A. Holderness

Advanced Level Inorganic Chemistry

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Advanced Level Inorganic Chemistry

A. Holderness

A new edition of the *Inorganic* section of *Inorganic and Physical Chemistry* revised by

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and a companion to *Advanced Level Physical Chemistry*

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Preface

The subjects which we study do not have their boundaries defined by God but by men. We take the totality of experience and (for various excellent reasons) call some parts of it 'science'. Science is divided, largely for the convenience of students, teachers, and users, into the disciplines of biology, physics, chemistry, and so on. Chemistry itself is further divided into the major areas of physical, inorganic, organic, and analytical chemistry. Those who practise and use science are crossing the barriers between subjects with increasing frequency and to increasing effect; for examples one has only to think of molecular biology and semiconductors. The social and economic consequences of scientific activity transcend subject boundaries. But the boundaries and subdivisions still prove useful for the purposes of teaching and learning.

This book is a new edition of the inorganic section of Albert Holderness's *Inorganic and Physical Chemistry*. It uses, as any book on inorganic chemistry must do, very many of the ideas developed in the companion volume on physical chemistry (*Advanced Level Physical Chemistry* by A. Holderness, revised by J. N. Lazonby). It is assumed that this can easily be referred to by the reader, and there are frequent references in this text to the physical chemistry volume.

It is always difficult to revise an established classic. Such is the pace of advance in chemical theory and practice that the new book has to incorporate discussion of ideas and techniques which were either totally unknown, or only dimly perceived, when the book was last revised. A conscious attempt has been made to retain as much as possible of the flavour and philosophy of the previous edition, while at the same time ensuring that the present work is a thoroughly up-to-date textbook. The material has been rearranged, and there have been major deletions and additions. SI units are used, and nomenclature is based on the recommendations of the Association for Science Education and the Examining Boards.

This book contains rather more descriptive and preparative material than is customary in contemporary inorganic chemistry texts at Advanced and Scholarship level, while at the same time covering the syllabus requirements for a theoretical background. It is hoped that this will enable the volume to be useful as a reference for both facts and ideas.

I am very grateful to John Lazonby for his detailed and helpful criticism of the text. Any errors and imperfections which remain are solely my responsibility. I am also grateful to Graham Taylor, Hamish MacGibbon, and Katherine Ross of Heinemann Educational Books for much encouragement and help. Above all, I am grateful to my wife and children for putting up with me during a task which proved tougher and longer than I had bargained for.

June 1979 *Martyn Berry*

Important note

All melting and boiling points are, unless otherwise stated, quoted for a pressure of 101 325 $\mathrm{N\,m^{-2}}$.

Where great accuracy is not essential, e.g. in industrial processes, pressures are often quoted in 'atmospheres', abbreviated to 'atm' (1 atm $\approx 10^5\,\mathrm{N\,m^{-2}}$).

Equations involving energy changes are written with the enthalpy change in the form (energy) × (amount of substance)$^{-1}$. The units for ΔH will thus be $\mathrm{kJ\,mol^{-1}}$. The use of '$\mathrm{mol^{-1}}$' does *not* imply 'per mole of any particular material formed or used up,' but 'per molar quantities as indicated by the equation.'

Hence, for example:

$$\mathrm{CO(g)} + \tfrac{1}{2}\mathrm{O_2(g)} \rightarrow \mathrm{CO_2(g)} \qquad \Delta H = -283\,\mathrm{kJ\,mol^{-1}}$$
$$\mathrm{2CO(g)} + \mathrm{O_2(g)} \rightarrow \mathrm{2CO_2(g)} \qquad \Delta H = -566\,\mathrm{kJ\,mol^{-1}}$$

(See e.g. Cvitaš and Kallay, *Chemistry in Britain*, June 1978, p. 290.)

About the questions

Most of the questions in this book are of the 'essay' type, although there are also many problems. Readers should remember that the chemistry examinations of an increasing number of Boards require an ability to cope with fixed response questions, usually in the form of an 'objective test' paper and a 'structured' paper. Considerations of space mean that there are no questions of these kinds in this book.

Thanks are due to the Oxford Delegacy of Local Examinations(O), the University of Cambridge Local Examination Syndicate(C), the Joint Matriculation Board(JMB), the University of London University Entrance and Schools Examination Council(L), and the Associated Examination Board (AEB) for permission to reproduce questions.

Contents

1

Introduction to inorganic chemistry

What is inorganic chemistry?

At the start of his classic textbook *Inorganic Chemistry* (New York: John Wiley, 1952), Professor Therald Moeller wrote:

> 'As opposed to organic chemistry, inorganic chemistry is properly a study of all chemical materials other than the hydrocarbons and their derivatives. Not only does inorganic chemistry embrace the properties and modes of preparation of such materials, but it goes beyond and seeks to account for and explain specific characteristics and observed similarities, differences, and trends in observed behaviours. Modern inorganic chemistry, unlike classical inorganic chemistry, is more than a descriptive science. It attempts to relate the properties of chemical substances to their structures, which in turn are related to the structures of the particles which combined to make those substances. Modern inorganic chemistry employs, therefore, both the experimental and theoretical approaches and requires familiarity with each. It is concerned with all the elements and with all the combinations in which these elements are found.'

This passage repays careful re-reading. It defines inorganic chemistry, and points out how the structures and properties of materials depend on the structures of the atoms of the elements of which they are composed. In the years since Professor Moeller's book, much progress has been made in *explaining* the myriad properties, similarities, differences, and trends which are observed in inorganic materials. Although we are very far from a complete interpretation and explanation of chemical behaviour, there is now a strong framework of theory which can be used both to hang the observed facts on and to make predictions. Most of the theory needed for our purposes can be found in the companion volume to this book, *Advanced Level Physical Chemistry*, and will be referred to and developed later in this chapter. Although it is not necessary to master *all* the theory before embarking on a study of inorganic chemistry—indeed, the immediate opportunity for a wide range of experiments and observations is one of the attractions of the subject—the reader is strongly advised to develop a knowledge and understanding of the unifying theory as soon as possible. This will lessen the need for memorizing many isolated details of factual information. It must be realized, though, that chemical theory is *not* fixed for ever, and that through research it improves with time; so that the reader should be prepared for change during the lifetime of this book. (For an important example of the way in which new observations can force theories to change, see p. 26).

Why study inorganic chemistry?

The fact that our environment consists very largely of inorganic materials would surely be reason enough for inorganic chemistry to be a worthwhile field of study. But, in addition, a great many important human activities depend on the application of inorganic chemical knowledge. Examples include the extraction and working of all metals; the construction industries of all kinds; semi-conductors; nuclear fuel technology; the supply of safe drinking water; the control and possible elimination of corrosion and pollution. Fossil fuels are not the only materials which are bound to become scarcer; the easily-discovered and easily-worked deposits of the ores of many metals have already been used up. The detection, winning, efficient use of, and recycling of metals form only one region of many fields in which an understanding of inorganic chemistry will become increasingly important. The social and economic impacts which result from the *right* (and, regrettably, sometimes the *wrong*) use of chemical knowledge should never be underestimated.

Sources of inorganic materials

Most inorganic materials of economic importance occur in the solid state as components of the Earth's crust. Most metals are found in combination with oxygen or sulphur. Only the most unreactive (e.g. gold) are found in the free state. A mass of rock which contains an unusually high proportion of a particular metal or group of metals is known as an *ore*. The ways in which the ores were deposited, and their detection and mining, are beyond the scope of this book. However, it should be pointed out that the extraction of metals from concentrated ore is a process of *reduction*. The ores, which are usually oxides or sulphides, contain metal ions; these must receive electrons to become free metal. Examples of ways in which this can be done include the extractions of iron (p. 432), copper (p. 456), and aluminium (p. 118).

Other solid materials of economic importance obtainable from the Earth's crust include calcium carbonate (p. 93), silica (p. 116), and sulphur (p. 310).

Many salts, particularly those of the alkali metals, are soluble in water. Such materials will be washed into the sea over many years. (This process may be observed occurring in the Dead Sea.) The main sources of sodium, potassium, and magnesium are either the sea or salt deposits formed by evaporation of sea-water in the distant past (see e.g. p. 43 and p. 69). Halide ions are also found in high concentration in rock salt and sea-water, which are therefore the main sources of chlorine (p. 50) and bromine (p. 371) respectively.

The atmosphere provides the industrially vital gas oxygen (p. 276). 'Fixation' of atmospheric nitrogen by the Haber process (p. 216) is essential for the production of fertilizers.

It is instructive to consider the composition of the Earth's crust, shown in Table 1.1.

Table 1.1 Composition of the Earth's crust, including waters and the atmosphere

Element	*Mass per cent*	*Element*	*Mass per cent*
Oxygen	49.5	Magnesium	1.9
Silicon	25.7	Hydrogen	0.88
Aluminium	7.5	Titanium	0.58
Iron	4.7	Chlorine	0.19
Calcium	3.4	Phosphorus	0.12
Sodium	2.6	Carbon	0.09
Potassium	2.4	All others	0.42

From Table 1.1 it can be seen that not only are many metals of major importance included within the 'all others" percentage of 0.42, but so also are the apparently common non-metals nitrogen and sulphur. Many rocks are roughly describable as 'aluminosilicates', that is materials containing aluminium, silicon, and oxygen. The final product of their weathering, as observed on sea shores, is often more or less impure silicon dioxide, i.e. sand.

The Periodic Table and its relation to atomic structure

The historic development of the Periodic Table is described in *Advanced Level Physical Chemistry*, pp. 58–61.

Table 1.2 The Periodic Table of the elements, showing the s-, p-, d-, and f-blocks

					1 H	2 He												
s–block														p–block				
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne	
11 Na	12 Mg						d – block					13 Al	14 Si	15 P	16 S	17 Cl	18 Ar	
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr	
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe	
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn	
87 Fr	88 Ra	89 Ac																
				58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu	f – block
				90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lw	actinides

A knowledge of the Periodic Table (Table 1.2) is essential if the reader wishes to have any mastery of inorganic chemistry. There is no alternative to *learning* it by heart—certainly as far as krypton, but preferably (except for the f-block elements: the lanthanides and actinides) in its entirety. It is immensely helpful to the student if he or she can immediately place an element in its correct *Period* (horizontal row) and *Group* (vertical column). Readers of this book could help each other to master the Table by use of the following exercises:

(1) Given an *atomic number*, place the element in its correct Period and Group, and give the symbol of the element.
(2) Given a *particular element*, identify the Period and Group and give the atomic number of the element.

Proficiency in using the Table can rapidly be gained, but must be reinforced by frequent revision. The exercises can later be extended to the electronic structures of the atoms of the elements concerned (see below).

The number of protons in the *nucleus* of each atom of a particular element is the same, and this number identifies the *atomic number* of that element (*Advanced Level Physical Chemistry*, p. 27). Thus, all atoms of sodium possess eleven protons, and the atomic number of sodium is eleven. The elements appear in the Periodic Table in the order of their atomic numbers. The number of protons in an atom *must* equal the number of electrons, if the atom is to be electrically neutral. And, as we shall see, the *number* of electrons determines the *arrangement* of electrons, and particularly the number of electrons in the outer quantum shell or energy level (see *Advanced Level Physical Chemistry*, p. 48 ff.) The number of electrons in the outer energy level largely determines the chemical behaviour of the 's-block' and 'p-block' elements. For 'd-block' elements, the number of electrons in the last two levels is important.

The argument in the last paragraph leads to this conclusion: if we know the position of an element in the Periodic Table, and hence its atomic number, we can write its detailed electron structure and hence *predict its chemical behaviour*. The advantages of this in terms of minimizing the need to remember facts are obvious and enormous, and the advisability of *thorough knowledge* of the Periodic Table is clear.

The evidence leading to ideas of electron structure in atoms is summarized in Chapter 5 of *Advanced Level Physical Chemistry*; the s, p, d, and f notation is also introduced in that chapter. It should be carefully read or re-read at this point, and any difficulties of understanding or interpretation discussed. An aid to memorizing the order of 'filling' the electron energy sub-levels in atoms is given in Figure 1.1.

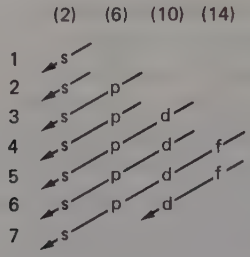


Figure 1.1 *Order of filling of energy levels*

Once the notation is mastered and the sequence of energy levels and sub-levels is known, the Periodic Table (Table 1.2) is immediately seen to reflect the electron energy levels or 'shells'. The first level is complete at helium; the second (with its s and p sub-levels) at neon; the third *appears* to be complete at argon, but after the 4s sub-level ten more electrons can be introduced into the 3d sub-level, corresponding to the first transition series Sc → Zn. This brings the number of electrons in the third energy level to its maximum of 18. The fourth electron energy level can contain 32 electrons. Eight (the s and p sub-levels) can go in at once; another ten (the 4d sub-level, corresponding to the second transition series, Y → Cd) follow later; and a final fourteen (the 4f sub-level, corresponding to the 'rare earths' or *lanthanides*, Ce → Lu) eventually complete the energy level. The sequence of filling of the sub-levels is clearly shown in Figure 1.1 and should be memorized at this stage.

The reader should now practise writing the full electron structures of elements, given their atomic numbers. For example, chlorine has an atomic number of 17. Its electron arrangement must therefore be: $1s^2 2s^2 2p^6 3s^2 3p^5$.

The ground state (i.e. *lowest energy*) electron arrangements in elements with atomic numbers 1 → 92 are given at the end of this book. The slightly anomalous behaviour of chromium and copper is explained on p. 393.

General trends within the Periodic Table

Since the Periodic Table provides the framework for the whole study of inorganic chemistry, a knowledge of the trends in chemical properties within the Table, and the reasons for those trends, gives a powerful way of systematizing the facts of inorganic chemistry and reducing the load on the memory.

The discussion which follows is to some extent simplified, and usually confined to elements in the s and p blocks of the Periodic Table. When generalizations are made, there are usually one or two exceptions with respect to particular properties or elements. The reasons for these anomalies are often quite complicated.

Metals and non-metals

Inspection of the Periodic Table reveals that the great majority of the elements (nearly 70 out of the first 92) are metals. Typically, metals are good conductors of heat and electricity, can readily form positive ions by loss of electrons, form solid ionic chlorides, and form basic oxides. Non-metals, on the other hand, typically are non-conductors, can readily form negative ions by gain of electrons, form volatile covalent chlorides, and form acidic or neutral oxides.

Metals form compounds by *ionic* bonding with non-metals; they can also form *alloys* with each other. Non-metals either bond ionically with metals, or *covalently* with each other. (Chapter 7 in *Advanced Leval Physical Chemistry*, which deals in detail with ionic and covalent bonding, should be closely studied at this point.) It should be realized that the properties of some elements are intermediate between those of typical metals and typical non-metals, and that the bonding in many compounds is intermediate in type between ionic and covalent. Metals which can exist in more than one *oxidation state* (see *Advanced Level Physical Chemistry*, p. 246 ff) can themselves show both metallic and non-metallic properties as judged from the properties of their compounds, with the lower oxidation state(s) resulting in more metallic properties than the upper. For example, lead(II) chloride, $PbCl_2$, is a solid which can be electrolysed when molten, whereas lead(IV) chloride, $PbCl_4$, is a volatile liquid which cannot be electrolysed and therefore contains no ions (see p. 205).

Trends within a Period

Study of any Period of the Table, for example the Period Na → Ar, reveals that the Period starts with an extremely reactive metal in Group I. The nature of the elements then changes gradually to non-metallic across the Period, reaching maximum non-metallic character in Group VII, before the Period ends with a chemically inert noble gas.

This behaviour can be correlated with the electron structure within the atoms. In the Group I elements, the outer energy level is occupied by a solitary electron, which is screened from the electrostatic attraction of the nucleus by one or more completed electron shells. It should there-

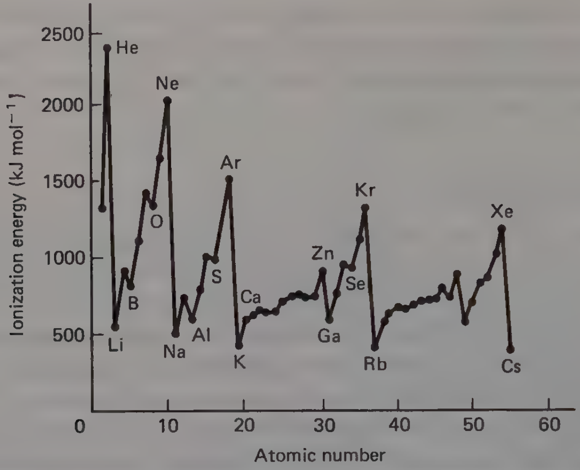


Figure 1.2 *Variation of first ionization energies with atomic number*

fore be comparatively easy to remove this electron, i.e. to *ionize* the atom. Inspection of a plot of first ionization energy against atomic number (Figure 1.2) reveals that, in any Period, the element in Group I has the lowest first ionization energy, i.e. it is the easiest element in that Period to remove an electron from.

The information in Figure 1.2, together with a plot of successive ionization energies for a particular element, provides evidence for the existence of energy levels and sub-levels (see *Advanced Level Physical Chemistry*, pp. 48–52).

The difficulty of removing an electron increases across the Period, and reaches a maximum at the noble gas. As the metallic character of an element depends largely on its readiness to lose electrons and become positively ionized, we can say that, in general, *metallic character decreases from left to right across a Period.* (We could equally well say that *non-metallic character increases* across a Period.)

Since metals characteristically lose electrons to become *positive* ions, the word *electropositive* is often used to describe them. Similarly, since non-metals characteristically gain electrons to become *negative* ions, the word *electronegative* is used to describe them. The statement above could therefore be made in this form: *elements become less electropositive* (*or more electronegative*) *across a Period.*

Trends within a Group

Further examination of Figure 1.2 shows that, as Group I is descended, the energy required to remove the first electron becomes less, i.e. the formation of positive ions becomes easier, so that the elements become more *electropositive*, more typically *metallic* in character, down the Group. This is to be expected because, as the number of completed electron levels becomes greater, their shielding of the outer electron from the attraction of the positive nucleus becomes greater, and it is in any case further away from the nucleus as the atomic size increases. Since both the atomic size and the shielding due to completed electron levels increases down *any* Group of the Periodic Table, we may expect that *as any Group is descended there will be an increase in electropositive (metallic) character*. This is perhaps best seen in Group V, where there is a gradual transition from a highly electronegative non-metal, nitrogen, to a fairly typical metal, bismuth.

The two major trends within the Periodic Table are therefore (a) an increase in non-metallic character from Group I to Group VII across a Period; and (b) an increase in metallic character down a Group. This means that the most reactive and typical metals are to be found at the bottom left-hand corner of the Table as usually printed, and the most reactive non-metals at the top right (ignoring the noble gases).

Inert pair effect

As a Group is descended, if the elements can exist in more than one oxidation state, then the lower state tends to become more stable. For example, in Group IV both the +2 and +4 states are possible. Tin(II) oxide, SnO, is unstable, and tin(IV) oxide, SnO_2, is stable; whereas lead(II) oxide, PbO, is stable, and lead(IV) oxide, PbO_2, is unstable (see p. 203).

The effect is most noticeable in p-block elements which follow immediately after the d-block section of the Periodic Table. It is thought that the shielding due to electrons in the d-orbitals is comparatively weak; this results in a decreased tendency for the s electrons to form bonds. The s electrons are known as the *inert pair*.

The elements thallium, lead, and bismuth best illustrate the effect.

The diagonal relationship

The two trends discussed above, which are (so to speak) at right angles to each other, give rise to the so-called *diagonal relationship*. For example, lithium shows some similarities in its properties to magnesium, beryllium to aluminium, and boron to silicon. The similarities are not great, and

Table 1.3 Covalent radii of the elements

1 H 0.037	2 He 0.120

s–block		d – block										p – block					
3 Li 0.123	4 Be 0.089											5 B 0.080	6 C 0.077	7 N 0.074	8 O 0.074	9 F 0.072	10 Ne 0.160
11 Na 0.157	12 Mg 0.136											13 Al 0.125	14 Si 0.117	15 P 0.110	16 S 0.104	17 Cl 0.099	18 Ar 0.191
19 K 0.203	20 Ca 0.174	21 Sc 0.144	22 Ti 0.132	23 V 0.122	24 Cr 0.117	25 Mn 0.117	26 Fe 0.116	27 Co 0.116	28 Ni 0.115	29 Cu 0.117	30 Zn 0.125	31 Ga 0.125	32 Ge 0.122	33 As 0.121	34 Se 0.117	35 Br 0.114	36 Kr 0.200
37 Rb 0.216	38 Sr 0.191	39 Y 0.162	40 Zr 0.145	41 Nb 0.134	42 Mo 0.129	43 Tc	44 Ru 0.124	45 Rh 0.125	46 Pd 0.128	47 Ag 0.134	48 Cd 0.141	49 In 0.150	50 Sn 0.140	51 Sb 0.141	52 Te 0.137	53 I 0.133	54 Xe 0.220
55 Cs 0.235	56 Ba 0.198	57 La 0.169	72 Hf 0.144	73 Ta 0.134	74 W 0.130	75 Re 0.128	76 Os 0.126	77 Ir 0.126	78 Pt 0.129	79 Au 0.134	80 Hg 0.144	81 Tl 0.155	82 Pb 0.154	83 Bi 0.152	84 Po –	85 At 0.140	86 Rn –
87 Fr –	88 Ra –	89 Ac –															

58 Ce 0.165	59 Pr 0.165	60 Nd 0.164	61 Pm	62 Sm 0.166	63 Eu 0.185	64 Gd 0.161	65 Tb 0.159	66 Dy 0.159	67 Ho 0.158	68 Er 0.157	69 Tm 0.156	70 Yb 0.170	71 Lu 0.156	f – block
90 Th 0.165	91 Pa –	92 U 0.142	93 Np –	94 Pu –	95 Am –	96 Cm –	97 Bk –	98 Cf –	99 Es –	100 Fm –	101 Md –	102 No –	103 Lw –	actinides

are only notable for elements which possess small atoms (see the discussion of the elements concerned in the appropriate chapters).

Atomic and ionic sizes

The sizes of atoms are usually given as *atomic (covalent) radii*, i.e. half the internuclear distance between two atoms of the same element joined by a single bond.

Atomic sizes decrease from left to right across a Period. The number of protons in the nucleus increases across a Period, without any extension of the energy levels occupied by the electrons. Consequently, the increasing nuclear charge attracts the electrons more strongly, and the atomic size decreases.

Atomic sizes increase down a Group. Increasing nuclear charge, which would pull the electrons in closer, is counteracted by the screening effect of extra electron shells, and also by the repulsion between individual electrons.

The similarity of the radii of most of the d-block elements in each Period should be noted. The ability of these metals to form alloys with each other is due in part to this similarity in size.

