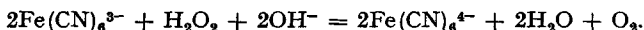


and oxidation can proceed more readily.

The standard redox potential of the cyanoferrate(III)–cyanoferrate(II) couple (+0.356 V) lies between these two values. As a result  $H_2O_2$  will oxidise a cyanoferrate(II) in acid solution:



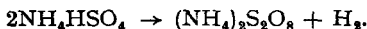
but in alkaline solution cyanoferrate(III) oxidises  $H_2O_2$ :



In the oxidation of aqueous  $H_2^{18}O_2$  by chlorine and  $MnO_4^-$ , and in the catalytic decomposition of hydrogen peroxide by  $Fe^{3+}$  and  $MnO_2$ , all the molecular oxygen that is released comes from the  $H_2O_2$ , none from the water. Evidently the O—O bond of the peroxide is not broken.

### Production of hydrogen peroxide

Formerly, its production was based on the electrolysis of ammonium sulphate in an excess of sulphuric acid between platinum electrodes at high current density; this produces a solution of the ammonium salt of perdisulphuric acid by oxidation at the anode and liberates hydrogen at the cathode:

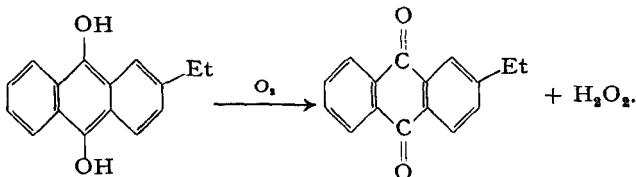


The solution, on heating at 40 mm pressure, hydrolyses and a distillate of water and  $\text{H}_2\text{O}_2$  is obtained:



The aqueous  $\text{H}_2\text{O}_2$  is concentrated to 85–90% by low-pressure fractionation, water being more volatile than hydrogen peroxide.

Now an autoxidation process is used in the manufacture of hydrogen peroxide. Air is passed through a 10% solution of 2-ethyl anthrahydroquinol in a mixture of benzene and 7–11 carbon-atom alcohols, or an alternative mixed solvent of a safer character.



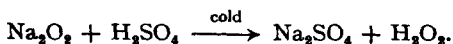
When the concentration of  $\text{H}_2\text{O}_2$  reaches about 5.5 g/l., the organic phase is extracted with water to give an 18% aqueous solution which is concentrated as described above. The 2-ethylanthraquinone which remains in the organic phase is reduced to the original compound with hydrogen in the presence of palladium on an inert support, the catalyst being suspended in the liquid by the stream of gas. The 2-ethylanthrahydroquinol solution is returned to the cycle.

### Peroxides

A peroxide contains, by definition, the anion  $(\text{O}-\text{O})^{2-}$  (p. 494) and produces  $\text{H}_2\text{O}_2$  when acidified. It is thus incorrect to apply the term to dioxides such as  $\text{NO}_2$  and  $\text{PbO}_2$ . Peroxides are formed by all Group IA and several Group IIA metals:  $\text{Li}_2\text{O}_2$ ,  $\text{Na}_2\text{O}_2$ ,  $\text{K}_2\text{O}_2$ ,  $\text{Rb}_2\text{O}_2$ ,  $\text{Cs}_2\text{O}_2$ , and  $\text{MgO}_2$ ,  $\text{CaO}_2$ ,  $\text{SrO}_2$ ,  $\text{BaO}_2$ .

The best known of these, sodium peroxide,  $\text{Na}_2\text{O}_2$ , is made by heating

sodium in oxygen. The pale yellow commercial material contains about 10%  $\text{NaO}_2$ . The compound  $\text{Li}_2\text{O}_2 \cdot \text{H}_2\text{O}_2 \cdot \text{H}_2\text{O}$  is precipitated when alcoholic  $\text{H}_2\text{O}_2$  is added to  $\text{LiOH}$ ; careful drying gives the anhydrous compound. The other peroxides of this group are made by controlled oxidation; either by using the calculated amount of air on the metal at  $300^\circ$ , or by passing the required amount of air through a solution of the metal in liquid ammonia at  $-50^\circ$ . The compounds all give  $\text{H}_2\text{O}_2$  on acid hydrolysis:



Belief in the existence of  $(\text{O}-\text{O})^{2-}$  ions in the Group I compounds is based on their reactions, not on their crystal structure which is unknown.

Of the Group IIA peroxides, that of barium is most stable. It is made by heating  $\text{BaO}$  in air or oxygen at  $400^\circ$ .  $\text{SrO}_2$  is made less easily; at  $400^\circ$  and 100 atmospheres the equilibrium mixture  $2\text{SrO} + \text{O}_2 \rightleftharpoons 2\text{SrO}_2$  contains about 15% of the strontium as  $\text{SrO}_2$ . Octahydrates of these two peroxides, and also  $\text{CaO}_2 \cdot 8\text{H}_2\text{O}$ , are precipitated by adding  $\text{H}_2\text{O}_2$  to the appropriate aqueous hydroxide. All the octahydrates can be dehydrated to the anhydrous peroxides. The monohydrate,  $\text{BaO}_2 \cdot \text{H}_2\text{O}$ , consists of  $\text{Ba}^{2+}$  ions and helical chains of peroxide groups, held together by hydrogen bonds. Anhydrous  $\text{MgO}_2$  is made by adding  $\sim 0.15M$   $\text{NaOH}$  to  $\text{MgSO}_4$  dissolved in 30%  $\text{H}_2\text{O}_2$  and drying the precipitate over phosphorus pentoxide.

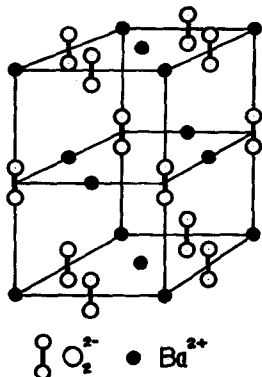


Fig. 284. Structure of  $\text{BaO}_2$ .

Of the Group IIB peroxides, anhydrous  $\text{ZnO}_2$  is prepared in a similar way to  $\text{MgO}_2$ , and  $\text{CdO}_2$  is made by the action of 30%  $\text{H}_2\text{O}_2$  on an ammoniacal solution of  $\text{CdSO}_4$  and drying the precipitate produced at  $120^\circ$ . Like  $\text{MgO}_2$ , the zinc and cadmium peroxides have the pyrites structure (p. 698) with an  $\text{O}-\text{O}$  distance, in the peroxide ion, of  $1.50 \text{ \AA}$ .

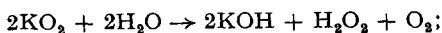
### Superoxides

The alkali metals other than lithium form coloured compounds of the formula  $MO_2$ , containing the anion  $O_2^-$  and termed superoxides (p. 494).  $NaO_2$  is formed only at high oxygen pressures, those of the other metals more easily. In  $NaO_2$  the arrangement of oxygen anions is not strictly ordered. The superoxides  $KO_2$  and  $BaO_2$  are similar in their structure and stability:

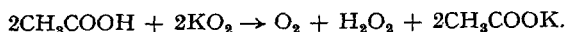
Ionic radius		O—O distance	
$K^+$	1.33 Å	$O_2^-$	1.28 Å
$Ba^{2+}$	1.35	$O_2^{2-}$	1.31

The paramagnetism of the superoxides suggests an ionic picture featuring the  $O_2^-$  anion; the moment of  $2.04\mu$  observed for  $KO_2$  is characteristic of one unpaired electron.

Canisters containing potassium superoxide are a source of oxygen for high-altitude climbing. In the presence of a little  $CuCl_2$ , it reacts with expired  $CO_2$ , one gram setting free 236 cc  $O_2$  at S.T.P. The compound reacts even with ice-cold water:



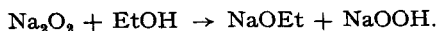
and with acetic acid in diethyl phthalate solution:



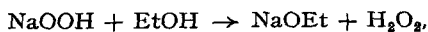
Potassium, rubidium and caesium also form oxides of the composition  $M_2O_3$ . When white  $K_2O_2$  is heated in oxygen at very low pressure red  $K_2O_3$  is produced. The magnetic susceptibilities of  $Rb_2O_3$  and  $Cs_2O_3$  are consistent with the presence of superoxide ions,  $O_2^-$ , and peroxide ions,  $O_2^{2-}$ , in the proportion 2 : 1.

### Hydroperoxides

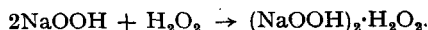
When sodium peroxide is added to ethyl alcohol containing a little sodium ethoxide, sodium hydroperoxide is produced:



In the absence of  $NaOEt$  the compound reacts with the alcohol:



Following this further reaction occurs:



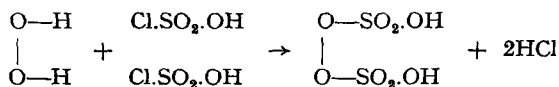
A compound in the same class, potassium hydroperoxide peroxohydrate  $(\text{KOOH})_2 \cdot 3\text{H}_2\text{O}_2$ , has also been isolated.

### Peroxoacids

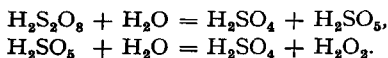
A peroxyacid is one which contains the peroxide linkage and either (i) is formed by the action of  $\text{H}_2\text{O}_2$  on the normal acid, or (ii) gives  $\text{H}_2\text{O}_2$  on treatment with dilute  $\text{H}_2\text{SO}_4$ . The empirical Riesenfeld test involves the addition of the acid or a salt to a 30% KI solution buffered to pH 7.5–8 with  $\text{NaHCO}_3$ . It is claimed that only true peroxyacids oxidise the KI to iodine under these conditions. However, the only unambiguous evidence for the peroxide link must come from determinations of structure.

### The peroxosulphuric acids

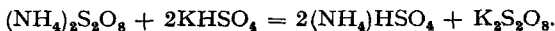
The best-characterised peroxyacids are those of Group VI. There are two peroxyacids of sulphur, peroxodisulphuric acid,  $\text{H}_2\text{S}_2\text{O}_8$ , and peroxomonosulphuric acid,  $\text{H}_2\text{SO}_5$ . The former is made by the electrolysis of 50%  $\text{H}_2\text{SO}_4$  at  $0^\circ$  with a Pt anode and a high current density; the  $\text{HSO}_4^-$  ions are oxidised at the anode to  $\text{H}_2\text{S}_2\text{O}_8$ . The acid can also be made by the action of 100%  $\text{H}_2\text{O}_2$  on chlorosulphuric acid:



The HCl is removed in a vacuum, leaving the colourless, crystalline  $\text{H}_2\text{S}_2\text{O}_8$ , m.p.  $65^\circ$ , which is stable when dry but hydrolyses easily:

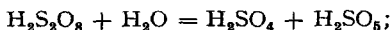


Ammonium peroxodisulphate,  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ , is produced at the anode when a mixture of  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{H}_2\text{SO}_4$  is electrolysed. The less soluble potassium salt can be precipitated by adding  $\text{KHSO}_4$  to the solution:

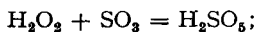


Peroxomonosulphuric acid,  $\text{H}_2\text{SO}_5$ , is made by

- (i) grinding  $\text{K}_2\text{S}_2\text{O}_8$  with concentrated  $\text{H}_2\text{SO}_4$ , allowing the slurry to stand, and then pouring it on to ice:

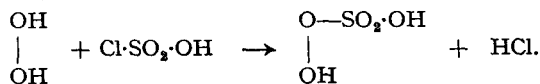


- (ii) treating  $\text{SO}_3$  with 100%  $\text{H}_2\text{O}_2$ :

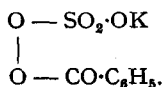




(iii) adding the calculated amount of anhydrous  $\text{H}_2\text{O}_2$  to well-cooled chloro-sulphuric acid:



Like  $\text{H}_2\text{S}_2\text{O}_8$ , it is a colourless crystalline solid, but differs in being mono-basic. The salts themselves are unstable, although a benzoyl derivative of the potassium salt has been made:



Both acids give the Riesenfeld reaction and oxidise  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$ . Unlike  $\text{H}_2\text{O}_2$ , however, neither acid has any action on  $\text{KMnO}_4$ ,  $\text{CrO}_3$  or  $\text{TiO}^{2+}$ . The two acids differ in their reactions with aniline and with KI at low pH:

	Potassium iodide	Aniline
$\text{H}_2\text{S}_2\text{O}_8$ :	$\text{I}_2$ set free slowly.	Oxidised to aniline black.
$\text{H}_2\text{SO}_5$ :	$\text{I}_2$ set free quickly.	Oxidised to nitrosobenzene.

### Sulphur-fluorine compounds containing peroxo groups

Peroxocompounds have been made from complex oxofluorides of sulphur. The compound  $\text{F}_5\text{SOF}$ , made by treating  $\text{SOF}_2$  with an excess of fluorine, is converted by ultraviolet irradiation into bis(pentafluorosulphur) peroxide,  $\text{F}_5\text{S}-\text{O}-\text{O}-\text{SF}_5$ , a dense, colourless liquid, b.p.  $49^\circ$ , which liberates iodine rather slowly from KI.

Peroxodisulphuryl difluoride,  $\text{FO}_2\text{S}-\text{O}-\text{O}-\text{SO}_2\text{F}$ , b.p.  $67^\circ$ , is produced in the electrolysis of fluorosulphuric acid and also in the catalytic fluorination of  $\text{SO}_3$  vapours by  $\text{F}_2$  when these are passed over  $\text{AgF}_2$  coated on copper ribbon. It can behave as an oxygenating agent (a), a fluorosulphonating agent (b) or as both (c):

- (a)  $\text{CO} + \text{S}_2\text{O}_5\text{F}_2 \rightarrow \text{CO}_2 + \text{S}_2\text{O}_5\text{F}_2$ .
- (b)  $\text{HgO} + 2\text{S}_2\text{O}_5\text{F}_2 \rightarrow \text{Hg}(\text{SO}_3\text{F})_2 + \text{O}_2 + \text{S}_2\text{O}_5\text{F}_2$
- (c)  $2\text{SOCIF} + 3\text{S}_2\text{O}_5\text{F}_2 \rightarrow 4\text{S}_2\text{O}_5\text{F}_2 + \text{Cl}_2$

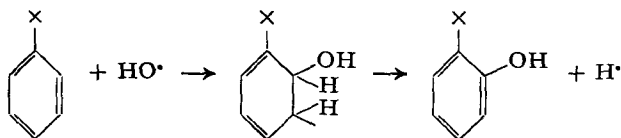
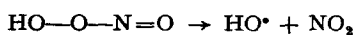
It liberates iodine rapidly from aqueous KI at room temperature.

### Group V peroxyacids

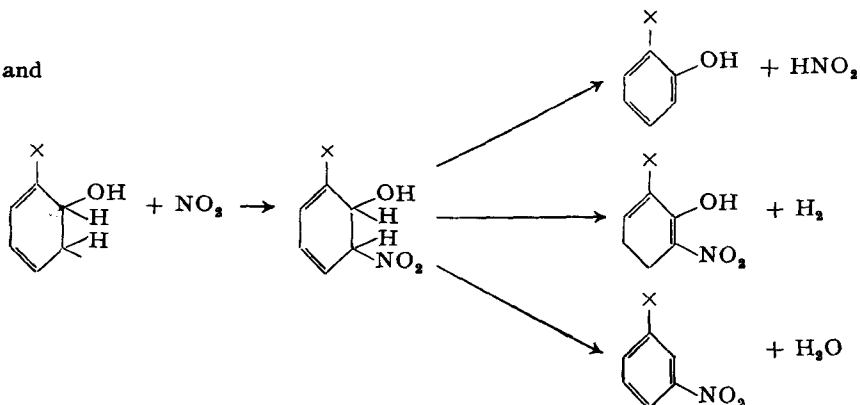
Peroxonitric acid,  $\text{HNO}_4$ , is reported to be formed when anhydrous  $\text{H}_2\text{O}_2$  is mixed with  $\text{N}_2\text{O}_5$  at  $-70^\circ$ . At high concentration the compound decom-

poses explosively below 0°; a 70% aqueous solution is moderately stable and weaker solutions hydrolyse rapidly. Unlike a solution of  $\text{HNO}_3$ ,  $\text{H}_2\text{O}_2$  or  $\text{HNO}_2$ , that of  $\text{HNO}_4$  liberates bromine from  $\text{KBr}$ . It oxidises aniline to nitrobenzene.

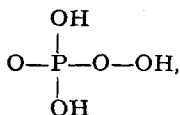
When  $\text{HCl}$  is added to sodium nitrite in 5% aqueous  $\text{H}_2\text{O}_2$  a fugitive, light-brown colour is produced which disappears with the evolution of oxygen. When the still brown liquid is run into  $\text{NaOH}$ , a bright yellow colour develops which may persist for upwards of 12 hours. The brown liquid is a dilute solution of peroxonitrous acid,  $\text{H}-\text{O}-\text{O}-\text{N}=\text{O}$ . Among other evidence for the presence of this compound is that the cold solution gives, with aromatic compounds, *o*-hydroxy and *m*-nitro derivatives. Their production can be explained by the following reactions:



and



A peroxomonophosphoric acid,  $\text{H}_3\text{PO}_5$ , presumably

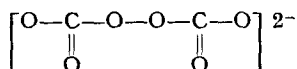


is obtained by the addition of ~14%  $\text{H}_2\text{O}_2$  to  $\text{P}_2\text{O}_5$  in acetonitrile which moderates the reaction. The aqueous solution oxidises aniline to a mixture of nitrosobenzene and nitrobenzene, and manganese(II) salts to perman-

ganates in the cold. Salts of peroxodiphosphoric acid can be made by the electrolysis of concentrated solutions of orthophosphates:  $2\text{K}_2\text{HPO}_4 \rightarrow \text{K}_4\text{P}_2\text{O}_8$ .

#### Group IV peroxyacids

When a concentrated solution of  $\text{K}_2\text{CO}_3$  is electrolysed, at about  $-15^\circ$ , with a high current density, the pale blue peroxocarbonate,  $\text{K}_2\text{C}_2\text{O}_6$ , is deposited at a smooth platinum anode. The compound responds to the Riesenfeld test, reacts with dilute  $\text{H}_2\text{SO}_4$  to give  $\text{H}_2\text{O}_2$  and with  $\text{MnO}_2$  to give oxygen, and oxidises  $\text{PbS}$  to  $\text{PbSO}_4$ . This electrolytically produced peroxocarbonate is believed to contain the ion

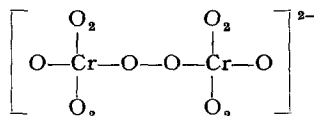


Several alkali-metal peroxocarbonates are claimed to have been made by passing  $\text{CO}_2$  into suspensions of their peroxides in ice-cold water. Later Group IA peroxocarbonates, for instance  $\text{M}_2\text{CO}_4 \cdot x\text{H}_2\text{O}$ ,  $\text{MHCO}_4$  and  $\text{M}_2\text{C}_2\text{O}_6$ , were obtained by treating saturated carbonate solutions with 30%  $\text{H}_2\text{O}_2$  and precipitating with alcohol. Some of these liberate iodine and oxygen, some oxygen only, from a neutral solution of KI.

#### Some peroxocompounds of transition metals

There is increasing interest in peroxocompounds of the transition metals and in organometallic peroxides, but only a few of the transition-metal peroxocompounds can be dealt with here.

When hydrogen peroxide is added to a dichromate in dilute  $\text{H}_2\text{SO}_4$  a blue colour is produced which fades rapidly unless extracted with ether. The ether extract contains  $\text{Et}_2\text{O} \cdot \text{CrO}_5$ . Organic bases give more stable co-ordination compounds such as  $\text{C}_5\text{H}_5\text{N} \cdot \text{CrO}_5$ . The addition of alcoholic  $\text{H}_2\text{O}_2$  and KOH to an ethereal solution of  $\text{CrO}_5$  yields a blue salt,  $\text{KCrO}_6 \cdot \text{H}_2\text{O}$ . The compound has 5 peroxy groups for every 2 chromium atoms and it has been suggested that the diamagnetic anion is

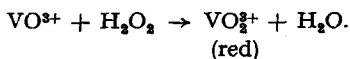


A series of red peroxochromates,  $\text{M}_2^+\text{CrO}_8$ , can be made by adding  $\text{H}_2\text{O}_2$  to soluble chromates under slightly alkaline conditions. Red magnesium

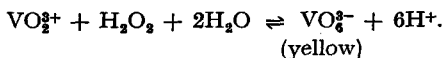
peroxochromate,  $Mg_3(CrO_8)_2 \cdot 13H_2O$ , is also known, as are the double salts of calcium, strontium and barium peroxochromates with alkali-metal peroxochromates,  $K_2Ca_5(CrO_8)_4 \cdot 19H_2O$  and  $K_2Ca_2(CrO_8)_2 \cdot 7H_2O$ . The  $CrO_8^{3-}$  anion has four peroxide groups per Cr atom, the centres of the O—O bonds being tetrahedrally arranged about the central Cr atom.

Hydrogen peroxide reacts with acidified molybdate solutions. The acid  $H_2Mo_2O_{11}$  is present in solutions of molybdate in concentrated perchloric acid to which  $H_2O_2$  has been added. The so-called 'permolybdic acid' is regarded as a salt of this acid with the cation  $[HMo_2O_6]^+$ , not itself peroxidic.

Vanadates, niobates and tantalates react with alkaline  $H_2O_2$  to give peroxo-salts formulated as  $M^I_3VO_8$ ,  $M^I_3NbO_8$  and  $M^I_3TaO_8$ . In strongly acid solution the vanadyl ion,  $VO^{2+}$ , gives a red colour with  $H_2O_2$ :



In weaker acid:



Titanium, zirconium and hafnium peroxo-compounds are produced by adding ammoniacal  $H_2O_2$  to their salts. The oxide salt,  $TiOCl_2$ , gives a compound formulated  $Ti(OH)_3OOH$ . This, with KOH, produces  $K_4TiO_8 \cdot 6H_2O$  which has been isolated as a solid; it does not, however, give the Riesenfeld reaction. In acid solution the  $(TiO)^{2+}$  ion reacts with  $H_2O_2$  to give the yellow colour ascribed to the hydrated  $(TiO_2)^{2+}$  ion. The discharge of this colour by fluoride ions is almost certainly due to  $TiF_6^{2-}$  formation. A solid,  $K_2(TiO_2)(SO_4)_2 \cdot 3H_2O$ , has been isolated which gives the Riesenfeld reaction.

### Peroxyhydrates

A compound of the empirical formula  $NaBO_3 \cdot 4H_2O$  is obtained by the action of  $Na_2O_2$  on a cold solution of borax,  $Na_2B_4O_7 \cdot 10H_2O$ , and also by the electrolysis of a solution of borax and  $Na_2CO_3$  with a platinum gauze anode. It does not free iodine from KI (see below). The substances  $LiBO_4 \cdot H_2O$  and  $KBO_5 \cdot H_2O$  have been made by adding  $\sim 14\%$   $H_2O_2$  to metaborate solutions and precipitating with alcohol.

There are so many similarities in the physical properties of  $H_2O_2$  and water that the existence of salts in which  $H_2O_2$  forms peroxyhydrates just as  $H_2O$  forms hydrates is not surprising. It is now known that the preparation from borax is such a compound, and that it is correctly formulated  $NaBO_2 \cdot H_2O_2 \cdot 3H_2O$ . The material is used in tooth powders and for rapid oxidation

of vat dyes. A peroxohydrate of sodium carbonate,  $2\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$ , made by adding  $\text{H}_2\text{O}_2$  to  $\text{Na}_2\text{CO}_3$  solution, is used in washing powders.

Peroxyhydrates can be distinguished from true peroxosalts by the ease with which ether extracts  $\text{H}_2\text{O}_2$  from their aqueous solutions, and by their failure to give the Riesenfeld reaction. Distinctions based on such empirical tests cannot, however, be considered wholly satisfactory, and the chemistry of peroxy-compounds will not be fully understood until there is more structural information.

#### FURTHER READING

- N. G. VANNERBERG, *Peroxides, Superoxides and Ozonides of the Metals of Groups IA, IIA, and IIB* in F. A. COTTON (Ed.), *Progress in Inorganic Chemistry*, Vol. 4, London, Interscience, 1962, p. 125.
- J. A. CONNOR AND E. A. V. EBSWORTH, *Peroxy Compounds of the Transition Metals* in H. J. EMELÉUS AND A. G. SHARPE (Eds.), *Advances in Inorganic Chemistry and Radiochemistry*, Vol. 6, New York, Academic Press, 1964, p. 279.

## The Halogens

### GROUP VIII B

Fluorine, chlorine, bromine, iodine and astatine are the terminal members of their respective periods and form a group in which the elements show a strong family relationship and also a very regular modification of properties. (The alkali metals, separated from the halogens by the noble gases, are the first members of these periods after Group 0 and have a similarly strong family relationship among themselves). The molecules of all the halogens are diatomic at room temperature and thus differ from the elements of Groups V and VI in which the first elements, nitrogen and oxygen alone are diatomic under these conditions. The m.p. of chlorine, bromine and iodine are very low compared with those of the previous members of their respective periods, sulphur, selenium and tellurium.

TABLE 93  
MELTING AND BOILING POINTS OF THE HALOGENS

	<i>F</i>	<i>Cl</i>	<i>Br</i>	<i>I</i>
Melting point (°C)	-233	-102	-7	113
Boiling point (°C)	-188	-35	59	183

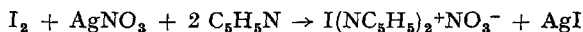
The halogens range in physical properties from an almost colourless gas ( $F_2$ ) through a dark-red, volatile liquid ( $Br_2$ ) to an almost black, crystalline solid made up of  $I_2$  molecules. The fall in volatility is due to an increase down the group of the Van der Waals force of attraction between the molecules. The deepening in colour is a consequence of an increase in the wave length of the charge-transfer bands with increasing atomic mass. The elements are all chemically active and, because of that, none is found in the free state in nature. Their activity makes them powerful disinfectants but dangerous when inhaled in any but very low concentrations.

As their electron configurations show, each element is a single p electron short of a noble-gas structure, and for this reason the dominating feature of their chemistry is the ease with which their atoms acquire an electron

TABLE 94  
ATOMIC PROPERTIES OF THE HALOGENS

	<i>F</i>	<i>Cl</i>	<i>Br</i>	<i>I</i>	<i>At</i>
Atomic number	9	17	35	53	85
Electron configuration	2s <sup>2</sup> 2p <sup>5</sup>	3s <sup>2</sup> 3p <sup>5</sup>	4s <sup>2</sup> 4p <sup>5</sup>	5s <sup>2</sup> 5p <sup>5</sup>	6s <sup>2</sup> 6p <sup>5</sup>
Covalent radius (Å)	0.72	0.99	1.14	1.33	
Ionic radius (Å) X <sup>-</sup>	1.36	1.81	1.95	2.16	

and become uninegative ions. That these anions are large has important structural consequences. Fluorine is always formally uninegative; however, the other elements can exhibit positive charge numbers in binary compounds, but only when in combination with strongly electropositive elements. Iodine forms a number of compounds in which unipositive iodine is stabilised by co-ordination, for example:



Ionisation energies in the group are generally high, but fall markedly with atomic number. Electron affinities show a maximum at chlorine. Nevertheless fluorine is the better oxidising agent in aqueous solution, and even when dry will usually replace chlorine from its compounds.

TABLE 95  
IONISATION ENERGIES, ELECTRON AFFINITIES AND  
ELECTRONEGATIVITIES OF THE HALOGENS

		<i>F</i>	<i>Cl</i>	<i>Br</i>	<i>I</i>
Ionisation energy	<i>I</i> (eV)	17.4	13.0	11.8	10.4
Electron affinity	<i>A</i> (eV)	3.74	4.02	3.78	3.44
Electronegativity		4.10	2.83	2.74	2.21
(Allred-Rochow scale)					

The redox potential,  $E^\circ$ ,  $X_2/2X^-$ , measures a free-energy change, usually dominated by the  $\Delta H$  term, but depending, as may be seen from the energy diagram (Fig. 285), on (a) the energy needed to break the molecule into atoms (the heat of dissociation), (b) the energy liberated when the atom is converted into a negative ion (the electron affinity), and (c) the energy set free on the hydration of the ion. For the fluorine molecule (b) is less than for the chlorine molecule but, since the energy needed to break the F—F bond is also less and the hydration energy more, the total energy drop is much greater.

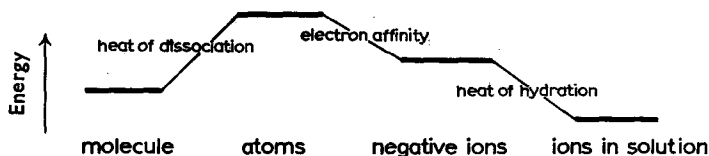


Fig. 285. Energetics of the change from free molecule to ion in solution.

Molecular fluorine is, in fact, an extremely powerful oxidising agent. In spite of their lower dissociation energies, bromine and iodine are weaker oxidising agents than chlorine; this is due to their smaller electron affinities and smaller hydration energies.

TABLE 96

PROPERTIES OF THE HALOGENS

	<i>F</i>	<i>Cl</i>	<i>Br</i>	<i>I</i>
Heat of dissociation of $X_2$ (kcal)	38	58	46	36
Hydration energy of $X^-$ (kcal)	122	89	81	72
$E^\circ, X_2/2X^-$ (V)	2.87	1.36	1.07	0.53

The great reactivity of fluorine largely stems from the low energy of the F—F bond. The more acceptable figure of 38 kcal, derived from a study of its dissociation between 500° and 850°, and from a Born-type treatment of heats of dissociation and heats of formation of alkali-metal fluorides together with their heats of sublimation and those of the metals concerned, has replaced the earlier larger value ( $\sim 70$  kcal). The F—F bond is weak because of repulsion between the non-bonding electrons; the stronger X—X bond, actually in  $Cl_2$  and  $Br_2$ , and relatively in  $I_2$ , is due to hybridisation of p and d orbitals. The weakness of the  $\sigma$  bond between atoms of the second period elements is also evident in the molecules  $H_2N-NH_2$  and  $HO-OH$ .

Another factor contributing to the exothermicity of many of the reactions of elementary fluorine is the short, strong bonds formed by its atoms with those of most other elements. When crystalline fluorides are formed their lattice energies are high because the  $F^-$  ion is comparatively small.

### Oxidation states of the halogens

The only oxidation state of fluorine which is stable in aqueous solution is the  $-1$ . The principal oxidation states of chlorine, bromine and iodine are  $-1$ ,  $+1$ ,  $+3$ ,  $+5$ , and  $+7$ . The oxoacids are all powerful oxidising



agents with respect to their reduction to the aqueous hydrogen halide, and even in alkaline solutions the higher oxidation states are easily reduced to  $-1$ .

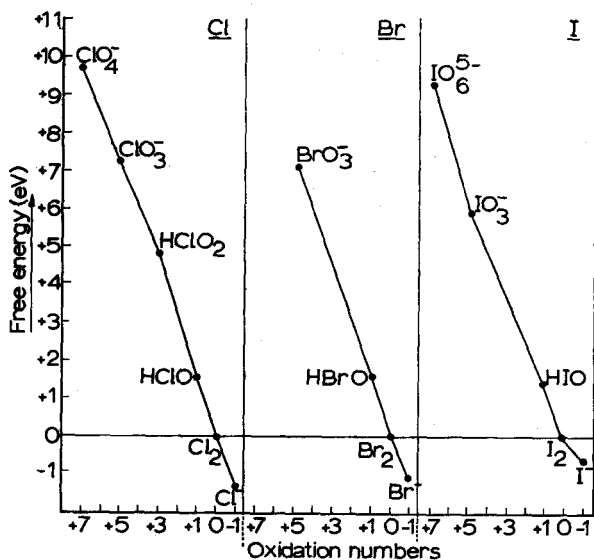


Fig. 286. Free energies of oxidation states relative to the elements at pH = 0.

All the points lie close to the straight line between the highest state and the lowest. This means that all except the  $-1$  state are oxidising and all except the  $-1$  and  $+7$  states are liable to disproportionate.

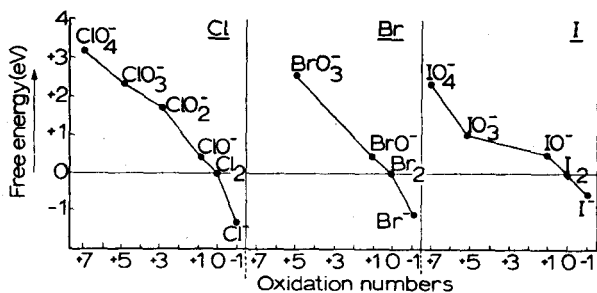


Fig. 287. Free energies of oxidation states relative to the elements at pH = 14.

At pH 14 the redox potentials, as indicated by the gradients of the graphs (Fig. 287), are lower. Features of these diagrams are the instability

of  $\text{Cl}_2$  and  $\text{Br}_2$  (and, to a lesser extent,  $\text{I}_2$ ), to disproportionation in alkaline solution, and the comparative stability of the  $\text{IO}_3^-$  ion. As in acid solution, the +3 state is an unstable one.

### Stereochemistry of positive halogen complexes

Halogens with a formally positive charge number occur in complexes in which the co-ordination numbers range from 2 to 7 and the other element present is either oxygen or another halogen which is more electronegative than the first. The complexes may be neutral molecules, but are usually ions. In complexes with oxygen, the halogen atom is surrounded by oxygen atoms; in interhalogen compounds the larger halogen atom is surrounded by the smaller halogen atoms. The number of bond pairs around the central atom can be increased by either (a) the use of some of its electrons to form  $\pi$  bonds with surrounding atoms, or (b) the promotion of some of its electrons to  $nd$  levels followed by the formation of  $\sigma$  bonds with the surrounding atoms.

The stereochemistry of typical complexes involving a formally positive halogen is summarised in Table 97.

TABLE 97  
STEREOCHEMISTRY OF HALOGEN COMPLEXES

<i>Electron pairs round central atom</i>	<i>Hybrids</i>	<i>Electrons used in <math>\pi</math> bonding</i>	<i>Lone pairs</i>	<i>Charge number of central atom</i>	<i>Shape of molecule or ion</i>	<i>Examples</i>
4	$sp^3$	1	2	+ 3	V-shaped	$\text{ClO}_2^-$
		2	1	+ 5	Trigonal pyramid	$\text{ClO}_3^-$ , $\text{BrO}_3^-$ , $\text{HIO}_3$
		3	0	+ 7	Tetrahedron	$\text{ClO}_4^-$ , $\text{IO}_4^-$
5	$sp^3d_{2s}$	0	3	+ 1	Linear	$\text{ICl}_2^-$ , $\text{I}_3$
		0	2	+ 3	T-shaped	$\text{ClF}_3$
		1	1	+ 5	Distorted tetrahedron	$\text{IO}_2\text{F}_2^-$
6	$sp^3d_y^2$	0	2	+ 3	Square	$\text{ICl}_4^-$
		0	1	+ 5	Square pyramid	$\text{IF}_5$
		1	0	+ 7	Octahedron	$\text{IO}_6^{5-}$
7	$sp^3d_y^2d_z$	0	0	+ 7	Pentagonal bipyramid	$\text{IF}_7$

All the molecules and ions employing four electron pairs are basically tetrahedral (p. 147), those employing five pairs, trigonal bipyramidal (p. 148), and those with six pairs, octahedral (p. 150). Bond directions are determined by the strong repulsive forces exerted by the lone-pair electrons on the bond pairs (Fig. 288).

In an unsymmetrical molecule some distortion of the simple shapes can occur. Thus  $\text{ClF}_3$  is not exactly T-shaped. Microwave spectroscopy shows the bond lengths and inter-bond angles to be as indicated in Fig. 289. This is consonant with the idea that lone pairs occupy two positions in a trigonal bipyramid arising from  $\text{sp}^3\text{d}_2$  hybridisation.

The maximum group charge number of +7 is less stable in iodine than in the earlier members of the group; in this respect iodine resembles bismuth and tellurium, the two elements which precede it in the period. The most stable oxide of iodine is  $\text{I}_2\text{O}_5$ , whereas  $\text{Cl}_2\text{O}_7$  is the only stable oxide of chlorine. Furthermore, the periodates are less stable than iodates ( $E^\circ$ ,  $\text{IO}_4^-/\text{IO}_3^- = +0.72$  V), but perchlorates are more stable than chlorates ( $E^\circ$ ,  $\text{ClO}_4^-/\text{ClO}_3^- = +0.17$  V).

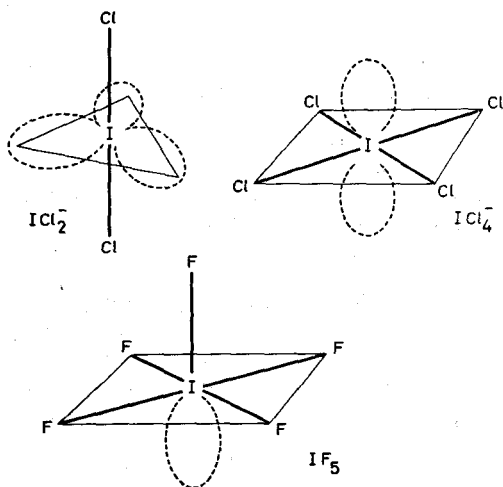


Fig. 288. Structures of  $\text{ICl}_2^-$ ,  $\text{ICl}_4^-$  and  $\text{IF}_5$ , showing positions occupied by lone pairs.

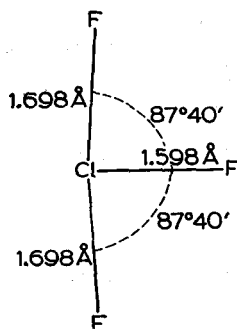


Fig. 289. Bond lengths and interbond angles of  $\text{ClF}_3$ .

### Occurrence and separation of the halogens

#### Fluorine

The principal source of fluorine (0.08% of the lithosphere) is fluorspar,  $\text{CaF}_2$ , but much fluorine is recovered from industrial effluent gases arising from the aluminium, iron and other industries.

High grade fluorspar is used for the manufacture of anhydrous hydrofluoric acid. The anhydrous acid is a source of fluorine itself, of the fluorides of many metals, and also of freons such as  $\text{CF}_2\text{Cl}_2$ .

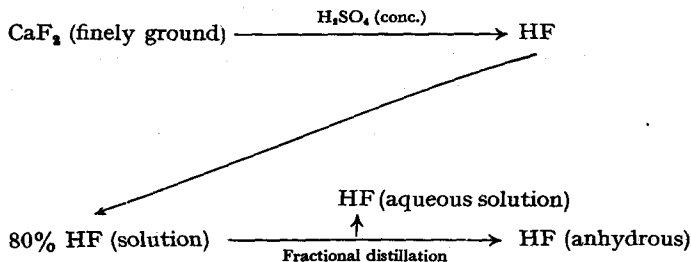


Fig. 290. Preparation of HF from fluorspar.

Industrial cells for preparing fluorine are rectangular steel vessels  $4' \times 1\frac{1}{2}'$  and  $2\frac{1}{2}'$  deep. The electrolyte,  $\text{KHF}_2$  together with up to 0.6 molar parts of HF kept molten at  $95\text{--}115^\circ$ , is electrolysed by a current of about  $0.5 \text{ amps/cm}^2$  between carbon anodes and sheet-steel cathodes. A monel metal diaphragm, perforated below the surface of the liquid but continuous above it, serves to keep separate the fluorine and hydrogen produced. Sealing and electrical insulation is provided by Teflon ( $\text{CF}_2$  polymer). There are small 10 amp cells convenient for laboratory work and very reliable in operation. Electrolysis depletes the cell of HF which is added from time to time in the anhydrous form. Liquid fluorine is now available in industrial quantities. Interest in the production of fluorine and its compounds has been stimulated by the use made of uranium hexafluoride for separating, by gaseous diffusion, the  $^{235}\text{U}$  isotope from the 99.28% of  $^{238}\text{U}$  in natural uranium, and of uranium tetrafluoride in the production of uranium metal (p. 619).

### Chlorine

The element (0.19% of lithosphere) is derived mainly from  $\text{NaCl}$  which is either crystallised from brines or mined. The gas is a product of the electrolysis of aqueous sodium chloride for caustic soda production, with carbon anodes and a mercury cathode. It is also a by-product of the manufacture of metallic sodium, and also of magnesium and calcium, by electrolysing the appropriate fused chloride. Its chief uses are as a bleach, a bactericide, and an industrial chemical.

*Bromine*

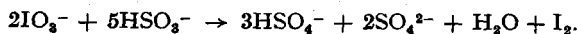
This element (0.01% of lithosphere), once largely derived from salt deposits, is now obtained chiefly from sea-water, by passing chlorine into it at pH 3.5:



The bromine is blown out with air and absorbed in  $\text{Na}_2\text{CO}_3$  solution to give bromate and bromide. On acidification the element can be distilled off:

*Iodine*

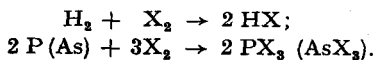
Iodine ( $10^{-4}$  % of lithosphere) is obtained mainly from iodates present in Chilean nitrates. Iodate-rich solutions are reduced with sodium bisulphite to liberate the element:

*Astatine*

This has not been detected as a product of natural radioactive decay. Astatine-211 is made by bombarding a cooled bismuth target with high-energy  $\alpha$ -particles, and evaporating it from the target under low pressure. Because of the short half-life (7.5 h) and consequent high activity, its chemistry has been studied by tracer methods only. This appears to closely resemble that of iodine, the element being soluble in organic solvents and forming  $\text{At}^-$  and  $\text{AtO}_3^-$  ions. It may possibly differ from the rest of the halogens in having an insoluble sulphide, for it is co-precipitated with  $\text{Bi}_2\text{S}_3$ .

**Reactions of the halogens**

Most metals combine directly with all the halogens and particularly readily with fluorine. Some non-metals also react:



The reactivity of the halogen decreases with atomic number. Fluorine, particularly, and chlorine to a lesser extent, often oxidise both metals and non-metals to higher states of oxidation than do bromine and iodine. Thus both fluorine and chlorine raise the charge number of phosphorus and arsenic to +5 in such compounds as  $\text{PCl}_5$  and  $\text{AsF}_5$ . Sulphur is converted to  $\text{SF}_6$  by fluorine, to  $\text{SCl}_2$  by chlorine and to  $\text{S}_2\text{Br}_2$  by bromine. The formation of  $\text{SF}_6$  from its elements may be pictured in terms of the energy changes shown in Fig. 291. The energy set free in the formation of  $\text{SF}_6$  is large; except in the  $\text{F}_2$  molecule itself, fluorine forms stronger bonds

than any of the other halogens. On the other hand the dissociation energy of fluorine is only about 38 kcal/mole, and there is therefore a net binding energy available, in spite of the considerable energy of the sulphur  $sp^3d^2$  valence state (*cf.* p. 113). Chlorine is more difficult to dissociate into atoms than fluorine and forms weaker bonds with sulphur. Insufficient energy is available to offset the valence state promotion energy for  $SCl_6$  formation, and such a compound is not known.

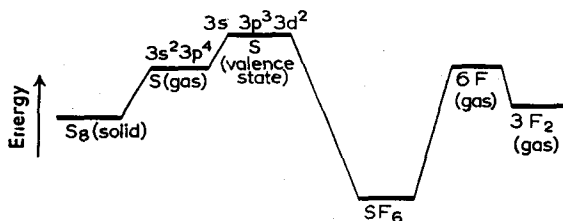


Fig. 291. Energetics of the formation of  $SF_6$  from its elements.

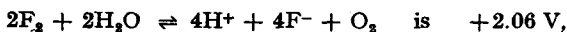
A halogen of lower atomic number oxidises the ion of another halogen of higher atomic number, both when the ion is in solution and in the crystal lattice.



The respective reactions of the halogens with water also illustrate the decrease in oxidising power with atomic number. For the reaction

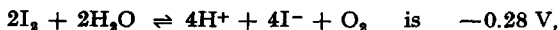


Since  $E^\circ, F_2/2F^-$  is +2.87 V, the redox potential for



equivalent to a standard free energy change  $\Delta G$  of -190 kcal. Fluorine accordingly sets free oxygen from water.

Since  $E^\circ, I_2/2I^-$  is +0.53 V, the redox potential for



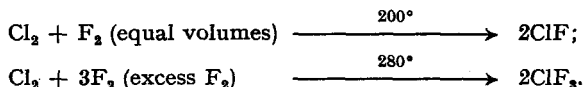
equivalent to a standard free energy change,  $\Delta G$ , of +25 kcal. Here the reaction takes the opposite direction and oxygen can oxidise the iodide ion to iodine. With chlorine and bromine the oxidation of water to oxygen is thermodynamically possible but has so high an activation energy that another course is followed:



This reaction is naturally strongly dependent on pH; the addition of alkali favours the formation of halide and hypohalite (p. 518).

### Interhalogen compounds

These are made by direct combination of the elements in a nickel tube; the product depends on the conditions, thus for instance:



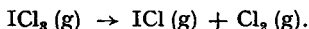
Bromine vapour diluted with nitrogen reacts with a limited supply of fluorine to give mainly  $\text{BrF}_3$ . With an excess of  $\text{F}_2$ ,  $\text{BrF}_5$  is the chief product. There are eleven interhalogen compounds which fall into the four classes shown in Table 98:

TABLE 98  
THE INTERHALOGEN COMPOUNDS

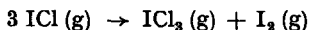
Type AX	AX <sub>3</sub>	AX <sub>5</sub>	AX <sub>7</sub>
ClF (b.p. $-100^\circ$ )	ClF <sub>3</sub> (b.p. $12^\circ$ )		
BrF (b.p. $20^\circ$ )	BrF <sub>3</sub> (b.p. $127^\circ$ )	BrF <sub>5</sub> (b.p. $40^\circ$ )	
BrCl (b.p. $5^\circ$ )			
ICl (solid, 2 forms)	ICl <sub>3</sub> (m.p. decomp. $101^\circ$ )	IF <sub>5</sub> (b.p. $97^\circ$ )	IF <sub>7</sub> (b.p. $4^\circ$ )
IBr (m.p. $36^\circ$ )			

For every class with more than one member, the boiling points increase as the difference between the electronegativities of the two halogens increases. The greatest increase is that between  $\text{BrF}_5$  and  $\text{IF}_5$ . Interhalogen compounds containing either three or four of the elements are not known, though the polyhalide ions  $\text{ClIBr}^-$  and  $\text{FICl}_3^-$  exist.

The conversion of  $\text{ICl}$  to  $\text{ICl}_3$  involves the promotion of two electrons of the iodine to orbitals of higher energy, and the consequent reduction of the net bond energy must largely determine the relative stabilities of the two chlorides. In fact,  $\text{ICl}_3$  is stable as a solid but decomposes when vaporised:



Neglecting the small entropy term in the free-energy change,  $\Delta H - T\Delta S$ , this implies that the net bond energy in  $\text{ICl}_3$  is less than that in  $\text{ICl}$ . Since the bond energies in  $\text{ICl}$  and  $\text{Cl}_2$  are 50 kcal and 58 kcal respectively, those in  $\text{ICl}_3$  must be less than  $\frac{1}{3}(50 + 58) = 36$  kcal. But if the bond energy of  $\text{ICl}_3$  were greater than 38.3 kcal, the reaction



would become thermodynamically feasible; it would proceed to a useful ex-

tent which it does not. The compatible range of bond energies is therefore small, as it is for any compound with a low heat of formation.

Interhalogen compounds of the AX type resemble the halogens themselves in physical properties (Fig. 292); the divergences are naturally greatest where differences in electronegativity are marked. In general compounds containing fluorine are more volatile than those in which it is replaced by chlorine, and so on down the group.

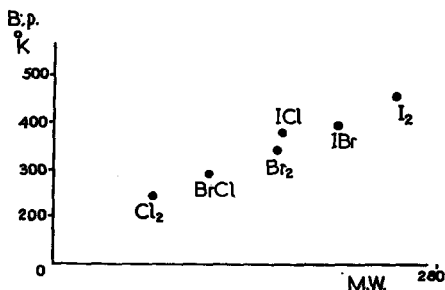


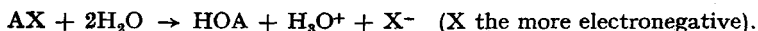
Fig. 292. Relation of boiling point to molecular weight in some halogen and interhalogen molecules.

The thermal stabilities of the diatomic compounds fall in the order  $IF > BrF > ClF > ICl > IBr > BrCl$ , corresponding to the difference in electronegativity between the two-atoms. The more polar the bond, the more thermally stable the molecule. The bond lengths, in the gas molecules, are:

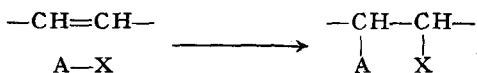
Br—F	1.756 Å	I—Br	2.470 Å
Cl—F	1.628 Å	I—Cl	2.321 Å
Br—Cl	2.138 Å		

The greater the difference in electronegativity the shorter the bonds compared with the sum of the two covalent radii (p. 516).

The AX compounds usually convert metals to mixed halides. The compounds are more reactive than the elements because the A—X bond energy is less than the X—X bond energy (X being the more electronegative element involved). Hydrolysis of these interhalogens usually proceeds:



They form addition compounds with olefins:

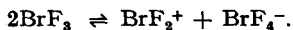


And they often do the same with alkali-metal halides:

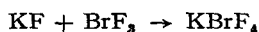




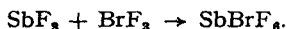
Of the  $AX_3$  compounds,  $ClF_3$  is the most reactive but  $BrF_3$  is more useful in preparative work. The liquid has a higher conductance:



It is a valuable fluorinating agent, converting many metals, their oxides and very many of their chlorides, bromides and iodides to fluorides. Some metal fluorides dissolve to give tetrafluorobromites:



or hexafluorobromates:



Chlorine trifluoride does not form corresponding compounds. Both  $ClF_3$  and  $BrF_3$  have high entropies of vaporisation, suggesting there is association in the liquid.  $ICl_3$  is much less reactive than the other two  $AX_3$  compounds. Thermal stabilities of the  $AX_3$ -type compounds are in the order:  $BrF_3 > ClF_3 > ICl_3$ . For the reaction  $AX_3 \rightleftharpoons AX + X_2$ ,  $\Delta G^\circ = +39$  kcal mole<sup>-1</sup> for  $BrF_3$ ,  $+16$  kcal mole<sup>-1</sup> for  $ClF_3$ , and  $+2$  kcal mole<sup>-1</sup> for  $ICl_3$ .

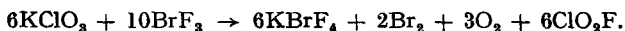
Of the  $AX_5$  compounds, bromine pentafluoride is the most reactive, resembling  $ClF_3$  in acting very violently, too violently to be used, undiluted, for the preparation of fluorides. Liquid  $IF_5$  is a good conductor:



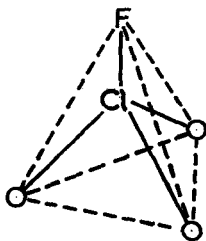
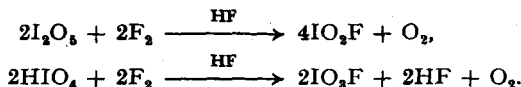
It reacts with KI at its boiling point to give  $KIF_6$ .

Iodine heptafluoride, the only example of the  $AX_7$  type, can be made by heating  $IF_5$  with  $F_2$  at 250–270°. It is comparable with  $ClF_3$  and  $BrF_5$  in its violent fluorinating action. In shape it is the unusual pentagonal bipyramid.

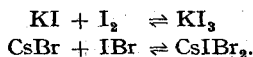
Several oxofluorides are known.  $ClO_2$  reacts with  $F_2$  to give chloryl fluoride,  $ClO_2F$ . The compound is produced by the action of  $BrF_3$  on potassium chlorate:



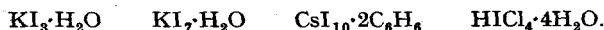
It forms solid additives with  $BF_3$  and  $SbF_5$ , regarded as chloronium salts  $ClO_2^+BF_4^-$  and  $ClO_2^+SbF_6^-$ . Perchloryl fluoride,  $ClO_3F$ , can be made by treating a perchlorate with fluorosulphuric acid. It is a colourless, inert, thermally stable gas in contrast with the reactive  $ClO_2F$ . Structurally  $ClO_3F$  is a tetrahedral molecule centred on the chlorine atom (Fig. 208).  $BrO_2F$  can be made by the direct fluorination of  $BrO_2$  at a low temperature.  $IO_2F$  and  $IO_3F$  are obtained by the reactions:

Fig. 293. Structure of  $\text{ClO}_3\text{F}$  molecule.*Polyhalide ions*

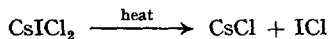
Halide ions, either in solution or in crystalline salts, frequently react with halogens and interhalogen compounds:



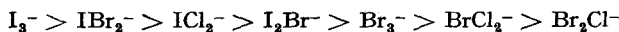
Many crystalline polyhalides contain solvent molecules, removal of which causes decomposition of the polyhalide:



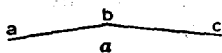
Polyhalides are unstable towards dissociation into monohalides and halogens or interhalogen compounds. The lighter halide atoms remain in the metal halide:



The products are not  $\text{CsI}$  and  $\text{Cl}_2$ , presumably because the former course is favoured energetically by the higher lattice energy of  $\text{CsCl}$ . For trihalides formed by the same metal, the order of thermal stability, based on dissociation pressures, is:

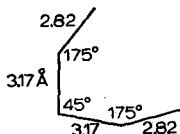


The polyhalide anions have interesting structures. The trihalides are almost linear:

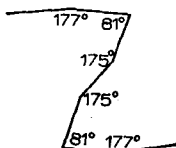


with  $\alpha$  in the range  $171$ – $179^\circ$ . Surprisingly the  $\text{I}_3^-$  and  $\text{Br}_3^-$  ions are both slightly unsymmetrical:  $ab \neq bc$ . The  $\text{ICl}_4^-$  ion in  $\text{KICl}_4 \cdot \text{H}_2\text{O}$  and the

$\text{BrF}_4^-$  ion in  $\text{KBrF}_4$  are both square (p. 520), but  $\text{I}_5^-$  in  $\text{NMe}_4\text{I}_5$  is approximately L-shaped:



The compound  $\text{Cs}_2\text{I}_8$  has a Z-shaped  $\text{I}_8^{2-}$  ion:



The L.C.A.O. method (p. 95) applied to polyhalide ions indicates that the bond angles should be either  $\sim 90^\circ$  or  $\sim 180^\circ$ , since only the p-functions of different atoms will overlap satisfactorily.

Polyhalogen cations are also known. Examples exist in the compounds  $\text{BrF}_2^+\text{SbF}_6^-$ ,  $\text{IF}_4^+\text{SbF}_6^-$  and  $\text{ICl}_2^+\text{SbCl}_6^-$ . The cation in the last has a  $\text{Cl}-\text{I}-\text{Cl}$  angle of  $95^\circ$ , again presumably mainly due to p-orbital overlap.

Acids formally corresponding to the polyhalide ions are not usually preparable, but the orange-yellow hydrate  $\text{HICl}_4 \cdot 4\text{H}_2\text{O}$  can be crystallised from a solution of  $\text{ICl}_3$  in aqueous  $\text{HCl}$ . The solution dissolves  $\text{RbF}$  and  $\text{CsF}$  to give  $\text{RbFICl}_3$  and  $\text{CsFICl}_3$ .

### Oxides

There are twelve oxides of the halogens. The fluorine compounds are better considered as oxygen fluorides.

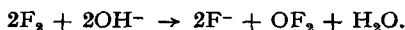
TABLE 99

PROPERTIES OF THE HALOGEN OXIDES

$\text{OF}_2$ (b.p. $-145^\circ$ )	$\text{Cl}_2\text{O}$ (b.p. $2^\circ$ )	$\text{Br}_2\text{O}$ (m.p. $-18^\circ$ )	
$\text{O}_2\text{F}_2$ (b.p. decomp. $-57^\circ$ )	$\text{ClO}_2$ (b.p. $11^\circ$ )	$\text{BrO}_2$ (stable as solid below $-40^\circ$ )	
$\text{O}_3\text{F}_2$ (decomp. $-163^\circ$ )	$\text{Cl}_2\text{O}_6$ (m.p. $4^\circ$ )		$\text{I}_2\text{O}_5$ (m.p. decomp. $300^\circ$ )
$\text{O}_4\text{F}_2$ (decomp. $-183^\circ$ )	$\text{Cl}_2\text{O}_7$ (b.p. $-92^\circ$ )	$\text{BrO}_3$ (stable as solid below $-80^\circ$ )	

*Fluorine*

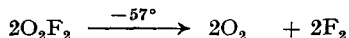
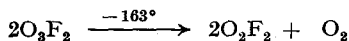
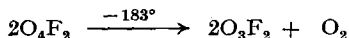
The colourless gas,  $\text{OF}_2$ , is made by the action of  $\text{F}_2$  on  $\text{NaOH}$  solution:



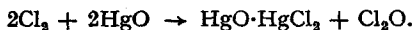
The bonding is essentially covalent because of the similar electronegativities of oxygen and fluorine and the structure is as shown in Fig. 294. The oxygen valence state is roughly tetrahedral ( $\text{sp}^3$ ), but in  $\text{OF}_2$  the  $\text{F}-\text{O}-\text{F}$  angle is  $103^\circ$ , which is less than the tetrahedral angle because the bond-pair-bond-pair repulsion is less than that caused by the lone pairs (p. 149).  $\text{OF}_2$  is neither explosive nor an acid anhydride; it reacts with bases to give  $\text{F}^-$  ions and free oxygen.

The compound  $\text{O}_2\text{F}_2$  is an orange-red solid produced at  $-165^\circ$  by passing an electric discharge through an oxygen-fluorine mixture at low pressure. It decomposes into its elements at  $-95^\circ$ , the boiling point.

The compounds  $\text{O}_3\text{F}_2$  and  $\text{O}_4\text{F}_2$  can be made similarly at lower temperatures; the first is a blood-red, viscous liquid, the second a red-brown solid. Their structures are uncertain. Decomposition temperatures are:

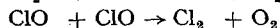
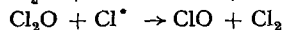
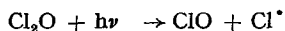
*Chlorine*

Orange dichlorine oxide,  $\text{Cl}_2\text{O}$ , is made by passing  $\text{Cl}_2$  over precipitated  $\text{HgO}$ :

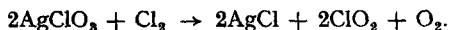


The liquid can be distilled at its b.p. ( $2^\circ$ ) but at higher temperatures the gas explodes. The molecule is V-shaped (Fig. 295), and the repulsion between the bond pairs is greater than in the fluorine compound, in accordance with the closer proximity of the electrons to the oxygen. The compound is formally the anhydride of hypochlorous acid.

The photochemical decomposition of  $\text{Cl}_2\text{O}$  has been shown to proceed through a free-radical chain reaction:



Chlorine dioxide,  $\text{ClO}_2$ , is best made by treating silver chlorate at  $90^\circ$  with dry chlorine and condensing the  $\text{ClO}_2$  by cooling:



It is a gas with little tendency towards dimerisation, showing the paramagnetism expected for the monomeric  $\text{ClO}_2$ . The bonds in the molecule are appreciably shorter than those in  $\text{Cl}_2\text{O}$ , having much more double-bond character (Fig. 296).

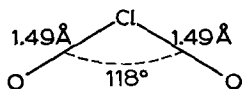
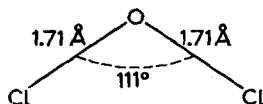
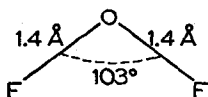
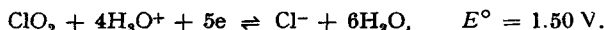


Fig. 294. Structure of  $\text{F}_2\text{O}$ . Fig. 295. Structure of  $\text{Cl}_2\text{O}$ . Fig. 296. Structure of  $\text{ClO}_2$ .

The odd-electron molecule is very reactive; when warmed the gas explodes unless diluted and it is a powerful oxidising agent, since for



The gas,  $\text{ClO}_2$ , can be looked upon as a mixed anhydride:



Dichlorine hexoxide,  $\text{Cl}_2\text{O}_6$ , results from mixing  $\text{ClO}_2$  with ozonised oxygen at  $0^\circ$ . It is a dark-red liquid, less explosive than  $\text{ClO}_2$ , and reacts with alkalis to give chlorate and perchlorate:



Though the molecular weight in carbon tetrachloride agrees with the formula  $\text{Cl}_2\text{O}_6$ , the weak paramagnetism of the aqueous solution suggests some dissociation to  $\text{ClO}_3$ . The dissociation energy  $\text{Cl}_2\text{O}_6 \rightarrow 2\text{ClO}_3$  is only 1.5 kcal mole<sup>-1</sup>.

Chlorine heptoxide,  $\text{Cl}_2\text{O}_7$ , is made by dehydrating perchloric acid with  $\text{P}_2\text{O}_5$  at a low temperature and distilling the product. The colourless, oily liquid is not so strong an oxidising agent as the other oxides of chlorine. It is the anhydride of perchloric acid. The structure is uncertain. It is more thermodynamically stable than any of the other oxides of chlorine.

### Bromine

Dibromine oxide,  $\text{Br}_2\text{O}$ , is a dark-brown liquid and is made in a similar way to  $\text{Cl}_2\text{O}$ . It is formally the anhydride of hypobromous acid.

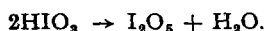
Bromine dioxide,  $\text{BrO}_2$ , is a yellow solid below  $-40^\circ$ ; above it is unstable. Prepared in a similar way to  $\text{O}_2\text{F}_2$ , it is less explosive than  $\text{ClO}_2$ . Hydrolysis gives bromide and bromate:



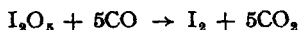
The action of a glow discharge on a mixture of bromine and oxygen between  $-10^\circ$  and  $20^\circ$  produces a white solid of crystalline appearance, stable below  $-70^\circ$ , which is  $\text{BrO}_3$ .

### Iodine

The only true oxide of iodine is di-iodine pentoxide,  $\text{I}_2\text{O}_5$ , made by dehydrating iodic acid at  $240^\circ$  in a stream of dry air:



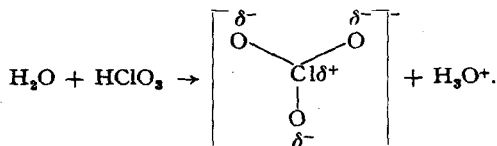
The white powder decomposes to iodine and oxygen above  $300^\circ$ . It is a fairly strong oxidising agent. The reaction



is quantitative at  $70^\circ$ , and is used for determining CO in gaseous mixtures. The oxides, empirically  $\text{I}_2\text{O}_4$  and  $\text{I}_4\text{O}_9$ , are of unknown structure, but are probably iodates of  $\text{IO}^+$  and  $\text{I}^{3+}$  respectively, viz.  $\text{IO}^+\text{IO}_3^-$  and  $\text{I}^{3+}(\text{IO}_3^-)_3$ .

### Oxoacids

Fluorine does not form an oxoacid; the element is more electronegative than oxygen. In the chlorine, bromine and iodine compounds the halogen atom in the oxoanion is positive in relation to the oxygen atoms, as indicated by the  $\delta$ 's:



Increase of the charge number of the halogen atom from +1 to +7 is accompanied by (i) increased thermal stability, (ii) decreased oxidising capacity, (iii) increased acid strength.

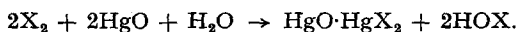
Periodic acid is exceptional in being more strongly oxidising than iodic acid:

	Cl	I
$E^\circ, \text{HOX}/\frac{1}{2}\text{X}_2$ (V)	+1.63	+1.45
$E^\circ, \text{HXO}_3/\frac{1}{2}\text{X}_2$ (V)	+1.47	+1.19
$E^\circ, \text{HXO}_4/\frac{1}{2}\text{X}_2$ (V)	+1.34	+1.38

Bromic acid is a particularly strong oxidising agent ( $E^\circ, \text{HBrO}_3/\frac{1}{2}\text{Br}_2 = +1.52$  V). Perbromic acid is unknown. The increasing stability of the oxoanions as the charge number of the halogen rises has already been discussed (p. 248).

### Hypohalous acids

These are weak acids ( $pK_a \sim 8$ ) which exist only in aqueous solution; indeed HOI is more correctly considered as iodine hydroxide (p. 535). Their aqueous solutions are made by shaking precipitated HgO in water with the particular halogen:



Sodium hypochlorite, used commercially in cotton bleaching, is made by the electrolysis of brine, the electrolyte being agitated to mix the anode and cathode products. At the cathode, the reaction  $2H^+ + 2e \rightarrow H_2$  increases the concentration of  $OH^-$ , while at the anode, the reaction  $2Cl^- \rightarrow Cl_2 + 2e$  releases chlorine. These combine:



and the solution becomes progressively stronger in NaOCl without chlorine being evolved.

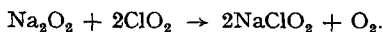
Hypohalite ions are all unstable to the disproportionation



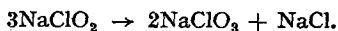
Because the activation energy for the hypochlorite reaction is rather large, conversion to  $ClO_3^-$  occurs rapidly only in hot solutions. The change is fast at about  $50^\circ$  for the hypobromite,  $OBr^-$ , and at room temperature for the hypoiodite,  $OI^-$ .

### Halous acids

Of these only chlorous acid,  $HClO_2$ , is known, and then only in solution. It is a stronger acid than hypochlorous ( $pK_a \sim 2$ ). Chlorites are best made by the reaction of  $ClO_2$  with peroxides:



Heating converts an alkali-metal chlorite to chloride and chlorate:



### Halic acids and halates

Chloric and bromic acids are obtainable only in aqueous solution, but  $HIO_3$  separates, as white crystals, when iodine is oxidised with fuming nitric acid. The acids are strong oxidising agents and fairly strong acids ( $pK_a \sim -2$ ).

Alkali-metal chlorates are much more soluble than bromates and iodates, and are conveniently made by the electrolysis of hot chloride solutions. Aqueous KCl (25%) is electrolysed at 70–75° till it is saturated with chlorate; it is then cooled and  $\text{KClO}_3$  crystallises.

Chlorate crystals contain the pyramidal  $\text{ClO}_3^-$  ion (Fig. 297). Formally, the chlorine has charge number +5 and forms  $\sigma$  bonds like nitrogen. But a lone pair from each O ligand overlaps a chlorine 3d orbital and can form a  $\pi$  bond by donation; thereby charge returns to the chlorine.

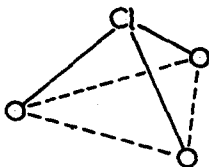
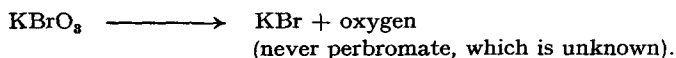
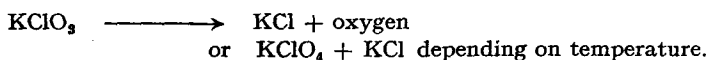


Fig. 297.  
Pyramidal structure of  $\text{ClO}_3^-$  ion.

Sodium iodate,  $\text{NaIO}_3$ , has orthorhombic symmetry, and discrete  $\text{IO}_3^-$  ions. Iodates follow the CsCl structural arrangement (p. 193) and chlorates and bromates that of NaCl (p. 193). However, the crystalline acid  $\text{HIO}_3$ , in its orthorhombic  $\alpha$ -form, appears to exist as separate tetrahedral molecules.

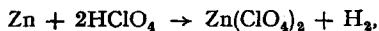
The thermal decomposition of the alkali-metal halates is complex:



Bromates of the heavier metals give mixtures of oxide, bromide and oxygen, others give oxide, bromine and oxygen. The alkali-metal iodates give periodate and iodide; other iodates react in a similar way to the bromates.

### Perhalic acids

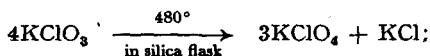
Only perchloric and periodic acids exist; neither perbromic acid nor perbromates occur. Perchloric acid distils as a colourless oily liquid when a perchlorate is heated with concentrated  $\text{H}_2\text{SO}_4$  at 10–20 mm pressure. The hot, concentrated liquid is liable to detonate in the presence of a trace of reducing agent, particularly a carbon compound. The cold, aqueous acid gives hydrogen with Zn and Fe, without any reduction of the chlorate ion:





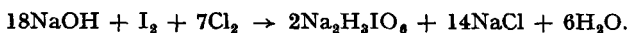
Perchloric acid is strongly ionised ( $pK_a \sim -11$ ). The tetrahedral  $\text{ClO}_4^-$  ion is the least polarised of anions and perchlorates are much used for adjusting the ionic strength of solutions without the risk of forming complexes with the cations present. Of the many crystalline hydrates, the monohydrate is the most interesting since the crystal is composed of  $\text{H}_3\text{O}^+$  and  $\text{ClO}_4^-$  ions and is isomorphous with  $\text{NH}_4\text{ClO}_4$ .

Perchlorates can be made by heating chlorates under controlled conditions:

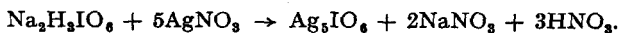


and by the electrolytic oxidation of cooled chlorate solutions at high current densities. Any chlorate remaining can be decomposed by  $\text{HCl}$  which does not react with the  $\text{ClO}_4^-$  ion. The potassium perchlorate is separated by fractional crystallisation. Perchlorates are often isomorphous with the permanganates and perrhenates. Most perchlorates are very soluble, but those of potassium, rubidium, caesium and ammonium are not.

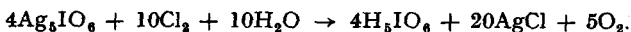
The periodate picture is more complicated because of the stability of paraperiodic acid,  $\text{H}_5\text{IO}_6$ . Thus when a stream of chlorine is passed through a boiling solution of iodine in an excess of caustic soda, a white precipitate of  $\text{Na}_2\text{H}_3\text{IO}_6$  is formed:



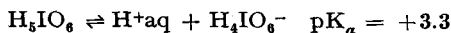
Treatment of a suspension of this with  $\text{AgNO}_3$  solution gives a black precipitate of silver paraperiodate:



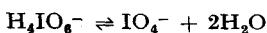
When chlorine is passed into a suspension of this salt, avoiding an excess of the gas, a solution is obtained from which, after filtration, paraperiodic acid,  $\text{H}_5\text{IO}_6$ , can be crystallised:

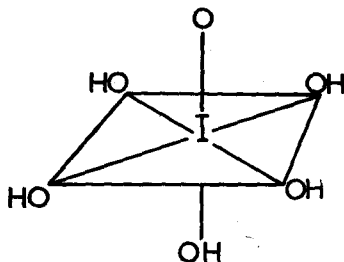


The colourless crystals contain octahedral molecules (Fig. 298), corresponding approximately to  $sp^3d^2$  hybridisation with secondary  $\pi$  bonding (p. 120).  $\text{HIO}_4$  is obtained by heating  $\text{H}_5\text{IO}_6$  in a vacuum at  $100^\circ$ . The acid is a powerful oxidising agent. In aqueous solution  $\text{HIO}_4$  is converted back to  $\text{H}_5\text{IO}_6$ , which is rather weakly ionised:



The  $\text{H}_4\text{IO}_6^-$  ion is in equilibrium with  $\text{IO}_4^-$  in the solution:



Fig. 298. Octahedral structure of  $H_5IO_6$ .

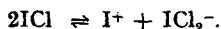
To sum up, the periodates are of four formula types:

- $KIO_4$  from metaperiodic acid,  $HIO_4$ ;  
 $Na_4I_2O_9$  from dimesoperiodic acid,  $H_4I_2O_9$ ;  
 $Pb_3(IO_6)_2$  from mesoperiodic acid,  $H_3IO_6$  (hypothetical);  
 $Ag_5IO_6$  from paraperiodic acid,  $H_5IO_6$ .

The salts, like the acids, are also powerful oxidisers, converting  $Mn^{2+}$  ions to  $MnO_4^-$ , and iodides to iodine.

### Compounds of cationic iodine

Molten  $ICl$  is a good electrical conductor and molten  $ICl_3$  an even better. When  $ICl$  is in solution in nitrobenzene or anhydrous acetic acid, transport evidence suggests the ionisation to be:

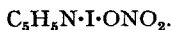


$I\text{Br}$  behaves similarly, giving  $I^+$  and  $Br^-$ . Non-aqueous solutions of  $ICl_3$  appear to contain  $ICl_2^+$  and  $Cl^-$  ions. As has been indicated (p. 532), and as  $K_b$  and  $K_a$  show,  $IOH$  is better considered as iodine hydroxide than as an acid, though made in a similar way to hypochlorous acid:

$$K_b = \frac{\{I^+\} \{OH^-\}}{\{IOH\}} = 3.2 \times 10^{-10}, \text{ whereas } K_a = \frac{\{H_3O^+\} \{IO^-\}}{\{HOI\}} = 2.5 \times 10^{-11}.$$

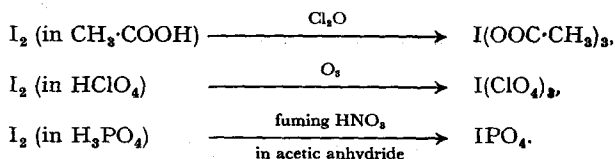
The unipositive iodine ion is stabilised by complexing with pyridine, and the salts  $I(\text{py})_2\text{NO}_3$  and  $I(\text{py})_2\text{ClO}_4$  are made by the action of iodine on silver nitrate or silver perchlorate dissolved in pyridine. Electrolysis of  $I(\text{py})_2\text{NO}_3$  in  $\text{CCl}_4$  gives iodine at the cathode only.

The compound  $I(\text{py})\text{NO}_3$  can also be made but it is a poor conductor in solution. It probably contains two-co-ordinate iodine also:



There is a wide range of evidence that the blue solutions obtained when  $I_2$  or  $ICl$  is dissolved in concentrated  $H_2SO_4$  or  $HSO_3F$  contain solvated  $I^+$  ions. The magnetic moment of 1.5 B.M. is attributed to a  $5s^25p^4$  cation in which the electronic energy bands are split by the interaction with solvent molecules.

Compounds of  $I^{3+}$  with oxoanions do not require stabilisation by complexing. They are made by oxidising solutions of iodine in the particular anhydrous acid:



Yellow iodyl sulphate,  $(IO)_2SO_4$ , is made from iodine and  $I_2O_5$  in concentrated  $H_2SO_4$ . It does not contain discrete  $IO^+$  ions, instead it has polymeric  $IO$ -chain cations.

#### FURTHER READING

- A. G. SHARPE, *Some General Aspects of the Inorganic Chemistry of Fluorine*, Quart. Rev., 11 (1957) 49.
- J. AROTSKY AND M. C. R. SYMONS, *Halogen Cations*, Quart. Rev., 16 (1962) 382.
- A. G. STRONG, *The Oxygen Fluorides*, Chem. Rev., 63 (1963) 607.
- E. H. WIEBENGA, E. E. HAVINGA AND K. H. BOSWIJK, *Structures of Interhalogen Compounds and Polyhalides* in H. J. EMELÉUS AND A. G. SHARPE (Eds.), *Advances in Inorganic Chemistry and Radiochemistry*, Vol. 3, London, Academic Press, 1961, p. 133.
- H. C. CLARK, *Halogen Fluorides and other Covalent Fluorides*, Chem. Rev., 58 (1958) 869.
- E. ANDERS, *The Nuclear and Chemical Properties of Astatine*, Ann. Rev. Nuclear Science, 9 (1959) 209.
- M. SCHMEISSER AND K. BRAENDLE, *Oxides and Oxyfluorides of the Halogens* in H. J. EMELÉUS AND A. G. SHARPE (Eds.), *Advances in Inorganic Chemistry and Radiochemistry*, Vol. 5, New York, Academic Press, 1963, p. 41.
- A. H. W. ATEN Jr., *The Chemistry of Astatine* in H. J. EMELÉUS AND A. G. SHARPE (Eds.), *Advances in Inorganic Chemistry and Radiochemistry*, Vol. 6, New York, Academic Press, 1964, p. 207.

# The Halides and Pseudohalides

## THE HALIDES

### General

#### Classes of halides

The halides may be divided broadly into two main classes:

- (i) those formed by metals which have ions of low charge;
- (ii) those formed by non-metals and by many B sub-group metals.

The first class comprises the saline halides with three dimensional, ionic lattices; they are salts with high m.p. and b.p. and are good conductors when fused. Most of the halides of elements of the first three A sub-groups belong to this class. The second class comprises the volatile, non-conducting halides which usually have molecular lattices. There are a few halides with some of the properties of each class, examples are those of beryllium and aluminium.

TABLE 100  
BOILING POINTS OF CHLORIDES (°C)

<i>Monohalides</i>		<i>Dihalides</i>		<i>Trihalides</i>		<i>Tetrahalides</i>	
LiCl	1380	BeCl <sub>2</sub>	490	BCl <sub>3</sub>	12.5	CCl <sub>4</sub>	76
NaCl	1440	MgCl <sub>2</sub>	1400	AlCl <sub>3</sub>	183*	SiCl <sub>4</sub>	57
KCl	1380	CaCl <sub>2</sub>	1600	ScCl <sub>3</sub>	1000	TiCl <sub>4</sub>	136

\* Sublimation temperature.

The classes are readily distinguished by considering the boiling points of the chlorides of the first three elements in Group I to IV (Table 100). Those to the left of the full lines are saline and those to the right are covalent. Beryllium and aluminium chlorides which are shown in boxes display both ionic and covalent character, the first being the more ionic the second the more covalent. Solid aluminium chloride has a layer-lattice structure, with a greatly distorted octahedral co-ordination of chlorine atoms around the aluminium atoms, but the vapour formed on sublimation at 183° contains Al<sub>2</sub>Cl<sub>6</sub> molecules in which there is tetrahedral arrangement of chlorine atoms around the aluminium atoms (p. 543). The solid can be liquified only under pressure.

The change from ionic to covalent halides is least abrupt in the lithium period. In it the boiling point of beryllium chloride is  $890^\circ$  below that of lithium chloride, whereas in the next period the sublimation point of aluminium chloride is  $1217^\circ$  below the boiling point of magnesium chloride.

The molar conductances of these compounds, measured at their melting points, also bring out the changes from ionic to covalent character which has just been described. Incidentally, the least readily melted halides are, broadly speaking, the best conductors when fused, and usually the transportation of current is mainly by the cations.

TABLE 101  
MOLAR CONDUCTANCES OF FUSED CHLORIDES  
(AT THEIR M.P.) IN  $\text{OHM}^{-1}$

<i>Monohalides</i>	<i>Dihalides</i>	<i>Trihalides</i>	<i>Tetrahalides</i>
LiCl ( $614^\circ$ ) 166	BeCl <sub>2</sub> ( $405^\circ$ ) 0.086	BCl <sub>3</sub> ( $-107^\circ$ ) 0	CCl <sub>4</sub> ( $-23^\circ$ ) 0
NaCl ( $800^\circ$ ) 134	MgCl <sub>2</sub> ( $714^\circ$ ) 29	AlCl <sub>3</sub> ( $193^\circ$ )* $1.5 \times 10^{-6}$	SiCl <sub>4</sub> ( $-70^\circ$ ) 0
KCl ( $770^\circ$ ) 104	CaCl <sub>2</sub> ( $782^\circ$ ) 52	ScCl <sub>3</sub> ( $939^\circ$ ) 15	TiCl <sub>4</sub> ( $-30^\circ$ ) 0

\* Under pressure.

As BeCl<sub>2</sub> shows, a rigid division into saline and volatile halides is not possible. Many metals which form ions such as  $M^{2+}$ ,  $M^{3+}$  or  $M^{4+}$ , give halides with intermediate properties. These compounds usually have either layer lattice structures (CdCl<sub>2</sub>, FeBr<sub>2</sub>, BiI<sub>3</sub>) or chain structures (PdCl<sub>2</sub>).

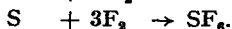
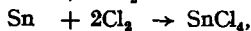
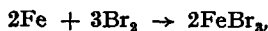
For a series of halides of the same metal, the covalence also increases with the size of the halogen atom; thus CaF<sub>2</sub> has an ionic crystal, and CaCl<sub>2</sub> has a very slightly deformed rutile structure, but CaI<sub>2</sub> has the CdI<sub>2</sub> layer lattice. Fluorides, as might be expected, tend to be saline, for instance AuF<sub>3</sub>, TiF<sub>3</sub> and PbF<sub>4</sub> are saline though the corresponding chlorides are volatile. An example of a halide combining saline and covalent characteristics is iron(III) chloride which is volatile (b.p.  $315^\circ$ ), soluble in organic solvents, dimeric in the vapour and readily hydrolysed, but, nevertheless, a good conductor of electricity when fused.

Halides frequently form hydrates which differ in properties from the anhydrous materials. Thus many  $M^{III}$  fluorides (e.g. AlF<sub>3</sub>) are quite insoluble when made by dry methods but the hydrates (e.g. AlF<sub>3</sub>·3.5H<sub>2</sub>O) produced from solutions dissolve readily in water. This is because the co-ordination of water molecules round cations greatly reduces the lattice energies and facilitates solution.

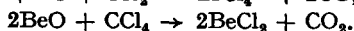
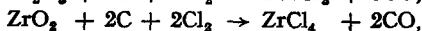
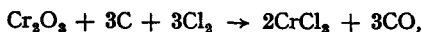
### Methods of preparation

Dry methods of preparation are obligatory when the product is easily hydrolysed.

- (i) Direct halogenation is a particularly versatile method, useful for all types of halide:



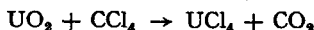
- (ii) Heating oxide or sulphide with carbon and chlorine, with carbon tetrachloride, or with phosgene, is usually a good method for non-saline metal halides:



- (iii) A mixture of  $\text{S}_2\text{Cl}_2$  and chlorine often converts an oxide, or even a sulphate, to a chloride. This is a common method of making the trichlorides of the lanthanides:

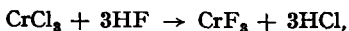


- (iv) Chlorine gives a mixture of chlorides with metallic uranium. The tetrachloride  $\text{UCl}_4$  results from heating the dioxide  $\text{UO}_2$  with  $\text{CCl}_4$ :



Probably  $\text{UCl}_6$  is first formed and decomposes to give  $\text{UCl}_4$ .