When a metal forms an ion, one or more electrons are removed from the atom. The number of protons now exceeds the number of electrons, and furthermore the repulsion between the electrons is reduced. For both these reasons, *a positive ion is always smaller than its parent atom.* The values in Table 1.4 should be compared with those for the covalent radii in Table 1.3. It will be seen that loss of two or more electrons (e.g. Mg^{2+}, Al^{3+}) results in a dramatic reduction in size.

Formation of a negative ion involves addition of one or more electrons to the neutral atom. Electrons now outnumber protons, and furthermore the repulsion between electrons is increased. *Hence a negative ion is always larger than its parent atom.*

The relative sizes of the ions involved are important in determining

Table 1.4 Ionic radii of some elements

Element	*Ionic radius (nm)*	*Element*	*Ionic radius (nm)*
Li(+1)	0.060	Ca(+2)	0.099
Na(+1)	0.095	Al(+3)	0.050
K(+1)	0.133	Cl(−1)	0.181
Rb(+1)	0.148	Br(−1)	0.195
Cs(+1)	0.169	I(−1)	0.216
Mg(+2)	0.065	O(−2)	0.140

the crystal structure of an ionic compound (see *Advanced Level Physical Chemistry*, p. 91).

Electronegativity

A covalent bond is thought to consist of a shared pair of electrons, usually one from each atom involved, located between the nuclei of the atoms. Unless the atoms are of the same element, the electrons will not be shared equally. The relative ability of atoms to attract bonding electrons to themselves is referred to as their *electronegativity*. It is obvious that a bond between atoms of different electronegativities will be *polarized*—partially negative at the end occupied by the more electronegative atom, and partially positive at the other. (See *Advanced Level Physical Chemistry*, p. 97.) If there is a sufficient difference in electronegativity between the two atoms, polarization will be virtually complete, and ionization will have resulted. The effect is summarized below:

A $:$ B A and B identical

$^{\delta-}$A $:$ B$^{\delta+}$ A more electronegative than B

$^{-}$A$:$ B^{+} A much more electronegative than B

As we have seen above, electronegativity increases across a Period from the alkali metal (Group I) to the halogen (Group VII). Electronegativity is more pronounced with *small* atoms (i.e. those towards the end of a Period or the top of a Group) since in these atoms, particularly those such as halogens with a comparatively high nuclear charge, the attraction of the nucleus for electrons is not completely eliminated by shielding.

An arbitrary but self-consistent table of electronegativities was developed by Pauling. He gave the most electronegative element, fluorine, an electronegativity value of 4.0, and related other elements to this. Some electronegativity values are given below.

Period Li → Ne	Li	Be	B	C	N	O	F	Ne
	1.0	1.5	2.0	2.5	3.0	3.5	4.0	—
Halogens	F	Cl	Br	I	At			
	4.0	3.0	2.8	2.5	2.2			
Alkali metals	Li	Na	K	Rb	Cs	Fr		
	1.0	0.9	0.8	0.8	0.7	0.7		

The important topic of bond polarity and the resulting forces between molecules (*intermolecular forces*) is discussed in Chapter 9 of *Advanced Level Physical Chemistry*.

Electron affinity

The removal of an electron to form a monopositive ion is always an *endothermic* process, i.e. it is a process which *absorbs* energy. Even for an alkali metal with large atoms, e.g. caesium, the value of the first ionization energy is $+382\ \mathrm{kJ\ mol^{-1}}$.

The gaining of *one* electron by an atom is, however, normally an *exothermic* process, i.e. it is a process which *releases* energy. As would be expected from the above discussion on electronegativity, the readiness to gain electrons is greatest for the smallest atoms in a Period or a Group. *Electron affinity* is a measure of this readiness to gain electrons, and is defined thus:

> The first electron affinity of an element is the enthalpy change when an electron is gained by each of one mole of isolated neutral atoms of the element in the gaseous state.

$$\mathrm{X(g) + e^- \rightarrow X^-(g)} \qquad \Delta H = -Y\ \mathrm{kJ\ mol^{-1}}$$

Notice the phrase *first electron affinity*. This is usually abbreviated to *electron affinity*. Once one electron is added, the atom becomes negatively charged, and therefore *repels* further electrons. Second electron affinities, i.e. for $\mathrm{X^-(g) + e^- \rightarrow X^{2-}(g)}$, are *always* endothermic.

Some electron affinity values are given in Table 1.5.

It is not generally realized that even an extremely electropositive element such as sodium has an exothermic electron affinity. The anomalous behaviour of fluorine may be due to the fact that the fluorine atom is so small that the incoming electron is affected by comparatively

Table 1.5 Some electron affinities

Element	*Electron affinity* ($\mathrm{kJ\ mol^{-1}}$)
F	− 354
Cl	− 370
Br	− 348
I	− 320
O	− 148
C	− 126
Na	− 78

strong repulsion from the nine electrons already around the nucleus, so diminishing the overall amount of energy released by the process.

Anomalous behaviour of the first elements in each Group

Study of the detailed material in the later Chapters of this book will reveal that the difference in properties between the first and second members of a Group is greater than that between subsequent members of the Group. The reason for this effect is essentially the small size, and consequently greater electronegative character, of the first element.

Another difference is seen in Groups IV to VII. Whereas, for example, sulphur—the second member of Group VI—can exert the Group oxidation number of six, oxygen cannot rise higher than two. This is because oxygen is so small that it has no d orbitals available for bonding. Its electron arrangement is $1s^2 2s^2 2p^4$: the second energy level has no d orbitals available. Sulphur's electron arrangement is $1s^2 2s^2 2p^6 3s^2 3p^4$. The 3d orbitals are empty but available for bonding if needed, so that sulphur can form compounds such as SF_6.

This property of the first elements in Groups is further discussed where appropriate in later chapters. When discussing trends in properties across a Period of the Periodic Table, it is advisable (unless otherwise instructed) to use as illustration the elements in the Period Na → Ar.

Group oxidation numbers

The *maximum* oxidation number (see *Advanced Level Physical Chemistry*, p. 246) attained by the typical elements in each Group is equal to the Group number. The first elements in each Group cannot, for the reasons given above, attain these oxidation numbers. Maximum oxidation numbers are shown below:

Group	I	II	III	IV	V	VI	VII	0
Period Li → Ne	1	2	3	4	3	2	1	0
Period Na → Ar	1	2	3	4	5	6	7	0

The common oxidation states for each Group, i.e. those most often met with in reasonably stable compounds, are as follows:

Group	I	II	III	IV	V	VI	VIII	0
Common oxidation states	+1	+2	+3	+4	−3 +3 +5	−2 +4 +6	−1 +5 +7	0

These oxidation states are discussed in detail in later Chapters.

A and B sub-Groups

Older forms of the Periodic Table contained A and B sub-Groups, which included the d-block elements. For example, the alkali metals were referred to as Group IA, and the coinage metals (Cu, Ag, Au) as group IB; Cr, Mo, and W were Group VIA, and O, S, Se, Te, and Po were Group VIB, etc.

There are certain similarities between the elements in the sub-Groups. For example, both Cr (in the old Group VIA) and S (in the old Group VIB) have a maximum oxidation state of + 6; they both form an acidic, volatile trioxide, and volatile compounds XO_2Cl_2. But the similarities are generally not great, and the A and B sub-Group notation has been discarded in favour of a number for each Group of elements in the s- and p-blocks, with separate treatment for the d-block elements.

Trends in compounds of the elements with oxygen and the halogens

The best compounds for illustrating trends in chemical properties within the Periodic Table are the oxides and halides.

(a) *Oxides*

There is a gradual change across a Period from strongly basic through amphoteric to strongly acidic, as the elements change from electropositive to electronegative. (If an explanation of the terms *acidic* and *basic* is required, see *Advanced Level Physical Chemistry*, p. 215ff. An *amphoteric* oxide is one which can dissolve in both acids and alkalis.) For example:

Group	I	II	III	IV	V	VI	VII
Oxide	Na_2O	MgO	Al_2O_3	SiO_2	P_4O_6	SO_2	Cl_2O
					P_4O_{10}	SO_3	Cl_2O_7
	basic		amphoteric	acidic			

The basic nature of oxides *increases* down a Group as electropositivity increases, provided the oxides show the elements in the same oxidation state. However, if a metal can form more than one oxide, *the higher the oxidation state of the metal, the more acidic the oxide* (see e.g. p. 394).

(b) *Halides*

The halides of the elements change from ionic to covalent across a

Period as electropositivity decreases. For example:

Group	I	II	III	IV	V	VI	VII
Chloride	NaCl	$MgCl_2$	$AlCl_3$	$SiCl_4$	PCl_3, PCl_5	S_2Cl_2	Cl_2
	ionic solids		easily sublimed solid	volatile and covalent			

The halides tend to become more ionic down a Group as electropositivity increases—generally less volatile, more resistant to hydrolysis, and easier to electrolyse when molten.

Questions

1. What, in electronic terms, is the characteristic chemical behaviour of a metallic element? Relate this behaviour to the characteristic nature of a metallic oxide, chloride and hydride, using the metal *potassium* in illustration.

2. Using the element *chlorine* in illustration, state in electronic terms the characteristic chemical behaviour of a non-metallic element. Relate this behaviour to the following facts: (a) a non-metal never displaces hydrogen from an acid to form a salt, (b) a non-metallic oxide is never basic, (c) a non-metal is characteristically a bad conductor of electricity.

3. State briefly how the 'reactivity series' of the metals has been arrived at. Place the metals Ag, Na, Mg, Zn and Pb in the order of this series. Justify your order by reference to (a) the behaviour of these metals with (i) water, (ii) dilute hydrochloric acid, (b) the action of heat on the nitrates and carbonates of the metals.

4. Calcium is classified as a metallic element in Group II of Mendeléeff's Periodic Table; sulphur is classified as a non-metal in Group VI of the table. Justify these placing fully by reference to the properties of these elements and their important compounds.

5. By reference to the properties of the elements, their oxides and hydrides, consider the statement that the elements of Group IV of the Periodic Table (C, Si, Sn and Pb) change from non-metallic to metallic in nature as their atomic masses increase.

6. Relate the classification of elements in the Periodic Table, from He to Ca, to the electronic arrangements shown in the atoms of these elements. How do these electronic arrangements determine the ability of these elements to enter into chemical combination?

7. This question is concerned with the elements of the second short period of the Periodic Table (sodium to argon inclusive). Discuss the trends observed on going across this period by reference to the following: (a) the reaction of the elements with dilute sulphuric acid; (b) the physical properties of the chlorides of these elements; (c) the action of water on these chlorides; (d) the chemical bonding present in the chlorides; (e) methods suitable for the preparation of the chlorides. Your answer to each section should be given separately. (L.)

8. Illustrate the gradation of properties across a short period of the Periodic

Table by considering for the elements lithium to fluorine (but excluding boron) the hydrides formed by each element, their bonding and their characteristic physical and chemical properties. (O.)

9. (a) Illustrate one of the trends in the Periodic Table by considering the acid-base properties of the oxides of formula, Na_2O, CaO, Al_2O_3, SiO_2 and P_2O_5.

(b) Rubidium follows potassium in Group I of the Periodic Table. From your knowledge of the chemistry of potassium and sodium and their compounds, discuss the properties you would expect to find for rubidium, and for its hydride, hydroxide and carbonate. (O.)

10. (a) Describe briefly *any two* developments which led to the modern form of the Periodic Table.

(b) In early forms of the Periodic Table certain elements were incorrectly placed. Name *two* such elements and explain why they were incorrectly placed.

(c) 'The properties of elements are *periodic functions* of their atomic numbers.' Explain the term in italics. Name *three* properties to which this statement refers and show by means of a labelled diagram the relationship which exists between *one* of them and atomic numbers.

(d) Give *two* reasons why hydrogen could be included with the alkali metals and *two* reasons why it could be included with the halogens. (A.E.B.)

11. (a) Describe and suggest reasons for the trends across and down the Periodic Table in (i) atomic radius, (ii) atomic volume and (iii) electronegativity.

(b) Discuss the bonding in (i) sodium chloride and (ii) hydrogen chloride.

(c) Describe and account for the bonding you would expect to be present in (i) rubidium chloride and (ii) iodine chloride (ICl). (J.M.B.)

12. 'The properties of the first member of a group of elements in the Periodic Table are not typical of the group as a whole.'

Discuss this with reference to the chemistry of the elements of Groups I (Li to Cs) and II (Be to Ba). You should include in your answer specific properties which differentiate lithium and beryllium as well as the reasons for the differentiation from other members of their respective groups. (J.M.B.)

13. The following is a table of electronegativities of some elements on a common scale:

Element	F	Cl	Br	Sn	Cs
Electronegativity	3.98	3.16	2.96	1.96	0.79

(a) (i) Explain the term electronegativity.
(ii) Account for the relative values of the electronegativities of the halogens.

(b) Show how the polarity of a covalent bond can be predicted using values of electronegativities.

(c) Name and describe the bonding present in caesium chloride and tin(IV) chloride. Show how the physical properties, melting point, boiling point, and hardness, of these two compounds can be related to the type of bonding present. (J.M.B.)

14. This question concerns the following elements whose electronegativities are listed

Al	1.5	C	2.5	H	2.1	N	3.0	P	2.1
B	2.0	Cl	3.0	Li	1.0	Na	0.9	S	2.5
Be	1.5	F	4.0	Mg	1.2	O	3.5	Si	1.8

(a) What is meant by the term *electronegativity*? What factors determine the electronegativity of an element?

(b) Arrange the elements according to their positions in the Periodic Table.

(c) What is the relationship between electronegativity and the position of elements (i) in a period, (ii) in a group?
In each case give a brief explanation.

(d) In what major respect do electronegativity and electron affinity differ?

(e) Arrange the following substances in order of increasing ionic character (i.e. putting the least ionic first).

$$CO_2,\quad LiCl,\quad MgF_2,\quad NaCl,\quad NH_3,\quad S_2Cl_2.$$

(f) State, with reasons, how you would expect electronegativity values to vary, if at all, across the first row of transition elements. (A.E.B.)

2

Elements of Group 0: The noble gases

Discovery of the noble gases

In 1894, Lord Rayleigh was engaged on the accurate determination of the densities of common gases. His work on nitrogen produced a most unexpected result. Several samples of nitrogen were prepared chemically by reactions such as the following:
Heating ammonium nitrite:

$$NH_4NO_2(aq) \rightarrow N_2(g) + 2H_2O(l)$$

Passing nitrogen oxide (nitric oxide) over red-hot iron:

$$4NO(g) + 3Fe(s) \rightarrow Fe_3O_4(s) + 2N_2(g)$$

After purification, all these chemically prepared samples of nitrogen showed constant densities. Agreement among them was well within the limits of experimental error, and the averaged value for the density of the gas was 1.2505 g dm^{-3} at s.t.p.

Also, samples of nitrogen were prepared from the atmosphere, the oxygen content of the air being removed in different ways. After full purification all these samples of atmospheric nitrogen showed a constant density but the values were about 0.5% higher than those for the chemically prepared samples, at an average value of 1.2575 g dm^{-3} at s.t.p. This was much outside possible experimental error.

Rayleigh and Ramsay attacked the problem in two ways. The more successful of them was to pass a quantity of air repeatedly over red-hot copper to absorb oxygen and red-hot magnesium to absorb nitrogen (as Mg_3N_2). The apparatus also included drying-tubes containing phosphorus(V) oxide, and soda-lime tubes to extract carbon dioxide. Eventually, a constant volume of gas remained, occupying only about 1% of the original volume of air. Its density relative to hydrogen was 19.94, against an original density of air of about 14.4. This residue was found to be inert towards heated metals, acids and alkalis, oxidizing agents, and other gases such as chlorine, oxygen, and fluorine. The gas was named argon (the Greek word for inactive).

Ramsay also used a modernized form of an experiment of Cavendish (1785). Cavendish had passed electric sparks through a mixture of air and oxygen, converting the nitrogen of the air to nitrogen dioxide. This gas and excess of oxygen were absorbed in 'liver of sulphur', i.e. a solution of potassium sulphide. A small volume of gas remained, estimated by Cavendish at about 1/120th of the volume of air used. This was mainly argon, but it went unrecognized.

The actual discovery of argon in the 1890s created great interest and some excitement in the chemical world, not merely because of its occurrence in so familiar a locale as the atmosphere, but because it appeared, at first as an awkward intruder, between potassium and calcium in the well-established Periodic Table of the elements. However, helium (which had previously been observed spectroscopically in the Sun), neon, krypton, and xenon were rapidly discovered and recognized as members of a complete new Group of the Table.

This Group was previously know as the Inert Gases or the Rare Gases. As will be seen, argon for one is certainly not rare, and xenon and krypton are not inert.

Helium

Helium is a gas with the following characteristics:

Relative atomic mass	4.003
Boiling point	4.2 K
Melting point	4 K at 100 atm
Solubility	0.0094 cm^3 in 1 cm^3 water at 273 K

Other than hydrogen, helium is the least dense element known; its density being 0.18 g dm^{-3} at s.t.p.

Isolation of helium

Helium is present in very minute proportions in the atmosphere (about 5 parts per million by volume). It is occluded in certain minerals containing radioactive metals, e.g. clèveite containing uranium, monazite containing thorium. The gas can be expelled by heating the minerals, preferably *in vacuo*. When prepared from clèveite, helium is accompanied by about 20% of nitrogen by volume.

Natural gas, occurring in Canada and in the United States, also contains helium though the amount is usually under 1% by volume. Accompanying gases can be removed by intense cooling and pressure, which liquefies them. Helium can be further purified by using the fact that, unlike most gases, it is not absorbed by charcoal at the temperature of liquid air.

Properties of helium

The gas is colourless, has no smell, and only a very slight solubility in water. It is monatomic. It was liquefied in 1908 by Onnes and solidified in 1926 by Keesom. At 2.18 K the liquid becomes a superfluid. Solidification required reduction of temperature to about 1 K and the application of pressure. Helium is chemically inert; it has not been found to form any true compounds. Like hydrogen, helium can diffuse through quartz at about 1400 K, and it diffuses slowly through glass at ordinary temperature.

Helium is a product of the radioactive disintegration of radium and similar elements; indeed, α-particles are helium nuclei. This is the source of the gas in clèveite. Helium is mainly composed of atoms, ^4_2He, but contains also a small proportion of the isotope, ^3_2He. Certain lines in the Sun's spectrum had been attributed to a hypothetical element, named helium, by Lockyer in 1868. These lines, especially a prominent yellow line, were found in the spectrum of the gas driven from clèveite, and the name was retained for it. This is why the name differs in ending from the-on of the other noble gases.

Uses of helium

(a) Helium is used in air-ships and in long-distance ballooning because of its low density and non-flammability. It is, however, expensive.
(b) Liquid helium is used to maintain certain metal alloys at temperatures low enough for them to become superconducting.
(c) A helium–oxygen mixture is used in deep-sea diving.
(d) Helium is used in thermometers for the measurement of very low temperatures.

Neon

This gas has the following characteristics:

Relative atomic mass	20.18
Boiling point	27 K
Melting point	24 K
Solubility	0.0114 cm^3 in 1 cm^3 water at 273 K

Isolation of neon

Neon occurs in the atmosphere (about 15 parts per million by volume) and is obtained by the fractional distillation of liquid air.

Properties of neon

The gas is colourless, has no smell, and is only slightly soluble in water. It is chemically inert and has never been found to form compounds. Like all the noble gases, it has a monatomic molecule, as is shown by the ratio of its specific heats ($C_p/C_v = 1.67$).

Neon has two principal isotopes, ${}^{20}_{10}Ne$ and ${}^{22}_{10}Ne$, with a very little of a third, ${}^{23}_{10}Ne$.

Uses of neon

Neon is used in 'neon signs' in advertising and display. When a high voltage is applied between electrodes in a glass tube containing neon at about 270 $N\,m^{-2}$ (2 mmHg) pressure, the gas gives a bright orange-red glow. With a trace of mercury present, a light blue glow is obtained.

Argon

This gas has the following characteristics:

Relative atomic mass	39.95
Boiling point	87 K
Melting point	84 K
Solubility	0.058 cm^3 in 1 cm^3 water at 273 K

Isolation of argon

Argon is obtained by the fractional distillation of liquid air. The atmosphere contains about 0.93% of argon by volume; in other words, there is about thirty times as much argon in the atmosphere as there is carbon dioxide. Argon is most certainly not a 'rare' gas.

Properties of argon

The gas is colourless, has no smell, and only slight solubility in water. It is monatomic. Argon has not been found to form any normal compounds. It forms a solid 'hydrate', $Ar.6H_2O$, and a 'compound' with 1,4-dihydroxybenzene (quinol). These materials are *clathrates*, i.e. 'cage' compounds in which the argon atoms are trapped in the lattice of the other material without any chemical bonds being formed by the argon. Argon has two principal isotopes, $^{40}_{18}Ar$ and $^{36}_{18}Ar$, with a little $^{38}_{18}Ar$.

Uses of argon

(a) Argon is used (usually mixed with about 5–10 per cent of nitrogen) in gas-filled electric light bulbs. It checks splintering of the filament and volatilization of material from it, which would blacken the bulb. It is too inert to react chemically with the filament. It is also used as part of the gas filling in fluorescent lamps.

(b) Argon is used as an inert atmosphere during the manufacture of titanium, and in the welding of titanium, aluminium, and stainless steel.

Krypton

This gas has the following characteristics:

Relative atomic mass	83.80
Boiling point	121 K
Melting point	104 K
Solubility	0.11 cm^3 in 1 cm^3 water at 273 K

Isolation of krypton

Krypton is obtained by the fractional distillation of liquid air, though it is present in the atmosphere to only a very minute extent (about 5 parts in 100 million by volume).

Properties of krypton

The gas is colourless, has no smell, and is slightly soluble in water. It is monatomic. It forms clathrates, as does argon. It is unreactive, and has been found to form only a few compounds (see below). The element has several isotopes with mass numbers ranging from 78 to 86; the two most abundant are $^{84}_{36}Kr$ and $^{86}_{36}Kr$.

Use of krypton

Krypton is used instead of argon in high efficiency, low voltage, electric lamps, e.g. miners' head lamps.

Xenon

This gas has the following characteristics:

Relative atomic mass	131.3
Boiling point	164 K
Melting point	133 K
Solubility	0.24 cm^3 in 1 cm^3 water at 273 K

Isolation of xenon

Xenon occurs in the atmosphere to the extent of only 6 parts by volume in 1000 million of air, but fractional distillation of liquid air is the only source of it.

Properties of xenon

Xenon is a colourless gas with no smell. It has a greater solubility in water than any other noble gas. It is monatomic. It forms clathrates, as do argon and krypton. There is now an extensive series of xenon compounds (see below). Xenon has several isotopes, the two most abundant being $^{132}_{54}Xe$ and $^{129}_{54}Xe$. The element has no common uses.

Radon

The element has the following characteristics:

Relative atomic mass	(222)
Boiling point	211 K
Melting point	202 K
Solubility	0.51 cm^3 in 1 cm^3 water at 273 K

Radon possesses three unstable isotopes. The most stable is $^{222}_{86}\text{Rn}$, which has a half-life of 3.8 days. Radon occurs in the atmosphere only to a very minute extent. It is formed when $^{226}_{86}\text{Ra}$ emits an α-particle. The very unstable isotopes, $^{219}_{86}\text{Rn}$ and $^{220}_{86}\text{Rn}$, are sometimes known as *actinon* and *thoron* respectively, because they occur in the radioactive decay series derived from actinium and thorium. The half-life of actinon is a few seconds, and that of thoron just under a minute.

General

Attention has already been drawn (*Advanced Level Physical Chemistry*, Chapters 6 and 7) to the important position occupied by the noble gases in theories of atomic structure and chemical bonding. Indeed, as indicated below, they were perhaps given too prominent a position in the historical and theoretical development of the subject.

It is worth noting the steady change in physical properties as relative atomic masses increase in this Group. This is not surprising since all the elements are monatomic and the only cohesive forces in the solid and liquid states will be very weak van der Waals' attractions (*Advanced Level Physical Chemistry*, p. 103).

The noble gas compounds

Until 1962, the only materials in which the noble gases appeared to form chemical bonds were the so-called '*clathrate compounds*'. These were shown to be not true compounds, but materials in which the gas atoms were trapped in 'cages' within the open crystal lattice of, for example, ice. In 1962 Bartlett found that the gas platinum hexafluoride, PtF_6 (cf. the gas UF_6, used in separating the fissionable isotope of uranium), could oxidize molecular oxygen and form the compound $O_2^+[PtF_6]^-$. Since the first ionization energy of xenon is in fact slightly less than that of the oxygen molecule, Bartlett deduced that PtF_6 should also react with xenon. The resulting yellow compound, although it was later shown to be more complex than the expected $Xe^+[PtF_6]^-$, was nonetheless the first compound of a noble gas ever made.

Since that time an extensive chemistry of xenon has been developed. Xenon can be made to react with fluorine under various conditions, and sometimes quite easily, to form the reasonably stable solids XeF_2, XeF_4, and XeF_6. These xenon fluorides can be used to form compounds containing xenon–oxygen bonds, such as XeO_3, $XeOF_4$, and $XeO_4{}^{2-}$; and even XeO_4 and $XeO_6{}^{4-}$, in which the oxidation state of xenon is + 8.

Not surprisingly, such xenate(VIII) compounds (perxenates) are among the most powerful known oxidizing agents.

Xenon will only form reasonably stable bonds with fluorine and oxygen, although a xenon chloride has been reported. A few fluoro-compounds of krypton are known, but no compounds of argon, neon or helium have so far been made. Compounds of radon are difficult to study because of the intense radioactivity and short half-life of radon.

XeF_2 is linear in shape and XeF_4 is square planar, but XeF_6 is a distorted octahedron, sometimes described as a 'floppy' molecule.

If the 'inert gas' theory of chemical bonding had not had such a strong hold on the minds of chemists and been taught so strongly at school and university, it is possible that compounds of the noble gases might have been made many years previously—as soon, indeed, as techniques for the safe handling of fluorine had been developed. The compounds of the noble gases provide us with an excellent example of the dangers of believing that a scientific theory is established fact, and of allowing accepted dogma to pass untested.

In 1933 Professor Don Yost, with A. Kaye, tried to prepare some xenon–halogen compounds. Addressing the first-ever international conference on noble gas compounds in 1963, Professor Yost said that: 'Quantum theory was coy about predicting the existence of stable noble gas compounds. With time it became virtually a *tradition* that such compounds could not exist in non-transitory form. Like many others in science and mathematics, this tradition now finds its resting place in Boot Hill, and we are all glad of it.... There may of course be some who say that if in spite of underdeveloped techniques we had worked harder and more exhaustively we would have succeeded in preparing one or more xenon fluorides. But the simple fact is that we didn't succeed. Mr Kaye and I will have to rest content with the fringe virtue of having said in print that we hadn't proved by our experiments that a xenon fluoride was *incapable* of existing'. The final sentence of this extract points another useful moral.

Questions

1. Write a general essay on the noble gases, covering their occurrence, extraction (in outline only) and uses, and considering their significance in the Periodic Table. Briefly discuss compound formation by these elements.

2. When the noble gas group of elements was discovered and entered late into the Periodic Table, it was designated 'Group 0'. Discuss the suitability of this numbering. By reference to examples drawn from this group, discuss (a) some uses of the elements, (b) methods of extraction, (c) isotopy, (d) the significance of Group 0 elements in theories of chemical bonding.

3

Hydrogen

Occurrence

Although most of the mass of the known Universe consists of hydrogen, since hydrogen is the fundamental material from which stars are formed, it is present to less than one per cent by mass in the crust of the Earth. Free hydrogen occurs in the atmosphere, but only in very small amounts. Small amounts of the gas are found occluded in a few minerals, e.g. in serpentine and blue clay, but almost all terrestrial hydrogen occurs in combination. It constitutes one-ninth by mass of the water of the rivers, lakes, and oceans; it occurs in the hydrocarbons of petroleum, C_nH_{2n+2}; as a constituent of coal; in hydrated minerals such as gypsum, $CaSO_4.2H_2O$, the hydrated aluminium silicate of clay, $Al_2Si_2O_7.2H_2O$, and a host of others; and in all animal and vegetable organisms.

Usual laboratory preparation of hydrogen

The most convenient way of preparing hydrogen in the laboratory is by the action of dilute hydrochloric acid (about 2 mol dm^{-3}) on granulated zinc (Figure 3.1).

$$Zn(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g)$$

Prepared in this way, hydrogen is likely to contain impurities such as sulphur dioxide, hydrogen sulphide, phosphine, and arsine, derived from impurities in the zinc. The same reaction occurs with dilute sulphuric acid, but is often too slow to be useful. It may be speeded up by addition of a little copper(II) sulphate solution.

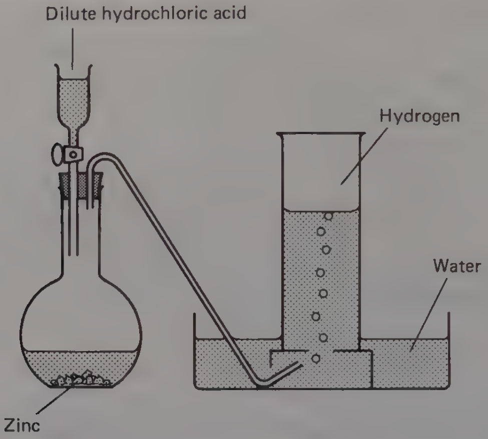


Figure 3.1 *Laboratory preparation of hydrogen*

Purification of hydrogen

After sweeping out air from the apparatus for a few minutes, the hydrogen may be purified by passing it through:

(a) saturated potassium manganate(VII) solution to remove reducing gases such as sulphur dioxide or hydrogen sulphide;

(b) 10% silver nitrate solution to remove any remaining amounts of phosphine (PH_3) or arsine (AsH_3);

(c) red-hot copper turnings to remove any oxygen.

The gas may then be dried over anhydrous, granular, calcium chloride. Concentrated sulphuric acid should not be used as drying agent because it is reduced slightly by hydrogen even at ordinary temperature.

$$H_2SO_4(l) + H_2(g) \rightarrow 2H_2O(l) + SO_2(g)$$

Such purified gas would probably be put to some experimental use, not collected; small amounts could be collected over mercury. The dry gas may also be collected by upward delivery in air, but then it is almost impossible to get rid of air as an impurity.

Other methods of preparing hydrogen on the laboratory scale

The following methods are little used as preparations but the reactions should be noted. Method 1(b) provides a method of manufacture. They may be grouped under the headings:

(1) from water; (2) from acids; (3) from alkalis; (4) from metallic hydrides.

1. *From water*

(a) *By the action of metals.* Sodium and potassium attack cold water vigorously. In the case of potassium, the hydrogen usually burns (with a flame tinged lilac by the potassium vaporized). Calcium and lithium attack cold water more slowly. The essential reaction is reduction of protons from the water by the metal atoms, so that the hydroxide of the metal is formed.

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$$

Then, for example: $2Na(s) + 2H^+(aq) \rightarrow 2Na^+(aq) + H_2(g)$

Overall: $2Na(s) + 2H_2O(l) \rightarrow 2NaOH(aq) + H_2(g)$

For calcium the overall equation is:

$$Ca(s) + 2H_2O(l) \rightarrow Ca(OH)_2(s) + H_2(g)$$

In this case, enough of the calcium hydroxide dissolves to make the solution alkaline; much of the solid remains in suspension to give the liquid a milky appearance (see p. 89).

Strongly heated zinc, magnesium, and iron decompose steam passed over them, liberating hydrogen. Metallic oxides are produced, not hydroxides, which are unstable at the temperatures employed.

$$\begin{aligned} Zn(s) + H_2O(l) &\rightarrow ZnO(s) + H_2(g) \\ Mg(s) + H_2O(l) &\rightarrow MgO(s) + H_2(g) \\ 3Fe(s) + 4H_2O(l) &\rightleftharpoons Fe_3O_4(s) + 4H_2(g) \end{aligned}$$

(b) *By the action of carbon or hydrocarbons.* Carbon, at 1300 K and higher temperatures, decomposes steam to produce water gas, containing (if pure) equal volumes of carbon monoxide and hydrogen.

$$C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$$

The water gas process is considerably more complex than this, and is dealt with more fully on p. 142.

If steam is heated with methane or the naphtha fraction from an oil refinery, *synthesis gas* is formed. For example, if methane is heated with steam under suitable conditions the reaction can be represented by:

$$CH_4(g) + H_2O(g) \rightarrow CO(g) + 3H_2(g)$$

Synthesis gas and water gas are used for the manufacture of hydrogen (see p. 31)

(c) *By electrolysis.* Water acidified by sulphuric acid is usually used in the laboratory for preparation of hydrogen by electrolysis. Platinum electrodes are suitable and the hydrogen is produced at the cathode.

$$2H^+(aq) + 2e^- \rightarrow H_2(g)$$

2. *Preparation of hydrogen from acids*

The use of zinc with dilute hydrochloric acid has already been described in this chapter.

All metals which are more electropositive than hydrogen liberate it from some acid, as in the examples below:

$$Mg(g) + 2H^+(aq) \rightarrow Mg^{2+}(aq) + H_2(g)$$

(dilute $HCl(aq)$ or $H_2SO_4(aq)$)

$$Fe(s) + 2H^+(aq) \rightarrow Fe^{2+}(aq) + H_2(g)$$

(dilute $HCl(aq)$ or $H_2SO_4(aq)$)

$$2Al(s) + 6H^+(aq) \rightarrow 2Al^{3+}(aq) + 3H_2(g)$$

(dilute $HCl(aq)$ with heat)

The action of zinc is the most convenient for laboratory preparations of hydrogen.

3. *Preparation of hydrogen from alkalis*

Zinc, aluminium, and silicon will all react with caustic alkali solution to liberate hydrogen. Powdered aluminium reacts with cold dilute caustic alkali (about 2 mol dm^{-3}) very rapidly; aluminium foil requires heat to start the reaction. Zinc and silicon both require heat.

$$2Al(s) + 2OH^-(aq) + 10H_2O(l) \rightarrow 2[Al(H_2O)_2(OH)_4]^-(aq) + 3H_2(g)$$

aluminate(III) ion

$$Zn(s) + 2OH^-(aq) + 2H_2O(l) \rightarrow [Zn(OH)_4]^{2-}(aq) + H_2(g)$$

zincate(II) ion

$$Si(s) + 2OH^-(aq) + H_2O(l) \rightarrow SiO_3{}^{2-}(aq) + 2H_2(g)$$

silicate(IV) ion

4. *Preparation of hydrogen from metallic hydrides*

The salt-like hydrides of lithium, sodium, potassium, and calcium react rapidly with cold water liberating hydrogen. The hydroxides of the metals are formed.

$$H^-(s) + H_2O(l) \rightarrow OH^-(aq) + H_2(g)$$

Industrial manufacture of hydrogen

(a) *Manufacture from methane and petroleum*

Hydrogen can be made by heating steam with either methane or the naphtha fraction from the distillation of crude oil, and then removing the carbon monoxide which is also formed. The hydrocarbon–steam mixture is heated to about 1200 K at a total pressure of 30 atm (about $3 \times 10^6\ \mathrm{N\,m^{-2}}$) in the presence of a nickel catalyst. The product is called *synthesis gas.*

For methane, the equation is:

$$CH_4(g) + H_2O(g) \rightarrow CO(g) + 3H_2(g)$$

The synthesis gas is then further heated with an excess of steam at 700 K and 30 atm in the presence of an iron catalyst.

$$CO(g) + 3H_2(g) + H_2O(g) \rightarrow CO_2(g) + 4H_2(g)$$

Carbon dioxide and the last traces of carbon monoxide can be removed as in the water gas process below.

(b) *Manufacture from water gas—the Bosch process*

For many years the starting material for the manufacture of hydrogen was coal, in the form of coke. As petroleum becomes scarcer and more expensive, this process may regain its former importance.

Steam is passed through a mass of coke at a minimum temperature of 1300 K. This produces water-gas. For details see p. 142.

$$C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$$

The water-gas is mixed with more steam and passed over a heated catalyst consisting of iron(III) oxide, Fe_2O_3, activated by chromium(III) oxide as promoter. This doubles the hydrogen yield and converts carbon monoxide to carbon dioxide, which is removed by solution in water at about 30 atm pressure, or by bubbling the gases through an alkali.

$$CO(g) + H_2(g) + H_2O(g) \rightarrow CO_2(g) + 2H_2(g)$$
$$CO_2(g) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$$

Remaining traces of carbon monoxide can be removed by passing the gases through an ammoniacal solution of copper(I) methanoate under pressure, or by absorption in molten sodium hydroxide under pressure to form sodium methanoate, $HCOO^-Na^+$.

(c) *By 'platforming'*

In 'platforming' processes in the petroleum industry, cyclohexane and similar saturated hydrocarbons are passed over a catalyst consisting of platinum spread on alumina as carrier. Pressures between 10 and 50 atm are used, and a temperature of about 770 K. Hydrogen is liberated and aromatic hydrocarbons produced. For example:

$$C_6H_{12}(g) \rightarrow C_6H_6(g) + 3H_2(g)$$

(d) *By electrolysis*

Hydrogen is obtained as a by-product in the manufacture of chlorine and sodium hydroxide by the electrolysis of brine (see p. 50).

Industrial uses of hydrogen

(a) *For the manufacture of ammonia (Haber's process)*

Hydrogen is used for this on a very large scale. Nitrogen obtained from the air (1 volume) is mixed with hydrogen (3 volumes). The gases are combined in the following conditions:

very high pressure (200–1000 atm, $2 \times 10^7 - 10^8$ N m^{-2})
670–770 K
with a catalyst (finely divided reduced iron activated by alkali or aluminia)

For fuller details of Haber's process, see p. 216.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

(b) *Hydrogen in the manufacture of margarine*

In a general way, fats are esters derived from the organic compound glycerol (propane-1,2,3-triol) and an acid of the type $C_nH_{2n+1}COOH$. For example, the chief constituent of beef and mutton fat is tristearin, of which the acid is octadecanoic acid (stearic acid), $C_{17}H_{35}COOH$. The liquid vegetable and animal oils, such as olive oil and whale oil, are similar, but the acid here is of the type $C_nH_{2n-1}COOH$, e.g. *cis*-octadec-9-enoic acid (oleic acid), $C_{17}H_{33}COOH$. Margarine manufacture converts oils to fats by providing the missing atoms.

The oil is heated at about 450 K with finely divided nickel present as catalyst. Hydrogen is passed in at about 5 atm (500 000 N m^{-2}) pressure. The unsaturation in the molecule of the oil is destroyed by the essential reaction:

$$\text{—CH=CH—} + H_2(g) \rightarrow \text{—}CH_2\text{—}CH_2\text{—}$$

The product is a fat which solidifies on cooling. It can be improved in texture by mechanical treatment and coloured yellow to simulate butter, and is then known as margarine.

(c) *Hydrogenation of coal*

The aim of this process is to convert coal into oil. Powdered coal is dispersed in heavy oil to make it flow and is subjected to the action of hydrogen at high pressure (about 250 atm, 2.5×10^7 N m^{-2}) and about 770 K with a catalyst present. Various catalysts have been tried, among them tin(II) ethanedioate and a mixture of 'molybdic acid' and sulphur. The resulting oil can be distilled to give petrol, lubricating oil and other fractions resembling those from natural petroleum.

(d) *Hydrogen in the manufacture of organic chemicals*

Hydrogen is a gas of rapidly increasing value in the production of organic chemicals. It is impossible to give a complete account of these processes for reasons of space. A typical case is the manufacture of methanol. Water-gas is mixed with hydrogen and passed over a mixture of zinc and chromium(III) oxides at about 720 K and 200 atm. Other products appear in small amount, e.g. propan-1-ol, $CH_3CH_2CH_2OH$.

$$CO(g) + 2H_2(g) \rightarrow \underset{\text{methanol}}{CH_3OH(l)}$$

(e) *Use of hydrogen for lifting*

At s.t.p. the mass of 1 dm^3 of hydrogen is 0.09 g, and the mass of 1 dm^3 of air is 1.29 g. Consequently, the theoretical lift per dm^3 of hydrogen at s.t.p. is 1.20 g, including the mass of the containing vessel. This is the maximum lift attainable but hydrogen suffers from the very severe defect of being dangerously flammable. This use of hydrogen is now limited to small-scale vessels for military and meteorological purposes. Helium has been used in airships (see p. 21).

Properties of hydrogen

Physical properties

Hydrogen is a colourless, odourless gas with the following characteristics:

Density	0.0899 g dm^{-3} at s.t.p. It is the least dense gas known.
Boiling point	20 K
Melting point	14 K
Solubility	0.0215 cm^3 in 1 cm^3 water at 273 K

Chemical properties

Hydrogen shows four important types of combination:

(a) Electrovalency in forming the hydrogen ion, H^+, hydrated in water as the ion, H_3O^+, and other hydrated-proton species.
(b) Electrovalency in forming the ion, H^-.
(c) Covalency.
(d) Hydrogen bonding.

Its chemical properties will be related to these modes of combination:

1. *Formation of ion,* H^+, *or* H_3O^+. This ion occurs in all aqueous solutions, because of the ionization of water, and in higher concentrations in acidic solutions. The ionization of, for example, hydrogen chloride in water can be written either as:

$$HCl(g) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)$$

or as: $$HCl(g) + aq \rightarrow H^+(aq) + Cl^-(aq)$$

Since the ion H_3O^+ is only one of the hydrated species found in the solution, the latter form of the equation is preferred.

Simple ionization of the hydrogen atom by loss of one electron would produce the hydrogen ion or proton, but in water it is invariably hydrated as shown. It is responsible for the following typical acidic properties.

(a) Change of colour in certain indicators, e.g. litmus to red, methyl orange to pink.
(b) Liberation of hydrogen with the more electropositive metals, e.g.:

$$Zn(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g)$$

(c) Neutralization of bases, the essence of which is the reaction:

$$H^+(aq) + OH^-(aq) \rightleftharpoons H_2O(l)$$

i.e. the reverse of the ionization of water.

(d) Liberation of carbon dioxide from carbonates:

$$2H^+(aq) + CO_3^{2-}(aq) \rightarrow H_2O(l) + CO_2(g)$$

2. *Formation of the ion,* H^-. Here the hydrogen atom forms an electron pair by accepting an electron from a strongly electropositive metal. Only metals of this type produce such hydrides. If lithium, sodium,

potassium, or calcium are heated in a current of dry hydrogen to about 600 K, the corresponding hydride is formed, e.g.:

$$2Na(l) + H_2(g) \rightarrow 2(Na^+H^-)(s)$$
$$Ca(s) + H_2(g) \rightarrow Ca^{2+}2H^-(s)$$

Lithium hydride can be used to make the complex hydride lithium tetrahydriodoaluminate(III) ('lithium aluminium hydride'), $LiAlH_4$

$$4LiH(s) + AlCl_3(s) \xrightarrow{\text{ether}} LiAlH_4(s) + 3LiCl(s)$$

This is used in ethoxyethane (ether) solution as a powerful reducing agent, particularly in organic chemistry. Sodium tetrahydridoborate(III) ('sodium borohydride'), $NaBH_4$, is also an excellent reducing agent, and unlike $LiAlH_4$ is soluble in water.

3. *Covalent compounds of hydrogen.* The number of these is very great. The following are typical. With *chlorine* at ordinary temperatures, hydrogen combines not at all in darkness, slowly in daylight and explosively in sunlight. Hydrogen burns in chlorine with a whitish flame and explodes with it if sparked. The product in all these cases is hydrogen chloride.

$$H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$$

With *oxygen*, hydrogen combines with dangerously explosive violence if sparked or heated to about red heat. Water vapour is catalytic to the reaction. Hydrogen also burns in oxygen or air. The product is water.

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$$

The oxy-hydrogen blow-pipe gives a temperature of about 3100 K and will melt platinum. It has been used in certain forms of welding.

Hydrogen will also combine directly, though only slightly, with *sulphur* at its boiling-point (717 K) to form hydrogen sulphide, H_2S, with *nitrogen* to give ammonia, NH_3 (see Haber's process, p. 216), and with *carbon* at about 1500 K to give methane, CH_4.

4. *Hydrogen bonding.* This is fully considered in Chapter 9 of *Advanced Level Physical Chemistry.*

Hydrogen as a reducing agent

At red heat, hydrogen acts as a reducing agent towards many metallic oxides. It makes electrons available by the reaction:

$$O^{2-} + H_2(g) \rightarrow H_2O(l) + 2e^-$$

and the electrons are taken up by the metallic ion, which is reduced, e.g.

$$Cu^{2+} + 2e^- \rightarrow Cu(s)$$

Such reactions are usually written thus:

$$CuO(s) + H_2(g) \rightarrow Cu(s) + H_2O(l)$$
$$PbO(s) + H_2(g) \rightarrow Pb(s) + H_2O(l)$$
$$Fe_2O_3(s) + 3H_2(g) \rightarrow 2Fe(s) + 3H_2O(l)$$

Hydrogen will not reduce the oxides of the more electropositive metals; the oxides of sodium, potassium, calcium, magnesium, aluminium, and zinc are unaffected by heating in hydrogen.

Molecular hydrogen is, for practical purposes, incapable of reducing materials in aqueous solution. Many substances unaffected by the passage of hydrogen gas can, however, be reduced if placed in an aqueous mixture in which hydrogen is being generated by chemical action (including electrolysis). Suitable sources of reduction in such cases are:

zinc and dilute sulphuric acid (acidic conditions)
sodium amalgam and dilute sulphuric acid (acidic conditions)
zinc or aluminium and caustic soda solution (alkaline conditions)
sodium amalgam and water (alkaline conditions)
zinc–copper or aluminium–mercury couple and water (neutral conditions)
sodium and ethanol (suitable for reducing many organic compounds)

Such reductions have been ascribed in the past to nascent hydrogen, that is, to hydrogen at the moment of its chemical production. This is incorrect. The reduction is brought about by electrons supplied by the metal, and this is helped by the solvent. The release of hydrogen from the solvent by action of the metal is, in these cases, merely a side-reaction.