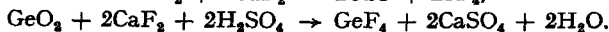
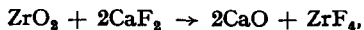
- (v) Fluorides are made by treating the chlorides with anhydrous HF:



by treating covalent halides with  $\text{SbF}_3$  in the presence of  $\text{SbCl}_5$  as catalyst:

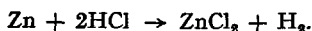


or by heating the oxides with  $\text{CaF}_2$  or a mixture of  $\text{CaF}_2$  and  $\text{H}_2\text{SO}_4$ :

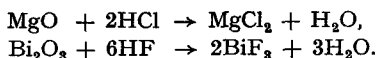


Wet methods are feasible when the halide is not hydrolysed, either because it is ionic or because it is insoluble. The products are frequently hydrated:

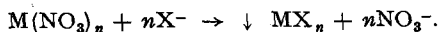
- (i) The metal may be dissolved in the aqueous halogen acid:



(ii) The oxide or hydroxide may be dissolved in the halogen acid:



(iii) Precipitation methods are frequently useful for non-hydrated metal halides:



The insoluble halides include the chlorides and bromides of the  $\text{Ag}^+$ ,  $\text{Cu}^+$ ,  $\text{Au}^+$  and  $\text{Tl}^+$  ions, of the  $\text{Pb}^{2+}$ ,  $\text{Pt}^{2+}$  and the mercury(I) ion,  $\text{Hg}_2^{2+}$ . The iodides of these metals, together with  $\text{HgI}_2$ ,  $\text{PdI}_2$ ,  $\text{BiI}_3$  and  $\text{AuI}_3$ , are also insoluble.

Certain ions are precipitated as fluoride from solutions of the corresponding chloride, for example, those of  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Cu}^{2+}$  and  $\text{Al}^{3+}$ ; but  $\text{AgF}$ ,  $\text{Hg}_2\text{F}_2$  and  $\text{TlF}$  are soluble.

### The structures of halides

#### *AB structures*

The alkali-metal halides have either NaCl type (6 : 6) or CsCl type (8 : 8) structures (p. 193). The ratios of the ionic radii,  $r_+/r_-$  in

KF	RbF	CsF
0.98	1.09	1.24

suggest that the structures should have 8 : 8 co-ordination (higher co-ordination is not consistent with overall electrical neutrality), yet they have the 6 : 6 NaCl structure. Ammonium chloride, bromide and iodide all possess two forms, that with the CsCl structure being stable below the respective transition temperatures and that with the NaCl structure above; the transition temperatures are:

$\text{NH}_4\text{Cl}$	$\text{NH}_4\text{Br}$	$\text{NH}_4\text{I}$
184.3°	137.8°	—17.6°

At a low temperature  $\text{NH}_4\text{Br}$  and  $\text{NH}_4\text{I}$  have a third form which is tetragonal. Hydrogen bonding imposes a wurtzite structure on  $\text{NH}_4\text{F}$  (Fig. 299). The copper(I) halides have the zinc blende structure (p. 202).

#### *AB<sub>2</sub> structures*

Difluorides usually have fluorite or rutile structures. Large ions such as  $\text{Hg}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Ba}^{2+}$  form a fluorite (8 : 4) lattice (p. 203); the smaller  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Mn}^{2+}$  cations give rise to the rutile (6 : 3) structure (p. 203). The crystals of some chlorides and bromides of metals with large bipositive cations are ionic.  $\text{CaCl}_2$  has a deformed rutile structure with four

$\text{Cl}^-$  ions 2.76 Å, and two  $\text{Cl}^-$  ions 2.70 Å, from the  $\text{Ca}^{2+}$ . However,  $\text{CaI}_2$  has the same layer lattice as  $\text{CdI}_2$  (p. 204).

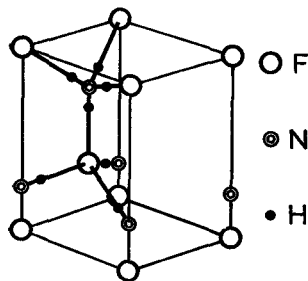


Fig. 299.  
Hexagonal unit cell of  $\text{NH}_4\text{F}$ .

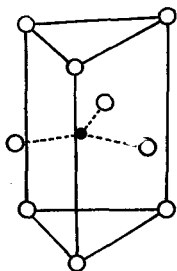


Fig. 300.  
Structure of  $\text{PbCl}_2$ .

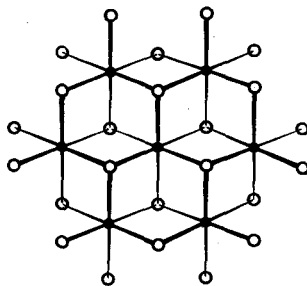


Fig. 301. Arrangement of octahedra in  $\text{CdCl}_2$ .

In  $\text{PbCl}_2$  the lead ion occupies the centre of a trigonal prism with six  $\text{Cl}^-$  ions at the corners and three outside the face centres.  $\text{SrBr}_2$  is similar (Fig. 300). But most dihalides form layer lattices.  $\text{CdCl}_2$  can be considered as an  $\text{NaCl}$  structure (p. 193) in which half the octahedral holes between the  $\text{Cl}$  atoms are unoccupied (Fig. 301).

$\text{CdI}_2$  can be considered as being made up of hexagonally close-packed iodine ions in which only half the octahedral holes are filled with cadmium ions.

Other halides of these layer types are:

$\text{CdCl}_2$  type:  $\text{FeCl}_2$ ,  $\text{CoCl}_2$ ,  $\text{NiCl}_2$ ,  $\text{NiI}_2$ ,  $\text{ZnCl}_2$ ,  $\text{MnCl}_2$ ;

$\text{CdI}_2$  type:  $\text{CaI}_2$ ,  $\text{MgI}_2$ ,  $\text{PbI}_2$ ,  $\text{MnI}_2$ ,  $\text{MgBr}_2$ ,  $\text{FeBr}_2$ .

The compounds  $\text{PdCl}_2$  (Fig. 302),  $\text{CuCl}_2$  and  $\text{CuBr}_2$  have chain structures:

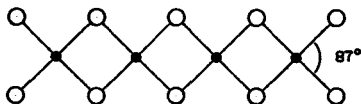


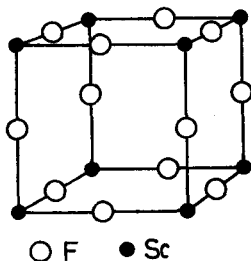
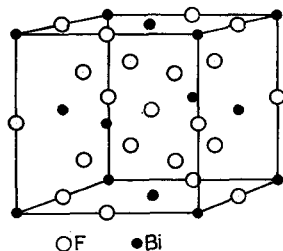
Fig. 302. Chain structure of  $\text{PdCl}_2$ .

### $\text{AB}_3$ types

The trifluorides of many lanthanides and actinides have very slightly distorted rhenium trioxide structures (Fig. 303). Examples are  $\text{CeF}_3$ ,  $\text{PrF}_3$ ,  $\text{NdF}_3$ ,  $\text{ScF}_3$ ,  $\text{EuF}_3$ ,  $\text{AcF}_3$ ,  $\text{UF}_3$  and  $\text{NpF}_3$ .

Bismuth trifluoride has the  $\text{CaF}_2$  structure with twelve extra fluorine atoms at the mid-points of the edges and one at the centre of the unit cell (Fig. 304).

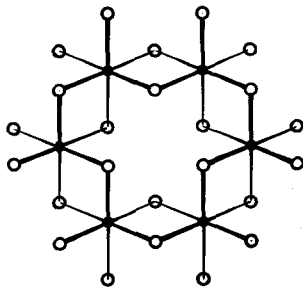


Fig. 303. Structure of  $\text{ScF}_3$ .Fig. 304. Cubic structure of  $\text{BiF}_3$ .

The chlorides and bromides of the lanthanides and actinides usually have the same structure as  $\text{PbCl}_2$  but with one third of the prisms lacking metal ions. Examples are  $\text{LaCl}_3$ ,  $\text{CeCl}_3$ ,  $\text{NdCl}_3$ ,  $\text{LaBr}_3$ ,  $\text{CeBr}_3$ ,  $\text{AcCl}_3$ ,  $\text{NpCl}_3$ .

The structure of  $\text{CrCl}_3$  (Fig. 305) is that of  $\text{CdCl}_2$  (Fig. 301) with the places of one third of the Cd atoms not filled. Crystalline  $\text{AlCl}_3$  is similar in structure to  $\text{CrCl}_3$ .

$\text{BiI}_3$  is similarly related to  $\text{CdI}_2$ . It can also be considered as a structure of close-packed iodine atoms in which only one third of the octahedral holes are filled. Other examples of this structure are  $\text{SbI}_3$ ,  $\text{AsI}_3$ ,  $\text{FeCl}_3$  and  $\text{CrBr}_3$ .

Fig. 305. Arrangement of octahedra in  $\text{CrCl}_3$ .

### Halides containing individual molecules

The halides of B, C, N, O, Si and S and the Gp.IVB, VB and VIB elements consist of finite molecules.  $\text{GeI}_4$  and  $\text{SnI}_4$  also contain individual tetrahedral molecules.  $\text{Al}_2\text{Br}_6$  molecules are present in aluminium bromide.  $\text{PCl}_5$  and  $\text{PBr}_5$  are interesting; the former contains tetrahedral  $\text{PCl}_4^+$  ions and octahedral  $\text{PCl}_6^-$  ions, the latter tetrahedral  $\text{PBr}_4^+$  ions and  $\text{Br}^-$  ions.

The hexachlorides of tungsten and uranium have a deformed hexagonal close-packing of chlorine atoms with metal atoms filling only one sixth of the octahedral holes.

### Halide molecules in the vapour state

The shapes of the free molecules in halide vapours are determined by mutual repulsion between electron pairs (p. 147) and may bear little relation to the disposition of atoms in the respective solid structures. The shapes of the molecules in the vapour depend largely on the electron configuration of the less electronegative element. Thus the  $\text{PCl}_5$  molecule is trigonal bipyramidal,  $\text{AsI}_3$  has a pyramidal molecule (Fig. 306). Aluminium chloride exists principally as the dimer,  $\text{Al}_2\text{Cl}_6$ , in the vapour just above the b.p. (Fig. 307), and  $\text{Fe}_2\text{Cl}_6$  is probably the same. The trihalides of gold are planar dimers (Fig. 308).

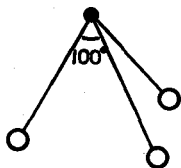


Fig. 306. Pyramidal structure of  $\text{AsI}_3$ .

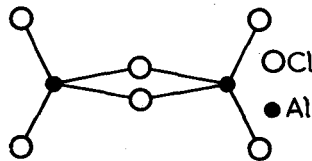


Fig. 307. Structure of  $\text{Al}_2\text{Cl}_6$ .

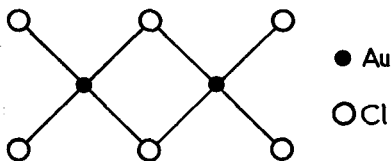


Fig. 308. Structure of  $\text{Au}_2\text{Cl}_6$ .

### Enthalpies of formation

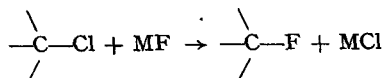
Of the alkali-metal halides, the fluorides have much the most negative enthalpies of formation. This is ascribed to the low heat of dissociation of the  $\text{F}_2$  molecule and the high lattice energies of the compounds themselves. In the fluorides the enthalpies of formation rise as the size of the cation increases, in the other halides they fall:

	<i>Li</i>	<i>Na</i>	<i>K</i>	<i>Rb</i>	<i>Cs</i>	
Fluorides	-145	-137	-135	-133	-132	kcal.
Chlorides	-97	-98	-104	-105	-107	kcal.

This is principally because the fraction  $\frac{1}{r_{\text{anion}} + r_{\text{cation}}}$  which occurs in the lattice energy formula (p. 102) decreases more rapidly in the fluoride series on account of the small size of the anion; this change has more effect than

have the decrease of ionisation energy and sublimation energy of the respective metals.

Lattice energy considerations are important in fluorination of an organic halide by alkali-metal fluorides:



Here  $\Delta G$  is largely dependent on the difference between the lattice energies of MF and MCl. As this difference is proportional to

$$\frac{1}{r_{M^+} + r_{F^-}} - \frac{1}{r_{M^+} + r_{Cl^-}} = \frac{r_{Cl^-} - r_{F^-}}{(r_{M^+} + r_{F^-})(r_{M^+} + r_{Cl^-})}$$

the greater the size of the  $M^+$  ion the smaller the energy needed to produce MCl from MF and the less the energy which has to be supplied by the C-Cl  $\rightarrow$  C-F change. Fluorine-exchanging ability therefore increases with

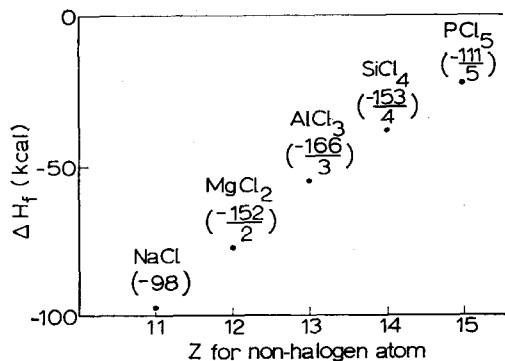


Fig. 309. Enthalpies of formation per g-atom of chlorine for chlorides of the third-period elements.

cation size for the fluorides of metals which form chlorides isomorphous with the fluorides. Incidentally, the difference between the lattice energy of AgF and AgCl is very small because of the partly covalent bonding in AgCl and this accounts for the specially high fluorinating power of AgF.

Trends in enthalpies of formation of halides through the Periodic Table are often surprisingly regular, as is shown for chlorides of elements of the third period in Fig. 309.

The enthalpy of formation (per halogen atom) of a halide plotted against the logarithm of the atomic number of its non-halogen atom displays a straight line relationship for compounds in which the maximum group

valency is achieved. This is shown for the chlorides of Groups I to IV (Fig. 310).

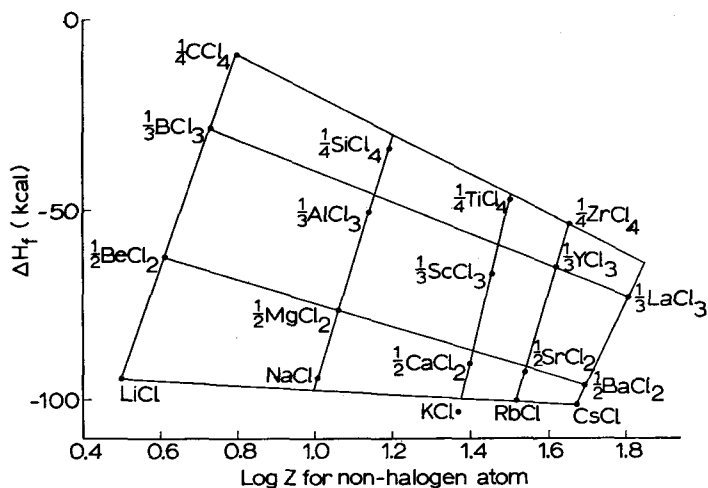
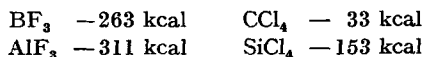


Fig. 310. Approximately linear relationships between enthalpies of formation and log  $Z$  for some simple chlorides.

Enthalpies of formation of chlorides, bromides and iodides decrease for the elements in going down Groups I, II, IIIA, IVA and VA. Elsewhere in the Periodic Table, enthalpies of formation usually increase down a group, but there are some irregularities, particularly in the first two periods, as appears from:



The fluorides of Group VIB are interesting, their enthalpies of formation,  $\Delta H_f$ , being  $\text{SF}_6$  -262 kcal,  $\text{SeF}_6$  -246 kcal and  $\text{TeF}_6$  -315 kcal. Fluorine apparently forms particularly strong bonds with atoms having orbitals available for  $\pi$ -bonding, such as the 4f orbitals in Te; in this kind of situation the halogen lone pairs could make a small contribution to bonding by back-donation (*cf.* p. 183).

The enthalpies of formation of hypothetical halides can be calculated by the Born-Haber treatment. For the halides for elements of variable charge number, the highest curve in Fig. 311 is the type commonly found for bromides and iodides.

According to simple theory, the reduction to be expected in enthalpy between a bromide and a chloride, or a chloride and a fluoride, is proportiona

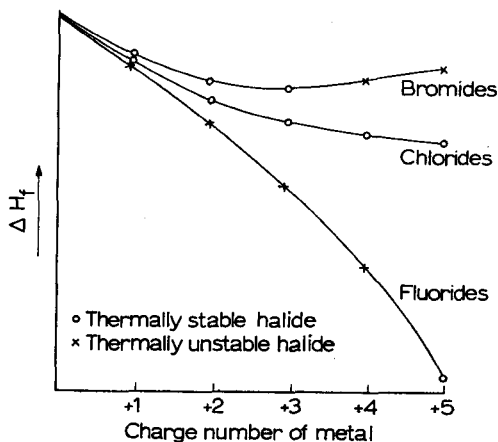
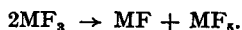


Fig. 311. Enthalpies of formation of halides related to thermal stability.

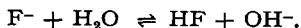
to the square of the charge number. This accounts for the form of the two lower curves. Both  $\text{MBr}_4$  and  $\text{MBr}_5$  are unstable and must liberate heat on conversion to  $\text{MBr}_3$ , whereas all the five chlorides are stable. When the curve becomes concave towards the charge number axis, as often happens for fluorides, the lower fluorides are metastable and heat must be liberated in the reaction



It is stressed that in halides of the non-metals, the charge numbers shown by the non-metal change by steps of two because of the necessity of forming singly occupied orbitals. The implied promotion of electrons in the valence state will, of course, occur only when the formation of the bonds results in a net binding energy (p. 113).

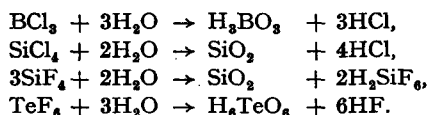
### Hydrolysis of halides

Most of the alkali-metal and barium halides dissolve in water without changing the pH, although there is undoubtedly some hydration of the ions. The alkali-metal fluorides give slightly alkaline reactions, however, because of the comparatively low ionisation of HF:

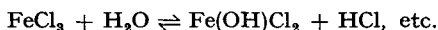


$\text{PbF}_4$  hydrolyses to give  $\text{PbO}_2$  and HF. This reaction is made possible by the high lattice energy of the  $\text{PbO}_2$  formed, and by the large energy of hydration of the four  $\text{F}^-$  ions.

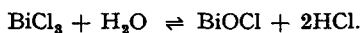
Most covalent halides hydrolyse readily:



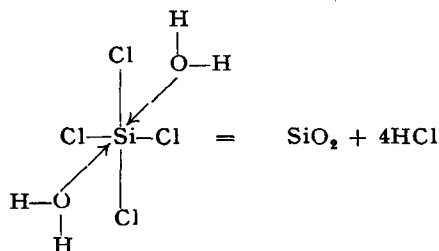
Halides of layer-lattice type often hydrolyse in stages and reversibly:



giving the solution a weakly acid reaction. Some hydrolyse reversibly to an oxide halide:



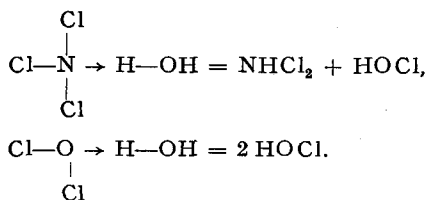
Hydrolysis is probably initiated by the donation of an electron pair to the central atom from the oxygen atom of the water molecule. Thus for example:



That Si—Cl bonds have some double bond character and involve the use of the 3d orbitals of Si, with donation from the chlorine lone pairs, is suggested by the very negative enthalpy of formation of  $\text{SiCl}_4$ . One d orbital is occupied in  $\text{sp}^2\text{d}$  hybridisation, but the empty 3d orbitals can also accept electrons from the oxygen of water.  $\text{CCl}_4$ , with its higher enthalpy of formation, is bound by simple  $\sigma$ -bonds and is not hydrolysed because there are no low-lying carbon orbitals of suitable symmetry to accept electrons from the water molecule.

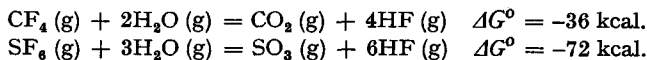
The fluoride  $\text{TeF}_6$  is much more readily hydrolysed than  $\text{SeF}_6$ ; it also has a much more negative enthalpy of formation than  $\text{SeF}_6$  which may be due, at least in part, to  $\pi$ -bonding in the Te—F bonds, made possible by the use of 4f electrons. For  $\text{SeF}_6$ ,  $\Delta H_f = -246$  kcal, for  $\text{TeF}_6$ ,  $-315$  kcal.

The hydrolysis of covalent halides in which the central atom has attained its maximum covalency but still has one or more lone pairs is initiated by the donation of electrons to a proton of the water molecule:



Such chlorides always yield HOCl instead of HCl on hydrolysis.  $\text{NF}_3$  and  $\text{F}_2\text{O}$  do not hydrolyse because the fluorine is too electronegative to permit the donation of electrons to another molecule.

It should be noted that stability in the presence of water is not entirely dependent on the thermodynamic properties of a halide. The free energy changes for the following reactions show that they are thermodynamically feasible:



The failure of appreciable hydrolysis to occur under ordinary conditions must be due to the magnitude of the activation energies; this would be expected to be considerable since in each case the central atom is exhibiting its maximum valency, and the formation of an activated complex would require complete reorganisation of the electronic structure.

### Colour of the halides

Halides, whether solid or in solution, are usually colourless unless the metal ion itself has a characteristic colour. The principal exceptions are certain anhydrous iodides:  $\text{AgI}$ , yellow;  $\text{PbI}_2$ , bright yellow;  $\text{BiI}_3$ , dark brown;  $\text{HgI}_2$ , scarlet.

### Hydrates

Sodium fluoride does not form a hydrate. The hydrate of sodium chloride,  $\text{NaCl} \cdot 2\text{H}_2\text{O}$ , separates from a saturated solution only below  $-10^\circ$ , whereas  $\text{NaBr}$  and  $\text{NaI}$  form both di- and penta-hydrates at the ordinary temperature.  $\text{CaF}_2$  is anhydrous but the other calcium halides form hydrates. By contrast, potassium and silver fluorides have hydrates,  $\text{KF} \cdot 2\text{H}_2\text{O}$ ,  $\text{AgF} \cdot 2\text{H}_2\text{O}$  and  $\text{AgF} \cdot 4\text{H}_2\text{O}$ , although their other halides are anhydrous. In  $\text{KF} \cdot 2\text{H}_2\text{O}$  each  $\text{K}^+$  and each  $\text{F}^-$  is surrounded approximately octahedrally by two  $\text{H}_2\text{O}$  molecules and four ions of opposite sign, each  $\text{H}_2\text{O}$  having two  $\text{K}^+$  and two  $\text{F}^-$  ions arranged tetrahedrally round it.

In very few instances is the degree of hydration of fluoride and chloride the same; where it is, as in



the structures are not yet known.

Electrostatic considerations provide a useful guide to the likelihood of hydrate formation. For a pair of ions  $A^+$  and  $B^-$  an over-all energy decrease is most likely to happen when  $r_{A^+}$  and  $r_{B^-}$  are large. Conversely when the ionic radii are small, as in  $\text{LiF}$  and  $\text{NaF}$ , a hydrate is not usually formed. As, however, the energy decrease in hydrate formation also depends on the energy change due to the hydration of individual ions, and as the smallest ions often have the greatest hydration energies, the formation of a hydrate depends on a rather fine energy balance. Thus  $\text{AgF}$ , for instance, with two small ions, forms a hydrate.

Many metallic dihalides form hexahydrates containing  $M(\text{H}_2\text{O})_6^{2+}$  ions. Examples are  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{FeCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ . The radius-ratio rule suggests that these hydrates should have a fluorite structure, but  $\text{Mg}(\text{H}_2\text{O})_6\text{Cl}_2$  is, in fact, less symmetrical. However,  $\text{Mg}(\text{NH}_3)_6\text{Cl}_2$  has a fluorite lattice.

Solubilities are closely related to the ease of hydrate formation. In the ionic halides, solubilities increase with the size of the halide ion; fluorides are often particularly insoluble. In the more covalent halides this order of solubility is usually reversed.

### Complex halides

These generally contain  $\text{MX}_4^{n-4}$  ions and  $\text{MX}_6^{n-6}$  ions, where  $n$  is the charge number of the metal. Many new fluoro-complexes containing metals with unusual charge numbers have been made by the use of  $\text{BrF}_3$  as a non-aqueous solvent and fluorinating agent: examples are  $\text{Cs}_2\text{CoF}_6$ ,  $\text{K}_3\text{CuF}_6$  and  $\text{KIrF}_6$ .

Where the central metal ion is small the fluoro-complexes are less stable in solution than the chloro-complexes, perhaps because appreciable  $\pi$ -bonding is possible only in the latter. The complex fluorides of base metals with large positive ions are more stable than the corresponding complex chlorides. Hydration energies also play a part in determining relative stabilities in solution.

Complex fluorides may be grouped into different structural types:

(i) Those with structures like simple halides:

$\text{KLaF}_4$  and  $\text{K}_2\text{UF}_6$  have the  $\text{CaF}_2$  structure (p. 203) with random arrangement of metal ions in the  $\text{Ca}^{2+}$  positions.  $\text{BaUF}_6$  and  $\text{BaThF}_6$  have the random lanthanum fluoride lattice ( $\text{LaF}_3$  has the  $\text{ReO}_3$  structure; see p. 683).



- (ii) Those with perovskite-type lattices (p. 206):  
 $\text{KMgF}_3$ ,  $\text{KZnF}_3$  and  $\text{KNiF}_3$  are examples.
- (iii) Uranium and thorium complexes with a fluorine deficiency:  
 $\text{Na}_3\text{UF}_7$  has a fluorite lattice with  $\text{U}^{4+}$  ions filling one quarter of the  $\text{Ca}^{2+}$  positions and  $\text{Na}^+$  the other three quarters; one eighth of the  $\text{F}^-$  positions are unoccupied. There are many uranium and thorium complexes with lattices of similar type.
- (iv) Complexes of Group IVA and VA elements of unusual formula:  
 $\text{K}_2\text{NbF}_7$  contains  $\text{NbF}_7^{2-}$  ions which have six fluorines at the corners of a trigonal prism and a seventh in a position normal to the centre of one face;  $(\text{NH}_4)_3\text{SiF}_7$  contains octahedral  $\text{SiF}_6^{2-}$  ions and discrete  $\text{F}^-$  ions. The  $\text{TaF}_8^{3-}$  ion has the rather unusual square antiprism structure (Fig. 312).

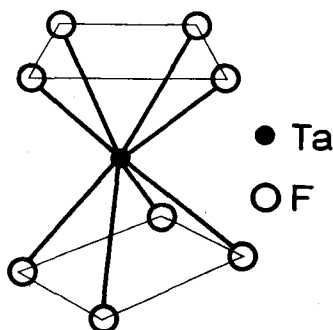


Fig. 312. The square antiprism of  $\text{TaF}_8^{3-}$ .

- (v) Fluoroaluminates:  
 These may contain  $\text{AlF}_6$  octahedra linked in chains or layers, for instance  $\text{Ti}_2\text{AlF}_5$  (Fig. 313).

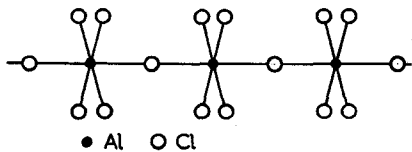


Fig. 313. Chain ions in  $\text{Ti}_2\text{AlF}_5$ .

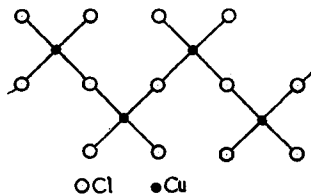


Fig. 314. Double-chain ions in  $\text{CsCuCl}_3$ .

The chloro-complexes usually contain finite complex anions. None has the perovskite structure of  $\text{KMgF}_3$ . The complex  $\text{CsAuCl}_3$  contains equal

numbers of square  $\text{AuCl}_4^-$  ions and linear  $\text{AuCl}_2^-$  ions in addition to  $\text{Cs}^+$  ions.  $\text{Cs}_2\text{CuCl}_4$  contains finite  $\text{CuCl}_4^{2-}$  ions, but  $\text{CsCuCl}_3$  has a double chain (Fig. 314).

In  $\text{K}_2\text{HgCl}_4$  and  $\text{K}_2\text{SnCl}_4$  there are chains based on octahedral arrangement round the noble metal (Fig. 315), and in  $\text{NH}_4\text{CdCl}_3$ , double chains (Fig. 316).

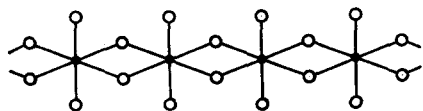


Fig. 315. Chain ions in  $\text{K}_2\text{HgCl}_4$ .

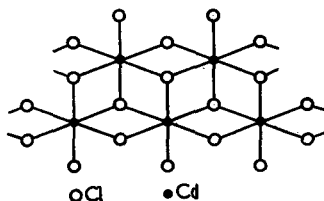


Fig. 316. Double chain ions in  $\text{NH}_4\text{CdCl}_3$ .

## THE PSEUDOHALOGENS AND PSEUDOHALIDES

### Pseudohalides

Several uninegative groups show a similarity to halide ions in both their ionic and covalent compounds. The corresponding pseudohalogen covalent dimer of four of these entities, cyanogen,  $(\text{CN})_2$ , thiocyanogen,  $(\text{SCN})_2$ , selenocyanogen,  $(\text{SeCN})_2$ , and azidocarbonyl disulphide,  $(\text{SCSN}_3)_2$ , have been isolated (Table 102).

TABLE 102

PSEUDOHALIDES IONS AND THE PSEUDOHALOGENS

<i>Pseudohalide</i>	<i>Ion</i>	<i>Pseudohalogen</i>
Cyanide	$\text{CN}^-$	cyanogen $(\text{CN})_2$
Cyanate	$\text{OCN}^-$	
Thiocyanate	$\text{SCN}^-$	thiocyanogen $(\text{SCN})_2$
Selenocyanate	$\text{SeCN}^-$	selenocyanogen $(\text{SeCN})_2$
Tellurocyanate	$\text{TeCN}^-$	
Azide	$\text{N}_3^-$	
Azidothiocarbonate	$\text{SCSN}_3^-$	azidocarbonyl disulphide $(\text{SCSN}_3)_2$
Isocyanate	$\text{ONC}^-$	

Characteristic reactions of pseudohalide ions and the pseudohalogens are given below.

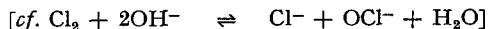
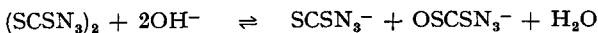
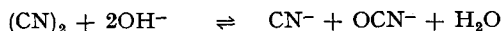
(1) With hydrogen, the uninegative groups form acids which are, however, very weak compared with the halogen acids.

$pK_a$  for  $\text{HN}_3$ , hydrazoic acid, = 4.4.

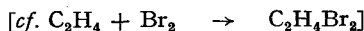
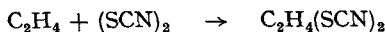
$pK_a$  for  $\text{HCN}$ , hydrocyanic acid, = 8.9.

(2) The silver and mercury(I) salts are like the corresponding halides in being insoluble.

(3) The pseudohalogens are volatile and react with alkalis in rather a similar manner to the halogens:

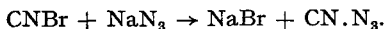


(4) They form addition compounds with olefines and other unsaturated molecules:



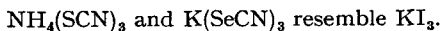
(5) Inter-pseudohalogen compounds and pseudohalogen-halogen compounds are known. Cyanogen chloride and bromide,  $\text{CNCl}$  and  $\text{CNBr}$ , result from the action of  $\text{Cl}_2$  and  $\text{Br}_2$  on  $\text{HCN}$ . Cyanogen fluoride has been identified spectroscopically among products of the fluorination of cyanogen.

Chloroazide,  $\text{ClN}_3$ , bromoazide,  $\text{BrN}_3$ , and iodoazide,  $\text{IN}_3$ , have also been made. In chloroform, thiocyanogen,  $(\text{SCN})_2$ , combines with chlorine to give white crystals of  $\text{SCNCl}$ . Cyanogen bromide reacts with sodium azide to give  $\text{CN} \cdot \text{N}_3$ :

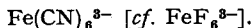


Such compounds as  $\text{CN}(\text{SCN})$  and  $\text{CN}(\text{SeCN})$  have been obtained in crystalline form.

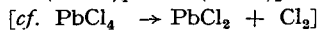
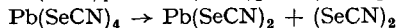
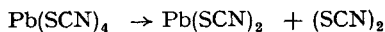
(6) The pseudohalides form ions analogous to polyhalide ions:



The well-known complexes are similar to the less numerous halide complexes:

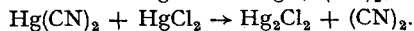


(7) Certain lead(IV) compounds are decomposed by heat to give the lead(II) salt and the free pseudohalogen:

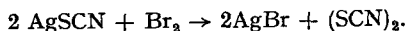


### Pseudohalogens

Cyanogen (p. 379) is made by heating  $\text{AgCN}$  alone or  $\text{Hg}(\text{CN})_2$  with  $\text{HgCl}_2$ :

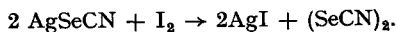


Thiocyanogen,  $(\text{SCN})_2$ , is released by the action of bromine on  $\text{AgSCN}$  suspended in ether:



The yellow solid polymerises irreversibly at room temperature giving an insoluble brick-red material. The dimer oxidises iodides to iodine and  $\text{Cu}^+$  to  $\text{Cu}^{2+}$  ions.

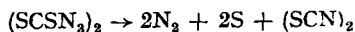
Selenocyanogen,  $(\text{SeCN})_2$ , also yellow and crystalline, is displaced by iodine from  $\text{AgSeCN}$ :



Azidocarbon disulphide,  $(\text{SCSN}_3)_2$ , is formed as white crystals when  $\text{KSCSN}_3$  is oxidised with hydrogen peroxide:



The compound decomposes at room temperature:



#### FURTHER READING

- L. BREWER AND E. BRACKETT, *The Dissociation Energies of Gaseous Alkali Halides*, Chem. Rev., 61 (1961) 425.
- L. BREWER, G. R. SOMAYAJULA AND E. BRACKETT, *Thermodynamic Properties of Gaseous Metal Dihalides*, Chem. Rev., 63 (1963) 111.

## The Transition Metals

The elements which constitute Groups IIIA to IB in the fourth, fifth and sixth periods of the Periodic Table are classified as the *transition elements*. They are metals characterised by having atoms which, either in their neutral state, or, in the case of the coinage metals, in their common oxidation states, have partly filled d or f shells.

### Division of transition elements into two groups

The elements can be divided into a 'd-block' and an 'f-block':

(i) The 'd-block' are the transition elements of Groups IVA to IB, together with scandium and yttrium. They all have partly filled d-shells (a) in their neutral atoms (Sc and Y), or (b) in their atoms when in certain oxidation states ( $\text{Cu}^{\text{II}}$ ,  $\text{Ag}^{\text{II}}$ ,  $\text{Au}^{\text{III}}$ ), or (c) in their atoms when they occur in a neutral state and in certain oxidation states.

(ii) The 'f-block' are the inner transition elements—the lanthanides of Period 6 and the actinides of Period 7. Most of these elements have partly filled f shells either in their neutral atoms or in some of their common oxidation states. Exceptions are La ( $5d^16s^2$ ) and Lu ( $4f^{14}5d^16s^2$ ). Nevertheless the fifteen elements from  $_{57}\text{La}$  to  $_{71}\text{Lu}$  inclusive are so similar that they are conveniently considered together, (p. 605) as are the fifteen elements from  $_{88}\text{Ac}$  to  $_{103}\text{Lw}$  (p. 617). The lanthanides and actinides have a general similarity to the Group IIIA elements, because +3 is nearly always an important oxidation state in them. Accordingly, the Group IIIA elements scandium and yttrium are described with the lanthanides in Chapter 32 (p. 605).

It is important to note that the lanthanides resemble one another far more closely than do the d-block elements. In the latter, the unfilled d orbitals are near the periphery of the atom and are consequently strongly influenced by the atoms or groups surrounding them. By contrast, the unfilled f orbitals of a lanthanide are overlaid with the 5s and 5p electrons and are thus rather thoroughly shielded from external influences; as a result the chemistry of the lanthanides depends hardly at all on the number and disposition of f electrons, and the properties of the elements are very

similar. The actinides do not resemble one another so closely as do the lanthanides because the 5f orbitals are not quite so well shielded from external influences as the 4f ones. The electron occupancy of the orbitals in the transition elements has been discussed on p. 77.

### Properties of the transition elements

#### Physical

Nearly all the transition elements have the simple h.c.p., f.c.c., or b.c.c. lattices characteristic of the true metals (p. 132) and display typical metallic properties—high tensile strength, ductility, malleability, high thermal and electrical conductivity. Their m.p. and b.p. are high; in any period, these rise to a maximum value at the Group VIA metal and then, except for Mn and Tc, regularly fall again (Table 103).

TABLE 103  
MELTING POINTS OF METALS OF GROUPS IVA TO IB (°C)

IVA	VA	VIA	VIIA	VIII	VIII	VIII	IB
Ti	V	Cr	Mn	Fe	Co	Ni	Cu
1725	1700	1920	1260	1535	1480	1455	1083
Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag
1860	2410	2620	2140	2450	1970	1560	960
Hf	Ta	W	Re	Os	Ir	Pt	Au
2200	2850	3370	3170	2700	2450	1770	1062

#### Chemical

Most of the metals dissolve easily in dilute acids. For the lanthanides,  $E^\circ$ ,  $\text{Ln}^{3+}/\text{Ln}$  is about  $-2.1$  V, and the actinides are about as active. The fourth-period d-block metals, with the exception of copper, are readily soluble in non-oxidising acids. Only the coinage metals and some that precede them in the fifth and sixth period show noble character. Because they have partly filled shells, many transition metals give compounds which are paramagnetic (p. 81). The promotion of an electron from one d orbital to another usually requires a quantum of energy appropriate to absorption in the visible spectrum; thus many transition-metal compounds are coloured, but often only weakly, as d—d transitions are 'forbidden' ones in the quantum-mechanical sense (p. 167).

The most important chemical characteristic of the transition metals is that nearly all of them exhibit several oxidation states (p. 230). The co-ordination number of the metal atom in a compound, the stereochemistry

of the atom and the nature of the bonds it forms are all, to some extent, dependent on the particular oxidation state. The structures of transition-metal compounds may be rationalised by means of purely electrostatic models (crystal-field theory, p. 154) or by means of covalent bond models (molecular orbital theory, p. 177); but the approaches made in the two models are complementary rather than contradictory and are effectively combined in ligand-field theory (p. 177).

### Atomic properties of the transition elements

The difference between a transition and a non-transition element arises primarily from the weak shielding of the nucleus afforded by d and f electrons compared with the strong shielding provided by s and p electrons (p. 124). A comparison of the ionisation energies and s—p promotion energies of the Group IA and IB elements emphasises the differences (Fig. 317).

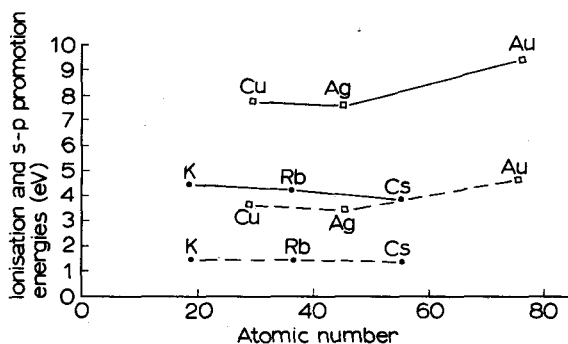


Fig. 317. Ionisation energies (joined by full lines) and s—p promotion energies (joined by dotted lines) for IA and IB metals.

A comparison of the radii of the unipositive ions provides a further illustration of the weakness of the shielding afforded by d electrons:

Ion	Outer configuration	Radius	Ion	Configuration	Radius
K <sup>+</sup>	3s <sup>2</sup> 3p <sup>6</sup>	1.33	Cu <sup>+</sup>	3s <sup>2</sup> 3p <sup>6</sup> 3d <sup>10</sup>	0.96
Rb <sup>+</sup>	4s <sup>2</sup> 4p <sup>6</sup>	1.48	Ag <sup>+</sup>	4s <sup>2</sup> 4p <sup>6</sup> 4d <sup>10</sup>	1.26
Cs <sup>+</sup>	5s <sup>2</sup> 5p <sup>6</sup>	1.69	Au <sup>+</sup>	4f <sup>14</sup> 5s <sup>2</sup> 5p <sup>6</sup> 5d <sup>10</sup>	1.37

The combined effects of the smaller radius of a transition-metal ion and the greater effective nuclear charge exerted at its surface makes its force

of attraction on ligand ions and dipoles much stronger than the force exerted by a non-transition ion of the same charge and an atomic number of the same order. This force can be considered to be proportional to  $Z^*/r^2$  ( $Z^*$  = effective nuclear charge (p. 70),  $r$  = ionic radius).

Values of  $Z^*/r^2$  for comparable transition and non-transition ions are as shown:

K <sup>+</sup>	0.26	Cu <sup>+</sup>	0.84
Cs <sup>+</sup>	0.20	Au <sup>+</sup>	0.86

The value for Au<sup>+</sup> is high because of the very large effective nuclear charge at the surface of the ion. The ten 5d electrons and the fourteen 4f electrons provide far weaker shielding than would equivalent numbers of s and p electrons.

### Oxidation states

The variability of oxidation states shown by individual transition metals arises from the fact that the energy required to remove successive d electrons is about the same as the extra energy obtainable from the formation of more bonds. In fact, the electrons are not completely removed from a metal atom and the oxidation number represents its formal rather than its actual charge. Nevertheless the total ionisation energy required to produce an isolated metal ion is a useful indication of the energy required for the elements to reach the same formal oxidation state in a compound. A comparison of the first four ionisation energies for nickel and platinum shows that, although the energy required to produce an Ni<sup>2+</sup> ion is less than that required to produce a Pt<sup>2+</sup> ion, the energy needed to produce Ni<sup>4+</sup> is much more than that needed to produce Pt<sup>4+</sup>.

	$I(1) + I(2)$ (eV)	$I(3) + I(4)$ (eV)	Total eV
Ni	25.8	91.2	117.0
Pt	27.6	69.5	97.1

Although the promotion energies for copper, silver and gold are smaller, the trends in them are almost certainly similar (*cf.* Fig. 317). Compounds of Ni<sup>2+</sup> are more thermodynamically stable than the corresponding Pt<sup>2+</sup> compounds (NiCl<sub>2</sub> is more stable than PtCl<sub>2</sub>); nevertheless a compound of Pt<sup>IV</sup> such as K<sub>2</sub>PtCl<sub>6</sub> is quite stable, whereas a corresponding nickel compound is unknown.

In general, high oxidation states (+4 upwards) are more stable in the 'd-block' elements of the fifth and sixth periods than in those of the fourth period. Elements of the fifth and sixth periods form predominantly covalent compounds, those of the fourth period predominantly ionic compounds.



### The electroneutrality principle

The stability of an oxidation state in a particular compounds depends not only on the promotion energies for the metal but also on the character of the ligands around the metal atom. A most useful concept for clarifying the relationship between a metal atom and its surrounding atoms is the *postulate of electrical neutrality*, which states:

- (i) that the electronic structure of a substance is such that each atom has a resultant charge not greater than  $\pm e/2$ ;
- (ii) that the resultant charges are possessed by the most electronegative and least electronegative atoms, and are distributed in such a way as to correspond to electrostatic neutrality (Pauling, 1948).

Consider an aquated transition-metal ion  $M(H_2O)_6^{n+}$ . The metal has an electronegativity of about 1.7, enabling it to form M—O bonds of about half ionic and half covalent character. This means that the six oxygen atoms transfer about three units of negative charge to the metal by electrons moving from them towards the metal; and if the metal is to be about electrically neutral in the aquated ion, it must have had a charge of about +3 originally. An application of the electroneutrality principle indicates that the formal oxidation state of a transition metal in a hexa-aquo ion should be about +3 in order that the ion may be stable towards oxidation and reduction. In fact, the most common oxidation states shown by transition metals in such ions are +2, +3 and +4. The charge is not held by the oxygen atoms, but is largely transferred to the twelve hydrogen atoms. Thus the charge possessed by the hydrated ion becomes spread over its surface, in accordance with elementary electrostatic theory.

### Co-ordination numbers

The electroneutrality principle is of importance in deciding the co-ordination number of a metal in a particular oxidation state. Thus in the isoelectronic series of cations,  $Ag^+$ ,  $Cd^{2+}$ ,  $In^{3+}$ , the chloride ion forms complexes  $AgCl_2^-$ ,  $CdCl_4^{2-}$  and  $InCl_6^{3-}$ , as would be expected from the principle if the metal-chlorine bonds are about 50% covalent. Considering different ligands, a metal ion  $M^{n+}$  can be converted into an atom of roughly zero charge by accepting a large negative charge from each of a few easily polarisable ligands, or, alternatively, a small negative charge from each of a larger number of ligands which are less easily polarised. Thus  $Fe^{3+}$  forms a 4-co-ordinate ion,  $FeCl_4^-$ , with  $Cl^-$  ions but a 6-co-ordinate ion,  $FeF_6^{3-}$ , with the less polarisable  $F^-$  ions. When the ligands are large enough, the co-ordinate ion number may be affected by steric considerations, but these

are usually thought to be of subsidiary importance. In general, the more electronegative the ligand the higher will be the most favoured co-ordination number.

Some readily polarisable groups such as the  $\text{CN}^-$  ion are, however, exceptions to the generalisation. Unlike the  $\text{Cl}^-$  ion, the  $\text{CN}^-$  ion forms the 6-co-ordinate  $\text{Fe}^{\text{III}}$  complex  $\text{Fe}(\text{CN})_6^{3-}$ . Although electrons attached to the carbon atoms are directed strongly towards the iron atom, the symmetry and the energy of the  $t_{2g}$  electrons of the metal are so favourable for the formation of  $d\pi-p\pi$  bonds with the ligand (p. 182) that much of the negative charge is 'back-donated' to the empty  $\pi^*$  orbitals of the  $\text{CN}^-$  ligands.

### Ligands stabilising oxidation states

A further consequence of the electroneutrality principle is that the highest oxidation states of the metals are stabilised by strongly electronegative, non- $\pi$ -bonding ligands. In the  $\text{MnO}_4^-$  ion, for example, the oxygen atoms exert sufficient attraction on the bonding electrons to prevent them from being attracted wholly to the metal. Charge numbers of +5 and +6 are particularly common among the oxo-complexes of transition metals ( $\text{VO}_4^{3-}$ ,  $\text{CrO}_4^{2-}$ ); and charge numbers of +7 ( $\text{MnO}_4^-$ ,  $\text{ReO}_4^-$ ) and even +8 ( $\text{OsO}_4$ ) are known.

High oxidation states are also stabilised by the strongly electronegative fluorine in fluoro-complexes, but chlorine and the less electronegative bromine and iodine have decreasing power to do this. Thus although  $\text{Fe}^{\text{III}}$  is stable in chloro- and bromo-complexes, in its iodo-complexes the highest oxidation state of iron is +2. The iron atom can be considered to capture completely the two electrons of one of the  $\text{Fe}-\text{I}$  bonds; and, as a consequence,  $\text{Fe}^{\text{III}}$  is reduced to  $\text{Fe}^{\text{II}}$  and iodine is liberated.

Low oxidation states are stabilised by ligands which have vacant orbitals of suitable symmetry and energy for the formation of strong  $\pi$  bonds with the metal. It is possible for the carbon atom of  $\text{CO}$  to direct electrons strongly towards a metal even in its zero oxidation state (for instance  $\text{Ni}^0$ ) because the negative charge added to the metal atom can be dissipated by back-donation into the  $\pi$  orbitals.

A particularly good example of a metal exhibiting many different oxidation states is ruthenium; some of its compounds are listed in Table 104. These compounds illustrate the principle outlined above; the highest oxidation states here are stabilised by oxide and fluoride ions, the intermediate states are stabilised by chloride ions and ammonia molecules, and the lowest states by  $\text{CO}$  molecules. The  $\text{O}^{2-}$  ion stabilises even higher oxidation states than

the F<sup>-</sup> ion, probably because it uses its second electron for  $\pi$  bonding to the metal. A neutral molecule like ammonia cannot stabilise as high an oxidation state as can a negative ion in which the co-ordinating atom is of similar electronegativity; thus the substitution of Cl<sup>-</sup> for NH<sub>3</sub> in Ru(NH<sub>3</sub>)<sub>6</sub><sup>2+</sup> enables the oxidation state of the ruthenium to be raised by one. In an ion like Ru(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup> the hydrogens tend to become so positive that the complex ion undergoes considerable dissociation as an acid.

TABLE 104

## OXIDATION STATES OF RUTHENIUM

<i>Charge number</i>	<i>Compound or ion</i>
0	Ru(CO) <sub>5</sub>
+2	[Ru(NH <sub>3</sub> ) <sub>6</sub> ] <sup>2+</sup>
+3	[RuCl(NH <sub>3</sub> ) <sub>5</sub> ] <sup>2+</sup>
+4	RuCl <sub>6</sub> <sup>2-</sup>
+5	RuF <sub>5</sub>
+6	RuF <sub>6</sub>
+7	RuO <sub>4</sub> <sup>-</sup>
+8	RuO <sub>4</sub>

**Lattice energy stabilising an oxidation state**

Major departures from the electroneutrality rule can occur in ionic lattice compounds when the loss of stability due to departure from electroneutrality is more than counterbalanced by a gain in lattice energy. In general, provided a closed electron shell in the metal atom is not broken, the increase in lattice energy which results from a higher positive charge on the cation compensates for the increased ionisation energy required. But as the cation becomes more highly charged, a limit of stability is reached when the anions become so highly polarised that they lose electrons completely to the metal and are oxidised.

**d-Shell occupancy and the stability of oxidation states**

Complexes in which the transition metal has a more than half-filled d shell tend to be more covalent, for a particular oxidation state and ligand, than complexes in which the transition metal has fewer d electrons, because of the increasing effective nuclear charge felt at the surface of the metal atom. The stability of such complexes is considerably affected by the

number of d electrons present. Complexes in which the metal has 6, 8, or 10 d electrons are much more numerous than those in which the metal has a  $d^7$  or  $d^9$  configuration; a single unpaired electron appears to react particularly freely with electrons on other atoms.

### $d^6$ complexes

Low-spin complexes of  $d^6$  ions are especially common and range over many oxidation states:

V <sup>-I</sup> V(CO) <sub>6</sub> <sup>-</sup>	Cu <sup>0</sup> Cr(CO) <sub>6</sub>	Mn <sup>I</sup> Mn(CO) <sub>5</sub> <sup>4-</sup>	Fe <sup>II</sup> Fe(CN) <sub>6</sub> <sup>4-</sup>	Co <sup>III</sup> Co(NH <sub>3</sub> ) <sub>6</sub> <sup>3+</sup>	Ni <sup>IV</sup> NiF <sub>6</sub> <sup>2-</sup>
--	--	--	---	--	--

The low-spin  $d^6$  configuration is particularly favourable for octahedral arrangement (p. 162).

### $d^7$ complexes

In agreement with the generalisation above, the  $d^7$  configuration is rather an uncommon one. Strikingly, for ruthenium, which exhibits every other oxidation state between 0 and 8, no Ru<sup>I</sup> ( $d^7$ ) compound has yet been prepared. But the configuration does occur in a few compounds of other metals with oxidation states as far apart as  $-1$  in Cr<sub>2</sub>(CO)<sub>10</sub><sup>2-</sup> and  $+3$  in K<sub>3</sub>NiF<sub>6</sub>.

### $d^8$ complexes

This again, like  $d^6$ , is a very common configuration, ranging over a wide range of oxidation states; 5-co-ordination is often observed in the low-spin complexes:

Cr <sup>-II</sup> [Cr(CO) <sub>5</sub> ] <sup>2-</sup>	Mn <sup>-I</sup> [Mn(CO) <sub>5</sub> ] <sup>-</sup>	Fe <sup>0</sup> Fe(CO) <sub>5</sub>	Co <sup>I</sup> [Co(PhNC) <sub>5</sub> ] <sup>+</sup>	Ni <sup>II</sup> [Ni(CN) <sub>5</sub> ] <sup>3-</sup>
---	---	--	--	--

### $d^9$ complexes

Oxidation states with a  $d^9$  configuration are moderately common, but in most cases the spare electron is paired off to achieve, in effect, a  $d^8$  arrangement. In Fe<sub>2</sub>(CO)<sub>8</sub><sup>2-</sup>, for example, there is a metal-metal bond. Paramagnetism in  $d^9$  complexes is consequently comparatively rare.

### $d^{10}$ complexes

This is almost as common as the  $d^6$  configuration. The most usual co-ordination number is four.

Fe-II [Fe(CO) <sub>4</sub> ] <sup>2-</sup>	Co-I [Co(CO) <sub>4</sub> ] <sup>-</sup>	Ni <sup>0</sup> Ni(CO) <sub>4</sub>	Cu <sup>I</sup> [Cu(CN) <sub>4</sub> ] <sup>3-</sup>	Zu <sup>II</sup> [Zn(CN) <sub>4</sub> ] <sup>2-</sup>
---	---	--	---	--

### Geometry stabilising oxidation states

There is another way in which d-shell occupancy can affect the stability of an oxidation state. A particular geometrical arrangement of ligands, enforced by the environment, can stabilise an otherwise unusual oxidation state. For example d<sup>3</sup> and low-spin d<sup>6</sup> configurations are favourable for octahedral co-ordination but not for tetrahedral.

We have outlined above some of the considerations which have a bearing on the stabilities of transition-metal compounds to oxidation and reduction. The subject is still somewhat empirical; very much more information is required about such things as promotion energies and ligand-field strengths before there can be a unified, quantitative theory.

### Ionic radii in transition series

Through any of the transition series there is a general downward trend in ionic radii which results from an increasing effective nuclear charge (p. 70). The trend is illustrated here by the bipoisitive ions of the first-row d-block elements:

Ion	Ti <sup>2+</sup>	V <sup>2+</sup>	Cr <sup>2+</sup>	Mu <sup>2+</sup>	Fe <sup>2+</sup>	Co <sup>2+</sup>	Ni <sup>2+</sup>	Cu <sup>2+</sup>	Zn <sup>2+</sup>
Radius (Å)	0.90	0.88	0.84	0.80	0.76	0.78	0.78	0.69	0.74

Minor variations in this trend are probably due to ligand-field effects caused by differences in the occupancy of t<sub>2g</sub> and e<sub>g</sub> orbitals in the ions.

Through the inner transition series of lanthanides there is a very considerable fall in the ionic radius, from 1.06 Å in La<sup>3+</sup> to 0.85 Å in Lu<sup>3+</sup>. (The radii of all the terpositive lanthanide ions are given on p. 605.) An important consequence of this lanthanide contraction is that the tendency for these elements to form covalent compounds increases from La to Lu, even though the principal oxidation number remains three.

### Hydrated ions of transition metals

Six co-ordinate, hydrated, bipoisitive and terpositive ions are particularly common among the transition metals (p. 558). The energies of hydration of these free ions are of considerable interest, and the variation of these

energies from one metal to another has been explained by the use of crystal-field theory (p. 177). The values for the bivalent ions of the fourth-period metals are shown in Fig. 318.

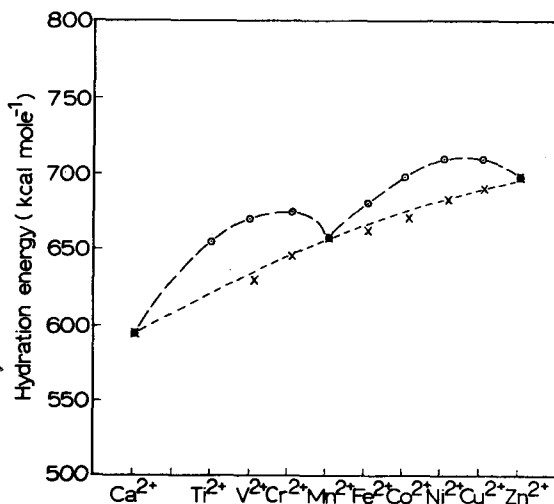


Fig. 318. Hydration energies of bivalent ions of Period 4 transition metals:  $\odot$ , experimental values;  $\times$ , after subtraction of ligand-field stabilisation energies.

It might be expected that the hydration energies would increase smoothly from  $\text{Ca}^{2+}$  to  $\text{Zn}^{2+}$  with the effective nuclear charge exerted at the surface of the free ion. But although the total occupancy of d orbitals increases steadily through the series the occupancies of the sets of  $t_{2g}$  and  $e_g$  orbitals do not. In  $\text{Ti}(\text{H}_2\text{O})_6^{2+}$  for example, there are two  $t_{2g}$  electrons but there is no  $e_g$  electron. The field created round the free ion by the approach of the water molecules releases a stabilisation energy of  $2 \times (2\Delta/5)$ , where  $\Delta$  is the crystal-field splitting. (p. 156). Thus the heat set free when the free  $\text{Ti}^{2+}$  ion is converted into its hexa-aquo complex is  $4\Delta/5$  greater than would be expected if the two electrons were distributed in a spherically symmetrical manner. For the  $\text{V}(\text{H}_2\text{O})_6^{2+}$  ( $t_{2g}^3$ ) ion, the extra energy released is  $6\Delta/5$ , but in the  $\text{Cr}(\text{H}_2\text{O})_6^{2+}$  ( $t_{2g}^3e_g$ ) ion it is only  $3\Delta/5$ , because the occupancy of the higher-energy  $e_g$  orbital reduces the stabilisation energy by  $3\Delta/5$  (p. 209), and in the  $\text{Mn}(\text{H}_2\text{O})_6^{2+}$  ion the stabilisation energy is zero because the occupancy is  $t_{2g}^3e_g^2$ , with a spherically symmetrical arrangement of d electrons.

The second part of the series from  $\text{Mn}^{2+}$  to  $\text{Zn}^{2+}$  repeats the pattern as

first the  $t_{2g}$  and then the  $e_g$  orbitals become doubly occupied. In  $Ni(H_2O)_6^{2+}$ , for example, ( $t_{2g}^6 e_g^2$ ), the stabilisation energy released when the aquo-complex is formed is  $6\Delta/5$  as in  $V(H_2O)_6^{2+}$ .

The ligand-field splittings for the ions can be determined from visible absorption spectra (p. 166) and the stabilisation energies can be calculated. When these stabilisation energies are subtracted from the experimental hydration energies a fairly smooth curve is obtained (Fig. 318).

Curves of very similar appearance to those for the hydration energies of the ions are obtained by plotting the stability constants (p. 583) of  $M^{II}$  complexes of a particular ligand for the same series of metals. The lattice energies of a series of salts such as the dichlorides also fall on a similar curve.

#### FURTHER READING

- C. J. SMITHELLS (Ed.), *Metals Reference Book*, 3rd. Edition, London, Butterworths, 1962.
- R. S. NYHOLM, *Electron Configuration and Structure of Transition-metal complexes*, Proc. Chem. Soc., (1961) 273.
- P. GEORGE AND D. S. MCCLURE, *Effect of Inner Orbital Splitting on the Thermodynamic Properties of Transition Metal Compounds and Coordination Complexes*, in F. A. COTTON (Ed.), *Progress in Inorganic Chemistry*, Vol. 1, New York, Interscience, 1959, p. 381.
- R. S. NYHOLM AND M. L. TOBE, *The Stabilisation of Oxidation States of the Transition Metals* in H. J. EMELÉUS AND A. G. SHARPE (Eds.), *Advances in Inorganic Chemistry and Radiochemistry*, Vol. 5, London, Academic Press, 1963, p. 1

## Complex or Co-ordination Compounds and Ions

### GENERAL

Various particular aspects of the subject of complex compounds and ions have been discussed earlier in the book (pp. 154–186, 205–6, 549–551); here we deal broadly with the subject as a whole.

### Introduction

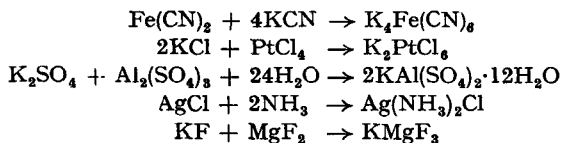
#### Definitions

A sufficient indication of what is meant by a complex is presented in the following definition: a complex molecule or ion is one in which an atom (A) is attached to other atoms (B) or groups of atoms (C) to a number in excess of the charge or oxidation number of the atom (A). In this definition (A) is the *central* or *nuclear atom* and (B) and (C) are *ligands*. An atom whether it be the atom (B) alone, or an atom in the group (C), which is directly attached to (A), is a *co-ordinating atom*. A ligand (C) with more than one potential co-ordinating atom is *multidentate* (*uni-, bi-, terdentate*).

A *chelate ligand* is one using more than one of its co-ordinating atoms. A complex with more than one nuclear atom is *polynuclear*. A *bridging group* is a group attached to two nuclear atoms in a polynuclear complex.

#### Examples

Two or more compounds capable of independent existence often combine:



These products differ widely in their behaviour, particularly in water.

Potassium hexacyanoferrate(II),  $\text{K}_4\text{Fe}(\text{CN})_6$ , dissolves in water to give a solution with none of the reactions of the  $\text{Fe}^{2+}$  ion; the metal is present as the  $\text{Fe}(\text{CN})_6^{4-}$  ion. A solution of  $\text{K}_2\text{PtCl}_6$  contains  $\text{PtCl}_6^{2-}$  ions and one of  $\text{Ag}(\text{NH}_3)_2\text{Cl}$ ,  $\text{Ag}(\text{NH}_3)_2^+$  ions. These are all complex ions.



The solution of an alum  $KAl(SO_4)_2 \cdot 12H_2O$ , on the other hand, gives reactions characteristic of  $K^+$ ,  $Al^{3+}$  and  $SO_4^{2-}$  ions. The brown caesium rhodium alum,  $CsRh(SO_4)_2 \cdot 12H_2O$ , behaves similarly in water. However, it can be partially dehydrated to the red  $CsRh(SO_4)_2 \cdot 4H_2O$ , and this does not produce a precipitate with  $BaCl_2$  immediately after it is dissolved because  $[Rh(H_2O)_4(SO_4)_2]^-$  ions, not  $SO_4^{2-}$  ions, are formed. The alums and other hydrates are often distinguished from the complex salts and are called lattice compounds, but evidently a sharp distinction is not always possible.

In solid  $K_2PtCl_6$  there are octahedral  $PtCl_6^{2-}$  ions. But  $KMgF_3$  is without discrete complex ions; the compound has the perovskite structure (p. 206). There is thus no simple way of defining a complex in terms of solid structure.

Not all complexes contain complex ions. The well-known 'nickel dimethylglyoxime', bis(dimethylglyoximate)nickel(II),  $[Ni(C_4H_7O_2N_2)_2]$  (p. 588) and bis(acetylacetonato)copper(II) (p. 588) are uncharged molecules.

Oxo-anions and halogeno-anions can be regarded as complexes. For example, the sulphate ion is formally an  $S^{6+}$  ion co-ordinated tetrahedrally to four  $O^{2-}$  ions, and the fluorosilicate ion is an  $Si^{4+}$  ion co-ordinated octahedrally to six  $F^-$  ions. These complex anions exist as such in crystals of their salts.

Potassium perchlorate,  $KClO_4$ , and potassium fluoroborate,  $KBF_4$ , both have the same structure with discrete complex ions. The compounds  $K_2SO_4$  and  $Cs_2HgBr_4$  have not only the same rhombic form but the same crystallographic axial ratios in which  $a : b : c = 1 : 0.74 : 0.57$ .

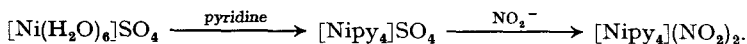
### Methods of preparing complexes

Here are classified and described some of the more important methods of preparing complexes. The reactions of complexes are dealt with in Chapter 31 (p. 590).

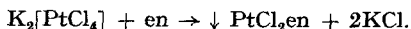
#### (i) *Substitution reactions in aqueous solution*

This, the commonest way of synthesis, involves the replacement of water molecules round the metal atom by other ligands. Thus when an excess of  $NH_3$  is added to an aqueous solution of  $CuSO_4$ , the co-ordinated water round the copper cation is replaced by ammonia molecules to give  $[Cu(NH_3)_4]^{2+}$  ions. Dark-blue  $Cu(NH_3)_4SO_4$  crystallises from the solution when ethanol is added. In certain cases the addition of a second anion to an aqueous solution enables an insoluble complex to be formed. Thus tetrapyrridinenickel(II) nitrite is precipitated as dark-blue crystals by

treating aqueous  $\text{NiSO}_4$  with pyridine and then slowly adding a solution of sodium nitrite:



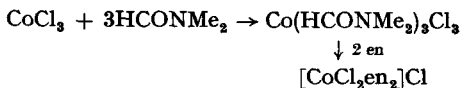
When a product is non-ionic it is often rather insoluble and separates as it is formed, for instance:



Here substitution of the chloroligands by ethylenediamine is incomplete. Generally, however, completely substituted complexes are easier to prepare than mixed complexes. In theory it should be possible to obtain intermediate products by limiting the concentration of the substituent, but in practice such products are usually difficult to isolate from the reaction mixture.

(ii) *Substitution reactions in non-aqueous solvents*

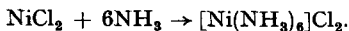
If the aquo-complex of the metal is too stable, either kinetically or thermodynamically, for easy substitution by the required ligand, or if the ligand is not water-soluble, a non-aqueous solvent can frequently be used. Solvents such as diethyl ether and dimethylformamide,  $\text{HCONMe}_2$ , have proved useful. Chromium(III) complexes with amine ligands are often made in dimethylformamide; in aqueous solution, however, the bases would precipitate hydrated chromium(III) oxide.



Many tetrahedral complexes formerly thought to be incapable of preparation on thermodynamic grounds have been made in solvents other than water. Thus compounds of  $\text{VCl}_4^-$  have been prepared in acetonitrile.

(iii) *Direct reaction between solid salt and liquid ligand*

Metal ammines can be made by allowing a solution of a metal salt in liquid ammonia to evaporate:

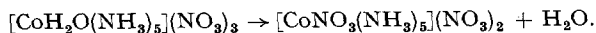


Similarly the addition of  $\text{PtCl}_2$  to liquid ethylenediamine gives  $[\text{Pten}_2]\text{Cl}_2$ . The direct reaction between a metal ion and a basic solvent is particularly useful when the presence of water would cause hydrolysis.

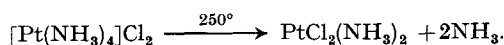
(iv) *Thermal decomposition of complexes*

What are effectively substitution reactions in the solid state may occur

when a solid complex is heated. A very simple example is the conversion of pale-pink  $[\text{Co}(\text{H}_2\text{O})_6]\text{Cl}_2$ , by heating, to blue  $\text{CoCl}_2$  (the 'invisible ink' reaction). The  $\text{Cl}^-$  ion can be considered to replace water molecules which are driven out of the co-ordination sphere when the compound is heated. Sometimes the loss of water from a complex ion occurs even at room temperature. Aquopenta-amminecobalt(III) nitrate,  $[\text{CoH}_2\text{O}(\text{NH}_3)_5](\text{NO}_3)_3$ , made by dissolving nitratopenta-amminecobalt(III) nitrate (below) in warm aqueous ammonia, loses water on standing in air:

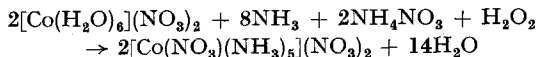


A similar transfer of anions to the co-ordination sphere can often be used to prepare complexes such as chloroammines:

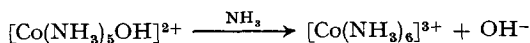


(v) *Substitution reactions accompanied by oxidation*

Cobalt(III) complexes can be made from aqueous  $\text{Co}^{\text{II}}$  salts because the redox potential of the  $\text{Co}^{\text{III}}/\text{Co}^{\text{II}}$  couple falls markedly in the presence of most complexing agents (p. 235). Cobalt(II) nitrate reacts with concentrated aqueous ammonia and  $\text{NH}_4\text{NO}_3$  in the presence of  $\text{H}_2\text{O}_2$  to give nitratopenta-amminecobalt(III) nitrate:

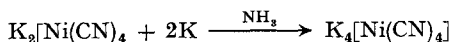


Sometimes the course of reaction is altered by the presence of a heterogeneous catalyst such as activated charcoal. Thus  $[\text{CoCl}(\text{NH}_3)_5]\text{Cl}_2$  is obtained when cobalt(II) chloride is treated with aqueous ammonia, hydrogen peroxide and ammonium nitrate, but when activated charcoal is also added the product is  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ . The action of the catalyst here is not fully understood; it may catalyse an otherwise very slow intermediate reaction such as:



(vi) *Reduction reactions*

Complexes in which the metal is in an unusually low oxidation state must be prepared in the absence of oxygen. An alkali metal in liquid ammonia is often useful as a reducing agent in these circumstances. Thus potassium tetracyanonickelate(II) is reduced to the tetracyanonickelate(0):



(vii) *More specialised methods*

The application of the trans-effect principle to the preparation of *cis*-

and *trans*-isomers is treated on p. 598. The resolution of optically active isomers can be carried out by making diastereoisomeric salts. For non-ionic racemates, however, separation is usually made by chromatographic means. Thus triglycinecobalt(III) has been resolved by pouring a solution of it through a column packed with starch. One isomer is preferentially absorbed on the starch because the N atoms are more favourably orientated for bond formation with the —OH groups of the starch molecules.

The preparation of organometallic compounds, sometimes classified as complexes, is treated elsewhere (p. 397).

### Methods of investigating the structure of a complex

The principles of some of the methods used for investigating structure are outlined briefly below. The list of methods is not complete, but it includes those of most general application.

#### (i) Stoichiometry of reaction

The formulae of the ions in an ionic complex may be determined by means of precipitation reactions. Thus from the complex  $[\text{CoCl}_2\text{en}_2] \text{Cl} \cdot \text{H}_2\text{O}$  only one-third of the chlorine is precipitated by  $\text{AgNO}_3$  solution, but from its isomer  $[\text{CoCl}(\text{H}_2\text{O})\text{en}_2]\text{Cl}_2$  two-thirds of the chlorine is so precipitated. Whence the distribution of the chlorine anions follows.

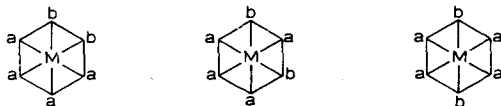
#### (ii) Molar conductance

Ions with unit charge have ionic conductances at infinite dilution of  $65 \pm 15 \text{ ohm}^{-1}$  with very few exceptions ( $\text{H}^+_{\text{aq}}$  and  $\text{OH}^-_{\text{aq}}$  are the main ones); doubly charged ions have conductances of about  $130 \text{ ohm}^{-1}$  and triply charged ones,  $195 \text{ ohm}^{-1}$ . Thus ionic salts of the types  $\text{MX}$ ,  $\text{MX}_2$  and  $\text{MX}_3$  ( $\text{X} = \text{uninegative ion}$ ) have molar conductances of about 130, 260 and  $390 \text{ ohm}^{-1}$  respectively. Whence a complex empirically  $\text{PtCl}_4(\text{NH}_3)_5$ , which has a molar conductance of  $404 \text{ ohm}^{-1}$  is probably  $[\text{PtCl}(\text{NH}_3)_5]\text{Cl}_3$ .

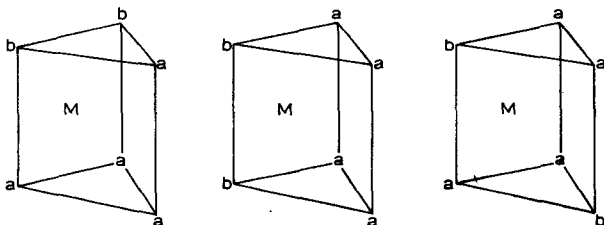
#### (iii) Abundance of the isomeric forms

The classical experiments of Werner on the cobaltammines, in which he used methods (i) and (ii) above, convinced him that these compounds of  $\text{Co}^{\text{III}}$  always had six groups in a co-ordination shell around the cobalt. He deduced the geometrical arrangement of the six groups from the number of isomers of a particular formula type he was able to make. Thus for compounds containing ions of the type  $[\text{Coa}_4\text{b}_2]^{n+}$  he was often able to make two isomers but never three. A planar hexagonal arrangement would

permit three isomers:



and so would a triangular prismatic one:



The only other symmetrical arrangement, the octahedral one, permits of only two:



The octahedral arrangement of the co-ordinated ligands in  $\text{Co}^{\text{III}}$  complexes thus deduced was supported by the fact that a complex ion like  $[\text{CoCl}_2\text{en}_2]^+$  had one *trans*-isomer and two enantiomeric *cis*-isomers (p. 578). No other arrangement around the cobalt could explain the number and character of these isomeric ions.

Similarly for  $\text{PtCl}_2(\text{NH}_3)_2$ , the fact that it exists in two forms (below) rules out the possibility of a tetrahedral arrangement of the four groups around the platinum.

(iv) *Dipole moment*

Measurement of dipole moment (p. 142) is often of value in deciding between two forms. Of the two forms of dichlorodiammineplatinum(II) the *cis*-form has a dipole moment but the *trans*-form has not:



Incidentally, the fact that the *trans*-form has zero moment indicates that the four ligands are arranged in a square planar configuration. A square pyramidal arrangement, for example, would be expected to have a moment, because Pt—Cl and Pt—NH<sub>3</sub> have different polarities, as is shown by the existence of a moment in the *cis*-form of the compound.

(v) *Optical rotatory dispersion*

Many complex ions are capable of being resolved into optical enantiomers. The effect of a particular enantiomer on the plane of polarisation of light depends not only on the arrangement of its atoms, but also on the wavelength of the light. The same isomer may rotate the plane to the right at one frequency and to the left at another. A rotatory dispersion curve is shown in Fig. 319.

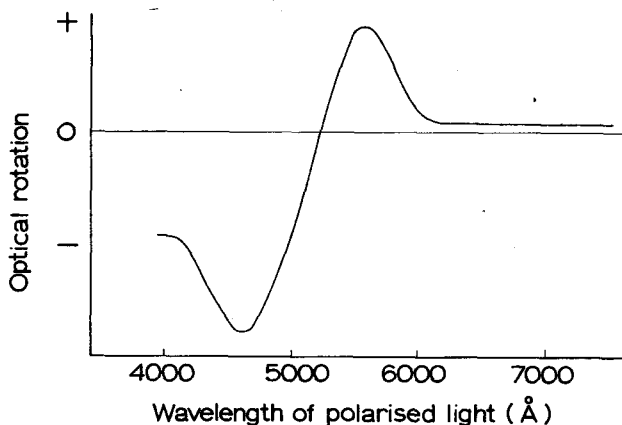


Fig. 319. Rotatory dispersion curve for (+)Coen<sub>3</sub><sup>3+</sup> ion.

Rotatory dispersion curves have been described for a large number of cobalt(III) and chromium(III) complexes, and the absolute configurations of some of the complexes have been assigned from the relation of their curves to the curve for the (+) Coen<sub>3</sub><sup>3+</sup> ion, for which the absolute configuration had been determined by means of X-ray diffraction.

(vi) *Infrared spectra*

Information about metal-ligand bonds can often be obtained from infrared absorption spectra. Comparison of the spectra of the urea complexes of Pt<sup>II</sup>, Pd<sup>II</sup>, Cr<sup>III</sup>, Fe<sup>III</sup>, Cu<sup>II</sup> and Zn<sup>II</sup> shows that in the first two the urea ligands are co-ordinated through the nitrogen atoms and in the other four

through the oxygen atoms. When co-ordination is through the oxygen the infrared absorption spectrum is similar to that of urea itself, although the C—O stretching frequency is a little lower in the complexes. But when co-ordination is through the nitrogen, the N—H stretching and deformation frequencies are reduced and the C—O stretching frequency increased; the spectra of the M—N complexes are quite different from the urea spectrum.

The infrared spectra of the two forms of  $[\text{CoNO}_2(\text{NH}_3)_5]^{2+}$  show that the stable, brown form is a nitro complex and the unstable red form a nitrito complex,  $[\text{Co}\cdot\text{ONO}\cdot(\text{NH}_3)_5]^{2+}$ . The symmetric and antisymmetric stretching frequencies of the  $\text{Co}-\text{N}\begin{matrix} \diagup \text{O} \\ \diagdown \text{O} \end{matrix}$  group are 1315 and 1430  $\text{cm}^{-1}$ ; those of the  $\text{Co}-\text{O}-\text{N}-\text{O}$  group are 1065 and 1460  $\text{cm}^{-1}$ .

(vii) *Visible absorption spectra*

With the increasing application of ligand-field and molecular-orbital theories to the interpretation of visible spectra, the measurement of the frequency of absorption peaks and their extinction coefficients has become an extremely valuable method of gaining information about structure. A series of compounds of a metal in a particular oxidation state have spectra of similar general form.

For octahedral complexes of nickel(II) there are absorption peaks at about 10,500, 13,000, 18,000, and 28,000  $\text{cm}^{-1}$ ; the extinction coefficients are usually less than 10. Examples are:

Complex	Absorption peak ( $\text{cm}^{-1}$ )	E	Complex	Absorption peak ( $\text{cm}^{-1}$ )	E
$\text{Ni}(\text{NH}_3)_6^{2+}$	10,750	4.0	$\text{Ni}(\text{en})_3^{2+}$	11,200	7.3
	13,500	5.0		12,400	5
	17,500	4.8		18,350	6.7
	28,200	6.3		29,000	8.6

The square complexes of nickel(II), such as bis(dimethylglyoxime)-nickel(II) have at most three bands, the one of lowest energy is at 15,000–18,000  $\text{cm}^{-1}$ ; the second and third bands are not often observable because of the high absorption of the ligands in the ultraviolet. The extinction coefficients of the bands are relatively high, usually in the range 100–300.

The tetrahedral  $\text{Ni}^{\text{II}}$  complex  $\text{NiCl}_4^{2-}$ , present in a mixture of  $\text{NiCl}_2$  and  $\text{LiCl}$  which has been melted, absorbs at 15,250 and 14,200  $\text{cm}^{-1}$ , with both extinction coefficients about 160. The spectra of octahedral, square, and tetrahedral nickel(II) are thus sufficiently different from one another to enable the three possible structures to be distinguished; minor variations

between spectra of the same type which arise from differences in ligand field strengths are not large enough to mask the major characteristics.

(viii) *Magnetic measurements*

The measurement of magnetic moments (p. 85) indicates the number of unpaired d electrons in a transition-metal complex, but this information is not always a reliable guide to the stereochemistry, as was once believed. The paramagnetic bis(acetylacetonato)nickel(II),  $\text{Ni}(\text{acac})_2$ , was formerly assumed to be 4-co-ordinate and tetrahedral. It was argued that a square planar arrangement of four ligands, with  $\text{dsp}^2$  hybrid orbitals, would be a diamagnetic, spin-paired complex in which the eight electrons of  $\text{Ni}^{\text{II}}$  were accommodated in the four d orbitals not occupied by ligand electrons. Thus the square structure was ruled out. The tetrahedral structure, however, would be expected to be paramagnetic, since if  $\text{sp}^3$  hybrid orbitals were used for bonding there would be two unpaired electrons in the d orbitals. When the structure was determined by X-ray analysis  $\text{Ni}(\text{acac})_2$  was found to have a trimeric structure in which the nickel was 6-co-ordinated (Fig. 320).

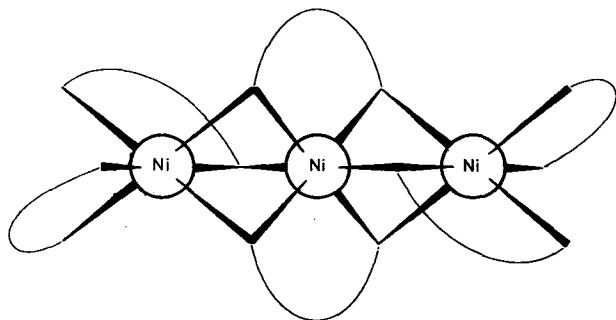


Fig. 320. Structure of  $\text{Ni}_3(\text{acac})_6$ , the bis(acetylacetonato)nickel(II) trimer.

This example has been mentioned to draw attention to the fact that there is no unequivocal magnetic criterion of stereochemistry based on the number of unpaired electrons, as was thought in the early days of the valence-bond theory.

However, information about the stereochemical arrangement of ligands can be derived from a consideration of deviations from spin-only values for the magnetic moments (p. 87). In octahedral complexes the orbital contributions to the moments are quenched in low-spin  $d^6$  and  $d^7$  complexes and in high-spin  $d^3$ ,  $d^4$ ,  $d^5$ ,  $d^8$  and  $d^{10}$  complexes, but the other configurations retain some orbital contribution to the moment. In tetrahedral complexes



orbital contribution to the moment is absent for  $d^1$ ,  $d^2$ ,  $d^6$  and  $d^7$  and may be present for  $d^3$ ,  $d^4$ ,  $d^8$  and  $d^9$ . For other arrangements with lower symmetry, orbital contribution is possible for fewer configurations:

Square pyramidal and square planar  $d^2$  and  $d^4$   
 Trigonal bipyramidal  $d^1$ ,  $d^3$ ,  $d^4$  and  $d^5$ .

Examples of the use of the deviation from spin-only values for diagnosing stereochemical arrangement are provided by tetrahedral  $Ni^{II}$  complexes which have higher moments than octahedral  $Ni^{II}$  complexes, as expected for a  $d^8$  arrangement; and by  $Co^{II}(d^7)$  tetrahedral complexes which have moments closer to the spin-only value than do their octahedral counterparts.