Atomic hydrogen

Langmuir (1912) showed that hydrogen at low pressure in contact with an electrically heated tungsten wire (temperature in excess of 2300 K) dissociated to some extent into the atomic state with great absorption of heat:

$$H_2(g) \rightarrow 2H(g) \quad \Delta H = +436 \text{ kJ mol}^{-1}$$

Atomic hydrogen is more effectively produced at atmospheric pressure by blowing hydrogen through an electric arc struck between tungsten electrodes. It is estimated that the hydrogen is about 60% dissociated at 4300 K. If the stream of atomic hydrogen is blown rapidly out of the tungsten arc, the atomic hydrogen will become molecular again with great liberation of heat as the H—H bonds are remade. Obviously, for recombination to occur the energy released must be removed, as otherwise it will be exactly the energy needed to break the bonds. A metal surface is suitable for this. If projected as a jet, atomic hydrogen has great heating effect and will even melt tungsten (m.p. 3670 K).

Occlusion behaviour of hydrogen

About the middle of the nineteenth century, Graham showed that hydrogen passes readily through both platinum and palladium at red-heat. If, however, palladium was heated to only about 370 K in hydrogen for some time, allowed to cool in the gas and then re-heated to about 520 K, the palladium gave out about 500 times its own volume of hydrogen. Hydrogen taken into palladium in this way is said to be *occluded*. Later work has shown that the metal occludes the gas most effectively when in a state of fine division, and may take in up to 900 times its own volume in favourable conditions. Rise of temperature reduces occlusion. If a palladium cathode is used in the electrolysis of water, no gaseous hydrogen will appear at the cathode until the metal is saturated with occluded hydrogen. Such a cathode then has strong reducing properties; it will liberate mercury from mercury chloride and convert iron(III) salts in solution to iron(II) salts.

$$Hg^{2+}(aq) + 2e^- \rightarrow Hg(l); \quad Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$$

This phenomenon of occlusion has been much investigated. The formation of various compounds has been claimed, but the accepted explanation involves the formation of a non-stoichiometric *interstitial compound*. To form this, the palladium lattice is not changed except to expand in all three dimensions and fit hydrogen atoms into the tetrahedral spaces between the atoms of palladium. Interstitial hydrides occur with some other metals, and are always formed with decreasing density because of the expansion of the metallic lattice. Salt-like hydrides of the CaH_2 type are denser than the metal.

Ortho-hydrogen and para-hydrogen

The hydrogen molecule contains two nuclei (protons) and two electrons. The electrons are paired with *opposed* spins or, by the Pauli exclusion principle, the molecule would not be stable.

The two protons, however, may have their spins in the same or opposite senses. If the same, the spins are said to be *parallel*, and the molecule is known as *ortho*-hydrogen. If opposed, the spins are said to be *anti-parallel*, and this gives *para*-hydrogen. Ordinary hydrogen at room temperature contains 25 per cent of the *ortho-* and 75 per cent of the *para*-type. *Ortho-* and *para*-hydrogen show no appreciable chemical differences; but they differ physically, especially in thermal conductance and specific heat. The *para*-variety has somewhat higher vapour pressure than ordinary hydrogen at corresponding temperatures. The *para*-form is the more stable, and the proportion of it in the mixture increases as the temperature is lowered.

Isotopy of hydrogen

Hydrogen exists in three isotopic forms, each with one electron and one proton, and with no neutron, one neutron and two neutrons respectively, as:

$^{1}_{1}H$	$^{2}_{1}D$	$^{3}_{1}T$
Protium	deuterium	tritium

Ordinary hydrogen is almost all protium. It has only a very small proportion of deuterium (1 in 4500) and no tritium to speak of. Tritium is formed by bombardment of lithium-6 with neutrons:

$$^{6}_{3}Li + ^{1}_{0}n \rightarrow ^{4}_{2}He + ^{3}_{1}H$$

The isotopes behave in the same way chemically, although the rates of reactions differ. Because of the large relative differences in mass, the physical properties of the isotopes differ considerably.

Deuterium is used as an isotopic 'label' in studying the mechanisms of organic reactions.

Tritium emits β-particles and has a half-life of 12.3 years. It has also been used as a 'label'.

If ordinary water is electrolysed over a long period the deuterium oxide in it becomes more concentrated, and can eventually be isolated. This is because ordinary hydrogen is liberated much more readily than deuterium.

Hydrogen and the Periodic Table

Hydrogen is difficult to classify in the Table. In one respect, it resembles the alkali metals, being able to ionize by loss of one electron per atom, though in aqueous solution the positive ion, or proton, is hydrated.

$$(H) - e^- \rightarrow H^+; \quad H^+ + aq \rightarrow H^+(aq)$$

Compare $Na - e^- \rightarrow Na^+$

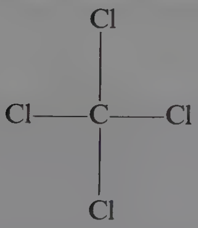
To this extent, hydrogen could be placed in Group 1 with the alkali metals.

Alternatively, hydrogen may behave like a halogen. In the same way as chlorine, it can take up one electron per atom, either by electrovalence or by covalent sharing, to produce a duplet of electrons resembling that of the helium atom. For example, in the alkali-metal hydrides, it forms the univalent anion, H^-.

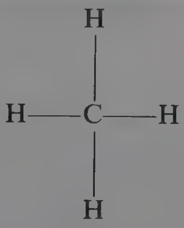
$$\tfrac{1}{2}H_2 + e^- \rightarrow H^-$$

$$\text{Compare} \quad \tfrac{1}{2}Cl_2 + e^- \rightarrow Cl^-$$

In many organic compounds, hydrogen combines by shared-pair covalency as chlorine does. Compare the compounds:



$$\begin{array}{ccc} & Cl & \\ & | & \\ Cl - & C & - Cl \\ & | & \\ & Cl & \end{array}$$



$$\begin{array}{ccc} & H & \\ & | & \\ H - & C & - H \\ & | & \\ & H & \end{array}$$

To this extent, hydrogen can be placed in Group VII. But the similarities with Group I and Group VII elements are only very limited; and hydrogen is best placed by itself at the head of the Table, associated with no particular Group.

Questions

1. Give an account of (a) *two* essentially different methods of preparing hydrogen in the laboratory, (b) *one* method of large scale preparation of this gas. Describe, in essential outline, *two* industrial uses of hydrogen.

2. Discuss the behaviour of hydrogen (a) as a reducing agent, (b) as an oxidising agent (i.e. an electron acceptor). Illustrate suitably.

3. Compare and contrast the physical and chemical properties of the simple hydrides of each of the following elements:

sodium, calcium, carbon, nitrogen, oxygen, and fluorine.

In your answer attempt to relate these properties to the type of bonding encountered in these hydrides. (L.)

4. Write a short account of the position of hydrogen in the Periodic Table. Give the name of (a) an ionic hydride, (b) a covalent hydride. In each case describe the formation and give the structure of the compound.

A solution of Fe^{3+} ions in dilute sulphuric acid is unaffected by the passage of hydrogen gas, but if metallic zinc is added reduction to Fe^{2+} occurs. Explain this in electronic terms.

The masses of equal volumes of hydrogen and a gas *Y* at the same temperature and pressure are 0.064 g and 0.576 g respectively. Calculate the relative molecular mass of *Y*. (A.E.B.)

5. (a) Give one example in each case of the formation of hydrogen from (i) a named acid, (ii) a named alkali, (iii) water.
   (b) Describe the structures of (i) sodium hydroxide, (ii) water, (iii) the oxonium ion (H_3O^+).
   (c) Explain why
      (i) water has a higher boiling point than hydrogen sulphide;
      (ii) hydrogen iodide is a stronger reducing agent than hydrogen chloride;
      (iii) the acidity of the hydrides of the elements from sodium to chlorine in the Periodic Table increases from left to right.
   (d) Deuterium, D, is an isotope of hydrogen. Starting with deuterium oxide, describe briefly how you would prepare (i) ND_3, (ii) C_2D_2. (A.E.B.)

4

Elements of Group I: The alkali metals

Group I includes the elements from lithium to caesium, usually referred to as the *alkali metals*. These form a very closely related group of elements. The main resemblances are:

(a) All are strongly electropositive and in their compounds show a constant oxidation state of +1. The electropositivity increases with relative atomic mass.
(b) All form strongly basic oxides, and their hydroxides are soluble in water forming alkalis. They do not form basic salts.
(c) All attack water, forming a hydroxide and hydrogen.
(d) All form hydrides of electrovalent type, $X^+ \ H^-$; all these yield hydrogen when water is added.
(e) Except for some salts of lithium, salts of these metals are almost all soluble in water.

The above similarities arise from the fact that all the elements show, in their electron structure, a single valency electron outside an octet or duplet, as:

Li	2.1
Na	2.8.1
K	2.8.8.1
Rb	2.8.18.8.1
Cs	2.8.18.18.8.1

Because of the shielding of this outer electron from the attraction of the nucleus by completed shells of electrons, the first ionization energies of these elements are very low, and decrease with increasing numbers of shielding shells. Hence the elements are all very reactive as metals, and reactivity increases down the Group.

In general, the hydroxides, carbonates, and sulphates of Group I are more stable to heat than those of other metals, and their nitrates do not decompose in the usual way.

Lithium

The metal is usually extracted by the electrolysis of fused lithium chloride, using a carbon anode and an iron cathode. Lithium resembles sodium and potassium in appearance, being silvery white, but is harder than either. It gives a carmine red flame-colour. It reacts with cold water comparatively slowly to form its hydroxide and liberate hydrogen.

$$2Li(s) + 2H_2O(l) \rightarrow 2LiOH(aq) + H_2(g)$$

Lithium is not a completely typical metal of Group I, because of the small size of its atom and consequent comparative lack of electropositive character. It shows general resemblance to the other metals of this Group in its oxidation state of + 1, general chemical activity, reaction with water and physical characteristics. But, in some respects, it resembles the elements of Group II. It can be said to have a 'diagonal relationship' (p. 9) with magnesium.

(a) Lithium chloride, LiCl, is very soluble in water and deliquescent like calcium chloride. Sodium and potassium chlorides are less soluble and not deliquescent.
(b) Lithium carbonate, Li_2CO_3, is only sparingly soluble in water and can be precipitated. This shows resemblance to magnesium and calcium carbonates, but sodium and potassium carbonates are easily soluble in water.
(c) Lithium phosphate(V), Li_3PO_4, is almost insoluble in water like $Ca_3(PO_4)_2$, but the corresponding salts of sodium and potassium are soluble.
(d) Lithium fluoride is almost insoluble in water like CaF_2; the fluorides of both sodium and potassium are soluble.

Sodium

Atomic number 11; electron arrangement 2.8.1 ($1s^2 2s^2 2p^6 3s^1$)
Sodium has only one isotope: mass number 23; relative atomic mass 22.99

Occurrence

Sodium compounds are very widely distributed in nature, the following being the principal modes of occurrence:

(a) *As common salt, sodium chloride*, NaCl. This compound occurs as rock salt in many areas, such as Cheshire and Worcestershire (England), Stassfurt (Germany), Castile (Spain), California, New York, Virginia and Ohio (USA) and in many other places. Sodium chloride also occurs in sea-water to the extent of almost 3 per cent. Rock salt is thought to have formed through the evaporation of prehistoric land-locked seas. A present-day example of the process is the Dead Sea in Israel, which contains a concentration of salts sufficient to raise the density of the water enough to make swimming difficult, and the shores of which support a small minerals industry.

(b) *As sodium nitrate*, $NaNO_3$. This compound occurs as Chile saltpetre. It is extensively used, for its nitrate content, as a fertilizer.

(c) *As sodium carbonate.* Soda lakes, for example in East Africa, show deposits round the lake shores and in the shallows, which contain the carbonate, $Na_2CO_3.10H_2O$, and the sesquicarbonate,

$$Na_2CO_3.NaHCO_3.2H_2O$$

(d) *As borax*, $Na_2B_4O_7.10H_2O$. For example, in Nevada, USA.

(e) *As cryolite*, Na_3AlF_6, *in Greenland.* This material has been used in the extraction of aluminium, p. 119, but is now almost exhausted.

Properties of sodium

Physical properties

Naturally occurring sodium consists of only one kind of atom, $^{23}_{11}Na$.

Melting point	371 K
Boiling point	1156 K
Density	0.962 g cm^{-3} at 273 K

Sodium is a soft silvery metal. It tarnishes readily in moist air (see below). Sodium conducts heat and electricity well. Its vapour is purple in colour and is monatomic.

Chemical properties

1. *With the atmosphere.* Sodium is very little attacked by dry air, but, if exposed to moist air at room temperature, the following changes occur:

(a) Oxidation to sodium monoxide

$$4Na(s) + O_2(g) \rightarrow 2Na_2O(s)$$

(b) Conversion to sodium hydroxide by water from the air; deliquescence of the sodium hydroxide produces a pool of solution.

$$Na_2O(s) + H_2O(l) \rightarrow 2NaOH(aq)$$

The alkaline liquid absorbs carbon dioxide from the air and forms a crystalline mass of washing soda, sodium carbonate, which may also contain some sodium hydrogencarbonate, $NaHCO_3$.

$$2NaOH(aq) + CO_2(g) + 9H_2O(l) \rightarrow Na_2CO_3.10H_2O(s)$$

If left for a prolonged period in the air, the washing soda may effloresce and leave a white powder consisting largely of the monohydrate, $Na_2CO_3.H_2O$. These changes require sodium to be protected from the atmosphere by a layer of oil or (more recently) a sheath of plastic material.

(c) If heated in air, sodium burns and forms a mixture of its monoxide and peroxide:

$$4Na(s) + O_2(g) \rightarrow 2Na_2O(s); 2Na(s) + O_2(g) \rightarrow Na_2O_2(s)$$

2. *Sodium as a reducing agent.* Sodium is a very vigorous reducing agent. It reduces many metallic compounds when heated with them in the absence of air, e.g.

$$BeCl_2(s) + 2Na(s) \rightarrow Be(s) + 2NaCl(s)$$
$$Al_2O_3(s) + 6Na(s) \rightarrow 2Al(s) + 3Na_2O(s)$$

It also reduces carbon dioxide when heated, forming carbon and sodium carbonate.

$$4Na(s) + 3CO_2(g) \rightarrow 2Na_2CO_3(s) + C(s)$$

In all these cases sodium is oxidized by electron loss and converted to sodium ion:

$$Na - e^- \rightarrow Na^+.$$

3. *With the halogen elements, sulphur, and hydrogen.* If sodium is heated in contact with the dry vapour of the halogen elements, dry sulphur or dry hydrogen, it combines readily to form the corresponding halide, sodium sulphide or sodium hydride.

$$2Na(s) + Cl_2(g) \rightarrow 2NaCl(s)$$
$$2Na(s) + S(g) \rightarrow Na_2S(s)$$
$$2Na(s) + H_2(g) \rightarrow 2NaH(s)$$

4. *With water.* Sodium attacks cold water rapidly with evolution of hydrogen and formation of sodium hydroxide solution.

$$2Na(s) + 2H_2O(l) \rightarrow 2NaOH(aq) + H_2(g)$$

The hydrogen does not burn unless the movement of the sodium is restricted.

5. *With ammonia.* Sodium dissolves readily in liquid ammonia to form a blue solution. This solution is used as a reducing agent in organic chemistry. If heated in a current of dry ammonia gas to about 620 K, sodium yields sodamide (see also p. 68).

6. *With mercury.* If pressed in small pieces under the surface of warm mercury, sodium will amalgamate with it. In the early stages, each addition of sodium usually produces a flash of light, and a liquid amalgam results. Later, the amalgamation is milder and the amalgam becomes solid. The amalgam reacts with water and (more rapidly) dilute sulphuric acid, liberating hydrogen and regenerating the mercury. This combination of sodium amalgam and water or dilute sulphuric acid is a valuable reducing agent. The amalgam is vital for the major method of manufacture of both sodium hydroxide and chlorine (p. 49).

Extraction of sodium metal

The conversion of its commonest compound, sodium chloride, to sodium is a reduction which is most conveniently performed at the cathode in electrolysis. The melting point of common salt (1074 K) is, however, rather high, and much electrical power is needed to keep large masses of sodium chloride molten. The Downs Process (following) is now the major method for producing sodium directly from common salt, but sodium has also been made by Castner's Process, that is by the electrolysis of fused sodium hydroxide. This has a much more convenient melting-point, 591 K, but has to be made itself from sodium chloride.

1. *Castner's Process for production of sodium by electrolysis of molten sodium hydroxide*

The iron container (Figure 4.1) is set in brick-work. The electrolyte (molten sodium hydroxide) is kept at about 620 K by the ring of gas burners. The cage of nickel wire serves to concentrate the sodium into a thicker layer and to prevent it from shorting the electrolysis by touching both anode and cathode. Hydrogen (produced as explained below)

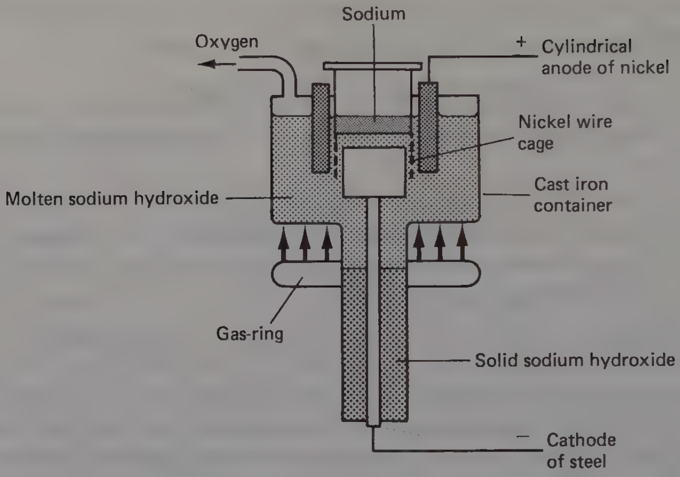


Figure 4.1 *Electrolysis of sodium hydroxide*

protects the sodium from oxidation. The metal is removed by a perforated ladle of such mesh that the liquid sodium is retained while the molten sodium hydroxide, of different surface tension, is not.

Sodium hydroxide yields ions Na^+ and OH^-.

Na^+	*OH^-*
Na^+ migrates to the cathode and is discharged, i.e. is reduced by electron gain.	OH^- migrates to the anode and is discharged, i.e. oxidized by electron loss.
$Na^+ + e^- \rightarrow Na(l)$	$OH^- \rightarrow e^- \rightarrow (OH)$
$2Na(l) + 2H_2O(g) - 2NaOH(l) + H_2(g)$	Then $4(OH) \rightarrow 2H_2O(g) + O_2(g)$ Some steam diffused to the cathode, is attacked there by sodium and liberates hydrogen (equation opposite).

Davy discovered sodium (1807) by electrolysis of sodium hydroxide between platinum electrodes.

2. *The Downs Process of production of sodium; electrolysis of fused sodium chloride*

The Downs cell has an outer iron shell, lined with fire-brick (Fig. 4.2). A diaphragm of iron gauze screens the carbon anode from the ring-shaped iron cathode which surrounds it. Chlorine escapes via the hood. Sodium

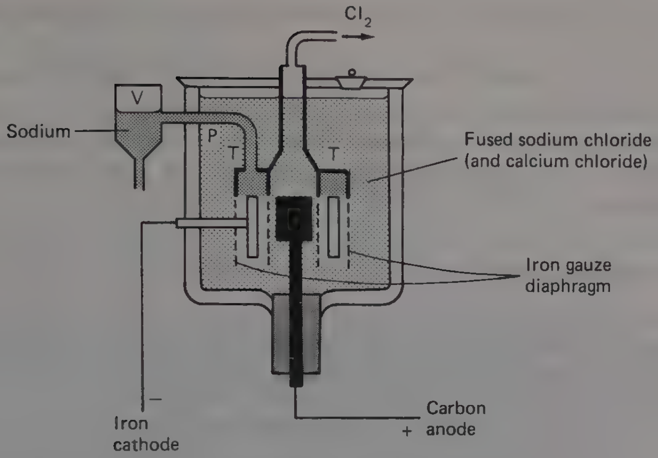


Figure 4.2 *Electrolysis of sodium chloride*

collects in the inverted trough T placed over the cathode, rises up the pipe P, and is tapped off through the iron vessel V. Calcium chloride (in earlier versions of the process, sodium fluoride) is added to the sodium chloride electrolyte to reduce the fusion temperature to about 800 K. (The melting point of pure sodium chloride is 1074 K.) Some calcium is discharged, but this does not mix with the sodium and is much denser, so that it can easily be separated. Sodium chloride consists of the ions Na^+ and Cl^-; when the salt is molten these ions are free to move to the electrodes.

Na^+	*Cl^-*
Na^+ migrates to the cathode and is reduced by electron gain.	Cl^- migrates to the anode and is oxidized by electron loss.
$Na^+ + e^- \rightarrow Na(l)$	$Cl^- - e^- \rightarrow Cl$
	Then $Cl + Cl \rightarrow Cl_2(g)$

Uses of sodium

(a) Sodium is important as a source of sodium peroxide, sodium cyanide and sodamide. See the account of these compounds (later in the present chapter) for details.

(b) A sodium–lead alloy is employed in the manufacture of tetraethyllead(IV), $Pb(C_2H_5)_4$, an anti-knock compound used in petrol (p. 205).

(c) Sodium is used as the heat-transfer fluid in fast-breeder nuclear reactors.
(d) An alloy of sodium and potassium is used in high-temperature thermometers. It is a liquid at room temperature.
(e) Sodium (like other alkali metals) emits electrons under the action of light. It is used in photo-electric cells in connection with television and films.

Sodium hydride, NaH (Na^+H^-)

This compound is made by heating sodium in a stream of hydrogen, well dried, at about 620 K. It is a salt-like hydride, a crystalline solid, an electrolyte when molten, giving hydrogen at the anode.

$$2Na(s) + H_2(g) \rightarrow 2NaH(s)$$

Sodium hydride yields hydrogen and sodium hydroxide solution when acted upon by cold water.

$$NaH(s) + H_2O(l) \rightarrow NaOH(aq) + H_2(g)$$

Oxides of sodium

(a) *Sodium monoxide*, Na_2O. This oxide is formed, along with some peroxide, when sodium is burnt in a limited supply of air.

$$4Na(s) + O_2(g) \rightarrow 2Na_2O(s); \; 2Na(s) + O_2(g) \rightarrow Na_2O_2(s)$$

It reacts violently with water to form sodium hydroxide solution.

$$Na_2O(s) + H_2O(l) \rightarrow 2NaOH(aq)$$

(b) *Sodium peroxide*, Na_2O_2. Sodium peroxide is manufactured by heating sodium metal in excess of air at about 600 K. The air is freed from carbon dioxide by passage through sodalime and dried. The sodium is contained in trays made of aluminium metal.

$$4Na(s) + 2O_2(g) \rightarrow 2Na_2O_2(s)$$

Sodium peroxide is usually encountered as a pale yellow solid, but if perfectly pure, it is white. It is stable when heated to moderate temperatures. It is little affected by dry air but moist air decomposes it as in (1) below.

Chemical properties of sodium peroxide

1. *Ice-cooled, dilute mineral acid* (HCl or H_2SO_4) acts upon sodium peroxide to produce hydrogen peroxide solution. It contains the corres-

ponding sodium salt as impurity, e.g.

$$Na_2O_2(s) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + H_2O_2(aq)$$

Acting as a weak acid, carbon dioxide combines with sodium peroxide, liberating oxygen.

$$2O_2^{2-} + 2CO_2(g) \rightarrow 2CO_3^{2-} + O_2(g)$$

Sodium peroxide is, therefore, useful in confined spaces, e.g. submarines, to absorb carbon dioxide and liberate oxygen, so regenerating breathable air.

2. *Sodium peroxide as an oxidizing agent.* Sodium peroxide is a most vigorous oxidizing agent. A mixture of fine saw-dust and sodium peroxide will inflame if slightly damped with water, and glacial ethanoic acid will inflame in contact with sodium peroxide. Many sulphides are converted to sulphates when fused with sodium peroxide.

$$S^{2-} + 4O_2^{2-} \rightarrow SO_4^{2-} + 4O^{2-}$$

Sodium peroxide converts a suspension of chromium(III) hydroxide, $Cr(OH)_3$, in water to sodium chromate(VI) solution (i.e. a *yellow* colour develops) when heated.

$$2Cr^{3+}(aq) + 4OH^-(aq) + 3O_2^{2-} \rightarrow 2CrO_4^{2-}(aq) + 2H_2O(l)$$

This reaction is used in tables for qualitative analysis in the identification of chromium. A mixture of sodium hydroxide and hydrogen peroxide solution is often preferred to sodium peroxide, being less dangerous to handle.

Sodium hydroxide, caustic soda, NaOH (Na^+OH^-)

This compound is a very important industrial chemical. It is now manufactured almost entirely from brine.

When a concentrated solution of common salt (i.e. brine) is electrolysed, the *cathode product is sodium hydroxide* solution and the *anode product is chlorine*. Since these products are capable of interaction, as for example,

$$2OH^-(aq) + Cl_2(g) \rightarrow Cl^-(aq) + ClO^-(aq) + H_2O(l)$$

it is essential to keep them apart by means of a diaphragm which separates them mechanically but still allows electrolysis to proceed.

1. *A method with mercury diaphragm; the Kellner-Solvay cell*

The apparatus is described by Figure 4.3. In the upper cell, sodium is

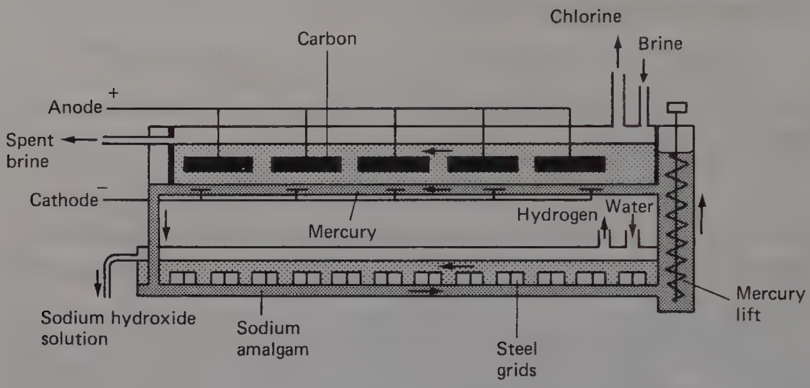


Figure 4.3 *Electrolytic production of sodium hydroxide*

discharged into the mercury cathode. This breakdown in the normal order of discharge of ions occurs because hydrogen cannot easily discharge on a mercury surface: it is said to have a *high overvoltage.* The process is helped because the discharged sodium amalgamates with the mercury. Chlorine is liberated at the anode.

At cathode	*At anode*
$Na^+ + e^- \rightarrow Na$	$Cl^- - e^- \rightarrow (Cl)$
$Na + Hg(l) \rightarrow NaHg(l)$	$(Cl) + (Cl) \rightarrow Cl_2(g)$

The sodium amalgam then flows into the lower cell. Here it encounters distilled water in contact with steel, on which hydrogen has only a very low over-voltage. Sodium hydroxide is at once formed with liberation of hydrogen. The solution (concentrated to 47%) is sent to users.

$$2NaHg(e) + 2H_2O(l) \rightarrow 2(Na^+OH^-)(aq) + H_2(g) + 2Hg(l)$$

Solid sodium hydroxide can be obtained by evaporation.
The product is of good quality but the capital cost of the mercury involved is very large.

It should be noticed that chlorine is produced in this process in the proportion of NaOH : Cl, i.e. 40 : 35.5 by mass. This method is now the only substantial source of industrial chlorine.

2. *A method with asbestos diaphragm: the Gibbs cell*

The arrangement of the Gibbs cell is shown diagrammatically in Figure 4.4. Concentrated brine is used at a temperature of about 360 K. The anode, a ring of carbon rods, is separated from the cathode, an iron gauze cylinder, by the porous asbestos diaphragm. Ions present are:

From common salt $Na^+ Cl^-$
From water $H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$

At cathode	*At anode*
H^+ and Na^+ migrate to this pole. H^+ discharges, hydrogen being much less electropositive than sodium and there being little over-voltage effect. $2H^+(aq) + 2e^- \rightarrow H_2(g)$ To maintain the ionic equilibrium of water ($K_w = 10^{-14}\ \text{mol}^2\ \text{dm}^{-6}$), more water ionizes. The excess of OH^-, with incoming Na^+, is equivalent to the production of sodium hydroxide in solution.	Cl^- discharges $2Cl^-(aq) - 2e^- \rightarrow Cl_2(g)$

The sodium hydroxide solution, produced on the outside (i.e. the cathode side) of the diaphragm, collects as shown and is run off and concentrated by evaporation. The product is cheaper than that from a

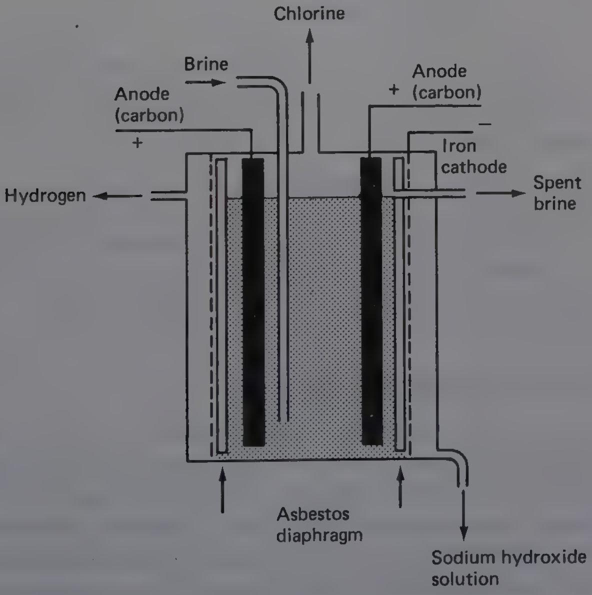


Figure 4.4 *Gibbs cell*

mercury cell, but is liable to contain sodium chloride which has penetrated the asbestos unchanged. Chlorine is a by-product as before.

Uses of sodium hydroxide

The uses of sodium hydroxide are so numerous that it is impossible to give an exhaustive list of them. The following are some of the more important.

(a) *In the manufacture of soap.* A fat or oil is boiled with aqueous sodium hydroxide. The products are an alcohol, propane-1,2,3-triol (glycerol), and the sodium salt of a carboxylic acid containing about 16 or 17 carbon atoms. This is the soap. Sodium octadecanote (sodium stearate), $C_{17}H_{35}COO^-Na^+$, and sodium *cis*-octadec-9-enoate (sodium oleate), $C_{17}H_{33}COO^-Na^+$, are typical soaps.

This hydrolysis (to give an alcohol and the salt of the acid) with sodium hydroxide is a general reaction of esters; the reaction is often know as *saponification*, because of its specific use in soap making.

(b) *In the purification of bauxite.* This occurs during the extraction of aluminium. For details, see p. 118.

(c) *In the extraction of phenols and methylphenols* (*cresols*) *from coal-tar.* These compounds are feebly acidic and form water-soluble sodium salts with sodium hydroxide solution.

$$C_6H_5OH(l) + NaOH(aq) \rightarrow C_6H_5O^-Na^+(aq) + H_2O(l)$$

If the aqueous layer is separated from the tar and acidified, the phenol is regenerated.

$$C_6H_5O^-Na^+(aq) + HCl(aq) \rightarrow C_6H_5OH(l) + H_2O(l)$$

(d) *In the textile industry.* Sodium hydroxide is used in bleaching and dyeing processes, in the manufacture of rayon and in the mercerizing of cotton, a process which gives the fabric a silky sheen.

Physical properties of sodium hydroxide

Sodium hydroxide is a white solid. It is very difficult to purify because of its marked deliquescent properties and tendency to absorb atmospheric carbon dioxide. It is only sparingly soluble in ethanol. (Potassium hydroxide is much more soluble.) The melting point of sodium hydroxide is 591 K. It is very soluble in water and dissolves with great evolution of heat. The dilute solution has a characteristic soapy feel. Concentrated solutions are very corrosive.

A pure solution of sodium hydroxide can be made by the action of sodium amalgam on cold, boiled-out, distilled water but it must be protected from atmospheric carbon dioxide.

$$2NaHg(l) + 2H_2O(l) \rightarrow 2(NaOH)(aq) + H_2(g) + 2Hg(l)$$

Chemical properties of sodium hydroxide

1. *As an alkali*

Sodium hydroxide is a very strong alkali, i.e. it is fully ionized to Na^+ and OH^- ions. It has the characteristic alkaline properties of affecting the colours of indicators (e.g. litmus turned blue; methyl orange turned yellow) and forming salts with acids, e.g.

$$Na^+OH^-(aq) + H^+Cl^-(aq) \rightarrow Na^+Cl^-(aq) + H_2O(l)$$

Sodium hydroxide solution precipitates the insoluble hydroxides of many metals from solutions of their salts, e.g.

$$Fe^{3+}(aq) + 3OH^-(aq) \rightarrow Fe(OH)_3(s)$$

In some cases the hydroxides are amphoteric and redissolve in excess of the alkali, e.g.

$$Zn(OH)_2(s) + 2OH^-(aq) \rightarrow [Zn(OH)_4]^{2-}(aq)$$

When warmed with any ammonium salt, sodium hydroxide liberates ammonia gas.

$$NH_4{}^+(aq) + OH^-(aq) \rightarrow NH_3(g) + H_2O(l)$$

Sodium hydroxide also has the property of saponifying organic esters to produce an alcohol and the sodium salt of the acid corresponding to the ester, as noted earlier. The process usually requires heat under reflux to prevent loss of the alcohol. A typical case is:

$$\underset{\text{(ester, ethyl ethanoate)}}{CH_3COOC_2H_5(l)} + NaOH(aq) \rightarrow \underset{\text{(sodium ethanoate)}}{CH_3COO^-Na^+(aq)} + \underset{\text{(ethanol)}}{C_2H_5OH(aq)}$$

2. *With metals*

Sodium hydroxide solution reacts with aluminium and zinc to produce hydrogen and *sodium aluminate(III)* or *sodium zincate(II)*, in solution. Aluminium powder reacts rapidly in the cold with dilute sodium hydroxide solution; aluminium foil and zinc need heat.

$$2Al(s) + 2OH^-(aq) + 10H_2O(l) \rightarrow 2[Al(H_2O)_2(OH)_4]^{2-}(aq) + 3H_2(g)$$
$$Zn(s) + 2OH^-(aq) + 2H_2O(l) \rightarrow [Zn(OH)_4]^{2-}(aq) + H_2(g)$$

3. *With non-metals*

(a) *Silicon*, with heat, liberates hydrogen from sodium hydroxide solution and leaves sodium silicate(IV) solution.

$$Si(s) + 2OH^-(aq) + H_2O(l) \rightarrow SiO_3{}^{2-}(aq) + 2H_2(g)$$

(b) *Yellow* (*white*) *phosphorus*, heated with 20% sodium hydroxide solution, gives a rather complex reaction of which the chief products are *phosphine gas*, PH_3, and *sodium phosphinate* (hypophosphite) solution. An inert atmosphere is needed. The equation for the main reaction is:

$$3OH^-(aq) + P_4(s) + 3H_2O(l) \rightarrow 3H_2PO_2{}^-(aq) + PH_3(g)$$

(Red phosphorus is inert to sodium hydroxide.)

(c) Chlorine shows two different reactions.
With cold, dilute sodium hydroxide solution it gives a pale yellow solution containing sodium chloride and sodium chlorate(I) (sodium hypochlorite).

$$2OH^-(aq) + Cl_2(g) \rightarrow Cl^-(aq) + OCl^-(aq) + H_2O(l)$$

With hot, concentrated sodium hydroxide solution, chlorine gives a colourless solution containing *sodium chloride* and *chlorate*(*V*). The formation of chlorate(V) ions in the hot mixture is due to disproportionation of the chlorate(I) ions to chlorate(V) ions and chloride ions:

$$3OCl^-(aq) \rightarrow ClO_3{}^-(aq) + 2Cl^-(aq)$$

So the overall reaction in the hot mixture is:

$$6OH^-(aq) + 3Cl_2(g) \rightarrow 5Cl^-(aq) + ClO_3{}^-(aq) + 3H_2O(l)$$

Bromine and iodine give corresponding reaction.

(d) *Sulphur*, with hot sodium hydroxide solution, gives a rather complex reaction in which the products are *sodium thiosulphate* and a *polysulphide* of sodium. A typical reaction among those possible is:

$$6OH^-(aq) + 12S(s) \rightarrow 2S_5{}^{2-}(aq) + S_2O_3{}^{2-}(aq) + 3H_2O(l)$$

Sodium carbonate

Sodium carbonate is a very important industrial chemical, occurring in the anhydrous form as *soda-ash*, Na_2CO_3, and as the decahydrate, $Na_2CO_3.10H_2O$, *washing soda*. Exposure to air causes the decahydrate to effloresce and fall gradually to a powder consisting mainly of the monohydrate, $Na_2CO_3.H_2O$.

Manufacture of sodium carbonate from common salt by the ammonia–soda (Solvay) process

This very important process was begun in Belgium (1861) by Solvay and in England (1873) by Brunner and Mond.

Stage 1. Ammoniation of brine

An almost saturated brine (containing about 28% by mass of sodium chloride) is allowed to flow down an ammoniating tower in which it encounters an upward current of ammonia. Mushroom-shaped baffles, set across the tower at short intervals, check the flow of brine and ensure its saturation by ammonia. Metallic impurities in the water may precipitate as hydroxides (e.g. $Fe(OH)_3$) and are filtered off. As ammonia dissolves, the temperature of the liquid rises and it is cooled over water-pipes to about 300 K.

Stage 2. Carbonation of the ammoniated brine

The ammoniated brine then flows down a carbonating tower and meets an upward current of carbon dioxide at a pressure of about 2.5 atm. Perforated hoods, placed at short intervals in the tower, check the flow of liquid and break up the carbon dioxide into very small bubbles, so ensuring good conditions for the reaction. The probable course of reactions in this tower is:

$$2NH_3(g) + CO_2(g) + H_2O(l) \rightarrow 2NH_4^+(aq) + CO_3^{2-}(aq)$$

$$CO_3^{2-}(aq) + CO_2(g) + H_2O(l) \rightarrow 2HCO_3^-(aq)$$

(the hydrogencarbonate ion)

There are then present the ions Na^+, Cl^- (from the brine), NH_4^+, and HCO_3^-. The least soluble combination of ions then precipitates out as sodium hydrogencarbonate, $NaHCO_3$, leaving the ions of ammonium chloride, NH_4^+ and Cl^-, in solution.

In total result, these reactions are exothermic; consequently, the temperature of the materials rises. This tends to inhibit precipitation of the hydrogencarbonate. To counter this adverse effect, the lower part of the tower is cooled. The precipitated sodium hydrogencarbonate is then filtered out by a form of vacuum filtration and washed free of ammonium compounds.

Stage 3. Conversion to sodium carbonate

The sodium hydrogencarbonate is heated to convert it to anhydrons sodium carbonate (soda-ash).

$$2NaHCO_3(s) \rightarrow Na_2CO_3(s) + H_2O(l) + CO_2(g)$$

The carbon dioxide is returned to the carbonating tower. By crystallization from hot water, the soda-ash then yields the decahydrate (washing soda), $Na_2CO_3.10H_2O$.

Sources of materials. Efficiency of the process

(a) *Brine* is obtained from natural deposits of common salt.

(b) *Carbon dioxide* is obtained by heating limestone quarried from natural deposits. This also yields quicklime.

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

(c) *Ammonia* is regenerated from the ammonium chloride left in solution after filtering off the sodium hydrogencarbonate. This is done by steam-heating the solution with lime from (b).

$$CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(s)$$

$$2NH_4Cl(aq) + Ca(OH)_2(s) \rightarrow CaCl_2(aq) + 2H_2O(l) + 2NH_3(g)$$

The ammonia is returned to the ammoniating tower. In theory, once the process is operating fully, it requires no further supplies of ammonia. In practice, slight losses are replaced by the addition of extra ammonium chloride before the heating with lime.

The process as a whole is very efficient. As a continuous-flow process, it requires relatively little labour. Its raw materials—brine, limestone, and a little ammonium chloride—are cheap and plentiful. The chief weakness of the Solvay process is its waste of the chlorine of the common salt. This is lost as calcium chloride (as in (c) above) for which there are no uses adequate to absorb the very large amount available.

Notice that the ammonia–soda process depends on the comparatively low solubility of sodium hydrogencarbonate in water (9 g in 100 g water at 288 K). This allows the hydrogencarbonate to precipitate and to be separated by filtration. A corresponding process for potassium hydrogencarbonate cannot be worked because this salt is much more soluble (27.7 g in 100 g water at 283 K) and will not precipitate.

Some sodium carbonate is now made by passing carbon dioxide (often in waste gases from combustion) through surplus sodium hydroxide solution obtained from the electrolysis of brine. Sodium hydrogencarbonate precipitates and is treated as above.

Uses of sodium carbonate

The uses of sodium carbonate are very extensive. The following must be considered as typical rather than exhaustive.

(a) *In the manufacture of glass and water-glass.* To manufacture ordinary soda-glass, sand (silica), calcium carbonate, and anhydrous sodium carbonate are fused together. The reactions, though really more complex, are usually written:

$$Na_2CO_3(s) + SiO_2(s) \rightarrow Na_2SiO_3(s) + CO_2(g)$$
$$CaCO_3(s) + SiO_2(s) \rightarrow CaSiO_3(s) + CO_2(g)$$

The mixture of silicates(IV), with some unchanged silica, is *glass*. In a similar process, but using only sodium carbonate with sand, the product is *water-glass*, sodium silicate(IV).

(b) *In the form of washing soda*, sodium carbonate has been extensively used as a *domestic water-softener*. It precipitates calcium ion from the water as chalk.

$$Ca^{2+}(aq) + CO_3{}^{2-}(aq) \rightarrow CaCO_3(s)$$

(c) Sodium carbonate is used in *papermaking* and some other industrial processes.

Properties of sodium carbonate

1. *Hydrates of sodium carbonate.* Sodium carbonate can be obtained anhydrous, as Na_2CO_3. The best method of making this form is to heat sodium hydrogencarbonate to constant mass.

$$2NaHCO_3(s) \rightarrow Na_2CO_3(s) + H_2O(l) + CO_2(g)$$

If crystallized from water below 305 K, sodium carbonate yields its decahydrate, $Na_2CO_3.10H_2O$. This forms transparent, colourless crystals which effloresce in air and crumble to a white powder, which is mainly the monohydrate, $Na_2CO_3.H_2O$. Over a narrow temperature range, 305.2–308.6 K, a heptahydrate, $Na_2CO_3.7H_2O$, can be crystallized. These various hydrates produce an unusual solubility curve for sodium carbonate, of the approximate form shown in Figure 4.5.

2. *Hydrolysis of sodium carbonate in solution.* Sodium carbonate, as the

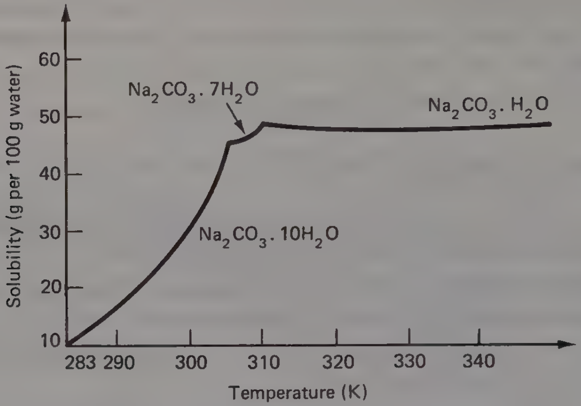


Figure 4.5 *Solubility curve of sodium carbonate*

salt of a weak acid and a strong base, is much hydrolysed in solution. The ionic situation is:

$$\begin{array}{lll} \text{From sodium carbonate:} & 2Na^+ & CO_3^{2-} \\ & & + \\ \text{From water:} & 2H_2O \rightleftharpoons 2OH^- & +\, 2H^+ \\ & & \upharpoonleft\downharpoonright \\ & & H_2CO_3 \end{array}$$

Ions in the proportion of two H^+ to one CO_3^{2-} are withdrawn to form undissociated molecules of the weak acid, carbonic acid, H_2CO_3. This disturbs the ionic equilibrium of water ($K_w = 10^{-14}$ mol^2 dm^{-6} at 298 K) and more water ionizes to restore this equilibrium. This produces an excess of the ion, OH^-, so that the solution has a pH much higher than 7 and reacts alkaline.

3. *With mineral acids.* Sodium carbonate reacts with all the dilute mineral acids liberating carbon dioxide.

$$2H^+(aq) + CO_3^{2-}(aq) \rightarrow H_2O(l) + CO_2(g)$$

4. *Precipitation of carbonates.* All common carbonates (except those of sodium, potassium and ammonium) are insoluble in water. Sodium carbonate solution will precipitate these insoluble carbonates from solutions of salts of the corresponding metals, e.g. calcium carbonate from a solution of calcium chloride.

$$Ca^{2+}(aq) + CO_3^{2-}(aq) \rightarrow Ca\,CO_3(s)$$

Where the corresponding base is weak, the hydrolysis of sodium carbonate solution (last section) may cause precipitation of a basic carbonate of the metal, e.g. basic copper carbonate is precipitated from copper(II) sulphate solution.

$$2Cu^{2+}(aq) + 2OH^-(aq) + CO_3^{2-}(aq) \rightarrow Cu_2(OH)_2CO_3(s)$$

5. *Conversion of sodium carbonate to sodium hydrogencarbonate.* For this topic, see the next section.