(ix) Nuclear magnetic resonance spectra

For certain complexes n.m.r. spectrometry is useful in the diagnosis of structure. The compounds  $RuXH[C_2H_4(PEt_2)_2]_2$ , where X is Cl, Br, I, SCN,  $NO_2$  or CN, are found to have five sharp, equally spaced bands with intensities in the approximate ratios 1:4:6:4:1 in the absorption region associated with the unique hydrogen atom. The hydrogen atom ( $I = \frac{1}{2}$ ) is evidently coupled to four other atoms for which  $I = \frac{1}{2}$ , all in the same position relative to itself, confirming the structure shown in Fig. 321.

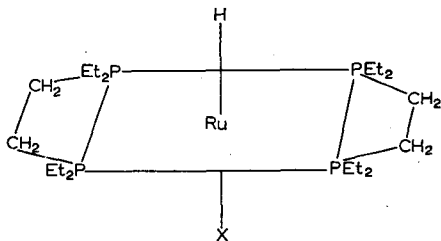


Fig. 321. Structure of  $RuXH[C_2H_4(PEt_2)_2]_2$ .

(x) X-ray analysis

This is also referred to as the absolute method, because it is the only one capable of supplying unequivocal evidence of structure. Its disadvantage is that it is much more laborious than magnetic and spectroscopic determinations. However, as more X-ray determinations of the structures of complexes are made, more examples of incorrect predictions from magnetic and spectroscopic data are disclosed.

For bis(trimethylphosphine oxide)cobalt(II) nitrate, X-ray analysis showed that the cobalt is 6-co-ordinate, with a very irregular arrangement of ligand atoms; there is a bidentate nitrate ion in the co-ordination sphere

and the whole is a molecule with no strict symmetry elements whatever. None of the previous indirect evidence suggested such an anomalous structure. For the given paramagnetic bis(benzylidiphenylphosphine)nickel(II) bromide, X-ray analysis reveals that the triclinic unit cell contains three molecules, two tetrahedral and one square planar, a stereochemical complication which could not have been disclosed by spectroscopic or magnetic evidence.

### Isomerism in complex compounds

Various types of isomerism occur in complex compounds.

#### 1. Ionisation isomerism

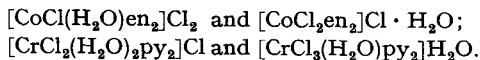
This kind of isomerism occurs when there is an interchange of groups between the co-ordination sphere of the nuclear atom and ions outside this sphere. Sulphatopenta-amminecobalt(III) bromide,  $[\text{Co}(\text{SO}_4)(\text{NH}_3)_5]\text{Br}$ , and bromopenta-amminecobalt(III) sulphate,  $[\text{CoBr}(\text{NH}_3)_5]\text{SO}_4$ , are such a pair of isomers. The former is red and in aqueous solution gives a precipitate of  $\text{AgBr}$  with  $\text{AgNO}_3$  but no precipitate with barium chloride; the latter is violet and gives an immediate precipitate with  $\text{BaCl}_2$ . It should be noticed that in these compounds an  $\text{SO}_4$  group occupies only one co-ordination position though it neutralises two ionic charges on the  $\text{Co}^{3+}$ ; thus the number of co-ordinate links formed by a ligand ion is not necessarily the same as the number of charges it carries.

An even more obvious example of ionisation isomerism is afforded by  $[\text{PtCl}_2(\text{NH}_3)_4]\text{Br}_2$  and  $[\text{PtBr}_2(\text{NH}_3)_4]\text{Cl}_2$ .

#### 2. Hydration isomerism

There are three isomers of  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ . The violet-grey form is shown, by its conductance and the fact that all the chlorine is precipitated immediately with  $\text{AgNO}_3$ , to be the hexa-aquochromium(III) chloride,  $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ . The dark green substance obtained from hot solutions is the dichlorotetra-aquo-salt,  $[\text{CrCl}_2(\text{H}_2\text{O})_4]\text{Cl} \cdot 2\text{H}_2\text{O}$ , from which  $\text{AgNO}_3$  removes only one third of the chlorine. The third compound, the chloropenta-aquochromium(III) dichloride hydrate,  $[\text{CrCl}(\text{H}_2\text{O})_5]\text{Cl}_2 \cdot \text{H}_2\text{O}$ , also green, yields two-thirds of its chlorine by precipitation with  $\text{AgNO}_3$ .

Other examples of hydration isomerism are found in the compounds:



The exact nature of the bonds holding water molecules in the co-ordination sphere and outside it is not always known. In some hydrates those out-

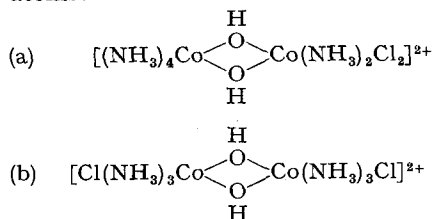
side the co-ordination sphere are held in the interstices of the crystal lattice, in others they are attached to the simple ions.

### 3. Co-ordination isomerism

This isomerism occurs when both cation and anion are complex. Typical examples are (a)  $[\text{Co}(\text{NH}_3)_6] [\text{Cr}(\text{CN})_6]$  and  $[\text{Cr}(\text{NH}_3)_6] [\text{Co}(\text{CN})_6]$ ; and (b)  $[\text{Pt}(\text{NH}_3)_4] [\text{PtCl}_4]$  and  $[\text{PtCl}(\text{NH}_3)_3] [\text{PtCl}_3(\text{NH}_3)]$ .

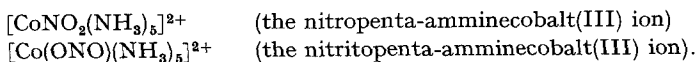
Co-ordination isomerism also occurs where a nuclear element is present in two states of different charge, as platinum is in  $[\text{Pt}(\text{NH}_3)_4] [\text{PtCl}_6]$  and  $[\text{PtCl}_2(\text{NH}_3)_4] [\text{PtCl}_4]$ .

A special type of co-ordination isomerism is co-ordination position isomerism. It can occur in bridged complexes such as the ions (a) and (b) below, in which ammonia and chloro ligands are differently placed relative to the two cobalt atoms:

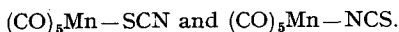


### 4. Linkage isomerism

The  $\text{NO}_2$  group may be co-ordinated to a metal atom either through the nitrogen atom to act as a nitro ligand ( $-\text{NO}_2$ ) or through one of the oxygens to act as a nitrito ligand ( $-\text{ONO}$ ). Examples are known of isomerism arising from this difference in linkage, for instance:

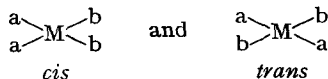


Other groups are capable of co-ordinating through different member atoms; for example the  $\text{CNS}^-$  ion can co-ordinate either through nitrogen or through sulphur. Linkage isomers of this type have been prepared recently:

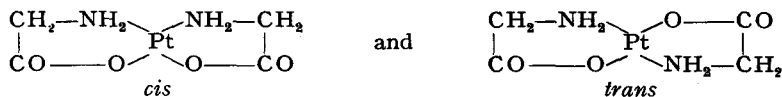


### 5. Geometrical isomerism

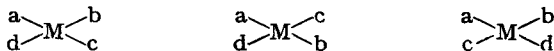
In the planar complexes of metals showing the co-ordination number four there is a possibility of *cis*- and *trans*-isomerism:



Examples are  $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$  and  $\text{Pd}(\text{NH}_3)_2(\text{NO}_2)_2$ ; both have *cis*- and *trans*-isomers. The type of isomerism also arises in planar chelate compounds containing unsymmetrical bidentate ligands. But it is not necessary for the two co-ordinating atoms of the bidentate ligand to be different; it is only necessary that the chelate ring have dissimilar halves:

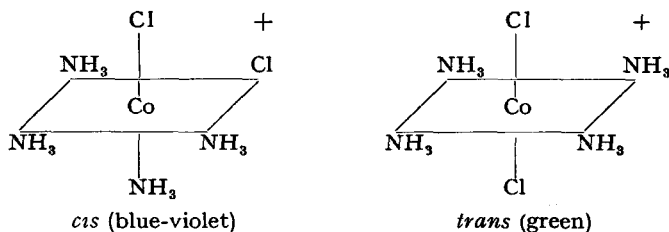


Geometrical isomerism cannot occur in the  $\text{Ma}_3\text{b}$  type of square complex, but the  $\text{Mabcd}$  type gives rise to three isomers:

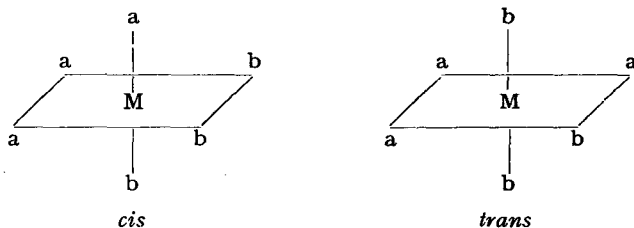


The first complex of this type to be obtained in three isomeric forms was  $[\text{PtNO}_2\text{pyNH}_3(\text{NH}_2\text{OH})]^+$ .

With 6-co-ordinate octahedral complexes, geometrical isomerism is also possible. *Cis*- and *trans*-isomerism is found in an ion such as  $[\text{CoCl}_2(\text{NH}_3)_4]^+$

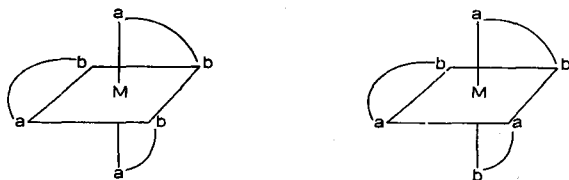


Complexes of the type  $\text{Ma}_3\text{b}_3$  exist in only two isomeric forms:



An example is trichlorotripyridinerhodium(III).

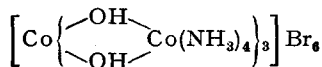
Unsymmetrical bidentate ligands can give rise to *cis*- and *trans*-isomers in a similar way:



The letters a and b represent different ends of an unsymmetrical bidentate ligand, not necessarily different co-ordinating atoms. An example is triglycinecobalt(III). In such an instance, both the *cis* and *trans*-form have each a pair of optical isomers.

### 6. Optical isomerism

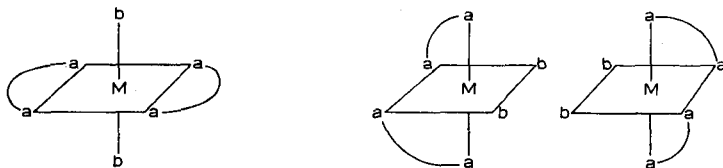
Werner showed (1908) that the element carbon is not a necessary constituent of an optical isomer when he resolved the compound



This kind of isomerism occurs when a compound can be represented by two asymmetrical structures, one of which is the mirror image of the other.

Resolution into optical enantiomers is usually achieved by similar methods to those of organic chemistry. Diastereoisomers of different solubility are made by forming a salt from a racemic mixture of active cations with an active anion such as, for example, d-bromocamphorsulphonate.

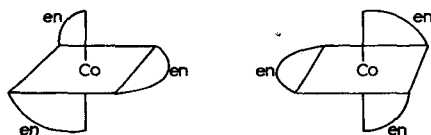
Six-co-ordinate complexes containing bidentate ligands afford many examples of optical isomerism. A particularly common type is  $M(aa)_2b_2$  ( $aa$  = bidentate ligand) for which the *cis*- but not the *trans*-form can be resolved into optical isomers.



*Trans*-form (symmetrical), not resolvable. Two *cis*-forms (unsymmetrical), resolvable.

An example is the dichloro-bis(ethylenediamine)cobalt(III) cation,  $[\text{CoCl}_2\text{en}_2]^+$ .

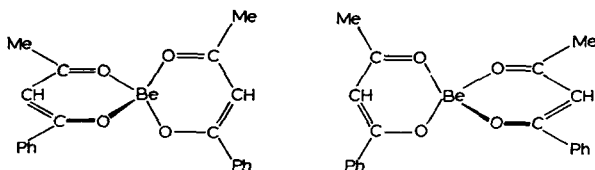
Octahedral complexes with three bidentate ligands also show optical isomerism. An example is the tris(ethylenediamine)cobalt(III) cation.



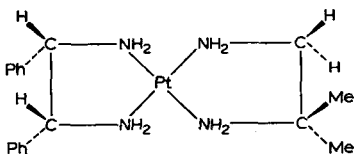
Multidentate ligands can also give rise to optical isomerism in octahedral complexes. A  $(\text{Co edta})^-$  complex ion has been resolved.

Optical isomerism should be possible in octahedral complexes  $\text{Mabcdef}$  which contain only unidentate ligands. Such a complex of  $\text{Pt}^{\text{IV}}$  has been made— $\text{PtBrClINO}_2\text{pyNH}_3$ . It should have fifteen geometrical isomers, each with a pair of optical enantiomers; a few of the different geometrical isomers of this compound have been made but none has been resolved.

By analogy with carbon, optically active tetrahedral complexes  $\text{Mabcd}$  are to be expected, but none has yet been prepared. However, tetrahedral complexes of  $\text{Be}^{\text{II}}$ ,  $\text{B}^{\text{III}}$  and  $\text{Zn}^{\text{II}}$  with unsymmetrical bidentate ligands have been made and resolved. An example is bis(benzoylacetato)beryllium(II).



Optical isomerism in square complexes is at present limited to a few examples. One of these is the compound



which can be seen to be without either a plane or an axis of symmetry.

## NOMENCLATURE OF COMPLEX COMPOUNDS

The formulae and names adopted for complex ions and compounds follow the main recommendations in *Nomenclature of Inorganic Chemistry*, 1959, issued by the International Union of Pure and Applied Chemistry; and in

*Handbook for Chemical Society Authors*, 1960 which has much other useful information. Those referring to mononuclear complexes have been summarised.

### Formulae

- (i) Place the symbol for the nuclear atom first, follow with the symbols for the ligands, and enclose the complex in square brackets.
- (ii) Indicate the charge number of the nuclear atom, when required, by Stock notation: Ni<sup>0</sup>, Cu<sup>I</sup>, Fe<sup>II</sup>.
- (iii) Place the ligands in the order (a) anionic, (b) neutral and cationic. Arrange the ligands within these classes in the sequences:
  - (a) (1) H<sup>-</sup>, O<sup>2-</sup>, OH<sup>-</sup>, I<sup>-</sup>, Br<sup>-</sup>, Cl<sup>-</sup>, F<sup>-</sup>;  
(2) other inorganic anions containing two or more elements, that with the smaller number of atoms first, and, when the number is the same, that with the central atom of larger atomic number first;  
(3) organic anions in alphabetical order.
  - (b) (1) H<sub>2</sub>O, NH<sub>3</sub>;  
(2) other inorganic ligands in this order of their central atoms: B, Si, C, Sb, As, P, N, Te, Se, S, I, Br, Cl;  
(3) organic ligands in alphabetical order.

### Names

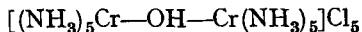
- (i) Cite names of ligands first, the name of the nuclear atom last.
- (ii) Names of complex cations and neutral molecules have no distinguishing termination; names of complex anions end in -ate.
- (iii) Cite ligands in their order in the formula. Names of the anionic ligands end in -o; those of the neutral, except aquo for H<sub>2</sub>O and ammine for NH<sub>3</sub>, and of the cationic are the same as for the molecule or cation.
- (iv) The anionic groups CN, O·NO, NO<sub>2</sub>, NO<sub>3</sub>, are named cyano, nitrito, nitro and nitrate. Anions derived from hydrocarbons are given the name of the radical, sometimes with an -o ending.
- (v) The groups NO, NS, CO, CS are termed nitrosyl, thionitrosyl, carbonyl and thiocarbonyl, and are treated as neutral in computing the oxidation number of the nuclear atom.
- (vi) The prefixes mono, di, tri, tetra, penta, hexa, hepta, octa, ennea, deca, hendeca and dodeca are used (without hyphen, except when two vowels are brought together as in the first example below) to indicate the numbers of the individual ligands in a complex. When, however, the name includes a numerical prefix with a different significance, then bis, tris and tetrakis are used, the group to which they refer being often placed in parentheses:

$[\text{Ni}(\text{CO})_2(\text{Ph}_3\text{P})_2]$  dicarbonyl-bis(triphenylphosphine)nickel;

and sometimes in cases like these:

$[\text{Fe}(\text{C}_5\text{H}_5)_2]\text{Cl}$  bis(cyclopentadienyl)iron (III) chloride, and  
 $\text{Ca}(\text{PCl}_6)_2$  calcium bis(hexachlorophosphate).

Details about formulae and names of polynuclear complexes can be found in *Nomenclature of Inorganic Chemistry* or the *Handbook for Chemical Society Authors*. It need only be mentioned here that a bridging group is indicated in the formula by separating it from the rest of the complex by hyphens, and in the name by prefixing it with  $\mu$ :-



$\mu$ -hydroxo-bis{penta-amminechromium(III)} chloride.

#### Examples of formulae and names

$[\text{Co}(\text{NH}_3)_6]^{3+}$  the hexa-amminecobalt(III) ion.

$[\text{Co}(\text{O}\cdot\text{NO})_3]^{3-}$  the hexanitritocobaltate(III) ion.

$[\text{Fe}(\text{CN})_6]^{4-}$  the hexacyanoferrate(II) ion.

$\text{K}_3[\text{Fe}(\text{CN})_6]$  potassium hexacyanoferrate(III).

$\text{CoCl}_2(\text{NH}_3)_4\text{Cl}$  dichlorotetra-amminecobalt(III) chloride.

$\text{K}[\text{Co}(\text{CN})(\text{CO})_2\text{NO}]$  potassium cyanodicarbonylnitrosylcobaltate (0).

$[\text{Co}(\text{NH}_3)_2(\text{en})_2]\text{Cl}_3$  diammine-bis(ethylenediamine)cobalt(III) chloride.

$[\text{Co}(\text{NO}_2)_3(\text{NH}_3)_3]$  trinitrotriamminecobalt(III).

$[\text{Pt}(\text{NH}_3)_6]\text{Cl}_4$  hexa-ammineplatinum(IV) chloride.

$[\text{CrCl}(\text{H}_2\text{O})(\text{en})_2]^{2+}$  the chloroaquo-bis(ethylenediamine)chromium(III) ion.

$\left[ \begin{array}{c} \text{NH}_3 \\ \diagdown \quad \diagup \\ (\text{NH}_3)_4\text{Co} \quad \text{Co}(\text{NH}_3)_4 \\ \diagup \quad \diagdown \\ \text{OH} \end{array} \right]^{4+}$  the octa-ammine  $\mu$ -amido  $\mu$ -hydroxo-dicobalt(III) ion.

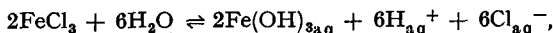
$\left[ \begin{array}{c} \text{OH} \\ \diagdown \quad \diagup \\ \text{CH}_3\text{C} = \text{N} \\ | \quad \diagdown \\ \text{CH}_3\text{C} = \text{N} \\ \diagup \quad \diagdown \\ \text{OH} \end{array} \right] \text{CoCl}_2$  dichlorodimethylglyoxime-N,N'cobalt(II).



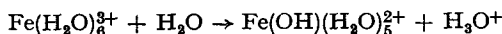
## COMPLEXES IN AQUEOUS SOLUTION

## Aquo-complexes

Dissolving a salt in water rarely gives unhydrated ions; the perchlorate ion,  $\text{ClO}_4^-$ , is a possible exception. The first step in the process of solution is probably hydration of the ions; it will be assumed in discussion that the number of water molecules in the solvated shell corresponds with the co-ordination number of the ion, although this is not always true. Relatively few salts give neutral solutions, and when  $\text{FeCl}_3$  or  $\text{CuSO}_4$  dissolve they must do more than yield  $\text{Fe}(\text{H}_2\text{O})_6^{3+} + 3\text{Cl}_{\text{aq}}^-$  or  $\text{Cu}(\text{H}_2\text{O})_2^{2+} + \text{SO}_4^{2-}{}_{\text{aq}}$ , for their solutions are acid. The naive explanation of the acidity of a  $\text{FeCl}_3$  solution as the simple hydrolysis indicated by the equation:



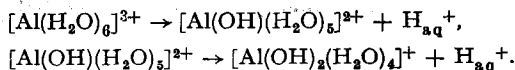
implies the solubility of the hydroxide, since the solution is clear and non-colloidal; furthermore, the analytical data do not comply with the law of mass action. The idea of the hydrated cation behaving as an acid is more probable:



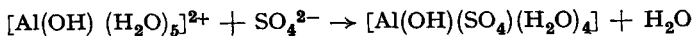
The loss of protons in this way will be the easier the greater the positive field about the cation. Elements of Period 3 exemplify this: the electrostatic field about  $\text{Na}^+$  being slight, it is only weakly hydrated; but the progressive increase in field about the following elements leads, successively, to the formation of  $\text{Mg}(\text{H}_2\text{O})_6^{2+}$ ,  $\text{Al}(\text{H}_2\text{O})_6^{3+}$ ,  $\text{Si}(\text{OH})_4$ ,  $\text{PO}(\text{OH})_3$ ,  $\text{SO}_3(\text{OH})^-$ ,  $\text{ClO}_4^-$  in acid solution, and of  $\text{Mg}(\text{OH})(\text{H}_2\text{O})_5^+$ ,  $\text{Al}(\text{OH})_4(\text{H}_2\text{O})_2^-$ ,  $\text{SiO}_2(\text{OH})_2^{2-}$ ,  $\text{PO}_4^{3-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{ClO}_4^-$  in alkaline solution.

These are mononuclear complexes, but the cation  $\text{Cr}_2(\text{OH})_2^{4+}$  exists in solution, and polynuclear complexes have proved to be frequent products of hydrolysis. Indeed, mercury(II) is one of the few metals which always gives mononuclear species:  $\text{Hg}(\text{H}_2\text{O})_2^{2+}$ ,  $\text{Hg}(\text{OH})(\text{H}_2\text{O})^+$ ,  $\text{Hg}(\text{OH})_2$ . Beryllium produces mainly  $\text{Be}_3(\text{OH})_3^{3+}$  which is presumed to have a cyclic structure. Iron(III) appears as the ions  $\text{Fe}(\text{OH})_2^+$  and  $\text{Fe}_2(\text{OH})_2^{4+}$ , the first being paramagnetic and the second diamagnetic.

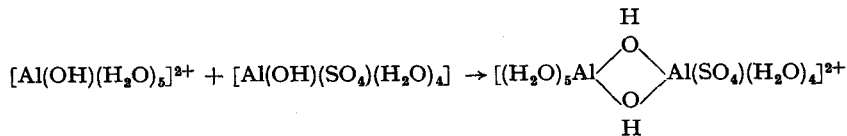
It is instructive to follow the behaviour of potassium alum which dissolves to give the ions  $\text{K}_{\text{aq}}^+$ ,  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$  and  $\text{SO}_4^{2-}{}_{\text{aq}}$ . The hexa-aquoaluminium ion is immediately soluble but tends in time, especially when the temperature is raised, to hydroxylate in stages by proton loss:



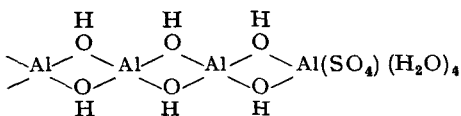
A water molecule in these aquo-complexes can be replaced by  $\text{SO}_4^{2-}$ :



The passage from solution to sol probably occurs by hydroxo-bridging



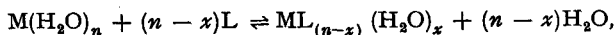
This and similar kinds of bridging produce polymers of indefinite size which eventually separate as precipitates:



The change from soluble complexes, through sols, to precipitates is accelerated when the pH is raised. It is characteristic of the precipitate that repeated washing with water fails to remove all the  $\text{SO}_4^{2-}$  anions; this is because they occupy a place in the co-ordination sphere of the  $\text{Al}^{3+}$  cation and are not merely adsorbed on the surface of the particles.

### Stability constants

Complex formation by replacement of molecules in the solvated shell of a metal cation in aqueous solution with, for example, unidentate ligands,



usually produces an equilibrium of two or more complexes. The reaction proceeds stepwise with an equilibrium constant for every step:

$$k_1 = \frac{[\text{M}(\text{H}_2\text{O})_{n-1}\text{L}]}{[\text{M}(\text{H}_2\text{O})_n] \times [\text{L}]}; \quad k_2 = \frac{[\text{M}(\text{H}_2\text{O})_{n-2}\text{L}_2]}{[\text{M}(\text{H}_2\text{O})_{n-1}\text{L}] \times [\text{L}]}; \quad k_n = \frac{[\text{ML}_n]}{[\text{M}(\text{H}_2\text{O})\text{L}_{n-1}] \times [\text{L}]}$$

The constants  $k_1, k_2 \dots k_n$  are the *consecutive stability constants*; since a ligand already co-ordinated repels an incoming ligand of the same type, their values nearly always decrease in the order  $k_1 > k_2 > \dots > k_n$ . Examples are

Cation	Ligand	$\log k_1$	$\log k_2$	$\log k_3$	$\log k_4$
$\text{Cu}^{2+}$	$\text{NH}_3$	4.3	3.6	3.0	2.3
$\text{Cd}^{2+}$	$\text{NH}_3$	2.6	2.1	1.4	0.9

The product of the consecutive stability constants is the *cumulative stability constant*,  $\beta$ :

$$k_1 \times k_2 \times k_3 \times \dots k_n = \frac{[ML_n]}{[M(H_2O)_n] \times [L]^n} = \beta$$

The symbol  $p\beta$ , that is  $\log \beta$ , is usually used as a measure of the stability of the ultimate complex. For  $Cu(NH_3)_4^{2+}$ ,  $p\beta$  is  $4.3 + 3.6 + 3.0 + 2.3 = 13.2$ ; and for  $Cd(NH_3)_4^{2+}$ ,  $p\beta$  is 7.0. A complex is regarded as stable when  $p\beta$  exceeds 8.

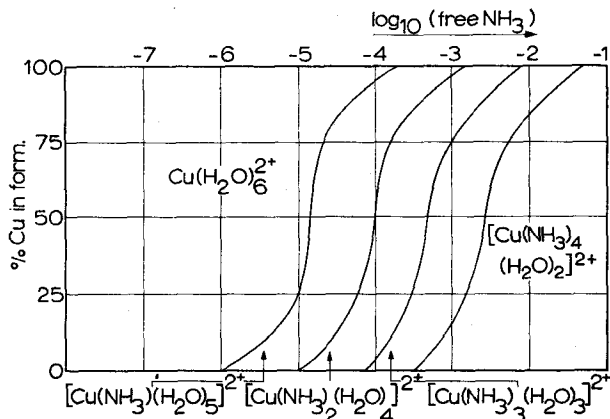


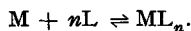
Fig. 322. Percentage of various copper(II) aquo-ammine complexes at different concentrations of free ammonia.

Fig. 322 is a plot of the percentage of the various aquo-ammine complexes of copper(II) present in an aqueous solution containing different concentrations of free ammonia. For example, when the concentration of free ammonia is  $10^{-4}$  mole  $l^{-1}$  the solution contains about 5% of the triammine, 45% of the diammine, 40% of the mono-ammine and 10% of aquated copper ions.

Stability constants are calculated from the concentrations of the species present in equilibrium mixtures containing the metal ion and the ligand in a wide range of proportions. Activity coefficients are kept constant by appropriate additions of a salt, usually sodium perchlorate, whose ions do not compete with those of the cation and ligand. Concentrations at different ionic strengths are extrapolated to zero ionic strength. It may be necessary to find the number of water molecules displaced at each step; the total of these is not necessarily the same as the co-ordination number of the

cation in the solid compound. Particularly in a polar solvent such as water, the ligands may not displace all the solvent molecules.

Ignoring hydration and charge, the equilibrium of a complex with its cation and ligands is expressed by:



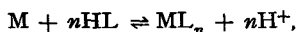
The total concentration of the metal, in the solvated cations and the complex,  $[M]_t$ , and the total concentration of the ligand, free and in the complex,  $[L]_t$ , can be found by analysis. The method of determining the concentration of the complex,  $[ML_n]$ , depends upon the system. When either the free ligand or the complex is coloured, or has a convenient absorption elsewhere in the spectrum, optical densities, *i.e.*  $\log$  (intensity of transmitted light/intensity of incident light), at a specific wave length are measured. Sometimes the concentrations of the uncomplexed metal ions are obtained potentiometrically with a suitable electrode. Polarography and extraction methods are also used, and occasionally the required information may be deduced from pH measurements.

To determine the stoichiometry of the reaction, Job's method of continuous variation is used:  $[ML_n]$  is plotted against  $[M]_t/\{[M]_t + [L]_t\}$  and a maximum in the curve indicates complex formation. Its composition corresponds to the position of the maximum.

With a complex of rather low stability, formation is not complete when M and L are in the proportion indicated by the plot and, as a result, the values of  $\beta$  drift as the ratio of metal to complexing agent is altered. But something very near the true value can be obtained by successive approximations.

Distribution methods for determining  $[M]$  depend on knowing the distribution coefficient for the metal ion or the ligand between two immiscible solvents. Thus free ammonia in equilibrium with the ammine complex of a metal can be determined from the ammonia concentration of a chloroform layer in equilibrium with the aqueous solution.

When the ligand is protonated, the equilibrium,



may be set up, then:

$$\beta = \frac{[ML_n] \times [H^+]^n}{[M] \times [HL]^n}.$$

Concentrations at equilibrium can be obtained from pH measurements. The method is applicable only when L is the anion of a weak acid; obviously it cannot be applied to the co-ordination of chloride and similar ions, for which the conjugate acid of the ligand is completely ionised before complex formation occurs.

### Factors affecting the stability of complexes

What follows applies to solid complexes and is even more significant for complexes in aqueous solution because these have to resist disruption by water.

#### 1. Electrostatic field round the cation

Of the complexes formed by an individual ligand with a metal anion in two different oxidation states, those in which the anion has the higher charge number are nearly always the more stable, for instance with hexacyanoferrate(II),  $\text{Fe}(\text{CN})_6^{4-}$ ,  $p\beta$  is 8.3, but with hexacyanoferrate(III),  $\text{Fe}(\text{CN})_6^{3-}$ ,  $p\beta$  is 31.0. This is understandable if the ligands are held by the electrostatic charge on the central ion; the smaller, more highly charged, iron(III) ion will exert a stronger attraction than the larger, lower charged, iron(II) ion.

When measured, the order of stability of complexes of these bivalent metal ions in Period 4 proved to be related, irrespective of the ligand, to the ionic radius:

Order of stability	$\text{Mn}^{2+}$	<	$\text{Fe}^{2+}$	<	$\text{Co}^{2+}$	<	$\text{Ni}^{2+}$	<	$\text{Cu}^{2+}$	<	$\text{Zn}^{2+}$
Ionic radius $\text{M}^{2+}(\text{\AA})$	0.91		0.83		0.82		0.78		0.69		0.74

#### 2. Distribution of charge

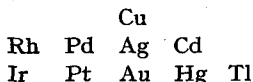
If complex formation be imagined to involve the donation of electron pairs from ligand to cation, and if the bonds were perfectly homopolar, then one unit of charge would be transferred for every bond formed. In these circumstances, a bivalent cation would accumulate a negative charge of four in becoming 6-co-ordinate, and the result would be a very unstable condition unlikely to persist. The stability of a complex increases as the Pauling 'postulate of neutrality' condition (p. 558) is approached, that is when each atom has a net charge between  $-\frac{1}{2}$  and  $+\frac{1}{2}$ . Consequently ions such as  $\text{Mg}^{2+}$ , for which  $E^\circ$ ,  $\text{M}^{n+}/\text{M}$  has a large negative value, attract electrons weakly and therefore form their strongest complexes with co-ordinating atoms of high electronegativity, for instance oxygen. At the other extreme, the noble metal ions with positive redox potentials accept electrons more readily, and form their strongest co-ordinate bonds with donor atoms such as sulphur and iodine which are easily polarised.

Acceptor metal ions are classified into two types:

Class(a) are acceptors which form their most stable complexes with the co-ordinating atoms N, O and F of the second period.

Class(b) are acceptors which form their most stable complexes with the co-ordinating atoms P, S, Cl, As, Br, I of later periods.

The class(b) acceptors lie in a roughly triangular area in the middle of the lower part of the Periodic Table:



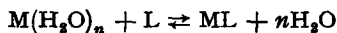
Neighbouring elements to right and left of this area have some class (b) character; the other metals, and those non-metals which fill the position of central atoms in complexes, are class (a) acceptors.

The class (b) acceptors are metals with positive redox potentials which accept electrons readily; they also have large complements of d electrons available for dative  $\pi$ -bonding. Their most stable complexes are formed with ligands like  $\text{PMe}_3$ ,  $\text{S}^{2-}$  and  $\text{I}^-$  which have vacant d orbitals, or like  $\text{CO}$  and  $\text{CN}^-$  which have vacant molecular orbitals of low energy.

### 3. Chelation

The stability of complexes is greatly increased by chelation; that is the formation of rings by polydentate ligands. Thus, for example, the stability constants of 6-co-ordinate  $\text{Ni}^{2+}$  with  $\text{NH}_3$  and  $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$  are, respectively,  $10^9$  and  $10^{19}$ . And the sexidentate EDTA ligand (p. 333) forms such stable soluble complexes that, for instance, the precipitation of  $\text{Ca}^{2+}$  by oxalate from alkaline solution is entirely prevented.

Measurements of the free energy changes and the heats of reaction associated with chelation usually show that there has been a considerable increase in entropy. This occurs because several molecules of solvent in the solvated ion are replaced by a smaller number of multidentate ligands, or even by one:

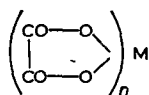


The reaction represented increases the number of entities in the solution  $\frac{1}{2}(n + 1)$  times; consequently it increases the disorder when  $n$  is greater than one.

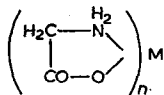
The enhanced stability of complexes containing chelated ligands is known as the *chelate effect*.

The size of the chelate ring is also of importance in the stabilisation of complexes; the optimum number of atoms in the ring is five, unless some of them are joined by double bonds. The following are examples:

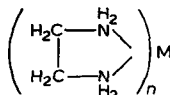
#### Bidentate ligands



Oxalato complexes

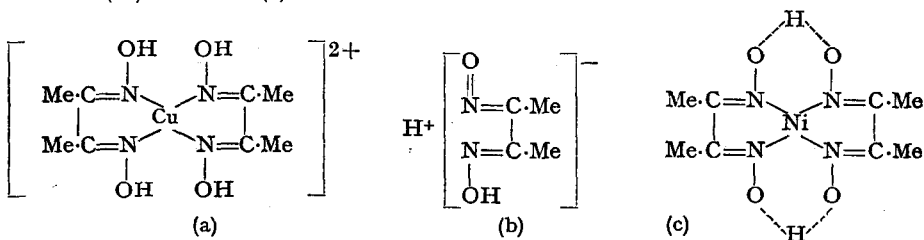


Glycine complexes

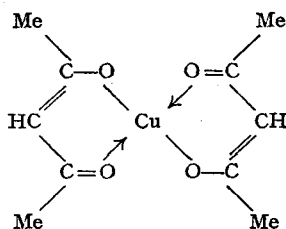


Ethylenediamine complexes

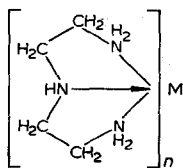
Dimethylglyoxime can act as a bidentate ligand in two ways: (i) as the whole molecule with a  $\text{Cu}^{2+}$  ion to form the bipositive bis(dimethylglyoxime) copper(II) ion (a), or (ii) as the ion derived from the dimethylglyoxime molecule (b) with a  $\text{Ni}^{2+}$  ion to form the uncharged bis(dimethylglyoximate) nickel(II) molecule (c):



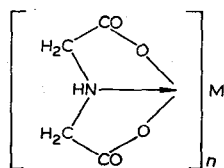
Another example of complex molecule which does not contain a complex ion is bis(acetylacetonato)copper(II):



### *Terdentate ligands*

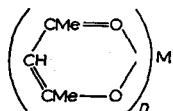


Diethylenetriamine complexes

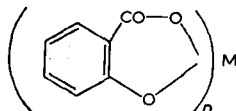


Imidodiacetate complexes

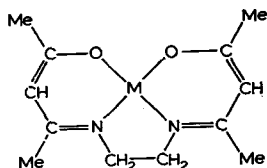
When some of the atoms in the ring are joined by double bonds the optimum size is six atoms. Examples:



Acetylacetonato complexes



Salicylato complexes

*Quadridentate ligand*

Bis(acetylaceton)ethylenedi-imine complex

In this the double-bonded rings are six-membered and the single-bonded ring five-membered.

The stability of a complex is affected by steric strain in some multidentate ligands. For example, ethylenediamine forms more stable complexes than its  $N,N'$ -tetramethyl derivative,  $\text{Me}_2\text{N}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NMe}_2$ ; this is because electron donation by the nitrogen atoms to the metal brings the Me groups close together.

## FURTHER READING

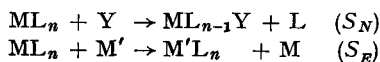
- J. LEWIS AND R. G. WILKINS (Eds.), *Modern Coordination Chemistry*, New York, Interscience, 1960.
- F. BASOLO AND R. C. JOHNSTON, *Coordination Chemistry*, New York, Benjamin, 1964.
- J. C. BAILAR JR. (Ed.), *The Chemistry of Coordination Compounds*, New York, Reinhold, 1956.
- F. J. C. ROSSOTTI AND H. ROSSOTTI, *The Determination of Stability Constants*, New York, McGraw-Hill, 1961.
- J. BJERRUM, G. SCHWARZENBACH AND L. G. SILLÉN, (Eds.), *Stability Constants of Metal-Ion Complexes*, London, The Chemical Society, Part I, *Organic Ligands*, 1957; Part II, *Inorganic Ligands*, 1958.
- A. B. P. LEVER (Ed.), *Coordination Chemistry Reviews*, Amsterdam, Elsevier, Vol. 1 (1966) etc.



## Substitution Reactions of Metal Complexes

### Classes of substitution reactions

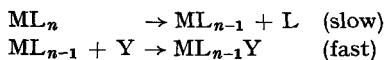
Substitution reactions in inorganic chemistry include the replacement of a ligand (L) in a co-ordination complex by another ligand (Y), and the replacement of a metal ion (M) by another metal (M'). In the terminology developed for organic reactions these are called  $S_N$  (substitution-nucleophilic) and  $S_E$  (substitution-electrophilic) reactions, respectively:



Although  $S_E$  reactions, such as that between  $\text{Hg}^{2+}$  and  $[\text{CoCl}(\text{NH}_3)_5]^+$ , are known, they are much less common than  $S_N$  and will not be considered here.

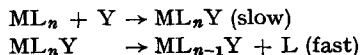
Turning to  $S_N$  reactions, one important class of these arises through changes in the oxidation state of the metal, but with this type of reaction we shall be less concerned than with reactions where neither oxidation nor reduction occurs. In the latter reactions, the substitution process can be looked upon as an acid-base reaction, with the metal ion (or positive species) acting as a Lewis acid (p. 249) and the ligands acting as bases.

Two different paths of nucleophilic substitution, each with a slow and a fast step, are generally recognised. The first can be formulated:



This is the  $S_N1$  (indicating substitution-nucleophilic-unimolecular) or dissociation mechanism. The reaction is termed unimolecular because only one species ( $\text{ML}_n$ ) is involved in the formation of the activated complex ( $\text{ML}_{n-1}$ ) with which further reaction occurs. As normally the activation energy for the first step will be high and that for the second step will be low, the rate of the overall reaction will depend upon  $[\text{ML}_n]$ , not upon  $[\text{Y}]$ . Thus the reaction will be of first order with respect to  $\text{ML}_n$  and of zero order with respect to Y. (Of course, if there are other competing mechanisms the order will be complex.) During the formation of an activated complex in an  $S_N1$  reaction, the co-ordination number of the metal is reduced.

The second path of nucleophilic substitution, also with two steps, can be formulated:

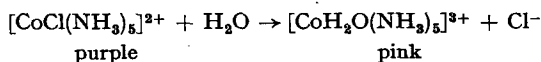


This is the substitution-nucleophilic-bimolecular,  $S_N2$ , or displacement mechanism. The rate of reaction depends on both  $[\text{ML}_n]$  and  $[\text{Y}]$ ; in fact, it is first order with respect to  $\text{ML}_n$ , first order with respect to  $\text{Y}$ , and thus second order overall. The activated complex is made by the addition of another ligand, and during its formation the co-ordination number of the metal is increased.

Unequivocal evidence in favour of an  $S_N1$  or an  $S_N2$  mechanism is usually difficult to obtain because the activated complex can rarely be detected directly. Furthermore, a mechanism which permits an almost simultaneous admission of  $\text{Y}$  to the co-ordination sphere of  $\text{M}$  and the ejection of  $\text{L}$  from it, is always a possibility.

### Methods of measuring rates of substitution

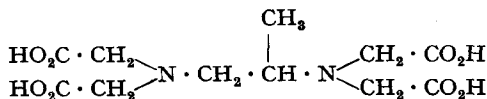
In a slow reaction, the time available allows rates to be measured by ordinary analytical methods. For instance, in the replacement:



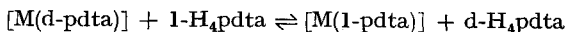
the progress of reaction may be followed

- (i) by determining the  $\text{Cl}^-$  ion in solution analytically;
- (ii) by observing the change in the optical density of the solution at an appropriate wavelength;
- (iii) by observing the change in electrical conductance;
- (iv) by measuring the pH; the complex ion  $[\text{CoH}_2\text{O}(\text{NH}_3)_5]^{3+}$  acts as an acid, with  $\text{p}K_a = 5.7$ .

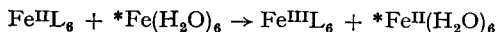
When complexes are formed from optically active ligands, rates of reaction can be followed polarimetrically. The compound 1, 2-propylenediaminetetraacetic acid (PDTA), also written  $\text{H}_4\text{pdta}$ :



is resolvable and acts as a quinquedentate or sexidentate ligand in the same way as EDTA (p. 333). If a metal complex containing one active form and the free optical antipode are mixed in equimolar quantities, the optical rotation tends towards zero as the reaction proceeds and the distribution of the isomers becomes random:



Radioisotopes are useful in the determination of reaction rates, particularly in electron-exchange reactions such as:



For fast reactions, flow techniques, relaxation spectrometry and line broadening n.m.r. methods (p. 19) are available.

### Factors affecting rates of substitution

Rates of substitution cover a wide range, and may depend on such variables as:

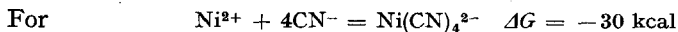
- (i) the charge number of the metal;
- (ii) the electronic configuration of the metal ion;
- (iii) the nature and geometrical arrangement of the ligands;
- (iv) the nucleophilic reagent;
- (v) the solvent;
- (vi) the influence of steric hindrance on the reaction.

For a metal ion of high charge number, substitution is usually slower than for an isoelectronic ion of lower charge number. The complex  $\text{MnH}_2\text{pdta}$ , made from the d-form of the acid, reacts with the l-form of the acid in aqueous solution at pH 6.3:



and the optical activity is reduced to zero in 5 minutes at 20°. The  $\text{Fe}^{\text{III}}$  complex (which is  $d^5$  like  $\text{Mn}^{\text{II}}$ ), formulated  $\text{FeHpdta}$ , does not undergo any measurable exchange with the optically isomeric acid in 2 days under the same conditions.

Complexes which react quickly in ligand replacement processes are termed *labile*, those which react slowly or not at all are called *inert*. Whether there is kinetic inertness or kinetic lability depends upon the activation energy of the reaction and has no connection with the thermodynamic stability of the species involved; this stability depends upon the free energy of formation.



but the replacement of  $^{12}\text{CN}^-$  by  $^{14}\text{CN}^-$ , when the latter is added to a solution of the complex, takes place too quickly to be measured by ordinary radiochemical techniques.

### Labile and inert octahedral complexes

Of the octahedral complexes of Period 4 transition metals, the most inert kinetically are those of chromium(III), a  $d^3$  system, and cobalt(III), a  $d^6$  system. In general, the octahedral complexes of transition metals of Periods 5 and 6 are more inert than those of their Period 4 congeners. Moreover, in these series the  $\text{Mo}^{\text{III}}$ ,  $\text{W}^{\text{III}}$ ,  $\text{Rh}^{\text{III}}$  and  $\text{Ir}^{\text{III}}$  states form particularly inert octahedral complexes.

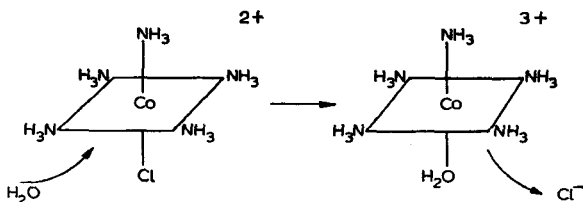
These facts have been interpreted by applying the molecular orbital theory of metal-ligand bonding (p. 177).

The six d electrons of a low-spin octahedral  $\text{Co}^{\text{III}}$  complex create regions of high electron density extending outwards from the faces of the octahedron formed by the ligands. These regions present a formidable barrier to  $S_N2$  attack by a nucleophile. Furthermore, whatever the mechanism by which an activated complex is formed, some of the stabilisation energy must be lost, and the loss will tend to be greatest for such complexes as have a low-spin  $d^6$  system or a  $d^3$  system, for both of which the stabilisation energy is great (p. 209). The formation of a 7-co-ordinate, pentagonal bipyramidal arrangement would involve a redistribution of d electrons in MO's of such high energy that the energy of activation of the process would be very large indeed.

For an  $S_N1$  process, in which a 5-co-ordinate activated complex would be formed, the energy levels of the trigonal bipyramidal structure are not favourable for six electrons unless one of the ligands which remains in the complex forms very strong  $\pi$  bonds to the metal. Loss of stabilisation will be least when one ligand is removed to leave the others in a square pyramidal, intermediate complex. In fact, application of the available thermochemical data to the process:



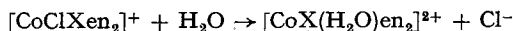
indicates the energy required would be about 94 kcal per mole; whereas the activation energy of the acid hydrolysis is only about 24 kcal. The most acceptable explanation of this is that when the Co-Cl bond is lengthened to some critical distance a solvent molecule slips in to replace the  $\text{Cl}^-$ :



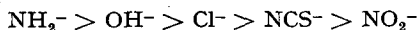
Obviously this process cannot be classified as either  $S_N1$  or  $S_N2$ .

### Effect of an inert substituent on the mechanism of replacement

The rates of acid hydrolysis (the reaction between the complex and solvent water at  $\text{pH} < 3$ ) of a series of complexes  $[\text{CoClXen}_2]^+$  ( $\text{X} = \text{NH}_2, \text{OH}, \text{Cl}, \text{NCS}, \text{NO}_2$ ) have been measured. The rate constants for the reactions:

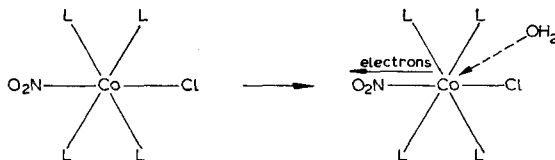


decrease in the order of the fall in electron-attracting power of  $\text{X}^-$



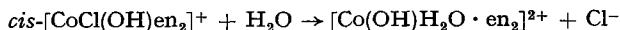
A basic group like  $\text{NH}_2$  tends to form  $\pi$  bonds with the metal by the donation of p electrons. This has the effect of reducing the positive charge on the metal atom, and facilitates breaking of the  $\text{Co}-\text{Cl}$  bond. Furthermore, the  $\pi$  bonding stabilises the 5-co-ordinate intermediate which is formed. Both effects weaken with the decreasingly basic  $\text{OH}^-$ ,  $\text{Cl}^-$  and  $\text{NCS}^-$  ligands; but, certainly in the cases where  $\text{X}$  is  $\text{OH}$  or  $\text{Cl}$ , the  $S_N1$  mechanism is favoured.

However the  $\text{NO}_2$  ligand is different, it tends to withdraw electrons and thus promotes an  $S_N2$  reaction by the formation of a 7-co-ordinate complex:



### Effect of the stereochemical arrangement of the ligands

The acid hydrolysis of the *cis*-isomer:



is considerably faster than that of the *trans*-isomer. The energy of activation is actually about 8 kcal mole<sup>-1</sup> less. This is believed to be due to the  $\text{OH}^-$  ligand, which is *cis* to the leaving group,  $\text{Cl}^-$ , and is in the most favourable position to donate electrons to an empty metal orbital by  $\pi$ -bonding. For complexes with electron-attracting ligands like  $\text{NO}_2$ , which do not form such  $\pi$  bonds, the hydrolysis of the *trans*-isomer is faster.

The position of an inert, electron-donating ligand also influences the configuration of the product of reaction. For the acid-hydrolysis of *cis*- and *trans*- $[\text{CoX}(\text{NCS})\text{en}_2]^+$  ( $\text{X} = \text{Cl}$  or  $\text{Br}$ ) the rate constants,  $k$ , the activation energies,  $E$ , and the percentage of *cis*- $[\text{Co}(\text{NCS})\text{H}_2\text{O} \cdot \text{en}_2]^{2+}$  in the product are as shown:

	$k$ at 25°	$E$ kcal mole <sup>-1</sup>	% <i>cis</i> product
<i>cis</i> -Cl-compound	$1.1 \times 10^{-5}$	20.8	100
<i>trans</i> -Cl-compound	$5 \times 10^{-8}$	30.4	~ 60
<i>cis</i> -Br-compound	$2.3 \times 10^{-5}$	23.1	100
<i>trans</i> -Br-compound	$5 \times 10^{-7}$	30.1	~ 70

When the NCS group is *cis* to the halogen, the orbitals of the two ligands overlap sufficiently for electrons to be directed towards the space vacated by the electrons originally employed in bonding M to X, without the need for a rearrangement of the electrons around the metal. This results in the formation of a square pyramidal transition state, and retention of the original configuration.

But if a *trans*-NCS group is to provide electrons to fill up the emptied orbital, a change of configuration to trigonal bipyramid or distorted square pyramid is necessary; the activation energy is high and the original configuration is not retained.

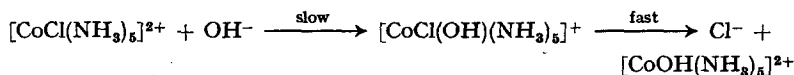
### Effect of the nucleophile on rates of replacement

#### (i) Octahedral complexes

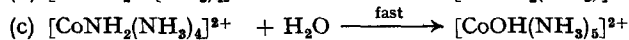
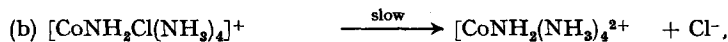
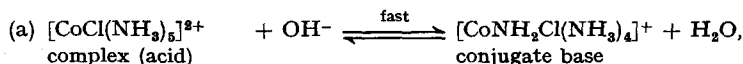
Attempts have been made to establish an order of increasing reactivity for nucleophiles by studying the base hydrolysis of cobaltammines (hydrolysis in aqueous solution at pH > 10). The rates of reaction are commonly a million times faster than in acid hydrolysis; the reactions usually exhibit overall second-order kinetics:

$$\text{Rate} \propto [\text{OH}^-][\text{cobaltamine}]$$

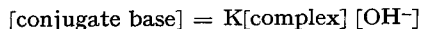
One explanation is that an  $S_N2$  mechanism operates; for instance:



But an  $S_N1CB$  (substitution, nucleophilic, unimolecular, conjugate-base) mechanism also accounts for the overall order of reaction:

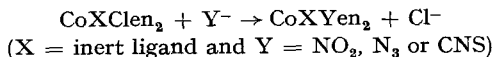


The speed of the rate-determining step (b) depends on [conjugate base]. If  $K$  = the equilibrium constant for the equilibrium (a), then

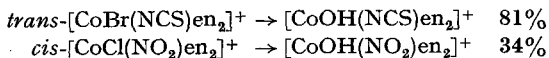


and the rate of the step (b) is proportional to  $[\text{complex}][\text{OH}^-]$ .

Both  $S_N2$  and  $S_N1CB$  mechanisms would therefore give second-order kinetics, and the same product in aqueous solution; but in a non-hydroxylic solvent different products should be obtained. It has been found that for:



the reaction is slow in dimethylsulphoxide, but fast in the presence of small amounts of  $\text{OH}^-$ , although the products are the same in both cases. Also, the rate depends on  $[\text{OH}^-]$ , not on  $[\text{Y}]$  or the nature of Y. These results support the idea of the initial formation of a 5-co-ordinate  $\text{CoXen}_2$  which then reacts quickly with Y. The  $S_N1CB$  mechanism should lead to extensive rearrangement for both *cis*- and *trans*-isomers, in agreement with experimental evidence:



Thus attempts to find a scale of nucleophilic reactivities applicable to octahedral complexes has proved unsuccessful. For square complexes, however, the establishment of such a series has been possible.

### (ii) Square complexes

The so-called square complexes are, through solvation, effectively tetragonal in most solvents (Fig. 323). The solvent molecules, S, are labile, and

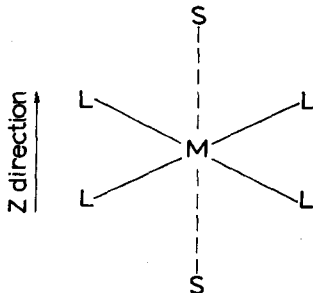
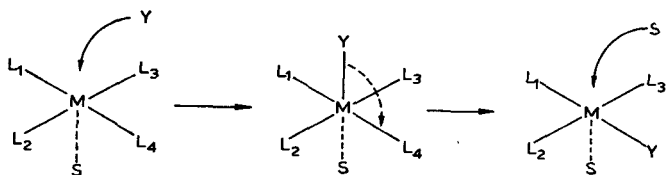


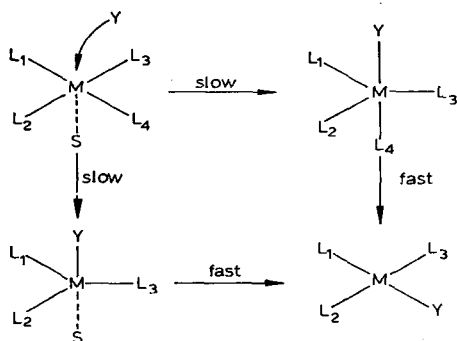
Fig. 323. Square complex converted to one of tetragonal symmetry by solvent molecules entering the co-ordination sphere ( $\text{M}-\text{S}$  distance long;  $d_z$  orbital contains two electrons in a typical square complex).

are replaceable by nucleophiles which can approach closer to M and cause the ejection of one of the ligands lying in the plane of the square.

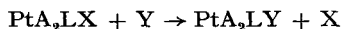
There are two possible mechanisms for this. The first involves the formation of a square-pyramidal, activated complex from which the most labile ligand ( $L_4$ ) is ejected:



The second mechanism by either path shown below, involves the formation of a 5-co-ordinate, trigonal bipyramidal activated complex:



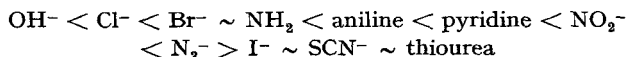
Experiments on  $Pt^{II}$  and  $Pd^{II}$  complexes of the type  $PtA_2LX$  show the rate law for the reaction:



to have the general form:

$$\text{Rate} = k_1[\text{complex}] + k_2[Y][\text{complex}]$$

Indeed,  $k_1$  is interpreted as a first-order rate constant for an  $S_N2$  reaction between complex and solvent. The values of  $k_2$  for different nucleophiles (Y) enable these reagents to be placed in the following order of reactivity towards platinum:

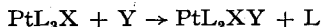


This order, with little variation from one  $Pt^{II}$  complex to another, is similar (except for  $OH^-$ ) to that for the reactivity of the same groups towards a typical organic substrate such as an alkyl halide.

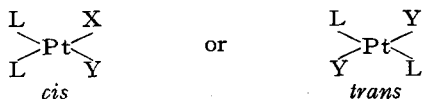


### Effect of ligands already in the complex: the *trans* effect

Ligand replacement reactions in square complexes such as those of  $\text{Pt}^{\text{II}}$  have some special features. For the reaction:

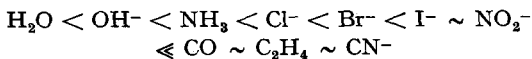


the reaction product may have either of the orientations:

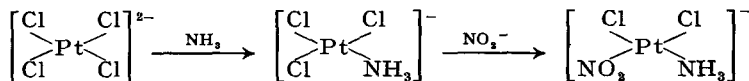


Experiment shows that the proportions of *cis*- and *trans*-isomers depend on the nature of the ligand X. Ligands vary in their power of directing an incoming nucleophilic ligand preferentially into a position *trans* to themselves.

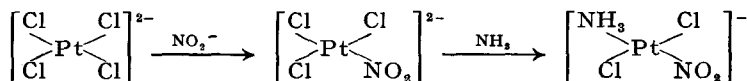
The order of the *trans*-directing strength for common ligands is indicated:



The discovery of the *trans*-effect has enabled the synthesis of many platinum complexes to be rationalised. Thus *cis*- $\text{PtCl}_2(\text{NO}_2)(\text{NH}_3)$ , is made by the action of ammonia on  $\text{PtCl}_4^{2-}$ , and of nitrite on the product:



The *trans*-isomer is obtained by reversing the order of reagent addition; this is because  $\text{NO}_2^-$  is more strongly *trans*-directing than  $\text{Cl}^-$ , but  $\text{NH}_3$  is weaker than  $\text{Cl}^-$ :



There are two approaches to the explanation of *trans*-directing characters in a ligand; but these are not mutually exclusive. The first is a thermodynamic approach. A large, highly polarisable ligand, like I, distorted by the positive charge on the central atom, is imagined to polarise that atom itself to some extent and thus weaken the bond between it and the opposite ligand.

The second approach is a kinetic one and assumes an  $\text{S}_{\text{N}}2$  reaction. It uses the idea that a ligand which can accept electrons donated back from the metal through  $d_{\pi}\text{-p}_{\pi}$  or  $d_{\pi}\text{-d}_{\pi}$  bonds (p. 182) will tend to reduce the electron

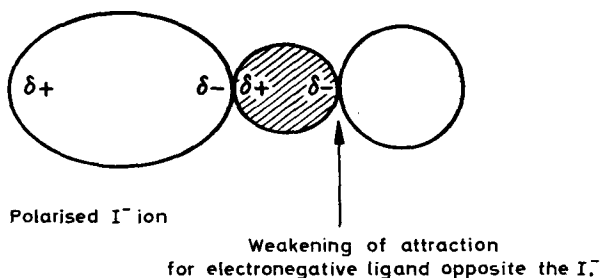
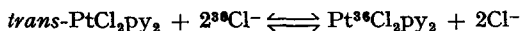


Fig. 324. Representation of polarisation of metal ion induced by highly polarisable ligand (signs show only polarisation effects; the central atom normally carries positive charge and the ligands are electron-donating).

density both above and below the bond situated on the other side of the metal atom, and thus open up the position for nucleophilic attack. This view is in better accord with the high position of ethylene in the *trans*-directing series, since this ligand cannot have a strong electrostatic effect. However, there is at present insufficient experimental evidence to enable a comprehensive theory to be formulated.

### Effect of the solvent

The following isotopic exchange has been studied in a number of solvents:



The results show that the solvents can be divided into two categories with respect to their influence on  $k_1$  and  $k_2$  in the rate equation for the forward reaction:

$$\text{Rate} = k_1[\text{complex}] + k_2[\text{Cl}^-][\text{complex}].$$

In water, ethanol, dimethylsulphoxide and methyl nitrite the rate is almost independent of  $[\text{Cl}^-]$ ; that is  $k_1 \gg k_2[\text{Cl}^-]$ . But in carbon tetrachloride, benzene, tertiary butanol, ethylene dichloride and ethyl acetate the reaction is of first order with respect to free chloride ion;  $k_2[\text{Cl}^-] \gg k_1$ . As explained above (p. 597),  $k_1$  can be considered as a rate constant for an  $S_N2$  reaction between complex and solvent.

The solvents of the first group are, in general, strongly co-ordinating and ionising ones, those in the second group co-ordinate weakly and do not promote ionisation. Apparently, the platinum(II) complex suffers nucleophilic attack by solvents like water and ethanol, but not by those like benzene and carbon tetrachloride. The co-ordinating solvent molecules all possess vacant

orbitals capable of bonding with the filled  $d_{xz}$  and  $d_{yz}$  orbitals of  $Pt^{II}$ . Thus their electron-donating oxygen atoms are able to approach more closely to the Pt and create favourable conditions for the displacement of chloride.

### Steric effect in replacement reactions

The importance of solvation above and below the plane in certain reactions of  $Pt^{II}$  complexes has been verified by blocking these positions by groups attached to ligands lying in the plane (Fig. 325).

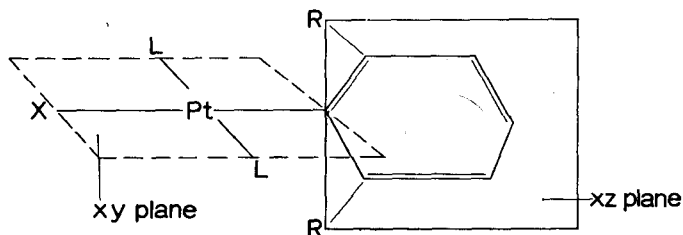
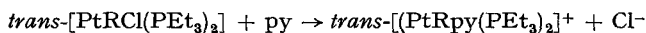


Fig. 325. R-groups above and below Pt sterically hinder the attachment of solvent molecules.

There is a marked reduction in reaction rates as steric shielding of the platinum by R groups is increased.

As an example, for the reactions in ethanol at 25°:



the rate constants,  $k_1$  are:

	$k_1 \text{ sec}^{-1}$
R = phenyl	$3 \times 10^{-5}$
R = <i>p</i> -tolyl	$6 \times 10^{-6}$
R = mesityl	$1 \times 10^{-6}$

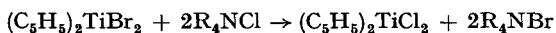
A similar but even more pronounced effect is observed for the analogous  $Pd^{II}$  and  $Ni^{II}$  complexes.

### Reactions of tetrahedral complexes

Tetrahedral complexes are generally labile, and relatively little kinetic work has been done on them. The mechanism of replacement reactions in the tetrahedral complexes of Si, Ge and Sn differ from those of carbon in that 5-co-ordinate intermediates can be formed with much less expenditure of energy because the co-ordination numbers of the atoms are more easily ex-

panded (p. 547). The dominant mechanism is  $S_N2$  displacement. Thus for optically active compounds of silicon of the type  $R'R''R'''SiX$  some substitutions occur with complete retention, some with complete inversion, of configuration; in the circumstances racemisation would result if the reaction were  $S_N1$ .

Solvent molecules seem to participate in some of the reactions of tetrahedral complexes. For instance, the bis(cyclopentadienyl)-titanium(IV) halides, which have distorted tetrahedral structures, react with ionic halides in benzene or tetrahydrofuran:



The rate of reaction is proportional to  $[R_4NCl]$ , suggesting an  $S_N2$  displacement process. But when  $LiCl$  is used instead of a quarternary ammonium chloride the rate is independent of  $[LiCl]$  and is slower. Presumably the rate-determining step is nucleophilic displacement by solvent molecules.

### Photochemistry of metal complexes

Metal-ligand systems usually show two kinds of absorption band:

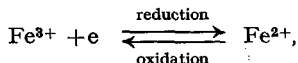
- (i) High-intensity ultraviolet absorption attributed to electron transfer (p. 184).
- (ii) Low-intensity absorption in the visible range due to d-d transition (p. 167).

Thus irradiation with ultraviolet rays should encourage redox processes, whereas visible light should promote substitution reactions by causing the promotion of electrons into antibonding orbitals where they cause repulsion between metal and ligand.

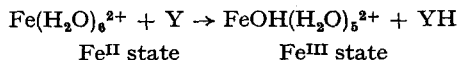
There is evidence that in  $Co^{III}$  complexes absorption in the charge-transfer band leads to reduction of  $Co^{III}$  to  $Co^{II}$ , but that absorption in the d-d transition band leads to substitutions. Thus for  $[CoNCS(NH_3)_5]^{2+}$  in aqueous solution, the ratio of reduction to substitution (hydration to  $[CoH_2O(NH_3)_5]^{3+}$ ) is 2.1 at 370  $m\mu$  (ultraviolet) but only 0.24 at 550  $m\mu$  (visible).

### Redox reactions

Although a redox process can be represented as an electron-transfer:

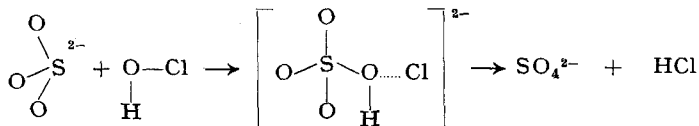


it does not necessarily occur by coupled electron-loss and electron-gain steps. Often a redox reaction involves the transfer of an atom or group rather than that of an electron:



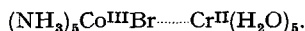
This is called an atom-transfer or a bridged, activated-complex mechanism. In the study of a redox reaction, the problem is usually to discover which atom or group is transferred.

The use of <sup>18</sup>O shows that oxidation of SO<sub>3</sub><sup>2-</sup> by hypochlorite, chlorite and chlorate occurs through the transfer of oxygen atoms. The reactions begin with a nucleophilic attack on an oxygen atom:



It has been possible to demonstrate the transfer of many univalent groups by using complexes of Cr<sup>II</sup> as a reducing agent. They are labile, while those of Cr<sup>III</sup> are inert; thus if an atom or group is transferred from a Cr<sup>II</sup> complex to one of Cr<sup>III</sup> it will remain part of the co-ordination sphere long enough to be detected. By the use of [CoX(NH<sub>3</sub>)<sub>5</sub>]<sup>2+</sup> to oxidise chromium(II) complexes, the transfer of X has been demonstrated for X<sup>-</sup> = NCS<sup>-</sup>, N<sub>3</sub><sup>-</sup>, CH<sub>3</sub>CO<sup>2-</sup> and Br<sup>-</sup>.

The evidence is that the reaction rate is increased when a good 'bridging' group is present so that a bridged complex can be formed; for instance:



Bridging by a Cl atom is probably the reason for the very rapid reaction between <sup>51</sup>Cr(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup> and [CrCl(H<sub>2</sub>O)<sub>5</sub>]<sup>2+</sup>, because the reaction between the two aquo-ions <sup>51</sup>Cr · aq<sup>2+</sup> and Cr · aq<sup>3+</sup> is extremely slow.

In the redox reactions of other aquo ions, however, the transfer of hydrogen atoms is considered as the most probable mechanism, although the evidence is indirect. The reactions between <sup>59</sup>Fe(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup> and FeOH(H<sub>2</sub>O)<sub>5</sub><sup>2+</sup> are about twice as fast in H<sub>2</sub>O as in D<sub>2</sub>O, the usual ratio of reaction rates for processes in which a hydrogen atom must move—for example *k<sub>H</sub>* / *k<sub>D</sub>* for the reactions of alkali metals with H<sub>2</sub>O and D<sub>2</sub>O.

Many redox reactions in aqueous solution are accelerated in the presence of small anions such as OH<sup>-</sup>, F<sup>-</sup> and Cl<sup>-</sup>. Examples are the acceleration of Eu<sup>II</sup>-Eu<sup>III</sup> exchange by chloride and of Ce<sup>III</sup>-Ce<sup>IV</sup> by fluoride. The lowering of the activation energy may owe something merely to a reduction of the coulombic repulsion between cations when a negative ion is placed between them, but such an effect appears to be small compared with that due to bridging.

However, electron transfer does seem to occur in some redox reactions, particularly when the geometrical arrangement of ligands round the metal is the same in both the oxidised and reduced states. The reaction is then said to proceed by an electron transfer or outer-sphere activated-complex mechanism.

The reactions of  $V^{2+aq}$  with oxidising agents such as  $Co^{III}(NH_3)_5L$  ( $L = H_2O, Cl, NH_3$ ) proceed through an outer-sphere complex rather than a bridged-complex mechanism such as in the  $Cr_{aq}^{2+}$  oxidation. A  $t_{2g}$  electron on the  $V_{aq}^{2+}$  ion is transferred, and its orbital overlaps an orbital on the oxidant. But with  $Cr_{aq}^{2+}$  the electron to be transferred is in an  $e_g$  orbital and is badly situated for overlap with a receiver orbital; consequently transference of the electron by means of a bridge provides a path of lower energy.

For an electron-transfer mechanism there is the critical requirement that reductant and oxidant should have similar structures. The Frank-Condon principle states that an electron moves so quickly compared with an atom that appreciable rearrangement of atoms is impossible during an electronic transition. If an electron is transferred from an  $Fe(CN)_6^{4-}$  ion to an  $Fe(CN)_6^{3-}$  ion the result would be an  $Fe(CN)_6^{4-}$  ion in which the Fe-C bonds are too short and an  $Fe(CN)_6^{3-}$  ion in which the Fe-C bonds are too long—both complexes being in high-energy states. Hence the process would create energy, and this description of the mechanism is therefore incorrect. Clearly the readjustment of the bond lengths must take place before the electron-jump occurs. The activation energy required to shorten the bonds in the  $Fe^{II}$  compound and lengthen those in the  $Fe^{III}$  compound is fairly small because the geometries of the two anions are similar.

Again in  $MnO_4^{2-}-MnO_4^-$  and  $IrCl_6^{3-}-IrCl_6^{2-}$  exchanges, where again both complexes are inert, the exchange rates are far faster than could possibly be explained by dissociation and atom transfer.

When, however, two ions are very different in their geometry or in the metal-ligand distances, electron-exchange reactions between them are usually slow. Thus for  $Co(NH_3)_6^{2+}$  and  $Co(NH_3)_6^{3+}$ , although both are octahedral, the Co-N distances and the electronic configuration round the cobalt atoms,  $t_{2g}^5, e_g^2$  and  $t_{2g}^6$  respectively, are quite dissimilar. Both must change before reaction can occur: this is the reason for the slowness of the redox process.

#### FURTHER READING

F. BASOLO AND R. G. PEARSON, *Mechanisms of Substitution Reactions of Metal Complexes*, in H. J. EMELÉUS AND A. G. SHARPE (Eds.), *Advances in Inorganic*

- Chemistry and Radiochemistry*, Vol. III, New York, Academic Press, 1961, p. 1.
- H. TAUBE, *Mechanisms of Redox Reactions of Simple Chemistry* in H. J. EMELÉUS AND A. G. SHARPE (Eds.), *Advances in Inorganic Chemistry and Radiochemistry*, Vol. I, New York, Academic Press, 1959, p. 1.
- J. HALPERN, *Mechanisms of Electron Transfer and Related Processes in Solution*, *Quart. Rev.*, 15 (1961) 207.
- N. SUTIN, *Electron Exchange Reactions*, *Ann. Rev. Nuclear Sci.*, 12 (1962) 285.

# The Lanthanides, Scandium and Yttrium

## GROUP IIIA

## THE LANTHANIDES

## Electronic structures and general properties

The lanthanides, for which the general symbol Ln is used, have electron configurations with  $5d^1 6s^2$  in common and a variable occupation of the 4f level. Although lanthanum itself has not an f electron in its ground state, the element has strong similarities with those which follow it, and it will be treated in what follows as a lanthanide. Classically called the Rare Earths, these elements are also referred to as the *inner-transition* elements because the 4f electron build-up takes place in the fourth quantum level, below the 5s, 5p and 6s electrons which are also present in these atoms. As the electronic diversity is in this lower shell, the elements are very similar chemically.

The small differences in properties arise principally from the 'lanthanide contraction'. Since, for every additional proton in a nucleus, the corre-

TABLE 105  
THE LANTHANIDES

	<i>Symbol</i>	<i>Z</i>	<i>Electron configuration</i>		<i>Common ionic charges</i>	<i>M<sup>3+</sup> radii</i>
Lanthanum	La	57	5d <sup>1</sup>	6s <sup>2</sup>	3	1.06
Cerium	Ce	58	4f <sup>1</sup>	5d <sup>1</sup> 6s <sup>2</sup>	3 4	1.03
Praseodymium	Pr	59	4f <sup>2</sup>	5d <sup>1</sup> 6s <sup>2</sup>	3 4	1.01
Neodymium	Nd	60	4f <sup>3</sup>	5d <sup>1</sup> 6s <sup>2</sup>	2 3 4	1.00
Promethium	Pm	61	4f <sup>4</sup>	5d <sup>1</sup> 6s <sup>2</sup>	3	0.98
Samarium	Sm	62	4f <sup>5</sup>	5d <sup>1</sup> 6s <sup>2</sup>	2 3	0.96
Europium	Eu	63	4f <sup>6</sup>	5d <sup>1</sup> 6s <sup>2</sup>	2 3	0.95
Gadolinium	Gd	64	4f <sup>7</sup>	5d <sup>1</sup> 6s <sup>2</sup>	3	0.94
Terbium	Tb	65	4f <sup>8</sup>	5d <sup>1</sup> 6s <sup>2</sup>	3 4	0.92
Dysprosium	Dy	66	4f <sup>9</sup>	5d <sup>1</sup> 6s <sup>2</sup>	3 4	0.91
Holmium	Ho	67	4f <sup>10</sup>	5d <sup>1</sup> 6s <sup>2</sup>	3	0.89
Erbium	Er	68	4f <sup>11</sup>	5d <sup>1</sup> 6s <sup>2</sup>	3	0.88
Thulium	Tm	69	4f <sup>12</sup>	5d <sup>1</sup> 6s <sup>2</sup>	2 3	0.87
Ytterbium	Yb	70	4f <sup>13</sup>	5d <sup>1</sup> 6s <sup>2</sup>	2 3	0.86
Lutetium	Lu	71	4f <sup>14</sup>	5d <sup>1</sup> 6s <sup>2</sup>	3	0.85



spending electron goes into the 4f shell which is too diffuse to screen the nucleus as effectively as a more localised inner shell, the attraction of the nucleus for the outermost electrons increases steadily with the atomic number of the lanthanide. This causes a fall in atomic size from lanthanum to lutetium. As may be seen in Table 105, the contraction is quite regular in  $\text{Ln}^{3+}$  ions. However, it should be noted that the changes in the metallic radii of the lanthanides are irregular (Table 106). These radii are inferred from the

TABLE 106  
PROPERTIES OF SOME LANTHANIDES

<i>Element</i>	<i>Structure</i>	<i>Metallic radius</i>	<i>Density</i>	<i>Atomic volume</i>
57 La	h.c.p.	1.87	6.2	22.4
62 Sm	h.c.p.	1.66	6.9	21.7
63 Eu	b.c.c.	2.04	5.2	29.2
64 Gd	h.c.p.	1.79	7.9	19.9
69 Tm	h.c.p.	1.74	9.3	18.2
70 Yb	f.c.c.	1.92	7.0	24.7
71 Lu	h.c.p.	1.74	9.7	18.0

structures of the metals, in which the outer electronic structure is strongly affected by the metallic bonding (pp. 124 and 132). The changes in atomic volume, also deduced from properties, are irregular.

The first three lanthanides, La, Ce and Pr, are dimorphous metals with h.c.p. and f.c.c. structures, and differ little in density. The rest of the metals are h.c.p., except Eu (b.c.c.) and Yb (f.c.c.), in which two the interatomic distances are greater and the densities lower (Table 106). These are lanthanides which have the greatest tendency to form bivalent ions. In the solids, the atoms probably donate only two electrons to the conduction bands of the metal; the 2+ ions which result will be larger and less strongly bound than the 3+ ions in the other solid metals. The first ionisation energies are about 6 eV and the second about 12 eV, comparable with those of calcium. The standard electrode potentials vary smoothly from  $-2.52$  V for the  $\text{La}^{3+}/\text{La}$  couple to  $-2.25$  V for  $\text{Lu}^{3+}/\text{Lu}$ .

The radii of the ions and the ionic charges are related to the electron configurations in Table 105; these result, as would be expected, in a dominant charge number of +3 and this charge is the only one displayed by La, Gd and Lu because empty, half-filled and filled 4f shells are particularly stable. Of the rest of the lanthanides Ce, Pr, Nd, Tb and Dy show in addition a charge number of +4 and Sm, Eu, Tm and Yb one of +2. Starting from the +3 state, the lanthanide +4 state is probably due to the loss of a 4f elec-

tron and the +2 state to the acquisition of one; for instance  $\text{Pr}^{4+}$  has  $4f^1$  and  $\text{Sm}^{2+}$  has  $4f^6$ .

The chemical properties of the early members of the series are similar to those of calcium but, with increasing atomic number, these give place to other properties more like those of aluminium. At the same time there is a progressive increase in the solubility of the potassium double sulphates.

### Sources and separations of the lanthanides

Though called rare, the elements are not particularly so. Three of them, namely Ce, La and Nd, are more common than lead, and thulium is about as abundant as iodine. The lanthanides tend to be in minerals which crystallise late from a magma since their ions are too large to replace other terpositive ions; hence they separate in the pegmatites. The 'light' lanthanides are extracted chiefly from monazite, predominantly phosphates of thorium, cerium, neodymium and lanthanum, and also from orthite. Monazite is a poor source of europium, which is more commonly associated as  $\text{Eu}^{2+}$  with alkaline earth minerals, and does not carry much of the 'heavy' lanthanides which are obtained from gadolinite,  $\text{FeBe}_2\text{Y}_2\text{Si}_2\text{O}_{10}$ , and xenotime,  $\text{YPO}_4$ .

#### *Extraction of lanthanides from monazite*

Monazite is digested with concentrated  $\text{H}_2\text{SO}_4$  to produce a paste of the sulphates containing phosphoric acid and an excess of sulphuric acid. The paste, separated by centrifugation, is dissolved in cold water, the sulphates being less soluble in hot water. The solution is neutralised with a previously prepared mixture of lanthanide oxides to precipitate thorium, zirconium and titanium. The addition of  $\text{Na}_2\text{SO}_4$  to the clear mother liquor throws down the light lanthanides (La to Sm) as double sulphates of variable composition; the heavy lanthanides (Gd to Lu), which comprise less than 4% of those present, remain in solution. Hot  $\text{NaOH}$  is added to the double sulphate precipitate of light fraction to give a mixture of hydrated oxides. This is washed free from  $\text{Na}_2\text{SO}_4$  and dried in air at  $100^\circ$ , the cerium being thus completely oxidised to  $\text{CeO}_2$ . The composition of the solid is roughly:  $\text{CeO}_2$  50%,  $\text{Nd}_2\text{O}_3$  20%,  $\text{La}_2\text{O}_3$  17%,  $\text{Pr}_2\text{O}_3$  8%,  $\text{Sm}_2\text{O}_3$  5%.

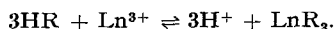
This mixture is extracted with dilute  $\text{HNO}_3$  to dissolve the more basic sesquioxides,  $\text{Ln}_2\text{O}_3$ ; and leave a residue of  $\text{CeO}_2$ . The crude  $\text{CeO}_2$  is dissolved in 85%  $\text{HNO}_3$  and added to an excess of dilute  $\text{H}_2\text{SO}_4$ , whereby the cerium is precipitated as the red, basic nitrate,  $\text{Ce}(\text{OH})(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$ . The dilute solution is used for leaching more of the dried hydroxide.

Separation of the light lanthanides, after removal of the Ce, has been accomplished in various ways, based mainly on solubility differences. Frac-

tional crystallisation of the double magnesium nitrates,  $2\text{Ln}(\text{NO}_3)_3 \cdot 3\text{Mg}(\text{NO}_3)_2 \cdot 24\text{H}_2\text{O}$ , was an early method. The heavy lanthanides from the double sulphate solution (above) and from ores such as xenotime have been separated by fractional crystallisation of either the bromates or the double ammonium oxalates.

#### *Separation by ion exchange*

When a solution containing a mixture of lanthanide ions is brought on to an exchange resin in its hydrogen form, the order of absorption follows the atomic number of the elements. Affinity for the resin decreases with radius of the hydrated ion:



Orderly displacement of the cations from the resin cannot be achieved by a concentrated solution of an ammonium salt. However, the addition of an acid which complexes with the lanthanide ions improves the separation. The distribution coefficients of adjacent lanthanides between citrate buffer solutions and Amberlite IR-1 differ by a factor of about two. The eluant is most efficient at low concentration and high pH.

On a large scale, light lanthanides have been absorbed on a cation resin in a 24-unit battery of Pyrex columns 10 ft by 4 in., and displaced with 0.1% citric acid buffered to pH 6 with ammonia. The eluate, collected in 40–50 litre fractions (about a day's run), contained up to 0.4 g/l of  $\text{Ln}_2\text{O}_3$ . Over 80% of each element present was obtained in a high state of purity from a single passage through the columns. Under these conditions, the elements were displaced in the reverse order of the atomic number. EDTA has proved an even more satisfactory complexing agent than citric acid and gives purer specimens than any other agent.

#### *Separation by solvent extraction*

Solutions of tri-*n*-butyl phosphate in kerosene flowing counter to a nitric acid solution of lanthanides removes them in the organic phase. Differences in the extraction coefficient are approximately equal from one element to the next. Gadolinium of about 95% purity has been separated from other lanthanides on a kilogram scale in this way.

### **The metals**

#### *Production*

The metals have been produced by methods which include:

- (i) electrolysis of the fused chlorides (*cf.* Ca),
- (ii) electrolysis of  $\text{CeO}_2$  in fused  $\text{CeF}_3$  (*cf.* Al),

(iii) reduction of the anhydrous chlorides with Na (*cf.* Ti),

(iv) reduction of the anhydrous fluorides with Mg (*cf.* U).

Metallothermic reduction by method (iii) has been used for the lighter lanthanides such as La, Ce and Ga, and by method (iv) for the heavier lanthanides because the fluorides are less volatile than the chlorides and they restrict loss by evaporation at the temperatures ( $> 1000^\circ$ ) employed. It is noteworthy that Sm, Eu and Yb, which have a reasonably stable +2 state are reduced only as far as the dichlorides and their separation from other lanthanides is facilitated. These metals themselves are obtained by reducing the oxides with lanthanum.

Metals produced in the various ways described may be purified by distillation and in other ways, but for all of them there are limits beyond which purification has not been carried.

### Physical properties

The melting points of the metals range from  $824^\circ$  for Yb to  $1652^\circ$  for Lu. With exceptions, there is a general rise in m.p. with atomic number. For metals, they are not very good conductors of heat and electricity and their mechanical characteristics are poor.

The metals are silvery-white. Those of the heavier lanthanides remain bright at room temperature, but the lighter rapidly become coated with oxide.

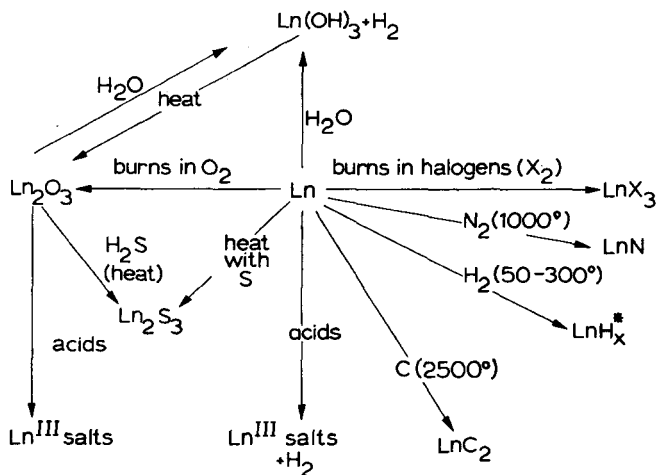


Fig. 326. Reactions of the lanthanides\* (Ln = lanthanide atom).

\* The hydrides are non-stoichiometric (p. 266) with  $x = 2.5$  to 3. Most of the carbides are acetylides (p. 381).

### Chemical properties

The chemical properties of the earlier lanthanides resemble those of calcium but, as the atomic number of the element increases, these give place to other properties more like those of aluminium. With this change there is also a progressive increase in the solubility of the potassium double sulphates. Figure 326 summarises the chemistry of these elements. Cerium provides two notable exceptions to the scheme: it combines with fluorine to give  $CeF_4$  and with oxygen to give  $CeO_2$ .

### Nature and properties of the ions

All the lanthanides have  $Ln^{III}$  compounds, this being the principal form in which the elements occur; complexes and ions with charge numbers other than +3 are rather uncommon (p. 611).

### Absorption spectra

Neither  $La^{3+}$  nor  $Lu^{3+}$  show absorption bands in the ultra-violet, visible or near infrared, but the rest do. The bands, which are narrow compared with those of the normal transition ions, move from red at  $Pr^{3+}$  to ultraviolet at  $Gd^{3+}$  and back to red again at  $Tm^{3+}$ . The energy changes involved are probably due to excitations within the 4f shell, since complexing agents, which alter the absorption spectra of normal transition ions by modifying their outer structure, have little effect on the lanthanide ions. An ion with  $n$  electrons in the 4f level generally has a similar absorption spectrum to one with  $14 - n$ , but the pairs  $Nd^{3+}$  ( $4f^3$ ),  $Er^{3+}$  ( $4f^{11}$ ), and  $Pm^{3+}$ ,  $Ho^{3+}$  are anomalous.

TABLE 107  
COLOURS OF LANTHANIDE 3+ IONS

$4f^1$	$Ce^{3+}$ (colourless)	$Yb^{3+}$ (colourless)	$4f^{13}$
$4f^2$	$Pr^{3+}$ (green)	$Tm^{3+}$ (green)	$4f^{12}$
$4f^3$	$Nd^{3+}$ (blue-violet)	$Er^{3+}$ (pink)	$4f^{11}$
$4f^4$	$Pm^{3+}$ (rose)	$Ho^{3+}$ (yellow)	$4f^{10}$
$4f^5$	$Sm^{3+}$ (cream)	$Dy^{3+}$ (cream)	$4f^9$
$4f^6$	$Eu^{3+}$ (colourless— u.v. absorption)	$Tb^{3+}$ (colourless— u.v. absorption)	$4f^8$
	$4f^7$ $Gd^{3+}$ (colourless—u.v. absorption)		

### Paramagnetism

The lanthanide ions, other than the  $4f^0$  type,  $La^{3+}$  and  $Ce^{4+}$ , and the  $4f^{14}$  type,  $Yb^{2+}$  and  $Lu^{3+}$ , are all paramagnetic, with both spin and orbital

moments (p. 87). For the  $J_0 \rightarrow J_1$  transition in  $\text{Sm}^{3+}$  and  $\text{Eu}^{3+}$ ,  $h\nu \sim kT$  and there is no simple expression for  $\mu$ , the magnetic moment, which receives contributions from some of the lower excited states of the ion as well as from the ground state. But in all other cases  $\mu$  is given to a near approximation by  $\mu = g \sqrt{J(J+1)}$  since  $h\nu$  is much greater than  $kT$ , and the Curie law is closely obeyed. The moments of isoelectronic ions ( $\text{Eu}^{2+}$ ,  $\text{Gd}^{3+}$ ,  $\text{Tb}^{4+}$  — all  $4f^7$ ) are very similar.

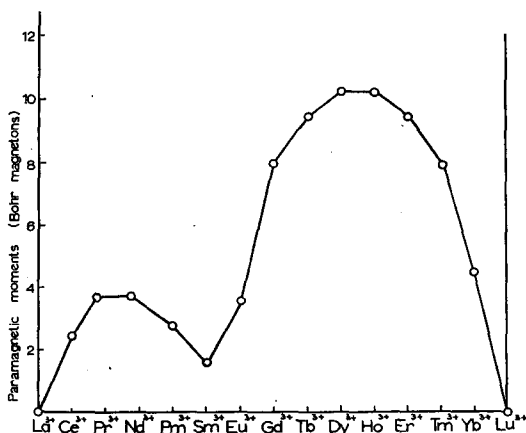
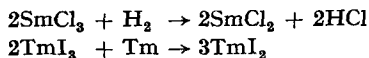


Fig. 327. Paramagnetic moments of trivalent lanthanide ions.

### Compounds of the lanthanides

#### The bivalent state

Sm, Eu, Tm and Yb form dihalides when the trihalides are reduced either with hydrogen or the metal:



In their structure the compounds usually resemble the corresponding barium compounds; for instance  $\text{SmF}_2$  and  $\text{YbF}_2$  have the fluorite structure, as has  $\text{BaF}_2$ , and  $\text{SmCl}_2$  is isostructural with  $\text{BaCl}_2$ .

Dihalides of Eu are made by reducing aqueous  $\text{Eu}^{3+}$  solutions with amalgamated zinc ( $E^\circ$ ,  $\text{Eu}^{3+}/\text{Eu}^{2+} = -0.43$  V). But all the other bivalent lanthanide ions reduce water ( $E^\circ$ ,  $\text{Sm}^{3+}/\text{Sm}^{2+} = -1.55$  V;  $E^\circ$ ,  $\text{Yb}^{3+}/\text{Yb}^{2+} = -1.15$  V)

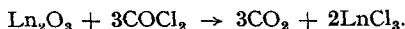
Sm, Eu and Yb have monoxides, obtained by reducing the  $\text{Ln}_2\text{O}_3$  compounds with the metal itself or with lanthanum in an inert atmosphere such

as argon at 1000–1300°. SmO and YbO have the NaCl structure. The sulphides EuS and YbS also have this structure. A sulphate  $\text{EuSO}_4$  has been made, it is isostructural with  $\text{BaSO}_4$ .

Aqueous  $\text{Eu}^{2+}$  solutions show intense, diffuse, absorption bands assigned to 4f–5d transitions.

#### *The terpositive state*

The anhydrous chlorides are best made by heating the oxides in carbonyl chloride or carbon tetrachloride vapour:



They are non-volatile, usually deliquescent, very soluble in water and fairly soluble in alcohol. They form crystalline hydrates, generally with either 6 or 7  $\text{H}_2\text{O}$  e.g.  $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ ;  $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$ . The hydrate  $\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$  has been shown to contain 8-co-ordinated, completely unsymmetrical  $[\text{Gd}(\text{H}_2\text{O})_6\text{Cl}_2]^+$  ions. This type of ion is probably rather common among hexahydrated lanthanide and actinide halides. When these hydrates are heated in air oxochlorides,  $\text{LnOCl}$ , are produced.

The hydroxides are precipitated by NaOH from solutions of  $\text{La}^{\text{III}}$  salts and are insoluble in an excess of the reagent. Like  $\text{Al}(\text{OH})_3$  they are precipitated by ammonia even in the presence of  $\text{NH}_4\text{Cl}$ . Their solubility products range from  $1.0 \times 10^{-19}$  for  $\text{La}(\text{OH})_3$  down to  $2.5 \times 10^{-24}$  for  $\text{Lu}(\text{OH})_3$ . The hydroxides are correctly formulated  $\text{Ln}(\text{OH})_3$ ; they are not hydrated oxides. Only those of the last two lanthanides, ytterbium and lutetium, show a little amphoteric character; heating with concentrated NaOH in an autoclave converts them to  $\text{Na}_3\text{Yb}(\text{OH})_6$  and  $\text{Na}_3\text{Lu}(\text{OH})_6$ . Apart from the exceptions mentioned, the hydroxides are converted into sesquioxides,  $\text{Ln}_2\text{O}_3$ , by heating in air. Lanthanum oxide, a very strong base, slakes like CaO on the addition of water and will then take up  $\text{CO}_2$ . The oxides of the other elements become progressively weaker bases as the size of the  $\text{Ln}^{3+}$  ion diminishes. The lanthanide oxides have particularly negative enthalpies of formation:

	$\text{La}_2\text{O}_3$	$\text{Pr}_2\text{O}_3$	$\text{Nd}_2\text{O}_3$	$\text{Sm}_2\text{O}_3$
$\Delta H_f$ (kcal mole <sup>-1</sup> )	–429	–427	–432	–433

The metals are therefore exceptionally strong reducing agents, comparable with the alkaline earth elements and aluminium. The oxides are refractory, but unlike  $\text{Al}_2\text{O}_3$  they dissolve in acids even after prolonged ignition. Lanthanide(III) oxides are of two structural types (p. 498):  $\text{La}_2\text{O}_3$ ,  $\text{Ce}_2\text{O}_3$ ,  $\text{Pr}_2\text{O}_3$  and  $\text{Nd}_2\text{O}_3$  are A-type oxides, the rest are C-type.

Normal carbonates of the lanthanides can be precipitated from solutions of  $\text{Ln}^{\text{III}}$  salts by  $\text{NaHCO}_3$ ; in this behaviour the lanthanides resemble magnesium. Many of the carbonates form hydrates. The carbonates are soluble in alkali-metal carbonate solutions, and compounds such as  $\text{K}_2\text{CO}_3 \cdot \text{Ce}_2(\text{CO}_3)_3 \cdot 3\text{H}_2\text{O}$  have been crystallised.

The nitrates are very soluble indeed and form double nitrates with magnesium,  $3\text{Mg}(\text{NO}_3)_2 \cdot 2\text{Ln}(\text{NO}_3)_3 \cdot 24\text{H}_2\text{O}$ ; these were formerly used for separations within this series of elements. Their solubilities increase with molecular weight.

The sulphates do not form alums. Small ions such as  $\text{Al}^{3+}$  ( $r = 0.50 \text{ \AA}$ ) can be surrounded octahedrally by six  $\text{H}_2\text{O}$  molecules, but the lanthanide ions ( $r > 0.85 \text{ \AA}$ ) are too large to co-ordinate water molecules in this way. Nevertheless there are many double sulphates,  $(\text{NH}_4)_2\text{SO}_4 \cdot \text{Ln}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$  being the commonest type.

The solubilities of lanthanide compounds resemble closely those of the Group IIA metals, as the following shows for a number of them.

Considerable solubility  $\text{LnCl}_3$ ,  $\text{LnBr}_3$ ,  $\text{LnI}_3$ ,  $\text{Ln}(\text{NO}_3)_3$ ,  $\text{Ln}(\text{ClO}_4)_3$ ,  $\text{LnAc}_3$ .  
 Low solubility  $\text{Ln}_2\text{O}_3$ ,  $\text{Ln}(\text{OH})_3$ ,  $\text{Ln}_2(\text{O}\bar{\text{X}})_3$ ,  $\text{Ln}_2(\text{CO}_3)_3$ ,  $\text{LnPO}_4$ ,  $\text{LnF}_3$ .  
 Variable solubility  $\text{Ln}_2(\text{SO}_4)_3$ .

#### *The quadripositive state*

With the exception of  $\text{Ce}^{3+}$ , the  $\text{Ln}^{3+}$  ions resist oxidation in aqueous solution. The standard redox potential of the  $\text{Ce}^{4+}/\text{Ce}^{3+}$  couple varies greatly with the nature of the anion present.

TABLE 108  
STANDARD REDOX POTENTIALS IN DIFFERENT MEDIA

<i>Medium</i>	$E^\circ, \text{Ce}^{4+}/\text{Ce}^{3+}$
HCl	+1.28 V
$\text{HNO}_3$	+1.61 V
$\text{HClO}_4$	+1.70 V

The figures suggest that the simple  $\text{Ce}^{4+}$  ion does not exist in aqueous solution, and the variations in redox potential seem too great to be caused merely by differences in its hydration. Because of its considerable charge and moderate size ( $r = 1.01 \text{ \AA}$ ), the ion has appreciable polarising power and may well form complexes with suitable anions.

The  $4+$  ion also occurs with praseodymium and terbium, but only in solids made by dry methods. When their nitrates, carbonates or hydroxides are



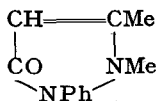
heated in air the final products are empirically  $\text{Pr}_6\text{O}_{11}$  and  $\text{Tb}_4\text{O}_7$ ; the corresponding cerium compounds give  $\text{CeO}_2$ . Pure  $\text{PrO}_2$  is made by heating the  $\text{Pr}_6\text{O}_{11}$  to  $300^\circ$  under 50 atmospheres of oxygen. The oxide  $\text{TbO}_2$ , has been made by treating  $\text{Tb}_2\text{O}_3$  with atomic oxygen at  $450^\circ$ . The dioxides  $\text{TbO}_2$ ,  $\text{PrO}_2$  and  $\text{CeO}_2$  have fluorite lattices;  $\text{Pr}_6\text{O}_{11}$  has a defect lattice in which one-twelfth of the oxygen positions of the  $\text{PrO}_2$  lattice are empty. Dark colour is often associated with defect lattices of this type; thus  $\text{Pr}_6\text{O}_{11}$  is black and  $\text{Tb}_4\text{O}_7$  brown.

Of the tetrafluorides,  $\text{CeF}_4$  and  $\text{TbF}_4$  can be made by direct fluorination of the trifluorides.  $\text{PrF}_3$  cannot be directly fluorinated, but fluorine converts it to  $\text{PrF}_4$  in the presence of about 10% of cerium fluoride.

Fluorocomplexes of  $\text{Ce}^{\text{IV}}$  and  $\text{Pr}^{\text{IV}}$  are known: colourless, diamagnetic  $\text{M}_3\text{CeF}_7$  and  $\text{M}_3\text{CeF}_6$  ( $\text{M} = \text{Na}, \text{Rb}, \text{Cs}$ ) are made by fluorinating  $\text{MCl}$  mixed with  $\text{CeO}_2$ . Fluorinating  $\text{Pr}^{\text{III}}$  salts mixed with alkali-metal fluorides gives such compounds as  $\text{NaPrF}_5$ ,  $\text{Na}_2\text{PrF}_6$  and  $\text{K}_2\text{PrF}_6$ . There is some evidence for  $\text{Cs}_3\text{NdF}_7$ . The chlorocomplexes  $\text{Rb}_2\text{PrCl}_8$  and  $\text{Cs}_2\text{PrCl}_8$  have been made.

### Complexes

In spite of a high charge, the ions are too large to cause much polarisation and relatively few complexes are formed. Complexes with unidentate ligands are uncommon; there are a few fluorocomplexes, and the compound anti-pyrine (Ap):

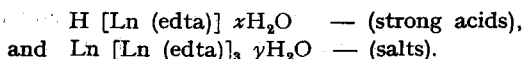


forms complexes of the type  $[\text{LnAp}_6]\text{X}_3$  ( $\text{X} = \text{Cl}, \text{NO}_3, \text{ClO}_4, \text{I}$ ) with several lanthanides, the methyl-substituted nitrogen being almost certainly the donor atom.

Complexes with chelating ligands such as oxine and various  $\beta$ -diketones are more common. Three types of ethylenediaminetetra-acetic acid (p. 333) complexes have been described (edta = the  $\{[\text{CH}_2\text{N}(\text{CH}_2\text{CO}_2)_2]_2\}^{4-}$  ion):

- (i)  $\text{HLn}(\text{edta})$
- (ii)  $\text{Ln}_4(\text{edta})_3$
- (iii)  $\text{NaLn}(\text{edta})$

Lanthanide oxides react with the acid to give (i) and (ii), these have been formulated as

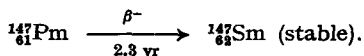


The addition of NaOH gives  $\text{Na}[\text{Ln}(\text{edta})]3\text{H}_2\text{O}$ . Evidence from X-ray diffraction, pH titration and ion migration studies suggests that in the  $[\text{Ln}(\text{edta})]^-$  ion the ethylenediaminetetra-acetate occupies only five coordination positions and possesses one uncomplexed  $-\text{COO}-$  group.

### Promethium

Discovery of the sequence of atomic numbers showed that there are 14 possible lanthanides. Attempts to find element 61, promethium, which lies between Nd and Sm, in natural occurrence have been unsuccessful because there is apparently no stable isotope.

Promethium-147 was separated by ion exchange from products of the slow-neutron fission of  $^{235}\text{U}$ , which contain 2.6% of the isotope. It is the one of longest half-life (2-3 years), and emits a soft  $\beta$  radiation (0.23 MeV) but no  $\gamma$  rays:



The same nuclide results from an  $(n,\gamma)$  reaction on  ${}_{60}^{146}\text{Nd}$  in the pile, followed by  $\beta^-$  emission from the  ${}^{147}\text{Nd}$  formed:



Though its specific activity is fairly high, the low  $\beta$  energy and the absence of  $\gamma$  radiation make it fairly safe to handle and chemical studies are possible. The chloride and nitrate have been made in mg amounts; their solutions are pink.

## SCANDIUM AND YTTRIUM

These elements are respectively the first *outer transition* elements of Periods 4 and 5 in the first of which the 3d electronic shell of the elements are filled, and in the second the 4d electronic shell. Their outermost electrons have a similar pattern to the corresponding electrons of the lanthanides and their properties greatly resemble those of the lanthanides. For this reason these elements of Group IIIA are included in this chapter.

### Scandium

Its  $3d^1 4s^2$  structure gives element 21 properties similar to the lanthanides and to lanthanum ( $5d^1 6s^2$ ) in particular. The covalent and ionic radii, 1.44 Å and 0.81 Å, respectively, are however much smaller than those of the lantha-

nides. In consequence the  $\text{Sc}^{3+}$  ion has a greater polarising power and more readily forms complexes: for instance crystalline  $\text{K}_3\text{ScF}_6$  can be obtained. The ionisation energies 1st, 6.56 eV; 2nd, 12.9 eV; 3rd, 24.8 eV are not much larger than those of the lanthanides so far as they are known, and the metal itself is almost as reactive.

Scandium is present in some of the lanthanide minerals, but thortveitite,  $\text{ScSi}_2\text{O}_7$ , is the usual source. The metal is made by the electrolysis of a fused mixture of  $\text{ScCl}_3$ ,  $\text{KCl}$  and  $\text{LiCl}$  on a zinc cathode followed by volatilisation of the Zn at low pressure from the Zn-Sc alloy so formed. The metal is dimorphous, with f.c.c. and h.c.p. forms. Its m.p. is rather high,  $\sim 1400^\circ$ .

Some important differences between scandium and the lanthanides are

- (i) scandium oxide is a weaker base,
- (ii) the chloride is more volatile,
- (iii) the nitrate,  $\text{Sc}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$ , is more easily decomposed by heat;
- (iv) the sulphate,  $\text{Sc}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ , is very soluble in both cold and hot water.
- (v) the chelate complexes with acetylacetonate and oxinate are more covalent in type than those of the lanthanides. Thus  $\text{Sc}(\text{acac})_3$  can be sublimed without decomposition; similar lanthanide acetylacetonates decompose at about  $200^\circ$ . Scandium oxinate is extracted almost quantitatively from aqueous solution by carbon tetrachloride in a single operation, again unlike the lanthanide oxinates.

Recently  $\text{Sc}^0$  and  $\text{Y}^0$  compounds,  $\text{Sc}(\text{dipy})_3(\text{THF})_3$  and  $\text{Y}(\text{dipy})_3(\text{THF})_3$  have been obtained by reducing the trichlorides with lithium in tetrahydrofuran (THF) containing 2,2'-dipyridyl.

## Yttrium

Element 39, with  $4d^1 5s^2$  electron configuration, is also similar to the lanthanides. It occurs with the lanthanides in minerals; the best source is xenotime,  $\text{YPO}_4$ . Yttrium has properties approximately midway between those of Sc and La; its compounds also resemble those of the heavy earths dysprosium and holmium, the ionic radius (0.90 Å) being similar.

## FURTHER READING

- N. E. TOPP, *Chemistry of the Rare-Earth Elements*, Amsterdam, Elsevier, 1965.  
F. H. SPEDDING AND A. M. DAANE (Eds.), *The Rare Earths*, New York, Wiley, 1961.  
R. C. VICKERY, *Chemistry of the Lanthanons*, London, Academic Press, 1953.  
M. D. TAYLOR, *Anhydrous Lanthanone Halides*, Chem. Rev., 62 (1962) 503.

Chapter 33

## The Actinides

Until the properties of neptunium and plutonium became known (1941), actinium, thorium, protactinium and uranium were treated as the last members of Sub-groups IIIA, IVA, VA and VIA respectively. There were chemical reasons for this: uranium forms complexes indicating variable charge and a particularly stable  $6+$  oxidation state which is typical of molybdenum and tungsten; and thorium nearly always occurs in a  $4+$  oxidation state. Thus they seemed to fit into Groups VI and IV. The existence of actinium(III) salts and their isomorphism with those of lanthanum, suggested membership of Group III. Very little was known of the properties of protactinium.

However, with the production of neptunium by McMillan (1940) and of plutonium and further trans-uranic elements by Seaborg and others (1944 to present), evidence for a different classification has accumulated. The similarity of the elements actinium and its successors to lanthanum and its successors became increasingly apparent. Actinium to mendelevium are indeed

TABLE 109  
ELECTRON CONFIGURATION OF THE ACTINIDES

		<i>Atomic no. (Z)</i>	<i>Probable electron configuration</i>	
Actinium	Ac	89	$6d^1$	$7s^2$
Thorium	Th	90	$6d^2$	$7s^2$
Protactinium	Pa	91	$5f^2$	$6d^1$ $7s^2$
Uranium	U	92	$5f^3$	$6d^1$ $7s^2$
Neptunium	Np	93	$5f^4$	$6d^1$ $7s^2$
Plutonium	Pu	94	$5f^6$	$7s^2$
Americium	Am	95	$5f^7$	$7s^2$
Curium	Cm	96	$5f^7$	$6d^1$ $7s^2$
Berkelium	Bk	97	$5f^9$	$7s^2$
Californium	Cf	98	$5f^{10}$	$7s^2$
Einsteinium	Es	99	$5f^{11}$	$7s^2$
Fermium	Fm	100	$5f^{12}$	$7s^2$
Mendelevium	Md	101	$5f^{13}$	$7s^2$

a closely related family and known as the *actinides* (*cf.* the lanthanides which begin thirty-two places earlier in the Periodic Table).

The actinides are characterised by the

- (i) increasing stability of the 3+ ion with atomic number;
- (ii) isomorphism of trichlorides, dioxides and many salts with corresponding lanthanide compounds;
- (iii) decrease in ionic radii with atomic number, analogous to the lanthanide contraction;
- (iv) character of the absorption spectra of the ions;
- (v) magnetic moments of the ions.

All the actinides are believed to have the outer electron configuration  $7s^2$  and to vary irregularly in the electron occupation of the 5f and 6d shells (Table 109).

### Ionic radii

TABLE 110

IONIC RADII OF THE ACTINIDES

	<i>Ac</i>	<i>Th</i>	<i>Pa</i>	<i>U</i>	<i>Np</i>	<i>Pu</i>	<i>Am</i>	<i>Cm</i>
$M^{3+}(\text{Å})$	1.11	—	—	1.03	1.01	1.00	0.99	0.98
$M^{4+}(\text{Å})$	—	0.99	0.96	0.93	0.92	0.90	0.89	—

These ionic radii, derived from X-ray diffraction data, should be compared with those of the lanthanides (p. 605). The size of an ion depends largely upon the quantum number of the outermost electrons and the effective nuclear charge (p. 70). In the 3+ ions of these elements the outermost electrons are in a completed 6p shell; the effective nuclear charge rises with atomic number because the screening effect of extra electrons in the 5f level fails to compensate entirely for the increased nuclear charge. Thus there is a contraction in the size of the ions, similar to the lanthanide contraction, from actinium to mendelevium. The contraction is, however, greater from element to element in the actinides.

### Occurrence and separation of the metals

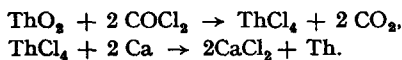
#### *Thorium*

The principal source of thorium is monazite (p. 607), a phosphate of cerium and lanthanum with up to 15% of thoria. It is dissolved in concentrated sulphuric acid and the thorium phosphate is precipitated with magnesium oxide. The washed phosphate heated with sodium carbonate gives crude

thoria,  $\text{ThO}_2$ , which is converted to the soluble oxalate and separated from the insoluble oxalates of cerium and lanthanum. After ignition of the oxalate to oxide the nitrate is made, purified by recrystallisation, and again calcined to thoria.

An alternative separation of thoria, based on the low solubility of lanthanides in a mixture of phosphoric and sulphuric acids, is to treat monazite at  $225^\circ$  with concentrated sulphuric acid and to leave most of the lanthanide sulphates behind by extracting the semi-solid mass with water. The crude thorium sulphate is crystallised by concentrating the liquor, washed with cold concentrated sulphuric acid to remove phosphoric acid and redissolved in 25% sulphuric acid. The solution of the sulphate is boiled with ammonium carbonate to precipitate basic thorium carbonate. This is washed with a very little dilute nitric acid and calcined to thoria.

The pure uncontaminated metal is difficult to obtain because it readily combines with hydrogen, oxygen, nitrogen and carbon. In bulk, the metal is best made by preparing the tetrachloride,  $\text{ThCl}_4$ , by heating thoria in phosgene, and reducing the tetrachloride with calcium:

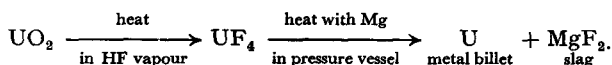


The metal may be purified (especially from  $\text{ThO}_2$ ) by the iodine method which has a fairly wide application to heavy metals. The crude metal powder is converted, by heating it in iodine vapour, to volatile  $\text{ThI}_4$ . The  $\text{ThI}_4$  vapour is dissociated to metal and iodine on a hot filament ( $1100\text{--}1200^\circ$ ), the liberated iodine being recirculated to react with more crude metal.

### *Uranium*

Uranium is extracted from pitchblende, essentially  $\text{U}_3\text{O}_8$ . The ore is washed, then fused with sodium carbonate and sodium nitrate. From the mass, dilute sulphuric acid extracts uranyl sulphate,  $\text{UO}_2\text{SO}_4$ . The addition of ammonium carbonate enables ammonium uranyl carbonate,  $(\text{NH}_4)_4\text{UO}_2(\text{CO}_3)_3$ , to be crystallised which, on ignition, yields pure  $\text{U}_3\text{O}_8$ .

Uranium is separated from low-grade ores by treating them in dilute sulphuric acid with manganese dioxide which, in spite of its insolubility, is able to oxidise  $\text{U}^{\text{IV}}$  to  $\text{U}^{\text{VI}}$  in the presence of 0.4 g/l of an iron salt. The uranium forms the soluble complex anion  $[\text{U}^{\text{VI}}(\text{SO}_4)_6]^{4-}$ . This is strongly and selectively absorbed on an anion exchange resin, by means of which it can be effectively separated from other ions. The uranium may be eluted from the resin with a solution of almost any salt other than a sulphate. Nitrates are best and give a liquor containing, typically, 20 g/l  $\text{UO}_2(\text{NO}_3)_2$ . From this  $\text{UO}_2$  is obtained by evaporation and ignition.



### *Plutonium*

The element occurs in pitchblende to the extent of about  $10^{-11}$  of the uranium present. The quantity, though extremely small, is nevertheless too high to be accounted for by neutrons from the  $^{235}\text{U}$  present acting on  $^{238}\text{U}$ . The extra neutrons required may result from  $(\alpha, n)$  reactions on the lighter elements present.

The production of plutonium and its separation from uranium are described below. The metal is obtained (*cf.* uranium) by the reduction of  $\text{PuF}_4$  with calcium.

## Transuranic elements from the nuclear reactor

### *The nuclear reactor*

An air-cooled graphite pile consists essentially of a stack of blocks of very pure graphite through which run many parallel channels arranged in a pattern calculated to make the most effective use of the available neutrons. In the channels are placed metallic uranium slugs sealed in magnox or steel cylinders and through the channels is blown cooling air. To control the neutron flux, rods of cadmium or other materials which absorb neutrons are automatically inserted into or withdrawn from the pile, and thus the power output is governed. A thick shield of concrete surrounds the pile.

Research reactors have openings through which materials for irradiation may be introduced and placed in a required neutron flux. Through others the graphite protrudes to form a 'thermal column' which makes the slower, 'thermal' neutrons available for experimental use. Both types of opening in the concrete are suitably shielded with cadmium and lead.

### *Plutonium*

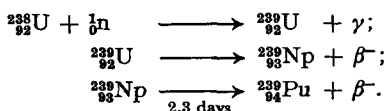
The element is produced almost entirely from uranium in the nuclear reactor.

The sequence of nuclear changes is:

1. A single neutron is absorbed by a  $^{235}\text{U}$  nucleus and causes instability leading to
  - (i) fission fragments which lose most of their kinetic energy in the uranium metal itself,
  - (ii)  $\gamma$ -rays which are absorbed mainly by the structure and shielding,
  - (iii) fast neutrons with energies of 0.5 to 1 MeV.
2. The fast neutrons lose energy by every collision with a carbon nucleus; they are thus continuously retarded and deflected back as slower neutrons into the uranium rods.

3. As the neutrons slow down their chance of capture increases. They are captured (i) by the structural materials of the pile and lost to the process; (ii) by the  $^{238}\text{U}$ , through resonance absorption, leading to the production of  $^{239}\text{Pu}$ ; and (iii) by the  $^{235}\text{U}$  ( $\sim 0.7\%$  of natural uranium) leading to fissions which generate about 2.5 fresh neutrons for every neutron captured. The geometry of the pile ensures that one of the fresh neutrons is captured by another  $^{235}\text{U}$ , thus maintaining a steady rate of fission of these nuclei and a steady neutron flux.

The sequence of nuclear reactions leading to the formation of  $^{239}_{94}\text{Pu}$  is:

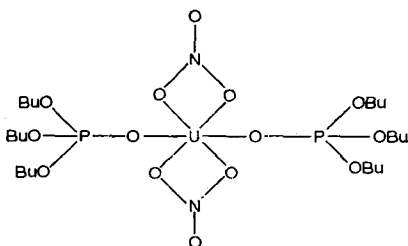


The nuclide  $^{239}_{94}\text{Pu}$  is an  $\alpha$ -emitter with a half-life of  $2.4 \times 10^4$  years.

Accumulation in the uranium of fission products, many of which absorb neutrons strongly, would eventually reduce the neutron flux below the intensity required to maintain the nuclear chain reaction. Accordingly the uranium is removed after a certain period and processed chemically, caesium-137, strontium-90 and the plutonium being extracted.

#### *Large-scale separation of plutonium*

One method for separating plutonium from uranium and from fission products makes use of the viscous liquid tributyl phosphate (TBP) dissolved in a water-insoluble organic solvent. Uranyl and plutonyl nitrates are extracted from aqueous nitric acid by solvent extraction with purified kerosene containing TBP. The nitrates go into solution as  $\text{MO}_2(\text{NO}_3)_2 \cdot 2\text{TBP}$  complexes:



in which the nitrate groups behave as bidentate ligands. The fission products remain in the aqueous phase.

The uranium- and plutonium-loaded kerosene is separated from the aqueous phase and washed with  $0.1M$   $\text{HNO}_3$  containing a reducing agent. The





column on which was poured 0.1 ml of a solution of transuranic elements in 0.05 M HCl. Elution with 0.4 M ammonium citrate, or ammonium  $\alpha$ -hydroxybutyrate, gave peaks of activity; the order of removal of the respective  $3^+$  ions was the reverse of their atomic number (Fig. 328). In this way einsteinium, element 99 (1952), fermium, element 100 (1954) and mendeleevium, element 101 (1955) were separated by Seaborg and his collaborators. The nuclide  $^{255}_{101}\text{Md}$  which undergoes spontaneous fission has a half-life of 3.5 hours. That this process could be studied so effectively on a sample consisting of 17 atoms gives an idea of the powerful experimental methods now available. More recently, elements 102 and 103 have been identified.

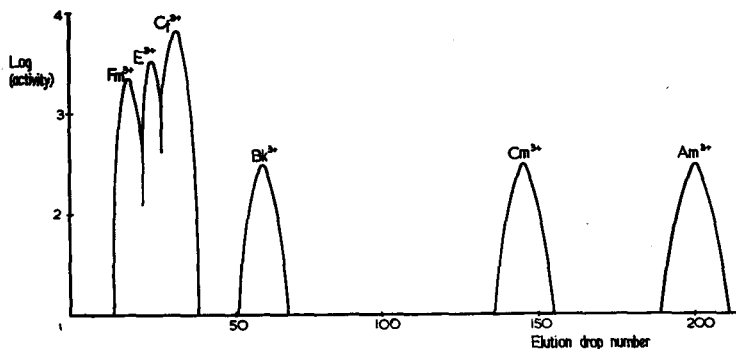


Fig. 328. Order of elution of trans-plutonium terpositive ions.

### The metals

The actinides are base metals which require the reduction of a chloride or fluoride with sodium or barium for their separation. Neptunium, for example, has been made by reducing its trifluoride with barium vapour at  $1200^\circ$ . Such drastic methods are needed because the heats of formation of the  $M^{4+}$  ions are as much as three times greater than that of the  $Pt^{4+}$  ion.

#### Physical properties

The metals are silvery white and all, except thorium and americium, have high densities.

TABLE 111  
PROPERTIES OF THE ACTINIDES

	<i>Ac</i>	<i>Th</i>	<i>Pa</i>	<i>U</i>	<i>Np</i>	<i>Pu</i>	<i>Am</i>	<i>Cm</i>
Melting point ( $^\circ\text{C}$ )	1100	1750	< 1600	1132	637	639	995	1340
Density ( $\text{g cm}^{-3}$ )		11.7	15.4	19.0	20.5	19.7	13.7	
Atomic volume		19.8	14.7	12.6	11.6	12.1	18.0	

The densities given in Table 111 are for the forms stable at room temperature. The metals Pa, U, Np and Pu have more complex crystal structures than the corresponding lanthanides. Plutonium assumes six different allotropic forms between room temperature and its melting point. Incidentally, there is not one of these phases for which the temperature coefficients of expansion and electrical resistance are both positive. Indeed plutonium is a most unusual metal.

The sudden increase in atomic volume at americium is interesting and paralleled by a similar increase at the corresponding lanthanide, europium.

### *Chemical properties*

The elements are reactive chemically. For the  $M^{3+}/M$  couples  $E^\circ$  values are about  $-1.9V$ . The metals tarnish in air; and in it finely divided thorium burns spontaneously. Larger pieces of the metal are attacked rapidly by oxygen at  $250^\circ$ , by nitrogen at  $800^\circ$ , and by boiling water. Hydrochloric and sulphuric acids react slowly, and nitric acid renders the metal passive.

Uranium ignites spontaneously in fluorine and, at about  $250^\circ$ , in chlorine, bromine and iodine vapour. It combines with sulphur at  $500^\circ$  and nitrogen at  $1000^\circ$ . The metal dissolves readily in hydrochloric and sulphuric acids giving  $U^{IV}$  salts; but nitric acid renders the metal passive.

### **Oxidation states**

Table 112 can usefully be compared with that giving the charge numbers associated with the lanthanides (p. 605). The comparison suggests that the 5f electrons are more easily removed than the 4f electrons. The spectra of actinide ions suggest that only ions with a charge greater than  $+3$  have 5f electrons outside the radon shell. It has been held that there is no necessary connexion between the presence of f electrons and the dominant  $+3$  charge number. This is relevant in view of other oxidation states which have been found for the lanthanides (p. 611). The most common ion in both series is  $3+$ , once thought to be the only charge displayed by curium, and still the only

TABLE 112  
OXIDATION STATES SHOWN BY ACTINIDES

<i>Ac</i>	<i>Th</i>	<i>Pa</i>	<i>U</i>	<i>Np</i>	<i>Pu</i>	<i>Am</i>	<i>Cm</i>	<i>Bk</i>	<i>Cf</i>
3	(3)	(3)	3	3	3	3	3	3	3
	4	4	4	4	4	(4)	(4)	4	
		(5)	(5)	(5)	(5)	(5)			
			(6)	(6)	(6)	(6)			

one shown by gadolinium, the corresponding lanthanide. The charge numbers shown in parentheses (Table 112) do not occur in simple hydrated ions in solution.

The oxo-ions containing  $M^{VI}$  are  $UO_2^{2+}$ ,  $NpO_2^{2+}$  and  $PuO_2^{2+}$  and those containing  $M^V$  are  $UO_2^+$ ,  $NpO_2^+$  and  $PuO_2^+$ .

The free energies of the oxidation state of elements 90–95, relative to the metal, calculated from redox potentials in aqueous solution at  $pH = 0$ , are shown in Fig. 329.

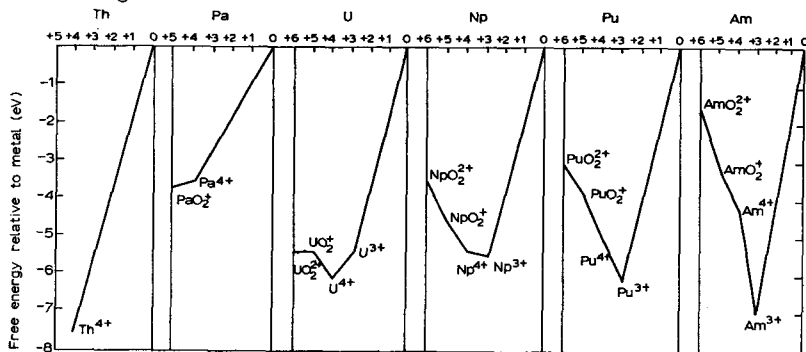
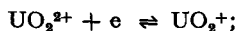


Fig. 329. Stabilities of oxidation states, elements 90–95. Free energies (eV) relative to the metal in aqueous solution at  $pH = 0$ .

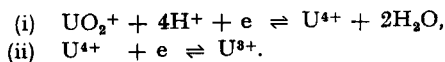
In all known compounds, actinium appears as  $Ac^{3+}$  with the radon structure, the hydrated ion occurring in aqueous solution of its salts. Thorium chemistry is dominated by the +4 state and the  $Th^{4+}$  ion is well characterised. Lower oxidation states have been reported for the iodides ( $ThI_3, ThI_2$ ), but their precise nature is uncertain and they do not alter the essential picture of the aqueous chemistry of thorium. This in many respects bears a closer resemblance to the chemistry of hafnium than to its lanthanide analogue, cerium. But, although the  $ThO^{2+}$  ion, occurs, it has less chemical importance than the zirconyl and hafnyl ions (p. 643).

Protactinium forms the ions  $Pa^{4+}$  and  $PaO_2^+$ ; the former is stable to disproportionation.

Uranium forms stable uranyl salts which give the  $UO_2^{2+}$  ion in solution, as indicated by absorption and Raman spectra. Polarographic reduction of a uranyl salt gives (a) a first stage at a half-wave potential little affected by acidity, presumably representing a simple electron transfer:



(b) a second wave, with an inflexion at half its height, which is irregular below this point and logarithmic above it, indicating a stepwise reduction:



In support of this view, the reduction of  $\text{U}^{\text{IV}}$  at a mercury cathode is reversible, whereas that of  $\text{U}^{\text{V}}$  is irreversible, and also heavily dependent on the hydrogen ion concentration. Solutions containing both  $\text{UO}_2^+$  and  $\text{U}^{3+}$  ions undergo rapid oxidation in air, as is to be expected from the redox potentials.

Neptunium gives a series of reactions analogous to those of uranium, but the stabilities of individual ions are different; thus, for instance,  $\text{NpO}_2^+$  is particularly stable relative to  $\text{NpO}_2^{2+}$ . A reagent as powerful as cerium(IV) sulphate is required to oxidise  $\text{NpO}_2^+$  to  $\text{NpO}_2^{2+}$ . Furthermore, the disproportionation of the  $\text{NpO}_2^+$  ion occurs only very slowly in solution:

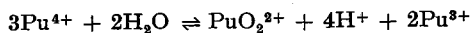


In this equilibrium, the product of the concentrations  $[\text{NpO}_2^{2+}]$  and  $[\text{Np}^{4+}]$  is only about 0.025 of  $[\text{NpO}_2^+]^2$  at 25°.

Plutonium also forms a similar series of cations. In solution, the  $\text{Pu}^{3+}$  ion is not oxidised by air.  $\text{PuO}_2^{2+}$  ions behave similarly to  $\text{UO}_2^{2+}$  ions when reduced at a dropping mercury cathode. The readily crystallised complexes, sodium plutonylacetate,  $\text{Na}[\text{PuO}_2\text{Ac}_3^-]$ , sodium uranylacetate,  $\text{Na}[\text{UO}_2\text{Ac}_3^-]$ , and sodium neptunylacetate,  $\text{Na}[\text{NpO}_2\text{Ac}_3^-]$ , are isomorphous. The +5 state of plutonium is much less stable than that of neptunium, a well-defined compound of  $\text{PuO}_2^+$  being unknown. Disproportionation occurs at all acidities:



Because the redox potentials for the couples  $\text{Pu}^{\text{IV}}/\text{Pu}^{\text{III}}$  and  $\text{Pu}^{\text{V}}/\text{Pu}^{\text{IV}}$  are about the same in solutions of moderate acidity, the 6+, 4+ and 3+ ions can coexist in about the same concentrations:



This is indicated in the free-energy diagram (Fig. 329) by the almost straight line through the free energies of the  $\text{Pu}^{\text{VI}}$ ,  $\text{Pu}^{\text{IV}}$  and  $\text{Pu}^{\text{III}}$  states.

The diagram for americium brings out particularly the extreme stability of the  $\text{Am}^{3+}$  state. This is shown by the very steep gradients of the lines to either side of it: for  $\text{Am}^{3+}/\text{Am}$   $E^\circ = -2.3$  V and for  $\text{Am}^{4+}/\text{Am}^{3+}$   $E^\circ = +2.7$  V. Thus  $\text{Am}^{3+}$  is not oxidised even by  $\text{Ag}^{2+}$  ions in nitric acid but is oxidised by ozone at a higher pH; moreover it is not reduced by zinc amalgam but is reduced by sodium amalgam. The corresponding  $\text{Cm}^{3+}$  ion is, however, unaffected by the reagents mentioned which either oxidise or reduce  $\text{Am}^{3+}$ .

Although the outermost electrons in the actinides are apparently more readily available for bonding than those in the lanthanides, even  $M^{VI}$  compounds occurring, the tendency to form  $M^{III}$  compounds increases with atomic number. Redox potentials indicate that this trend is greater than in the lanthanides. The fact that curium (III) is dominant (*cf.* gadolinium in the lanthanides), and that berkelium gives also  $Bk^{IV}$ , lends support to the suggestion that each of these states has a half-filled  $5f$  shell with its characteristic stability.

### Oxides, hydroxides and oxosalts

For the actinide series up to curium, moderate heating of the nitrate yields the dioxide, except for uranium ( $UO_3$ ), protactinium ( $Pa_2O_5$ ), and actinium ( $Ac_2O_3$ ). Orange-red  $UO_3$  decomposes at  $700^\circ$  to give black  $U_3O_8$ . The dioxide  $UO_2$  is made by the reduction of  $U_3O_8$  with  $CO$ . The dioxides have the fluorite structure. Curium has a white oxide,  $Cm_2O_3$ , and plutonium and americium form similar compounds. The neptunium oxide,  $Np_3O_8$ , corresponding to  $U_3O_8$ , is made by the action of  $NO_2$  at  $\sim 300^\circ$  on the hydroxide precipitated from  $Np^V$  or  $Np^{VI}$  solutions. For plutonium,  $PuO_2$  is the highest oxide yet produced. Non-stoichiometric phases (p. 215) are common among the actinide oxides.

The addition of ammonia to separate solutions of  $Np$ ,  $Pu$  and  $Am$  salts precipitates  $Np(OH)_4$ , a mixture of  $Pu(OH)_4$  with  $Pu(OH)_3$ , and  $Am(OH)_3$  respectively. Only for the actinides beyond plutonium is the tri-hydroxide,  $M(OH)_3$ , sufficiently stable to be isolated.

Both uranium(VI) and plutonium(VI) form oxoanions. Uranium gives mono-, di-, tri-, tetra-, penta- and hexa-uranates; the common diuranates,  $M_2U_2O_7$ , correspond only formally to the dichromates. Barium hydroxide precipitates the triplutonate,  $BaPu_3O_{10}$ , from solutions containing  $PuO_2^{2+}$ .

### Halides

Uranium hexafluoride is important because it is used to separate  $^{235}U$  from  $^{238}U$  by means of the diffusion of this compound. The pale yellow crystals melt at  $69^\circ$  under 2 atmospheres pressure and have a vapour pressure of 760 mm at  $56^\circ$ , so that they are very easily sublimed. The hexafluoride is made by the action of fluorine on the metal in the presence of some chlorine; otherwise  $UF_4$  is formed. Fluorination by chlorine trifluoride is also employed.  $UF_6$  is stable to air, oxygen, chlorine and iodine, but is easily hydrolysed and readily reduced to the tetrafluoride by hydrogen at the ordinary temperature. The molecule is octahedral and the dipole

moment zero. The hexafluorides of neptunium and plutonium, the first orange and the second dark brown, have a similar molecular structure.

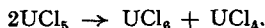
The uranyl halides  $UO_2X_2$  are very stable, being salts of the  $UO_2^{2+}$  ion and not covalent molecules like  $SO_2Cl_2$  and  $CrO_2Cl_2$ . There are corresponding neptunium and plutonium compounds.

TABLE 113  
THE HALIDES OF SOME ACTINIDES

	<i>Ac</i>	<i>Th</i>	<i>U</i>	<i>Np</i>	<i>Pu</i>	<i>Am</i>	<i>Cm</i>
VI			$UF_6, UCl_6$	$NpF_6$	$PuF_6$		
V			$UF_5, UCl_5$	—			
IV		$ThX_4$	$UX_4$	$NpF_4, NpCl_4, NpBr_4$	$PuF_4$	$AmF_4$	$CmF_4$
III	$AcF_3, AcCl_3, AcBr_3$		$UX_3$	$NpX_3$	$PuX_3$	$AmX_3$	$CmF_3$
II	—		—	—	—	—	—

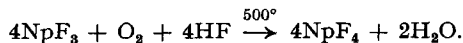
X = F, Cl, Br and I.

Substances empirically represented by  $UF_5$  and  $UCl_5$  are known but not their structures.  $UCl_5$  disproportionates readily:



Thorium appears with certainty only in the +4 state in its halides. The tetrahalides are all obtainable in the anhydrous condition and all, except the fluoride, can be sublimed in a vacuum without decomposition. The hydrated fluoride is insoluble in dilute acid; the rest are soluble in acid and hydrolysed by water.

The crystalline tetrahalides of uranium are all stable and are the normal result of either direct union of the elements or action of the halogen acid on the metal. Neptunium tetrafluoride, a pale green solid, is also known:



The corresponding chloride and bromide are made by heating the dioxide with carbon tetrachloride and aluminium bromide respectively. The only tetrahalide of plutonium yet isolated is the fluoride,  $PuF_4$ , although the tetrachloride appears to exist in solution. Americium forms a tetrafluoride and also a complex fluoride,  $KAmF_5$ .

With the exception of thorium, the actinides form trihalides. For uranium and neptunium, reduction of the  $MX_4$  compounds with hydrogen is

necessary, but for the elements from plutonium onwards the action of the carbon tetrahalide or aluminium halide on the dioxide is usually employed. The trifluorides are insoluble but the rest dissolve to give solutions containing  $M^{3+}$  ions.

A golden, diamagnetic compound, empirically  $ThI_2$ , is obtained by heating  $ThI_4$  with thorium at  $800^\circ$ . The structure is unknown, but the material is unlikely to be a true  $Th^{II}$  compound.

### Other compounds

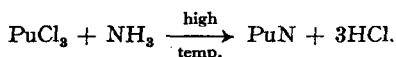
The sulphides are made by dry methods and are all compounds of lower charge number.

The disulphides of thorium and uranium are essentially covalent compounds; but materials of the formula  $M_2S_3$  appear to be semi-metallic, except for  $Pu_2S_3$  which is covalent. This again emphasises the increasing stability of compounds with the charge number +3 as the atomic number increases. Some of the sulphides, notably  $US$ , can be used as refractories.

TABLE 114  
SULPHUR COMPOUNDS OF SOME ACTINIDES

<i>Ac</i>	<i>Th</i>	<i>U</i>	<i>Np</i>	<i>Pu</i>
	ThS	US		
$Ac_2S_3$	$Th_2S_3$	$U_2S_3$	$Np_2S_3$	$Pu_2S_3$
		UOS	$NpOS$	
	$ThS_2$	$US_2$		

Plutonium, like uranium, forms both a mononitride and a monocarbide; all have the sodium chloride structure:



The hydrolysis of uranium monocarbide,  $UC$ , yields hydrated  $UO_2$  and a gas containing 85%  $CH_4$ , 11%  $H_2$  and some  $C_2$  and  $C_3$  hydrocarbons.

Uranium also forms a dinitride,  $UN_2$ , with a fluorite structure.

Uranium usually dissolves in acids to give  $U^{IV}$  salts. The sulphate crystallises as the tetrahydrate which heating converts to the hemihydrate, but further loss of water leads to decomposition. Plutonium sulphate is similar. Double sulphates of formula  $M^I_4 M^{IV}(SO_4)_4$  (where  $M^I = NH_4$ ,  $K$  or  $Rb$  and  $M^{IV} = Th^{IV}$ ,  $U^{IV}$  or  $Pu^{IV}$ ) have been made. Migration experiments indicate that these are true complexes.

Plutonium forms a nitrate of  $Pu^{IV}$  but the only nitrates of uranium are those of  $U^V$  and  $U^{VI}$ , namely  $UO_2(NO_3)$  and  $UO_2(NO_3)_2$ .



### Isomorphism in the actinide group

Isomorphism among compounds of the actinides is common and only a few examples need be given. The dioxides,  $\text{MO}_2$ , of thorium, uranium, neptunium, plutonium and americium all have a fluorite lattice. The trihalides of the transuranic elements are isomorphous not only with the corresponding trihalides of actinium and uranium but also with those of the lanthanides. Isomorphism is also exhibited in many of the actinide complex halides; thus thorium, uranium and plutonium form the isomorphous series  $\text{KM}_2\text{F}_9$ , and, together with neptunium, they also form another series,  $\text{KM}_2\text{F}_9$ . Plutonium has a number of complex nitrates  $\text{M}_2^{\text{I}}\text{Pu}(\text{NO}_3)_6$ , of which the ammonium salt  $(\text{NH}_4)_2\text{Pu}(\text{NO}_3)_6$  is isomorphous not only with  $(\text{NH}_4)_2\text{Th}(\text{NO}_3)_6$  but with  $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$  too. Examples might be multiplied to show that similarities exist between the crystalline compounds of the actinides which are comparable with those displayed by lanthanide compounds.

### Absorption spectra

Further evidence for electronic structures of the lanthanides, which are based on 5f electrons, is furnished by the absorption spectra of their compounds. The absorption bands are sharply defined and may be explained, as they are for the lanthanides, by characteristic atomic transitions involving 5f electrons rather than those electrons engaged more actively in bond formation. It is noteworthy that the spectra of the 3+ ions show particular resemblances to their lanthanide analogues, for example  $\text{U}^{3+}$  and  $\text{Nd}^{3+}$ ,  $\text{Pu}^{3+}$  and  $\text{Sm}^{3+}$ , and particularly  $\text{Am}^{3+}$  and  $\text{Eu}^{3+}$ .

### Magnetic properties

The paramagnetism of appropriate ions of the transuranic elements and that of the corresponding lanthanide ions discloses a remarkable parallelism (Fig. 330).

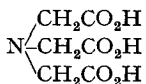
The moments of the lanthanide ions agree closely with theoretical prediction (p. 87) but those of the transuranic ions are somewhat lower than expected, possibly because the 5f electrons of the transuranic ions are less effectively screened from the crystal field which quenches the orbital contribution than are the 4f electrons of the lanthanide ions. The variation of paramagnetic moment with the number of unpaired electrons differs radically from the variation which occurs in elements of the first and second transition series where the maximum is five (p. 88).

The magnetic properties lend credence to a 5f structure: those of  $\text{UCl}_3$  indicate 5f<sup>3</sup> for  $\text{U}^{\text{III}}$  (*cf.*  $\text{Nd}^{\text{III}}$ ) and those of  $\text{PuO}_2^{2+}$ , with two unpaired



in benzene can be used for the solvent-extraction of  $\text{UO}_2^{2+}$ ,  $\text{Np}^{4+}$  and  $\text{Pu}^{4+}$ . A crystalline  $\text{UO}_2(\text{TTA})_2 \cdot 2\text{H}_2\text{O}$  has been isolated.

Nitrogen-ligands are also of interest.  $\text{ThCl}_4$  and  $\text{ThBr}_4$  form monopyridino complexes. Of the chelate complexes those from EDTA and oxine are well known.  $\text{Th}^{\text{IV}}$  and  $\text{U}^{\text{IV}}$  EDTA complexes  $\text{M}(\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_8) \cdot 2\text{H}_2\text{O}$  can be crystallised.  $\text{UO}_2^{2+}$  forms rather unstable complexes with EDTA and nitrilotriacetic acid:



#### FURTHER READING

- J. J. KATZ AND G. T. SEABORG, *The Chemistry of the Actinide Elements*, New York, Wiley, 1957.
- G. T. SEABORG, *Man-made Transuranium Elements*, London, Prentice-Hall, 1963.
- L. E. J. ROBERTS, *The Actinide Oxides*, Quart. Rev., 15 (1961) 442.
- J. J. KATZ AND I. SHEFT, *The Actinide Halides* in H. J. EMELÉUS AND A. G. SHARPE (Eds.), *Advances in Inorganic Chemistry and Radiochemistry*, Vol. II, New York, Academic Press, 1960.
- L. B. ASPREY AND B. B. CUNNINGHAM, *Unusual Oxidation States of Some Actinide and Lanthanide Elements* in F. A. COTTON (Ed.), *Progress in Inorganic Chemistry*, Vol. II, New York, Interscience, 1960.
- D. BROWN AND A. G. MADDOCK, *Protactinium*, Quart. Rev., 17 (1963) 289.
- A. E. COMYNS, *The Co-ordination Chemistry of the Actinides*, Chem. Rev., 60 (1960) 115.
- A. H. W. ATEN, JR. AND J. KOOI (Eds.), *Actinides Reviews*, Amsterdam, Elsevier, Vol. 1 (1967) etc.

Chapter 34

**Titanium, Zirconium and Hafnium**

GROUP IVA

**Atomic and general properties**

The transition elements of Group IVA, titanium, zirconium and hafnium, all have the  $(n - 1)d^2ns^2$  electron configuration. They differ from the transition elements of the later groups of the Periodic Table in their tendency to form  $M^{IV}$  compounds to the exclusion of those in which lower charge numbers occur; especially is this true of Zr and Hf. As in other transition elements, there is a distinct break in properties between the element in Period 4 and those in Periods 5 and 6.

TABLE 115  
ATOMIC PROPERTIES OF GROUP IVA ELEMENTS

	<i>Ti</i>	<i>Zr</i>	<i>Hf</i>
Atomic number	22	40	72
Electron configuration	3d <sup>2</sup> 4s <sup>2</sup>	4d <sup>2</sup> 5s <sup>2</sup>	5d <sup>2</sup> 6s <sup>2</sup>
Covalent radius (Å)	1.36	1.48	—
Metallic radius (Å)	1.47	1.60	1.58
Ionic radius $M^{4+}$ (Å)	0.68	0.80	0.81

The metallic and ionic radii of Hf are very close to those of Zr, in spite of the great increase in atomic number. This is because of the lanthanide contraction (p. 124), which accompanies the filling of the 4f shell (completed at Lu, the element preceding Hf), and which is largely responsible for the

TABLE 116  
IONISATION ENERGIES AND ELECTRODE POTENTIALS OF GROUP IVA ELEMENTS

	<i>Ti</i>	<i>Zr</i>	<i>Hf</i>
Ionisation energy <i>I</i> 1 (eV)	6.83	6.95	5.5
" " 2 "	13.63	13.97	14.8
" " 3 "	28.14	24.00	
" " 4 "	43.24	33.8	
$E^\circ, MO^{2+}/M$ (V)	-0.95	-1.53	-1.68

exceptional similarity between Zr and Hf, unmatched by a pair of elements in any other subgroup.

The first ionisation energies are all fairly low. The small 4+ ion which is invoked in  $M^{IV}$  compounds does not exist as such, since it takes a considerable share of the electron density of the ligands. Nor does the  $M^{4+}$  ion appear in aqueous solutions. Its place is taken by cations containing oxygen. These are shown in Table 116 as  $MO^{2+}$ , but the cations are almost certainly more complex.

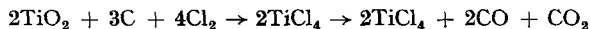
### Preparation and properties of the elements

The elements, like many true metals, have h.c.p. lattices. Their atomic radii and atomic volumes are similar, especially those of zirconium and hafnium. As the atomic weight of Hf (178.6) is almost twice that of Zr (91.2) their densities differ by a factor of two. Titanium is not only much less dense than Zr but also than succeeding elements of the first transition series. The metals are typical transition elements in having high m.p. and b.p. They are evidently strongly reducing; but they are so easily rendered passive that they are not very reactive at room temperature and have a remarkable resistance to corrosion.

#### *Titanium*

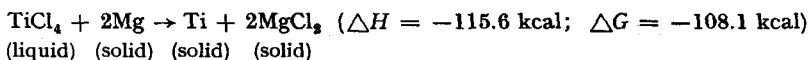
The element (0.6% of the earth's crust) is abundant but difficult to extract. It is commonly associated with siliceous rocks, but the principal workable ores are ilmenite,  $FeTiO_3$ , and rutile, a tetragonal form of  $TiO_2$ . Interest in the element has been stimulated by the need for a light, strong, corrosion-resistant metal for supersonic aircraft, and its manufacture has posed metallurgical problems. Reduction of  $TiO_2$  with carbon is unsatisfactory because the very stable carbide is also produced. The ease with which the metal combines with both oxygen and nitrogen at high temperatures makes other reduction methods difficult. The commercial production of titanium is by the metallothermic reduction of titanium tetrachloride.

In this process chlorine is passed over ilmenite or rutile heated to  $\sim 900^\circ$  with carbon and the  $TiCl_4$  vapour formed is condensed.



The liquid (b.p.  $136^\circ$ ) is purified by fractional distillation.

The tetrachloride vapour at atmospheric pressure is reduced with molten Mg at  $800^\circ$ , air being excluded by purging with argon.

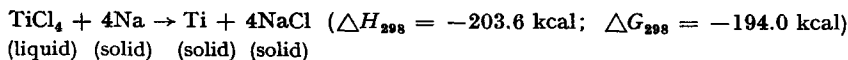


The magnesium chloride which is molten is tapped from the reactor when ~60% of the Mg has been used, in order to allow the  $\text{TiCl}_4$  vapour to continue to attack the Mg until 85% of the metal has reacted. Further consumption of Mg is undesirable since its presence prevents the loss of product titanium metal through the reactions:



The cold solid may be chipped from the reactor mechanically and the Mg and  $\text{MgCl}_2$  leached from the chips with dilute acid. Or, alternatively, without removal from the reactor, the Mg and  $\text{MgCl}_2$  may be distilled from the Ti under a high vacuum.

Reduction with molten sodium is also much employed:



It is arranged that all the Na is converted to NaCl and that some  $\text{TiCl}_4$  remains. Most of the molten NaCl is forced out of the reactor under argon pressure. The cold solid is then removed from the reactor mechanically and treated with 2%  $\text{HNO}_3$  to dissolve the impurities.

The fragments of titanium are melted in a water-cooled copper crucible, by striking an arc between them and a compressed titanium-sponge cathode, the operation being conducted in an atmosphere of argon.

Very pure titanium can be made by the iodine method in which  $\text{TiI}_4$  vapour is decomposed on a hot wire.

The metal is unusual in igniting spontaneously in oxygen, at 25 atm. and room temperature, when a fresh surface is exposed by fracture. The reaction is self-propagating and leads to the complete combustion of massive pieces, through a superficial melting and rapid diffusion of the oxide into the metal leaving a new surface of metal for oxidation. Similarly  $\text{ZrO}_2$  dissolves in molten Zr, and this metal also behaves like Ti; but Mg, Al, Nb and Ta, whose oxides are not soluble in the metal, do not show the phenomenon.

TABLE 117  
PROPERTIES OF GROUP IVA ELEMENTS

	<i>Ti</i>	<i>Zr</i>	<i>Hf</i>
Density (g/cc)	4.50	6.53	13.07
Atomic volume	10.64	14.0	13.7
Melting point (°C)	1725	1860	2200
Boiling point (°C)	3260	4750	

The mechanical properties of titanium are comparable with those of steel; but it is more difficult to fabricate owing to the readiness with which it takes up, and is hardened and embrittled by, oxygen and nitrogen. Its strength, lightness, resistance to corrosion and its low thermal expansion have led to its employment in high-speed aircraft, naval and military projects and chemical research and industry.

The non-stoichiometric, interstitial cubic compounds TiB, TiB<sub>2</sub>, TiC and TiN are very stable, strongly exothermic, and refractory. TiC is widely used in association with WC for tipping high-speed tools.

### *Zirconium*

The principal ores of zirconium (0.025% of the lithosphere) are the silicate zircon, ZrSiO<sub>4</sub>, and the oxide baddeleyite, ZrO<sub>2</sub>. Treatment of these with carbon and chlorine at red heat gives crude ZrCl<sub>4</sub>, which, after purification, can be reduced with Mg in a modification of the titanium process. For metal of higher purity the decomposition of ZrI<sub>4</sub> is used.

The metal is much softer than titanium. Its principal uses at present are as a 'getter' to remove traces of oxygen and nitrogen from thermionic valves, in bullet-proof alloy steels and, because of its low cross-section for neutron capture, in alloys for cladding the metallic fuel elements used in some atomic reactors. Hafnium must be separated as completely as possible (see below) from zirconium which is to be used in reactors, because of the high cross-section for neutron capture of hafnium.

### *Hafnium*

This element, predicted from atomic number sequence, was the first element to be discovered by X-ray methods. It was found in zirconium minerals which usually contain about 0.1%, but occasionally up to 7% of hafnium. Because of its very close resemblance to zirconium separation is difficult.

Both HfCl<sub>4</sub> and ZrCl<sub>4</sub> form surprisingly stable complexes with phosphoryl chloride, (HfCl<sub>4</sub>)<sub>3</sub>(POCl<sub>3</sub>)<sub>2</sub> and (ZrCl<sub>4</sub>)<sub>3</sub>(POCl<sub>3</sub>)<sub>2</sub>, which afford a method of separating the elements because the boiling point of the first is 5° lower than the second. Fractional crystallisations of the hexafluoro-compounds, oxo-chlorides and oxalates have also been fairly successful. But chromatographic separation has proved much better. The chlorides dissolved in anhydrous methanol are passed through a column of silica gel. A 1.9*N* solution of anhydrous HCl in methanol is used for elution, and preferentially carries forward the zirconium. Finally the Hf is removed with 7*N* H<sub>2</sub>SO<sub>4</sub>.

Solvent extraction from an acidified thiocyanate solution has also been successful.

### Reactions of the metals

Although unreactive at low temperatures, the metals combine directly at high temperatures with the halogens, oxygen, sulphur, nitrogen, carbon, boron and hydrogen. The interstitial hydrides are non-stoichiometric and not  $Ti^{II}$  or  $Zr^{II}$  compounds in a strict sense.

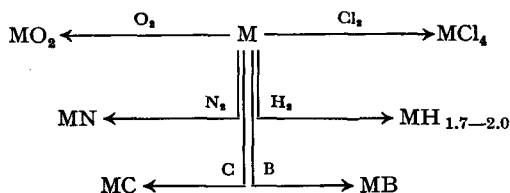


Fig. 331. Outline chemistry of Group IVA elements ( $M = Ti, Zr$  or  $Hf$ ).

The metals decompose steam on strong heating. Titanium dissolves in hot  $HCl$  to give  $TiCl_3$ , but resists attack by cold acids. Zirconium and hafnium dissolve even less readily in mineral acids, but all three metals dissolve in the presence of  $F^-$  ions, titanium giving salts of the  $Ti^{3+}$  ion, Zr and Hf giving zirconyl and hafnyl salts. The metals are remarkably resistant to corrosion by weakly acid solutions such as those of  $H_2S$ ,  $SO_2$ ,  $FeCl_3$  (hot and cold) and even of  $H_2CrO_4$ . Hot and cold alkalis do not react with them.

### Oxidation states

In this sub-group the +4 state is much the most important.  $Ti^{4+}$ , the smallest of the  $M^{4+}$  ions, appears in tetrahedral molecules such as  $TiCl_4$ , although the bonds will really be predominantly covalent (as is suggested by the fact that  $TiCl_4$  is a liquid at room temperature).  $Ti^{IV}$  is also found in anions such as the octahedral  $TiF_6^{2-}$ , and in complex molecules such as the octahedral  $Ti(acac)_2Cl_2$ .  $Zr^{IV}$  and  $Hf^{IV}$  also exist in tetrahedral molecules ( $ZrCl_4$  in the vapour) and octahedral complex ions ( $ZrCl_6^{2-}$  in  $Li_2ZrCl_6$ ).

$Ti^{III}$  compounds are known and the oxidation state +3 occurs in aqueous solution as the  $Ti(H_2O)_6^{3+}$  ion, an octahedral complex with a paramagnetic susceptibility which indicates a single d electron. Aqueous solutions containing  $Ti^{III}$  are violet and are produced when titanium(IV) compounds are reduced; the redox potential for  $Ti^{4+}/Ti^{3+}$  is about +0.05V. Such solutions may in turn be used for reducing  $Fe^{3+}$  to  $Fe^{2+}$ , chlorates and perchlorates to chlorides, and nitro-compounds to amines. There is no evidence that  $Zr^{III}$  and  $Hf^{III}$  exist in solution, but  $ZrI_3$  can be made by reducing  $ZrI_4$  with aluminium and  $ZrBr_3$  by reducing  $ZrBr_4$  with powdered zinc.

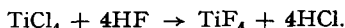


The +2 state appears in  $\text{TiCl}_2$ ,  $\text{TiBr}_2$ ,  $\text{TiI}_2$  and  $\text{TiO}$ ; all are made by heating the corresponding  $\text{Ti}^{\text{IV}}$  compound with the metal. Titanium forms a biscyclopentadienyl,  $(\pi\text{-C}_5\text{H}_5)_2\text{Ti}$ , and a cyclopentadienyl carbonyl,  $(\pi\text{-C}_5\text{H}_5)_2\text{Ti}(\text{CO})_6$ ; both of these are  $\text{Ti}^{\text{II}}$  compounds. Dihalides of zirconium are known:  $\text{ZrBr}_2$  has been made by passing  $\text{ZnBr}_4$  vapour with hydrogen over hot aluminium wire.

The oxidation state +1 has not yet been observed in this group. But, to go a step further, tris(dipyridyl)titanium,  $\text{Ti}(\text{dipy})_3$ , which is made by reducing  $\text{TiCl}_4$  with lithium in the presence of dipyridyl in the solvent tetrahydrofuran provides an example of  $\text{Ti}^0$ . None of the metals of this sub-group forms a carbonyl, a type of compound which usually provides an example of zero oxidation state in the 'd-block' metals.

### Halides

Tetrafluorides result from the action of anhydrous HF on the chlorides:

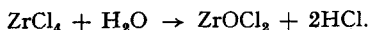


The white solids form stable complexes:



The  $\text{TiF}_6^{2-}$  ion is unstable to hydrolysis. It is converted rapidly to  $\text{TiOF}_4^{2-}$ . Surprisingly, some hexafluorozirconates, such as  $\text{K}_2\text{ZrF}_6$ , do not contain  $\text{ZrF}_6^{2-}$  ions, but instead  $\text{ZrF}_8$  units formed by the sharing of  $\text{F}^-$  ions.

The tetrachlorides are made by passing chlorine over the dioxides heated with carbon.  $\text{TiCl}_4$  is a colourless, strongly fuming liquid but  $\text{ZrCl}_4$  and  $\text{HfCl}_4$  are solids. The vapours are monomeric. Water hydrolyses them:



This oxide chloride crystallises from the solution as the octahydrate,  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ , which has a tetragonal structure containing  $\text{Zr}_4(\text{OH})_8^{8+}$  ions. Phase studies of zirconium tetrachloride—alkali-metal chloride systems indicate the formation of chlorozirconates,  $\text{M}_2^+\text{ZrCl}_6$ . Ammonium chlorotitanate,  $(\text{NH}_4)_2\text{TiCl}_6$ , is precipitated when  $\text{NH}_4\text{Cl}$  is added to a solution of  $\text{TiCl}_4$  in concentrated HCl.

The tetrabromides and tetraiodides are made by direct combination of the elements. Some are coloured;  $\text{TiBr}_4$  is yellow and  $\text{TiI}_4$  red-brown, in accordance with the position of the ligands in the spectrochemical series (p. 159). They are solids of low m.p.; the crystals have a cubic lattice and contain tetrahedral molecules. Some bromo-complexes have been made, for instance  $(\text{NH}_4)_2\text{TiBr}_6 \cdot 2\text{H}_2\text{O}$ , but they are much less stable than the fluoro-compounds; iodo-complexes are unknown; the stability falls rapidly with the more easily polarisable halogens.

Titanium trichloride,  $\text{TiCl}_3$ , is the most important trihalide. Its hexahydrate, like  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  (p. 575), has a green and a violet form. Rubidium and caesium chlorides give complexes containing  $\text{TiCl}_5^{2-}$  ions. The crystals,  $\text{M}_2\text{TiCl}_5 \cdot \text{H}_2\text{O}$ , are green but the solutions are violet. The colour change is associated with a change in the number of co-ordinated water molecules in the complex (*cf.* p. 663).  $\text{TiF}_3$  is best made from titanium hydride and  $\text{HF}$  at  $700^\circ$ . It is a blue solid, stable to air, water and even concentrated  $\text{H}_2\text{SO}_4$ . Its magnetic susceptibility (1.75 B.M.) is appropriate to the  $\text{Ti}^{3+}$  ion with one d electron.

The trihalides  $\text{ZrX}_3$  ( $\text{X} = \text{F}, \text{Cl}, \text{Br}$  or  $\text{I}$ ) and  $\text{HfBr}_3$ , are known. They are oxidised by water to the +4 state, and therefore are without an aqueous solution chemistry.

Pure titanium dichloride is a dark-brown powder, spontaneously inflammable in air. It is made by passing an electrode-less discharge through  $\text{TiCl}_4$  mixed with hydrogen at low pressure. It sets free hydrogen from water. Chlorocomplexes  $\text{MTiCl}_3$  and  $\text{M}_2\text{TiCl}_4$  can be made by melting  $\text{TiCl}_2$  with alkali metal halides.

Titanium dibromide, which is made by reducing  $\text{TiBr}_4$  with  $\text{Ti}$ , has been shown to have a  $\text{CdI}_2$  structure.  $\text{ZrBr}_2$  and  $\text{ZrI}_2$  are obtained, mixed with the corresponding trihalides, when  $\text{ZrBr}_4$  and  $\text{ZrI}_4$  are reduced with hydrogen or the metal.

### Oxides

Both  $\text{TiO}_2$  and  $\text{ZrO}_2$  are manufactured for use as white pigments.  $\text{TiO}_2$  from ilmenite by conversion to the sulphate, followed by hydrolysis (Fig. 332). The usual method is, however, the vapour-phase oxidation of  $\text{TiCl}_4$ , attained by passing the vapour with air through a flame produced by burning a hydrocarbon in an excess of oxygen.

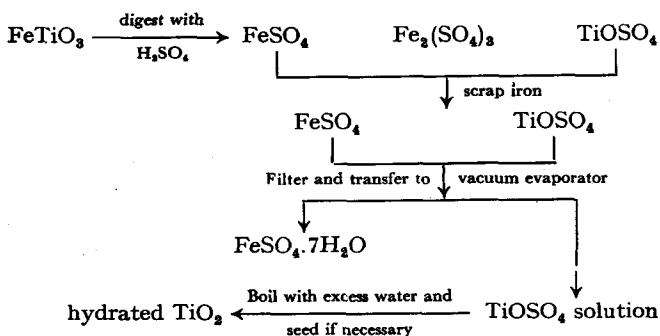


Fig. 332. Manufacture of  $\text{TiO}_2$  from ilmenite.

The refractory oxide is white when cold but resembles  $\text{SnO}_2$  in becoming yellow when hot. It has three crystalline forms, the tetragonal rutile, the slender tetragonal prisms of anatase and the flat plates of orthorhombic brookite. The pigment grades are either anatase or rutile. Rutile has 6 : 3 co-ordination and is isomorphous with cassiterite,  $\text{SnO}_2$  (Fig. 333). In anatase, linear molecules of  $\text{TiO}_2$  are present (Fig. 334).

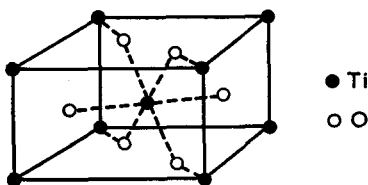


Fig. 333. Unit cell of rutile.

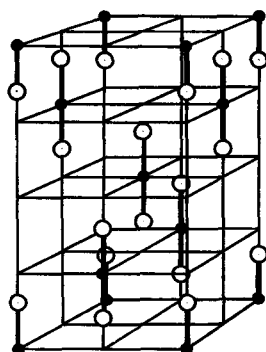


Fig. 334. Lattice of anatase.

Zirconia (m.p. 2700°) is used as a refractory and also as a pigment, mainly for white enamels. It is made from zircon [Fig. 335, (i)] or baddeleyite [Fig. 335, (ii)].

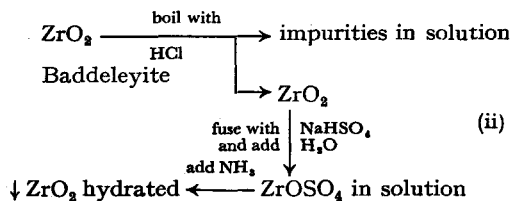
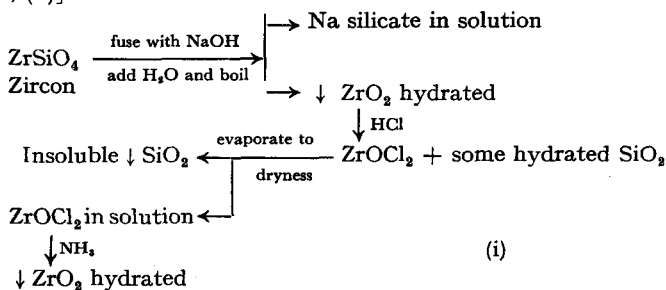


Fig. 335. Manufacture of zirconia, (i) from zircon, (ii) from baddeleyite.

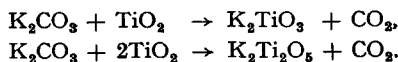
The hydrated oxides of titanium, zirconium, and hafnium, obtained by adding alkali to solutions of the  $M^{IV}$  salts, are soluble in acids. Heating these materials produces oxides which resist solution, as it does with  $Al_2O_3$  and  $Cr_2O_3$ .

Hydrated  $TiO_2$  dissolves in concentrated alkalis to give hydrated compounds such as  $M_2TiO_3 \cdot nH_2O$ , of unknown structure. Zirconium dioxide is, however, rather more basic in character; it is almost insoluble in aqueous alkalis.

White  $TiO_2$  is converted to dark violet  $Ti_2O_3$  by strong heating in hydrogen at atmospheric pressure. At very high pressures of hydrogen, the face-centred cubic, non-stoichiometric  $TiO$  is produced. A stable titanium(III) oxide can be made by heating  $TiO_2$  in hydrogen and  $TiCl_4$  vapour at  $1000^\circ$ .

### Complex oxides

Hydrated  $TiO_2$  is insoluble in alkalis but reacts, when heated, with lithium, sodium and potassium carbonates to give the compounds  $M_2TiO_3$  and  $M_2Ti_2O_5$ :



Most compounds formulated as titanates are complex oxides rather than salts. One of these, perovskite,  $CaTiO_3$ , gives its name to the perovskite structure (Fig. 336) of which other examples are  $SrTiO_3$ ,  $BaTiO_3$  and  $CaZrO_3$

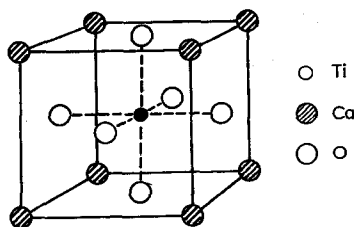


Fig. 336. Perovskite structure.

The barium compound, however, appears in four other crystalline forms: hexagonal, tetragonal, orthorhombic and trigonal. The tetragonal (s.g. 6.0) has a very high dielectric constant which varies markedly with temperature. It is used for high value capacitances. One form has piezoelectric properties and is employed in transducers to convert electrical into mechanical energy, in ultra-sonic applications and in gramophone pick-ups. The material is made by heating  $BaCO_3$  with  $TiO_2$ . It is ground, made to shape with a binding material, and fired like a ceramic.

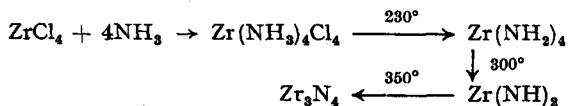
Some of the complex oxides of titanium have spinel structures (p. 500); examples are  $Mg_2TiO_4$  and  $Zn_2TiO_4$ , made by heating the respective oxides with  $TiO_2$ , and  $Mn^{II}Ti_2^{III}O_4$ , produced when  $MnO_2$  and  $TiO_2$  are heated together at  $1400^\circ$ . In  $Ba_2TiO_4$ , however, titanium is tetrahedrally co-ordinated to oxygen; the compound is a true titanate.

A number of complex oxides of zirconium are known; they are produced by strongly heating metal oxides, or nitrates, with  $ZrO_2$ . The calcium example,  $CaZrO_3$ , is a perovskite; but several of the  $M_2^{II}ZrO_4$  compounds are known to be spinels.

### Binary compounds with other non-metals

Hard, refractory borides such as  $TiB$  and  $TiB_2$  can be made by direct combination of the elements at high temperature. The carbides  $TiC$  and  $ZrC$ , made in the same way, have similar properties.

Both  $Ti$  and  $Zr$  form compounds of the  $M_3N_4$  type.  $Ti_3N_4$  is made by the reaction between  $TiBr_4$  and  $KNH_2$  in liquid ammonia. It decomposes on heating to give  $TiN$  and nitrogen.  $Zr_3N_4$  is made by the following series of reactions:



Although it is more stable than  $Ti_3N_4$ , strong heating converts it to  $ZrN$ . The interstitial nitrides, like the carbides  $TiC$  and  $ZrC$ , have the  $NaCl$  structure; alternatively they may be regarded as cubic close-packed arrangements of  $Ti$  atoms with nitrogens in the octahedral holes. As the metals have h.c.p. lattices, these have not been simply expanded to admit the  $N$  atoms.

A large number of sulphides, selenides and tellurides have been made by heating the elements together in evacuated silica tubes, and by the thermal decomposition of the higher compounds. The solids have compositions represented by  $MX$ ,  $M_2X_3$ ,  $MX_2$ ,  $MX_3$  and  $MX_4$ ; not all the variants have been produced, and many of the phases are non-stoichiometric (p. 215).

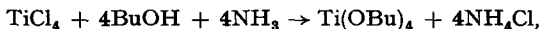
### Aqueous solution chemistry

Titanium(III) exists in aqueous solution as the blue-violet  $Ti(H_2O)_6^{3+}$  ion; the absorption spectrum of this ion is discussed on p. 158. The alum  $RbTi(SO_4)_2 \cdot 12H_2O$  contains the hexa-aquo ion, as does the violet form of  $TiCl_3 \cdot 6H_2O$ .

Although salts of the metals in the +4 state have formulae such as  $\text{TiOSO}_4 \cdot \text{H}_2\text{O}$ ,  $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  and  $\text{ZrO}(\text{C}_2\text{O}_4)$ , it is probable that  $\text{MO}^{2+}$  ions are not present in aqueous solution. Titanium(IV) perchlorate solutions contain  $\text{Ti}(\text{OH})_2(\text{H}_2\text{O})_4^{2+}$  ions, probably octahedral in form. But the ions in zirconium(IV) solutions appear to be of much greater complexity. In the crystal of  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  there are  $\text{Zr}_4(\text{OH})_8^{8+}$  ions (p. 638).

### Organometallic and related compounds

Unlike Ge, Sn and Pb, the transition metals of Group IV do not form strong metal-carbon  $\sigma$ -bonds. The best-known compounds of titanium with organic groups are derivatives of orthotitanic acid containing Ti—O—C bonds and not, therefore, truly organometallic compounds.  $\text{TiCl}_4$  reacts with sodium alkoxides or with primary alcohols in the presence of sufficient ammonia to neutralize all the HCl formed:



The products are alkyl orthotitanates. With secondary alcohols the reaction is less satisfactory. Intermediate products such as  $\text{Ti}(\text{OBu})_2\text{Cl}_2$  can be isolated when a smaller quantity of base has been used.  $\text{ZrCl}_4$  reacts in a similar way to  $\text{TiCl}_4$ . The alkyl titanates are solids or liquids at ordinary temperature. They are not monomeric even in the liquid phase, and  $\text{Ti}(\text{OEt})_4$  is a tetramer in the solid.