Sodium hydrogencarbonate, baking soda, $Na^+HCO_3^-$

Manufacture

Sodium hydrogencarbonate occurs as a precipitate during the course of the ammonia–soda process (p. 55) but is all converted to sodium carbonate. Industrially, sodium hydrogencarbonate is manufactured by saturating a wet mush of sodium carbonate and water with carbon dioxide.

$$Na_2CO_3(s) + H_2O(l) + CO_2(g) \rightarrow 2NaHCO_3(s)$$

The hydrogencarbonate is washed with cold water and dried.

Uses of sodium hydrogencarbonate

1. *In baking powders.* A typical baking powder contains three ingredients —sodium hydrogencarbonate, a weak acid, and rice powder. During baking, heat decomposes the sodium hydrogencarbonate, liberating carbon dioxide and steam, the bubbles of which raise the cake mixture and make it light.

$$2NaHCO_3(s) \rightarrow CO_2(g) + H_2O(l) + Na_2CO_3(s)$$

The remaining carbonate would impart a bitter taste to the product, so is converted by the weak acid present to a tasteless salt, with production of more carbon dioxide. Tartaric acid was much used at one time but is now largely replaced by acid sodium phosphate(V). The rice powder is a diluent and also serves to absorb moisture.

2. *In health salts.* Typical health salts contains sodium hydrogencarbonate, and a weak, solid acid, e.g. tartaric acid or acid sodium phosphate(V). When water is added, the two dissolve and the acid attacks the hydrogencarbonate, liberating carbon dioxide and producing the well-known effervescent effect.

$$HCO_3^-(aq) + H^+(aq) \rightarrow CO_2(g) + H_2O(l)$$

Properties of sodium hydrogencarbonate

This compound is a white solid, usually occurring as powdery crystals.

1. *Action of heat.* Sodium hydrogencarbonate begins to decompose rapidly at about 330 K into sodium carbonate, water, and carbon dioxide.

$$2NaHCO_3(s) \rightarrow Na_2CO_3(s) + H_2O(l) + CO_2(g)$$

2. *Hydrolysis; precipitation of carbonates.* Sodium hydrogencarbonate is hydrolysed to some extent in solution.

$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + H_2CO_3(aq)$$

The hydrolysis is, however, much less than that of the normal carbonate (p. 58). For this reason, sodium hydrogencarbonate solution can precipitate normal carbonates of certain metals from solutions of their salts while sodium carbonate solutions precipitates basic carbonates. This is true for lead, magnesium, and zinc. The typical behaviour is:

Sodium hydrogencarbonate

$$Mg^{2+}(aq) + 2HCO_3^-(aq) \rightarrow MgCO_3(s) + H_2O(l) + CO_2(g)$$

Sodium carbonate

$$2Mg^{2+}(aq) + 2OH^-(aq) + CO_3^{2-}(aq) \rightarrow Mg_2(OH)_2CO_3(s)$$

Laboratory preparation of sodium carbonate and sodium hydrogencarbonate from sodium hydroxide

A suitable apparatus for this preparation is show in Figure 4.6. A rapid

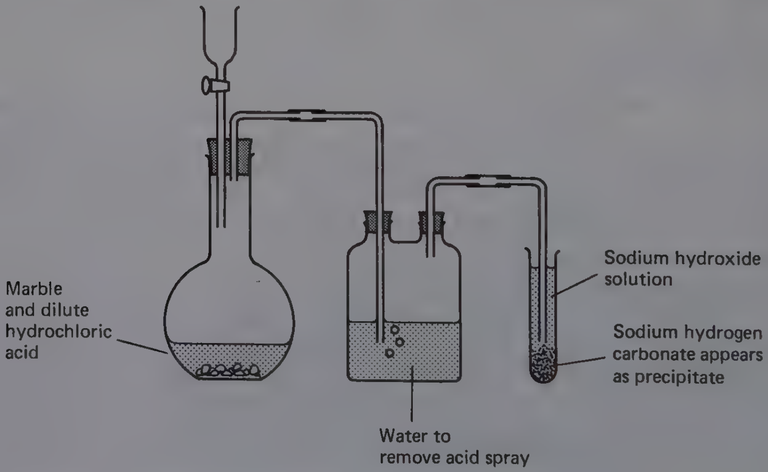


Figure 4.6 *Sodium carbonate and hydrogencarbonate from sodium hydroxide*

stream of carbon dioxide is passed through the concentrated solution of sodium hydroxide. The sodium hydroxide is first converted to sodium carbonate and then to sodium hydrogencarbonate.

$$2OH^-(aq) + CO_2(g) \rightarrow CO_3{}^{2-}(aq) + H_2O(l)$$
$$CO_3{}^{2-}(aq) + CO_2(g) + H_2O(l) \rightarrow 2HCO_3{}^-(aq)$$

The sodium hydrogencarbonate precipitates (more readily if surrounded by cold water). It is filtered, washed with cold water, and dried.

If the filtrate is boiled, the sodium hydrogencarbonate still contained in it is decomposed to form sodium carbonate.

$$2HCO_3{}^-(aq) \rightarrow H_2O(l) + CO_2(g) + CO_3{}^{2-}(aq)$$

After evaporation of the liquid to small bulk and cooling, washing-soda crystals will separate out and can be filtered off, washed with a little cold, distilled water and allowed to dry.

Sodium chloride, common salt, NaCl

The modes of occurrence of common salt were mentioned on p. 43.

Rock salt is obtained by mining from natural deposits. Brine may be obtained by flooding underground salt beds with water through a boring. When saturated, the liquid may be pumped to the surface. Much brine is used industrially, e.g. in the ammonia–soda process (p. 55) and in the electrolytic production of sodium hydroxide and chlorine (p. 49).

Properties of sodium chloride

Sodium chloride is a white solid, normally crystallizing anhydrous in face-centred cubes. Its melting-point is 1074 K. It has a high solubility in water at room temperature (36.0 g in 100 g water at 293 K), but its solubility increases only slightly with rise of temperature (39.8 g in 100 g water at 373 K). Its solubility in ethanol is slight.

Uses of sodium chloride

(a) Sodium chloride is widely used in connection with food, e.g. as a flavouring, in preserving fish, meat and butter, and in curing bacon.
(b) It is used in the making of soap to salt out the soap from solution after its production by alkaline hydrolysis ('saponification') of fat.
(c) Common salt is used as a glaze for common earthenware such as drain-pipes.

(d) Sodium chloride has very important industrial uses:
   (i) By electrolysis (p. 49), brine yields sodium hydroxide and chlorine.
   (ii) By electrolysis (p. 46), fused sodium chloride yields sodium. Sodium has also been produced by electrolysis of fused sodium hydroxide from (i).
   (iii) By the ammonia–soda process (p. 55), brine yields the various forms of sodium carbonate and, indirectly, sodium hydrogencarbonate.
   (iv) The chlorine from (i) above can be applied to the manufacture of bleaching powder, sodium chlorate(I) (sodium hypochlorite) and sodium chlorate(V), and for other purposes.

Purification of common salt

The best way of purifying common salt is the following. Warm distilled water is stirred with the given sample of common salt till some is left undissolved. The liquid is cooled and any solid which crystallizes out is filtered off, leaving a saturated, cold solution of common salt. Into this saturated solution is passed hydrogen chloride gas (by an inverted funnel just immersed in the liquid to prevent the solution passing into the gas generation apparatus—the so-called 'sucking back'). Fine crystals of common salt will deposit from the liquid and can be filtered off, washed with cold distilled water, and dried in a warm oven. Repetitions of the process will tend to give still purer samples.

The explanation of the method is as follows. In the saturated solution of common salt, before the passage of hydrogen chloride, there is equilibrium between undissolved solute and the ions in the saturated solution. As hydrogen chloride dissolves and ionizes,

$$\mathrm{HCl(g) + aq \rightleftharpoons H^{+}(aq) + Cl^{-}(aq)}$$

there is a great rise in the concentration of chloride ion Cl^-. This tends to cause the Na^+ and Cl^- ions to withdraw from solution as a crystalline precipitate of common salt. Other metallic ions, e.g. K^+, Mg^{2+}, Ca^{2+} may be present, but only in *low concentration* in the solution, so that their chlorides do not precipitate with the sodium chloride.

Sodium nitrate, chile saltpetre, $NaNO_3$

Extraction

Sodium nitrate occurs in the almost rainless areas near the west coast of South America. Rainfall would have washed this very soluble material out of the soil long ago. It is associated with pebbles, sand, and clay in a material known as *caliche*, which may contain up to 30% of sodium nitrate by mass. The material is broken up by explosive charges, extracted with water and the sodium nitrate purified (up to 95–6% of $NaNO_3$) by crystallization. The mother liquor left contains sodium iodate(V), $NaIO_3$; iodine is recovered from it.

Sodium nitrate is also produced by modern nitrogen fixation processes, e.g. the catalytic oxidation of ammonia by air.

Uses of sodium nitrate

(a) Sodium nitrate is chiefly used as a nitrogenous fertilizer in farming and horticulture.

(b) Nitric acid can be made from sodium nitrate by distilling with concentrated sulphuric acid (p. 242). The nitric acid has a low boiling point and is easily distilled off. This method has been superseded by oxidation of ammonia (see p. 217).

$$NaNO_3(s) + H_2SO_4(l) \rightarrow NaHSO_4(s) + HNO_3(l)$$

(c) Potassium nitrate is manufactured from sodium nitrate.

Properties of sodium nitrate

Sodium nitrate forms white, cubic crystals of melting point 589 K. It is very soluble in water (88.0 g in 100 g water at 293 K). Commercial samples are deliquescent and turn damp in air. For this reason, the non-deliquescent potassium nitrate is preferred for many purposes, especially in gunpowder and fireworks.

When heated considerably above its melting-point, sodium nitrate decomposes, giving off *oxygen* and leaving *sodium nitrite*.

$$2NaNO_3(s) \rightarrow 2NaNO_2(s) + O_2(g)$$

Sodium nitrite, $NaNO_2$

Manufacture

The only important large-scale source of sodium nitrite today is the oxidation of ammonia (p. 217). The oxides of nitrogen resulting from the oxidation of ammonia by air, with red-hot platinum gauze as catalyst,

$$4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g)$$
$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$$

are absorbed in sodium carbonate solution.

$$CO_3^{2-}(aq) + NO(g) + NO_2(g) \rightarrow 2NO_2^-(aq) + CO_2(g)$$

Sodium nitrite can be crystallized from the solution.

Laboratory preparation of sodium nitrite

To prepare sodium nitrite, sodium nitrate is heated alone or (at a reduced temperature) with lead or carbon.

$$2NaNO_3(s) \rightarrow 2NaNO_2(s) + O_2(g)$$
$$NaNO_3(s) + C(s) \rightarrow NaNO_2(s) + CO(g)$$
$$NaNO_3(s) + Pb(s) \rightarrow NaNO_2(s) + PbO(s)$$

In the last two cases, the product is extracted with hot water, the solution is filtered and the nitrite obtained by evaporation and crystallization of the solution. Sodium nitrite is mainly important as the usual source of nitrous acid. If a cooled solution of sodium nitrite is acidified by dilute hydrochloric acid or dilute sulphuric acid, free nitrous acid is produced in a pale blue solution. This mixture is used in the diazotization of aromatic amines, e.g. in the dyestuffs industry.

$$NO_2^-(aq) + H^+(aq) \rightleftharpoons HNO_2(aq)$$

Sodium sulphate, Na_2SO_4

Manufacture

Most of the sodium sulphate used in industry is made by heating common salt with concentrated sulphuric acid in the proportions of $2NaCl : H_2SO_4$. The reaction occurs in two stages, the first at moderate temperatures,

$$NaCl(s) + H_2SO_4(l) \rightarrow NaHSO_4(s) + HCl(g)$$

and the second at red heat,

$$NaHSO_4(s) + NaCl(s) \rightarrow Na_2SO_4(s) + HCl(g)$$

The second reaction is very hard to achieve under laboratory conditions. The product is known as *salt-cake*. The hydrogen chloride is absorbed in water to produce hydrochloric acid as a by-product.

Uses of sodium sulphate

(a) Sodium sulphate can be used as an alternative to anhydrous sodium carbonate in the manufacture of glass and water-glass, p. 57.

$$Na_2SO_4(s) + SiO_2(s) \rightarrow Na_2SiO_3(s) + SO_3(g)$$

(b) Sodium sulphate is used in the manufacture of *sodium sulphide* and *sodium thiosulphate*. For these, see later sections of this chapter.

(c) Sodium sulphate is used as Glauber's salt, $Na_2SO_4.10H_2O$, in medicine.

Properties of sodium sulphate

If crystallized from water below 305 K, sodium sulphate gives its decahydrate, $Na_2SO_4.10H_2O$, which is known as *Glauber's salt*. This form is efflorescent, forming the anhydrous salt on exposure to air. The solubility curve of sodium sulphate is discontinuous, having the approximate form shown in Figure 4.7. The curve from A to B is the solubility curve of the decahydrate, $Na_2SO_4.10H_2O$. At B (305.6 K), this hydrate is converted to the anhydrous salt, Na_2SO_4, of which the curve BE is the solubility curve. Rapid heating or cooling behyond the transition point of 305.6 K will yield limited extensions, BD and BC, of these curves, showing clearly that B is the point of intersection of the two. A heptahydrate, $Na_2SO_4.7H_2O$, is also known.

Sodium hydrogensulphate (sodium bisulphate), $NaHSO_4$

Laboratory preparation

Neutralization of sodium hydroxide solution by dilute sulphuric acid,

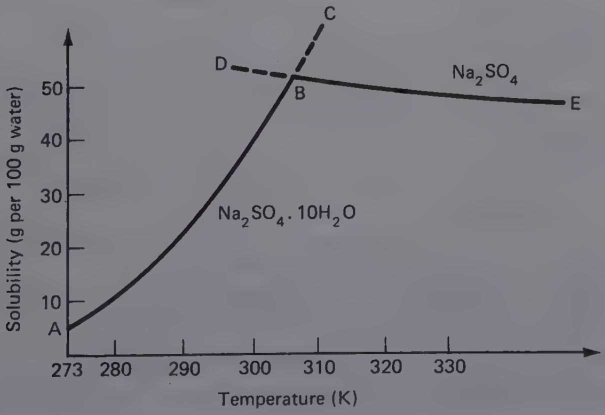


Figure 4.7 *Solubility curve of sodium sulphate*

using methyl orange or litmus as indicator, produces normal sodium sulphate.

$$2NaOH(aq) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + 2H_2O(l)$$

If the relative proportion of sodium hydroxide solution to sulphuric acid is halved, the product is sodium hydrogensulphate in solution.

$$NaOH(aq) + H_2SO_4(aq) \rightarrow NaHSO_4(aq) + H_2O(l)$$

On sufficient evaporation and cooling, the liquid will yield crystals of a monohydrate, $NaHSO_4.H_2O$. A solution of this material in water is quite acidic because of the ionization:

$$HSO_4^-(aq) \rightleftharpoons H^+(aq) + SO_4^{2-}(aq)$$

The monohydrate loses its water when heated and the anhydrous salt fuses at 573 K. Further heating produces sodium 'pyrosulphate', $Na_2S_2O_7$, and then anhydrous sodium sulphate.

$$2HSO_4^- \rightarrow S_2O_7^{2-} + H_2O(g)$$
$$S_2O_7^{2-} \rightarrow SO_4^{2-} + SO_3(g)$$

Sodium hydrogensulphide, NaHS

Laboratory preparation

A quantity of sodium hydroxide solution is saturated with hydrogen sulphide, giving the successive reactions:

$$2NaOH(aq) + H_2S(g) \rightarrow Na_2S(aq) + 2H_2O(l)$$
$$Na_2S(aq) + H_2S(g) \rightarrow 2NaHS(aq)$$

The solution will yield crystals of the hydrate, $NaHS.3H_2O$, but any attempt to dehydrate it will hydrolyse the salt. The anhydrous salt can be obtained by the action of hydrogen sulphide on sodium ethoxide in excess of ethanol.

$$\underset{\text{(in ethanol)}}{C_2H_5ONa} + H_2S(l) \rightarrow NaHS(s) + C_2H_5OH(l)$$

When heated, it yields the normal sulphide.

$$2NaHS(s) \rightarrow Na_2S(s) + H_2S(g)$$

Sodium sulphide, Na_2S

A quantity of sodium hydroxide solution is divided into two equal portions. One of these is saturated with hydrogen sulphide, yielding sodium hydrogensulphide in solution as described above. The unchanged half of the alkali is then added, producing sodium sulphide in solution.

$$NaHS(aq) + NaOH(aq) \rightleftharpoons Na_2S(aq) + H_2O(l)$$

After evaporation and cooling, the hydrate, $Na_2S.9H_2O$ will crystallize and can be filtered off, washed with a little cold distilled water and allowed to dry.

Manufacture

Sodium sulphate, salt-cake, Na_2SO_4, is reduced by heating in a revolving furnace with finely powdered coal at about 1300 K. The main reaction is:

$$Na_2SO_4(s) + 4C(s) \rightarrow Na_2S(s) + 4CO(g)$$

but other products also occur. The solid product is extracted with water and, as above, yields the hydrate, $Na_2S.9H_2O$. Sodium sulphide solution is used in stripping hair from hides before tanning and in the production of dyes.

Sodium thiosulphate, 'hypo', $Na_2S_2O_3.5H_2O$

Laboratory preparation

A solution of sodium sulphite is boiled gently in a porcelain dish for 20–30 minutes with powdered sulphur always present. The sulphite is oxidized to sodium thiosulphate.

$$SO_3^{2-}(aq) + S(s) \rightarrow S_2O_3^{2-}(aq)$$

After evaporation to small bulk and cooling, the solution will deposit colourless crystals of the hydrate, $Na_2S_2O_3.5H_2O$. These may be filtered off, washed with a little cold distilled water and dried.

Properties and uses of sodium thiosulphate

1. *Action of mineral acids.* If acidified by dilute sulphuric acid or dilute hydrochloric acid, sodium thiosulphate solution yields *sulphur dioxide* (tested by decolorization of potassium manganate(VII) solution on filter-paper) and a *white precipitate* of amorphous *sulphur.*

$$S_2O_3^{2-}(aq) + 2H^+(aq) \rightarrow H_2O(l) + SO_2(g) + S(s)$$

Sulphites with mineral acid yields sulphur dioxide but *no sulphur.*
2. *Action with iodine.* At ordinary temperature, sodium thiosulphate solution reacts with iodine (usually in potassium iodide solution) to give *sodium iodide* and *sodium tetrathionate.*

$$2S_2O_3^{2-}(aq) + I_2(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)\ \text{(tetrathionate ion)}$$

This reaction is much used in quantitative analysis to estimate iodine or materials which liberate iodine quantitatively from potassium iodide solution, e.g. chlorine, bromine, bleaching powder, copper(II) salts.
3. *Use in photography.* For this, see p. 480.

Sodamide, $NaNH_2$

Sodamide is prepared by heating sodium (usually electrically) to about 700 K and passing into it a current of dry ammonia gas. The reaction is carried out in an iron vessel.

$$2Na(l) + 2NH_3(g) \rightarrow 2NaNH_2(l) + H_2(g)$$

On cooling, sodamide becomes a white, wax-like solid. It reacts with cold water, liberating ammonia.

$$NaNH_2(s) + H_2O(l) \rightarrow NaOH(aq) + NH_3(g)$$

Sodamide also reacts with white-hot carbon as described in the preparation of sodium cyanide below.

Sodium cyanide, NaCN

Manufacture

Sodamide, prepared as above, is run molten on to white-hot charcoal. Sodium cyanide is formed in a two-stage reaction, with sodium cyanamide as intermediate product.

$$\begin{aligned} 2NaNH_2(l) + C(s) &\rightarrow \underset{\text{(sodium cyanamide)}}{Na_2CN_2(l)} + 2H_2(g) \\ Na_2CN_2(l) + C(s) &\rightarrow 2NaCN(l) \end{aligned}$$

The sodium cyanide is extracted by hot water; the liquid is filtered and sodium cyanide crystallized out.

Properties and uses

(a) Sodium cyanide is very poisonous, as are all soluble cyanides. It is a white solid, readily soluble in water and much hydrolysed in solution because hydrogen cyanide is such a weak acid. For a discussion of this see under potassium cyanide (p. 76).

(b) Sodium cyanide is used in the extraction of silver (p. 475) and gold.

Detection and determination of sodium

Sodium compounds impart an intense *yellow* colour to the bunsen flame. The test is very sensitive so, unless the colour is strong and persistent, it probably indicates only a trace of sodium, probably an impurity.

Provided that the solution contains no cations but those of the alkali metals, Na^+ can be detected by addition of solution of potassium 'pyroantimonate', which produces a slow precipitation of sodium pyroantimonate.

$$2Na^+(aq) + H_2Sb_2O_7{}^{2-}(aq) \rightarrow Na_2H_2Sb_2O_7(s)$$

Potassium

Atomic number 19; electron arrangement 2.8.8.1. ($1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$). Potassium has three isotopes of mass numbers, in order of abundance, 39, 41, 40; relative atomic mass 39.10

Occurrence of potassium compounds

(a) The following potassium compounds occur in the Stassfurt deposits in Germany, which up to the war of 1914, were the World's chief source of potassium: *sylvine*, KCl; carnallite, $KCl.MgCl_2.6H_2O$; *kainite*, $K_2SO_4.MgSO_4.MgCl_2.6H_2O$; and *leonite*, $K_2SO_4.MgSO_4.4H_2O$. More recently, the Dead Sea region and areas in the USA and USSR have been worked for similar compounds. There are also large deposits of potassium compounds in North Yorkshire, UK.

(b) Potassium occurs quite frequently in rocks as silicate, e.g. in *orthoclase felspar*, $K_2O.Al_2O_3.6SiO_2$ and *potash mica* $KH_2Al_3(SiO_4)_3$.

Extraction of potassium

Potassium can be obtained by electrolysis of fused potassium hydroxide; compare Castner's method for sodium, p. 45. The extraction of potassium is, however, more difficult because it is more soluble in fused potassium hydroxide than sodium is in fused sodium hydroxide.

At cathode	*At anode*
$K^+ + e^- \rightarrow K$	$OH^- - e^- \rightarrow (OH)$
	$4(OH) \rightarrow 2H_2O(g) + O_2(g)$

The electrolysis of fused potassium cyanide has also been used. Potassium is more volatile than sodium, so that potassium has also been prepared by heating potassium chloride with sodium.

Properties of potassium

The metal is solid in ordinary conditions, soft enough to be cut with a knife and showing a silvery surface when freshly cut. It tarnishes rapidly in damp air. Its melting-point is 336 K and its boiling-point 1033 K.