Aryltitanates can be made by reaction between  $\text{TiCl}_4$  and phenols in the presence of ammonia. Phenyl orthotitanate is a bright-red solid. Like the alkyl esters, the aryltitanates and zirconates are hydrolyzed rapidly in moist air.

Titanium-nitrogen compounds can be made similarly;  $\text{TiS}_2$  or  $\text{TiCl}_4$  reacts slowly with aniline in anhydrous benzene to give  $\text{Ti}(\text{NHC}_6\text{H}_5)_4$ .

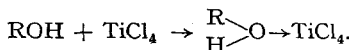
The first organotitanium compound to be made with a Ti—C  $\sigma$  bond in it was the solid  $\text{C}_6\text{H}_5\text{Ti}(\text{OPr}^i)_3$ ; this is obtained from the reaction between phenyl lithium and isopropylorthotitanate. Although rapidly oxidised by air or water, it is thermally stable at room temperature in an inert atmosphere.

Although the Group IVA metals do not form many sigma-bonded organometallic compounds they show general resemblance to the transition metals in their ability to form  $\pi$ -bonded organometallic compounds. Deep-red, diamagnetic bis(cyclopentadienyl)titanium dichloride,  $(\pi\text{-C}_5\text{H}_5)_2\text{TiCl}_2$ , is made by treating  $\text{TiCl}_4$  with  $\text{C}_5\text{H}_5\text{Na}$  in tetrahydrofuran. The corresponding fluoride, bromide and iodide are known; so are  $(\pi\text{-C}_5\text{H}_5)_2\text{ZrBr}_2$  and  $(\pi\text{-C}_5\text{H}_5)_2\text{HfCl}_2$ ; all are stable in air.

Bis(cyclopentadienyl)titanium,  $(\pi\text{-C}_5\text{H}_5)_2\text{Ti}$ , is made by the action of  $\text{C}_5\text{H}_5\text{Na}$  on  $\text{TiCl}_2$ . In contrast to the  $\text{Ti}^{\text{IV}}$  compounds, it is exceedingly sensitive to air.

### Complexes

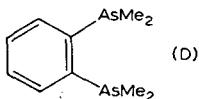
The tetrachlorides and tetrabromides of Ti and Zr (but not the fluorides) act as Lewis acids and give addition complexes particularly with oxygen compounds such as alcohols, ethers and carboxy compounds:



$\text{TiCl}_4$  forms several dark-red phosphine adducts such as  $\text{TiCl}_4 \cdot 2\text{PET}_3$  and  $\text{TiCl}_4 \cdot 2\text{PPh}_3$ .

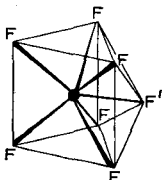
The Group IVA metals form chelates with oxygen donors such as catechol and acetylaceton. The tetraoxalatozirconate(IV) ion,  $\text{Zr}(\text{C}_2\text{O}_4)_4^{4-}$ , has a dodecahedral arrangement of oxygen atoms (p. 673) around the zirconium atom.

But complexes of bidentate ligands with donor atoms other than oxygen are also known. Orthophenylene-bis(dimethylarsine):



forms complexes  $\text{MCl}_4\text{D}$  and  $\text{MCl}_4\text{D}_2$  with Ti, Zr and Hf tetrachlorides.  $\text{TiCl}_4\text{D}_2$  has 8-co-ordinate Ti. This is the first example to be found of 8-co-ordination in a first-row, d-block metal complex.

The complex halides are of interest. The compounds  $\text{Na}_3\text{ZrF}_7$  and  $\text{Na}_3\text{HfF}_7$  are reported to contain pentagonal bipyramidal  $\text{MF}_7^{3-}$  ions, but  $(\text{NH}_4)_3\text{ZrF}_7$  is held to contain a 7-co-ordinate ion of different shape:



The Zr is at the centre of a triangular prism with F atoms at the six corners and a seventh (F') projecting from the centre of one side.

## FURTHER READING

- J. J. GRAY AND A. CARTER, *Chemistry and Metallurgy of Titanium Production*, Royal Institute of Chemistry Monograph, No. 1, London, 1958.
- I. SHIIBARA, W. T. SCHWARTZ AND H. W. PORT, *Chemistry of Titanium Alkylides and Organometallic Compounds*, Chem. Rev., 61 (1961) 1.
- W. FISCHER, *The Separation of Zirconium and Hafnium by Liquid-liquid Partition*, Angew. Chem., Intern. Ed., 5 (1966) 15.



## Vanadium, Niobium and Tantalum

## GROUP VA

## Atomic and general properties

The atoms of these elements have five valence electrons in the configuration  $(n-1)d^3ns^2$  for vanadium and tantalum or  $(n-1)d^4ns^1$  for niobium. The difference in configuration is without apparent effect on their chemistry.

TABLE 118  
ATOMIC PROPERTIES OF GROUP VA ELEMENTS

	<i>V</i>	<i>Nb</i>	<i>Ta</i>
Atomic number	23	41	73
Electron configuration	$3d^34s^2$	$4d^45s^1$	$5d^36s^2$
Metallic radius (Å)	1.34	1.46	1.46
Ionic radius $M^{4+}$ (Å)	0.64		
$M^{5+}$ (Å)	0.56	0.70	0.73

The first ionisation energies lie in the usual range for transition metals (6—8 eV). The standard electrode potentials are, however, not accurately known because the metals are so easily rendered passive that the preparation of reversible electrodes is difficult. Although the approximate values show them to be strongly reducing, the metals are unreactive towards cold acids.

TABLE 119  
IONISATION ENERGIES AND ELECTRODE POTENTIALS OF GROUP VA ELEMENTS

	<i>V</i>	<i>Nb</i>	<i>Ta</i>
Ionisation energy <i>I</i> (eV)	6.74	6.77	7.0
$E^\circ$ , $M^{4+}/M$ (V)	-1.5		
$M^{5+}/M$ (V)		-0.6	-0.7

Again, in this sub-group there is a very distinct break in properties after Period 4. Vanadium is considerably different from niobium and tantalum which are very similar to each other, although this similarity is not so marked

as that between zirconium and hafnium. However vanadium, niobium and tantalum are typical transition metals, displaying a wide variety of charge numbers in their compounds.

The metals all crystallise with a b.c.c. lattice. The small radius of the tantalum atom (inferred from measurements on the metal) is reflected in the high density of the element. The metals all have high m.p. (*cf.* iron, m.p. 1535°)

TABLE 120

PHYSICAL PROPERTIES OF GROUP VA ELEMENTS

	V	Nb	Ta
Density (g/cc)	6.1	8.4	16.6
Atomic volume	8.3	10.8	10.9
Melting point (°C)	1860	2410	2850

### Occurrence, separation and properties of the elements

#### Vanadium

The element (0.02% of the lithosphere) is very widely distributed—more than 60 vanadium minerals have been described—but there are few workable ores. Carnotite,  $K(UO_2)VO_4 \cdot xH_2O$ , is a source of both uranium and vanadium; vanadinite,  $Pb_5(VO_4)_3Cl$ , which is isomorphous with apatite, is also worked-up for the element (Fig. 337).

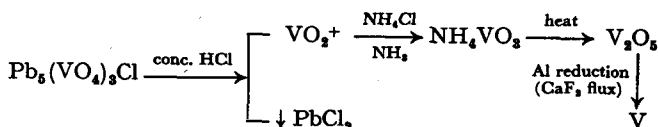
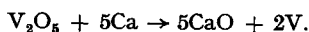


Fig. 337. Working-up of vanadinite.

Vanadium of high purity has been obtained by reducing  $V_2O_5$  with calcium, some  $CaCl_2$  being added to flux the lime formed:



Even purer metal has been made by the iodine process: the sublimation and thermal decomposition of  $VI_2$ .

The metal forms a stable carbide,  $V_4C_3$ , and is used as ferrovanadium to refine the grain and carbide structure of steel and to improve its hardness at high temperatures. Amongst its numerous applications are incorporation in high-speed tool steels and in steels for exhaust-valve and other springs.

### Niobium and tantalum

The two elements (both rare,  $\sim 3 \times 10^{-5}\%$ ) are extracted (Fig. 338) from a mineral which is a mixed niobate and tantalate of iron and manganese,  $(\text{Fe, Mn})(\text{Nb, Ta, O}_3)_2$ . When it contains more niobium than tantalum it is known as columbite, otherwise as tantalite. The two metals are separated from each other by the process outlined in Fig. 338.

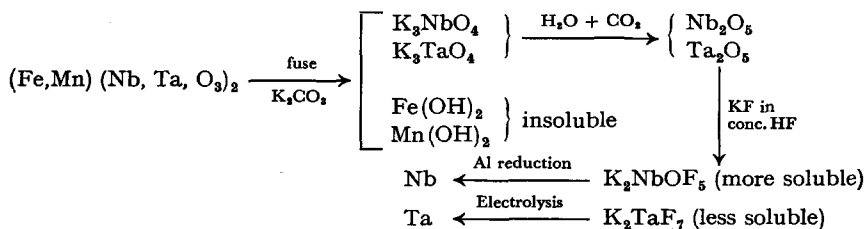


Fig. 338. Extraction of niobium and tantalum from columbite (tantalite).

Niobium and tantalum can also be separated by solvent extraction; Nb is extracted almost quantitatively from HCl solution by methyldioctylamine in xylene while Ta remains in the acid.

Chromatographic methods have been used to separate Nb and Hf from ores containing Ti and other metals. The fluorides were adsorbed on paper pulp; elution with methyl ethyl ketone saturated with water extracted the tantalum; equilibration of the column with a 1% solution of HF in the ketone arrested the movement of Ti, Zr and Sn; the niobium was then extracted with M.E.K. containing 12.5% of 40% aqueous HF.

Niobium is used to inhibit intergranular corrosion in austenitic steels and as carbide in hard carbide tool compositions. The metal is in commercial production and a more extensive use of it may be expected.

Tantalum is resistant to corrosion and for this reason is employed both in chemical research and in plant construction. The element has minimal foreign body reactions in human tissue and finds a place in surgery. It is used in electrolytic rectifiers and in capacitors. These applications are possible because of the thin anodic film formed on the metal in oxoacid electrolytes.

### Chemical behaviour of the metals

Although unreactive at room temperature, the metals combine with other elements very readily on heating. All three burn in oxygen to the pentoxides. Vanadium combines on heating with chlorine to form  $\text{VCl}_4$  and with nitrogen to give VN. The metals do not dissolve in cold mineral acids, but vanadium dissolves in perchloric acid and in ammonium persulphate to give metavanadic acid,  $\text{HVO}_3$ ; it also dissolves slowly in hot concentrated sulphuric

acid, hot HCl and hot dilute HNO<sub>3</sub>. The metals all react with fused alkalis, hydrogen being liberated; vanadates and corresponding salts are formed.

### Oxidation states

The charge number +5 is much the most common in this group. Niobium and tantalum form pentahalides with all four halogens, and also have the oxides Nb<sub>2</sub>O<sub>5</sub> and Ta<sub>2</sub>O<sub>5</sub>. Vanadium has a fluoride VF<sub>5</sub>, an oxide V<sub>2</sub>O<sub>5</sub> and oxidetrihalides such as VOCl<sub>3</sub> and VOB<sub>3</sub>; but the highest bromide is the unstable VBr<sub>4</sub> and the highest iodide VI<sub>3</sub>. Vanadates, niobates and tantalates containing the metals in the +5 state have a great variety of compositions.

The +4 state is an important one, in vanadium particularly. It is represented by halides such as VCl<sub>4</sub> and VBr<sub>4</sub>, by vanadyl compounds such as VOCl<sub>2</sub> and VOSO<sub>4</sub> and by the dark-blue oxide VO<sub>2</sub>. The oxides NbO<sub>2</sub> and TaO<sub>2</sub> are well characterised. Of the tetrahalides of these metals NbI<sub>4</sub> and TaI<sub>4</sub> are best known.

The +3 state is represented in vanadium by the basic V<sub>2</sub>O<sub>3</sub>, a black solid with the corundum structure (p. 497). All the trihalides of vanadium are known and the V(H<sub>2</sub>O)<sub>6</sub><sup>3+</sup> ion exists in the aqueous solution. The 3+ state is less important in Nb and Ta, but some of the trihalides are known.

Violet solutions containing aquated V<sup>2+</sup> ions can be produced by the reduction of vanadyl (VO<sup>2+</sup>) or vanadium(III) salts with zinc. The relation between the four highest oxidation states of vanadium in aqueous solution is shown in Table 121.

TABLE 121  
VANADIUM COMPOUNDS IN SOLUTION

Vanadium charge number	+5	+4	+3	+2
Most common corresponding species and appropriate reducing agents	VO <sub>3</sub> <sup>-</sup>	VO <sup>2+</sup>	V <sup>3+</sup>	V <sup>2+</sup>
Colour in aqueous solution	Colourless	Blue	Green	Violet
Redox potential		+1.0V	+0.3V	-0.2V
Typical compounds	NH <sub>4</sub> VO <sub>3</sub>	VOCl <sub>3</sub> VOSO <sub>4</sub>	V <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	VSO <sub>4</sub>
Typical complexes		VO(SCN) <sub>4</sub> <sup>2-</sup>	V(NH <sub>3</sub> ) <sub>6</sub> <sup>3+</sup>	V(CN) <sub>6</sub> <sup>4-</sup>

The lowest oxidation states are, as usual, stabilised by π-bonding ligands. Vanadium(I) is represented by V(dipy)<sup>+</sup> and V<sup>0</sup> by the carbonyl V(CO)<sub>6</sub>.

and the trisdarsine compound  $V(\text{Me}_2\text{P}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{PMe}_2)_3$ . Niobium forms a trisdipyridyl, obtained as violet crystals when  $\text{NbCl}_5$  is reduced with lithium in tetrahydrofuran in the presence of dipyridyl. The  $-1$  state is represented in all three elements by the carbonylates which contain  $\text{M}(\text{CO})_6^-$  ions.

### Halides

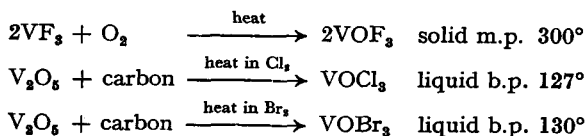
Vanadium forms the halides and oxohalides tabulated in Table 122.

TABLE 122  
HALIDES AND OXOHALIDES OF VANADIUM

Charge number	Fluorides	Chlorides	Bromides	Iodides
+2		$\text{VCl}_2$		$\text{VI}_2$
+3	$\text{VF}_3$ $\text{VF}_3\cdot 3\text{H}_2\text{O}$	$\text{VCl}_3$ $\text{VCl}_3\cdot 6\text{H}_2\text{O}$	$\text{VBr}_3$ $\text{VBr}_3\cdot 6\text{H}_2\text{O}$	$\text{VI}_3$ $\text{VI}_3\cdot 6\text{H}_2\text{O}$
+4	$\text{VF}_4$ $\text{VOF}_2$	$\text{VOCl}_2$ $\text{VOCl}_2$	$\text{VOBr}_2$	
+5	$\text{VF}_5$ $\text{VOF}_3$	$\text{VOCl}_3$	$\text{VOBr}_3$	

There is only one pentahalide; this is  $\text{VF}_5$  and is formed when  $\text{VF}_4$  is heated to  $600^\circ$  in nitrogen.

However, there are three vanadyl trihalides. Vanadyl trifluoride is a white solid, the other two are liquids; they are made thus:



Vanadyl trichloride is reduced to  $\text{VOCl}_2$  when it is heated with zinc in a sealed tube, or passed, with hydrogen, through a red-hot tube; both are strongly reducing conditions.

The brown liquid  $\text{VCl}_4$  is made by direct combination of the elements, but  $\text{VF}_4$  only by the action of dry  $\text{HF}$  on  $\text{VCl}_4$ :



The trihalides,  $\text{VBr}_3$  and  $\text{VI}_3$ , result from heating the respective elements together; but  $\text{VCl}_3$  is produced by the action of  $\text{HCl}$  gas on the metal. They are dark-coloured solids which crystallise from water as green hexahydrates.

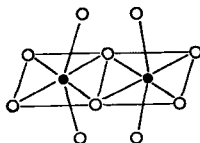
The yellow crystalline  $\text{VF}_3$  is obtained by prolonged heating of  $\text{VCl}_3$  with dry  $\text{HF}$ .

When  $\text{VCl}_3$  is heated to  $800^\circ$  in nitrogen,  $\text{VCl}_4$  distils off leaving  $\text{VCl}_2$ :



The residue dissolves in water to a violet solution which soon evolves  $\text{H}_2$  and turns green.  $\text{VBr}_3$  is now known to behave similarly. Vanadium di-iodide,  $\text{VI}_2$ , obtained by heating the tri-iodide at reduced pressure, has been used in the preparation of pure vanadium by the iodine method.

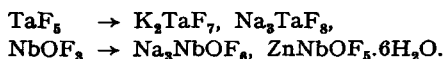
The important halides of niobium and tantalum are the pentahalides and the oxide halides  $\text{NbOCl}_3$ ,  $\text{NbOBr}_3$  and  $\text{TaOBr}_3$ . The pentahalides themselves are usually made by passing the halogen over the pentoxide heated with carbon. The pentachlorides and pentabromides are monomeric in the vapour phase but X-ray diffraction studies on the crystals show them to be made up of  $\text{M}_2\text{X}_{10}$  units containing two distorted octahedra joined along one edge:



Reduction of the pentachlorides is difficult. Heating with aluminium reduces  $\text{TaCl}_5$  to the tetrachloride, the vapour of which deposits black crystals on cooling; these liberate hydrogen from water. The tetrabromides and tetraiodides have been made by heating the pentahalides with the metals in sealed tubes.

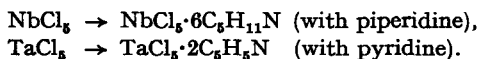
The oxide fluorides  $\text{NbO}_2\text{F}$  and  $\text{TaO}_2\text{F}$  are of structural interest, having the  $\text{ReO}_3$  lattice (p. 683) with a random distribution of O and F in the oxygen positions.

The halides form many complexes. In particular, the fluorides and oxide fluorides combine with other metallic fluorides:



The  $\text{TaF}_6^{3-}$  ion in  $\text{Na}_3\text{TaF}_6$  has the form of a slightly distorted square antiprism (Fig. 339).

Addition compounds with organic bases are also commonly formed, particularly by the pentachlorides:





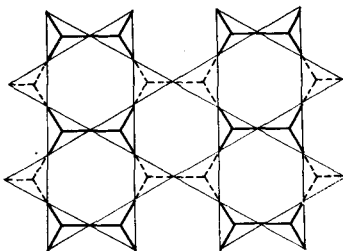
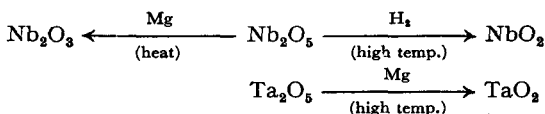


Fig. 340. Arrangement of  $\text{VO}_4$  tetrahedra in solid  $\text{V}_2\text{O}_5$ .

trates the general rule that as more electrons become involved in bonding the less complete is their transfer from one atom to another. Put in another way, the higher the charge number of an element in a compound the less ionic its character.

Two compounds,  $\text{VO}(\text{OH})_2$  and  $\text{V}_3\text{O}_5(\text{OH})_4$ , have been identified by X-ray diffraction. The rose-coloured crystals of the former are obtained on concentrating, in an inert atmosphere, the acid solution of a vanadate after reducing it with  $\text{SO}_2$ . Black crystals of the latter result from reducing vanadic acid with zinc in the presence of concentrated  $\text{NH}_4\text{Cl}$ . The basic trihydroxide  $\text{V}(\text{OH})_3$  is precipitated, green and flocculent, when ammonia is added to  $\text{VCl}_3$  solution.

The pentoxides of niobium and tantalum are more difficult to reduce than  $\text{V}_2\text{O}_5$ .



The pentoxides are more acidic than the dioxides  $\text{ZrO}_2$  and  $\text{HfO}_2$  of Group VA. Fusion of  $\text{Ta}_2\text{O}_5$  with caustic alkalis gives polytantalates of the form  $\text{M}_3\text{Ta}_6\text{O}_{19}$ ; meta- and pyrotantalates ( $\text{Ca}(\text{TaO}_3)_2$ ,  $\text{Ca}_2\text{Ta}_2\text{O}_7$ ) are also known.

A compound  $\text{NaNbO}_3$ , with the perovskite structure, has been obtained by heating  $\text{Nb}_2\text{O}_5$  with sodium carbonate. The orthoniobate  $\text{Na}_3\text{NbO}_4$  has been extracted with ethanol from an  $\text{Nb}_2\text{O}_5$ — $\text{NaOH}$  melt. Niobates of the  $\text{M}_4\text{Nb}_2\text{O}_7$  type are also known.

## Binary compounds with other non-metals

### Carbides

Very hard carbides result from strongly heating the oxides with carbon. They are empirically  $\text{MC}$  and have the  $\text{NaCl}$  structure. Vanadium also forms



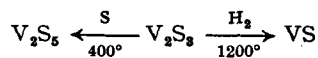
$V_4C_3$  which has a defect structure, carbon atoms being missing from some of the lattice positions.

### Nitrides

The elements combine with nitrogen at high temperatures to give the hard, very stable nitrides VN, NbN and TaN. They are not attacked by cold acids, but steam reacts with them at high temperatures to give the oxides and  $NH_3$ . The unstable higher nitrides  $Ta_3N_5$  and  $VN_2$  are made by heating the appropriate halides with ammonia.

### Sulphides

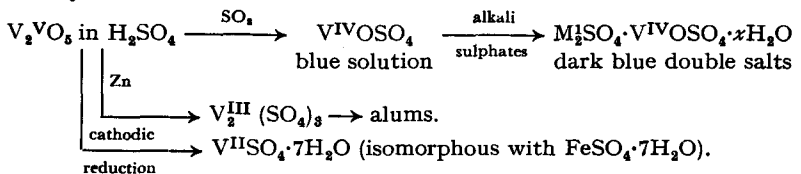
The most stable sulphide of vanadium is  $V_2S_3$ , made by passing  $CS_2$  over  $V_2O_5$ . It can be converted into  $V_2S_5$  and VS.



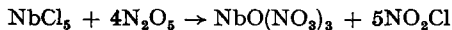
Reduction of  $Ta_2O_5$  with  $CS_2$  at white heat gives  $TaS_2$ , the only sulphide of tantalum.  $NbS_2$  is made by direct combination of the elements. The  $VS_4^{3-}$  ion is of interest because of its strong purple colour which is like that of  $MnO_4^-$ ; presumably it also owes its colour to charge-transfer absorption, as there are no partly filled d orbitals.

### Oxoacid salts of vanadium and niobium

The only oxoacid salts of importance are the sulphates of vanadium. A solid sulphate has not been obtained from a solution of  $V_2O_5$ , that is vanadium with charge number +5, in  $H_2SO_4$ , but reduction of the solution gives sulphates of vanadium with charge numbers +4, +3 and +2 respectively:



A nitrate of niobium,  $NbO(NO_3)_3$ , has been made by treating  $NbCl_5$  with  $N_2O_5$  at  $30^\circ$ :



### Organometallic compounds

As with the other transition metals, the  $\pi$ -bonded organometallic compounds are more numerous than the  $\sigma$ -bonded ones. The cyclopentadienyl

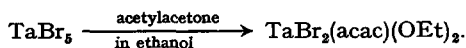
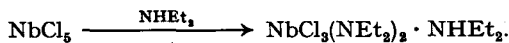
compounds are of interest. Pale-green, paramagnetic  $(\pi\text{-C}_5\text{H}_5)_2\text{VCl}_2$  is made by treating  $\text{VCl}_4$  with sodium cyclopentadienide; the dark-purple, paramagnetic  $(\pi\text{-C}_5\text{H}_5)_2\text{V}$  is made by treating  $\text{VCl}_3$  with the same reagent. A 'sandwich' structure has been proposed for the latter as a result of X-ray examination. The compound is soluble in most organic solvents and is very sensitive to air.

Reduction of  $(\pi\text{-C}_5\text{H}_5)_2\text{VCl}_2$  with amalgamated zinc gives  $(\pi\text{-C}_5\text{H}_5)_2\text{VCl}$ ; this reacts with phenyl-lithium to give  $(\pi\text{-C}_5\text{H}_5)_2\text{VC}_6\text{H}_5$  in which the phenyl group is  $\sigma$ -bonded to the metal.

From  $\text{NbBr}_5$  the bis(cyclopentadienyl)niobium(V) tribromide  $(\pi\text{-C}_5\text{H}_5)_2\text{NbBr}_3$  has been made by treatment with sodium cyclopentadienide.

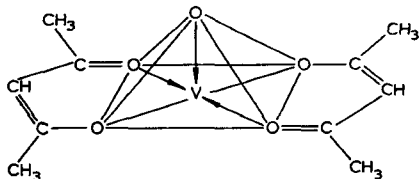
### Complexes

The metals of this sub-group form many complexes. In the oxidation state +5, high co-ordination numbers often occur, as in the  $\text{TaF}_8^{3-}$  ion already mentioned and in the  $\text{NbF}_7^{2-}$  and  $\text{TaF}_7^{2-}$  ions which have the same shape as  $\text{ZrF}_7^{3-}$  (p. 644). Many of the pentahalides react with oxygen and nitrogen donors:



$\text{NbCl}_5$  and  $\text{TaCl}_5$  form 1:1 adducts with  $\text{POCl}_3$  which are monomeric in benzene. In some organic solvents,  $\text{NbCl}_5$  reacts with  $\text{HCN}$  to give the complex acid  $\text{HNbCl}_5\text{CN}$ ; the triethylammonium salt of this acid,  $\text{Et}_3\text{NH}[\text{NbCl}_5\text{CN}]$ , has been isolated.

Vanadium in the +4 state forms chelate complexes with salicylic acid, catechol and  $\beta$ -diketones. Examples are  $\text{M}^I_2[\text{VO}(\text{OC}_6\text{H}_4\text{CO}_2)_2]$ ,  $\text{M}^I_2[\text{VO}(\text{C}_6\text{H}_4\text{O}_2)_2]\text{C}_6\text{H}_6\text{O}_2 \cdot x\text{H}_2\text{O}$  and  $\text{VO}(\text{acac})_2$ . In the last compound the vanadium atom is near the space centre of a square pyramid of oxygen atoms:



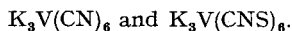
Vanadium(III) halides form 5-co-ordinate 1:2 adducts with some nitrogen and sulphur donors:



This oxidation state is also represented in chelate oxalate,  $\beta$ -diketone and catechol complexes:



The last compound is a dark-green solid, insoluble in water, but soluble in many organic solvents. Cyano and thiocyanato complexes are also known:



Vanadium(II) is represented by  $\text{K}_4\text{V}(\text{CN})_6$ . There are double sulphates of the schönite type, such as  $\text{K}_2\text{V}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ , but these are lattice compounds rather than complexes.

#### FURTHER READING

- F. FAIRBROTHER, *The Chemistry of Niobium and Tantalum*, Amsterdam, Elsevier, 1967.  
J. SELBIN, *The Chemistry of Oxovanadium(IV)*, Chem. Rev., 65 (1965) 153.

# Chromium, Molybdenum and Tungsten

## GROUP VIA

### Atomic and general properties

Although both chromium and molybdenum have the  $d^5s^1$  configuration, in contrast to the  $d^4s^2$  configuration of tungsten, the main break in properties comes, as in the previous sub-groups of transition elements, after Period 4. Chromium differs from the other two elements in forming the cations of lower charge,  $Cr^{2+}$  and  $Cr^{3+}$ . These cations are similar to cations formed by other elements of the first transition series.

Notwithstanding the difference in their electronic configuration, the metallic and ionic radii of molybdenum, in Period 5, and tungsten, in Period 6, are almost identical and their physical and chemical properties have much in common. The effect of the lanthanide contraction on elements of the third transition series, observed in Groups IVA and VA is again apparent in tungsten.

TABLE 123  
ATOMIC PROPERTIES OF GROUP VIA ELEMENTS

	<i>Cr</i>	<i>Mo</i>	<i>W</i>
Atomic number	24	42	74
Electron configuration	$3d^5 4s^1$	$4d^5 5s^1$	$5d^4 6s^2$
Metallic radius <i>M</i> (Å)	1.27	1.39	1.39
Ionic radius $M^{3+}$ (Å)	0.64		
$M^{2+}$ (Å)	0.55	0.68	0.68
$M^{6+}$ (Å)	0.52	0.62	0.67

The metals are silvery white and rather soft when pure. All are used in technical alloys and for giving special properties to steels. The m.p. are very high, every metal being at the peak melting point of its own transition series, and the m.p. of tungsten is, consequently, higher than that of any other metal. Molybdenum, like the common  $\alpha$ -forms of chromium and tungsten, has a b.c.c. structure. In addition chromium has a h.c.p.  $\beta$ -form and tungsten an f.c.c.  $\beta$ -form.

TABLE 124

PHYSICAL PROPERTIES OF GROUP VIA ELEMENTS

	<i>Cr</i>	<i>Mo</i>	<i>W</i>
Density (g/cc)	7.1	10.4	19.3
Atomic volume	7.3	9.4	9.5
Melting point (°C)	1920	2620	3370

The first ionisation energies are not abnormally high for transition metals, but the metals are relatively inert since they easily become passive. Judged potentiometrically, chromium is a strong reducing agent, and molybdenum a moderate one; but again, as for the Group VA metals, reactivity is inhibited by the formation of an adherent oxide film.

TABLE 125

IONISATION ENERGIES AND ELECTRODE POTENTIALS OF GROUP VIA ELEMENTS

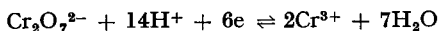
	<i>Cr</i>	<i>Mo</i>	<i>W</i>
Ionisation energy <i>I</i> (eV)	6.76	7.18	7.98
$E^\circ$ , $M^{3+}/M$ (V)	-0.71	-0.2	
$M^{4+}/M$ (V)			-0.05

The free energies of oxidation states relative to the metals in aqueous solution at pH = 0 are shown in Fig. 341.

Of species of these elements in the +6 state only  $Cr_2O_7^{2-}$  is strongly oxidising, as is indicated by the steep downward gradient of the line from  $Cr^{VI}$  to  $Cr^{III}$ :

$$E^\circ, Cr_2O_7^{2-}/Cr^{3+} = +1.33V \text{ at } pH = 0.$$

The value of the redox potential is strongly dependent on pH, since the reversible electrode reaction is



In alkalis, the potential is much smaller, and chromates can be made from  $Cr^{III}$  salts.

The +6 state has little oxidizing power in molybdenum and tungsten. These elements usually appear in aqueous solution in this oxidation state.

The  $Cr^{3+}$  ion is related in an interesting way to the other  $M^{3+}$  ions of the first transition series, namely  $Ti^{3+}$ ,  $V^{3+}$ ,  $Mn^{3+}$ ,  $Fe^{3+}$  and  $Co^{3+}$ . The first two of these are reducing agents, the last three, following  $Cr^{3+}$ , are oxidising.

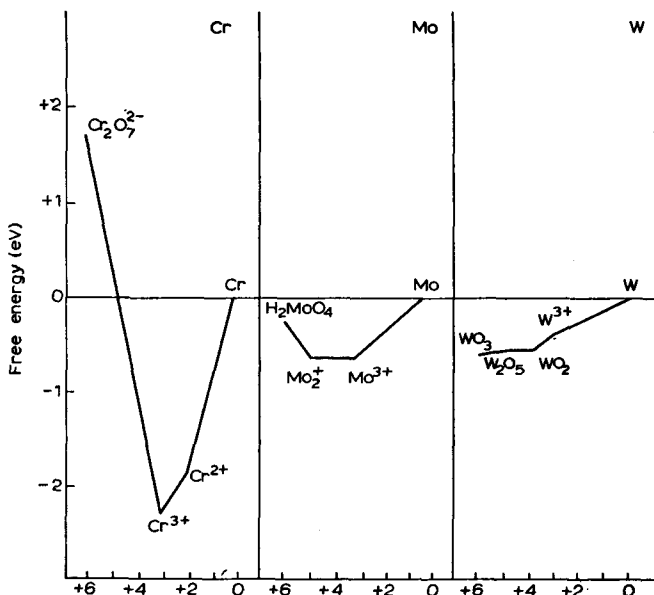


Fig. 341. Free energies of the oxidation states of Group VIA metals relative to the metals in aqueous solution at  $\text{pH} = 0$ .

Evidently  $\text{Ti}^{3+}$  with a  $3d^1$  configuration, and  $\text{V}^{3+}$ , with a  $3d^2$  configuration, tend to lose electrons to achieve an inert gas configuration; but  $\text{Mn}^{3+}$  ( $3d^4$ ),  $\text{Fe}^{3+}$  ( $3d^5$ ) and  $\text{Co}^{3+}$  ( $3d^6$ ) tend to receive electrons and fill the  $3d$  shell. The  $\text{Fe}^{3+}$  ion does this weakly because the half-filled  $d$  shell is rather stable; but  $\text{Cr}^{3+}$  ( $3d^3$ ), between  $\text{V}^{3+}$  and  $\text{Mn}^{3+}$ , is less oxidising than even  $\text{Fe}^{3+}$ .

Chromium(II) ions are among the strongest known reducing agents in aqueous solution,

$$E^\circ, \text{Cr}^{3+}/\text{Cr}^{2+} = -0.4 \text{ V},$$

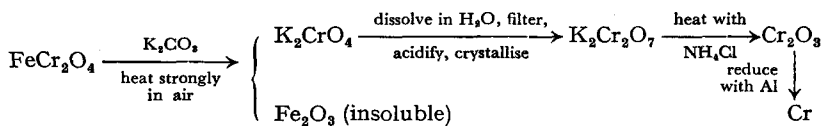
this redox potential being almost low enough to imply the reduction of water. A chromium(II) solution can remove oxygen completely from a mixture of gases.

### Occurrence, separation and properties of the elements

#### Chromium

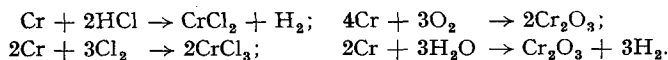
The element (0.02% lithosphere) is produced from chromite,  $\text{FeCr}_2\text{O}_4$ . Direct reduction of this compound with carbon yields ferrochrome, an iron-chromium alloy used in making stainless steel. Chromium is obtained free

from iron by converting the chromite first to a soluble chromate, then to the oxide  $\text{Cr}_2\text{O}_3$ , and finally to metal:



Electrolytic chromium is deposited from aqueous chromic acid acidified with sulphuric acid.

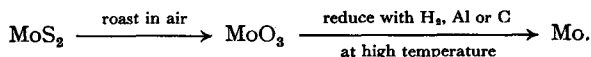
In the passive condition chromium is corrosion-resistant. It is therefore used as a protective electro-plating on ferrous metals and as a component of stainless steels. The metal dissolves slowly in cold dilute  $\text{HCl}$  and  $\text{H}_2\text{SO}_4$ , not at all in  $\text{HNO}_3$ , but rapidly in hot  $\text{HCl}$  and in hot conc.  $\text{H}_2\text{SO}_4$ . It reacts with chlorine and bromine when heated, with oxygen at the temperature of the oxy-hydrogen flame, and with steam at red heat:



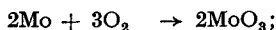
### *Molybdenum*

The element ( $10^{-4}\%$  of the lithosphere) occurs as molybdenite,  $\text{MoS}_2$ . The sulphide has a remarkably easy cleavage, similar to that of graphite; it also is used, suspended in oil, as a lubricant, particularly at high temperatures.

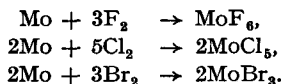
Molybdenite is the source of commercial molybdenum; it is first converted to the trioxide which is then reduced:



The metal is used in toughening steel and for supporting tungsten filaments in electric lamps and other devices. It burns in oxygen at red heat:



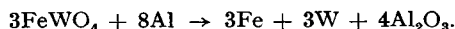
and reacts with halogens to give the halides:



The metal dissolves in hot concentrated  $\text{H}_2\text{SO}_4$  and aqua regia, but not in  $\text{HF}$  or in alkali solutions, though it reacts with fused alkalis.

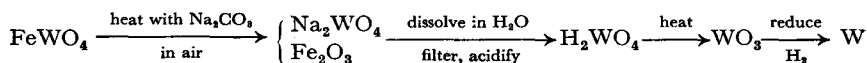
*Tungsten*

The element (10<sup>-4</sup>% lithosphere) and its compounds are largely made from scheelite, CaWO<sub>4</sub>, and wolframite, an isomorphous mixture of ferberite, FeWO<sub>4</sub>, and huebnerite, MnWO<sub>4</sub>. About 90% of the tungsten produced in the world (15,000 tons) is used in the manufacture of ferrous alloys, mainly tool steels. For this purpose ferro-tungsten is made by reducing high grade concentrates of ferberite, low in manganese, with aluminium powder (or ferro-silicon) in a thermit reaction:



Alternatively, wolframite or scheelite may be reduced with anthracite or coke in an arc furnace, with or without fluxing agents such as CaF<sub>2</sub>.

A pure metal for lamp filaments (2-4% of the total production of metal) is made by reducing pure WO<sub>3</sub> with hydrogen:



The reactivity is very similar to that of Mo but the chloride formed by the action of chlorine is the hexachloride, WCl<sub>6</sub>, and the bromide by bromine is WBr<sub>6</sub>.

**Oxidation states**

Table 126 lists some of the compounds representing the oxidation states 0 to +6. Lower states are known in the carbonylate anions, for instance -2 in Cr(CO)<sub>5</sub><sup>2-</sup> and Mo(CO)<sub>5</sub><sup>2-</sup>, -1 in Cr<sub>2</sub>(CO)<sub>10</sub><sup>2-</sup>.

TABLE 126

REPRESENTATIVE COMPOUNDS OF OXIDATION STATES 0 TO +6

Charge number	Cr	Mo	W
0	K <sub>6</sub> Cr(CN) <sub>6</sub> , Cr(C <sub>6</sub> H <sub>6</sub> ) <sub>2</sub>	Mo(dipy) <sub>3</sub>	W(CO) <sub>6</sub>
+1	Cr(dipy) <sup>+</sup>	(π-C <sub>5</sub> H <sub>5</sub> )MoC <sub>6</sub> H <sub>6</sub>	
+2	CrCl <sub>2</sub>	Mo(diars) <sub>2</sub> Br <sub>2</sub>	W <sub>6</sub> Cl <sub>8</sub> <sup>4+</sup>
+3	Cr <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	MoBr <sub>2</sub> NH <sub>2</sub> , Mo(acac) <sub>3</sub>	K <sub>2</sub> W <sub>2</sub> O <sub>9</sub>
+4	K <sub>2</sub> CrF <sub>6</sub>	MoO <sub>2</sub> , Mo(CN) <sub>8</sub> <sup>4-</sup>	WBr <sub>4</sub>
+5	CrF <sub>5</sub>	MoCl <sub>5</sub> , MoF <sub>5</sub>	WBr <sub>5</sub>
+6	CrO <sub>2</sub> Cl <sub>2</sub> , K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	MoOF <sub>4</sub>	WO <sub>3</sub>

The 0 and +1 states are stabilised by π-bonding ligands such as CO and C<sub>5</sub>H<sub>5</sub>, but there is also a complex cyanide of Cr<sup>0</sup>, K<sub>6</sub>Cr(CN)<sub>6</sub>, a green



solid precipitated when  $K_3Cr(CN)_6$  is reduced with potassium in liquid ammonia.

Although the three metals all form dihalides, those of Mo and W are very different from those of Cr. The molybdenum compound with the empirical formula  $MoCl_2$  does not have the simple  $Mo^{2+}$  ion; its structure is  $[Mo_6Cl_8]Cl_4$ , the complex cation being cubic, with chlorine atoms at the eight corners and molybdenum atoms on the six faces of the cube (Fig. 342). Ions like  $Mo_6Cl_8^{4+}$  are known as metal cluster ions. Tungsten forms a similar compound but, unlike the Mo complex which is not attacked by aqua regia, it is easily oxidised.

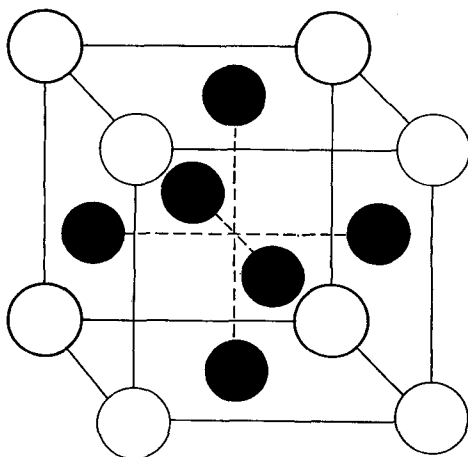


Fig. 342. Metal cluster ion  $Mo_6Cl_8^{4+}$ .

The +3 state is important in chromium; the  $Cr^{3+}$  salts are extremely stable to both oxidation and reduction in acid solution (p. 659). Several trihalides of Mo and W are known. And  $Mo^{III}$  appears in a large number of complexes, but there are very few complexes based on  $W^{III}$ .

Quadripositive Mo and W form chlorides, oxides and sulphides:  $MO_2$  and  $WO_2$  have a distorted rutile structure, and  $MoS_2$  has a layer lattice.

The +5 state is more common in molybdenum than in tungsten.  $MoCl_5$  produced by heating the metal in chlorine, is the highest chloride of molybdenum. Complex cyanides of both Mo and W in which the charge number is +5, are exceptionally stable and cannot be oxidised even by  $KMnO_4$ . In these two elements the +6 state is the one most readily assumed; it is exemplified by the hexafluorides, trioxides and acids (e.g.  $H_2MO_4$ ).

## Halides

The known halides are tabulated in Table 127.

TABLE 127

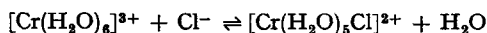
HALIDES OF CHROMIUM, MOLYBDENUM AND TUNGSTEN

Charge	Cr	Mo	W
+2	CrF <sub>2</sub> , CrCl <sub>2</sub> , CrBr <sub>2</sub> , CrI <sub>2</sub>	MoCl <sub>2</sub> , MoBr <sub>2</sub> , MoI <sub>2</sub>	WCl <sub>2</sub> , WBr <sub>2</sub> , WI <sub>2</sub>
+3	CrF <sub>3</sub> , CrCl <sub>3</sub> , CrBr <sub>3</sub> , CrI <sub>3</sub>	MoF <sub>3</sub> , MoCl <sub>3</sub> , MoBr <sub>3</sub> , MoI <sub>3</sub>	WBr <sub>3</sub>
+4	CrF <sub>4</sub>	MoF <sub>4</sub> , MoCl <sub>4</sub> , MoBr <sub>4</sub> , MoI <sub>4</sub>	WF <sub>4</sub> , WCl <sub>4</sub> , WBr <sub>4</sub>
+5	CrF <sub>5</sub>	MoF <sub>5</sub> , MoCl <sub>5</sub>	WCl <sub>5</sub> , WBr <sub>5</sub>
+6		MoF <sub>6</sub>	WF <sub>6</sub> , WCl <sub>6</sub> , WBr <sub>6</sub>

The table illustrates the usual composition trends to be found in the halides of a transition-metal series. Metals of Periods 5 and 6 form more of the higher halides than do metals of Period 4. Thus molybdenum and tungsten, like the Group IV and Group V metals which precede them, form several halides in which the metal has a  $d^0$  configuration, all the outer  $d$  and  $s$  electrons being used in bonding. The +6 state is particularly strongly represented in tungsten; especially noticeable is this because the charge number +6 is unusual in metal chlorides and bromides. Moreover, it is interesting that five distinct bromides of tungsten are known.

The chromium(II) halides are made by the action of hydrogen halides on the metal at 700° (CrF<sub>2</sub>, CrCl<sub>2</sub> and CrBr<sub>2</sub>) or by direct combination of the elements (CrI<sub>2</sub>). The  $d^4$  configuration gives rise to Jahn-Teller distortion: in the CrF<sub>2</sub> crystal there is a tetragonal arrangement of fluoride ions round the chromium ion, with four of the F<sup>-</sup> ions at 2.00 Å and two at 2.43 Å distance.

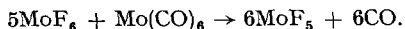
Red-violet chromium trichloride can be made by heating the metal with chlorine or the oxide Cr<sub>2</sub>O<sub>3</sub> with carbon tetrachloride. The colour of a CrCl<sub>3</sub> solution varies with temperature and chloride-ion concentration. In a cold, dilute, aqueous solution the octahedral [Cr(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup> ion has a violet colour. The addition of chloride ion, particularly if accompanied by heat, produces a green solution due to the [Cr(H<sub>2</sub>O)<sub>5</sub>Cl]<sup>2+</sup> ion:



Three isomers of  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  can be crystallised from the aqueous solutions under different conditions (p. 575).

The trifluoride has several hydrates; the bromide has two hydration isomers, one violet and one green, the tri-iodide is known only as the hydrate  $\text{CrI}_3 \cdot 9\text{H}_2\text{O}$ .

The most stable pentahalides are  $\text{MoCl}_5$  and  $\text{WBr}_5$ , both made by direct combination of the elements at high pressure. The dark-green crystals of molybdenum(V) chloride contain  $\text{Mo}_2\text{Cl}_{10}$  molecules similar in structure to  $\text{Nb}_2\text{Cl}_{10}$  (p. 651). But in the vapour, the compound (b.p.  $268^\circ$ ) is monomeric. The pentafluoride  $\text{MoF}_5$ , a yellow solid, is made by reducing  $\text{MoF}_6$  with  $\text{Mo}(\text{CO})_6$ :



It has a tetrameric structural unit (Fig. 343). But the arrangement of the fluorine atoms around the Mo atoms is only approximately octahedral.

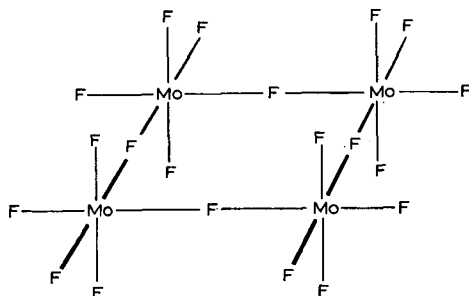


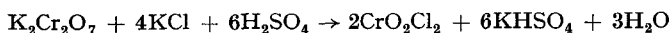
Fig. 343. Tetramer of molybdenum(V) fluoride.

Chromium pentafluoride is a crimson powder made by the action of fluorine on powdered chromium at  $400^\circ$  and 200 atm.

Tungsten hexafluoride is a colourless liquid and molybdenum hexafluoride a white solid; both are made by direct fluorination of the metals.  $\text{WCl}_6$  is a dark-blue solid. These covalent compounds are all hydrolysed by water.

### *Oxohalides*

The three metals all form oxochlorides,  $\text{MO}_2\text{Cl}_2$ . Chromyl chloride, familiar as a distinguishing test for a chloride, is the yellow distillate produced when a chloride is heated with  $\text{K}_2\text{Cr}_2\text{O}_7$  and concentrated  $\text{H}_2\text{SO}_4$ :



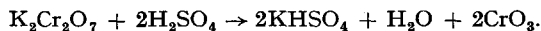
The liquid is immediately hydrolysed by water, unlike the solid molybdenyl chloride,  $\text{MoO}_2\text{Cl}_2$ , which dissolves and ionises to  $\text{MoO}_2^{2+}$  and  $2\text{Cl}^-$ .

Oxofluorides such as  $\text{MoOF}_4$ ,  $\text{MoO}_2\text{F}_2$  and  $\text{WOF}_4$  are solids; they form many oxofluoro-complexes  $\text{M}^{\text{I}}_2(\text{MoO}_3\text{F}_2)$ ,  $\text{M}^{\text{I}}_2(\text{MoO}_2\text{F}_4)$ ,  $\text{M}^{\text{I}}_2(\text{WO}_2\text{F}_4)$ .

There are also oxohalides of the metals in their +5 states.  $\text{CrOCl}_3$  and  $\text{MoOCl}_3$  have been made. The chromium compound disproportionates above  $0^\circ$  into  $\text{CrO}_2\text{Cl}_2$  and a  $\text{Cr}^{\text{III}}$  compound. An oxochloride of  $\text{Cr}^{\text{III}}$ ,  $\text{CrOCl}$ , has been made by heating  $\text{Cr}_2\text{O}_3$  with  $\text{CrCl}_3$ .

### Oxides

There is a full series of  $\text{M}^{\text{VI}}$  oxides. The trioxides  $\text{MoO}_3$  (white) and  $\text{WO}_3$  (yellow) are produced when the metals, their other oxides, or their sulphides are heated in air or oxygen. The dark-red, crystalline  $\text{CrO}_3$  is less stable and cannot be made by direct combination of the elements. The oxide separates when a saturated dichromate solution is treated with concentrated  $\text{H}_2\text{SO}_4$ .



It differs from  $\text{MoO}_3$  and  $\text{WO}_3$  in being very soluble in water, but it does not appear to form any crystalline hydrates.  $\text{MoO}_3$  has, surprisingly, a layer lattice;  $\text{CrO}_3$  and  $\text{WO}_3$  have the rhenium trioxide structure (Fig. 344).

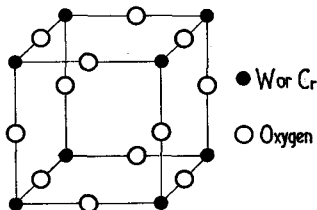


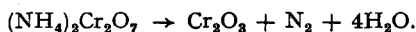
Fig. 344.  $\text{CrO}_3$  structure.

The slow decomposition of  $\text{CrO}_3$ , or of  $\text{CrO}_2\text{Cl}_2$  in oxygen gives first a solid which X-ray analysis and magnetic measurements show to be  $\text{Cr}_5\text{O}_{13}$ . Further decomposition yields an oxide varying in composition from  $\text{CrO}_{2.38}$  to  $\text{CrO}_{2.48}$ , and, finally, the ferromagnetic  $\text{CrO}_2$ , with a rutile structure, is produced.

At a high temperature,  $\text{MoO}_3$  and  $\text{WO}_3$  are reduced by hydrogen, through the violet  $\text{Mo}_2\text{O}_5$  and blue  $\text{W}_2\text{O}_5$ , to the violet  $\text{MoO}_2$  and brown  $\text{WO}_2$ . The last two can also be made by reducing  $\text{MoO}_3$  and  $\text{WO}_3$  with ammonia. The blue compounds of molybdenum and tungsten, formed by reducing molybdic and tungstic acids with zinc,  $\text{SO}_2$  and other reducing agents, are of unknown constitution. They probably contain the elements in both the +5 and +6 states.

When HCl is added to a hot solution of a tungstate the insoluble, yellow acid,  $\text{H}_2\text{WO}_4$ , separates. A cold solution yields soluble, colourless  $\text{H}_2\text{WO}_4 \cdot \text{H}_2\text{O}$ . The material which separates when nitric acid is added to a cold solution of ammonium molybdate is the hydrate  $\text{MoO}_3 \cdot \text{H}_2\text{O}$ . It is yellow when cold, but becomes colourless when it is heated, being converted to  $\text{H}_2\text{MoO}_4$ .

Chromium(III) oxide,  $\text{Cr}_2\text{O}_3$ , is very much the most stable oxide of chromium. It is a product of the oxidation of the metal and of the thermal decomposition of ammonium dichromate:

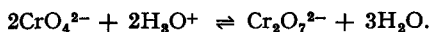


It resembles  $\text{Al}_2\text{O}_3$  in having a corundum structure, in being insoluble in water, and in resisting solution in mineral acids particularly after having been heated. The ionic radii of the  $3+$  ions,  $\text{Al}^{3+}$  0.50 Å and  $\text{Cr}^{3+}$  0.64 Å, are similar enough to allow the formation of many isomorphous compounds, exemplified in the fluorides and the alums.

Black chromium(II) oxide,  $\text{CrO}$ , is most conveniently made by dissolving the mercury out of chromium amalgam with dilute  $\text{HNO}_3$  which, under these conditions, oxidises the chromium only as far as  $\text{CrO}$ . It can also be obtained by heating  $\text{Cr}_2\text{O}_3$  and  $\text{CrC}$  together.

### Chromates, molybdates and tungstates

Alkali-metal chromates can be crystallised only from alkaline solutions; when the pH is low dichromates are obtained:



Insoluble chromates such as  $\text{Ag}_2\text{CrO}_4$ ,  $\text{BaCrO}_4$  and  $\text{PbCrO}_4$  are, however, precipitated from acid solution, the last named being an important pigment, chrome yellow.

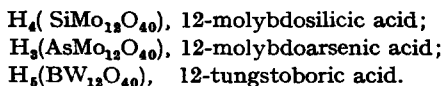
Normal molybdates and tungstates are obtained from solutions when the pH is kept within certain limits. When  $\text{MoO}_3$  is dissolved in an excess of hot concentrated ammonia  $(\text{NH}_4)_2\text{MoO}_4$  crystallises on cooling, but the salt obtained from a near-neutral solution is  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ . The tendency to form polyanions is even more marked with tungsten. When wolframite is roasted with sodium carbonate, the aqueous extract of the mass yields the compound  $\text{Na}_{10}\text{W}_{12}\text{O}_{41} \cdot 28\text{H}_2\text{O}$ .

### Polyacids

#### *Heteropoly acids*

The yellow precipitate obtained in the ammonium molybdate test for

phosphate is  $(\text{NH}_4)_2\text{H}(\text{PMo}_{12}\text{O}_{40})\text{H}_2\text{O}$ . When washed with dilute  $\text{NH}_4\text{NO}_3$  it becomes  $(\text{NH}_4)_3(\text{PMo}_{12}\text{O}_{40})$ . This molybdophosphate is an example from the series of heteropolyacid salts formed by Mo and W. Some other members are



These are known, from the number of Group VI atoms in the anion as 12-acids; the hetero-atom may also be one of the following: Ti, Ge, Sn, Zr and Hf. There are also a few 12-acid salts containing the ions:  $(\text{MW}_{12}\text{O}_{42})^{n-12}$  and  $(\text{MMo}_{12}\text{O}_{42})^{n-12}$  ( $\text{M} = \text{Ce}^{\text{IV}}$  or  $\text{Th}^{\text{IV}}$  and  $n$  is the charge number of the hetero-atom). In the  $(\text{MMo}_{12}\text{O}_{42})^{n-12}$  anions there is probably octahedral co-ordination of the oxygen atoms around the central hetero-atom.

6-acids of molybdenum are also known; they have the general formula,



where M can be I, Te, Fe, Cr, Al, Co, Ni, Rh, Cu or Mn, and its charge number  $12 - m$ .

The structure of a 12-acid anion  $(\text{MMo}_{12}\text{O}_{40})^{n-8}$  can be represented as a tetrahedron round the central metal atom, surrounded by twelve  $\text{MoO}_6$  or  $\text{WO}_6$  octahedra; every tetrahedron corner is shared by three octahedra, every one of which shares an oxygen with its neighbours. The four resulting  $\text{Mo}_3\text{O}_{13}$  groups share corners to give  $[\text{MMo}_{12}\text{O}_{40}]^{n-8}$  ions, where  $n =$  charge number of M. The large open spaces in this type of anion allow the inclusion of water molecules. Hydrates are, in fact, numerous.

In the 6-acids, six  $\text{MoO}_6$  octahedra are joined by sharing edges to form a hexagonal annulus, in the centre of which is an octahedral arrangement of bonds round the hetero-atom; the central atoms of the known 6-acids all show octahedral stereochemistry (Fig. 345).

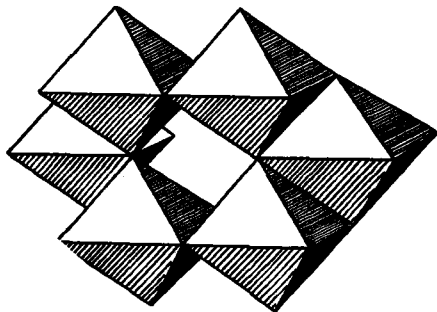


Fig. 345. Arrangement of  $\text{MoO}_6$  octahedra in a 6-acid.

Molybdenum also forms salts of 9-acids, *e.g.*  $H_6(MnMo_9O_{32})$ , and salts of the more complex 10- and 11-acids with molybdenum atom: hetero-atom ratios of 10 and 11 respectively.

Work on the structure of polyanions is beginning to shed light on a formerly intractable problem, yet there are still many unexplained anomalies. One of the most striking is the existence of surprisingly high ionic charges; the well-characterised  $Fe^{III}_5H[SiW_{12}O_{40}]_2 \cdot 52H_2O$  must contain an anion with a charge  $-8$ .

### Isopolyacids

In addition to heteropolyacids there are isopolyacids, the commonest of which are the parent acids of the paramolybdates,  $H_6[Mo_7O_{24}]$ , and of the paratungstates,  $H_5[HW_6O_{21}]$ . The structure of the  $[Mo_7O_{24}]^{6-}$  ion is like that of the 6-acid anions (above) but with a central, octahedrally co-ordinated Mo atom. From more acidic solutions, octamolybdates,  $MI_4[Mo_8O_{26}]$ , can be obtained. These have a structure similar to that shown in Fig. 345 but with two additional octahedrally co-ordinated molybdenum atoms, one on each side of the central annulus.

### Tungsten bronzes

When alkali-metal tungstates are reduced by heating with tungsten or by electrolysis in the fused state, intensely coloured, unreactive substances are obtained with semi-metallic properties; they are good conductors of electricity. These *tungsten bronzes* have the general formula  $M_xWO_3$  ( $M = Li, Na, \text{ or } K; x < 1$ ). The compounds have defect lattices with the alkali-metal atoms

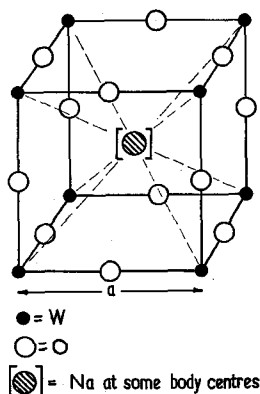


Fig. 346. Structure of a tungsten bronze

occupying only a fraction of the places indicated in Fig. 356. When  $x$  is large ( $\sim 0.9$ ) the  $a$  dimension is large (3.85 Å) too, and the bronze is golden yellow. Reduction of  $x$  reduces  $a$  and intensifies the colour in this non-stoichiometric phase (p. 215).

The formula implies that tungsten exhibits a charge between +5 and +6 but it is most convenient to regard all the tungsten ions in the structure as  $W^{6+}$ , the electrons from the sodium atoms being imagined as part of the free 'electron gas' of the whole lattice. This concept is in accord with the electrical conductance, metallic appearance, and low paramagnetic susceptibilities of the tungsten bronzes.

### Binary compounds with other non-metals

The metals of this sub-group do not form definite hydrides.

They react at high temperatures with carbon and nitrogen to give hard, refractory carbides and nitrides. These generally have the character of interstitial compounds, but there are phases of stoichiometric composition:  $M_2C$ ,  $M_2N$ ,  $MC$  and  $MN$  ( $M = Mo$  and  $W$ ). The mononitrides and monocarbides have cubic, close-packed arrangements of metal atoms with N or C atoms in octahedral holes. The best-characterised chromium carbide is  $CrC$ : there is a nitride  $CrN$  which is a violet powder.

There are various types of interstitial borides.  $MoB$  and  $WB$  have structures similar to that of  $FeB$  (p. 347).  $MoB_2$  and  $WB_2$  resemble  $AlB_2$ .

A monosulphide  $CrS$  is obtained by direct combination of the elements at high temperatures. The dark-green, paramagnetic  $Cr_2S_3$  is formed by the action of  $H_2S$  on  $Cr_2O_3$ .

Molybdenum forms several sulphides; the most important is molybdenite,  $MoS_2$ .

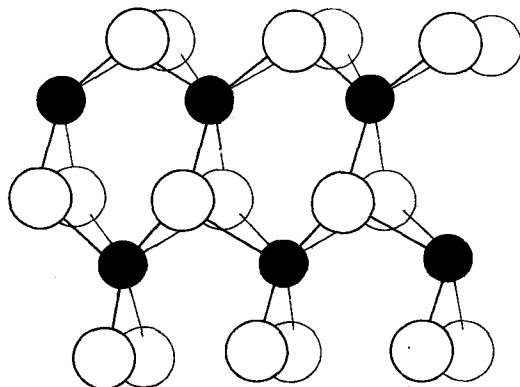


Fig. 347. Eclipsed arrangement of S atoms in molybdenite,  $MoS_2$ .



$\text{MoS}_2$ , which has a layer lattice rather like  $\text{CdI}_2$  but with the layers of S atoms eclipsed instead of staggered (Fig. 347).

Molybdenite resembles graphite in being an excellent lubricant and is added to engine oils for that purpose. A trisulphide  $\text{MoS}_3$  is precipitated when  $\text{H}_2\text{S}$  is passed into an acidified molybdate solution. The sulphides  $\text{WS}_2$  and  $\text{WS}_3$  resemble the molybdenum compounds.

### Organometallic compounds and $\pi$ -complexes

The metals all have  $\pi$ -bonded organometallic derivatives.

Chromium forms a cyclopentadienyl compound similar to ferrocene (p. 699). Cyclopentadienylsodium reacts with anhydrous chromium(II) chloride in tetrahydrofuran to give red  $(\text{C}_5\text{H}_5)_2\text{Cr}$ . By oxidising this, compounds containing the  $(\text{C}_5\text{H}_5)_2\text{Cr}^+$  ion are easily obtained. The compound  $(\text{C}_5\text{H}_5)_2\text{Cr}$  enters into a complex reaction with carbon monoxide; in addition to  $(\text{C}_5\text{H}_5)_2\text{Cr}_2(\text{CO})_6$ , a salt,  $[(\text{C}_5\text{H}_5)_2\text{Cr}]^+[\text{C}_5\text{H}_5\text{Cr}(\text{CO})_3]^-$ , is obtained; but, at temperatures over  $250^\circ$ , the principal product is  $\text{Cr}(\text{CO})_6$ .

Molybdenum pentachloride reacts with  $\text{C}_5\text{H}_5\text{MgBr}$  to give cations  $[(\text{C}_5\text{H}_5)_2\text{MoCl}]^+$  and  $[(\text{C}_5\text{H}_5)_2\text{MoCl}_2]^+$ ;  $\text{WCl}_6$  gives  $[(\text{C}_5\text{H}_5)_2\text{WCl}_2]^+$ .

Several mixed cyclopentadiene compounds of chromium are known. Chromium(III) acetylacetonate gives with  $\text{C}_5\text{H}_5\text{MgBr}$  cyclopentadienylchromium acetylacetonate in which the chromium atom is  $\pi$ -bonded to  $\text{C}_5\text{H}_5$  but is also part of a chelate ring. Cyclopentadienylbenzenechromium, in which both  $\text{C}_5\text{H}_5$  and  $\text{C}_6\text{H}_6$  rings are  $\pi$ -bonded to the metal, has been isolated from the reaction of  $\text{C}_5\text{H}_5\text{MgBr}$ ,  $\text{C}_6\text{H}_5\text{MgBr}$  and  $\text{CrCl}_3$ , followed by hydrolysis.

Dibenzenechromium, which has a sandwich structure with a Cr atom between parallel benzene rings, can be made by heating  $\text{CrCl}_2$  with benzene,  $\text{AlCl}_3$  and aluminium, then hydrolysing the product to obtain  $\text{Cr}(\text{C}_6\text{H}_6)_2^+\text{Cl}^-$  and reducing this salt with sodium dithionite. The dark-brown, diamagnetic solid decomposes at  $300^\circ$  into chromium and benzene. There is a similar compound of molybdenum.

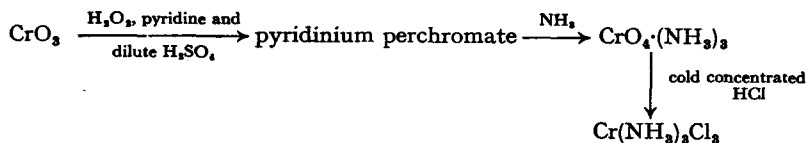
Although  $(\text{C}_6\text{H}_6)_2\text{Cr}$  contains the same number of bonding electrons as  $(\text{C}_5\text{H}_5)_2\text{Fe}$  it is much less stable to electrophiles; attempts to effect aromatic substitution as in ferrocene always causes decomposition.

### Complexes

There are not many complexes containing the metals in the +2 state. Chromium forms amines, for instance  $\text{Cr}(\text{NH}_3)_6\text{Cl}_2$ , which are high-spin  $d^4$  complexes and, as such, exhibit Jahn-Teller distortion (p. 164) to a

tetragonal symmetry. There are some low-spin cyanocomplexes such as  $K_4Cr(CN)_6$ . Molybdenum(II) is represented by high-spin orthophenylenebisdimethyldiarsine complexes,  $Mo(diars)_2X_2$  ( $X = Cl, Br, I$ ).

Chromium(III) complexes ( $d^3$  configuration) are very common; there are many ammine complexes of this oxidation state. The purple chloropentamminechromium(III) dichloride,  $[Cr(NH_3)_5Cl]Cl_2$ , is made by bubbling air through a solution of  $CrCl_2$ ,  $NH_4Cl$  and  $NH_3$  in water. It can be converted into hexa-amminechromium(III) trichloride,  $[Cr(NH_3)_6]Cl_3$  (yellow), by treating its cold, concentrated solution with ammonia. A violet dichlorotetra-amminechromium(III) chloride,  $[Cr(NH_3)_4Cl_2]Cl$ , exists and also the triammine,  $Cr(NH_3)_3Cl_3$ . Werner (1910) made the latter by the reactions:



Cyano- and thiocyanato-complexes of chromium are also common. Among the more interesting of these is Reinecke's salt,  $NH_4[Cr(NH_3)_2(SCN)_4]H_2O$ , made by adding  $(NH_4)_2Cr_2O_7$  slowly to melted  $NH_4SCN$ , washing with, and recrystallising from, alcohol. The octahedral ion has the form shown in Fig. 348.

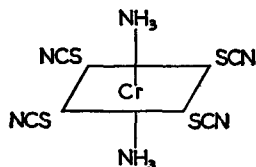
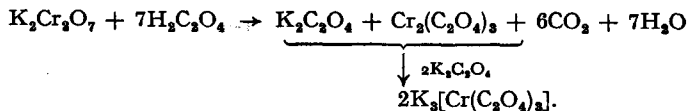


Fig. 348. Structure of  $[Cr(NH_3)_2(SCN)_4]^-$  ion present in Reinecke's salt.

Some of the oxalato-complexes of chromium(III) are also of interest. Potassium trioxalatochromate(III),  $K_3Cr(C_2O_4)_3 \cdot 3H_2O$ , is obtained by adding potassium oxalate to the solution obtained by reducing  $K_2Cr_2O_7$  with oxalic acid:



The anion of the blue crystalline compound was resolved by Werner (1912) into dextrorotatory and laevorotatory forms (Fig. 349, A). Potassium dioxalato-diaquochromate,  $K[Cr(C_2O_4)_2(H_2O)_2]$ , exists in *cis*- and *trans*-forms,

the former (Fig. 349, B (i)) showing purple-green dichroism and the latter (Fig. 349, B (ii)) being mauve.

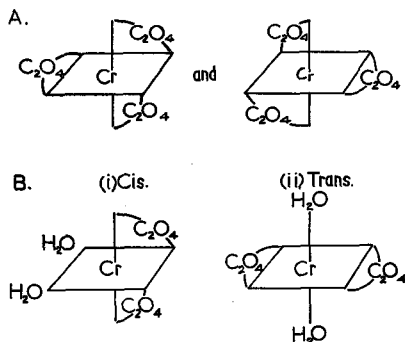
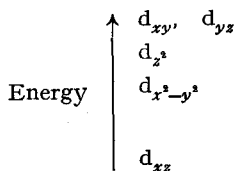


Fig. 349. A. *d*- and *l*-forms of  $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$  ion.  
B. *cis*- and *trans*-forms of  $[\text{Cr}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]^-$  ion.

Molybdenum(III) exists in neutral, anionic and cationic complexes.  $\text{MoCl}_3$  and  $\text{MoBr}_3$  form the adducts with pyridine  $\text{Mo}(\text{py})_3\text{X}_3$ , but the halides undergo solvolysis in liquid ammonia, methylamine and dimethylamine to give products such as  $\text{MoBr}_2\cdot\text{NH}_3$  and  $\text{MoBr}_2\cdot\text{NMe}_2\cdot\text{NHMe}_2$ . The complex anions include many octahedral ones of the  $\text{MoX}_6^{3-}$  type in which X is a halogen or pseudohalogen. The complex  $\text{Mo}^{\text{III}}$  cations include  $\text{Mo}(\text{dipy})_3^{3+}$  and  $\text{Mo}(o\text{-phen})_3^{3+}$ . Tungsten(III), however, forms few complexes; these are mainly complex halides. The  $\text{W}_2\text{Cl}_9^{3-}$  ion in  $\text{K}_3\text{W}_2\text{Cl}_9$  has the same structure as the  $\text{Ti}_2\text{Cl}_9^{3-}$  ion (p. 358).

Molybdenum(IV) and tungsten(IV) are represented by interesting 8-coordinate cyanocomplexes containing  $\text{Mo}(\text{CN})_8^{4-}$  ions.  $\text{K}_4\text{Mo}(\text{CN})_8$  is made by treating a  $\text{K}_2\text{MoCl}_6$  solution with KCN in the presence of air. These octacyanocomplexes are remarkably stable to heat and hydrolysis. The free acid  $\text{H}_4[\text{Mo}(\text{CN})_8]\cdot 6\text{H}_2\text{O}$  can be isolated as crystals when the potassium salt is acidified with HCl. The acid is oxidised to  $\text{H}_3\text{Mo}(\text{CN})_8\cdot 3\text{H}_2\text{O}$  by  $\text{KMnO}_4$ . Molybdenum(IV) has only one d electron. The arrangement of eight  $\text{CN}^-$  ligands around the metal atom in the  $\text{Mo}(\text{CN})_8^{4-}$  ion is such as to stabilise one d orbital relatively to all the others:



The structure of the  $\text{Re}(\text{CN})_8^{3-}$  ion is similarly stabilised. In solid  $\text{K}_4\text{Mo}(\text{CN})_8$  the complex ion is dodecahedral (Fig. 350).

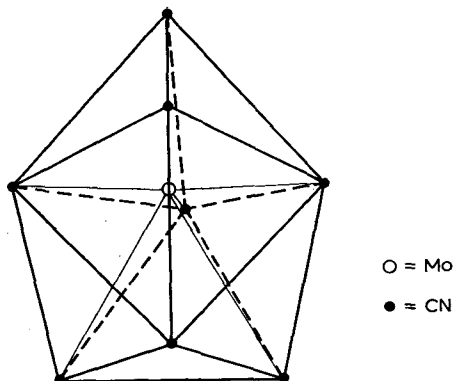


Fig. 350. Dodecahedral structure of  $\text{Mo}(\text{CN})_8^{4-}$  ion.

The oxidation state +5 is represented by some fluoro- and oxohalide complexes of molybdenum and tungsten, such as  $\text{M}^{\text{V}}\text{MoF}_6$ ,  $\text{M}^{\text{V}}\text{WF}_6$ ,  $\text{M}^{\text{V}}_2[\text{MoOCl}_5]$  and  $\text{M}^{\text{V}}[\text{MoOBr}_4]$ . There are also the cyanocomplexes like  $\text{K}_3\text{W}(\text{CN})_8$ , made by the oxidation of aqueous solutions of the corresponding +4 complexes (above).

Molybdenum(VI) and tungsten(VI) exist in anionic complexes containing oxygen and fluorine as ligands. Examples are  $[\text{MoOF}_5]^-$  and  $[\text{WOF}_5]^-$ ,  $[\text{MoO}_3\text{F}_3]^{3-}$  and  $[\text{WO}_3\text{F}_3]^{3-}$ .

Chromium(VI) oxide reacts with alkali metal and ammonium iodate on heating to give the compounds  $\text{M}^{\text{VI}}\text{CrIO}_6$ . The ammonium salt contains a complex  $\text{CrIO}_6^-$  ion which has a tetrahedral arrangement of oxygens around the chromium, one of the oxygens being shared with a trigonal arrangement around the iodine.

#### FURTHER READING

- F. A. COTTON, *Transition-Metal Compounds Containing Clusters of Metal Atoms*, Quart. Rev., 20 (1966) 389.  
 W. H. HARTFORD AND M. DARRIN, *Chemistry of Chromyl Compounds*, Chem. Rev., 58 (1958) 1.  
 P. C. H. MITCHELL, *Oxo-species of Molybdenum(V) and Molybdenum(VI)*, Quart. Rev., 20 (1966) 103.

## Manganese, Technetium and Rhenium

### GROUP VIIA

#### Atomic and general properties

The properties of manganese stand apart from those of technetium and rhenium, elements which resemble one another closely. The break in descending the sub-group is similar but more marked than that between vanadium and niobium in Group VA and that between chromium and molybdenum in Group VIA. Nevertheless, as in these earlier sub-groups, there is enough in common among these Group VIIA elements for it to be advantageous to treat them as a family. Manganese, technetium and rhenium are demonstrably metallic. They each have a total of seven s and d electrons available for valency orbitals. Their dioxides are all stable and their +7 state is clearly characterised in the permanganate, pertechnetates and perrhenates, which have the  $\text{MO}_4^-$  anion. In the main, technetium and rhenium differ from manganese in the instability of the +2 state and other low oxidation states. Manganese has a stable  $d^5$  electronic arrangement and is commonly bivalent.

TABLE 128

ATOMIC PROPERTIES OF GROUP VIIA ELEMENTS

	<i>Mn</i>	<i>Tc</i>	<i>Re</i>
Atomic number	25	43	75
Electron configuration	$3d^5 4s^2$	$4d^5 5s^2$	$5d^5 6s^2$
Metallic radius (Å)	1.26	1.36	1.37
Ionic radius, $\text{M}^{2+}$ (Å)	0.80		

The densities of the metals are normal for the position they occupy in their respective periods in the Periodic Table. The m.p. of technetium and rhenium are particularly high, that of the latter being exceeded among metals only by tungsten.

Though the first and second ionisation energies of manganese are similar to those of magnesium, the standard electrode potential  $E^\circ$ ,  $\text{Mn}^{2+}/\text{Mn}$  is much less negative than that for magnesium because of the much greater heat of sublimation (p. 228).

TABLE 129

## PHYSICAL PROPERTIES OF GROUP VIIA ELEMENTS

	<i>Mn</i>	<i>Tc</i>	<i>Re</i>
Density (g/cc)	7.4	11.5	20.5
Atomic volume	7.4	8.6	8.8
Melting point (°C)	1260	2150	3170

The redox potentials for technetium and rhenium (Table 130) are for the reactions:

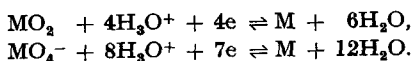


TABLE 130

## IONISATION ENERGIES AND ELECTRODE POTENTIALS OF GROUP VIIA ELEMENTS

		<i>Mn</i>	<i>Tc</i>	<i>Re</i>
Ionisation energy <i>I</i>	1 (eV)	7.43	7.28	7.87
	2 (eV)	15.46	15.26	
<i>E</i> °, <i>M</i> <sup>2+</sup> / <i>M</i> (V)		-1.05		
MO <sub>2</sub> / <i>M</i> (V)			+0.27	+0.25
MO <sub>4</sub> <sup>-</sup> / <i>M</i> (V)		+0.79	+0.47	+0.34

The free energies of some of the oxidation states relative to the metal in aqueous solution at pH 0 are given in Fig. 351. A striking point is the very great stability of Mn<sup>II</sup> to both oxidation and reduction. The Mn<sup>VI</sup> state is unstable to disproportionation in acid solution but is more stable at high pH. Thus K<sub>2</sub>MnO<sub>4</sub> (which is isomorphous with K<sub>2</sub>CrO<sub>4</sub>) is converted by as weak an acid as H<sub>2</sub>CO<sub>3</sub> into KMnO<sub>4</sub> and MnO<sub>2</sub>:



Technetium and rhenium salts corresponding to Mn<sup>2+</sup> salts are not known. The formal charge +7 is dominant in Tc and Re; compounds in this state have far less oxidising power than MnO<sub>4</sub><sup>-</sup>. Free permanganic acid exists only in aqueous solution and the oxide decomposes explosively above 0°. The corresponding compounds of Tc and Re are, however, stable.

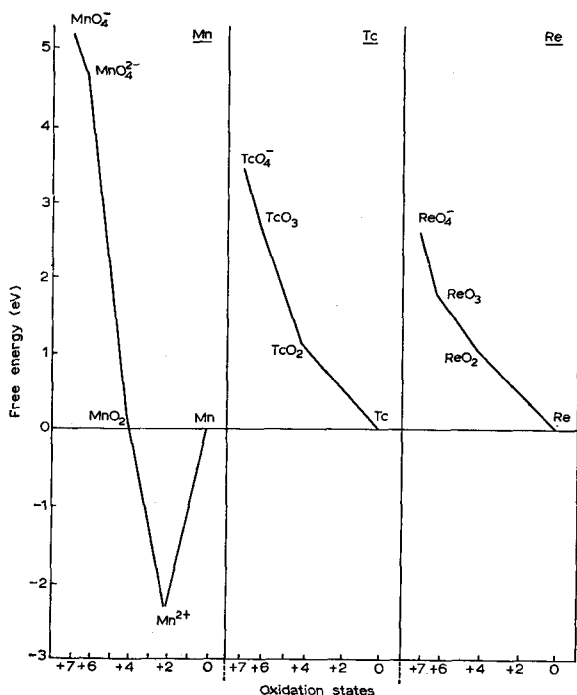


Fig. 351. Free energies of oxidation states relative to the metal in aqueous solution at pH = 0.

### Occurrence and preparation of the elements

#### *Manganese*

The element (0.08% of the earth's crust) occurs principally as oxides, pyrolusite, a tetragonal form of  $MnO_2$ , being the most important. The metal is made in small quantities by aluminothermic reduction of  $MnO_2$ , or by electrolysis of  $MnSO_4$  solution. Pure manganese has three forms, an  $\alpha$ -cubic, a  $\beta$ -cubic, and a face-centred tetragonal, the last with an axial ratio 0.937. The metal is reactive; it combines with the halogens, oxygen, sulphur, carbon, nitrogen (Fig. 352) and with most of the metalloids. It liberates hydrogen from dilute  $HCl$  and  $H_2SO_4$  in the cold and from steam at red heat.

Its most important use is for improving the mechanical properties of steel, almost every grade of which contains manganese. It combines with the sulphur which would otherwise remain as  $FeS$  and make the steel brittle when hot. The  $MnS$  forms harmless inclusions, thereby improving the

rolling and forging properties of the steel. The rest of the manganese acts as a deoxidiser while the metal is molten and improves its strength, toughness and response to heat-treatment after solidification. For this purpose ferromanganese (80% Mn, 20% Fe) and spiegeleisen (25% Mn, 5% C, 70% Fe) are made by blast-furnace reduction of mixed oxides.

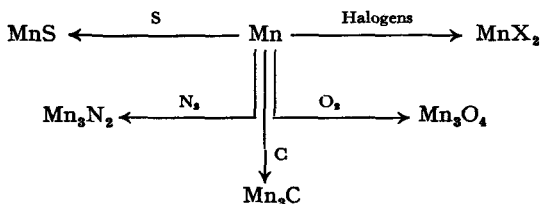
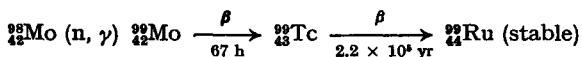


Fig. 352. Reactions of manganese.

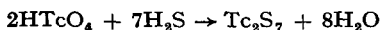
### Technetium

The element occurs terrestrially in trace amounts as technetium-99, a fission product of uranium, and has also been observed in spectra of the sun and certain stars. In 1937, the 90-day technetium-97 was made by bombarding molybdenum with high-energy deuterons from a cyclotron. The isotope more useful as a tracer is the 60-day technetium-95. The long-lived technetium-99, the most useful isotope for studying the element, is obtained by long irradiation of molybdenum in an atomic pile:



Technetium-99 also forms about 6% of the fission products of uranium; and a pile operating at 100 megawatts yields about 2.5 g per day. This is the principal source of the metal.

The hot, acid solution of fission-product waste, to which an excess of perchloric acid has been added to provide a chlorate carrier for the technetate, is treated with tetraphenyl tetrachloroarsenate,  $\text{Ph}_4\text{AsCl}_4$ . The precipitate, consisting of  $\text{Ph}_4\text{AsTeO}_4$  with its carrier  $\text{Ph}_4\text{AsClO}_4$ , is filtered off; the caesium, strontium, lanthanide and other fission elements remain in solution. The technetium is recovered by dissolving the precipitate of technetate and chlorate in concentrated sulphuric acid and electrolysing the solution between platinum electrodes. The black  $\text{TcO}_2$  which is deposited is dissolved in perchloric acid which oxidises it to  $\text{Tc}_2\text{O}_7$ . The heptoxide is distilled out of the solution into water and separated therefrom by precipitating  $\text{Tc}_2\text{S}_7$  with hydrogen sulphide:



The heptasulphide is reduced to metal by heating it in a stream of hydrogen.



The metal is bright and silvery; it tarnishes in moist air and, like rhenium, burns in oxygen to the heptoxide. It dissolves in  $\text{HNO}_3$  and concentrated  $\text{H}_2\text{SO}_4$ , but not in  $\text{HCl}$ .

### Rhenium

The element remained undiscovered till 1925 largely because it was sought in manganese ores. In fact its only appreciable occurrence is in molybdenite,  $\text{MoS}_2$ , some Norwegian minerals containing as much as 20 p.p.m. of Re. The metal is usually made by reducing  $\text{NH}_4\text{ReO}_4$  with hydrogen at  $400^\circ$  but the sulphide  $\text{Re}_2\text{S}_7$ , the chloride  $\text{ReCl}_5$ , and the oxide  $\text{ReO}_2$  are also readily reduced. It is not employed industrially at present, but has possibilities as a hydrogenation catalyst:

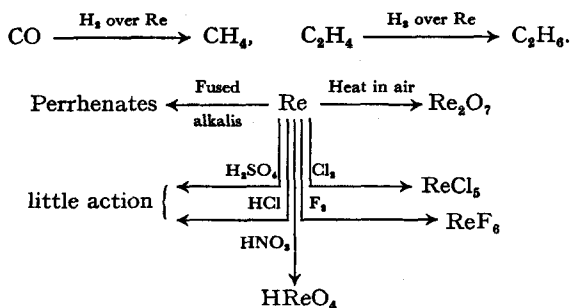


Fig. 353. Reactions of rhenium.

### Oxidation states

Representative compounds and ions with the metals in various oxidation states are shown in Table 131.

TABLE 131

COMPOUNDS AND IONS OF OXIDATION STATES  $-1$  TO  $+7$

Charge number	Manganese	Technetium	Rhenium
-1	$\text{Mn}(\text{CO})_5^-$		$\text{Re}(\text{CO})_5^-$
0	$\text{Ph}_3\text{PMn}(\text{CO})_4$	$\text{Tc}_2(\text{CO})_{10}$	$\text{Re}_2(\text{CO})_{10}$
+1	$\text{Mn}(\text{CO})_5\text{Cl}$	$\text{K}_5\text{Tc}(\text{CN})_6$ , $\text{Tc}(\text{CO})_5\text{Cl}$	$\text{Re}(\text{CO})_5\text{I}$
+2	$\text{Mn}(\text{H}_2\text{O})_6^{2+}$	$(\text{C}_5\text{H}_5)_2\text{Tc}$	$\text{Na}_2\text{Re}(\text{CN})_5$
+3	$\text{MnF}_3$	$[\text{Tc}(\text{diars})_2\text{Cl}_2]\text{Cl}$	$\text{Re}_2\text{Br}_6$
+4	$\text{MnF}_4$ , $\text{MnO}_2$	$\text{TcO}_2$ , $\text{K}_2\text{TcF}_6$	$\text{ReF}_4$
+5	$\text{Na}_3\text{MnO}_4$	$\text{TcOBr}_3$	$\text{ReBr}_5$
+6	$\text{MnO}_4^{2-}$	$\text{TcF}_6$	$\text{ReO}_3$
+7	$\text{MnO}_4^-$ , $\text{MnO}_3\text{F}$	$\text{TcO}_4^-$ , $\text{Tc}_2\text{S}_7$	$\text{ReO}_3\text{F}$

As usual, the lowest states are stabilised by ligands such as the CO molecule, the highest by fluoride and oxide ions. In this group of the Periodic Table the range of oxidation states is very wide indeed, but the +5 ( $d^2$ ) state is rather uncommon.

### Halides

The halides and oxohalides of the sub-group are tabulated in Table 132.

TABLE 132

HALIDES AND OXOHALIDES OF GROUP VIIA ELEMENTS

<i>Charge number</i>	<i>Manganese</i>	<i>Technetium</i>	<i>Rhenium</i>
+2	MnF <sub>2</sub> , MnCl <sub>2</sub> , MnBr <sub>2</sub> , MnI <sub>2</sub>		
+3	MnF <sub>3</sub>		ReCl <sub>3</sub> , ReBr <sub>3</sub> , ReI <sub>3</sub>
+4	MnF <sub>4</sub>	TcCl <sub>4</sub>	ReF <sub>4</sub> , ReBr <sub>4</sub> , ReI <sub>4</sub>
+5			ReF <sub>5</sub> , ReCl <sub>5</sub> , ReBr <sub>5</sub>
		TcOBr <sub>3</sub>	ReOF <sub>3</sub>
+6		TcF <sub>6</sub> , TcCl <sub>6</sub>	ReF <sub>6</sub> , ReCl <sub>6</sub>
			ReOF <sub>4</sub> , ReOCl <sub>4</sub> , ReOBr <sub>4</sub>
+7			ReF <sub>7</sub>
			ReOF <sub>5</sub>
			ReO <sub>2</sub> F <sub>3</sub>
	MnO <sub>3</sub> F	TcO <sub>3</sub> F	ReO <sub>3</sub> F, ReO <sub>3</sub> Cl, ReO <sub>3</sub> Br

Features of note in the table are (a) the absence of higher iodides, (b) the absence of high-oxidation states of Mn except for MnO<sub>3</sub>F, (c) the existence of many oxofluorides of rhenium.

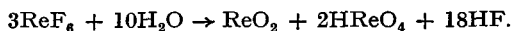
The dihalides of manganese, except MnF<sub>2</sub>, are obtained as soluble, rose-pink hydrates when the metal is dissolved in the halogen acid.

The only trihalide of manganese, MnF<sub>3</sub>, is made by the action of F<sub>2</sub> on MnI<sub>2</sub>. The trifluoride gives with water MnO<sub>2</sub> and the sparingly soluble MnF<sub>2</sub>.

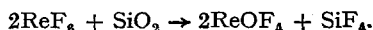
The blue tetrafluoride, MnF<sub>4</sub>, has been obtained by heating MnF<sub>3</sub> with fluorine at 400°. ReBr<sub>4</sub> and ReI<sub>4</sub> are made by reducing perrhenic acid with HBr and HI respectively. TcCl<sub>4</sub> has been made by heating Tc<sub>2</sub>O<sub>7</sub> and CCl<sub>4</sub> in a closed tube.

Rhenium pentachloride, ReCl<sub>5</sub>, is made by heating Re in Cl<sub>2</sub>. When the compound is heated in an inert atmosphere, it is converted into the violet, crystalline ReCl<sub>3</sub>. Direct combination of Re and Br<sub>2</sub> at 300° gives dark-green ReBr<sub>3</sub>.

Golden-yellow crystals of  $\text{TcF}_6$ , m.p.  $33^\circ$ , have been obtained by heating the metal in fluorine. Rhenium combines with  $\text{F}_2$  under a little pressure to produce a pale-yellow solid,  $\text{ReF}_7$ , which is the highest binary metal fluoride known. At  $125^\circ$  under atmospheric pressure the product is  $\text{ReF}_6$ , m.p.  $19^\circ$ . This hydrolyses:



It also reacts with silica and glass:



Rhenium hexafluoride is reduced by  $\text{H}_2$ ,  $\text{SO}_2$ , Re, Zn and Al to  $\text{ReF}_4$ , m.p.  $124.5^\circ$ .

The oxofluoride of manganese is made by the action of anhydrous HF on  $\text{KMnO}_4$  at a low temperature:



The dark-green crystals of  $\text{MnO}_3\text{F}$  melt at  $-38^\circ$  and explode at  $0^\circ$ . The many oxohalides of rhenium are present in the crude halide preparations unless air and moisture have been rigorously excluded. As would be expected the compound  $\text{ReO}_3\text{F}$  is much more stable than  $\text{MnO}_3\text{F}$ . The low-melting, yellow solid, pertechnyl fluoride,  $\text{TcO}_3\text{F}$ , is made by the action of fluorine on  $\text{TcO}_2$  at  $150^\circ$ .

The elements display a wide range of complex halides. Manganese(II) forms complexes of the types  $\text{M}^{\text{II}}\text{MnF}_3$ ,  $\text{M}^{\text{I}_2}\text{MnCl}_4$  and  $\text{M}^{\text{I}_4}\text{MnCl}_6$ . Moreover,  $\text{MnCl}_2$  and  $\text{MnBr}_2$  react with salts like the pyridinium and tetramethylammonium halides to give tetrahedral  $\text{MnX}_4^{2-}$  complexes.

Manganese(III) complexes such as  $\text{M}^{\text{I}_2}\text{MnF}_5$  and  $\text{M}^{\text{I}_2}\text{MnCl}_5$  are known. When  $\text{MnO}_2$  is added to a solution of HCl in  $\text{CCl}_4$ , a dark-green colour is produced and a salt  $(\text{Et}_4\text{N})_2\text{MnCl}_5$  can be extracted after the addition of tetraethylammonium chloride.

The  $\text{ReCl}_4^-$  ion is of interest. It was once thought to be an example of the otherwise unknown phenomenon of spin-pairing enforced by a tetrahedral field. However the ion in  $\text{CsReCl}_4$  has been proved to exist as  $\text{Re}_3\text{Cl}_{12}^{3-}$  in which there is a triangle of Re atoms, each 7-co-ordinate (Fig. 354).

The most common complex halides of Mn and Re are those in which the metal has a +4 charge; examples are  $\text{M}^{\text{I}_2}\text{MnCl}_6$ ,  $\text{M}^{\text{I}_2}\text{ReCl}_6$  and, particularly, the corresponding fluoro-complexes. This +4 state of Re is obtained from states of higher charge in the formation of these compounds:



The fluoro-compound  $\text{K}_2\text{ReF}_6$  is made in good yield by the action of anhydrous HF on  $\text{K}_2\text{ReI}_6$ , but the acid  $\text{H}_2\text{ReF}_6$  cannot be isolated.

The  $\text{Mn}^{\text{IV}}$  complexes are spin-free with 3 unpaired electrons. The magnetic susceptibilities of the complex chlorides of  $\text{Re}^{\text{IV}}$  and  $\text{Tc}^{\text{IV}}$  increase with temperature and the magnetic moment approaches that expected for 3 unpaired electrons.

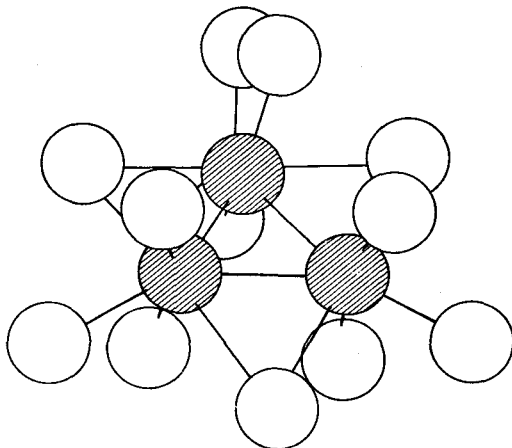


Fig. 354. The  $\text{Re}_3\text{Cl}_{12}^{3-}$  anion in  $\text{CsReCl}_4$ .

### Oxides

The known oxides of manganese, technetium and rhenium are given below.

$\text{MnO}$	—	—
$\text{Mn}_3\text{O}_4$	—	—
$\text{Mn}_2\text{O}_3$	—	—
$\text{MnO}_2$	$\text{TcO}_3$	$\text{ReO}_2$
—	$\text{TcO}_3$ (reported)	$\text{ReO}_3$
$\text{Mn}_2\text{O}_7$	$\text{Tc}_2\text{O}_7$	$\text{Re}_2\text{O}_7$

### Manganese

The monoxide,  $\text{MnO}$ , occurs as the grey-green mineral manganosite (cubic  $\text{NaCl}$  structure) and the corresponding hydroxide,  $\text{Mn}(\text{OH})_2$ , occurs as pyrochroite. Made by the thermal decomposition of the oxalate or carbonate,  $\text{MnO}$  is readily oxidised. Heating in air at  $250\text{--}300^\circ$  converts it to  $\text{Mn}_2\text{O}_3$ . The precipitated hydroxide is oxidised by air even at room temperature.

$\text{Mn}_3\text{O}_4$ , found in nature as hausmannite, is formed when any of the other oxides of manganese is heated in air to  $1000^\circ$ . The oxide is a normal spinel (p. 207) but is tetragonal instead of octahedral because of Jahn-Teller distor-

tion. The  $\text{Mn}^{3+}$  ( $d^4$ ) ion is, like a  $d^8$  ion, particularly stable in a square, 4-coordinate environment, and tends to occupy octahedral rather than tetrahedral sites. But because of the electronic degeneracy due to there being one electron in the  $e_g$  level, the octahedral arrangement of oxygen around the cation is distorted to tetragonal.

$\text{Mn}_2\text{O}_3$  has  $\alpha$ - and  $\beta$ -forms, corresponding to those of  $\text{Fe}_2\text{O}_3$  (p. 697). Another oxygen compound of  $\text{Mn}^{\text{III}}$  is the mineral manganite,  $\text{MnO}(\text{OH})$ .

Manganese dioxide exists principally as pyrolusite, a mineral with a rutile-like structure. Pyrolusite is used (a) for making ferromanganese and manganese itself, (b) in dry batteries, (c) for rendering glass colourless, (d) as a drier in paint, and (e) for making  $\text{MnSO}_4$  which is used for treating manganese-deficient soils. The purest  $\text{MnO}_2$  is made by decomposing  $\text{Mn}(\text{NO}_3)_2$  at  $200^\circ$ , followed by dehydration of the residue at  $500^\circ$  in oxygen, but the product is always stoichiometrically deficient in oxygen.

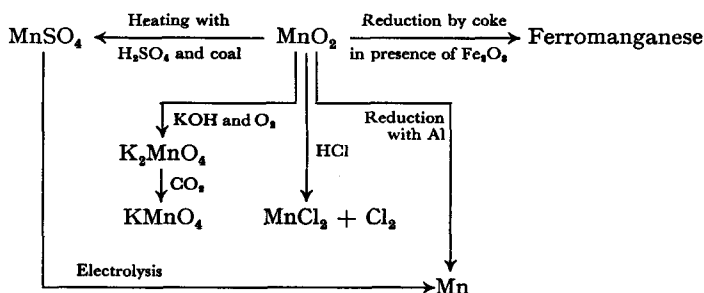
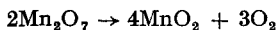


Fig. 355. Reactions of manganese dioxide.

Manganese heptoxide,  $\text{Mn}_2\text{O}_7$ , very much the least stable oxide of manganese, separates when powdered  $\text{KMnO}_4$  is added to concentrated  $\text{H}_2\text{SO}_4$  and the mixture is cooled to  $-20^\circ$ . It is a dark olive-green liquid which can be distilled below  $0^\circ$  but which explodes at  $10^\circ$ :



### *Technetium and rhenium*

Technetium dioxide is the most thermally stable oxide of technetium, it sublimates at  $\sim 1000^\circ$  and is formed when either of the other oxides or ammonium pertechnetate,  $\text{NH}_4\text{TeO}_4$ , is heated; The oxide dihydrate is precipitated when pertechnetates are reduced and is oxidised back to  $\text{TcO}_4^-$  by hydrogen peroxide. Rhenium dioxide results from heating  $\text{Re}_2\text{O}_7$  with the metal at  $600^\circ$  or from reducing an acid solution of  $\text{HReO}_4$  with zinc. It is less thermally stable than  $\text{TcO}_2$ , being converted to the heptoxide and rhenium

at high temperatures. Both technetium and rhenium dioxides have the same distorted rutile structure as manganese dioxide.

Technetium trioxide has been reported as a product of heating  $\text{TeO}_3\text{Br}$ , but little is yet known about it. However, rhenium trioxide (red or purple) is well established. It was first made by reducing  $\text{Re}_2\text{O}_7$  with the metal at  $300^\circ$ , and is obtained, in almost quantitative yield, by the thermal decomposition of  $\text{Re}_2\text{O}_7(\text{C}_4\text{H}_8\text{O}_2)_3$ , the addition compound of  $\text{Re}_2\text{O}_7$  with dioxan. When it is strongly heated,  $\text{ReO}_3$  disproportionates:



It has a very simple structure (Fig. 356), related to that of  $\text{CrO}_3$  and  $\text{MoO}_3$ .

Both technetium and rhenium form heptoxides. The first,  $\text{Tc}_2\text{O}_7$ , a pale yellow, hygroscopic solid (m.p.  $300^\circ$ ), is made by heating the metal or the other oxides to  $200^\circ$  in air. The heptoxides are not isostructural. Both are very hygroscopic and give solutions of pertechnetic and perrhenic acid respectively.

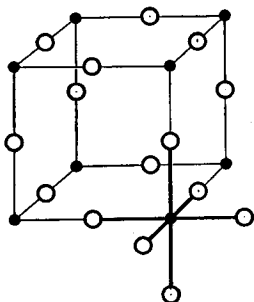


Fig. 356. Structure of rhenium trioxide.

### Manganates and rhenates

Manganese has the well-known, green manganate ion  $\text{MnO}_4^{2-}$  which is formed when a manganese compound is fused with an alkali-metal hydroxide and an oxidising agent. Several of its salts have been prepared. The soluble manganates are stable only in alkaline solution; in acid the ion disproportionates into  $\text{MnO}_4^-$  and hydrated manganese dioxide:



One of the most stable manganates,  $\text{BaMnO}_4$ , is made by adding concentrated  $\text{KMnO}_4$  to boiling saturated  $\text{Ba}(\text{OH})_2$ :



Its magnetic moment indicates the presence of one unpaired electron. The material provides a non-toxic green pigment.

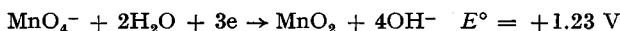
Rhenium has also an oxo-anion,  $\text{ReO}_3^{2-}$ , in which the charge number of the metal is  $+4$ . The ion is very readily oxidised and, in contrast to the  $\text{MnO}_4^{2-}$  anion, is immediately decomposed by water.

### Permanganates, pertechnetates and perrhenates

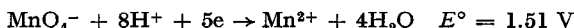
#### *Permanganates*

The stability of the permanganate ion  $\text{MO}_4^-$  over a wide range of pH makes the permanganates very useful oxidising agents. Potassium permanganate,  $\text{KMnO}_4$ , is manufactured by the electrolytic oxidation of the alkaline manganate solution. It is used in volumetric oxidimetry, in the industrial production of such things as saccharin and benzoic acid, and for bleaching waxes. The  $\text{MnO}_4^-$  anion is much used in the volumetric determination of manganese since  $\text{Mn}^{2+}$  is quantitatively oxidised to it in dilute nitric acid by insoluble oxidising agents like sodium bismuthate.

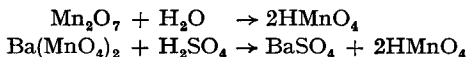
In alkali  $\text{MnO}_4^-$  reacts as an oxidising agent thus:



and in acid oxidation occurs thus:



Anhydrous  $\text{HMnO}_4$  has not been isolated but aqueous solutions can be made:



The acid is strongly dissociated in aqueous solution.

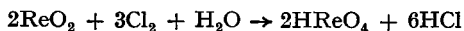
Permanganates have a weak temperature-dependent paramagnetism, although  $\text{Mn}^{\text{VII}}$  is without unpaired electrons, the  $\text{MO}_4^-$  being a tetrahedral ion with the manganese in the  $d^0$  electronic state.

#### *Pertechnetates and perrhenates*

Colourless pertechnetetic acid,  $\text{HTcO}_4$ , solution is made by dissolving  $\text{Tc}_2\text{O}_7$  in water, or by oxidising technetium compounds with nitric acid. On evaporation, the solution yields dark-red crystals claimed to be the anhydrous acid. The tetrahedral pertechnetate ion,  $\text{TeO}_4^-$ , the only oxo-anion of technetium formed in acid and alkaline solutions, differs from  $\text{MnO}_4^-$  in being stable in alkali. It is a stronger oxidising agent than the perrhenate ion,  $\text{ReO}_4^-$ . The alkali-metal and ammonium pertechnetates are colourless, their solubilities lie between those of the corresponding permanganates and perrhenates.

tes and are very similar to those of the perchlorates. The thermal decomposition of  $\text{NH}_7\text{TcO}_4$  gives pure technetium dioxide.

Solutions of perrhenic acid, which are also colourless, are made by (a) dissolving  $\text{Re}_2\text{O}_7$  in water, (b) oxidising  $\text{Re}_2\text{S}_7$  or the metal with nitric acid, or (c) oxidising a suspension of  $\text{ReO}_2$  in water with chlorine.



When evaporated the solutions become yellowish green and leave a solid of the same colour. Anhydrous  $\text{HReO}_4$  has not been isolated, and further heating results in the almost colourless  $\text{Re}_2\text{O}_7$ . The solutions of the acid contain only the tetrahedral  $\text{ReO}_4^-$  ion, but heavy metal ions precipitate mesoperrhenates  $\text{M}^{\text{II}}_3(\text{ReO}_4)_2$  which have the  $\text{ReO}_5^{3-}$  ion. Perrhenic acid is a strong monobasic acid, dissolving magnesium, iron and zinc with the evolution of hydrogen. Although not a strong oxidising agent, it oxidises  $\text{HBr}$  to bromine; it is reduced by the powerful reducing agents tin(II) chloride and hydrazine to a mixture of  $\text{ReO}_2$  and the metal.

The alkali-metal perrhenates are colourless, stable and, except for sodium perrhenate, not very soluble. Potassium perrhenate is precipitated when  $\text{KCl}$  and  $\text{HReO}_4$  solutions are mixed. It is less soluble (1.2 g/1000 g,  $25^\circ$ ) than potassium perchlorate. The sodium and ammonium salts are more soluble, and the latter when heated in air gives a mixture of oxides and when heated in nitrogen,  $\text{Re}_3\text{N}$  and metal. A large number of other perrhenates have been described.

### Sulphides

Manganese has two sulphides  $\text{MnS}$  and  $\text{MnS}_2$ . Hydrated manganese(II) sulphide is the pink precipitate given by  $\text{Mn}^{2+}$  when treated with alkali sulphides. In air it rapidly becomes brown through oxidation, but in the absence of oxygen can be dehydrated to the green cubic  $\text{MnS}$  with a rock-salt structure. It can also be obtained with wurtzite and zinc blende structures. The disulphide, which occurs as hauerite, has a cubic structure.

Technetium and rhenium have the isomorphous sulphides  $\text{TcS}_2$ ,  $\text{ReS}_2$  and  $\text{Tc}_2\text{S}_7$ ,  $\text{Re}_2\text{S}_7$ . The higher sulphides are precipitated from  $\text{HTcO}_4$  and  $\text{HReO}_4$  solutions in hydrochloric acid by hydrogen sulphide. The disulphides are obtained from the heptasulphides by heating in a vacuum. All the sulphides are dark coloured and stable in air.

### Potassium nonahydridorhenate

The dark-brown solid formed by reducing a solution of  $\text{KReO}_4$  with potassium in moist ethylenediamine has a paramagnetic susceptibility too low



for the presence of even one unpaired electron. It was first thought to be a rhenide,  $KRe$ , but n.m.r. and infrared spectroscopy showed it to contain metal-hydrogen bonds. Later the positions of the Re and K atoms were found by X-ray diffraction, and those of the H atoms, independently, by neutron diffraction. The compound is, in fact,  $K_2ReH_9$ , dipotassium nonahydridorhenate(VII). In Fig. 357 part of the unit cell is shown, to illustrate the environment of the Re atom. This is surrounded by 9 hydrogen atoms, six at the corners of a triangular prism, and three on extensions of normals from the Re atom to the vertical sides of the prism.

The arrangement constitutes an  $ReH_9^{2-}$  ion. The potassium ions are arranged in exactly similar positions to the hydrogens in a larger prism turned (about the common vertical axis) through  $60^\circ$  with respect to the first. If the hydrogen is considered to be co-ordinated as  $H^-$  ions, and if each hydrogen donates two electrons to the co-ordination sphere of the metal, then the rhenium is seen to have the formal charge number  $+7$ . The observed near-diamagnetism of the compound is thereby explained.

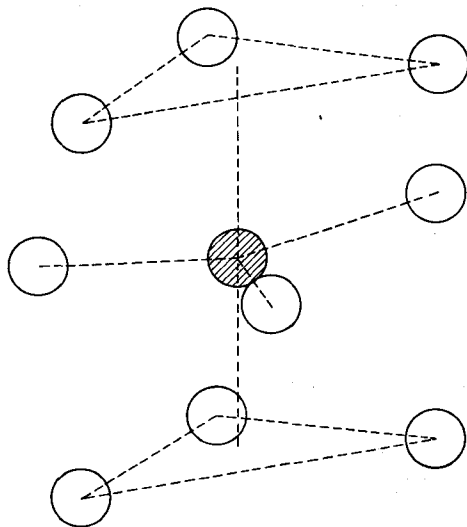


Fig. 357. Environment of Re atom in  $ReH_9^{2-}$  ion in solid  $K_2ReH_9$ . The  $K^+$  ions lie on extensions of lines drawn through H and Re atoms.

### Organometallic compounds and $\pi$ -complexes

Air-sensitive, amber-brown crystals of  $(C_5H_5)_2Mn$ , m.p.  $173^\circ$ , are made by treating manganese dihalides with sodium cyclopentadienide. Its infrared spectrum suggests that the compound is much more ionic than the other

transition-metal cyclopentadienyls. Possibly the stability conferred on the  $Mn^{2+}$  ion by the  $d^5$  (half-filled shell) configuration is responsible. The compound reacts with CO at high pressure to give the pale-yellow, diamagnetic  $(\eta-C_5H_5)Mn(CO)_3$  in which the cyclopentadienyl ring evidently contributes six electrons to the bonding (noble gas rule, p. 388). The compound resembles ferrocene (p. 699) in undergoing typical aromatic substitution in the ring. It reacts with diphenylacetylene to give an interesting complex  $(\eta-C_5H_5)Mn(CO)_2(PhC \equiv CPh)$  in which the metal is bonded by  $\pi$ -electrons of the  $C \equiv C$  bond occupying the position vacated by the CO group.

The reaction between  $C_5H_5Na$  and  $ReCl_5$  in tetrahydrofuran is unique in that a hydride  $(C_5H_5)_2ReH$  is the only organo-rhenium compound formed. The compound is diamagnetic and basic; its hydrogen atom is hydridic, not protonic. It was in this compound that the characteristics of a bond between hydrogen and a transition metal were first recognised (p. 722).



The reaction between  $C_5H_5Na$  and  $TcCl_4$  in tetrahydrofuran produces a purple solution which, when reduced with  $NaBH_4$ , gives air-sensitive, yellow crystals of  $[C_5H_5]_2Tc$ . The infrared spectrum of this contains no metal-hydrogen stretching frequency.

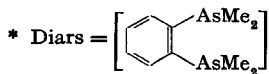
It is claimed that the dibenzenetchnetium cation  $(C_6H_6)_2Tc^+$  is produced in small quantities by the neutron irradiation of dibenzenechromium.

### Complexes

The +1 state is represented by hexacyano complexes,  $K_5M(CN)_6$ , for all three metals. The preparation of the olive-green technetium compound,  $K_5Tc(CN)_6$ , is typical; it is made by reducing a pertechnetate with potassium amalgam in the presence of  $CN^-$  ions.

The +2 state is common in manganese but rather uncommon in rhenium, and rare in technetium. The  $d^5$  configuration is rather unfavourable for the formation of low-spin octahedral complexes (p. 161) but they exist in  $Mn(CN)_6^{4-}$  and  $Mn(CNR)_6^{2+}$ . The high-spin amines of  $Mn^{II}$  are rather unstable, but there are octahedral complexes with chelating liquids such as ethylenediamine and the oxalate ion. Manganese(II) has some tetrahedral complexes, mainly salts of  $MnX_4^{2-}$  ( $X = Cl, Br, I$ ) with large cations such as  $Me_4N^+$ .

$Tc^{II}$  and  $Re^{II}$  exist in the compounds  $MCl_2(diars)_2^*$ , made by reducing  $M^{VII}$  compounds in methanol in the presence of  $Cl^-$  ions and the diarsine.



$\text{Re}^{\text{II}}$  also occurs in  $\text{Na}_3\text{Re}(\text{CN})_5$ , made by reducing  $\text{HReO}_4$  with sodium amalgam in the presence of sodium cyanide.

The +3 state is rather uncommon in this sub-group. However, several ligands lower the  $\text{Mn}^{\text{III}}/\text{Mn}$  redox potential sufficiently for the aqueous manganese(II) compound to be oxidised by air.

Examples of this are the low-spin  $\text{K}_3\text{Mn}(\text{CN})_6$  and the high-spin  $\text{Mn}(\text{acac})_3$ , made by the air-oxidation of  $\text{Mn}^{\text{II}}$  compounds in the presence of the respective ligands. Technetium(III) and rhenium(III) compounds  $[\text{M}(\text{halogen})_2(\text{diars})_2]\text{ClO}_4$  have been made by a method similar to that for the  $\text{M}^{\text{II}}\text{Cl}_2(\text{diars})_2$  above, but with the use of weaker reducing agents.

The +4 state for manganese is not common—it exists in some hexachloro- and hexafluorocomplexes. Technetium(IV), in addition to its halide complexes, forms some cyanocomplexes. Thus  $\text{TcO}_2 \cdot 2\text{H}_2\text{O}$  dissolves in alkali cyanides to give  $\text{Tc}(\text{OH})_3(\text{CN})_4^{3-}$  which can be isolated as the dark-brown thallium salt.  $\text{K}_2\text{TcI}_6$  and  $\text{KCN}$  react in methanol to give the dark-red  $\text{K}_2\text{Tc}(\text{CN})_6$ . But similar reactions with the corresponding rhenium compound produce the  $\text{Re}^{\text{V}}$  complexes  $\text{Re}(\text{OH})_4(\text{CN})_4^{3-}$  and  $\text{K}_3\text{Re}(\text{CN})_8$ .

The +5 state in technetium is represented by  $[\text{TcCl}_4(\text{diars})_2]\text{ClO}_4$ ; this provided the first example of 8-co-ordinate technetium.

Higher oxidation states than +5 in this sub-group are represented mainly by the oxo-complexes and complex halides. But another particularly interesting complex is the rhenium(VI) compound tris(*cis*-1,2-diphenylethene-1,2-dithiolato)-rhenium:

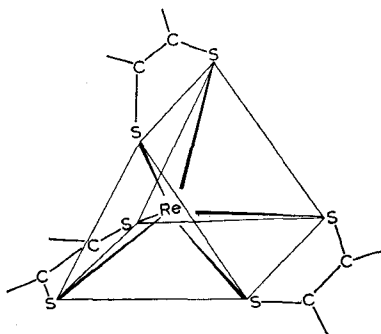
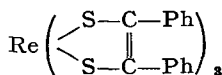
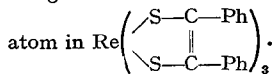


Fig. 358. Trigonal prismatic arrangement of bidentate sulphur ligands around rhenium



If was the first known example of a trigonal prismatic complex. The arrangement of sulphur and carbon atoms is shown in Fig. 358; the phenyl rings, not shown in the figure, are twisted out of the S—C—C—S planes. Although the trigonal prismatic arrangement of sulphur atoms around a metal atom exists in crystals such as  $\text{MoS}_2$  and  $\text{WS}_2$ , this configuration is extremely rare in complexes, where 6-co-ordination usually means either octahedral symmetry or some minor deviation from it.

#### FURTHER READING

- R. COLTON AND R. D. PEACOCK, *An Outline of Technetium Chemistry*, Quart. Rev., 16 (1962) 299.
- A. A. WOLF, *An Outline of Rhenium Chemistry*, Quart. Rev., 15 (1961) 372.
- R. COLTON, *The Chemistry of Rhenium and Technetium*, New York, Wiley, 1965.
- R. D. PEACOCK, *The Chemistry of Technetium and Rhenium*, Amsterdam, Elsevier, 1966.

## Iron, Cobalt and Nickel

### GENERAL FEATURES OF GROUP VIII

The elements of Group VIII carry the first, second and third transition series from the manganese sub-group to the copper sub-group. The three triads of atoms have electronic structures which run from  $3d^6 4s^2$  to  $3d^8 4s^2$ , from  $4d^7 5s^1$  to  $4d^{10}$  and from  $5d^6 6s^2$  to  $5d^9 6s^1$  respectively. In physical and chemical properties they change along the periods from resembling an element of the manganese sub-group to resembling an element of the copper sub-group.

TABLE 133

THE THREE A-TYPE SUBGROUPS

First Triad	Fe ( $3d^6 4s^2$ )	Co ( $3d^7 4s^2$ )	Ni ( $3d^8 4s^2$ )
Second Triad	Ru ( $4d^7 5s^1$ )	Rh ( $4d^8 5s^1$ )	Pd ( $4d^{10}$ )
Third Triad	Os ( $5d^6 6s^2$ )	Ir ( $5d^9$ )	Pt ( $5d^9 6s^1$ )

Although there are vertical similarities between the nine elements of Group VIII, the practice of considering them as three separate triads is justified by strong 'horizontal' relationships. This feature is emphasised by the difference between the chemistry of iron, cobalt and nickel in the First Triad, and that of their congeners ruthenium, rhodium and palladium in the Second Triad, and osmium, iridium and platinum in the Third Triad. The break in properties between elements of the first transition series and those of the second and third series occurs in all the sub-groups containing transition metals. It affords the reason for a separate treatment of the First Triad.

### GROUP VIII: THE FIRST TRIAD

#### General

Considered as metals, iron, cobalt and nickel are similar to the metals preceding them in the Fourth Period; thus titanium, vanadium, chromium and manganese, like cobalt and nickel, feature as alloying elements in steel making. The chemistry, however, of iron, cobalt and nickel differs that of these transition elements; in particular they do not form stable oxo-anions such

as  $\text{VO}_3^-$ ,  $\text{CrO}_4^{2-}$  and  $\text{MnO}_4^-$ . The ferrate ion,  $\text{FeO}_4^{2-}$ , is known, but is very unstable and, incidentally, a stronger oxidising agent than the  $\text{MnO}_4^-$  ion. Neither cobalt nor nickel forms oxo-anions.

In this respect, the metals illustrate the greatly reduced tendency of d electrons to function as valency electrons once the d level is more than half filled. However, the small ionic radii of the 2+ and 3+ cations, together with the presence of unfilled d orbitals, favour complex formation. The complexes of  $\text{Co}^{\text{III}}$ , anionic, cationic and neutral, are particularly numerous.

The radii, ionisation energies and standard electrode potentials of the elements are summarised in Table 134.

TABLE 134  
RADI, IONISATION ENERGIES  
AND ELECTRODE POTENTIALS OF Fe, Co AND Ni

	<i>Fe</i>	<i>Co</i>	<i>Ni</i>
Atomic number	26	27	28
Metallic radius (Å)	1.26	1.26	1.25
Ionic radius $M^{2+}$ (Å)	0.76	0.78	0.78
$M^{3+}$ (Å)	0.67	0.65	
Ionisation energy <i>I</i> 1 (eV)	7.90	7.86	7.63
2 (eV)	16.16	17.3	18.2
$E^\circ, M^{3+}/M$ (V)	-0.44	-0.28	-0.25
$M^{3+}/M^{2+}$ (V)	+0.77	+1.84	

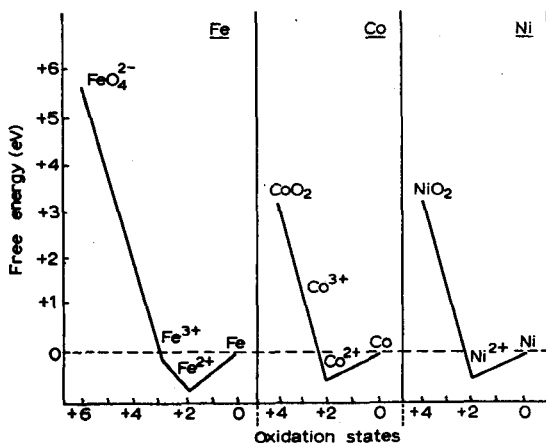


Fig. 359. Free energies of the oxidation states of Fe, Co and Ni, relative to the metals, at  $\text{pH} = 0$ .

The free energies of the oxidation states of these three elements relative to the metals are illustrated in Fig. 359, those of the highest state having been deduced indirectly. The principal points of interest brought out by the plots are the relatively high stability of the +3 state and the existence of a +6 state for iron. Whereas, for cobalt and nickel only the +2 state is thermodynamically stable in an acidified aqueous solution.

### Separation and properties of the metals

Iron, cobalt and nickel have typical metallic structures (Table 135). Their melting points, though somewhat lower than that of chromium in Group VI (p. 658), are characteristically high. The metals are ferromagnetic.

TABLE 135  
THE METALLIC STRUCTURES OF Fe, Co AND Ni

Fe	<i>a</i>	b.c.c.	$\gamma$	f.c.c.
Co	<i>a</i>	h.c.p.	$\beta$	f.c.c.
Ni	<i>a</i>	h.c.p.	$\beta$	f.c.c.

TABLE 136  
DENSITY, ATOMIC VOLUME AND MELTING POINT OF Fe, Co AND Ni

	<i>Fe</i>	<i>Co</i>	<i>Ni</i>
Density (g/cc)	7.9	8.7	8.9
Atomic volume	7.1	6.7	6.7
Melting point (°C)	1535	1480	1455

#### *Iron*

The element makes up 4.7% of earth's crust and may be the most important constituent of its interior. The principal ores are haematite,  $\text{Fe}_2\text{O}_3$ , magnetite,  $\text{Fe}_3\text{O}_4$ , limonite,  $\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ , and siderite,  $\text{FeCO}_3$ . The metal is of the greatest economic importance, world output exceeding two hundred million tons per annum. Roasting of the ores converts them to  $\text{Fe}_2\text{O}_3$  which is reduced in a blast furnace by carbon monoxide. The pig iron so made contains about 4% carbon and about 0.5% each of sulphur, phosphorus and silicon. Oxidation of the impurities by  $\text{Fe}_2\text{O}_3$  in the open-hearth furnace, or by air in the Bessemer converter, leaves a purer iron which is made into steel by addition of a manganese-carbon-iron alloy. Many alloy steels have special properties such as toughness, hardness, and resistance to corrosion.

Pure iron is soft and malleable. It is chemically reactive, being pyrophoric

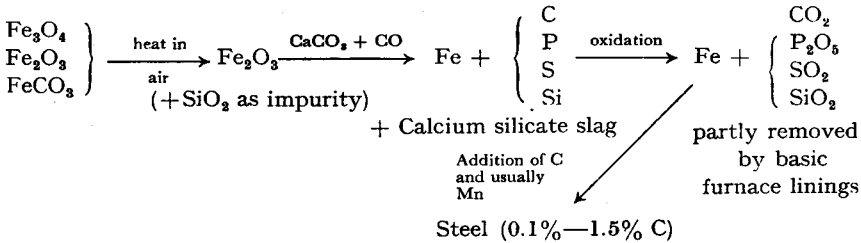


Fig. 360. Production of iron and steel from iron ores.

when in a fine state of division; and it rusts readily in moist air through the combined agency of  $\text{H}_2\text{CO}_3$  and  $\text{O}_2$ . The hydrated oxide, known as rust, is porous and does not protect the metal beneath as the closely adhering  $\text{Al}_2\text{O}_3$  protects aluminium.

*Cobalt*

The element ( $4 \times 10^{-3}\%$  of the earth's crust) occurs principally as smaltite,  $\text{CoAs}_2$ , and cobaltite,  $\text{CoAsS}$ . It is obtained as a by-product in the smelting of arsenical ores of nickel and copper. Its extraction involves oxidation to  $\text{Co}_3\text{O}_4$ , iron and arsenic being removed as slag, followed by aluminothermic reduction of the cobalt oxide:

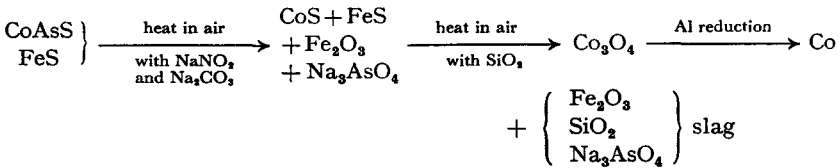


Fig. 361. Production of cobalt from ores.

Cobalt dissolves more readily than iron or nickel in dilute mineral acids. It is attacked by oxygen and steam at high temperatures but not at all by hydrogen or nitrogen. The metal is used in corrosion-resistant alloys and in alloys for permanent magnets.

*Nickel*

The element ( $10^{-2}\%$  of the earth's crust) is found as pentlandite,  $\text{NiS}$ , with  $\text{FeS}$  as impurity. It is used in the fabrication of chemical plant, as an alloying metal to increase the corrosion resistance of steel, as a catalyst in hydrogenation reactions, and as a coinage metal. Alloyed with chromium it gives Nichrome for resistance heaters; with zinc and copper it forms German silver.

The sulphide ores are oxidised in the presence of silica which enables the iron to be removed as a silicate slag. The nickel oxide left is reduced at



350° by water gas to an impure metal, leaving the iron as ferric oxide. Purification is based on the formation and decomposition of gaseous  $\text{Ni}(\text{CO})_4$ . Carbon monoxide is passed over the impure metal at 60° and the gas containing a few per cent of the tetracarbonyl is brought into contact with agitated nickel pellets at 200°. The pellets grow as nickel is deposited on them; the CO is recirculated (Fig. 362).

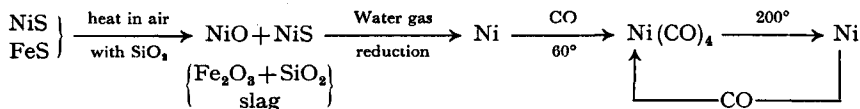


Fig. 362. Production of nickel from ore.

Nickel is very malleable and is not attacked by air or water at the ordinary temperature. It is used for electroplating, in storage batteries (p. 698), and in alloy steels.

The three metals liberate hydrogen from dilute hydrochloric and sulphuric acids. Concentrated nitric acid renders them passive. They react on heating with oxygen, sulphur and the halogens. Boron, carbon, silicon and phosphorus combine with all of them, generally forming non-stoichiometric compounds, many of the interstitial-lattice type.

### Oxidation states

The lowest oxidation states occur in  $\pi$ -bonded complexes such as the carbonyls and carbonylate anions, and the highest in fluorocomplexes or, in the case of iron, oxo-anions—the usual pattern for transition metals. But the range of oxidation states falls sharply compared with that of the preceding elements manganese and chromium (pp. 678, 661).

Zero oxidation state is particularly common in nickel. The diamagnetic carbonyl,  $\text{Ni}(\text{CO})_4$ , is tetrahedral. When the CO molecules are replaced by other  $\pi$ -bonding ligands such as isonitriles or phosphorus trihalides, other tetrahedral diamagnetic ( $d^{10}$ ) complexes are formed; examples are  $\text{Ni}(\text{CNC}_6\text{H}_5)_4$  and  $\text{Ni}(\text{PX}_3)_4$ . The complex cyanide  $\text{K}_4\text{Ni}(\text{CN})_4$  (p. 568) is an instance of the rather unusual occurrence of zero oxidation state in an anion.

Charge +1 occurs in the diamagnetic, bipyramidal  $\text{Co}(\text{NCPH})_5^+$  ion in which cobalt has the  $d^8$  configuration favourable for this geometrical arrangement. The nickel +1 state has the  $d^9$  configuration and is uncommon. The diamagnetic  $\text{Ni}_2(\text{CN})_6^{4-}$  ion is planar, with a metal-metal bond.

Charge +2 is very common in Fe, Co and Ni, and both high- and low-spin complexes (p. 162) are known. A high-spin  $\text{Fe}^{\text{II}}$  complex is  $\text{Fe}(\text{NH}_3)_6^{2+}$  in which the configuration  $t_{2g}^4 e_g^2$  has four singly occupied orbitals. On the other hand,  $\text{Fe}(\text{CN})_6^{4-}$  in  $\text{K}_4\text{Fe}(\text{CN})_6$  is diamagnetic with a closed subshell,  $t_{2g}^6$ . An

example of a high-spin  $\text{Co}^{\text{II}}$  complex is  $\text{CoCl}_4^{2-}$ , which is tetrahedral; another is the octahedral  $\text{Co}(\text{NH}_3)_6^{2+}$ . Although all such complexes have three singly occupied d orbitals their magnetic moments vary from 4.3 to 5.6  $\mu$ , owing to orbital contributions (p. 87) which depend on ligand-field strength. Similarly, the low-spin complexes with 4 co-ordination and only one singly occupied d orbital have moments of up to 2.9  $\mu$ , owing to large orbital contributions. In 6 co-ordination these drop to about 1.9  $\mu$ . Nickel commonly forms square  $\text{Ni}^{\text{II}}$  complexes (p. 164) which are diamagnetic. High-spin  $\text{Ni}^{\text{II}}$  compounds also exist; for instance in the tetrahedral  $\text{NiCl}_4^{2-}$  ion, present in solutions of nickel chloride in fused caesium chloride, and the same ion is present in the tetrachloronickelate,  $(\text{Et}_4\text{N})_2\text{NiCl}_4$ , prepared from an alcoholic solution. They are usually formed with the more electronegative ligands and are green or blue, whereas the low-spin compounds are orange or red.

TABLE 137

REPRESENTATIVE COMPOUNDS AND IONS OF OXIDATION STATES -2 TO +6 OF IRON, COBALT AND NICKEL

Charge	Fe	Co	Ni
-2	$\text{Fe}(\text{CO})_4^{2-}$	—	—
-1	—	$\text{Co}(\text{CO})_4^-$	$\text{Ni}_2(\text{CO})_8^{2-}$
0	$\text{Fe}(\text{CO})_5$	$\text{K}_4\text{Co}(\text{CN})_4$	$\text{Ni}(\text{PF}_3)_4$ , $\text{K}_4\text{Ni}(\text{CN})_4$ , $\text{K}_4\text{Ni}_2(\text{CN})_6$
+1	$(\pi\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_4$ , $\text{Fe}(\text{H}_2\text{O})_5\text{NO}$	$\text{Co}(\text{dipy})_3^+$ , $\text{Co}(\text{NCC}_6\text{H}_5)_5\text{ClO}_4$	
+2	$\text{Fe}(\text{H}_2\text{O})_6^{2+}$ , $\text{FeCl}_2$ , $(\pi\text{-C}_5\text{H}_5)_2\text{Fe}$	$\text{Co}(\text{H}_2\text{O})_6^{2+}$ , $\text{CoCl}_4^{2-}$	$\text{Ni}(\text{H}_2\text{O})_6^{2+}$ , $\text{Ni}(\text{en})_3^{2+}$
+3	$\text{FeF}_6^{3-}$ , $\text{FeO}(\text{OH})$ , $\text{K}_3\text{Fe}(\text{CN})_6$	$\text{Co}(\text{NH}_3)_6^{3+}$ , $\text{K}_3\text{Co}(\text{CN})_6$	$\text{Ni}(\text{diars})_2\text{Cl}_2^+$ , $\text{NiBr}_3(\text{PMe}_3)_3$
+4	$\text{Fe}(\text{diars})_2\text{Cl}_2^{2+}$ , $\text{Ba}_2\text{FeO}_4$	$\text{CoF}_6^{2-}$	$\text{K}_2\text{NiF}_6$
+5	$\text{FeO}_4^{3-}$	—	—
+6	$\text{K}_2\text{FeO}_4$	—	—

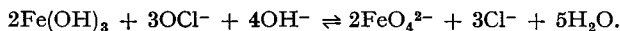
Charge +3 is also common. As Table 134 (p. 691) shows,  $\text{Fe}^{3+}$  is an electron acceptor ( $E^\circ = 0.77$  V), and iron(III) salts are readily hydrolysed, the brown colour of their aqueous solutions being largely due to  $\text{Fe}(\text{OH})^{2+}$ . The  $\text{Co}^{3+}$  ion is clearly an even more powerful oxidising agent ( $E^\circ = 1.84$  V), and simple cobalt(III) salts are therefore difficult to make, since they liberate oxygen from water and are reduced to cobalt(II). It is only in co-ordination that  $\text{Co}^{\text{III}}$  becomes commonplace. There are many octahedral  $\text{Fe}^{\text{II}}$  complexes;

$\text{FeF}_6^{3-}$  is of high-spin type with configuration  $t_{2g}^3 e_g^2$  and  $\text{Fe}(\text{CN})_6^{3-}$ , with a higher ligand field (p. 159), is low-spin  $t_{2g}^5$ . Nickel is less ready to form  $\text{Ni}^{\text{III}}$  complexes, though an interesting series has been made by treating the square nickel dioxime chelates with chlorine.

Charge +4 occurs much less commonly. Treatment of alcoholic  $\text{FeCl}_3$  with  $o\text{-C}_6\text{H}_4(\text{AsMe}_2)_2$  gives a brilliant red precipitate of  $[\text{Fe}^{\text{III}}\text{Cl}_2 \cdot 2\text{C}_6\text{H}_4(\text{AsMe}_2)_2]\text{FeCl}_4$ . A nitrobenzene solution of this compound, when heated with 15*N*  $\text{HNO}_3$ , gives  $[\text{Fe}^{\text{IV}}\text{Cl}_2 \cdot 2\text{C}_6\text{H}_4(\text{AsMe}_2)_2](\text{FeCl}_4)_2$  containing  $\text{Fe}^{\text{IV}}$  in the cationic complex. The perchlorate of the cation can also be made in a fairly pure state, and magnetic measurements suggest a  $t_{2g}^4$  state. The  $\text{Co}^{\text{IV}}$  state is poorly represented, but  $\text{Ni}^{\text{IV}}$  exists in the oxide  $\text{NiO}_2$  and in the  $[\text{NiCl}_2 \cdot 2\text{C}_6\text{H}_4(\text{AsMe}_2)_2]^{2+}$  ion.

Charge +5 is unimportant.

Charge +6 occurs in the ferrates, which are made by hypochlorite oxidation of  $\text{Fe}(\text{OH})_3$  suspended in alkali:



The potassium and barium salts have been isolated. The carmine-red  $\text{BaFeO}_4$  is structurally similar to  $\text{BaSO}_4$  and  $\text{BaCrO}_4$ .

### Halides

The metals all form dihalides. Anhydrous  $\text{FeF}_2$  and  $\text{FeCl}_2$  can be made by passing HF or HCl over the heated metal,  $\text{CoF}_2$  by the action of HF on  $\text{CoCl}_2$ , and the others by direct combination of the elements. The reaction between iron and bromine gives  $\text{FeBr}_2$  with iron in excess, and  $\text{FeBr}_3$  with bromine in excess. The colour deepens with increasing polarisability of the anion; both  $\text{CoI}_2$  and  $\text{NiI}_2$  are black.  $\text{CoCl}_2$  forms blue crystals of the rhombohedral system with the cadmium chloride structure. The colour of a solution of  $\text{CoCl}_2$  varies with temperature and concentration from pink to blue, the latter being favoured by higher temperatures and concentrations and by the presence of concentrated HCl. The blue colour is due to the  $\text{CoCl}_4^{2-}$  ion (p. 701). The most common hydrate,  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ , is red. The hydrate  $\text{FeCl}_2 \cdot 6\text{H}_2\text{O}$  has been shown, by X-ray diffraction, to contain *trans* octahedral  $\text{FeCl}_2(\text{H}_2\text{O})_4$ , not  $\text{Fe}(\text{H}_2\text{O})_6^{2+}$  ions.

The three trihalides,  $\text{FeF}_3$ ,  $\text{FeCl}_3$  and  $\text{FeBr}_3$ , are formed by direct combination of the elements;  $\text{CoF}_3$  is made by passing fluorine over  $\text{CoCl}_2$  at 150°. Nickel forms no trihalide. The vapour density of iron(III) chloride shows some of the dimer to be present below 750°, but molecular weight determinations made in organic solvents indicate monomeric  $\text{FeCl}_3$ . In the crystal of  $\text{FeCl}_3$  there is a layer structure rather similar to that of  $\text{CrCl}_3$  (p. 542).

### Oxides

$\text{FeO}$ ,  $\gamma\text{-Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$  are closely related structurally. In all, the oxygen atoms have c.c.p. arrangement. If stoichiometric  $\text{FeO}$  existed, all the octahedral spaces would be filled with Fe atoms, giving effectively a sodium chloride lattice of  $\text{Fe}^{2+}$  and  $\text{O}^{2-}$  ions. Stoichiometric  $\text{FeO}$  is, however, unknown. The atom ratio of the 'iron-rich' limit is 48.56% iron. Removal of  $\text{Fe}^{2+}$  ions from the ideal structure and replacement by two-thirds of their number of  $\text{Fe}^{3+}$  ions gives  $\text{FeO}$  deficient in iron—this is a more accurate picture than an excess of oxygen. When three-quarters of the original  $\text{Fe}^{2+}$  ions are replaced by  $\text{Fe}^{3+}$  ions the compound has the composition  $\text{Fe}_3\text{O}_4$ , that is  $\text{Fe}^{\text{II}}(\text{Fe}^{\text{III}}\text{O}_2)_2$ , and a spinel structure. Removal of more iron atoms gives  $\gamma\text{-Fe}_2\text{O}_3$  in which all the original  $\text{Fe}^{2+}$  are replaced by  $\text{Fe}^{3+}$  ions. The addition of oxygen to iron and its lower oxides appears to take place by the formation of close-packed layers of oxygen atoms on the surface followed by diffusion of the iron atoms into these layers. The side of the unit cell containing 32 oxygen atoms decreases linearly as the proportion of iron to oxygen atoms decreases.

$\gamma\text{-Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$  are both ferromagnetic. The rhombohedral, paramagnetic haematite, or  $\alpha\text{-Fe}_2\text{O}_3$ , is the stable form; although it has only one crystal structure it occurs in three colours, grey, yellow and red.

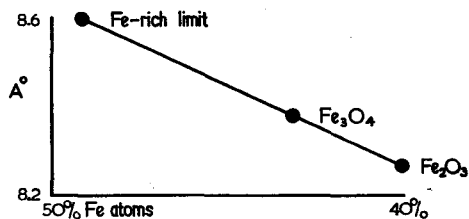


Fig. 363. Cell sizes of iron oxides.

$\text{CoO}$  and  $\text{NiO}$  also have the sodium chloride structure. When dry,  $\text{CoO}$  is stable at room temperature but, when wet, is easily oxidised to  $\text{CoO}(\text{OH})$ ; this compound is also obtained as a black precipitate when cobalt(III) complexes are decomposed by alkali. Dry  $\text{CoO}$  is oxidised to  $\text{Co}_3\text{O}_4$  when heated in air, but further oxidation to  $\text{Co}_2\text{O}_3$  does not occur.  $\text{NiO}$  is thermally stable and is made by strongly heating the carbonate or nitrate.

Only the hydrated oxides of cobalt(III) and nickel(III) are precipitated by alkali hypochlorites from cobalt(II) and nickel(II) solutions. Iron(III) hydroxide has two crystalline forms in the orthorhombic system,  $\alpha\text{-FeO}(\text{OH})$ , dark brown needles, and  $\gamma\text{-FeO}(\text{OH})$ , thin red plates. All other hydrates of  $\text{Fe}_2\text{O}_3$  are mixtures of these with either  $\text{Fe}_2\text{O}_3$  or absorbed water.

A hydrate of  $\text{NiO}_2$  is the depolarising agent in the Edison storage battery, which has nickel plates and an alkaline electrolyte.

### Sulphides

The monosulphides occur as hexagonal crystals which always show a deficiency of metal atoms without heterogeneity of structure (Fig. 364).

As  $\text{Fe}^{3+}$  ions oxidise  $\text{H}_2\text{S}$ ,  $\text{HS}^-$  and  $\text{S}^{2-}$ , the precipitation of  $\text{Fe}_2\text{S}_3$  free from sulphur is impossible. Monohydrated iron(III) oxide reacts with dry  $\text{H}_2\text{S}$  to give primarily  $\text{Fe}_9\text{S}_8$  some of which disproportionates into  $\text{FeS}_2$  and  $\text{FeS}$ . A cobalt(III) sulphide cannot be precipitated from aqueous solution and there is no unequivocal evidence for its formation or that of  $\text{Ni}_2\text{S}_3$  in dry reactions. However, disulphides are known, of which the most important is  $\text{FeS}_2$ . In its commonest form, pyrites, Fe atoms and  $\text{S}_2$  pairs are arranged in a sodium chloride-type structure with the axes of the sulphur pairs parallel to the four trigonal axes (Fig. 365).

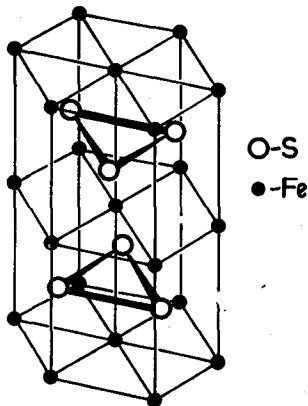


Fig. 364. Hexagonal unit cell  $\text{FeS}$ .  
(There are always some vacant Fe positions.)

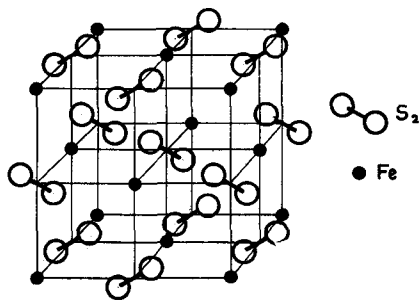
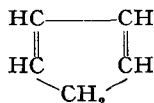


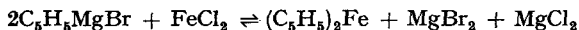
Fig. 365. Unit cell of  $\text{FeS}_2$ .

### Organometallic compounds and $\pi$ -complexes

Dicyclopentadienyliron(II), or 'ferrocene', can be made by heating finely divided iron with cyclopentadiene



or by treating  $\text{FeCl}_2$  with a Grignard compound of cyclopentadiene:



or, in better yield, by treating anhydrous  $\text{FeCl}_2$  in tetrahydrofuran with sodium cyclopentadienide. The solid (m.p.  $173^\circ$ ) is remarkably stable, and is unaffected by  $\text{NaOH}$  and  $\text{HCl}$  even at the boiling point. The complex is diamagnetic, has zero dipole moment, and all its  $\text{CH}$  bonds are alike: Fourier analyses has confirmed a 'sandwich' structure with the iron atom lying between two  $\text{C}_5\text{H}_5$  pentagons. The rings show aromatic rather than

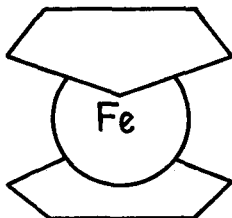


Fig. 366. Structure of ferrocene (dicyclopentadienyl iron(II)).

olefinic reactivity; the existence of only three acetyl ethyl ferrocenes proves that the rings can rotate freely.

The compound has an extensive chemistry of aromatic substitution. It can be oxidised to a blue, water-soluble cation  $(\text{C}_5\text{H}_5)_2\text{Fe}^+$ . Ferrocene has been considered as an additive for promoting the smokeless combustion of fuel oils.

The compound  $(\text{C}_5\text{H}_5)_2\text{Co}$  has been made by treating  $\text{Co}(\text{SCN})_2$  in liquid ammonia with sodium cyclopentadienide. It is extremely readily oxidised to the cation  $(\text{C}_5\text{H}_5)_2\text{Co}^+$ , which is isoelectronic with ferrocene.

Biscyclopentadienylnickel has been made by a similar method to that for the cobalt compound. Its green, paramagnetic crystals are moderately stable to air.

Sigma-bonded organometallic compounds of these metals are few in number, but perfluoroalkyl derivatives such as  $(\text{Ph}_3\text{P}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{PPh}_3)\text{Ni}(\text{C}_2\text{F}_5)\text{I}$  have been made which are crystalline and stable to air.

### Complexes

Although some of the complexes of these metals have already been considered in our discussion of oxidation states, their chemistry is so extensive that many other aspects are worthy of attention.

*Bipositive states**(i) Iron(II)*

Most of the complexes of iron(II) ( $d^6$ ) are octahedral; but diamagnetic compounds are far less common than among the isoelectronic  $\text{Co}^{\text{III}}$  compounds, not unnaturally in view of the smaller charge on the iron. The six-co-ordinate, diamagnetic complexes include the hexacyanoferrates(II) and the tris(*ortho*-phenanthroline) iron(II) ions. The octahedral  $[\text{Fe}(\text{phen})_3]^{2+}$  ion (Fig. 367) is blood-red; it is oxidised to pale blue  $[\text{Fe}(\text{phen})_3]^{3+}$  without any structural change.  $E^\circ$  for the system = 1.14 V, making the compound, also known as ferroin, a most useful redox indicator for the oxidation of  $\text{Fe}^{2+}$  ion ( $E^\circ$ ,  $\text{Fe}^{3+}/\text{Fe}^{2+} = 0.77$  V) by cerium(IV) ion ( $E^\circ$ ,  $\text{Ce}^{4+}/\text{Ce}^{3+} = 1.45$  V).

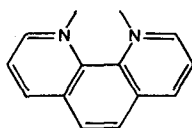
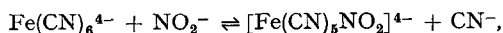
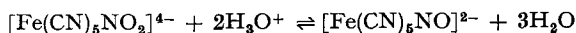


Fig. 367. The (phen) group in octahedral  $[\text{Fe}(\text{phen})_3]^{2+}$  ion.

The pentacyanonitrosylferrates, (the 'nitroprussides') are of interest. Cyano complexes in general do not easily form mixed complexes by replacement of  $\text{CN}^-$  groups and, in the hexacyanocomplexes of iron, only one  $\text{CN}^-$  can be replaced by  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ ,  $\text{CO}$ ,  $\text{NO}_2$  (nitro) or  $\text{NO}$  (nitroso). Acidification of a  $\text{K}_4\text{Fe}(\text{CN})_6\text{-KNO}_2$  mixture gives first the pentacyanonitroferrate(II) ion,  $[\text{Fe}(\text{CN})_5\text{NO}_2]^{4-}$ :

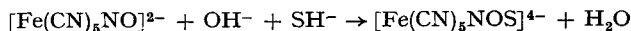


and then the pentacyanonitrosylferrate(II) ion, the 'nitroprusside' ion:



The red sodium salt,  $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}] \cdot 2\text{H}_2\text{O}$ , is diamagnetic; surprisingly since the  $\text{NO}$  group is an odd-electron group which must confer paramagnetism should it be co-ordinated in the normal way. If the group is considered as co-ordinating in the form  $\text{NO}^+$ , however, not only is the diamagnetism comprehensible but the charge on the iron becomes clear: it is, in fact, +2.

The  $\text{SH}^-$  ion in alkaline solution converts the nitroprusside ion to purple  $[\text{Fe}(\text{CN})_5\text{NOS}]^{4-}$ :



Prussian blue, precipitated from potassium hexacyanoferrate(II) (ferrocyanide),  $\text{K}_4\text{Fe}(\text{CN})_6$ , solution by a little less than an equivalent of  $\text{FeCl}_3$ , is known to have the composition  $\text{KFe}[\text{Fe}(\text{CN})_6]$ . Its structure (Fig. 368) is

somewhat similar to that of a tungsten bronze. The cubic unit cell has an iron atom at each corner and a CN pair occupying the middle of each side. Half of the iron atoms have 6 carbon atoms as nearest neighbours and half have 6 nitrogen ones. There are potassium atoms at only half of the cube centres. Iron(III) cyanide has the same lattice with nothing at the cube centres; whereas  $K_2Fe_2(CN)_6$ , made by the action of  $FeCl_2$  on  $K_4Fe(CN)_6$ , has potassium atoms at all the cube centres.

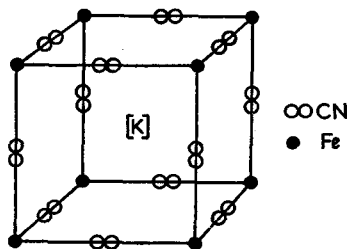


Fig. 368. Structure of soluble Prussian blue.

High-spin octahedral iron(II) complexes are common. The pale-green hexa-aquoiron(II) ion,  $Fe(H_2O)_6^{2+}$ , present in aqueous solution, owes its colour to a single absorption band with a peak at about  $10,000\text{ cm}^{-1}$  in the infrared which spreads into the red of the visible spectrum.

Tetrahedral  $Fe^{II}$  complexes are not common, but some complex halide ions  $FeX_4^{2-}$  are known to have this geometry. Salts of  $FeCl_4$  with large cations are almost colourless; their spectra, from solutions in liquids such as chloro-acetonitrile, show a single d-d band at about  $4050\text{ cm}^{-1}$  with  $\epsilon_{\text{max}}$  about  $80\text{ litre mole}^{-1}\text{ cm}^{-1}$ . There is a square complex  $Fe(C_6Cl_5)_2(PPhEt_2)_2$ .

### (ii) Cobalt(II)

This state ( $d^7$ ) occurs in octahedral, tetrahedral and square complexes. With strong-field ligands the tendency for the complex to oxidise to  $d^6$  type ( $Co^{III}$ ) is very strong (p. 705). Hydrated cobalt salts are usually pink: they contain the  $Co(H_2O)_6^{2+}$  ion which absorbs weakly ( $\epsilon_{\text{max}} = 10.2$ ) at  $18,000\text{ cm}^{-1}$ , in the blue part of the spectrum. The high-spin octahedral  $Co^{II}$  complexes have magnetic moments of 4.7 to 5.2 B.M.; there are large orbital contributions (p. 87). The low-spin octahedral complexes such as  $Co(\text{diars})_3^{2+}$ , however, have moments little above the spin-only value for one unpaired electron.

Tetrahedral  $Co^{II}$  complexes are formed when halide and thiocyanate ions are added to aqueous  $Co^{2+}$  solutions; they can be isolated as salts such as quaternary ammonium salts,  $R_4NCoX_4$ . These compounds are deep-blue,

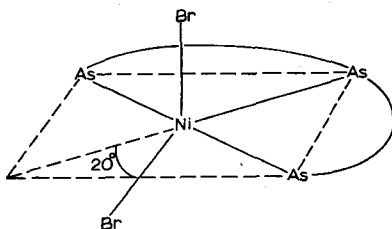


with rather strong ( $\epsilon_{\text{max}} \sim 600$ ), broad absorption bands in the orange and red part of the visible spectrum. The compounds are, of course, all high-spin and, like the high-spin octahedral complexes, their magnetic moments are considerably higher than the value calculated from the spin-only formula.

Low-spin, square planar  $\text{Co}^{\text{II}}$  complexes are also known; one is bis(dimethylglyoximate)cobalt(II), which is similar in structure to the nickel(II) compound.

### (iii) Nickel(II)

Most of these are octahedral and paramagnetic or square planar; but several tetrahedral (high-spin) complexes are known and some of even lower symmetry. The compound  $\text{MeAs}(\text{CH}_2\text{CH}_2\text{AsMe}_2)_2\text{NiBr}_2$  has a distorted, square pyramidal structure:



Octahedral complexes include  $\text{Ni}(\text{H}_2\text{O})_6^{2+}$ ,  $\text{Ni}(\text{NH}_3)_6^{2+}$  and  $\text{Ni}(\text{edta})^{2-}$ , [ $\text{H}_4(\text{edta}) = \text{ethylenediaminetetra-acetic acid}$ ]. Their magnetic moments are in the range 2.9–3.4 B.M. (p. 88), indicating some orbital contribution; their absorption spectra (p. 170) contain four bands in the visible and near ultraviolet, with  $\epsilon_{\text{max}}$  usually  $\sim 10$  litre mole $^{-1}$  cm $^{-1}$ . Hydrated nickel salts containing  $\text{Ni}(\text{H}_2\text{O})_6^{2+}$  are apple-green, but the complexes with nitrogen ligands are usually blue or purple because of the shift of the peaks in the stronger ligand field:

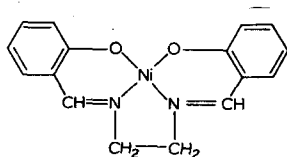
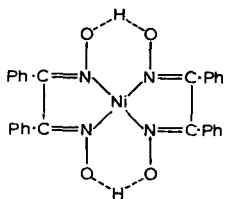
$\text{Ni}(\text{H}_2\text{O})_6^{2+}$		$\text{Ni}(\text{NH}_3)_6^{2+}$	
Wave number	$\epsilon$	Wave number	$\epsilon$
8,500	2.0	10,750	4.0
13,500	1.8	13,150	5.0
15,400	1.5	17,500	4.8
25,300	5.2	28,200	6.3

It should be noted that where there are several absorption peaks a general shift to lower wavelengths (higher energies) does not necessarily mean a

shift in colour towards red as in the simple  $d^1$  case (p. 158). In the examples above, the ammine is a deeper blue than the aquo ion because the principal absorption peak in the visible range is that at  $17,500\text{ cm}^{-1}$  which is in the ultraviolet, whereas for the aquo ion the absorption at  $25,300\text{ cm}^{-1}$  lies in the violet.

Several of the paramagnetic nickel(II) complexes, once thought to be tetrahedral on stoichiometric grounds, have been found to be associated and octahedral (p. 573). Nevertheless, increasing numbers of authentic tetrahedral complexes are being discovered: examples are  $\text{NiI}_2(\text{PPh}_3)_2$ ,  $\text{NiI}_2(\text{py})_2$  and the chelate isopropyl- and *sec*-butyl-salicylaldehyde complexes. They are usually blue compounds and their absorption in the red part of the spectrum ( $\sim 15000\text{ cm}^{-1}$ ) is fairly strong ( $\epsilon \sim 160\text{ litre mole}^{-1}\text{ cm}^{-1}$ ).

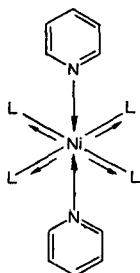
Typical square planar nickel(II) complexes are uncharged complexes:



Bis (diphenylglyoxime)nickel(II)      Salicylaldehyde ethylenediamine nickel(II)

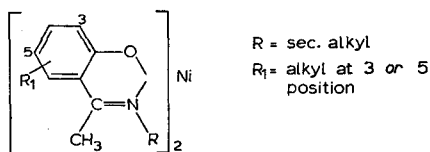
The compounds are usually pink: there are at most three bands in the visible absorption spectrum, the strongest being at about  $22,000\text{ cm}^{-1}$  ( $\epsilon \sim 150\text{ to }350$ ).

Many square planar  $\text{Ni}^{\text{II}}$  complexes which are diamagnetic in the solid state become paramagnetic in solution. Bis(*N*-methylsalicylaldehyde)nickel(II) shows weak absorption bands which indicate that some of the nickel atoms are in a triplet ground state even in the diamagnetic solid. When the solid is dissolved in chloroform these bands become stronger, and the compound becomes paramagnetic ( $\mu = 2.3\text{ B.M.}$ ) The solvent weakens the ligand field and uncoupling of spin occurs. In pyridine the same compound has the type of absorption spectrum characteristic of a paramagnetic octahedral  $\text{Ni}^{\text{II}}$  complex and the magnetic moment reaches  $3.1\text{ B.M.}$  Molecules of the base can enter the fifth and sixth co-ordination positions, thereby raising the energy of the  $d_z^2$  orbital and causing the ligands in the  $xy$  plane to be repelled:



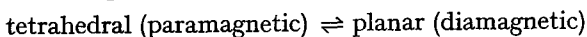
Another way in which planar nickel(II) complexes are converted into tetragonal or octahedral ones is by association either in solution or in the crystal.

There is evidence for equilibria between diamagnetic planar and paramagnetic tetrahedral isomers in solution and melts. The phenomenon is shown by a number of bis(*N*-sec-alkylsalicylaldimine)nickel(II) complexes:



Of the solids, some are diamagnetic and some paramagnetic ( $\mu \sim 3.3$  B.M.). When dissolved in toluene the diamagnetic ones become paramagnetic, the paramagnetic ones less so.

The existence of equilibria between conformational isomers:



is evident from the absorption spectra.

#### *Terpositive states*

##### *(i) Iron(III)*

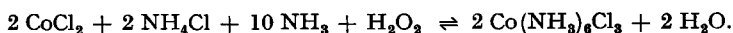
Most iron(III) complexes are octahedral, but tetrahedral cations such as  $\text{FeCl}_4^-$  are known and there is the pentagonal bipyramidal  $[\text{Fe}(\text{edta})(\text{H}_2\text{O})]^-$ . Of the octahedral complexes, those with ligands such as oxalate, phosphate and  $\beta$ -diketones, which co-ordinate through oxygen atoms, are much more common than those formed from nitrogen donors. Addition of ammonia to an iron(III) salt, even in the presence of ammonium chloride, merely causes the precipitation of hydrated iron(III) oxide. But dipyriddy and *ortho*-phenanthroline, which exert ligand fields strong enough to cause spin-pairing, form stable complexes. Among the halogen and pseudohalogen complexes are  $\text{FeF}_6^{3-}$ ,  $\text{Fe}(\text{CN})_6^{3-}$ ,  $\text{Fe}(\text{CNS})_6^{3-}$ ; anions containing five of one type of ligand and one of another are rather common;  $[\text{Fe}(\text{CN})_5(\text{H}_2\text{O})]^{2-}$  and  $[\text{FeF}_5(\text{H}_2\text{O})]^{2-}$  are examples.

Iron(III) ( $d^5$ ) compounds might be expected to have very similar absorption spectra to those of the isoelectronic  $Mn^{II}$  (p. 171), but the weak  $d-d$  transitions are in fact masked by the spread into the visible spectrum of strong charge-transfer peaks belonging to the near ultraviolet.

(ii) *Cobalt(III)*

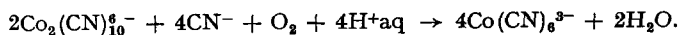
There is a wide range of cobalt(III) complexes with nitrogen donors, and most of the pioneer investigation of transition-metal complexes was done on the cobaltamines.

Although cobalt(II) salts are oxidised only with extreme difficulty ( $E^\circ$ ,  $Co^{3+}/Co^{2+} = +1.84$  V),  $H_2O_2$  or even air will oxidise  $Co^{II}$  to a complex of  $Co^{III}$  in the presence of cyanide or ammonia ( $E^\circ$ ,  $Co(CN)_6^{3+}/Co(CN)_6^{4-} = -0.83$  V). Hexa-amminecobalt(III) chloride,  $Co(NH_3)_6Cl_3$ , is readily made by oxidising an ammoniacal  $CoCl_2$  solution containing  $NH_4Cl$  in the presence of active charcoal as catalyst:

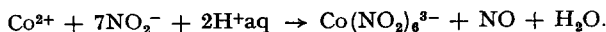


This is a cobaltamine of the so-called 'luteo' series containing the  $Co(NH_3)_6^{3+}$  ion. Treatment of  $Co(NO_3)_2$ ,  $NH_4NO_3$  and  $NH_3$  with  $H_2O_2$  in the absence of charcoal produces one of the 'purpureo' series, nitratopenta-amminecobalt(III) nitrate,  $[Co(NH_3)_5NO_3](NO_3)_2$ . Other series such as the 'roseo' aquopenta-amminecobalt(III) chloride,  $[Co(NH_3)_5H_2O]Cl_3$ , and 'violeo' chloroaquotetra-amminecobalt(III) chloride,  $[Co(NH_3)_4H_2OCl]Cl_2$ , can be made by suitable methods. The classical names, now falling into disuse, indicate the colours. The colour changes observed in passing from one series to another conform nicely to the spectrochemical series (p. 159). In all, over two thousand cobaltamines are known.

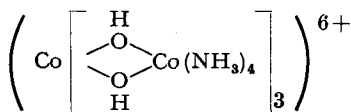
Hexacyanocobaltates(III) contain the extremely stable  $Co(CN)_6^{3-}$  ion. An excess of KCN added to a  $Co^{2+}$  solution gives  $K_6[Co_2(CN)_{10}]$ , which is precipitated from aqueous solution by alcohol. When boiled with even a weak acid such as acetic, aerial oxidation to the hexacyanocobaltate(III),  $K_3Co(CN)_6$ , occurs:



'Cobaltinitrites' are also complexes of  $Co^{III}$ . Addition of  $KNO_2$  to a  $Co^{II}$  solution made acid with acetic acid gives a yellow precipitate of potassium hexanitrocobaltate(III),  $K_3Co(NO_2)_6$ :



When the violet salt, chloroaquotetra-amminecobalt(III) sulphate,  $[Co(NH_3)_4(H_2O)Cl]SO_4$ , is treated with cold alkali the asymmetric ion



is produced. The chloride of this ion was the first purely inorganic (non-carbon) compound to be resolved (Werner, 1914).

Another type of polynuclear cobalt complex is produced by aerial oxidation of ammoniacal  $\text{Co}(\text{NO}_3)_2$  solution. This is the  $\mu$ -peroxo-bis{pentaamminecobalt(III)} ion,  $[(\text{NH}_3)_5\text{Co}-\text{O}-\text{O}-\text{Co}(\text{NH}_3)_5]^{4+}$ . Further oxidation gives the quinquepositive ion  $[(\text{NH}_3)_5\text{CoO}_2\text{Co}(\text{NH}_3)_5]^{5+}$ . It was shown, by electron-spin resonance, to contain cobalt atoms of identical oxidation number, not  $\text{Co}^{\text{III}}$  and  $\text{Co}^{\text{IV}}$  as previously thought. X-ray studies indicated the axis of  $\text{O}-\text{O}$  to be perpendicular to the  $\text{Co}-\text{Co}$  axis.

All Cobalt(III) complexes except  $\text{CoF}_6^{3-}$  have singlet ground states and are diamagnetic (p. 162). The energy level diagram for the  $d^6$  ion in the octahedral field, with only the singlet states shown, has the form illustrated in Fig. 369.

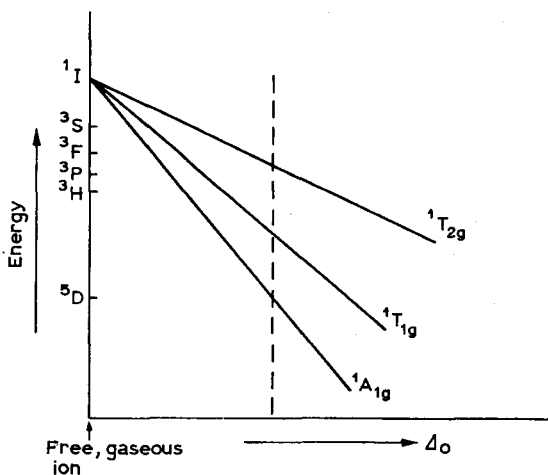


Fig. 369. Energy level diagram for  $d^6$  ion in an octahedral field (singlet states only).

There are usually two absorption bands in the visible spectrum. For symmetrical complexes,  $\text{CoX}_6$ , each of these bands, when plotted on a wave-number scale, is almost perfectly symmetrical about its peak. But for less symmetrical complexes such as  $\text{CoX}_4\text{Y}_2$  there is considerable splitting of the  ${}^1\text{T}_{1g}$  state. Furthermore, the splitting is greater for the *trans* form than for the *cis* form of such a complex. For the *trans* the absorption peak at the lower

energy ( ${}^1A_{1g} \rightarrow {}^1T_{1g}$ ) transition is split into two peaks, for the *cis* the peak differs from that of the symmetrical  $\text{CoX}_6$  in having a 'shoulder'. Moreover because a *cis* octahedral isomer is without a centre of symmetry the intensity of absorption is stronger. Typical absorption curves for *cis* and *trans* isomers of the  $\text{CoX}_4\text{Y}_2$  type are illustrated in Fig. 370.

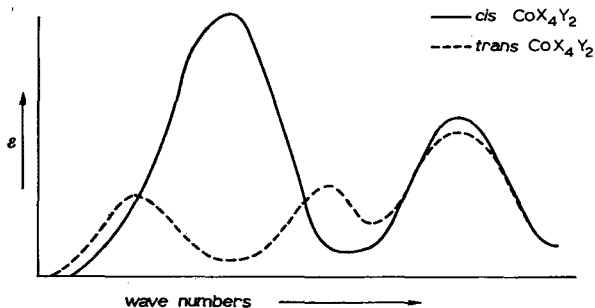


Fig. 370. Typical absorption curves for *cis* and *trans*  $\text{CoX}_4\text{Y}_2$  isomers.

### (iii) Nickel(III)

This is an unusual oxidation state in nickel, but a few complexes with the element in this state are known. The trimethylphosphine complexes of nickel(II) halides,  $\text{NiX}_2(\text{PMe}_2)_2$ , are oxidised to nickel(III) complexes even by atmospheric oxygen. When the appropriate nitrosyl halide is used as the oxidising agent the compounds formed are  $\text{NiX}_3(\text{PMe}_2)_2$ ; they are monomeric in solution.

### Higher oxidation states

Complexes containing these metals in oxidation states above +3 are rather uncommon. Some of them have been mentioned in the review of charge numbers on page 694.

### FURTHER READING

- P. L. PAUSON, *Ferrocene and Related Compounds*, *Quart. Rev.*, 9 (1955) 391.  
 M. ROSENBLUM, *The Chemistry of the Iron Group Metallocenes*, New York, Wiley, 1965.  
 R. S. NYHOLM, *The Stereochemistry and Valence States of Nickel*, *Chem. Rev.*, 53 (1953) 263.  
 R. S. YOUNG (Ed.), *Cobalt*, American Chemical Society Monograph, New York, Reinhold, 1960.

## The Platinum Metals

### GROUP VIII: THE SECOND AND THIRD TRIADS

The second triad of Group VIII, ruthenium, rhodium and palladium, and the third triad, osmium, iridium and platinum, because of their frequent occurrence together and the properties the elements have in common, are collectively known as the *platinum metals*. Vertical relationships are much stronger between members of these triads than between them and iron, cobalt and nickel. The second and third triad respectively complete the second and third series of transition elements and there are notable similarities between technetium and ruthenium and again between rhenium and osmium especially in their response to oxidation. However, apart from this comparative ease of oxidation the two elements have many properties which justify their membership of these two triads of rare metals of high melting point and density. The ground-state electronic configurations of the platinum metals are in doubt, but the tendency to complete the  $(n-1)d$  level at the expense of the  $ns$  level increases across each triad, platinum being an exception. The almost uniform atomic radii naturally lead to great physical similarity between the elements. Because the radii of  $Pd^{2+}$  and  $Pt^{2+}$  are so small, the metals rarely form uncomplexed cations. Indeed complexed cations are a characteristic of all the platinum metals.

TABLE 138

ATOMIC PROPERTIES OF THE PLATINUM METALS

	<i>Ru</i>	<i>Rh</i>	<i>Pd</i>	<i>Os</i>	<i>Ir</i>	<i>Pt</i>
Atomic number	44	45	46	76	77	78
Electron configuration	$4d^7 5s^1$	$4d^8 5s^1$	$4d^{10}$	$5d^6 6s^2$	$5d^9$	$5d^9 6s^1$
Metallic radius (Å)	1.34	1.34	1.37	1.35	1.36	1.38
Ionic radius $M^{3+}$ (Å)			0.50			0.52
$M^{3+}$ (Å)		0.69				
$M^{4+}$ (Å)	0.65			0.67	0.66	

Although the first ionisation energies are not much greater than those of other elements of the particular transition series to which they belong and all are lower than that of zinc (9.4 eV), the standard electrode potentials of

the platinum metals are very high, these being determined in part by the sublimation energies which are high. A tendency to assume passivity also increases the resistance of some of the metals to attack. Only platinum, osmium and palladium are soluble in aqua regia, and then, almost certainly, as complexes such as  $\text{PtCl}_6^{2-}$ .