When exposed to air, potassium shows a set of changes analogous to those detailed for sodium on p. 43 except that solid potassium carbonate is not obtained at the end. This compound is deliquescent and is left in a pool of solution. Potassium is stored under oil to prevent these changes.

Potassium is feebly radioactive, emitting beta-rays (electrons) from the isotope of mass number 40.

Potassium is very reactive (more so than sodium) and shows the following typical behaviour:

1. *With water.* Potassium reacts violently with water in the cold. Hydrogen is liberated and burns with the lilac flame characteristic of the presence of potassium compounds. Potassium hydroxide is left in solution.

$$2K(g) + 2H_2O(l) \rightarrow 2K^+(aq) + 2OH^- + H_2(g)$$

2. *With air or oxygen.* Heated in air under reduced pressure, potassium forms mainly its *monoxide*, K_2O, and any remaining potassium can be distilled off *in vacuo*. With excess oxygen, the *peroxide* K_2O_2 is formed (cf. sodium). When oxygen is passed into a solution of potassium in liquid ammonia, the *superoxide* $K^+O_2^-$ is produced.
3. *With hydrogen.* Potassium, when heated in *dry* hydrogen, produces *potassium hydride*, K^+H^-, a white solid resembling sodium hydride in chemical behaviour (p. 48).
4. *With chlorine.* Potassium combines readily with *dry* chlorine when heated to form *potassium chloride*, a white solid forming cubic crystals. It behaves correspondingly with bromine and iodine.

$$2K(s) + Cl_2(g) \rightarrow 2KCl(s)$$

5. *With ammonia.* Heated in *dry* ammonia gas, potassium forms

potassamide, a white solid resembling sodamide (p. 68) in chemical behaviour.

$$2K(s) + 2NH_3(g) \rightarrow 2KNH_2(s) + H_2(g)$$

6. *As a reducing agent*. Potassium is a most vigorous reducing agent because of its ready ionization by electron loss, $K - e^- \rightarrow K^+$. When heated, potassium will reduce most of the gases containing oxygen, e.g.

$$N_2O(g) + 2K(s) \rightarrow K_2O(s) + N_2(g)$$

Heated with the oxides of silicon or boron, it reduces them to the corresponding elements,

$$SiO_2(s) + 4K(s) \rightarrow Si(s) + 2K_2O(s)$$
$$B_2O_3(s) + 6K(s) \rightarrow 2B(s) + 3K_2O(s)$$

and gives a similar reduction if heated with the chlorides of magnesium and aluminium.

$$MgCl_2(s) + 2K(s) \rightarrow 2KCl(s) + Mg(s)$$
$$AlCl_3(s) + 3K(s) \rightarrow 3KCl(s) + Al(s)$$

Potassium monoxide, K_2O

The preparation of this compound was mentioned in the last section. Potassium monoxide is the ordinary basic oxide of potassium. It combines with water to produce the alkali, potassium hydroxide, and, through this reaction, has the usual salt-forming behaviour with acids.

$$O^{2-} + H_2O(l) \rightarrow 2OH^-(aq)$$
$$OH^-(aq) + H^+(aq) \rightleftharpoons H_2O(l)$$

Potassium hydroxide (caustic potash), K^+OH^-

Manufacture

(a) By electrolysis of potassium chloride solution in a mercury-cathode cell. This process is almost identical with that used for the manufacture of sodium hydroxide from brine (p. 49). The reactions are similar, substituting K for Na, and the potassium hydroxide is similarly purified.

(b) Potassium hydroxide can also be prepared by heating potassium carbonate (or potassium sulphate) solution with slaked line.

$$K_2CO_3(aq) + Ca(OH)_2(s) \rightleftharpoons 2KOH(aq) + CaCO_3(s)$$

Properties

Potassium hydroxide closely resembles sodium hydroxide, but is more soluble in both water and ethanol. It is a white solid, melting-point 633 K. The chemical behaviour of potassium hydroxide is almost identical with that of sodium hydroxide (p. 53) and need not be separately described. Potassium hydroxide is preferred to sodium hydroxide for absorption of carbon dioxide or sulphur dioxide because of its greater solubility, and because potassium carbonate and sulphite are more soluble than the corresponding sodium salts and do not separate out.

Uses

(a) Potassium hydroxide is the electrolyte in the nickel-iron electric storage battery.
(b) If boiled with oil or fat, potassium hydroxide solution yields soft soap. The reaction resembles the (hard) soap manufacture using sodium hydroxide, described on p. 52.

Potassium nitrate (saltpetre or nitre), KNO_3

Manufacture and uses

Potassium nitrate is manufactured by the reaction between sodium nitrate (Chile saltpetre) and potassium chloride in specially chosen conditions.

$$K^+Cl^-(aq) + Na^+NO_3^-(aq) \rightleftharpoons K^+NO_3^-(s) + Na^+Cl^-(aq)$$

Strictly speaking, there is no true chemical reaction here but merely a choice of conditions which reverses the ionic pairing. The important factor is the solubilities of the four reagents. These are:

Reagent	*Solubilities in g per 100 g water at*	
	291 K	373 K
Potassium chloride	37.4	56.6
Sodium nitrate	87.5	175.5
Potassium nitrate	31.2	247.0
Sodium chloride	36.0	39.8

From these figures, it is clear that, near the boiling point of water, sodium chloride is the least soluble of the four salts; near room temperature, potassium nitrate is the least soluble. This situation suggests the following technique.

Very concentrated, almost boiling solutions of potassium chloride and sodium nitrate are mixed. The least soluble salt at this temperature, sodium chloride, precipitates and is filtered off from the hot mixture. The filtrate is allowed to cool. At room temperature, potassium nitrate becomes the least soluble salt and crystallizes out. Very little sodium chloride crystallizes because its solubility falls so little between 373 K and 293 K. The potassium nitrate finds its chief use in the manufacture of gunpowder and fireworks. (Sodium nitrate cannot be used because it is hygroscopic.)

Like sodium nitrate, potassium nitrate decomposes when heated to give potassium nitrite and oxygen.

$$2KNO_3(s) \rightarrow 2KNO_2(s) + O_2(g)$$

Gunpowder

Gunpowder consists, chemically, of a mixture of potassium nitrate, wood charcoal, and sulphur in the approximate proportions of 6:1:1 respectively by mass. Its explosive effect arises from the sudden production, by combustion of the gunpowder in an enclosed space, of a volume of gas which is very large compared with the volume of the solid gunpowder, and further expanded by heat of reaction. These gases are mainly carbon dioxide and nitrogen, with some carbon monoxide. The main reaction is:

$$2KNO_3(s) + S(s) + 3C(s) \rightarrow K_2S(s) + N_2(g) + 3CO_2(g)$$

Potassium chloride, KCl

This salt occurs naturally as *sylvine*, but is obtained mainly from *carnallite*, $KCl.MgCl_2.6H_2O$. The crushed carnallite is steam-heated with liquor (from previous similar operations) containing magnesium chloride. Potassium chloride and magnesium chloride dissolve from the carnallite. After an hour or so, during which undissolved material settles out, the hot liquid is decanted. When cooled, it deposits crude potassium chloride which can be further purified by recrystallization.

Potassium chloride crystallizes in white, cubic crystals, melting at 1041 K. It closely resembles sodium chloride in chemical behaviour. It is less soluble in water than sodium chloride at low temperature (KCl 27.6 g, NaCl 35.7 g at 273 K) but more soluble at high temperature

(KCl 56.6 g, NaCl 39.8 g at 373 K in 100 g of water). Potassium chloride is used as a fertilizer. It is also used as a source of potassium hydroxide and potassium nitrate.

Potassium carbonate, K_2CO_3

Manufacture

This compound cannot be made by a process analogous to the ammonia–soda process for sodium carbonate because, though the reactions would occur, potassium hydrogencarbonate is too soluble to precipitate.

Potassium carbonate is usually made by the following (Precht) process. Solid hydrated magnesium carbonate is added to a concentrated solution of potassium chloride and carbon dioxide is passed through the suspension. A precipitate of magnesium potassium hydrogencarbonate is formed.

$$2KCl(aq) + 3[MgCO_3.3H_2O](s) + CO_2(g) \rightarrow 2[MgCO_3.KHCO_3.4H_2O](s) + MgCl_2(aq)$$

This precipitate is filtered off and treated with magnesium oxide in water below 293 K. Hydrated magnesium carbonate is precipitated, filtered out, and used again. Potassium carbonate can be crystallized from the solution.

$$2[MgCO_3.KHCO_3.4H_2O](s) + MgO\,(suspension) \rightarrow 3[MgCO_3.3H_2O](s) + K_2CO_3(aq)$$

Potassium carbonate crystallizes as $K_2CO_3.3H_2O$ between 283 K and 298 K. It is dehydrated to $K_2CO_3.H_2O$ at 373 K and to K_2CO_3 at 403 K. It is very soluble in water (112 g in 100 g water at 293 K) and is deliquescent. It is used as a drying agent for organic liquids and is very effective in salting-out ethanol from aqueous mixtures. It is used in the manufacture of hard glass, i.e. glass of high melting-point.

Potassium hydrogencarbonate (potassium bicarbonate), $KHCO_3$

This compound can be precipitated by passing carbon dioxide into a cold, saturated solution of potassium carbonate (which is much more soluble than the hydrogencarbonate).

$$CO_3^{2-}(aq) + H_2O(l) + CO_2(g) \rightarrow 2HCO_3^-(aq)$$

It decomposes when heated (as sodium hydrogencarbonate does), to leave potassium carbonate and liberate carbon dioxide and steam.

$$2KHCO_3(s) \rightarrow K_2CO_3(s) + H_2O(l) + CO_2(g)$$

Potassium hydrogencarbonate has no large-scale uses.

Potassium sulphate, K_2SO_4

Potassium sulphate is chiefly important as a fertilizer (*sulphate of potash*) and in the manufacture of potash alum. It is prepared on the large scale from the complex salt, kainite, $K_2SO_4.MgSO_4.MgCl_2.6H_2O$, occurring in the Stassfurt deposits. When cooled, a hot, saturated solution of kainite deposits the double sulphate, $MgSO_4.K_2SO_4.6H_2O$. This is filtered off, redissolved and treated with potassium chloride solution. The following reaction occurs:

$$MgSO_4.K_2SO_4.6H_2O(aq) + 2KCl(aq) \rightarrow 2K_2SO_4(s) + MgCl_2(aq) + 6H_2O(l)$$

When cooled, the solution deposits potassium sulphate which is not very soluble in water (11.1 g in 100 g water at 293 K). Potassium sulphate crystallizes anhydrous, in contrast to the much hydrated $Na_2SO_4.10H_2O$.

Sulphides of potassium; potassium sulphide, K_2S; potassium hydrogensulphide, KHS

If a solution of potassium hydroxide is saturated with hydrogen sulphide, a hydrate of potassium hydrogensulphide, $(2KHS).H_2O$, can be crystallized from the solution after evaporation and cooling.

$$KOH(aq) + H_2S(g) \rightarrow KHS(aq) + H_2O(l)$$

To prepare potassium sulphide, a solution of potassium hydroxide is divided into two equal parts. One of them is saturated with hydrogen sulphide, giving the reaction stated above; the other half of the alkali is then added.

$$KHS(aq) + KOH(aq) \rightarrow K_2S(aq) + H_2O(l)$$

A hydrate of normal potassium sulphide, $K_2S.5H_2O$, can be crystallized from the solution. Polysulphides of potassium also exist, such as K_2S_2, K_2S_5, and K_2S_6.

When potassium carbonate is fused with sulphur, a material, named in early days *liver of sulphur*, is formed. The name arose from the maroon colour of the material. It contains polysulphides of potassium, potassium sulphate, and potassium thiosulphate, $K_2S_2O_3$. A solution of liver of sulphur is used as a horticultural spray against insects and mildew.

Potassium cyanide ('prussic acid'), KCN

This salt is produced when potassium hexacyanoferrate(II) (potassium ferrocyanide) is heated to bright red heat,

$$K_4Fe(CN)_6(s) \rightarrow 4KCN(s) + Fe(s) + 2C(s) + N_2(g)$$

In industry a mixture of sodium and potassium cyanides, made by heating potassium hexacyanoferrate(II) with sodium, is often used instead of either of the pure cyanides.

$$K_4Fe(CN)_6(s) + 2Na(s) \rightarrow 4KCN(s) + 2NaCN(s) + Fe(s)$$

In either case, the cyanide can be extracted by hot water and crystallized.

Potassium cyanide is the soluble cyanide most commonly used as a laboratory reagent. It is very much hydrolysed in solution because hydrocyanic acid is so weak. The ionic situation is:

$$\begin{array}{llll} \text{From potassium cyanide:} & K^+ & CN^- & \\ & & + & \\ \text{From water:} & H_2O \rightleftharpoons OH^- + & H^+ & \\ & & \upharpoonleft\downharpoonright & (A) \\ & & HCN & \end{array}$$

Removal of hydrogen ion to form unionized hydrocyanic acid molecules disturbs the ionic equilibrium of water ($K_w = 10^{-14}$ mol^2 dm^{-6}). More water ionizes to restore the equilibrium, putting OH^- ion into excess. The pH of the solution rises above 7 and the solution reacts alkaline. The strong base, potassium hydroxide, remains fully ionized as K^+OH^-. The solution has the almond smell of hydrogen cyanide, HCN, which is very volatile. If well boiled in a fume cupboard, a dilute solution of potassium cyanide loses hydrogen cyanide as vapour. As it boils off, equilibrium (A) above is disturbed, and, in accordance with Le Chatelier's Principle, more HCN molecules are produced. This increases the hydrolysis by removing more H^+, and, eventually, all hydrogen cyanide will be eliminated, leaving K^+ and OH^- ions in water, i.e. a solution of potassium hydroxide. Some hydrolysis will also occur producing potassium methanoate and ammonia.

$$HCN(g) + 2H_2O(l) \rightarrow HCOO^-NH_4^+(aq)$$

$$HCOO^-NH_4^+(aq) + K^+OH^-(aq) \rightarrow HCOO^-K^+(aq) + NH_3(g) + H_2O(l)$$

Potassium cyanide is often known as prussic acid, though it is, of course, the potassium salt of the acid, HCN. Like all soluble cyanides, it is very poisonous.

Potassium thiocyanate, KCNS

Potassium thiocyanate can be prepared directly by fusing potassium cyanide with sulphur. The produce may be extracted with a hot ethanol–water mixture and, after evaporation and cooling, the solution gives colourless, deliquescent crystals of potassium thiocyanate.

$$\mathrm{KCN(l) + S(l) \rightarrow KCNS(l)}$$

On the larger scale, potassium thiocyanate can be made by fusing a mixture of potassium hexacyanoferrate(II) and potassium carbonate with sulphur.

Uses of potassium thiocyanate

1. *In testing for iron(III) ion in solution.* A blood-red coloration is given by a reaction usually written as:

$$\mathrm{Fe^{3+}(aq) + 3CNS^{-}(aq) \rightleftharpoons \underset{\text{(blood-red)}}{Fe(CNS)_3(aq)}}$$

but it is probably more complex.
2. *In titrating silver ion in solution* (*Volhard's method*). Potassium thiocyanate is used in the burette, and, in the titration, a precipitate of silver thiocyanate is formed. The indicator is iron(III) ion (supplied as iron alum), which gives a blood-red coloration, as in (1) above, at the end-point, i.e. when potassium thiocyanate passes into excess. The titration can be carried out in acidic solution.

Detection of potassium

Potassium compounds give a characteristic lilac colour to a bunsen flame. Provided that the ions of the alkali metals are the only cations in the solution, potassium ions can be detected by:

(a) 20 per cent chloric(VII) acid and ethanol, which give a white precipitate of potassium chlorate(VII).

$$\mathrm{K^{+}(aq) + ClO_4{}^{-}(aq) \rightarrow K^{+}ClO_4{}^{-}(s)}$$

(b) Sodium hexanitrocobaltate(III) (sodium cobaltinitrite) solution, which gives a yellow precipitate of potassium hexanitrocobaltate(III).

$$3K^+(aq) + Co(NO_2)_6^{3-}(aq) \rightarrow K_3Co(NO_2)_6(s)$$

Questions

1. Mainly by a labelled sketch of apparatus and ionic equations, describe the extraction of sodium metal from *either* sodium hydroxide *or* common salt. How, and in what conditions, does sodium react with (a) water, (b) hydrogen, (c) chlorine, (d) ammonia, (e) oxygen?

2. Describe the essential chemistry of the Solvay process for converting common salt into 'washing soda'. (Give no diagrams and mention only such features of the plant as are essential to the success of the process.) How, and in what conditions, does sodium carbonate react with (a) carbon dioxide, (b) silica?

3. Describe and explain (a) the behaviour of sodium hydrogen carbonate when heated, (b) the behaviour of sodium with mercury, (c) the action of heat on sodium nitrate, (d) the effect of heating sodium sulphite solution with sulphur. What occurs if (i) the product of (b) is added to water, (ii) the product of (d) is acidified in aqueous solution?

4. Give an account of the manufacture of *solid sodium hydroxide* from common salt by electrolysis. How, and in what conditions, does sodium hydroxide react with (a) silica, (b) carbon dioxide, (c) aluminium, (d) chlorine? Briefly discuss *two* important uses of sodium hydroxide in industry.

5. (a) Describe the manufacture of sodium hydroxide and chlorine from sodium chloride. Give a simple sketch of the cell and explain the principles which are involved.

Mention two uses of sodium hydroxide and two uses of chlorine.

(b) When a pellet of sodium hydroxide is put on a watch glass and left in the air, it gradually changes to a colourless liquid. On further exposure to the air, the liquid first turns into colourless transparent crystals, and then into a white opaque solid whose mass is 55% greater than that of the original sodium hydroxide. Explain fully these changes. [H 1, C 12, O 16, Na 23.] (O.)

5

Elements of Group II

Group II of the Periodic Table contains the group of elements from beryllium to radium. These are often referred to as the *alkaline earth* metals. Beryllium, consisting of very small atoms, behaves anomalously: its compounds are largely covalent. It is not considered further here. Magnesium, calcium, strontium, and barium form a closely related group. The chief points of chemical similarity can be summarized as follows. (See also p. 9.)

(a) All the metals are strongly electropositive and attack water, though magnesium will only react at an appreciable rate with boiling water or steam.

(b) All the oxides react vigorously with water and produce strongly basic hydroxides. The reaction of magnesium oxide is the least vigorous.

(c) Salts of all the metals show little or no tendency to hydrolysis, except for some of those of magnesium.

(d) All the metals form salt-like hydrides, $M^{2+}.2H^-$, which are attacked by water with evolution of hydrogen.

(e) Strontium and barium show no tendency to form complex ions; calcium and magnesium show only slight tendency.

(f) In their compounds, all the metals show an invariable oxidation state of + 2, associated with removal of the two outermost electrons. The ease of such ionization increases with increased shielding of the nucleus by completed shells of electrons. For this reason, the reactivity of the metals increases down the Group.

(g) All the carbonates are almost insoluble in water; all are decomposed by heat, with increasing difficulty in the order:

$$MgCO_3 \rightarrow CaCO_3 \rightarrow SrCO_3 \rightarrow BaCO_3$$

Among the slight *differences* are:

(i) Magnesium sulphate is freely soluble in water. Calcium sulphate is much less soluble than magnesium sulphate, but is considerably more soluble than the sulphates of strontium and barium.

(ii) Barium chromate(VI) will precipitate in the presence of dilute ethanoic acid. The other Group II chromates(VI) remain in solution.

Magnesium

Atomic number 12; electron arrangement 2.8.2 ($1s^2 2s^2 2p^6 3s^2$). Magnesium has three isotopes of mass number, in order of abundance, 24, 26 and 25; relative atomic mass 24.31.

Occurrence

1. *As carbonate.* Magnesium carbonate occurs as *magnesite*, $MgCO_3$, and also as the double carbonate, $MgCO_3.CaCO_3$, *dolomite*.
2. *As sulphate.* Magnesium occurs as sulphate in $MgSO_4.7H_2O$, *Epsom salt*, in $MgSO_4.H_2O$, *kieserite*, and $KCl.MgSO_4.3H_2O$, *kainite*.
3. The double *chloride*, $KCl.MgCl_2.6H_2O$, is much used for the extraction of magnesium. It is known as *carnallite*.
4. Various *silicates* of magnesium occur, e.g. olivine, Mg_2SiO_4, and asbestos, a complex form of $CaMg_3(SiO_3)_4$.

Sea-water contains about 0.13 per cent of magnesium by mass and a process of extraction from this source is now in operation. Magnesium also occurs in all plant and animal tissues, especially in chlorophyll in plants.

Extraction of magnesium

Magnesium is extracted by *electrolytic* reduction and by *chemical* reduction.

1. *Electrolytic reduction*

In recent years, this process has been applied to the extraction of magnesium from sea-water, which typically contains about one million tonnes of magnesium per cubic kilometre. Shorn of its technical complications (which are considerable), the extraction of magnesium from sea-water by the Dow process is essentially as follows.

Lime is prepared by heating oyster shells or dolomite (as sources of calcium carbonate) and is used to precipitate magnesium hydroxide from sea-water.

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$
$$CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(s)$$
$$Mg^{2+}(aq) + 2OH^-(aq) \rightarrow Mg(OH)_2(s)$$

After settling, during which it thickens, the precipitate is washed, then converted to magnesium chloride by solution in hydrochloric acid. Anhydrous magnesium chloride is recovered by evaporation in a current of hydrogen chloride (to prevent hydrolysis) and is electrolysed (Figure 5.1).

The density of magnesium is low enough for it to float on the electrolyte. To protect the metal from anodic chlorine, the anode is enclosed in a porcelain sheath by which the chlorine is conducted away. The electrolyte contains some sodium chloride to make the operating temperature about 1000 K (melting point of magnesium 923 K). Magnesium is protected from atmospheric oxidation by a thin coating of electrolyte. It is skimmed from the surface and cast into blocks.

At the cathode	*At the anode*
$Mg^{2+} + 2e^- \rightarrow Mg(l)$	$2Cl^- - 2e^- \rightarrow Cl_2(g)$

The anodic chlorine is converted to hydrochloric acid and used again in the early part of the process.