TABLE 139

IONISATION ENERGIES AND ELECTRODE POTENTIALS OF THE PLATINUM METALS

	<i>Ru</i>	<i>Rh</i>	<i>Pd</i>	<i>Os</i>	<i>Ir</i>	<i>Pt</i>
<i>I</i> (eV)	7.5	7.7	8.3	8.7	9.2	9.0
$E^\circ$ , $M^{2+}/M$ (V)	+0.45	+0.6	+1.0	+0.85	+1.1	+1.0

### Stability of oxidation states in aqueous solution

The free energies of oxidation states up to +4, relative to the metal, are illustrated in Fig. 371. Notable features of the diagram are the relative stability of the +3 state in the elements Ru and Os, the tendency of this state to disproportionation in Rh and Ir (*cf.* their congeners), and the absence of the +3 state in Pd and Pt (*cf.* Ni).

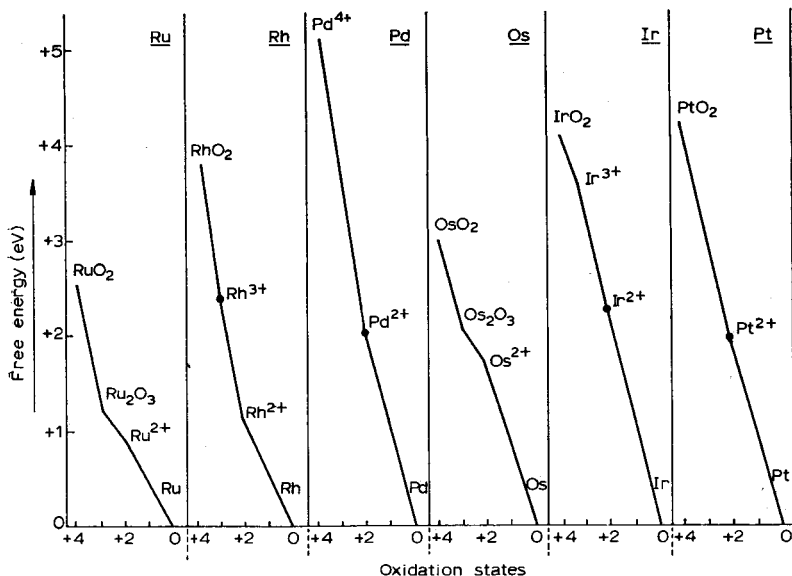


Fig. 371. Free energies of oxidation states of the platinum family, relative to the metal, in aqueous solution at  $\text{pH} = 0$ .



Higher oxidation states of Ru and Os exist in solution, for instance in  $\text{RuO}_4^-$  and  $\text{OsO}_4(\text{OH})_2^{2-}$ , but they are unstable at low pH and their redox potentials are in doubt.

### The elements: preparation and properties

The six metals together comprise about  $2 \times 10^{-5} \%$  of the lithosphere and are often found native. Osmiridium is a natural alloy of osmium and iridium. Important ores are sperrylite,  $\text{PtAs}_2$ , cooperite, PtS, and braggite, (Pt, Pd, Ni)S. The Sudbury (Canada) nickel and copper sulphide deposits contain about 2 ppm of the platinum metals, other than osmium. The metals, along with copper and gold, are segregated in the undissolved sludges from the electro-refining of Ni and Cu and in the involatile residues after the removal of  $\text{Ni}(\text{CO})_4$  in the carbonyl process. The Sudbury separation (Fig. 372) begins with an extraction by hot aqua regia in which only platinum, palladium and gold dissolve; the various metals are recovered as indicated:

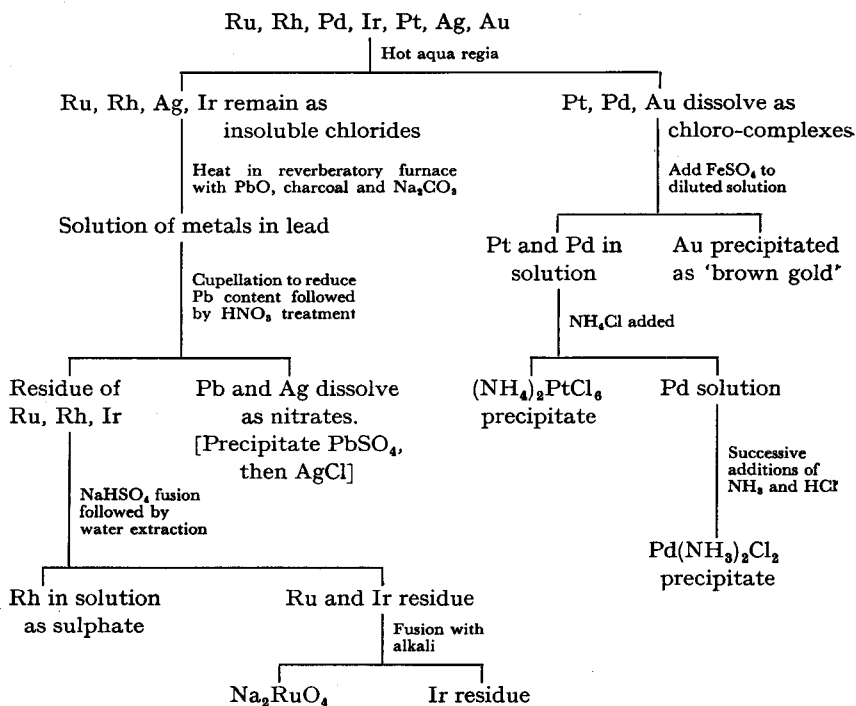


Fig. 372. Separation of the platinum metals.

The densities of the metals fall into two groups, those in the third triad being the highest of all the elements, nevertheless the atomic volumes are slightly greater than those of iron, cobalt and nickel. Ruthenium and osmium have h.c.p. structure, the rest f.c.c. Melting points decrease with atomic number rather quickly in each triad, but all are high.

TABLE 140  
PHYSICAL PROPERTIES OF THE PLATINUM METALS

	<i>Ru</i>	<i>Rh</i>	<i>Pd</i>	<i>Os</i>	<i>Ir</i>	<i>Pt</i>
Density (g/cc)	12.2	12.4	11.9	22.5	22.4	21.4
Atomic volume	8.6	8.8	9.0	8.5	8.6	9.1
Melting point (°C)	2500	1970	1560	2700	2450	1770

Platinum and palladium are useful in catalysis. Many of the elements are resistant to corrosion: platinum is employed for electrodes and crucibles and extensively for spinnerets to extrude rayon, and rhodium provides a surfacing material for searchlight mirrors. Palladium is used for purifying hydrogen which diffuses rapidly and selectively through the warm metal.

The metals are relatively unreactive. Of them platinum does not react with oxygen, palladium alone dissolves in nitric acid, and platinum, osmium and palladium dissolve in aqua regia. Only osmium and ruthenium form volatile oxides,  $\text{MO}_4$ , or, when fused with alkalis and oxidising agents, compounds like the osmates and ruthenates,  $\text{M}^{\text{I}}_2\text{OsO}_4$  and  $\text{M}^{\text{I}}_2\text{RuO}_4$ . Palladium and ruthenium acquire oxide coatings on heating to  $600^\circ\text{--}800^\circ$ , but these decompose and leave bright metal at  $1000^\circ$ . The metals all react with chlorine at temperatures of  $400^\circ$  and above. The oxides and sulphides, a few of the sulphates, and some of the halides are the only uncomplexed compounds.

### Oxidation states

A few examples of negative oxidation states are known; rhodium forms the carbonylate anion  $\text{Rh}(\text{CO})_4^-$  and there is some evidence for the  $\text{Ru}(\text{CO})_4^{2-}$  anion.

In their oxidation states, ruthenium and osmium bear a relation to iron rather similar to that of Mo and W to Cr. High charge numbers occur, in for instance  $\text{OsO}_4$ , but  $\text{OsF}_6$  is the highest fluoride. The value of the maximum charge falls abruptly from ruthenium to rhodium and from osmium to iridium. Indeed the general charge pattern of the preceding transition elements changes at this point in the Periodic Table; thereafter the elements tend to

show less diversity of charge number. This is evinced by the closer relationship between Ni, Pd, Pt than between the respective members of both the Co, Rh, Ir and the Fe, Ru, Os vertical groupings.

TABLE 141

REPRESENTATIVE COMPOUNDS AND IONS OF OXIDATION STATES 0 TO +8  
OF THE PLATINUM METALS

Charge number	Ru	Rh	Pd	Os	Ir	Pt
0	Ru(CO) <sub>5</sub>	Rh <sub>2</sub> (CO) <sub>8</sub>	Pd(NCR) <sub>2</sub>	Os(CO) <sub>5</sub>	Ir(NH <sub>3</sub> ) <sub>5</sub>	Pt(PR <sub>3</sub> ) <sub>4</sub>
+1		Rh <sub>2</sub> (CO) <sub>4</sub> Cl <sub>2</sub>		Os(NH <sub>3</sub> ) <sub>6</sub> Br		
+2	Ru(NH <sub>3</sub> ) <sub>6</sub> <sup>2+</sup>	[Rh(dipy) <sub>2</sub> Cl] <sup>+</sup>	PdO	Os(CN) <sub>6</sub> <sup>4-</sup>	Ir(NH <sub>3</sub> ) <sub>4</sub> Cl <sub>2</sub>	PtO
+3	[Ru(NH <sub>3</sub> ) <sub>5</sub> Cl] <sup>2+</sup>	[RhCl <sub>2</sub> en <sub>2</sub> ] <sup>+</sup>	PdF <sub>3</sub> *	Os(NH <sub>3</sub> ) <sub>6</sub> Br <sub>3</sub>	IrCl <sub>6</sub> <sup>3-</sup>	
+4	RuO <sub>2</sub>	RhF <sub>6</sub> <sup>2-</sup>	PdCl <sub>6</sub> <sup>2-</sup>	OsCl <sub>6</sub> <sup>2-</sup>	IrO <sub>2</sub>	PtCl <sub>6</sub> <sup>2-</sup>
+5	RuF <sub>5</sub>			Os <sub>2</sub> OCl <sub>8</sub>	IrF <sub>6</sub> <sup>-</sup>	PtF <sub>6</sub> <sup>-</sup>
+6	RuF <sub>6</sub>	RhF <sub>6</sub>		OsF <sub>6</sub>	IrF <sub>6</sub>	PtF <sub>6</sub>
+7	RuO <sub>4</sub> <sup>-</sup>			OsOF <sub>5</sub>		
+8	RuO <sub>4</sub>			OsO <sub>4</sub>		Pt(CO) <sub>2</sub>

\* See p. 722.

The charge numbers +1 and +5 are uncommon. The +6 state occurs in hexafluorides of all the elements, except palladium, for which the highest fluoride is PdF<sub>3</sub>. The +7 state is found in Ru and Os, as is also the +8 state. The compound Pt(CO)<sub>2</sub>F<sub>8</sub>, formally a Pt<sup>VIII</sup> complex, is of uncertain structure; it is a very reactive, yellow solid made by treating PtF<sub>4</sub> with CO under pressure.

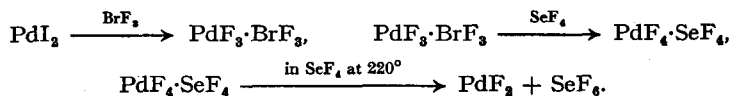
### Halides

The principal halides, many made by direct combination of the elements at 250–800°, are shown in Table 142.

The lower halides are obtained from higher halides in various ways:

- (i) by heating at very low pressures: 2OsCl<sub>3</sub> → 2OsCl<sub>2</sub> + Cl<sub>2</sub>,
- (ii) by heating with the metal: 2IrF<sub>6</sub> + Ir → 3IrF<sub>4</sub>, or
- (iii) by reducing with iodine or sulphur: 3RuF<sub>5</sub> + I<sub>2</sub> → 3RuF<sub>3</sub> + 2IF<sub>3</sub>.

Palladium trifluoride, PdF<sub>3</sub>, is, however, best made by the action of fluorine on PdCl<sub>2</sub>. Pure PdF<sub>2</sub> has been obtained by the following steps:



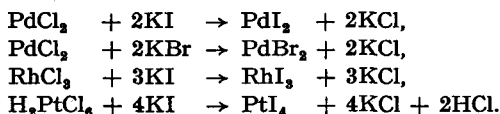
Platinum(IV) chloride, PtCl<sub>4</sub>, is made from H<sub>2</sub>PtCl<sub>6</sub>. Platinum is dissolved

TABLE 142  
PRINCIPAL HALIDES OF THE PLATINUM METALS

Charge number	Ru	Rh	Pd	Os	Ir	Pt
+1				OsI		
+2			PdF <sub>2</sub> PdCl <sub>2</sub> PdBr <sub>2</sub>	OsCl <sub>2</sub>		PtCl <sub>2</sub> PtBr <sub>2</sub> PtI <sub>2</sub>
+3	RuF <sub>3</sub> RuCl <sub>3</sub> RuBr <sub>3</sub> RuI <sub>3</sub>	RhF <sub>3</sub> RhCl <sub>3</sub> RhBr <sub>3</sub> RhI <sub>3</sub>	PdI <sub>2</sub> PdF <sub>3</sub>	OsI <sub>2</sub> OsCl <sub>3</sub> OsBr <sub>3</sub> OsI <sub>3</sub>	IrF <sub>3</sub> IrCl <sub>3</sub> IrBr <sub>3</sub> IrI <sub>3</sub>	
+4	RuF <sub>4</sub> RuCl <sub>4</sub>	RhF <sub>4</sub>		OsF <sub>4</sub> OsCl <sub>4</sub> OsBr <sub>4</sub>	IrF <sub>4</sub> IrCl <sub>4</sub>	PtF <sub>4</sub> PtCl <sub>4</sub> PtBr <sub>4</sub> PtI <sub>4</sub>
+5	RuF <sub>5</sub>			OsF <sub>5</sub>		PtF <sub>5</sub>
+6	RuF <sub>6</sub>	RhF <sub>6</sub>		OsF <sub>6</sub>	IrF <sub>6</sub>	PtF <sub>6</sub>

in aqua regia and the liquid evaporated down several times with concentrated HCl to decompose nitrosyl complexes originally formed. The product is impure chloroplatinic acid, H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O, which, when heated in Cl<sub>2</sub> at 370°, gives the red-brown PtCl<sub>4</sub>. A corresponding chloride of palladium is not known.

Bromides and iodides are often made most satisfactorily by precipitation reactions, being generally much less soluble than the corresponding chlorides:



The method is not always applicable, however. The compound (H<sub>3</sub>O)<sub>2</sub>OsI<sub>6</sub> can be crystallised from the solution made by dissolving OsO<sub>2</sub> in hot, aqueous HI. On strong heating it gives dark-grey compounds with the compositions OsI<sub>3</sub>, OsI<sub>2</sub> and OsI, but of these only the di-iodide has a distinctive X-ray diffraction pattern. The preparation of PtBr<sub>4</sub> is similar to that of PtCl<sub>4</sub>; platinum is dissolved in a mixture of nitric acid and bromine to give H<sub>2</sub>PtBr<sub>6</sub> which, on drying and warming, yields 2HBr and PtBr<sub>4</sub>.

Most of the halides are highly coloured solids whose volatility usually increases with the charge number of the metal; some of the higher fluorides are easily vaporised:

$\text{OsF}_6$  (m.p.  $35^\circ$ , b.p.  $47^\circ$ )  $\text{IrF}_6$  (m.p.  $44^\circ$ , b.p.  $53^\circ$ )  $\text{PtF}_6$  (m.p.  $57^\circ$ , subl. p.  $155^\circ$ )

Platinum hexafluoride,  $\text{PtF}_6$ , obtained in the fluorination of platinum, is a dark-red solid, m.p.  $57^\circ$ . Its vapour was found to oxidise molecular oxygen to  $\text{O}_2^+$ , a result which stimulated work which led to the discovery of the first compound of cationic xenon,  $\text{XePtF}_6$  (p. 299).

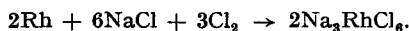
### Halogen complexes

The principal fluoro- and chloro-ions are shown in Table 143.

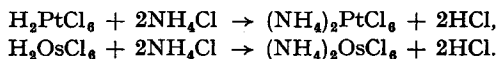
TABLE 143  
FLUORO- AND CHLORO-IONS OF THE PLATINUM METALS

Charge number	<i>Ru</i>	<i>Rh</i>	<i>Pd</i>	<i>Os</i>	<i>Ir</i>	<i>Pt</i>
+2			$\text{PdCl}_4^{2-}$			$\text{PtCl}_4^{2-}$
+3	$\text{RuF}_6^{3-}$ $\text{RuCl}_6^{3-}$	$\text{RhF}_6^{3-}$ $\text{RhCl}_6^{3-}$		$\text{OsCl}_6^{3-}$	$\text{IrF}_6^{3-}$ $\text{IrCl}_6^{3-}$	
+4	$\text{RuF}_6^{2-}$ $\text{RuCl}_6^{2-}$	$\text{RhF}_6^{2-}$ $\text{RhCl}_6^{2-}$	$\text{PdF}_6^{2-}$ $\text{PdCl}_6^{2-}$	$\text{OsF}_6^{2-}$ $\text{OsCl}_6^{2-}$	$\text{IrF}_6^{2-}$ $\text{IrCl}_6^{2-}$	$\text{PtF}_6^{2-}$ $\text{PtCl}_6^{2-}$
+5	$\text{RuF}_6^-$			$\text{OsF}_6^-$	$\text{IrF}_6^-$	$\text{PtF}_6^-$

The chloro-complexes can sometimes be made by heating the metal with an alkali-metal chloride in a stream of chlorine:



Another common method of preparation is to add  $\text{NH}_4\text{Cl}$  or  $\text{KCl}$  to the complex chloro-acid, ammonium and potassium salts being sparingly soluble as a rule:



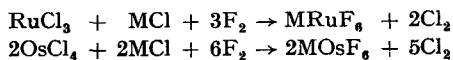
The ammonium salt is frequently used in purification processes as it gives the metal on heating. The addition of  $\text{KCl}$  to a  $\text{Na}_3\text{RhCl}_6$  solution precipitates the 5-co-ordinate  $\text{K}_2\text{RhCl}_5$ .

Ruthenium(III) exists in  $\text{RuCl}_4^-$ ,  $\text{RuCl}_5^{2-}$  and  $\text{RuCl}_7^{4-}$ , ions of unknown structure, as well as in  $\text{RuCl}_6^{3-}$ .

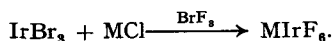
Platinum resists attack by concentrated aqueous  $\text{HCl}$  except in the presence of  $\text{KCl}$  or  $\text{RbCl}$  which, by forming insoluble chloroplatinates, disturb the equilibrium which is normally in favour of the metal. Similarly, gaseous  $\text{HCl}$  reacts with  $\text{Pt}$  in the presence of  $\text{KCl}$ :  $\text{K}_2\text{PtCl}_4$  is first formed and subsequently disproportionates to  $\text{Pt}$  and  $\text{K}_2\text{PtCl}_6$ , on cooling.

Of all the chloro-complexes, only the chloroplatinates(II) and (IV) are not hydrolysed in aqueous solution at pH 7. The rest give precipitates of hydrated oxides under these conditions.

Of the fluorides,  $K_3RuF_6$  is made by fusing  $RuCl_3$  with  $KHF_2$ , and  $K_3RhF_6$  by fusing  $K_3Rh(NO_2)_6$  with  $KHF_2$ . Fluorocomplexes of +5 states can be made by fluorination of mixtures of alkali-metal halides with platinum-group halides:



Bromine trifluoride is also used as the fluorinating agent:



These +5 complexes are unstable in water or dilute aqueous alkali. Thus when  $KIrF_6$  is treated with dilute  $KOH$  it is converted to  $K_2IrF_6$ , an  $Ir^{IV}$  complex, which remains unchanged by the water. The hexafluororuthenates and hexafluoroosmates(IV) are made similarly.

There are bromocomplexes corresponding to some of the chlorocomplexes listed above; among the most important are the salts of  $IrBr_6^{2-}$ ,  $OsBr_6^{2-}$  and  $PtBr_4^{2-}$ . Few iodocomplexes are known.

### Oxides

The principal oxides are shown in Table 144.

TABLE 144

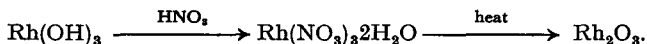
PRINCIPAL OXIDES OF THE PLATINUM METALS

Charge number	<i>Ru</i>	<i>Rh</i>	<i>Pd</i>	<i>Os</i>	<i>Ir</i>	<i>Pt</i>
+2			PdO			PtO
+3		$Rh_2O_3$				
+4	$RuO_2$			$OsO_2$	$IrO_2$	$PtO_2$
+8	$RuO_4$			$OsO_4$		

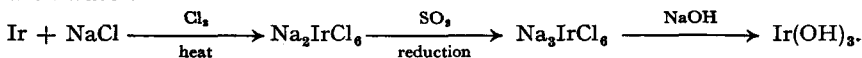
The dominant charge +2 of Pd is shown in its oxide; this remains after heating  $PdCl_2$  with  $NaNO_3$  at  $600^\circ$  and leaching out the soluble sodium salts. In the tetragonal lattice (Fig. 373) the metal atoms have four coplanar bonds, as in the  $Pd^{II}$  complexes; the oxygens are tetrahedrally co-ordinated. PtO is isomorphous with PdO but, as normally prepared by the cautious heating of black  $Pt(OH)_2$  precipitated from  $H_2PtCl_4$  by NaOH, is deficient in oxygen.

Yellow  $Rh(OH)_3$  is thrown down when a very slight excess of alkali is

added to an  $\text{RhCl}_3$  solution. The black  $\text{Rh}_2\text{O}_3$  is best prepared from it by first making the nitrate and heating this:



The oxide has the rhombohedral  $\text{Fe}_2\text{O}_3$  structure. Dark-green  $\text{Ir}(\text{OH})_3$  can be obtained by heating  $\text{Na}_3\text{IrCl}_6$  to redness with  $\text{NaOH}$  and washing the solid with water.



This hydroxide is the best starting point for the  $\text{Ir}^{\text{III}}$  compounds; the corresponding oxide is not known.

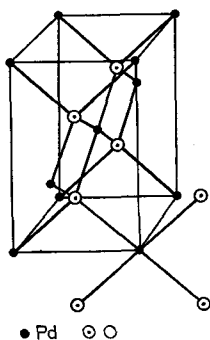
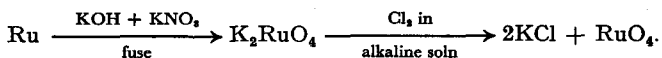


Fig. 373. Structure of  $\text{PdO}$ , showing tetragonal unit cell.

Dark-blue  $\text{Ir}(\text{OH})_4$  is precipitated when  $\text{Na}_2\text{IrCl}_6$  solution is boiled with sodium bromate at pH 6. When heated in an inert atmosphere at  $500^\circ$  it is converted to black  $\text{IrO}_2$ , also obtainable by direct combination, as is  $\text{RuO}_2$ . But  $\text{OsO}_2$  can only be prepared by the reduction of  $\text{OsO}_4$ . The three oxides have the rutile structure (p. 640). Platinum cannot be directly oxidised, being in this respect the most noble of the six metals;  $\text{PtO}_2$  is made by fusing  $\text{H}_2\text{PtCl}_6$  with  $\text{NaNO}_3$  at  $500^\circ$  and washing the residue free of sodium salts.

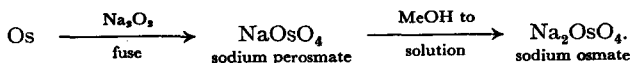
The tetroxides of ruthenium and osmium are solids of low m.p. ( $\text{RuO}_4$ ,  $25^\circ$ ;  $\text{OsO}_4$ ,  $41^\circ$ ).  $\text{RuO}_4$  volatilises when a stream of  $\text{Cl}_2$  is passed through an alkaline solution of a ruthenate and is conveniently prepared by oxidising potassium ruthenate with periodic acid



It sublimes in a vacuum but decomposes explosively above  $600^\circ$ .

The much more stable  $\text{OsO}_4$  is made by heating finely divided Os in oxygen: it can be boiled without decomposition.

These two metals, ruthenium and osmium, form oxo-anions similar to those of manganese and rhenium.



Violet crystals of  $\text{K}_2\text{OsO}_4$  are precipitated when an excess of KOH is added to a solution of the sodium salt. Thermally stable oxides corresponding to these oxo-anions are not known.

### Sulphides

The platinum metals form the sulphides given in Table 145.

TABLE 145

SULPHIDES OF THE PLATINUM METALS

Charge number	Ru	Rh	Pd	Os	Ir	Pt
+2			PdS			PtS
+3		$\text{Rh}_2\text{S}_3$			$\text{Ir}_2\text{S}_3$	
+4	$\text{RuS}_2$	$\text{RhS}_2$	$\text{PdS}_2$	$\text{OsS}_2$	$\text{IrS}_2$	$\text{PtS}_2$

Although the six metals form disulphides, these are not the same structurally.  $\text{RuS}_2$ ,  $\text{RhS}_2$  and  $\text{OsS}_2$  have a cubic, pyrites structure (Fig. 365, p. 698) containing  $\text{S}_2^{2-}$  ions; they are therefore compounds exhibiting the +2 state, but  $\text{PtS}_2$  has the  $\text{CdI}_2$  lattice (p. 204).

Both Rh and Ir form sulphides of the type  $\text{M}_2\text{S}_3$  when their trichlorides are heated in  $\text{H}_2\text{S}$ .

$\text{PdS}$ , made by direct combination, and  $\text{PtS}$ , by the reduction of  $\text{PtS}_2$ , have tetragonal structures.

The platinum metals also react with selenium and tellurium. For some of them, many phases have been identified, e.g.  $\text{Pd}_4\text{Se}$ ,  $\text{Pd}_{14}\text{Se}_5$ ,  $\text{PdSe}$ ,  $\text{PdSe}_2$ , and there is evidence for non-stoichiometry.

### Oxoacid salts

The sulphates of rhodium and iridium form yellow alums with the sulphates of K,  $\text{NH}_4$ , Rb, Cs and  $\text{Ti}^{\text{IV}}$ . The salts themselves are formulated  $\text{Rh}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$  and  $\text{Ir}_2(\text{SO}_4)_3 \cdot 12\text{H}_2\text{O}$ . Like palladium(II) sulphate,  $\text{PdSO}_4 \cdot 2\text{H}_2\text{O}$ , they are made by the action of  $\text{H}_2\text{SO}_4$  on the metals.

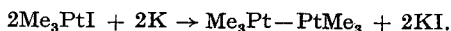


Palladium(II) nitrate,  $\text{Pd}(\text{NO}_3)_2$ , can be crystallised from a solution of palladium in nitric acid. In these salts, the metal again shows its dominant +2 charge and its similarity to nickel.

Platinum does not form salts of the oxoacids.

### Organometallic compounds and $\pi$ -complexes

Platinum, unlike the other Group VIII metals, forms some thermally stable alkyl compounds in which there is little or no  $\pi$ -bonding. Orange crystals of  $\text{Me}_3\text{PtI}$  are obtained from the reaction between  $\text{PtCl}_4$  and  $\text{MeMgI}$  by treating the product with water and afterwards extracting with benzene. The solid is insoluble in water and is not attacked by concentrated acids and alkalis, but it reacts with potassium to give  $\text{Pt}_2\text{Me}_6$ :



Tetramethylplatinum has an interesting structure. The molecule is a cubic tetramer in which every platinum is octahedrally co-ordinated to methyl groups; three of these are terminal groups and three bridging groups to other platinum atoms (Fig. 374).

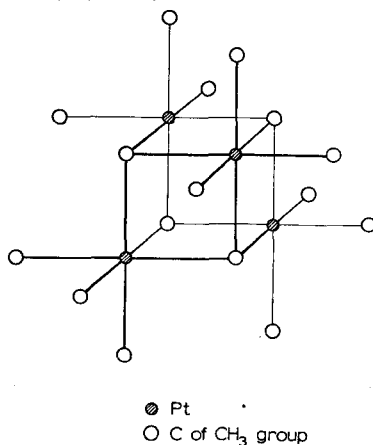


Fig. 374. Tetramethylplatinum: cubic structure of the tetrameric molecule.

Octahedral arrangements in  $\text{Pt}^{\text{IV}}$  compounds are frequently preserved by such unusual types of co-ordination.

Trimethylplatinum acetylacetonate, made by the action of  $\text{Me}_3\text{PtI}$  on acetylacetonone, has a dimeric molecule (Fig. 375). This dimer reacts with dipyrindyl to give the monomeric  $\text{Me}_3\text{Pt}(\text{dipy})(\text{O}_2\text{C}_5\text{H}_7)$  in which the octa-

hedral arrangement around the platinum is preserved through co-ordination, not, however, to the two oxygens of the  $\beta$ -diketone, but to the methylenic carbon atom (Fig. 376).

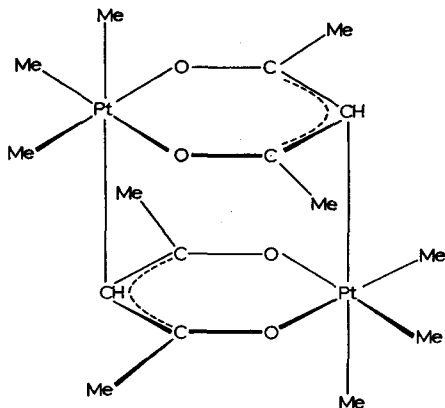


Fig. 375. Dimeric molecule of trimethylplatinum acetylacetonate.

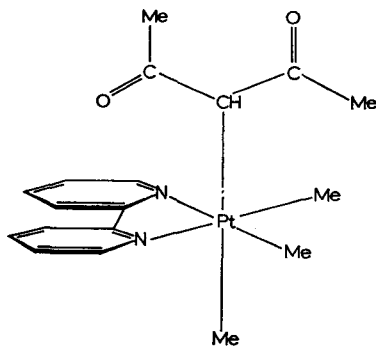
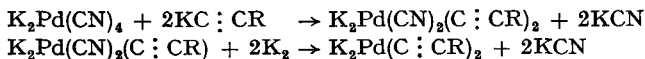


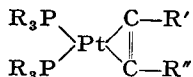
Fig. 376. Co-ordination of platinum to methylenic carbon atom in  $\text{Me}_3\text{Pt}(\text{dipy})(\text{O}_2\text{C}_5\text{H}_7)$ .

Of the many olefin complexes formed by the platinum metals some have already been discussed (p. 402). Complex acetylides are also known. Those of  $\text{Pd}^{\text{II}}$  and  $\text{Pd}^0$  have been prepared in liquid ammonia by the reactions:



Similar platinum complexes are similarly made. These are all true acetylido-complexes containing metal-carbon  $\sigma$  bonds similar to those in cyano-complexes. In another interesting group of acetylene complexes,  $(\text{R}_3\text{P})_2\text{Pt}$

( $R_1C : CR_2$ ), the structures are best explained by considering the metal to be  $\sigma$ -bonded to both the carbons of the acetylene group:

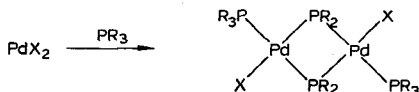
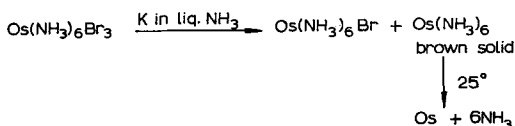
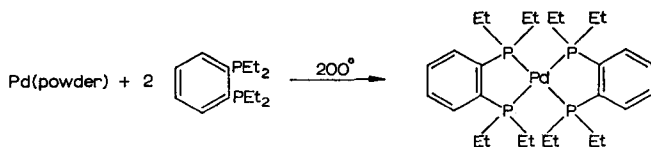


The cyclopentadienyls of ruthenium and osmium resemble ferrocene in being stable in air and capable of aromatic substitution without decomposition. Yellow  $(\pi-C_5H_5)_2Rh$  and colourless  $(\pi-C_5H_5)_2Os$  are made by treating  $RuCl_3$  and  $OsCl_4$  respectively with  $C_5H_5Na$ .

The ions  $(C_5H_5)_2Rh^+$  and  $(C_5H_5)_2Ir^+$ , made by treating the acetylacetonates with  $C_5H_5MgBr$ , can be reduced to the biscyclopentadienyls by  $NaBH_4$ .

### Complexes

Many complexes are formed by this family of metals. The metals exhibit high oxidation states in some of the complex halides, and there are many examples of low oxidation states of which three are given:

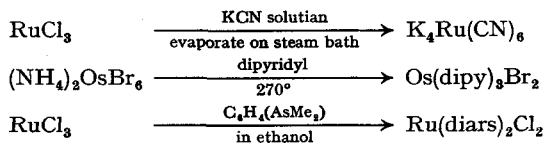


But the most common charge numbers are +2, +3 and +4.

#### *Bipositive states*

##### (i) $Ru^{II}$ and $Os^{II}$

The  $d^6$  complexes of these are diamagnetic, octahedral, and usually inert. They are obtained by the direct action of the ligands on compounds in which the metals are in higher oxidation states:



In these reactions the KCN, dipyridyl and diarsine all act as reducing agents.

(ii)  $\text{Pd}^{\text{II}}$  and  $\text{Pt}^{\text{II}}$

These complexes are formally of  $d^8$  configuration; they are diamagnetic, and usually square planar. Palladium and platinum are typical Class b acceptors (p. 586). Their most stable complexes are formed with donors such as phosphorus, arsenic, sulphur and chlorine. Oxygen-donor ligands produce only a few unstable complexes, although there are many complexes with nitrogen ligands.

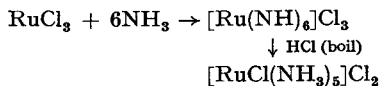
There are a few octahedral complexes of platinum(II) such as  $[\text{PtCl}_5\text{NO}]^{2-}$  and  $[\text{PtCl}(\text{NO})(\text{NH}_3)_4]^{2+}$ .

*Terpositive states*

(i)  $\text{Ru}^{\text{III}}$  and  $\text{Os}^{\text{III}}$

These  $d^7$  complexes are all low-spin, with one unpaired electron. Ruthenium(III) complexes are much more common than those of osmium(III).

Ruthenium halides react with ammonia to give hexa-ammines, which are changed to acidopenta-ammines by boiling with acid:



Complexes of osmium(III) with nitrogen ligands are not common, but  $[\text{Os}(\text{NH}_3)_6]^{3+}$ ,  $[\text{OsBr}(\text{NH}_3)_5]^{2+}$  and  $[\text{Os}(\text{dipy})_3]^{3+}$  occur.

Only a few  $\text{Ru}^{\text{III}}$  and  $\text{Os}^{\text{III}}$  complexes with oxygen donors are known—mainly  $\beta$ -diketone and oxalato chelates.

In keeping with the Class b character (p. 586) of these metals, they form stable complexes with phosphines and arsines. Examples are  $\text{RuX}_3(\text{PPh}_3)_3$  and  $[\text{Os}(\text{diars})_2\text{X}_2]^+$ .

(ii)  $\text{Rh}^{\text{III}}$  and  $\text{Ir}^{\text{III}}$

There are many stable complexes of these  $d^6$  states.

The cationic complexes resemble those of  $\text{Co}^{\text{III}}$  (also  $d^6$ ), and the structures, where known, are octahedral. They are all diamagnetic; even a weak-field ligand like  $\text{F}^-$  causes spin-pairing in the  $\text{RuF}_6^{3-}$  ion.

There is a well-defined  $\text{Rh}(\text{H}_2\text{O})_6^{3+}$  ion in rhodium alums and in the perchlorate  $\text{Rh}(\text{H}_2\text{O})_6(\text{ClO}_4)_3$ ; this is notable because aquo ions of this type are uncommon among second and third row d-block elements. Salts of *cis*- $[\text{Rh}(\text{en})_2\text{Cl}_2]^+$  have been resolved into optical isomers. The  $[\text{Rh}(\text{dipy})_3]\text{X}_3$  salts ( $\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{SCN}, \text{ClO}_4$ ) are yellow because of charge-transfer bonds in the blue region of the spectrum.

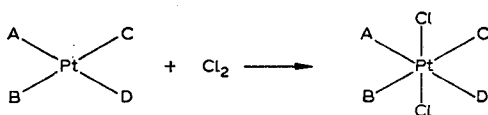
Rhodium(III) forms many more anionic complexes than does cobalt(III); they are usually more labile than the cationic and neutral complexes.

### (iii) Palladium and platinum

The +3 state probably does not exist in the true sense in either of these metals, for instance,  $\text{PdF}_3$  is actually  $\text{Pd}^{\text{II}}[\text{Pt}^{\text{IV}}\text{F}_6]$  and  $\text{PtBr}_3\text{en}$  contains equal numbers of  $\text{PtBr}_2\text{en}$  and  $\text{PtBr}_4\text{en}$  groupings.

### Quadripositive states

$\text{Ru}^{\text{IV}}, \text{Rh}^{\text{IV}}, \text{Pd}^{\text{IV}}, \text{Os}^{\text{IV}}$  and  $\text{Ir}^{\text{IV}}$  occur principally in complex halides but there is a greater range of  $\text{Pt}^{\text{IV}}$  complexes, some of which can be made by *trans* addition:

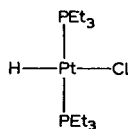
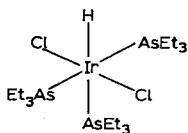
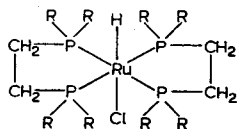


In the product the equatorial positions of the octahedral  $\text{Pt}^{\text{IV}}$  complex have the same arrangement as in the square  $\text{Pt}^{\text{II}}$  complex. The  $\text{Pt}^{\text{IV}}$  complexes are invariably octahedral; they provide a particularly extensive range of amines, from  $\text{Pt}(\text{NH}_3)_6^{4+}$  through  $\text{PtX}(\text{NH}_3)_5^{3+}$ , all the way to  $\text{PtX}_6^{2-}$  ( $\text{X} = \text{Cl}, \text{Br}, \text{SCN}, \text{NO}_2$ ). Ethylenediamine, hydrazine and hydroxylamine are other nitrogen donors which appear in these complexes.

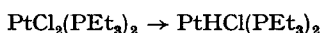
### Hydridocomplexes

When ligands which exert a strong field are attached to a transition metal it acquires some of the  $\sigma$ -bonding character of a B sub-group metalloid. Thus it can form metal-metal bonds, as in  $\text{Mn}_2(\text{CO})_{10}$ , and strong  $\sigma$ -bonds to hydrogen, as in carbonyl hydrides, *e.g.*  $\text{MnH}(\text{CO})_5$ , cyclopentadienyl hydrides, *e.g.*  $\text{ReH}(\text{C}_5\text{H}_5)_2$ , and carbonylcyclopentadienyl hydrides, *e.g.*  $\text{MoH}(\text{C}_5\text{H}_5)(\text{CO})_3$ .

The platinum metals form a particularly interesting series of molecular hydrides in which stabilisation is due to tertiary phosphines and amines. Examples are:



These hydrides are usually made by reduction of the corresponding halogen complexes:



The reducing agents which have been used include  $\text{LiAlH}_4$  in tetrahydrofuran,  $\text{H}_3\text{PO}_2$  in alcohol and  $\text{NH}_2\cdot\text{NH}_2$  in water.

In these compounds hydrogen acts as an anionic ligand, the metal retains the same charge number, co-ordination number and stereochemistry as it has in the halogen compound from which the hydride is made. Thus *trans*- $\text{PtHBr}(\text{PET}_3)_2$  has the slightly distorted square planar structure (Fig. 377).

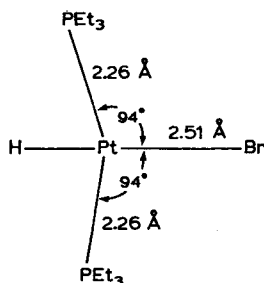


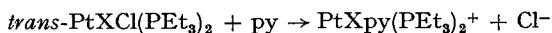
Fig. 377. Bond lengths and bond angles in *trans*- $\text{PtHBr}(\text{PET}_3)_2$ .

The chemical shifts in the proton magnetic resonance spectrum are very large (20–30 p.p.m.)—well removed from those due to organic substituents on the phosphorus atoms. In a compound such as  $\text{PtHBr}(\text{PET}_3)_2$  the hydrogen resonance is split into a triplet by the two equivalent  $^{31}\text{P}$  nuclei ( $I = \frac{1}{2}$ ) and there is further large splitting by  $^{195}\text{Pt}$ .

The infrared absorption spectra show a strong, sharp band due to metal-hydrogen bond stretching, but the position of the band varies a great deal from one compound to another (1726–2242  $\text{cm}^{-1}$ ). In platinum complexes of the *trans*- $\text{PtHX}(\text{PET}_3)_2$  type the M—H stretching frequency is reduced by X ligands of increasing *trans* effect (p. 598).

X	$\text{NO}_3$	Cl	Br	I	$\text{NO}_2$	SCN	CN
M—H stretching frequency ( $\text{cm}^{-1}$ )	2241	2183	2178	2156	2150	2112	2041

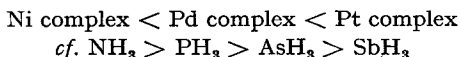
The hydrogen itself exerts a strong *trans* effect. In the process:



the rate of reaction is  $10^6$  times faster for  $X = \text{H}$  than for  $X = \text{Cl}$ . The hydrogen produces a strong ligand field at the metal; the d—d transition bands in the spectra of these compounds are shifted right into the ultraviolet range, and usually masked by charge-transfer bands, but the available evidence is that  $\text{H}^-$  lies near  $\text{CN}^-$  in the spectrochemical series (p. 159).

The dipole moments of these compounds are of interest. For *trans*- $\text{PtHCl}(\text{PEt}_3)_2$  the moment is  $4.2D$ . As the usual moment associated with a transition-metal to chlorine bond is about  $2D$  the  $\text{M}-\text{H}$  moment appears to be about  $2.5D$ , with  $\text{H}$  positive, in conflict with the idea that the hydrogen is co-ordinated as hydride ion. However, some of the moment is due to the distortion from square symmetry (Fig. 377) which places positive P atoms towards the hydrogen; furthermore the presence of the hydrogen has the effect of lengthening the metal-chlorine bond.

Thermal stabilities of analogous hydridocomplexes in any group of transition elements usually rise with the atomic mass of the element. Thus in the nickel group  $\text{PtHCl}(\text{PEt}_3)_2$  is stable enough to be distilled at  $130^\circ$  ( $10^{-2}$  mm pressure); the palladium compound  $\text{PdHCl}(\text{PEt}_3)_2$  is rather unstable even in the solid state; but the corresponding nickel compound has not been isolated, although its n.m.r. spectrum has disclosed its presence in the solution made by reducing  $\text{NiCl}_2(\text{PEt}_3)_2$  with  $\text{LiAlH}_4$ . The order of thermal stability of these transition-metal hydridocomplexes is thus the reverse of that found for hydrides of a B-sub-group:



The arsine- and phosphine-stabilised hydridocomplexes of the platinum metals are usually octahedral or square, but the trigonal bipyramidal  $\text{RhH}(\text{CO})(\text{PPh}_3)_3$  has been made by reducing the square planar  $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$  with hydrazine in alcohol.

The  $\pi$ -bonding ligands  $\text{PH}_3$  and  $\text{AsR}_3$  which stabilise the metal-hydrogen  $\sigma$  bonds are also effective in stabilising metal-carbon  $\sigma$  bonds and there are some organometallic compounds similar to these hydrides. *Trans*- $\text{PtHCl}(\text{PEt}_3)_2$  reacts reversibly with ethylene to give *trans*- $\text{PtClEt}(\text{PEt}_3)_2$ .

The existence of a hydridocomplex without a  $\pi$ -bonding ligand has now been established. The dichlorobis(ethylenediamine)rhodium(III) cation has been reduced to  $[\text{RhH}_2\text{en}_2]^+$  by  $\text{NaBH}_4$  in aqueous solution.

## FURTHER READING

- J. R. MILLER, *Recent Advances in the Stereochemistry of Nickel, Palladium and Platinum*, in H. J. EMELÉUS AND A. G. SHARPE (Eds.), *Advances in Inorganic Chemistry and Radiochemistry*, Vol. 4, London, Academic Press, 1962, p. 133.
- W. P. GRIFFITH, *Osmium and its Compounds*, *Quart. Rev.*, 19 (1965) 254.
- J. CHATT, *Hydrido- and Related Organo-Complexes of Transition Metals*, *Proc. Chem. Soc.*, (1962) 318.



## Copper, Silver and Gold

## GROUP IB

Copper, silver and gold are traditionally the coinage metals because of their resistance to corrosion under ordinary atmospheric conditions. All have the  $(n-1)d^{10}ns^1$  electron configuration and a  $^2S$  ground state. Although they have filled d orbitals, the elements are considered respectively the final members of the first, second and third transition series because they are all capable of forming ions with incomplete d shells. They lie well to the right in the Periodic Table and have ionisation energies about twice as large as those of potassium, rubidium and caesium, the elements which begin the fourth, fifth and sixth periods. The coinage metals show a considerable tendency to form covalent compounds. The  $s^1$  electrons account for the +1 oxidation state shown by all, but d electrons frequently participate in bonding and the formal +2 and +3 states which occur bring features of the chemistry of copper, silver and gold close to those of the other transition elements.

TABLE 146  
ATOMIC PROPERTIES OF GROUP IB ELEMENTS

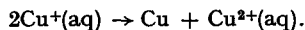
	<i>Cu</i>	<i>Ag</i>	<i>Au</i>
Atomic number	29	47	79
Electron configuration	$3d^{10} 4s^1$	$4d^{10} 5s^1$	$5d^{10} 6s^1$
Metallic radius (Å)	1.28	1.43	1.44
Ionic radius, $M^+$ (Å)	0.96	1.26	1.37

TABLE 147  
IONISATION ENERGIES AND ELECTRODE POTENTIALS OF  
GROUP IB ELEMENTS

	<i>Cu</i>	<i>Ag</i>	<i>Au</i>
Ionisation energy $I$ (eV)	7.72	7.87	9.22
$E^\circ, M^+/M$ (V)	+0.522	+0.799	+1.68
$M^{2+}/M$ (V)	+0.337	+1.39	
$M^{3+}/M$ (V)			+1.42

The hydrated ions occur in aqueous solutions and the standard electrode potentials are known (Table 147).

It is of interest that silver ions become less resistant to reduction with increasing charge, whereas those of copper and gold become more so; this is due to a relatively high heat of hydration of the  $\text{Cu}^{2+}$  and  $\text{Au}^{3+}$  ions. The second ionisation energy of copper is high, 20.2 eV, but the large heat of hydration of  $\text{Cu}^{2+}$  compared with that of  $\text{Cu}^+$  makes the hydrated  $\text{Cu}^{2+}$  ion much the more stable in aqueous solution. Thus soluble copper(I) compounds always disproportionate:



A comparison of the equilibrium of copper ions with that of silver ions is striking:

$$\frac{\{\text{Cu}^{2+}\}}{\{\text{Cu}^+\}^2} = 1.2 \times 10^6 \quad \frac{\{\text{Ag}^{2+}\}}{\{\text{Ag}^+\}^2} \approx 10^{-17} \quad (\text{at } 25^\circ)$$

An appreciable concentration of  $\text{Ag}^{2+}$  does not occur in aqueous solution. Gold resembles copper in the stability of its unipositive ion, which undergoes a similar disproportionation:



On reduction, both  $\text{Cu}^{\text{II}}$  and  $\text{Au}^{\text{III}}$  salts usually give the metal.

The free energies of the oxidation states of copper, silver and gold relative to the metals in aqueous solution at  $\text{pH} = 0$  are represented graphically in Fig. 378.

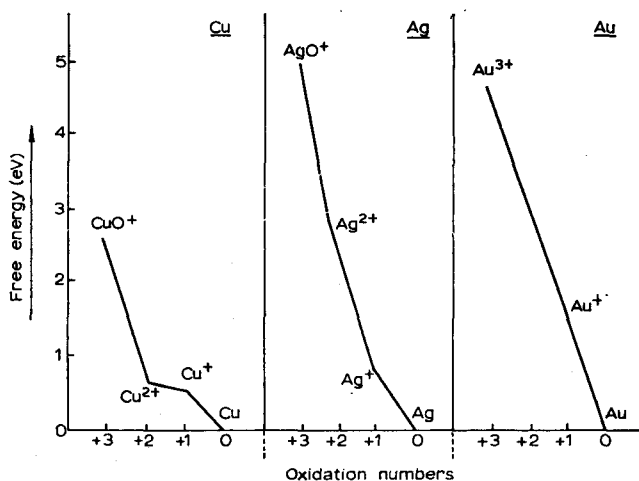


Fig. 378. Free energies of the oxidation states of the group IB elements relative to the metals at  $\text{pH} = 0$ .

### Properties, occurrence and extraction of the metals

Compounds of these elements are all readily reduced to the metals; these are relatively soft, very malleable and have high thermal and electrical conductivity. Gold and silver resist oxidation at any temperature, and silver and copper remain untarnished in dry air free from hydrogen sulphide. The densities of all the metals are high. Their atomic volumes are low, that of gold being particularly so because of the lanthanide contraction associated with the filling of the 4f shell. The metals have c.c.p. structure and their m.p. and b.p. are moderately high.

TABLE 148

PHYSICAL PROPERTIES OF GROUP IB ELEMENTS

	<i>Cu</i>	<i>Ag</i>	<i>Au</i>
Density (g/cc)	8.9	10.5	19.3
Atomic volume	7.1	10.3	10.2
Melting point (°C)	1083	960	1062
Boiling point (°C)	2310	1950	2600

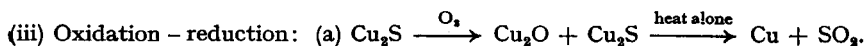
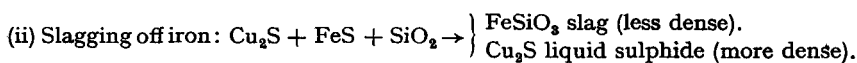
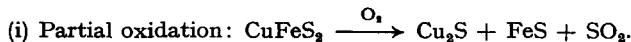
The metals all occur native, gold almost exclusively so. Copper makes up about  $7 \times 10^{-3}\%$  of the lithosphere mainly as copper pyrites  $\text{CuFeS}_2$ , cuprite,  $\text{Cu}_2\text{O}$ , and malachite,  $\text{Cu}_2(\text{OH})_2\text{CO}_3$ ; silver about  $2 \times 10^{-5}\%$  mainly as argentite,  $\text{Ag}_2\text{S}$ , horn silver,  $\text{AgCl}$ , and pyrargyrite,  $\text{Ag}_3\text{SbS}_3$ ; gold about  $5 \times 10^{-7}\%$  mainly as metal. Their extraction from ores is chemically relatively easy.

#### *Copper*

Oxide and carbonates ores are readily reduced by heating with coke and a flux:



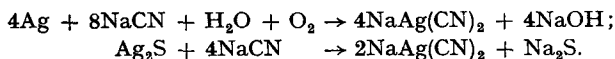
The main source is copper pyrites which is relieved of volatile arsenic and antimony by roasting, after which it is slagged and reduced.



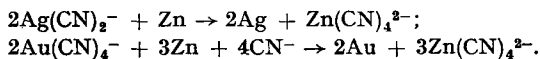
Copper is refined electrolytically, the silver and gold present separating as an anode sludge.

### Silver and gold

Whether present as metal or compound, these elements can be extracted from the finely divided ore by means of aqueous sodium cyanide. The cyanide ion reduces the oxidation potential of the noble metal so that atmospheric oxygen brings it into solution as a soluble complex:



The sodium sulphide is largely oxidised to  $\text{Na}_2\text{SO}_4$  by air and the reverse reaction is thereby impeded. The silver and gold are precipitated from their solution as cyano-ions, after this has been filtered, by the addition of zinc:



Silver and gold are recovered during the purification of lead (p. 411) and nickel (p. 693).

### Reactions of the metals

Copper reacts with the halogens and with oxygen. In oxygen at a dull red heat black  $\text{CuO}$  is formed; this is converted to red  $\text{Cu}_2\text{O}$  at  $900^\circ$ . The metal dissolves in nitric acid and in hot, concentrated sulphuric acid, but is not attacked by non-oxidising, dilute acids (*e.g.*  $\text{HCl}$ ) in the absence of air.

Although silver and gold are noble metals in the electrochemical sense, they are not particularly unreactive. Some of their principal reactions are summarised in Figs. 379 and 380.

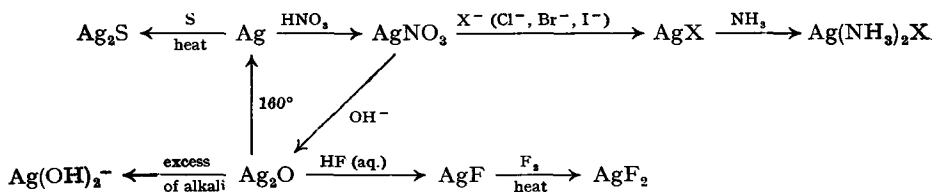


Fig. 379. Reactions of silver.

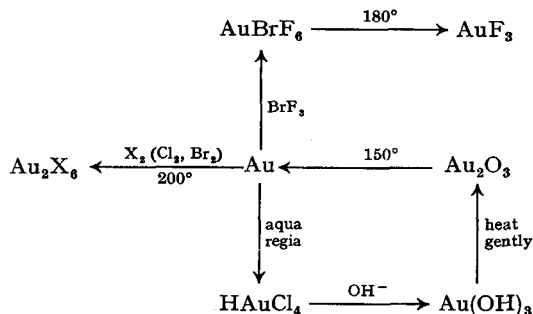


Fig. 380. Reactions of gold.

### Oxidation states

The range of charge numbers in this group is limited to +1, +2 and +3. Zero and negative oxidation states are not known; none of the metals forms a carbonyl, or carbonyl hydride, although carbonyl halides have been made.

In the simple compounds of the unipositive metals the bonding is largely covalent. Oxides and sulphides and many of the halides are insoluble in water. The water-soluble compounds, except silver fluoride, are those with complex ions, such as  $\text{Cu}(\text{CN})_3^{2-}$ ,  $\text{Cu}(\text{NH}_3)_2^+$  and  $\text{Ag}(\text{NH}_3)_2^+$ , the solutions always being colourless. In these ions the metal is unipositive with a non-bonding  $d^{10}$  shell and the ligands tend to be in linear or trigonal planar arrangement as they are with the non-transition metals.

The metals appear with charge +2 in many complexes,  $\text{Cu}^{\text{II}}$  compounds being particularly common. The  $d^9$  configuration often gives square structures, with four ligands in the plane, and distorted octahedral structures in which two more ligands are attached, by somewhat longer bonds, above and below the plane (p. 165). Copper(II) compounds of both types occur. The most important silver(II) compound is the oxide  $\text{AgO}$ , but the solid is diamagnetic and confirms the artificiality of the ionic model, in which the  $\text{Ag}^{2+}(d^9)$  would give a spin paramagnetism. On the other hand a solution of  $\text{AgO}$  in  $\text{HNO}_3$  is paramagnetic, indicating bipoisitive silver in the resulting complex ion. Gold alone appears to have no  $\text{M}^{\text{II}}$  complexes.

Both copper and gold form  $\text{M}^{\text{III}}$  complexes. Copper appears with charge +3 in  $\text{CuF}_6^{3-}$ , whose paramagnetism indicates two singly occupied  $d$  orbitals; this is a high-spin complex (p. 162) and the expected shape is regular octahedral, the non-bonding electrons being  $t_{2g}^6 e_g^2$ . Gold, with its higher electronegativity, can obtain an adequate share of electrons from

a smaller number of ligands (p. 558) and occurs more commonly in 4 coordination, examples being  $\text{AuCl}_4^-$  and  $\text{AuBr}_4^-$  which are square.

### Halides

The monohalides of copper and silver, with the exception of  $\text{AgF}$ , are almost insoluble in polar solvents. Copper(I) halides all have the zinc blende structure and they show a predominantly covalent character in agreement with the observed lattice energies (p. 102) (Table 149).

TABLE 149  
LATTICE ENERGIES OF COPPER(I) HALIDES

	$U_{\text{expt.}}$ (kcal mole <sup>-1</sup> )	$U$ as calc. on ionic model (kcal mole <sup>-1</sup> )	Difference
CuCl	221.9	216.0	+5.9
CuBr	216.0	208.0	+8.0
CuI	213.4	199.0	+14.4

Silver iodide is the only silver halide with an adamantine structure; in it the two elements have covalent radii in the ratio 1.26 : 1.33. In contrast both  $\text{AgCl}$  (1.26 : 0.99) and  $\text{AgBr}$  (1.26 : 1.14) have a rock-salt structure and an ionic character. For  $\text{AgI}$  the difference is sufficiently large to indicate considerable deviation from ionic bonding; its more covalent character is reflected in the insolubility of  $\text{AgI}$  in  $\text{NH}_3$ . Above 146°,  $\text{AgI}$  exhibits an unusual form of defect structure (p. 215). The suggestion that colour in  $\text{AgBr}$  and  $\text{AgI}$  is due to ionic deformation (increasing covalent character) is questionable as  $\text{AgF}$  is yellow. The fluoride alone forms a hydrate,  $\text{AgF} \cdot \text{H}_2\text{O}$ .

TABLE 150  
LATTICE ENERGIES OF SILVER(I) HALIDES

	$U_{\text{expt.}}$ (kcal mole <sup>-1</sup> )	$U$ as calc. on ionic model (kcal mole <sup>-1</sup> )	Difference
$\text{AgF}$	217.7	219 (NaCl structure)	-1.3
$\text{AgCl}$	205.7	203 (NaCl structure)	+2.7
$\text{AgBr}$	201.7	197 (NaCl structure)	+4.7
$\text{AgI}$	199.2	190 (ZnS structure)	+9.2

Gold(I) fluoride is unknown, and the chloride, bromide and iodide are not very thermally stable and decrease in stability in that order, AuI being an endothermic compound ( $\Delta H = +5.52$  kcal). With the exception of AuI, the monohalides are converted by water to the trihalide and metal, the chloride the most readily, possibly because it is the most soluble.

Copper(II) fluoride,  $\text{CuF}_2$ , made from fluorine and copper, is an ionic compound. The covalent anhydrous chloride,  $\text{CuCl}_2$ , consists of infinite chains packed so that individual copper atoms show square 4-co-ordination (Fig. 381) and have, as nearest neighbours in the next chain, two chlorine atoms. In the hydrate  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  there are no chains. It probably has a distorted octahedral structure, the Cu—Cl (2.30 Å) and Cu—O (1.97 Å) lengths indicating predominant covalence. Anhydrous  $\text{CuBr}_2$  has a structure similar to  $\text{CuCl}_2$  and is without a stable hydrate.

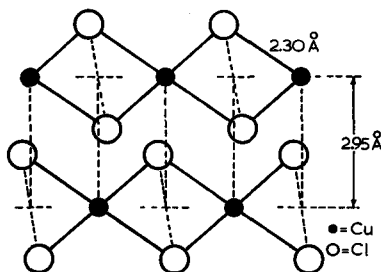
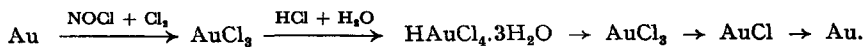


Fig. 381. Arrangement of Cu and Cl atoms in anhydrous  $\text{CuCl}_2$ .

Silver (II) fluoride,  $\text{AgF}_2$ , made by the action of fluorine on Ag or  $\text{AgCl}$ , is fairly stable, the equilibrium pressure of fluorine over the solid at  $700^\circ$  being only 80 mm. It is, nevertheless, a useful fluorinating agent.

Gold(III) but not gold(II) halides are known. The metal dissolves in aqua regia to a yellow solution which gives hydrogen tetrachloroaurate(III) trihydrate on evaporation:



Heating the tetrachloroaurate gives first red  $\text{AuCl}_3$ , then yellow  $\text{AuCl}$  and finally gold. Gold(III) chloride also results from the disproportionation of  $\text{AuCl}$  in the presence of water:



### Oxides

The isomorphous copper(I) and silver(I) oxides,  $\text{Cu}_2\text{O}$  and  $\text{Ag}_2\text{O}$ , are of unusual structure. The metal atoms have two collinear bonds and the

oxygens four tetrahedral bonds in a cubic structure similar to that of cristobalite. The low co-ordination, 4:2, is indicative of covalence. The structure represented in Fig. 382 is not the complete picture. An identical framework, in which the structure shown is moved forward so that the oxygens marked A take up the positions B, interpenetrates it without cross-connection by M—O bonds. The interpenetrating structure is unique in crystal chemistry. Both oxides form solid solutions with the metal.

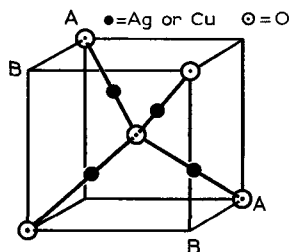
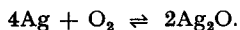


Fig. 382. Diagram illustrating how  $\text{Ag}_2\text{O}$  and  $\text{Cu}_2\text{O}$  are built up structurally.

Silver(I) oxide is made by heating finely divided silver at  $300^\circ$  under oxygen at 15 atm. pressure:



The material of approximately the same composition, precipitated by alkali from aqueous silver salts, cannot be completely freed of water without decomposition; that precipitated from alcoholic solution is the hydroxide,  $\text{AgOH}$ , which can be made only in this way. Silver oxide is decomposed completely into silver and oxygen at  $300^\circ$  under normal pressure. It gives an alkaline reaction in water, the solubility though slight is in conformity with a low lattice energy. Its enthalpy of formation is only  $-7.3 \text{ cal mole}^{-1}$ .

Copper(I) oxide, more thermally stable and insoluble, is precipitated from aqueous solution without water of hydration. Its heat of formation, 40 kcal, though low for a metal oxide, is appreciably above that of  $\text{Ag}_2\text{O}$ .

Compounds of  $\text{Cu}^{\text{I}}$  in the solid, dry condition are not oxidised by air, but its soluble complexes in this oxidation state are very readily converted to the  $\text{Cu}^{\text{II}}$  condition. For instance, a colourless solution of  $\text{Cu}(\text{NH}_3)_2^+$  becomes blue immediately on exposure to air, even while being poured out.

Gold(I) oxide is unknown, as are all binary compounds of the element in this oxidation state. A hydrated material, precipitated from a  $\text{KAuBr}_2$  solution by alkali, cannot be dehydrated without loss of oxygen.



The copper(II) oxide structure involves 4 : 4 co-ordination, with a tetrahedral bond arrangement round the oxygen and coplanar bonds round the copper atoms. The Cu—O distance of 1.95 Å indicates a large degree of covalency (Fig. 383).

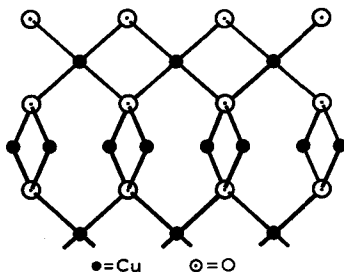


Fig. 383. Arrangement of Cu and O atoms in CuO.

Crystalline  $\text{Cu}(\text{OH})_2$  is made by adding ammonia to boiling  $\text{CuSO}_4$  solution until the green precipitate first formed turns blue, then washing and digesting with  $\text{NaOH}$  solution. The hydroxide is converted by boiling water to black  $(\text{CuO})_4 \cdot \text{H}_2\text{O}$  which loses all its water at dull red heat without further decomposition. Copper(II) oxide and sulphide are less stable than the corresponding copper(I) compounds, into which they are converted at a higher temperature:



The solution of  $\text{Cu}(\text{OH})_2$  in ammonia contains both  $[\text{Cu}(\text{NH}_3)_2](\text{OH})_2$  and  $[\text{Cu}(\text{NH}_3)_4](\text{OH})_2$ .

Silver(II) oxide,  $\text{AgO}$ , has the zinc blende structure (p. 202). It is made by (i) the action of boiling water on  $\text{Ag}_2\text{O}_3$  (the black crystals formed on the anode when 10%  $\text{AgNO}_3$  is electrolysed); (ii) precipitation from  $\text{AgNO}_3$  with potassium persulphate; (iii) oxidising silver(I) oxide with hot alkaline  $\text{KMnO}_4$ . The compound is not a peroxide since it does not give hydrogen peroxide when acidified. Both the solid  $\text{Ag}_2\text{O}_3$  and a solution of  $\text{AgO}$  in concentrated  $\text{HNO}_3$  are dark-coloured and paramagnetic, suggesting the presence in each of the  $\text{Ag}^{2+}$  ion with a  $4s^24p^64d^9$  structure. Solutions of silver(II) oxide are easily decomposed in oxidising acids other than nitric acid. The couple  $\text{Ag}^{2+}/\text{Ag}^+$  has the very high redox potential of 1.98 volts; thus a solution of  $\text{Ag}^{2+}$  ions in nitric acid is a particularly strong oxidising agent.

Anodic oxidation of silver nitrate in the presence of pyridine gives the orange-red  $[\text{Ag}(\text{pyr})_4](\text{NO}_3)_2$ . Dipyridyl compounds are also known,

$[\text{Ag}(\text{dipyr})_2]\text{X}_2$  where  $\text{X} = \text{NO}_3, \text{HSO}_4, \text{ClO}_4$  and  $\frac{1}{2}(\text{S}_2\text{O}_8)$ ; they are much more stable than  $\text{AgO}$ .

Gold(III) hydroxide is made by the action of  $\text{MgO}$  on  $\text{HAuCl}_4$ . Unlike  $\text{Cu}(\text{OH})_2$  it dissolves in hot alkalis; yellow crystals of potassium aurate,  $\text{KAuO}_2 \cdot 3\text{H}_2\text{O}$ , can be recovered from such a solution.

### Other binary compounds

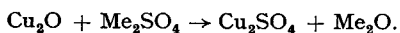
Copper nitride,  $\text{Cu}_3\text{N}$ , is a dark-green solid made by treating  $\text{CuF}_2$  with  $\text{NH}_3$  at  $280^\circ$ , or by heating the metal to redness in ammonia. It has a reversed rhenium oxide structure; in it the cubic unit cell has nitrogen atoms at the corners and copper atoms at the mid-points of the edges.

The sulphides  $\text{Cu}_2\text{S}$  and  $\text{Ag}_2\text{S}$ , and the corresponding selenides are known; copper also forms  $\text{CuS}$  and  $\text{CuSe}$ . All are insoluble in water. Gold gives  $\text{Au}_2\text{S}$  and  $\text{Au}_2\text{S}_3$ , the latter being hydrolysed by water.

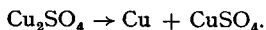
Copper(I) sulphide has a high thermal stability. It is not very reactive, being very slowly attacked by chlorine and by sodium carbonate at a dull red heat.

### Oxoacid salts

Copper(I) sulphate is the only ionic  $\text{Cu}^{\text{I}}$  compound. It is made by heating  $\text{Cu}_2\text{O}$  with dimethyl sulphate:



It is decomposed immediately in water:



This is to be expected from the redox potentials of the  $\text{Cu}^+/\text{Cu}$  and  $\text{Cu}^{2+}/\text{Cu}$  couples. The  $\text{Cu}^+$  ion is, however, stabilised by complexing and appears as colourless crystals of  $[\text{Cu}(\text{NH}_3)_2]_2\text{SO}_4$ ; these are produced when ethyl alcohol is added to a solution made by dissolving  $\text{Cu}_2\text{O}$  in an aqueous solution of ammonium sulphate and ammonia.

Copper(II) sulphate pentahydrate,  $\text{Cu}(\text{H}_2\text{O})_4\text{SO}_4 \cdot \text{H}_2\text{O}$ , has four water molecules and an oxygen from each of two  $\text{SO}_4^{2-}$  anions octahedrally arranged about the  $\text{Cu}^{2+}$  cation. The fifth water molecule is hydrogen-bonded to oxygen atoms. The positions of all the water molecules and hydrogen bonds have been determined by neutron refraction. The  $\text{H}-\text{O}-\text{H}$  angles of all the water molecules are near the tetrahedral angle, the  $\text{O}-\text{H}\cdots\text{O}$  angles between  $154-176^\circ$ , and the  $\text{O}-\text{O}-\text{O}$  angles between  $105-130^\circ$ ; so that some of the hydrogen bonds are bent, one by as much as  $26^\circ$ . The corresponding ammine hydrate,  $\text{Cu}(\text{NH}_3)_4\text{SO}_4 \cdot \text{H}_2\text{O}$ , is known, but not a

penta-ammine because the hydrogen bonding between  $\text{NH}_3$  molecules is too weak to hold a fifth  $\text{NH}_3$ .

Copper(II) nitrate has the hydrates  $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Cu}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$ . Attempts to dehydrate them produce basic salts. However, the anhydrous salt has been made by dissolving copper in a mixture of  $\text{N}_2\text{O}_4$  and ethyl acetate, separating the crystalline  $\text{Cu}(\text{NO}_3)_2 \cdot \text{N}_2\text{O}_4$  formed, and decomposing it by heat. The  $\text{N}_2\text{O}_4$  is driven off at  $85^\circ$  and further heating of the anhydrous  $\text{Cu}(\text{NO}_3)_2$  in a vacuum at  $150\text{--}200^\circ$  enables it to be purified by sublimation on to a cold finger. The volatile nitrate is monomeric both in the vapour and in organic solvents such as dioxan, ethyl acetate and nitrobenzene. Some thermal decomposition of the solid to  $\text{CuO}$  begins at  $150^\circ$ , but the vapour is stable to  $225^\circ$ .

The molecule has a 'sandwich' form and bonding is evidently due to an overlap of d orbitals of the copper with  $\pi$  orbitals of the  $\text{NO}_3$  groups, but the latter orbitals are not identical or equivalent (Fig. 384).

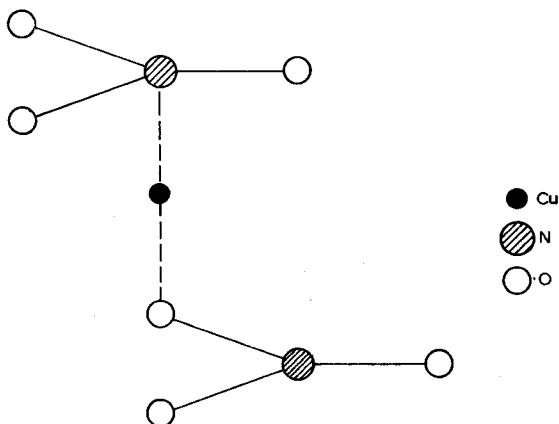


Fig. 384. Molecule of  $\text{Cu}(\text{NO}_3)_2$  in vapour.

Copper nitrate and other anhydrous, volatile nitrates have also been prepared from the anhydrous chlorides of the respective metals by treating them with an excess of dinitrogen pentoxide. The chlorine is evolved as  $\text{NO}_2\text{Cl}$  and the excess of reagent and the co-ordinated oxides of nitrogen are removed by warming the product. The method is of general application and has enabled volatile  $\text{Zr}(\text{NO}_3)_4$  to be made.

Copper(II) acetate monohydrate is interesting for its magnetic properties. The moment decreases as the temperature falls, suggesting a temperature-

dependent equilibrium between the diamagnetic  $d^{10}$  and the paramagnetic  $d^9$  configurations, with a Cu—Cu bond energy of only about 1 kcal/mole<sup>-1</sup>. The compound has a dimeric structure (Fig. 385).

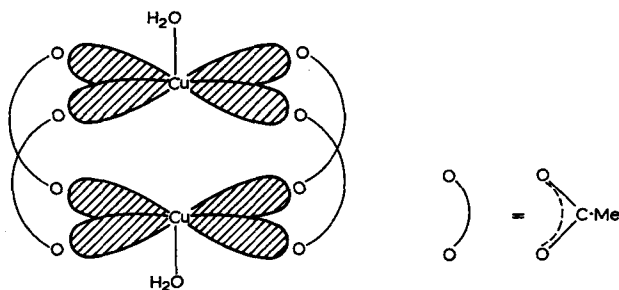


Fig. 385. Dimer of copper(II) acetate monohydrate, illustrating  $\delta$ -bonding.

The copper atoms have square pyramidal arrangements of oxygens around them. Interaction between the two copper atoms is pictured as being due to the face-to-face overlap of the  $d_{x^2-y^2}$  orbitals, shown in the diagram. This type of bonding, called  $\delta$ -bonding, though it is extremely weak compared with  $\sigma$ - and  $\pi$ -bonding, can lead to diamagnetism through the coupling of spins.

Silver nitrate is notable for a high solubility considerably increased by temperature (215 g per 100 g of water at 20° and 910 g at 100°). Attempts to volatilise  $\text{AgNO}_3$  have failed.

That normal silver carbonate can be precipitated from solution,



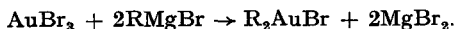
is in contrast with the formation of basic copper(II) carbonates under similar conditions, and conforms with the more basic character of  $\text{Ag}_2\text{O}$ .

Silver perchlorate is not only deliquescent and very soluble but forms a monohydrate. It also dissolves in benzene and toluene, recrystallising from the latter as  $\text{AgClO}_4 \cdot \text{C}_7\text{H}_8$ . Solubility in organic solvents is thus shown to be an unreliable guide to covalent character, for silver perchlorate is considerably ionised both in water and nitromethane.

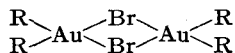
Oxoacid salts of gold are uncommon; one of the more stable, yellow  $\text{Au}_2(\text{SeO}_4)_3$ , crystallises from a solution of gold in hot selenic acid.

### Organometallic compounds

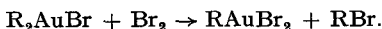
Gold resembles platinum in forming numerous  $\sigma$ -bonded alkyl derivatives. The halides  $\text{AuCl}_3$  and  $\text{AuBr}_3$  react with Grignard reagents to give colourless solids,  $\text{R}_2\text{AuX}$ :



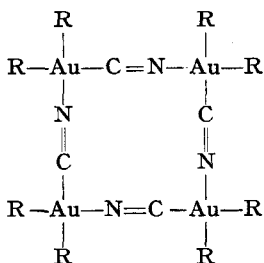
The compounds are insoluble in water but soluble in organic solvents. The molecules are dimeric and halogen-bridged:



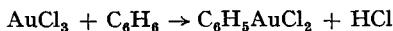
They react with halogens to give red monoalkyl derivatives:



The cyanides  $\text{R}_2\text{AuCN}$  are tetrameric:



Aryl compounds cannot be made from Grignard reagents, but yellow solids of the general formula  $\text{ArAuCl}_2$  are prepared by dissolving  $\text{AuCl}_3$  in the aromatic hydrocarbon:



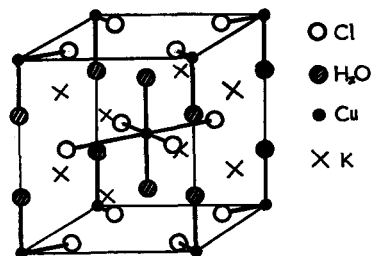
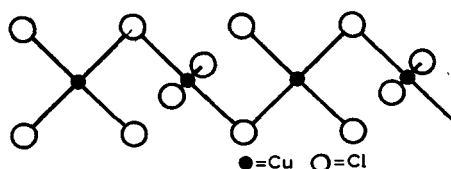
## Complexes of copper, silver and gold

### *Complex halides*

The  $\text{M}^{\text{I}}$  complexes are mainly of the type  $\text{M}[\text{CuX}_2]$  in which the covalency of the metal is limited to two and of which all the elements provide examples.

Of the  $\text{M}^{\text{II}}$  complexes,  $\text{K}_2\text{CuCl}_4 \cdot 2\text{H}_2\text{O}$  (Fig. 386) has a tetragonal unit cell with features deriving from both  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  and  $\text{CuCl}_2$ . In anhydrous  $\text{Cs}_2\text{CuCl}_4$ , the  $[\text{CuCl}_4]^{2-}$  anion is not planar but a flattened tetrahedron; in solution the absorption spectrum is different from that of the solid, possibly because the anion reverts to a planar configuration on hydration.

In the weak ligand field exerted by the halogen ions (p. 159) the metal has four electrons in  $e$  orbitals and only five in the three  $t_2$  orbitals which point in the direction of the ligands; thus the ligands are able to approach more closely and form stronger bonds.

Fig. 386. Structure of  $K_3CuCl_4 \cdot 2H_2O$ .Fig. 387. Spiral arrangement of atoms in  $(CuCl_3^{2-})_n$  ions.

The  $Cu^{II}$  complex  $CsCuCl_3$  consists of  $Cs^+$  ions and infinite chain  $(CuCl_3^{2-})_n$  ions. The co-ordination in these is planar but the sharing of corners by the  $CuCl_3$  units gives them a spiral arrangement (Fig. 387).

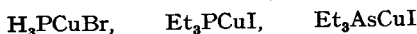
The  $Cu^{III}$  complex  $K_3CuF_6$  has been prepared; but only the fluorine compound occurs, as so often happens with the highest co-ordination number. Its paramagnetic moment corresponds to two unpaired electrons and suggests the  $t_{2g}^6 e_g^2 Cu^{III}$  configuration with regular octahedral form.

Gold(III) complexes are particularly stable. The  $AuBr_4^-$  ion in  $K[AuBr_4] \cdot 2H_2O$  is square.  $CsAuCl_3$  contains both  $Au^I$  and  $Au^{III}$  and can be formulated  $Cs_2[(AuCl_2)(AuCl_4)]$ . The compound  $(C_7H_7)_2S \cdot AuBr_2$ , made by the action of benzyl sulphide on  $AuBr_3$ , contains separate molecules of  $(C_7H_7)_2S \cdot AuBr$  and  $(C_7H_7)_2S \cdot AuBr_3$  in a highly disordered structure.

#### Other complexes

##### The +1 state

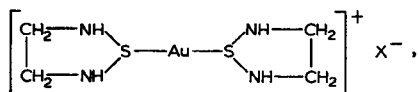
The three metals of the sub-group form amines containing linear  $M(NH_3)_2^+$  ions. There are similar alkylamine and pyridine complexes. Phosphine, and substituted phosphines, and arsines react with monohalides of the metals to form rather unstable complexes:



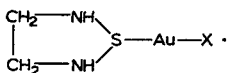
These are tetrameric in benzene. A full structural determination on  $(Et_3AsCuI)_4$  has shown it to have a structure based on interpenetrating tetrahedra of copper and arsenic atoms (Fig. 388).

The silver compounds are similar, but  $Ph_3PAuCl$  has been shown to be monomeric.

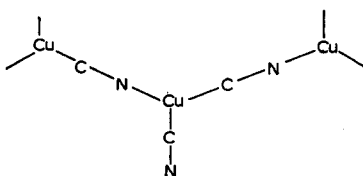
Complexes of the unipositive metals with oxygen donors are few and unimportant but there are many with sulphur donors. Copper(I) forms thiourea complexes with 1, 2, 3 and 4 thiourea molecules per copper atom; silver(I) complexes are similar. Gold(I) halides form two series of compounds with ethylenethiourea, the salts



and the covalent compounds



The unipositive metals form cyanocomplexes of empirical formula  $\text{M}(\text{CN})_2^-$ . The silver and gold complexes are monomeric but  $\text{KCu}(\text{CN})_2$  has been shown to contain spiral, polymeric ions:



Copper(I) amines react with alkynes to give yellow or red polymers in which the copper atom of one  $\text{R}\cdot\text{C}:\text{C}:\text{C}\cdot\text{CN}$  unit is  $\pi$ -bonded to the  $\text{---C}:\text{C---}$  bond of another. Both the amines and the chlorocuprates(I) absorb carbon monoxide.

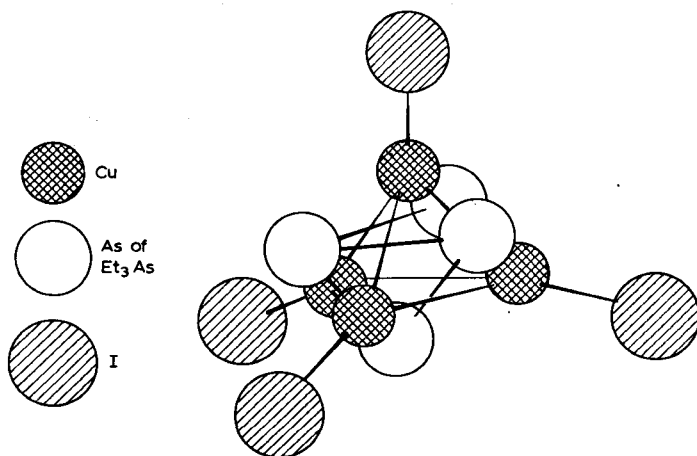
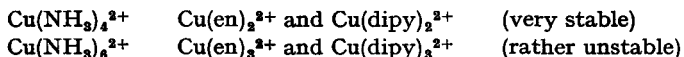


Fig. 388. Structure of  $[\text{Et}_3\text{AsCuI}]_4$ .

*The +2 state*

Copper(II) forms many complexes with nitrogen ligands. The four-co-

ordinate complexes are usually much more stable than the six-co-ordinate ones, although many of these exist:



Glycine reacts with  $\text{Cu}^{\text{II}}$  salts to give square planar diglycinecopper,  $(\text{NH}_2\text{CH}_2\text{CO}_2)_2\text{Cu}$ , co-ordinated through both oxygen and nitrogen. There are also numerous complexes with chelating oxygen donors, such as  $\beta$ -diketones,  $\beta$ -ketoesters, catechol and salicylic acid.

The best known silver(II) complexes are those formed by oxidising  $\text{Ag}^+$  with persulphate in the presence of ligand molecules such as pyridine and dipyriddy:  $[\text{Ag}(\text{py})_4]\text{S}_2\text{O}_8$  is isomorphous with its  $\text{Cu}^{\text{II}}$  analogue which is known to have square planar geometry. Gold(II) complexes are not known.

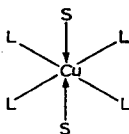
### The +3 state

Copper(III) is uncommon, but occurs in  $\text{K}_3\text{CuF}_6$  and in the blue-grey, diamagnetic  $\text{KCuO}_2$ . Silver(III) occurs in  $\text{KAgF}_4$ , made by heating a mixture of  $\text{KF}$  and  $\text{AgF}$  in fluorine, and in periodate complexes made by oxidising  $\text{Ag}^+$  with persulphate in the presence of periodate ions.

Gold(III) complexes are more common than terpositive complexes of the other two metals. Four-, five-, and six-co-ordination occurs. Chelating nitrogen, phosphorous and arsenic donors are particularly important.

### Effect of solvent on the spectra of copper(II) complexes

Bipositive copper ( $d^9$ ) can be considered to form square planar complexes in which the odd electron occupies the  $d_{x^2-y^2}$  orbital. When additional ligands are available they occupy the fifth and sixth co-ordination positions, but as the  $d_{z^2}$  orbital is doubly occupied, these ligands will not approach so closely as those in the plane; the complex thus becomes tetragonal. With the compound in solution the apical positions can be occupied by solvent molecules; the more basic the solvent the stronger the ligand field so created:



The square planar energy diagram for a  $d^9$  system is given on the left of the diagram shown in Fig. 389. As solvent molecules approach the  $\text{Cu}$  atom the  $d_{z^2}$ ,  $d_{xz}$  and  $d_{yz}$  orbitals increase in energy; at the same time the ligands in the  $xy$  plane move away from the copper and the  $d_{x^2-y^2}$  and  $d_{xy}$  energies



fall (right of diagram). The extent of this effect depends on the particular solvent.

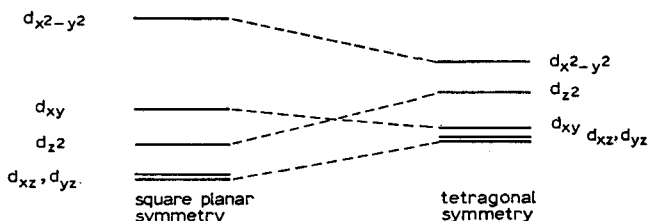


Fig. 389. Changes in energy levels as square planar symmetry is converted to tetragonal.

The absorption spectrum of copper(II) acetylacetonate in a variety of solvents illustrates this (Table 151).

TABLE 151  
EFFECT OF SOLVENT ON THE SPECTRUM OF  $\text{Cu}(\text{acac})_2$

Wave number ( $\text{cm}^{-1}$ )	Transition	Dioxan	<i>n</i> -Pentanol	Pyridine	Piperidine
$\nu_1$	$\left. \begin{matrix} d_{xz} \\ d_{yz} \end{matrix} \right\} \rightarrow d_{x^2-y^2}$	17,500	17,100	15,900	15,100
$\nu_2$	$d_{xy} \rightarrow d_{x^2-y^2}$	15,100	15,200	14,800	14,800
$\nu_3$	$d_{z^2} \rightarrow d_{x^2-y^2}$	13,500	13,000	12,100	11,300

As the solvent becomes more basic, the  $d_{xz} \rightarrow d_{x^2-y^2}$  transition involves a smaller energy change, as does also the  $d_{z^2} \rightarrow d_{x^2-y^2}$  transition, but the  $d_{xy} \rightarrow d_{x^2-y^2}$  transition is almost unchanged. However, the identification of absorption bands in terms of orbital transitions is rarely as simple as in this  $d^9$  case.

#### FURTHER READING

- J. A. McMILLAN, *Higher Oxidation States of Silver*, Chem. Rev., 62 (1962) 65.  
 B. R. JAMES AND R. J. P. WILLIAMS, *Oxidation-reduction Potentials of Cupric Compounds*, J. Chem. Soc. (1961) 2007.  
 W. MANCH AND W. C. FERNELIUS, *The Structure and Spectra of Nickel(II) and Copper(II) Complexes*, J. Chem. Educ., 38 (1961) 192.  
 J. W. LAIST, *Copper, Silver and Gold*, in M. C. SNEED, J. M. MAYNARD AND R. C. BRASTED (Eds.), *Inorganic Chemistry*, Vol. 2, Princeton, N.J., 1954.

Chapter 41

## Zinc, Cadmium and Mercury

### GROUP IIB

Zinc, cadmium and mercury differ from the members of other sub-groups found in this part of the Periodic Table in the ease with which they are melted and volatilised; thus they have much lower melting points than copper, silver and gold, just before them, and much lower boiling points than gallium, indium and thallium, just after them, in their respective periods. Another characteristic feature of the metals is their stability towards air at room temperature. They are, however, oxidised at moderate temperatures by air.

Individually the elements show many other differences from Cu, Ag and Au. Their electron configurations are  $d^{10}s^2$  with  $^1S$  ground state. The covalent radii are greater, but the bivalent ions, with their complete d shells, are smaller than the univalent ions of Group IB.

TABLE 152  
ATOMIC PROPERTIES OF GROUP IIB ELEMENTS

	<i>Zn</i>	<i>Cd</i>	<i>Hg</i>
Atomic number	30	48	80
Electron configuration	$3d^{10}4s^2$	$4d^{10}5s^2$	$5d^{10}6s^2$
Covalent radius (Å)	1.31	1.48	1.49
Metallic radius (Å)	1.38	1.54	1.57
Ionic radius, $M^{2+}$ (Å)	0.74	0.97	1.10

Although zinc, cadmium and mercury do not exist in high oxidation states like the platinum metals, and form no compounds in which the d shell is other than completely filled, they resemble the transition metals in the way in which they form complexes, particularly with nitrogen, halogen, oxygen and sulphur donors. The complexes of  $Hg^{II}$  are usually much more stable thermodynamically than those of  $Zn^{II}$  and  $Cd^{II}$ .

The first ionisation energies are larger than those of the coinage metals, the increased size of the s orbital being overshadowed by the greater effective nuclear charge. Univalent ions are not observed, although the second

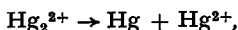
ionisation potentials are large, because the  $d^{10}$  shell is very stable. In this the elements resemble those of Group IIA.

The standard electrode potentials of the three metals show a remarkable range, evidently due to the high energies of hydration of the  $Zn^{2+}$  and  $Cd^{2+}$  ions; this is because the sum of the first and second ionisation energies is about the same in all three.

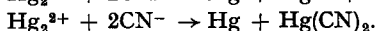
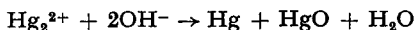
TABLE 153  
IONISATION ENERGIES AND ELECTRODE POTENTIALS  
OF GROUP IIB ELEMENTS

	Zn	Cd	Hg
Ionisation energy $I_1$ (eV)	9.39	8.99	10.43
"          " $I_2$ (eV)	17.89	16.84	18.65
$E^\circ, M^{2+}/M$ (V)	-0.763	-0.402	+0.854
$M_2^{2+}/2M$ (V)			+0.789

The redox potentials for the  $Hg^{2+}/Hg$  and  $Hg_2^{2+}/Hg$  couples indicate that for the disproportionation reaction:



the free energy change,  $\Delta G$ , is equal to +3.0 kcal. The mercury(I) ion is seen to be stable to disproportionation, but by only a small margin. In the presence of anions which reduce the activity of  $Hg^{2+}$  by causing complex formation or the precipitation of mercury(II) compounds, the forward reaction (above) with the liberation of mercury is favoured:



In fact, most ligands tend to encourage the disproportionation of mercury(I) ions, and complexes containing the metal in this oxidation state are only possible when the metal-ligand bonds are predominantly ionic in character, as in the  $[Hg_2(P_2O_7)_2]^{6-}$  anion.

### Physical properties of the metals

The individual metals are less dense than the corresponding coinage metals; the m.p. is distinctly lower, the b.p. strikingly lower. Mercury is the only metal liquid at room temperature, though liquid gallium can be supercooled below this point.

The elements have not the close-packing of atoms which is typical of

true metals. Zinc and cadmium have distorted h.c.p. structure with axial ratios  $\sim 1.87$  instead of the ideal 1.63 (Fig. 390). These are contributory factors to their low tensile strengths; the ultimate tensile stress of zinc is 7.5 tons per sq. in., whereas that of copper is 15 tons. In solid mercury there is even greater distortion of the hexagonal pattern; every atom has six neighbours at 3.00 Å and a further six at 3.47 Å.

TABLE 154

## PHYSICAL PROPERTIES OF GROUP IIB ELEMENTS

	<i>Zn</i>	<i>Cd</i>	<i>Hg</i>
Density (g/cc)	7.1	8.6	13.6
Atomic volume	9.2	13.0	14.0
Melting point (°C)	419	321	-39
Boiling point (°C)	907	768	357

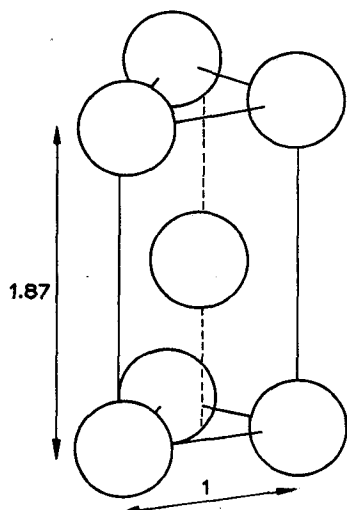


Fig. 390. Inter-atomic spacing in cadmium.

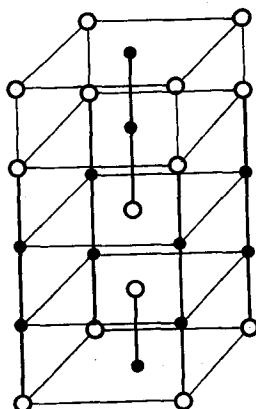
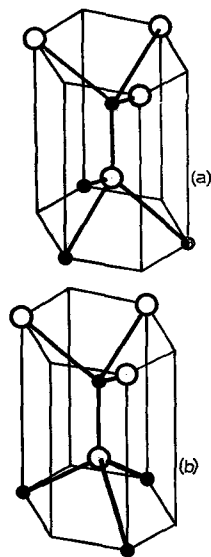
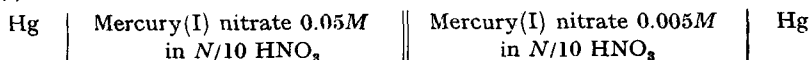
Fig. 391. Tetragonal unit cell of  $\text{Hg}_2\text{Cl}_2$ .

Fig. 392. Relation between (a) blende and (b) wurtzite in terms of arrangement of atoms.

### Ions in salts of the metals in a unipositive state

Mercury displays the cation  $\text{Hg}_2^{2+}$  in mercury(I) salts. The evidence for the form of this ion is set out below:

(i) The cell



has an e.m.f.  $\sim 0.029 \text{ V}$  at  $25^\circ$ .

$$\text{Since} \quad E \sim \frac{RT}{ZF} \ln \frac{0.05}{0.005} = \frac{0.059}{Z}$$

$Z$ , the charge on the cation reversible at the electrodes, equals 2 and the cation must be bipoisitive.

(ii) A simple cation does not produce a Raman spectral line because it is without vibrational energy. Mercury(I) salts give a line, not ascribable to the anion, indicating that the cation is capable of vibration. Hence more than one atom is present.

(iii) The tetragonal unit cell of  $\text{Hg}_2\text{Cl}_2$  contains linear  $\text{Cl}-\text{Hg}-\text{Hg}-\text{Cl}$  units (Fig. 391).

The  $\text{Hg}_2^{2+}$  ion involves an electron-pair bond. This type of metal-metal bonding is rare, but occurs in  $\text{Mn}_2(\text{CO})_{10}$  and in  $[\text{Ni}_2(\text{CN})_6]^{4-}$ . The  $\text{Hg}_2^{2+}$  ion is but little more stable than the  $\text{Hg}^{2+}$  ion; hence the reduction of a mercury(II) salt normally yields the metal.

Cadmium dissolves in cadmium(II) halides to form stable compounds of cadmium(I). The salt  $\text{Cd}_2(\text{AlCl}_4)_2$  has been isolated in the pure state. Raman spectroscopy of a molten mixture of two moles of this salt with one mole of  $\text{Cd}(\text{AlCl}_4)_2$  has indicated the existence of the  $\text{Cd}_2^{2+}$  ion. A species  $(\text{ZnX})_2$  has been found in zinc-zinc halide systems at  $285-350^\circ$ , but it disproportionates at room temperature.

### Occurrence, extraction and outline chemistry

#### Zinc

The element (0.02% of the earth's crust) occurs almost entirely as  $\text{ZnS}$ ; this has two forms (Fig. 392), the much commoner, cubic zinc blende or sphalerite, and the rarer, hexagonal wurtzite (p. 745). Iron and cadmium are nearly always present as substitutional impurities and the ore also serves to concentrate a number of much rarer elements such as indium, gallium and germanium. The sulphide is easily converted to oxide by roasting in air. From the oxide the metal distils when it is heated in a retort with carbon.

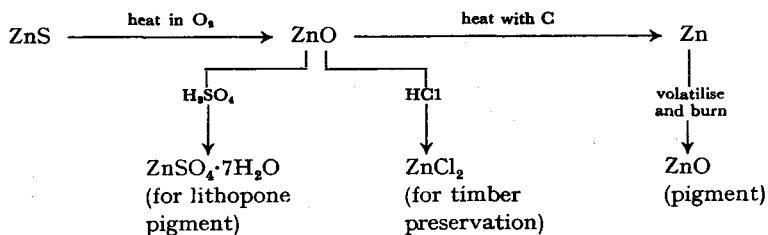


Fig. 393. Outline industrial chemistry of Zn.

The metal is used for 'galvanising' steel. An alloy with ~4% Al and 0.15–1.25% Cu is being increasingly employed for die-casting.

### Cadmium

The metal ( $2 \times 10^{-5}\%$  of the earth's crust) is derived exclusively from zinc ores; the mineral greenockite, CdS, is without economic importance. Its lower b.p. enables cadmium metal, which may amount to 0.5% of crude zinc, to be separated by distillation. It is used in electroplating, in bearing metals, in fusible alloys, and in atomic reactors to absorb neutrons.

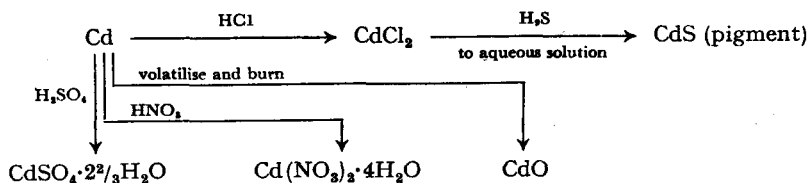


Fig. 394. Outline chemistry of Cd.

### Mercury

The element ( $10^{-4}\%$  of the earth's crust) has only one important ore; red, rhombohedral cinnabar, HgS. Heating in air converts this to the metal and  $\text{SO}_2$ , the oxide being thermally unstable.

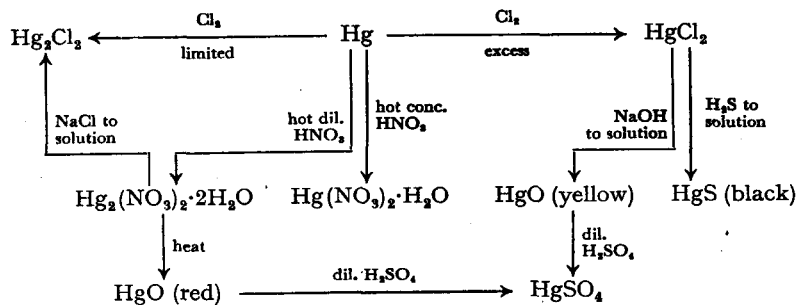


Fig. 395. Outline chemistry of Hg.

## Halides

*Zinc*

Zinc fluoride,  $ZnF_2$ , is made by dissolving the oxide in aqueous HF. The hydrate  $ZnF_2 \cdot 4H_2O$  which crystallises from the solution can be converted into the anhydrous salt by heating it to  $100^\circ$ . The hygroscopic white solid, m.p.  $872^\circ$ , is rather sparingly soluble in water (1.5 g per 100 g at  $25^\circ$ ); the solution is used for preserving wood.

Zinc chloride,  $ZnCl_2$ , can be made by dissolving the sulphide, the oxide or the metal in dilute HCl and crystallising in a stream of HCl gas to inhibit hydrolysis. Unlike  $ZnF_2$ , it is extremely soluble in water (432 g per 100 g at  $25^\circ$ ), the process being strongly exothermic. Anhydrous  $ZnCl_2$  crystallises in three different modifications,  $\alpha$ ,  $\beta$ , and  $\gamma$ , in which the Zn—Cl distances are, respectively, 2.34, 2.31, and 2.27 Å, but in all three the zinc ions are surrounded tetrahedrally by chloride ions. The small (0.74 Å)  $Zn^{2+}$  ion has a strong tendency towards tetrahedral co-ordination in its compounds. The solid chloride is easily fused (m.p.  $262^\circ$ ); the liquid is a conductor of electricity.

The bromide and iodide of zinc are similar to the chloride, although not isomorphous with it.

Complex halides of the types  $M^iZnX_3$ ,  $M^i_2ZnX_4$  and  $M^i_3ZnX_5$  are known. They are much less stable in solution than those of cadmium. The compound  $KZnF_3$  has a perovskite structure and does not contain a complex ion (p. 641).

*Cadmium*

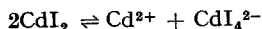
Colourless crystals of  $CdF_2$  can be made by evaporating to dryness a solution of the metal in HF or by adding aqueous  $NH_4F$  to a  $CdCl_2$  solution. The chloride is obtained by heating the metal or its oxide in chlorine or by heating the hydrate in a stream of HCl. The bromide and the iodide are similar but  $CdI_2$  does not form a hydrate.

TABLE 155  
PHYSICAL PROPERTIES OF CADMIUM HALIDES

	$CdF_2$	$CdCl_2$	$CdBr_2$	$CdI_2$
Melting point ( $^\circ C$ )	1100	568	567	388
Boiling point ( $^\circ C$ )	1758	964	960	715
Solubility at $25^\circ$ (g/100 g)	4.5	120	115	85
Form	Cubic fluorite		Hexagonal (layer)	

$\text{CdF}_2$  has the cubic fluorite lattice but the chloride, bromide and iodide form hexagonal crystals based on layer lattices (p. 204). The distances between the layers increase from the chloride to the iodide, with a corresponding reduction in lattice energies. These differences affect the physical properties (Table 155).

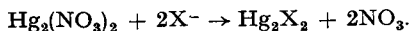
Cadmium halides form autocomplexes in concentrated solution. The anomalous transport number of cadmium in  $\text{CdI}_2$  solution was noticed by Hittorf (1859) and correctly attributed to the equilibrium:



The  $\text{CdI}_4^{2-}$  ion results from adding an excess of iodide ion to  $\text{CdI}_2$  solution; the Raman spectrum of this and the similar  $\text{CdBr}_4^{2-}$  ion have been examined. The spectrum of the latter has a pattern very like that of the isoelectronic  $\text{SnBr}_4$ .

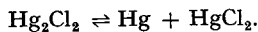
### *Mercury(I)*

Mercury(I) fluoride is made by treating freshly-prepared mercury(I) carbonate with aqueous HF. The other mercury(I) halides are made by precipitation from aqueous solutions of  $\text{Hg}_2(\text{NO}_3)_2$ :



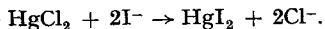
The chloride and bromide are colourless, the iodide is bright yellow. The fluoride is cubic, the other halides are tetragonal (p. 745); the Hg—Hg distance varies from 2.43 Å in  $\text{Hg}_2\text{F}_2$  to 2.69 Å in  $\text{Hg}_2\text{I}_2$ . Only the fluoride is appreciably soluble in water, the others resemble the  $\text{Cu}^{\text{I}}$ ,  $\text{Ag}^{\text{I}}$ ,  $\text{Au}^{\text{I}}$  and  $\text{Tl}^{\text{I}}$  compounds in their slight solubility.  $\text{Hg}_2\text{F}_2$  decomposes slowly in aqueous solution to give HF, HgO and Hg.

$\text{Hg}_2\text{Cl}_2$  and  $\text{Hg}_2\text{Br}_2$  vaporise easily; although diamagnetic, the vapours have densities which indicate HgCl and HgBr as the molecular formulae, but the reason may be the disproportionation:



### *Mercury(II)*

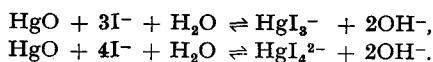
Mercury(II) fluoride, made by the action of fluorine on  $\text{Hg}_2\text{Cl}_2$ , is used to convert organic chlorides to fluorides. The most common halide of mercury is the very poisonous, corrosive, colourless  $\text{HgCl}_2$ , made by the action of chlorine on the metal. The colourless  $\text{HgBr}_2$  and the red  $\text{HgI}_2$  are much less soluble in water and can be made by precipitation from aqueous solution:





Except for fluoride, the mercury(II) halides are too covalent to allow the free  $\text{Hg}^{2+}$  to appear; its presence must be associated with autocomplex formation. In  $\text{HgCl}_2$ , mercury has a distorted octahedral symmetry, but the structure is really molecular because two of the pairs of  $\text{Hg}-\text{Cl}$  distances, 3.34 Å and 3.63 Å, are greater than the sum of the Van der Waals radii for mercury and chlorine (3.30 Å). Mercury(II) iodide contains layers of fully corner-linked  $\text{HgI}_4$  tetrahedra. In the vapour the chloride, bromide and iodide are all linear monomers. The fluoride is an ionic compound with the fluorite structure.

Anionic complexes, with halogens other than fluorine, can be made by the addition of halide ion to solutions of  $\text{Hg}^{\text{II}}$  compounds. Iodide solutions particularly, and bromide and chloride to a lesser extent, dissolve  $\text{HgO}$ :



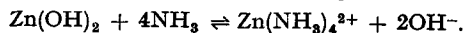
The solution can be made quite strongly alkaline without causing precipitation (Nessler's reagent). The complex ion  $\text{HgI}_4^{2-}$  is tetrahedral.

## Oxides

### Zinc

Zinc oxide occurs to a limited extent as the mineral zincite, which has the wurtzite structure; it is usually made industrially by burning the metal in air. The pure oxide is used as a white pigment (Chinese white) and as a filler in soft rubber. When heated  $\text{ZnO}$  becomes yellow but without change in the structure of the phase. The hot oxide is bleached by oxygen and its colour is restored by zinc vapour. The coloured oxide has about 0.03% of zinc over the stoichiometric ratio; the zinc is present as atoms occupying octahedral interstices in the lattice.

The hydroxide  $\text{Zn}(\text{OH})_2$  is formed as a white, voluminous precipitate when aqueous sodium hydroxide is added to a solution of a zinc salt. The precipitate is soluble in an excess of sodium hydroxide, giving zincate ions of unknown structure, but probably  $\text{Zn}(\text{OH})_4^{2-}$  and  $\text{Zn}(\text{OH})_3 \cdot \text{H}_2\text{O}^-$ . The solids  $\text{Na}_2\text{Zn}(\text{OH})_4$  and  $\text{NaZn}(\text{OH})_3$  have been separated from these solutions. The latter is interesting from the point of view of structure because it contains a distorted trigonal bipyramidal arrangement of oxygen atoms round the zinc. Zinc hydroxide, which exists in five distinct crystalline modifications, is also soluble in acids and in aqueous ammonia:



### Cadmium

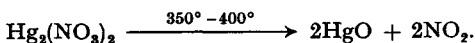
Cadmium oxide is obtained as a brown powder by the pyrolysis of carbon-

ate or nitrate, but strong ignition in oxygen converts it to deep-red, cubic crystals. It has the NaCl structure, an example of the tendency of cadmium to show octahedral symmetry, a distinction from zinc which is usually tetrahedrally co-ordinated.

White cadmium hydroxide is precipitated by the addition of sodium hydroxide solution to a solution of  $\text{Cd}^{2+}$  ions. The solid, which has the brucite ( $\text{Mg}(\text{OH})_2$ ) structure, is soluble in aqueous ammonia and in acids, but is practically insoluble in an excess of alkali. The hydroxide is, in fact, best considered as purely basic; unlike  $\text{Zn}(\text{OH})_2$  it is without amphoteric character.

### *Mercury*

The normal, orthorhombic form of mercury(II) oxide can be precipitated in a yellow form by adding cold, aqueous NaOH to  $\text{Hg}(\text{NO}_3)_2$  solution, or in a red form by adding hot, aqueous  $\text{Na}_2\text{CO}_3$ . The red form, which gives the same X-ray pattern but contains larger particles than the yellow, is also the product of the pyrolysis of mercury(I) nitrate:



A hexagonal form of HgO is also known. It is precipitated by adding NaOH to solutions of  $\text{K}_2\text{HgI}_4$  containing a small excess of KI. It is usually precipitated as fine, red crystals but it too has a more finely-divided yellow form. Both the orthorhombic and the hexagonal forms of HgO are based on zig-zag Hg—O—Hg—O—Hg chains, which are planar in the former and spiral in the latter. There is no evidence for a mercury(II) hydroxide, nor is there a mercury(I) oxide.

## Sulphides

### *Zinc*

Zinc sulphide occurs principally as blende; the hexagonal wurtzite is comparatively rare. The white sulphide precipitated when ammonium sulphide is added to a  $\text{Zn}^{2+}$  solution is amorphous and is readily soluble in dilute mineral acids, but it gradually changes to a less soluble form. This, heated with aqueous  $\text{H}_2\text{S}$  under pressure, gives blende, but heated with  $\text{H}_2\text{S}$  gas gives wurtzite.

### *Cadmium*

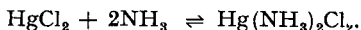
Cadmium sulphide occurs as the mineral greenockite. When made by heating cadmium oxide and sulphur, it has the wurtzite form, but the precipitate obtained by adding  $\text{H}_2\text{S}$  to a weakly acidic  $\text{Cd}^{2+}$  solution has the blende structure.

### Mercury

The stable modification of mercury(II) sulphide, the mineral cinnabar, is isostructural with the hexagonal form of HgO. In the Hg—S—Hg chains, the bond distance, 2.36 Å, is equal to the sum of the diagonal covalent radii; every mercury atom has two other pairs of sulphur atoms, at 3.10 and 3.30 Å respectively, which give it an effectively octahedral environment. The black mercury(II) sulphide precipitated from solution is a metastable form with the blende structure. The mineral metacinnabar, s.g. 7.60, which also has the cubic blende structure, is much less common than cinnabar.

### Mercury-nitrogen compounds

Mercury forms direct covalent as well as co-ordinate links with nitrogen. Mercury(II) chloride reacts with gaseous ammonia to give 'fusible white precipitate':



The  $[\text{Hg}(\text{NH}_3)_2]^{2+}$  ions are arranged at the face centres of cubes of  $\text{Cl}^-$  ions with their axes randomly arranged along the a, b and c axes of the crystal. The crystal contains finite  $[\text{Hg}(\text{NH}_3)_2]^{2+}$  ions (Fig. 396).

Treatment of  $\text{HgCl}_2$  with aqueous ammonia gives 'infusible white precipitate',  $\text{HgNH}_2\text{Cl}$ , containing indefinitely long chains of  $[-\text{Hg}-\text{NH}_2-]^{+}$  with  $\text{Cl}^-$  ions between them in an orthorhombic structure (Fig. 397). The infusibility and low solubility is ascribed to the chain structures.

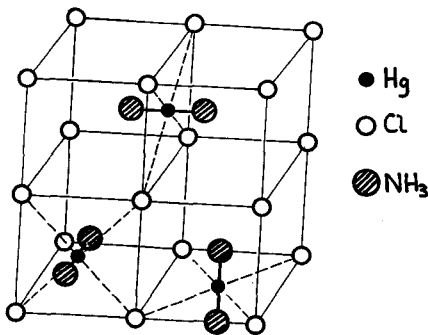


Fig. 396. Random arrangement of  $[\text{Hg}(\text{NH}_3)_2]^{2+}$  ions in 'fusible white precipitate',  $\text{Hg}(\text{NH}_3)_2\text{Cl}_2$ .

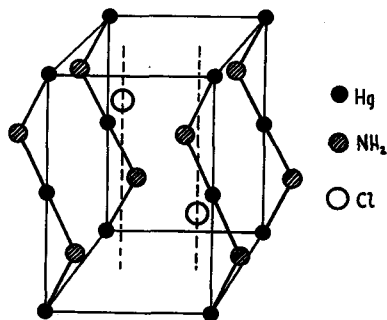


Fig. 397. Orthorhombic cell of 'infusible white precipitate'  $\text{HgNH}_2\text{Cl}$ , showing zig-zag chains  $(-\text{Hg}-\text{NH}_2-)_n$ .

When HgO is warmed with aqueous ammonia the compound  $\text{Hg}_2\text{NOH}\cdot 2\text{H}_2\text{O}$ , Millon's base, is produced. This has a  $\text{Hg}_2\text{N}^+$  network of cristobalite type with  $\text{OH}^-$  ions and water molecules held in the network by ionic, hydrogen bond and dispersion forces (Fig. 398).

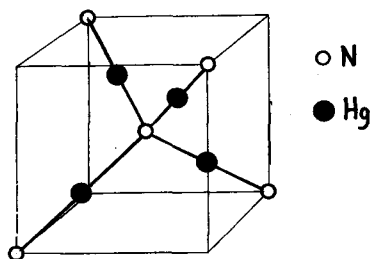
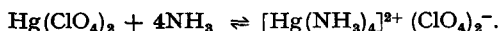


Fig. 398. Arrangement of  $\text{Hg}_2\text{N}^+$  network in Millon's base,  $\text{Hg}_2\text{NOH}\cdot 2\text{H}_2\text{O}$ .

The Hg—N distances in all these compounds are similar ( $\sim 2.06 \text{ \AA}$ ). The iodide corresponding to Millon's base,  $\text{Hg}_2\text{NI}\cdot\text{H}_2\text{O}$ , is the precipitate produced from Nessler's reagent by ammonia. The nitrogen atom uses  $\text{sp}^3$ -hybrid orbitals in these compounds; the collinear bonds of the Hg probably involve  $\text{sp}$  hybridisation.

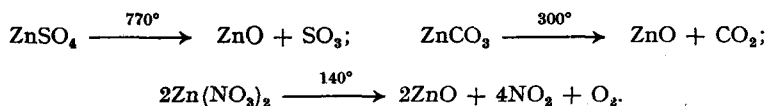
When ammonia reacts with  $\text{Hg}(\text{ClO}_4)_2$ , a compound of much greater ionic character than  $\text{HgCl}_2$  is formed, a complex tetra-ammine in which there are co-ordinate links between nitrogen and mercury:



A mercury(I) compound reacts with aqueous ammonia to give free mercury together with the ammine formed by the corresponding mercury (II) compound under the same conditions. Thus  $\text{Hg}_2\text{Cl}_2$  gives a black precipitate which is a mixture of finely divided mercury and infusible white precipitate.

### Oxoacid salts

The carbonates, nitrates, and even the sulphates are thermally unstable:



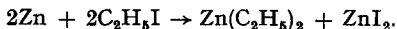
Zinc carbonate is decomposed on boiling with an excess of  $\text{Na}_2\text{CO}_3$  solution: the phosphate is much more stable,  $\text{Zn}_3\text{P}_2\text{O}_7$  being used in the gravimetric determination of the metal.

Cadmium sulphate forms the hydrate  $\text{CdSO}_4\cdot 2\frac{2}{3}\text{H}_2\text{O}$  with an interesting structure. There are two sets of  $\text{Cd}^{2+}$  ions with slight different environments; all are octahedrally surrounded by two  $\text{H}_2\text{O}$  molecules and four sulphate oxygens. There are four kinds of crystallographically nonequivalent  $\text{H}_2\text{O}$

molecules; three-quarters of the  $\text{H}_2\text{O}$  molecules are attached to  $\text{Cd}^{2+}$  ions and one quarter of them have as neighbours two other water molecules and two sulphate oxygen atoms.

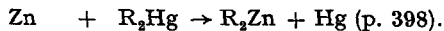
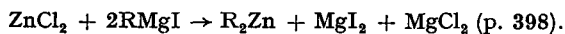
### Organometallic compounds

Zinc dialkyls can be made by treating the metal or, preferably, a zinc-copper couple, with the appropriate alkyl iodide in an autoclave at  $150^\circ$ :



The substances made by refluxing alkyl iodides with zinc, and once thought to be zinc alkyl iodides of the form  $\text{R}-\text{Zn}-\text{I}$ , are not true compounds, but mixtures of the zinc alkyl with zinc iodide. The use of  $^{65}\text{Zn}$  as a radioactive tracer has demonstrated that there is no exchange of zinc atoms between diethyl zinc and zinc iodide in solution as there would be if the compound  $\text{C}_2\text{H}_5\text{ZnI}$  existed.

Other preparative methods for the zinc dialkyls are:

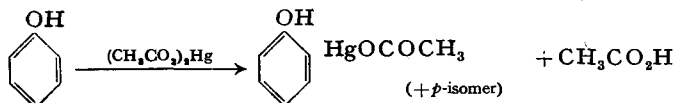


Dimethyl zinc and diethyl zinc are volatile liquids which can be distilled unchanged in the absence of air but are oxidised immediately if air is present. The compounds are monomeric in the vapour and in benzene solution. The infrared and Raman spectra of  $(\text{CH}_3)_2\text{Zn}$  indicate a linear  $\text{C}-\text{Zn}-\text{C}$  arrangement and eclipsed methyl groups.

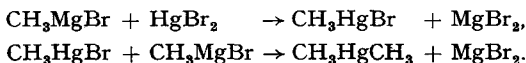
Diaryl derivatives of zinc can be made from the metal and the corresponding mercury aryls; they are white, crystalline solids.

Cadmium alkyls are best made by treating cadmium bromide with Grignard reagents in ether, the aryls from  $\text{CdBr}_2$  and lithium aryls in the same solvent. Of the alkyls, only  $(\text{CH}_3)_2\text{Cd}$  can be kept for long without decomposition, the others deposit cadmium slowly in the dark and rapidly in daylight.

Organomercury compounds, which are stable to air and water, are nevertheless sufficiently reactive towards other metals to be of considerable value in the synthesis of their organometallic compounds (p. 399). The mercury-carbon bond is a rather weak one ( $\sim 15$  kcal), and the lack of reactivity towards oxygen is probably due mainly to the weakness of the  $\text{Hg}-\text{O}$  bond. Organomercury compounds can, in fact, be made by treating aromatic compounds, as well as alkenes and alkynes, with mercury-oxygen compounds such as basic salts. This process of *mercuration* goes particularly smoothly with substituted benzene derivatives:

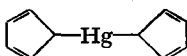


Alkyls of mercury, as well as alkylmercury halides, can be made by treating mercury(II) bromide with Grignard reagents in ether:



The alkylmercury halides are well-characterised compounds containing a linear arrangement C—Hg—X. Dimethyl mercury, b.p. 92°, and diethyl mercury, b.p. 159° are monomers in the vapour.

Zinc and mercury both form cyclopentadienyl compounds but they are quite different in character. Biscyclopentadienylzinc is made in low yield by the action of  $\text{C}_5\text{H}_5\text{Na}$  on  $\text{ZnCl}_2$  in ether. It is air-sensitive, rapidly hydrolysed by water, and only slightly soluble in organic solvents. The similarity of its infrared spectrum to that of bis(cyclopentadienyl)magnesium suggest that it too has a 'sandwich' structure in which the bonding is largely ionic. Bis(cyclopentadienyl)mercury, made from  $\text{C}_5\text{H}_5\text{Na}$  and  $\text{HgCl}_2$  in tetrahydrofuran, is stable to water, soluble in most organic solvents, and capable of forming Diels–Adler adducts (p. 397). Sigma bonding between the mercury atom and the cyclopentadiene groups is indicated.



### Complexes

Of the oxygen complexes, those of zinc are the most stable. Its chelate compounds include acetylacetonate and dioxalato complexes, and a basic acetate,  $\text{Zn}_4\text{O}(\text{CH}_3\text{COO})_6$ , very similar in properties to that of beryllium (p. 331), with a tetrahedral structure centred on the oxygen atom.

The acetylacetonate monohydrate,  $\text{Zn}(\text{acac})_2\text{H}_2\text{O}$  contains 5-co-ordinate zinc; five oxygen atoms are arranged around the zinc atom at the corners of a distorted trigonal bipyramid. Six-co-ordinate zinc complexes are not common; one interesting example is hydrazinium sulphatozincate,  $(\text{N}_2\text{H}_5)_2\text{Zn}(\text{SO}_4)_2$ . In the solid, zinc is co-ordinated to one nitrogen of each cation and doubly co-ordinated to each sulphate group acting as a bidentate ligand. A number of six-co-ordinate complexes of mercury(II) with oxygen donors have been prepared; they have the general formula  $\text{HgL}_6(\text{ClO}_4)_2$ , in which L represents dimethyl sulphoxide, thioxan oxide, tetrahydrothiophen oxide or pyridine N-oxide.

Sulphur forms more stable complexes than oxygen with these metals. In alkali-metal polysulphide solutions, HgS gives the  $\text{HgS}_2^{2-}$  ion. The metal halides all form addition compounds with thioethers (Fig. 399).

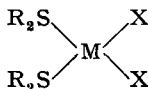


Fig. 399. Addition compounds with thioethers of metal halides of Group IIB.  
R = alkyl, M = Zn, Cd or Hg, X = halogen.

Tetrahedral co-ordination is usual among the sulphur complexes. Tetra-thiocyanatomercurates contain the tetrahedral  $\text{Hg}(\text{SCN})_4^{2-}$  ion in which the Hg—S distances are equal to the sum of the tetrahedral covalent radii. The compound formulated  $\text{Ba}_2\text{ZnS}_3$ , made by the action of  $\text{H}_2\text{S}$  on  $\text{BaZnO}_2$ , has been shown to contain  $\text{ZnS}_4$  tetrahedra linked into chains which are held together by  $\text{Ba}^{2+}$  ions.

Salts of the three metals form amines, principally tetrahedral complex ions of the form  $[\text{M}(\text{NH}_3)_4]^{2+}$ , but in addition mercury salts form linear diammine complexes, and zinc and cadmium octahedral hexa-ammines,  $[\text{M}(\text{NH}_3)_6]^{2+}$ . Ethylenediamine produces 6-co-ordinate complexes,  $[\text{M}(\text{en})_3]^{2+}$ , with all three cations.

The chlorocomplexes of mercury are of structural interest. The anions usually contain distorted  $\text{HgCl}_6$  octahedra linked in ribbons and layers. Thus  $\text{NaHgCl}_3$  contains a 'double-ribbon' anion (Fig. 400).

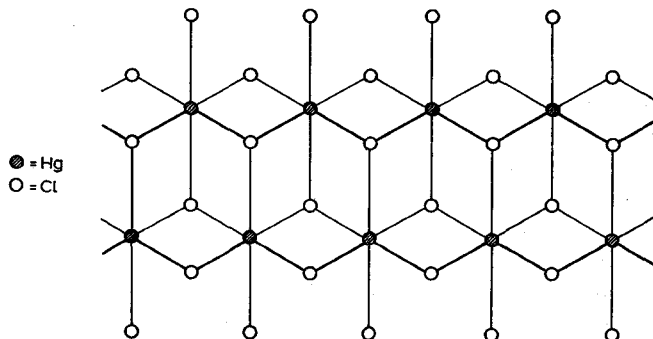
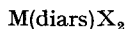


Fig. 400. Extended 'double-ribbon' structure of anion in  $\text{NaHgCl}_3$ .

The dihalides, other than the fluorides, of all three metals form complexes with *o*-phenylenebisdimethylarsine; these are non-electrolytes:



in which the metal atoms are co-ordinated tetrahedrally with two arsenic and two halogen atoms.

#### FURTHER READING

- W. N. LIPSCOMB, *Structures of Mercury-Nitrogen Compounds*, Anal. Chem. 25 (1953) 737.
- H. M. CYR, *Zinc, Cadmium and Mercury*, in M. C. SNEED, J. M. MAYNARD AND R. C. BRATED (Eds.), *Comprehensive Inorganic Chemistry*, Vol. 4, Princeton, N.J., Van Nostrand, 1954.



APPENDIX

**The Elements**

ATOMIC WEIGHTS AND OTHER DATA

The scale of atomic weights has as its denominator the integral number 12 as the relative mass of the atom of the principal isotope of carbon,  $^{12}\text{C}$ .

Name	Symbol	Atomic Number	Atomic Weight	Commonest natural isotope	
				Mass Number	Abundance in %
Actinium	Ac	89	(227)		
Aluminium	Al	13	26.982	27	100
Americium	Am	95	(243)		
Antimony	Sb	51	121.75	121	57.26
Argon	Ar	18	39.948	40	99.60
Arsenic	As	33	74.922	75	100
Astatine	At	85	(210)		
Barium	Ba	56	137.34	138	71.7
Berkelium	Bk	97	(249)		
Beryllium	Be	4	9.012	9	100
Bismuth	Bi	83	208.980	209	100
Boron	B	5	10.811	11	81.3
Bromine	Br	35	79.904	79	50.6
Cadmium	Cd	48	112.40	114	28.8
Caesium	Cs	55	132.905	133	100
Calcium	Ca	20	40.08	40	96.92
Californium	Cf	98	(251)		
Carbon	C	6	12.01115	12	98.9
Cerium	Ce	58	140.12	140	88.45
Chlorine	Cl	17	35.453	35	75.4
Chromium	Cr	24	51.996	52	83.7
Cobalt	Co	27	58.933	59	100
Copper	Cu	29	63.546	63	69
Curium	Cm	96	(247)		
Dysprosium	Dy	66	162.50	164	28.2
Einsteinium	Es	99	(254)		
Erbium	Er	68	167.26	168	26.9
Europium	Eu	63	151.96	153	52.2
Fermium	Fm	100	(253)		
Fluorine	F	9	18.998	19	100

Name	Symbol	Atomic Number	Atomic Weight	Commonest natural isotope	
				Mass Number	Abundance in %
Francium	Fr	87	(223)		
Gadolinium	Gd	64	157.25	158	24.8
Gallium	Ga	31	69.72	69	60
Germanium	Ge	32	72.59	74	36.5
Gold	Au	79	196.967	197	100
Hafnium	Hf	72	178.49	180	35.4
Helium	He	2	4.0026	4	99.9998
Holmium	Ho	67	164.930	165	100
Hydrogen	H	1	1.00797	1	99.985
Indium	In	49	114.82	115	95.8
Iodine	I	53	126.904	127	100
Indium	Ir	77	192.2	193	61.5
Iron	Fe	26	55.847	56	91.6
Krypton	Kr	36	83.80	84	57.02
Lanthanum	La	57	138.91	139	99.91
Lawrencium	Lw	103			
Lead	Pb	82	207.19	208	52.3
Lithium	Li	3	6.939	7	92.6
Lutetium	Lu	71	174.97	175	97.5
Magnesium	Mg	12	24.312	24	79.0
Manganese	Mn	25	54.938	55	100
Mendelevium	Md	101	(256)		
Mercury	Hg	80	200.59	202	29.7
Molybdenum	Mo	42	95.94	98	24.0
Neodymium	Nd	60	144.24	144	23.9
Neon	Ne	10	20.183	20	90.0
Neptunium	Np	93	(237)		
Nickel	Ni	28	58.71	58	67.9
Niobium	Nb	41	92.906	93	100
Nitrogen	N	7	14.0067	14	99.6
Nobelium	No	102			
Osmium	Os	76	190.2	192	41
Oxygen	O	8	15.9994	16	99.76
Palladium	Pd	46	106.4	108	26.7
Phosphorus	P	15	30.974	31	100
Platinum	Pt	78	195.09	195	33.7
Plutonium	Pu	94	(242)		
Polonium	Po	84	(210)		
Potassium	K	19	39.102	39	93.08
Praseodymium	Pr	59	140.907	141	100
Promethium	Pm	61	(147)		

Name	Symbol	Atomic Number	Atomic Weight	Commonest natural isotope	
				Number Mass	Abundance in %
Protactinium	Pa	91	(231)		
Radium	Ra	88	226.05		
Radon	Rn	86	(222)		
Rhenium	Re	75	186.2	187	62.9
Rhodium	Rh	45	102.905	103	100
Rubidium	Rb	37	85.47	85	72.8
Ruthenium	Ru	44	101.07	102	31.5
Samarium	Sm	62	150.35	152	27
Scandium	Sc	21	44.956	45	100
Selenium	Se	34	78.96	80	49.9
Silicon	Si	14	28.086	28	92.18
Silver	Ag	47	107.868	107	51.35
Sodium	Na	11	22.9898	23	100
Strontium	Sr	38	87.62	88	82.56
Sulphur	S	16	32.064	32	95.0
Tantalum	Ta	73	180.948	181	100
Technetium	Tc	43	99		
Tellurium	Te	52	127.60	130	34.35
Terbium	Tb	65	158.924	159	100
Thallium	Tl	81	204.37	205	70.5
Thorium	Th	90	232.038	232	100
Thulium	Tm	69	168.934	169	100
Tin	Sn	50	118.69	120	32.9
Titanium	Ti	22	47.90	48	73.4
Tungsten	W	74	183.85	184	30.7
Uranium	U	92	238.03	238	99.28
Vanadium	V	23	50.942	51	99.75
Xenon	Xe	54	131.30	132	26.93
Ytterbium	Yb	70	173.04	174	31.8
Yttrium	Y	39	88.905	89	100
Zinc	Zn	30	65.37	64	48.9
Zirconium	Zr	40	91.22	90	51.6

# Subject Index

- Absorption spectra, electronic, 158, 166, 572, 742
- Acetic acid as a solvent, 245
- Acetylene molecule, 115
- Acetylides, 381
- Acid-base equilibria, 239
- Acidity constant ( $K_a$ ), 239
- Acids, charge types, 238
- Acid strength and molecular structure, 247
- Actinides, 617
  - atomic properties, 617
  - complexes, 631
  - halides, 627
  - isomorphous compounds, 630
  - magnetic properties, 630
  - metals, 618, 623
  - oxidation states, 624
  - oxides, 627
  - redox potentials, 625
- Actinium, 617
- Adamantine compounds, 201
- Alloys, interstitial, 199
  - substitutional, 197
- Allred-Rochow electronegativity scale, 128
- Alpha particle, 21
- Alumina, 343
- Aluminate ion, structure, 344
- Aluminium,
  - atomic properties, 336
  - complexes, 350
  - extraction, 338
  - halides, 339
  - organometallic compounds, 349
  - oxide, 343
  - physical properties, 337
  - reactions, 338
  - unipositive, 348
- Aluminothermic reduction, 339
- Alums, 347
- Americium, 617
  - ions, 624
  - production, 622
  - separation, 623
- Ammonia, 283
  - as a solvent, 243
  - molecular structure, 118, 284
- Ammonium ion, 285
- Amphiboles, 211
- Amphiprotic solvents, 242
- Anatase, structure, 640
- Angular momentum,
  - orbital, 62
  - spin, 66
- Anion water, 213
- Anisodesmic solids, 191
- Antiferromagnetism, 175
- Antimony,
  - allotropy, 461
  - atomic properties, 459
  - extraction, 462
  - halides, 463
  - organometallic compounds, 469
  - oxides, 465
  - reactions, 463
  - sulphides, 467
- Aprotic solvents, 247
- Argon,
  - atomic properties, 295
  - clathrates, 299
  - separation from air, 297
  - physical properties, 296
- Arsenic,
  - allotropy, 461
  - atomic properties, 459
  - extraction, 462
  - halides, 463
  - organometallic compounds, 468
  - oxides, 465
  - reactions, 463
  - sulphides, 466
- Arsine, 288, 292
- Astatine,
  - atomic properties, 516
  - production, 522
- Atmosphere, composition of, 34
- Atomic hydrogen, 258
- Atomic mass ( $M$ ), 11
- Atomic number ( $Z$ ), 6

- Atomic oxygen, 473  
Atomic pile, nuclear reactor, 620  
Atomic weight (mass), 8, 758  
Aufbau principle, 75  
- applied to molecules, 94  
Austenite, 200  
Autoprotolysis constant, 240  
Azides, 454, 551  
Azidocarbon disulphide, 553
- Balmer series, 59  
Barium,  
- atomic properties, 322  
- complexes, 333  
- extraction, 325  
- halides, 326  
- oxides, 328  
- oxoacid salts, 330  
- peroxide, 328  
- physical properties, 322  
- reactions, 325  
- sulphides, 329  
Bases, charge types, 238  
Berkelium, 617  
- production, 622  
- separation, 623  
Beryl structure, 211  
Beryllium,  
- alloys, 323  
- atomic properties, 322  
- chloride molecule, 115  
- comparison with aluminium, 335  
- complexes, 332  
- extraction, 323  
- halides, 326  
- hydride, 268  
- hydroxide, 323  
- organometallic compounds, 333  
- oxide, 328  
- oxide acetate (basic acetate), 331  
- oxoacid salts, 330  
- physical properties, 322, 323  
Beta diketone complexes, 333  
Beta particle, 6, 21  
Bidentate ligands, 565, 587  
Bimolecular substitution mechanisms, 591  
Binding energy, nuclear, 11  
Bismuth,  
- atomic properties, 459  
- extraction, 462  
- halides, 463  
- oxide, 465  
- oxoacid salts, 468  
- reactions, 463  
- sulphide, 467  
Bloch orbitals, 94  
Body-centred cubic structure, 192  
Bohr magneton, 74, 86  
Bohr radius of hydrogen atom, 57  
Bond,  
- covalent, 97, 107  
- ionic, 99  
- ion-dipole, 134  
- energies, 126  
Boranes, 268  
Borates, 344  
Borazine, 277  
Borazon, 346  
Boric acid, 344  
Borides, 346  
Born equation of free energy, 243  
Born-Haber cycle, 102  
Borohydrides, 278  
Boron,  
- atomic properties, 336  
- complexes, 350  
- halides, 339  
- hydrides, 268  
- nitride, 345  
- organometallic compounds, 348  
- oxide, 342  
- physical properties, 337  
- reactions, 338  
Bragg equation, 187  
Bravais lattices, 191  
Bridged structures, 268, 271  
Bromine,  
- atomic properties, 516  
- fluorides, 526  
- oxides, 528, 530  
- physical properties, 515, 517  
- production, 522  
- reactions, 522  
- stereochemistry, 519  
- trifluoride as a solvent, 250  
Buffer action, 241
- Cadmium,  
- atomic properties, 743  
- chloride structure, 541

- complexes, 756
- halides, 748
- iodide structure, 541
- organometallic compounds, 754
- oxide, 750
- physical properties, 744
- reactions, 747
- sulphate hydrate, 753
- sulphide, 751
- Caesium,
  - atomic properties, 308
  - chloride lattice, 193
  - halides, 312
  - metal, 310
  - oxides, 313
  - physical properties, 309
  - sulphides, 314
- Calcium,
  - atomic properties, 322
  - complexes, 333
  - extraction 324
  - fluoride structure, 203
  - halides, 326
  - oxides, 328
  - oxoacid salts, 330
  - physical properties, 322, 323
  - reactions, 325
- Californium, 617
  - production, 622
  - separation, 623
- Carbides,
  - covalent, 382
  - interstitial, 382
  - salt-like, 381
- Carbon,
  - allotropy, 365
  - atomic properties, 363
  - dioxide, 372
  - halides, 367
  - monoxide, 370
  - suboxide, 370
  - sulphides, 378
- Carbonylate ions, 389
- Carbonyls, 383
- Carbonyl halides, 390
- Carbonyl hydrides, 390
- Carboranes, 276
- Carriers for radionuclides, 39
- Cementite, 200
- Cerium, 605
  - compounds, 613
  - Charge (oxidation) number, 230
  - Charge-transfer spectra, 184
  - Chelate effect, 587
  - Chelate ligands, 565, 588
  - Chemical cell, evaluation of free energy, 224
  - Chlorine,
    - atomic properties, 516
    - fluorides, 520, 526
    - interhalogen compounds, 524
    - oxides, 528, 530
    - oxoacids, 531
    - oxofluorides, 526
    - physical properties, 515, 517
    - production, 521
    - reactions, 522
    - stereochemistry, 519
    - trifluoride molecule, 149
  - Chlorocomplexes, 550
  - Chromium,
    - atomic properties, 657
    - complexes, 575, 670
    - extraction, 660
    - halides, 663
    - organometallic compounds, 670
    - oxidation states, 658, 661
    - oxides, 665
    - physical properties, 658, 660
  - Class a and class b acceptors, 586
  - Clathrates, 200, 299
  - Close-packed hexagonal structure, 132
  - Cluster ions, 662, 680
  - Cobalt,
    - atomic properties, 691
    - complexes, 577, 593, 701, 705
    - extraction, 693
    - halides, 696
    - oxidation states, 694
    - oxides, 697
    - physical properties, 692
  - Cohesive forces in crystals, 191
  - Complexes, 565
    - determination of structure, 569
    - high- and low-spin, 160
    - in aqueous solution, 582
    - labile and inert, 593
    - nomenclature, 579
    - preparation, 566
    - stability, 586

- stability constants, 583
- substitution reactions, 590
- thermal decomposition, 567
- Complex ions in crystals, 205
- Conjugate acid-base pair, 238
- Conjugated bonding, 131
- Co-ordinated water, 212
- Co-ordination isomerism, 576
- Co-ordination number,
  - crystallographic, 102
  - in complexes, 558
- Copper,
  - atomic properties, 726
  - complexes, 169, 584, 738, 741
  - extraction, 728
  - halides, 731
  - oxidation states, 730
  - oxides, 732
  - oxoacid salts, 735
  - nitrate, 736
  - physical properties, 728
  - sulphides, 735
- Corundum structure, 497
- Covalency maxima, 119
- Cristobalite, 204
- Cryolite, 352
- Crystal field theory, 154
- Crystal growth, 217
  - defects, 219
- Cubic lattice, types of, 192
- Curie of radioactivity, 22
- Curie-Weiss law, 87
- Curium, 617
  - production, 622
  - separation, 623
- Cyanates, 552
- Cyanide ion, structure, 182
- Cyanides, 551
- Cyanogen, 379, 551
- Cyclopentadienides, 396
- Cyclopentadienyls, 403
  
- Debye units, 143
- Debye-Scherrer X-ray powder diffraction, 187
- Decay constant, 21
- Defect structures, 215
- Deuterium, 259
  - exchange reactions, 261
- Delta bonding, 737
  
- Diagonal similarities in the Periodic Table 319, 335
- Diamond, 365
- Diborane structure, 271
- Dielectric constant, 142, 243
- Diffusion, separation of isotopes by,
  - gaseous, 9
  - thermal, 9
- Dinitrogen pentoxide, 438
- Dinitrogen tetroxide, 250, 436
- Dinitrogen trioxide, 435
- Diphosphine, 287
- Dipole moments, 142, 570
- Dispersion forces, 136
- Distillation, separation of isotopes by molecular, 10
- Dithionates, 489
- Dysprosium, 605
  
- Earth, composition of hydrosphere and lithosphere, 34
- E.D.T.A., 333, 579, 614
- Effective nuclear charge, 70
- Eigenvalues, 55
- Einsteinium, 617
- Einstein mass-energy equation, 10
- Electrodes, reversible, 223
- Electrolytes, weak and strong, 240
- Electron, 5
  - affinity, 84, 103
  - capture, 25
  - compounds, 198
  - configurations, 77
  - deficient molecules, 270
  - diffraction, 188
  - excess compounds, 303
  - spin, 65
  - spin resonance, 88
  - transfer, 41
- Electronegativity, 127
- Electroneutrality principle, 558
- Electrophilic substitution, 590
- Elements,
  - abundance, cosmic, 32
  - abundance, terrestrial, 34
  - genesis, 31
  - list of, 758
- Ellingham diagrams, 373
- Erbium, 605
- Ethylenediamine complexes, 587

- Ethylene molecule, 117  
Europium, 605  
Excited states of atom, 58
- Face-centred cubic structure, 132, 192  
Fermium, 617  
Ferrocene, 699  
Ferroun, 700  
Ferromagnetism, 84  
Feynman-Hellmann principle, 93  
Fission products, 29  
Fluorine,  
- atomic properties, 516  
- compounds with oxygen, 528  
- interhalogen compounds, 524  
- molecule, 108  
- nitrate (pernitryl fluoride), 439  
- physical properties, 515, 517  
- production, 521  
- reactions, 522  
Fluoroaluminates, 351  
Fluorocarbons, 368  
Fluoro complexes, 549  
Force constants of bonds, 138  
Formic acid as a solvent, 245  
Francium, 308, 309  
Free-energy diagrams, 233  
Frenkel defects in crystals, 215  
Fundamental particles, 30  
Fusible white precipitate, 752
- Gadolinium, 605  
Gallium,  
- atomic properties, 354  
- halides, 357  
- halogeno-complexes, 358  
- nitride, 360  
- organometallic compounds, 360  
- oxides, 359  
- physical properties, 355  
- reactions, 356  
- sulphate, 360  
- sulphide, 360  
Gamma radiation, 21, 23  
Geiger-Muller tube, 36  
Genesis of elements, 31  
Geochronometry, 43  
Geometrical isomerism, 576  
Germanium,  
- atomic properties, 407  
- halides, 412  
- oxides, 415  
- physical properties, 409  
- reactions, 411  
- sulphides, 416  
Germanium, 417  
Gold,  
- atomic properties, 726  
- complexes, 732, 738  
- halides, 731  
- organometallic compounds, 737  
- oxidation states, 727, 730  
- oxides, 733  
- physical properties, 728  
Gouy balance, 85  
Graphite, 365  
Graphite compounds, 380  
Grimm-Sommerfeld rule, 201  
Ground state of atom, 71  
Group velocity, 51
- Hafnium,  
- atomic properties, 633  
- physical properties, 635  
- separation from zirconium, 636  
- reactions, 637  
Half-life, radioactive, 21  
Halides,  
- classification, 537  
- complex, 549  
- hydrates, 548  
- hydrolysis, 546  
- molecules in vapour state, 542  
- preparation, 539  
- structure of solids, 540  
- thermochemistry, 543  
Hartree field, 70  
Heavy water (deuterium oxide), 259  
Helium,  
- atomic properties, 295  
- separation from natural gas, 297  
- physical properties, 296  
Helium II, 296  
Heterodesmic solids, 192  
Heteropolyacids, 666  
Hexagonal close-packing, 132  
Holmium, 605  
Homodesmic solids, 191  
Homopolar crystals, 196  
Hume-Rothery rules, 198



- Hund's rules, 74  
 Hybridisation, 107, 109  
 Hybrid orbitals, 111  
 Hydrates, structure of, 212  
 Hydration isomerism, 575  
 Hydrazine, 285  
 Hydrazoic acid, 453  
 Hydrides,  
   – aluminium, 279  
   – carbon, 280  
   – germanium, 283  
   – indium, 280  
   – metallic, 266  
   – saline, 265  
   – silicon, 280  
   – tin, 283  
 Hydridocomplexes of transition metals,  
   722  
 Hydrofluoric acid as a solvent, 246  
 Hydrogen atom, wave mechanical treat-  
   ment, 55  
 Hydrogen bond, 135, 289, 293  
 Hydrogen-bridged structures, 271  
 Hydrogen, 254  
   – bromide, 292  
   – chloride, 292  
   – fluoride, 110, 112, 293  
   – iodide, 292  
   – isotopes, 254, 259, 262  
   – molecule, 97  
   – molecule ion ( $H_2^+$ ), 94  
   – ortho and para, 255  
   – overvoltage, 259  
   – peroxide, 504  
   – persulphide, 291  
   – polysulphides, 291  
   – production, 262  
   – selenide, 291  
   – spectrum, 58  
   – sulphide, 290  
   – telluride, 291  
 Hydroperoxides, 508  
 Hydroxylamine, 454  
 Hydroxonium ion, 237  
 Hyperons, 31  
  
 Ice, structure, 289  
 Indium,  
   – atomic properties, 354  
   – complexes, 358, 361  
   – halides, 357  
   – organometallic compounds, 360  
   – oxides, 359  
   – physical properties, 355  
 Induced nuclear reactions, 26  
 Inert complexes, 593  
 Infusible white precipitate, 752  
 Interhalogen compounds, 524  
 Interstitial alloys, 199, 266  
 Iodine,  
   – atomic properties, 516  
   – cationic, 535  
   – chlorides, 526  
   – fluorides, 150, 526  
   – oxide, 528, 531  
   – oxoacids, 531  
   – physical properties, 515, 517  
   – production, 522  
   – reactions, 522  
   – stereochemistry, 519  
 Ion-dipole bonds, 134  
 Ion exchange,  
   – actinide separation, 622  
   – lanthanide separation, 608  
   – separation of tracers, 38  
 Ionisation energy, 82  
 Ionisation isomerism, 575  
 Iridium,  
   – atomic properties, 708  
   – complexes, 714, 720  
   – halides, 712  
   – oxidation states, 709, 711  
   – oxides, 715  
   – physical properties, 711  
   – separation, 710  
   – sulphate, 717  
   – sulphides, 717  
 Iron,  
   – atomic properties, 691  
   – complexes, 700, 704  
   – extraction, 692  
   – halides, 696  
   – organometallic  $\pi$ -complexes, 698  
   – oxidation states, 694  
   – oxides, 697  
   – physical properties, 692  
   – sulphides, 698  
   – (II) sulphide structure, 698  
 Isocyanates, 551  
 Isodesmic solids, 191

- Isomerism in complex compounds, 575  
Isopolyacids, 668  
Isotopes, 6  
- relative abundance of naturally occurring, 8, 35  
- separation, 9  
Isotope dilution analysis, 44  
Isotopic exchange reactions, 40  
Jahn-Teller effect, 164, 196, 205  
K-electron capture, 25  
Krypton,  
- atomic properties, 295  
- clathrates, 299  
- fluorides, 306  
- physical properties, 296  
- separation from air, 297  
Lability of complexes, 593  
Landé *g*-factor, 74, 86  
Lanthanide contraction, 124  
Lanthanides,  
- atomic properties, 605, 606  
- complexes, 614  
- compounds, 611  
- densities, 606  
- ions, 610  
- metals, 608  
- oxides, 498, 612  
- paramagnetic moments, 611  
- physical properties, 609  
- reactions, 609  
- sources, 607  
Lanthanum, 605  
- compounds, 611  
- oxide, 498  
Lattice,  
- crystal, 190  
- energy, 192  
- point, 190  
- water, 212  
Layer lattices, 189, 204  
L.C.A.O. approximation, 95  
Lead,  
- atomic properties, 407  
- extraction, 410  
- halides, 412  
- oxides, 415  
- oxoacid salts, 417  
- physical properties, 409  
- reactions, 412  
- sulphides, 416  
- tetraacetate, 417  
- tetraethyl, 419  
Lewis acids, 249  
Ligand-field splitting, 157  
Ligand-field stabilisation, 563  
Ligand-field theory, 177  
Ligands, 565  
- bi- and terdentate, 565, 587, 588  
- nomenclature, order in formulae and names, 579  
Lithium,  
- alloys, 311  
- aluminium hydride, 280  
- atomic properties, 308  
- borohydrides, 278  
- halides, 312  
- organometallic compounds, 316  
- oxides, 313  
- oxoacid salts, 315  
- physical properties, 309  
- separation of isotopes, 310  
- similarities to magnesium, 319  
- sulphides, 314  
Lowry-Brønsted theory of acids and bases, 237  
Lutetium, 605  
Madelung constant, 102  
Magnesium,  
- atomic properties, 322  
- complexes, 332  
- extraction, 324  
- halides, 326  
- nitride, 329  
- organometallic compounds, 334  
- oxide, 328  
- oxoacid salts, 330  
- physical properties, 322  
- reactions, 326  
- sulphides, 329  
Magnetic measurements, 85, 573  
Magnetic susceptibility, 85  
Manganese,  
- atomic properties, 674  
- complexes, 687  
- halides, 679  
- organometallic  $\pi$ -complexes, 686  
- oxidation states, 678

- oxides, 681
- physical properties, 675
- reactions, 677
- sulphides, 685
- Mass number (*A*), 6, 7
- Mass spectrograph, determination of atomic mass, 8
- Mendelevium, 623
- Mercury,
  - atomic properties, 743
  - complexes, 755
  - halides, 749
  - ions, 746
  - nitrogen compounds, 752
  - occurrence, 746
  - organometallic compounds, 754
  - oxide, 751
  - physical properties, 744
  - reactions, 747
  - sulphide, 751
- Meson, 31
- Metal-carbon bonds, 393
  - relative reactivity of, 399
- Metals, classification, 197
  - electronic structure, 132
- Methane molecule, 117
- Methanides, 382
- Methyl radical, 116
- Mica, 211
- Miller indices of crystals, 217
- Mole, definition, 9
- Molecular orbitals, 94, 177
- Molybdenum,
  - atomic properties, 657
  - complexes, 670
  - extraction, 660
  - halides, 663
  - oxidation states, 661
  - oxides, 665
  - physical properties, 658
- Monazite, 607
- Mössbauer spectra, 46
- Mullikan notation of MO's, 107
- Multiplet state, 72
  
- Neodymium, 605
- Neon,
  - atomic properties, 295
  - physical properties, 296
  - separation from air, 297
- Nephelauxetic series, 175
- Neptunium, 622
  - ions, 625
  - halides, 628
  - oxidation states, 624
  - production, 622
- Nessler's reagent, an anionic Hg<sup>II</sup> compound, 750
- Neutrino, 23
- Neutron, 5
  - activation analysis, 45
  - decay, 31
  - diffraction, 189
  - resonance capture, 29
- Nickel,
  - arsenide structure, 202
  - atomic properties, 691
  - complexes, 702, 707
  - dimethylglyoxime, 588
  - extraction, 693
  - halides, 696
  - organometallic compounds, 699
  - oxidation states, 694
  - oxides, 697
  - physical properties, 692
  - sulphides, 698
- Niobium,
  - atomic properties, 646
  - chromatographic separation from tantalum, 648
  - complexes, 655
  - extraction, 648
  - halides, 650
  - nitride, 654
  - oxidation states, 649
  - oxides, 652
  - physical properties, 647
  - reactions, 648
  - sulphide, 654
- Nitrides, 452
- Nitrogen,
  - active, 425
  - atomic properties, 420
  - halides, 427
  - hybridisation of AO's, 422
  - molecule, 107, 421
  - oxidation states, 423
  - oxides, 431
  - oxoacids, 441
  - preparation and properties, 424

- sulphides, 450
- Nitronium compounds, 438
- Nitrosonium compounds, 434
- Nitrosyl,
  - carbonyls, 391
  - chloride as solvent, 251
  - compounds, 435
- Nitryl halides, 439
- Noble-gas compounds, 299
- Noble-gas electronic structure rule, 386
- Nomenclature of inorganic chemistry, 579
- Nonahydridorhenate(VII) ion, 686
- Non-localised MO's, 129
- Non-protonic solvents, 250
- Non-stoichiometric compounds, 215, 697
- Nuclear,
  - binding energy per nucleon, 13
  - fission products, 29
  - magnetic resonance spectroscopy, 14
  - quadrupole coupling, 19
  - reactions, 26
  - reactor, 30, 620
  - spin, 13
- Nucleation in crystal growth, 218
- Nucleons, 6
- Nucleophilic substitution, 590, 595
- Nucleus, 5
  - collective model, 13
  - liquid drop model, 12
  - shell model, 12
- Nuclide, 7
  
- Olefin complexes, 719
- Olefin compounds of metals, 402
- Olivine, 210
- Operator, Hamiltonian, 55
- Optical isomerism, 578
- Optical rotatory dispersion, 571
- Orbitals, atomic, 58
  - order of filling, 76
  - valence, 69
- Orbitals, crystal (Bloch), 94
- Orbitals, molecular, 94
  - bonding and antibonding, 95
  - L.C.A.O. approximation, 95
  - localised, 114
  - principle of overlap density, 98
  - non-localised, 129
- Order-disorder transition, 198
  
- Organometallic compounds, 393 (*see also under pertinent metals*)
  - reactions, 400
  - uses, 405
- Orthophenanthroline complexes, 700
- Osmium,
  - atomic properties, 708
  - complexes, 714, 720
  - halides, 712
  - oxidation states, 709, 711
  - oxides, 715
  - physical properties, 711
  - separation, 710
  - sulphides, 717
- Oxidation number, 230
- Oxidation-reduction electrode, 223
  - processes, 222
- Oxidation state, 230
- Oxides,
  - classification, 494
  - compared with sulphides, 501
  - complex, 499
  - distribution of classes through Periodic Table, 495
  - non-stoichiometry, 502
  - preparation, 495
  - structures, 496
  - thermochemistry, 502
- Oxine (8-hydroxyquinoline), thallium tris-complex with, 361
- Oxygen,
  - allotropy, 473
  - atomic, 473
  - atomic properties, 470
  - fluorides, 529
  - isotope  $^{18}\text{O}$ , 472
  - molecule, 108
  - paramagnetism, 109
  - physical properties, 472
  - stereochemistry, 478
- Ozone, 473
  
- Pair production, 25
- Palladium,
  - atomic properties, 708
  - complexes, 714, 720
  - halides, 712
  - hydride, 266
  - oxidation states, 709, 711
  - oxides, 715

- physical properties, 711
  - separation, 710
  - sulphides, 717
  - Paramagnetism, 86
  - Pauli exclusion principle, 69
  - Pauling's rules for ionic crystals, 195
  - Periodic Classification, 80
  - Periodic Table, 81
  - Permanganates, 684
  - Perovskite structure, 206
  - Peroxides, 313, 328, 506
  - Peroxoacids of
    - carbon, 512
    - chromium, 512
    - nitrogen, 510
    - phosphorus, 511
    - sulphur, 509
  - Peroxo-compounds of titanium, 513
  - Peroxyhydrates, 513
  - p-wave functions, 60
  - Phase velocity of a wave, 51
  - Phosphides, 453
  - Phosphonitrilic compounds, 455
  - Phosphorus,
    - allotropy, 426
    - atomic properties, 420
    - halides, 148, 428
    - hybridisation of AO's, 423
    - hydrides, 287
    - molecule, 422
    - oxidation states, 423
    - oxides, 439
    - oxoacids, 444
    - stereochemistry, 422
    - sulphides, 450
  - Photochemistry, 601
  - Pile, atomic, 29, 620
  - Pitchblende, 619
  - pK values (acid-base equilibria in water), 240
  - Planck's constant, 50
  - Planets, composition, 33
  - Platinum,
    - atomic properties, 708
    - complexes, 714, 720
    - halides, 712
    - organometallic compounds, 718
    - oxidation states, 709, 711
    - oxides, 715
    - physical properties, 711
  - separation, 710
  - sulphides, 717
  - Plutonium,
    - atomic properties, 617, 618
    - halides, 628
    - oxidation states, 624
    - oxides, 627
    - production, 620
    - separation from uranium, 621
    - sulphides, 629
  - Point defects in crystals, 220
  - Polonium,
    - atomic properties, 470
    - halides, 480
    - oxides, 484
    - oxoacid salts, 493
    - physical properties, 472
    - production, 477
  - Polyacids, 666
  - Polyhalides of the alkali metals, 312
  - Polynuclear complexes, 565, 581
  - Polyphosphates, 448
  - Polysulphides, 291
  - p orbitals, 61
  - Positive ray analysis, 7
  - Positron, 24
  - Potassium,
    - atomic properties, 308
    - halides, 312
    - oxides, 313
    - oxoacid salts, 315
    - physical properties, 309
    - radioactive isotope, 309
    - sulphides, 314
  - Praseodymium, 605
  - Probability density, electron, 52, 58
  - Promethium, 605
  - Protactinium, 617
  - Protogenic solvents (acidic), 245
  - Protolysis, 239
  - Proton, 5
  - Protophilic solvents (basic), 243
  - Prussian blue structure, 701
  - Pseudohalogens, 551
  - Pyrites structure, 698
  - Pyrolusite, 682
  - Pyroxenes, 210
- Quantisation of energy, 54, 63
- Quantum numbers, 69

- Radii,
  - covalent, 122
  - ionic, 103
  - metallic, 125
  - Van der Waals, 124
- Radioactivation analysis, 45
- Radioactive tracers, 37
- Radioactivity, 21
- Radiocarbon dating, 44
- Radiometric analysis, 44
- Radionuclide production, 37
- Radium,
  - atomic properties, 322
  - extraction, 326
  - physical properties, 322
- Radius ratio rule, 193, 330
- Radon,
  - atomic properties, 295
  - isotopes, 298
  - physical properties, 296
- Raman spectra, 141
- Reaction mechanisms, 590, 592, 595, 597, 599
- Reaction rates, methods of measurement, 591
- Redox potentials, 225
- Reinecke's salt, 671
- Reversible cells, 224
- Rhenium,
  - atomic properties, 674
  - extraction, 678
  - halides, 679
  - oxidation states, 678
  - oxides, 681
  - physical properties, 675
  - reactions, 678
  - sulphides, 685
- Rhodium,
  - atomic properties, 708
  - complexes, 714, 720
  - halides, 712
  - oxidation states, 709, 711
  - oxides, 715
  - physical properties, 711
  - separation, 710
  - sulphides, 717
- Riesefeld test for peroxoacids, 509
- Rubidium,
  - atomic properties, 308
  - halides, 312
  - metal, 310
  - oxides, 313
  - physical properties, 309
  - radioactive isotope, 309
  - sulphides, 314
- Russell-Saunders coupling, 73, 87
- Ruthenium,
  - atomic properties, 708
  - complexes, 714, 720
  - halides, 712
  - oxidation states, 709, 711
  - oxides, 715
  - physical properties, 711
  - separation, 710
  - sulphide, 717
- Rutile structure, 203, 640
- Rydberg constant, 59
  
- Saline hydrides, 265
- Samarium, 605
  - halides, 611
- Scandium, 615
  - fluoride structure, 542
- Schrödinger equation, 54
- Scintillation counting, 36
- Screening constants, 70
- Screw dislocation in crystals, 219
- Selenium,
  - allotropy, 476
  - atomic properties, 470
  - halides, 480
  - oxidation states, 477
  - oxides, 484
  - oxoacids, 490
  - physical properties, 471
  - production, 476
  - reactions, 472
  - seleninyl halides, 492
  - stereochemistry, 479
- Selenocyanogen, 553
- Self-diffusion, 39
- Semiconductors, 409
- Schottky defects in crystals, 215
- Sigma bonds, 95
- s functions, 58
- Silanes, 280
- Silica, crystalline forms, 375
  - gel, 376
- Silicam, 417
- Silicate structures, 209

- Silicon,  
 - atomic properties, 363  
 - halides, 367  
 - nitride, 379  
 - oxides, 375  
 - reactions, 367  
 - sulphides, 378  
 Silicones, 377  
 Silver,  
 - atomic properties, 726  
 - extraction, 729  
 - halides, 731  
 - iodide structure, 215  
 - oxidation states, 727, 730  
 - oxides, 733  
 - oxoacid salts, 737  
 - physical properties, 728  
 - reactions, 729  
 - sulphides, 735  
 Silyl halides, 281  
 Sodium,  
 - atomic properties, 308  
 - chloride lattice, 193  
 - complexes, 318  
 - halides, 312  
 - metal, 310  
 - organometallic compounds, 316  
 - oxides, 313  
 - oxoacid salts, 315  
 - peroxide, 506  
 - physical properties, 309  
 - sulphides, 314  
 Solvent extraction for separation of tracers from non-isotopic fission products, 38  
 - lanthanide separation, 608  
 Solvents, non-aqueous, 242  
 s orbitals, 58  
 Spectra,  
 - atomic, 64  
 - electronic absorption, 166, 572  
 - electron spin resonance, 88  
 - infrared absorption, 137, 387, 571  
 - microwave, 141  
 - Mössbauer, 46  
 - nuclear magnetic resonance, 14, 449, 481, 574  
 - nuclear quadrupole resonance, 20  
 - Raman, 141  
 Spectrochemical series, 159  
 Spectroscopic series (classical), 62  
 - states, 71  
 Spinel structure, 207  
 Spin-orbit coupling, 91  
 Stabilisation of oxidation states, 559  
 Stability constants, 583  
 Stellar energy, 27  
 Stereochemistry,  
 - Group V, 422, 423  
 - Group VI, 479  
 - Group VII, 519  
 Steric effects in replacement reactions, 600  
 Steric strain, 589  
 Strontium,  
 - atomic properties, 322  
 - extraction, 325  
 - halides, 326  
 - oxides, 328  
 - physical properties, 322  
 - reactions, 326  
 Substitutional alloys, 197  
 Substitution reactions, 590  
 - solvent effects, 599  
 - steric effects, 600  
 Sulphur,  
 - allotropy, 474  
 - atomic properties, 470  
 - dioxide as solvent, 251  
 - halides, 480  
 - hexafluoride molecule, 150  
 - hydrides, 290  
 - nitride, 450  
 - oxidation states, 477  
 - oxides, 483  
 - oxoacids, 486  
 - physical properties, 471  
 - reactions, 471  
 - stereochemistry, 479  
 - sulphinyl and sulphonyl halides, 491  
 - tetrachloride structure, 481  
 - trioxide structures, 485  
 Sulphuric acid as a solvent, 245  
 Superconductivity of heat by helium II, 296  
 Superoxides, 313, 608  
 Tantalum,  
 - atomic properties, 646  
 - halides, 650

- nitrides, 654
- oxidation states, 649
- oxides, 652
- physical properties, 647
- reactions, 648
- sulphide, 654
- Technetium,
  - atomic properties, 674
  - halides, 679
  - oxidation states, 678
  - oxides, 681
  - pertechnetic acid, 684
  - physical properties, 675
  - separation from fission products, 677
  - sulphides, 685
- Tellurium,
  - atomic properties, 470
  - extraction, 476
  - halides, 480
  - oxidation states, 477
  - oxides, 484
  - oxoacids, 491
  - oxoacid salts, 493
  - physical properties, 471
  - reactions, 472
  - stereochemistry, 479
- Tellurocyanates, 551
- Terbium, 605
- Terdentate ligands, 588
- Thallium,
  - atomic properties, 354
  - complexes, 358, 361
  - halides, 357
  - oxide, 359
  - physical properties, 355
  - reactions, 356
  - salts, 359
- Thiocyanogen, 551
- Thionates, 487, 489
- Thiosulphates, 488
- Thorium, 617
  - extraction, 618
  - halides, 628
  - oxidation states, 624
- Three-centre bonds, 274
- Thulium, 605
- Tin,
  - atomic properties, 407
  - halides, 412
  - organometallic compounds, 418
  - oxides, 415
  - physical properties, 409
  - reactions, 411
  - sulphides, 416
- Titanates, 641
- Titanium,
  - atomic properties, 633
  - complexes, 644
  - halides, 638
  - metal, 636
  - nitrides, 642
  - organometallic compounds, 643
  - oxide, 639
  - physical properties, 635
  - reactions, 637
- Trans* effect, 598
- Transition metals, 554
  - atomic properties, 556
  - d-shell occupancy and stability of oxidation state, 560
  - hydrated ions, 562
  - properties, 555
  - oxidation states, 557
- Transuranic elements, 617
  - production, 620
- Tributyl phosphate, use in solvent extraction, 621
- Tritium, 6, 262
- Tungsten,
  - atomic properties, 657
  - bronzes, 206, 668
  - complexes, 670
  - extraction, 661
  - halides, 663
  - oxidation states, 661
  - oxides, 665
  - physical properties, 658
  - polyacids, 666
  - redox relationships, 659
- Uncertainty principle, 52
- Unimolecular substitution mechanisms, 590
- Unit cell, 190
  - types, 191
- Uranium,
  - atomic properties, 617
  - extraction, 619
  - halides, 627
  - metal, 623



- oxidation states, 624
- oxides, 627
- sulphides, 629
- Valence states, 112
- Valentinite structure, 501
- Vanadium,
  - atomic properties, 646
  - carbides, 653
  - complexes, 655
  - extraction, 647
  - halides, 650
  - nitrides, 654
  - organometallic compounds, 654
  - oxidation states, 649
  - oxides, 652
  - oxosalts, 654
  - physical properties, 647
  - reactions, 648
  - sulphides, 654
- Van der Waals forces, 136
- Vector addition of orbital and spin angular momenta, 66
- Water as a solvent, 106
- Water of crystallisation, 212, 314
- Water,
  - maximum density, 289
  - molecule, 118
  - redox potentials, 290
  - structure of liquid, 288, 289
- Wave,
  - equation, 53
  - function, 53
  - mechanics, 50
  - packet, 51
- Wigner energy in graphite, 220
- Wurtzite structure, 202, 745
- Xenon,
  - atomic properties, 295
  - clathrates, 299
  - compounds, 299
  - extraction from air, 297
  - fluorides, 300
  - hydrates, 299
  - oxides, 304
  - physical properties, 296
  - uses, 298
- X-ray diffraction, 187
- Ytterbium, 605
- Yttrium, 615
- Zeeman effect, 64, 66
- Zeise's salt, 402
- Zeolites, 212
- Zeolite water, 212
- Zinc,
  - atomic properties, 743
  - blende, 202, 745
  - complexes, 755
  - extraction, 746
  - halides, 748
  - metal structure, 745
  - organometallic compounds, 754
  - oxide, 750
  - reactions, 747
  - sulphide, 745, 751
- Zirconium,
  - atomic properties, 633
  - complexes, 644
  - halides, 638
  - metal, 636
  - nitrides, 642
  - oxide, 639
  - physical properties, 635
  - reactions, 637
  - separation from hafnium, 636
- Zone refining of germanium, 410

**HESLOP**  
**ROBINSON**

## About this book

"Inorganic Chemistry" broke new ground as a text-book and had a favourable reception when it appeared in 1960, rapidly running through several reprintings and into a second edition. During this time inorganic chemistry has been developing quickly through the application of more sophisticated methods of observing reactions and structure, and further integration of the subject has become possible. Hence the third edition has been largely rewritten and is virtually a new book. What has been retained has been brought into line with current theory. There are new sections on organometallic chemistry and on reaction mechanisms; there is considerable expansion of the treatment of oxidation and reduction and of spectroscopic and other methods of investigating structure. However, many of the popular features remain, such as the thorough treatment of structural chemistry and the full consideration of periodic relationships. The book remains a reasonably-priced, handy text-book suitable for study up to honours level.

**ELSEVIER PUBLISHING COMPANY**  
AMSTERDAM - LONDON - NEW YORK

**Inorganic  
Chemistry**

**THIRD  
EDITION**

**ELSEVIER**