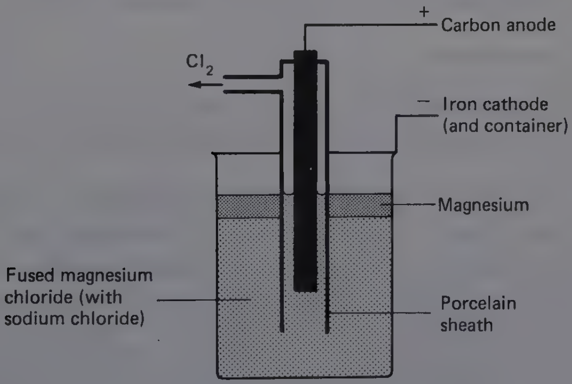


Figure 5.1 *Extraction of magnesium*

2. *Production of magnesium by chemical reduction*

More than one process is available for this purpose. The following (Pidgeon process) is typical. Dolomite is heated to produce a mixture of calcium and magnesium oxides.

$$CaCO_3.MgCO_3(s) \rightarrow MgO(s) + CaO(s) + 2CO_2(g)$$

It is mixed with ferrosilicon, which is a source of silicon containing some iron. The mixture is heated electrically, in a retort of chromium steel, to a temperature of about 1500 K at a very low pressure (400 N m^{-2}, about 3 mmHg).

$$2MgO(s) + CaO(s) + Si(s) \rightarrow CaSiO_3(l) + 2Mg(g)$$

The magnesium vaporizes and condenses to an almost pure solid in a condenser attached to the retort. It can be removed after cooling.

Uses of magnesium

(a) Magnesium is chiefly employed in the production of light alloys for use in engineering, e.g. *elektron* (95% Mg; 5% Zn). Other alloys containing upwards of 85 per cent of magnesium, alloyed with some, or all, of Al, Zn, Mn, and Ni, are in use. *Duralumin* and *magnalium* also contain small amounts of magnesium.
(b) Magnesium powder, mixed with an oxidizing agent such as potassium chlorate(V), burns brilliantly. It is now out of date as a photographic flash-powder, but is used in fireworks and flares.
(c) Grignard reagents, made by reacting magnesium with halogenoalkanes in rigorously dry ethoxyethane, are widely used in the synthesis of organic compounds.
(d) Magnesium is used in the extraction of titanium metal.

Properties of magnesium

Magnesium is silvery-white in appearance. It melts at 923 K, and boils at 1380 K. If heated at very low pressure, it will give a crystalline sublimate.

1. *With air*. Dry air does not attack magnesium. Damp air slowly puts on to it a layer of oxide, which later forms hydroxide and carbonate.

Magnesium takes fire in air, at about 900 K if in ribbon or powder form, to burn with a brilliant bluish-white flame. The product contains its oxide and nitride.

$$2Mg(s) + O_2(g) \rightarrow 2MgO(s)$$
$$3Mg(s) + N_2(g) \rightarrow Mg_3N_2(s)$$

If the product is damped and warmed, *ammonia* is evolved.

$$MgO(s) + H_2O(l) \rightarrow Mg(OH)_2(s)$$
$$Mg_3N_2(s) + 6H_2O(l) \rightarrow 3Mg(OH)_2(s) + 2NH_3(g)$$

2. *With water. Reducing action.* Clean magnesium attacks cold water only very slowly, and the reaction is not rapid even at 373 K. But it burns brilliantly if heated in steam, producing its oxide and *hydrogen.*

$$Mg(s) + H_2O(l) \rightarrow MgO(s) + H_2(g)$$

A silica tube is desirable here; glass usually breaks.

This is an example of the vigorous *reducing action* of magnesium, which is essentially the conversion of magnesium to its ions:

$$Mg - 2e^- \rightarrow Mg^{2+}$$

3. *With acids.* Dilute hydrochloric and sulphuric acids react with magnesium, liberating *hydrogen.*

$$Mg(s) + 2H^+(aq) \rightarrow Mg^{2+}(aq) + H_2(g)$$

Magnesium is said to react slowly with very dilute nitric acid to give some hydrogen. More concentrated nitric acid yields *oxides of nitrogen* in the usual way, e.g.

$$3Mg(s) + 8HNO_3(aq) \rightarrow 3Mg(NO_3)_2(aq) + 4H_2O(l) + 2NO(g)$$

Hot, concentrated sulphuric acid yields *sulphur dioxide.*

$$Mg(s) + 2H_2SO_4(l) \rightarrow MgSO_4(aq) + 2H_2O(l) + SO_2(g)$$

Alkalis do not react with magnesium.

4. *With non-metals.* When heated, magnesium combines with several non-metals—chlorine, sulphur, nitrogen, and phosphorus—often with great violence.

$$Mg(s) + Cl_2(g) \rightarrow MgCl_2(s)$$
$$Mg(s) + S(s) \rightarrow MgS(s)$$
$$3Mg(s) + N_2(g) \rightarrow Mg_3N_2(s)$$
$$6Mg(s) + P_4(s) \rightarrow 2Mg_3P_2(s)$$

Magnesium oxide (magnesia), MgO

Magnesium oxide may be prepared by strong heating of the nitrate, carbonate, or hydroxide of magnesium. The nitrate may be prepared by the action of nitric acid on magnesium. The carbonate or hydroxide may be prepared by precipitation, as below. If magnesium is burnt in air, as previously mentioned, the oxide is contaminated with nitride.

$$2Mg(s) + O_2(g) \rightarrow 2MgO(s)$$
$$3Mg(s) + N_2(g) \rightarrow Mg_3N_2(s)$$

It can be purified by addition of water, followed by strong heating.

$$MgO(s) + H_2O(l) \rightarrow Mg(OH)_2(s)$$
$$Mg_3N_2(s) + 6H_2O(l) \rightarrow 3Mg(OH)_2(s) + 2NH_3(g)$$

On heating, $Mg(OH)_2(s) \rightarrow MgO(s) + H_2O(l)$

Properties

Magnesium oxide is a white powder. It is only slightly soluble in water (0.001 g in 100 g water at 293 K), though the solubility seems to vary with the heat treatment the oxide has received. A *higher* heating temperature tends to produce a *lower* solubility in the oxide. Though only slightly soluble in water, magnesium oxide is quite a strong base, i.e. the dissolved material is highly ionized and the solution has an alkaline reaction, even though the solubility is low.

$$MgO(s) \rightarrow Mg^{2+}(aq) + \underset{\text{in solution}}{O^{2-}(aq)}$$
$$O^{2-}(aq) + H_2O \rightarrow 2OH^-(aq)$$

Magnesium oxide readily forms salts with the dilute mineral acids, e.g.,

$$Mg^{2+}O^{2-}(s) + 2H^+SO_4{}^{2-}(aq) \rightarrow Mg^{2+}SO_4{}^{2-}(aq) + H_2O(l)$$

Uses

(a) Magnesium oxide has a very high melting point (about 3100 K). Consequently, it is used as a refractory lining for furnaces, especially if a basic reaction is wanted in the lining (see p. 434).
(b) Magnesium oxide is used as 'magnesia' in medicine to correct acidity in the stomach. Magnesium ions have an aperient action.

Magnesium hydroxide, $Mg(OH)_2$

Magnesium hydroxide can be precipitated from solutions of magnesium salts by caustic alkali solution.

$$Mg^{2+}(aq) + 2OH^-(aq) \rightarrow Mg(OH)_2(s)$$

Magnesium hydroxide has the same reaction with dilute mineral acids as the oxide (above).

Magnesium carbonate, $MgCO_3$

This compound occurs naturally as *magnesite*, $MgCO_3$, and in *dolomite*, $MgCO_3.CaCO_3$. It is best known in *basic* forms. These are made by the action of sodium carbonate solution (in which there is much hydrolysis and a considerable concentration of hydroxide ion, OH^-) on a solution of a magnesium salt, usually the sulphate. These basic carbonates are used in the manufacture of toothpastes and face powders.

A *normal* hydrated magnesium carbonate can be precipitated by the action of sodium hydrogencarbonate solution on magnesium sulphate solution. This is possible because sodium hydrogencarbonate is much less hydrolysed in solution than sodium carbonate, so that the concentration of OH^- remains insignificant.

$$Mg^{2+}(aq) + 2HCO_3^-(aq) + 2H_2O(l) \rightarrow MgCO_3.3H_2O(s) + CO_2(g)$$

If wanted pure, the precipitate can be filtered, washed with hot, distilled water and dried.

Magnesium carbonate is *not* precipitated in Group V of the tables of Qualitative Analysis along with the carbonates of calcium, strontium and barium. It is thought that in the presence of ammonium ion (from ammonium carbonate) and chloride ion (from HCl added earlier), magnesium forms an anion as:

$$Mg^{2+}(aq) + 3Cl^-(aq) + NH_4^+(aq) \rightarrow NH_4^+MgCl_3^-(aq)$$

So little free Mg^{2+} is available that the solubility product of magnesium carbonate is not reached, and this salt does not precipitate.

All the above forms of magnesium carbonate are converted to the oxide by heat.

Magnesium chloride, $Mg^{2+}(Cl^-)_2$

Magnesium chloride occurs *in carnallite*, $KCl.MgCl_2.6H_2O$, and since Mg^{2+} and Cl^- ions are present in sea water, it must be said to occur there.

Preparation

Solution of magnesium metal, its oxide, hydroxide or carbonate in dilute hydrochloric acid gives a solution of magnesium chloride, from which crystals of the hydrate, $MgCl_2.6H_2O$, can be obtained. This cannot be dehydrated directly to the anhydrous salt because, when heated, it undergoes hydrolysis to a basic compound:

$$MgCl_2.6H_2O(s) \rightleftharpoons Mg(OH)Cl(s) + HCl(g) + 5H_2O(l)$$

Stronger heating will leave magnesium oxide.

$$Mg(OH)Cl(s) \rightarrow MgO(s) + HCl(g)$$

Heating in a current of hydrogen chloride will produce anhydrous magnesium chloride, because the continual presence of the acidic gas inhibits hydrolysis by reversing the above reactions. Also, if magnesium chloride is mixed in solution with an equimolar mass of ammonium chloride, the double salt, $MgCl_2.NH_4Cl.6H_2O$, can be crystallized. When heated, this salt leaves anhydrous magnesium chloride.

$$MgCl_2.NH_4Cl.6H_2O(s) \rightarrow MgCl_2(s) + NH_3(g) + HCl(g) + 6H_2O(l)$$

The strongly acidic HCl prevents hydrolysis.

Probably the best way of preparing the anhydrous chloride is to heat magnesium in a current of *dry* chlorine or *dry* hydrogen chloride. Apparatus suitable for this is given on p. 367.

$$Mg(s) + Cl_2(g) \rightarrow MgCl_2(s)$$
$$Mg(s) + 2HCl(g) \rightarrow MgCl_2(s) + H_2(g)$$

Industrially (p. 81), magnesium chloride is made from magnesium hydroxide extracted from sea-water.

Magnesium sulphate, $MgSO_4$

Kieserite, $MgSO_4.H_2O$, occurs in the Stassfurt deposits. If boiled with water and crystallized, kieserite yields the common heptahydrate, $MgSO_4.7H_2O$, known as *Epsom salt*, from its occurrence in springs at Epsom. Several other hydrates, e.g. $MgSO_4.6H_2O$, have been described. Epsom salt is freely soluble in water (35.5 g in 100 g water at 293 K) and is used in medicine as a purgative, in tanning and dyeing, and in soap manufacture.

Detection and estimation of magnesium

In the tables of Qualitative Analysis, magnesium does not precipitate as sulphide, hydroxide or carbonate. It is therefore left to pass into Group VI with the alkali metals. In these conditions, magnesium ion can be detected in solution by the addition of *ammonia* and *sodium* *phosphate(V)* solution. This causes precipitation, usually slowly, of a white, *crystalline* solid, *magnesium ammonium phosphate(V)*.

$$Mg^{2+}(aq) + NH_4^+(aq) + PO_4^{3-}(aq) + 6H_2O(l) \rightarrow MgNH_4PO_4.6H_2O(s)$$

The same process can be used to determine magnesium quantitatively. The precipitate is filtered, washed with dilute ammonia and heated to constant weight at about 1000 K. It leaves magnesium heptaoxodiphosphate(V) (magnesium pyrophosphate), which is weighed.

$$2MgNH_4PO_4.6H_2O(s) \rightarrow Mg_2P_2O_7(s) + 13H_2O(g) + 2NH_3(g)$$

Magnesium constitutes the fraction $2Mg/Mg_2P_2O_7$, i.e. 48/222, of the mass of the 'pyrophosphate.'

Calcium

Atomic number 20; electron arrangement 2.8.8.2 ($1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$). Calcium has isotopes of mass number, in order of abundance, 40, 44, 42, 43, 46 and 48; relative atomic mass 40.08.

Occurrence

Calcium compounds are widespread in the Earth's crust. They appear in the following principal forms.

1. *As calcium carbonate*, $CaCO_3$. *Chalk, limestone, marble, calcspar*, and *Iceland spar* are all forms, more or less impure, of *calcite*, which crystallizes in the hexagonal system (density 2.72 g cm^{-3}). Calcite also occurs in eggshells and, to some extent, in animal bones.

Crystallizing in the rhombic system is *aragonite* (density, 2.92 g cm^{-3}).

Dolomite is the double carbonate, $CaCO_3.MgCO_3$. Both dolomite and limestone occur in enormous masses, forming mountain ranges or groups.

2. *As calcium sulphate*. This compound occurs as *anhydrite*, $CaSO_4$, and as *gypsum*, $CaSO_4.2H_2O$.
3. *As calcium fluoride*, CaF_2. *Fluorspar* is calcium fluoride.
4. *As calcium phosphate*. Calcium phosphate(V), $Ca_3(PO_4)_2$, occurs in animal bones and as *apatite*, $Ca_3(PO_4)_2.CaF_2$.

Extraction and uses of calcium

Calcium is usually extracted by electrolysis of *fused calcium chloride*

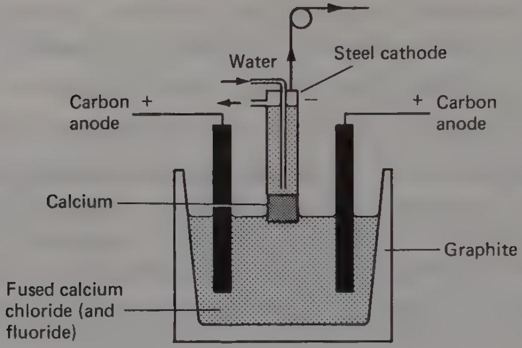


Figure 5.2 *Extraction of calcium*

containing about one-sixth of its weight of *calcium fluoride*, so ensuring a fusion temperature of 920 K. The *cathode* is a water cooled *steel* tube and the *anode* is made of *graphite* (Figure 5.2). Solid calcium (m.p. 1123 K) adheres to the cathode, which is raised as calcium accumulates, so that the calcium itself soon becomes the effective cathode. A layer of electrolyte protects the calcium from oxidation. When the full limit of cathode rise is reached, the calcium is detached and the steel cathode lowered again to the electrolyte.

After melting (in argon to prevent oxidation), the adhering electrolyte is removed, leaving calcium of about 95 per cent purity. Distillation *in vacuo* gives a purer product.

At the cathode	*At the anode*
$Ca^{2+} + 2e^- \rightarrow Ca(s)$	$Cl^- - e^- \rightarrow (Cl)$
	$(Cl) + (Cl) \rightarrow Cl_2(g)$

Calcium is used

(a) as a deoxidant for metals such as copper, aluminium, and special steels;
(b) for hardening lead in bearing-alloys (Ca 3%; Pb 97%);
(c) for the manufacture of 'hydrolith' (see below).

Calcium is important in biological systems.

Properties of calcium

Calcium is silvery white, soft enough to be cut with a knife when pure, of very low density (1.55 $g\,cm^{-3}$) and melting point 1123 K.

1. *Action with air.* On exposure to air at room temperature, calcium tarnishes, forming in succession its oxide, hydroxide, and carbonate.

$$2Ca(s) + O_2(g) \rightarrow 2CaO(s)$$
$$CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(s)$$
$$Ca(OH)_2(s) + CO_2(g) \rightarrow CaCO_3(s) + H_2O(l)$$

When gently heated in air, it burns forming a mixture of calcium oxide and nitride, Ca_3N_2. This liberates ammonia when water is added.

$$Ca_3N_2(s) + 6H_2O(l) \rightarrow 3Ca(OH)_2(s) + 2NH_3(g)$$

2. *Action with water.* Calcium reacts briskly with water; unlike the alkali metals, it sinks. *Hydrogen* is evolved and calcium hydroxide (slaked lime) is formed. This is only sparingly soluble, and tends to precipitate on the metal and stop the action. As the reaction proceeds, a white suspension of calcium hydroxide is seen.

$$2H_2O(l) \rightleftharpoons 2H^+(aq) + 2OH^-(aq)$$
$$Ca(s) + 2H^+(aq) \rightarrow Ca^{2+}(aq) + H_2(g)$$
$$Ca^{2+}(aq) + 2OH^-(aq) \rightarrow Ca(OH)_2(s)$$

3. *Action with hydrogen.* Heated in *dry* hydrogen, calcium produces *calcium hydride* (see also next section).

$$Ca(s) + H_2(g) \rightarrow CaH_2(s)$$

Calcium has no reaction with *alkalis*.

Calcium hydride, CaH_2

Calcium hydride is produced as mentioned immediately above. It is a salt-like hydride, a colourless solid, which yields *hydrogen* when cold water is added to it.

$$CaH_2(s) + 2H_2O(l) \rightarrow Ca(OH)_2(s) + 2H_2(g)$$

It is used, as 'hydrolith', for generating hydrogen in this way on the small scale.

Calcium oxide (quicklime), CaO

Manufacture

Calcium oxide is made on the large scale by heating calcium carbonate. Limestone is usually used; very pure quicklime can be obtained from marble. The reaction is reversible.

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

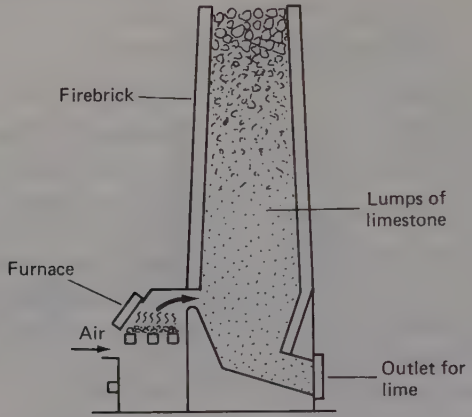


Figure 5.3 *Production of quicklime*

At 1170 K, the equilibrium pressure of carbon dioxide slightly exceeds one atmosphere so that, at this temperature, decomposition is rapid and virtually complete if the gas is allowed to escape freely or, better, removed by a draught of air.

In a modern vertical lime kiln, lump limestone is fed in at the top and the firing is by producer gas. A temperature of 1100–1300 K is maintained and quicklime is removed at the base (Figure 5.3).

Laboratory preparation of calcium oxide

Calcium oxide is not often made on the laboratory scale. The manufacture (described above) may be imitated by heating chalk, marble or slaked lime in a gas-fired muffle-furnace giving a temperature near to 1300 K.

Properties of calcium oxide

Pure quicklime is an amorphous white solid, though, as manufactured, it is usually in somewhat discoloured lumps. It is highly refractory, sustaining a temperature of about 2900 K without decomposition, and then melting. Under intense heat, it becomes incandescent, a fact once used in the now out-dated 'lime-light', employed in the theatre and magic lantern shows.

1. *Action with water*. If cold water is added to quicklime, there is hissing and the material swells, cracks and crumbles to a white powder, *calcium hydroxide* or *slaked lime*, with much steam evolved. This is the *slaking* of quicklime. The liveliness of this reaction explains the name *quick*lime—

quick as in the phrase 'the quick and the dead'. The reaction is strongly exothermic.

$$CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(s) \qquad \Delta H = -65\ kJ\ mol^{-1}$$

2. *With chlorine.* At red heat, calcium oxide reacts with chlorine producing *calcium chloride*:

$$2CaO(s) + 2Cl_2(g) \rightarrow CaCl_2(s) + O_2(g)$$

The reactions of *damp* 'quicklime' are really reactions of 'slaked lime' and will be considered in the next section. Similarly, the reactions of quicklime as a basic oxide with dilute acids are also reactions of slaked lime because of the presence of water in the acids.

Uses of calcium oxide

1. Great quantities of 'quicklime' are slaked for use in the building industry in mortar and plaster; in the manufacture of bleaching powder, and for many other industrial purposes.
2. If 'quicklime' is slaked with a concentrated solution of sodium hydroxide and the product is dried by heat, 'sodalime' is formed. For many purposes it is equivalent to sodium hydroxide, but has the advantages of non-deliquescence and a higher melting point. It is used as a drying agent and absorbent of carbon dioxide.
3. Calcium oxide is sometimes used as a drying agent for materials which react with concentrated sulphuric acid and calcium chloride, e.g. ethanol or ammonia gas.

Calcium hydroxide (slaked lime), Ca $(OH)_2$

Manufacture

Calcium hydroxide is made by the action of water on calcium oxide. This was fully described above. The laboratory preparation is similar. Any excess water may be dried off by heating in a steam-oven.

Properties of calcium hydroxide

1. Calcium hydroxide is a white solid, usually in powder form. It is only sparingly soluble in water and shows the unusual property of a *decreasing* solubility as temperature rises, e.g. 0.17 g in 100 g water at 283 K, 0.059 g at 353 K. A solution of calcium hydroxide in water is known as *lime water* and is much used as a test for carbon dioxide.

This gas produces a 'milkiness' in the lime water by precipitating fine white particles of calcium carbonate (see also p. 151).

$$Ca(OH)_2(aq) + CO_2(g) \rightarrow CaCO_3(s) + H_2O(l)$$

Lime water is not, however, a satisfactory *absorbent* for carbon dioxide; it is too dilute. Potassium hydroxide solution should be used. Water containing a large excess of undissolved calcium hydroxide is known as *milk of lime* and finds considerable use, especially when hot, as a cheap industrial alkali.

2. *With acids.* Calcium hydroxide is strongly *basic.* It reacts readily with dilute hydrochloric and nitric acids, forming the corresponding calcium salts in solution, e.g.

$$Ca(OH)_2(s) + 2H^+(aq) + 2Cl^-(aq) \rightarrow CaCl_2(aq) + H_2O(l)$$

The corresponding reaction with dilute sulphuric acid is unsatisfactory. Calcium sulphate is only sparingly soluble and tends to precipitate on undissolved lime. This may make the reaction incomplete.

3. *With ammonium salts.* Calcium hydroxide reacts with ammonium salts when *heated* (better if damped) to liberate ammonia gas.

$$NH_4{}^+(s) + OH^-(s) \rightarrow NH_3(g) + H_2O(l)$$

4. *With chlorine.* Calcium hydroxide can give several different reactions with chlorine if conditions are varied.

(a) Solid calcium hydroxide *at ordinary temperature* yields *bleaching-powder.* (For manufacturing conditions, see p. 363). The reaction is usually written in the approximate form:

$$Ca(OH)_2(s) + Cl_2(g) \rightarrow CaOCl_2(g) + H_2O(l)$$

(b) *At red heat*, the products are *calcium chloride* and *oxygen.*

$$2Ca(OH)_2(s) + 2Cl_2(g) \rightarrow 2CaCl_2(s) + 2H_2O(l) + O_2(g)$$

(c) *Cold* 'milk of lime' produces a mixture of *calcium chloride* and *calcium hypochlorite.*

$$Ca(OH)_2(s) + Cl_2(g) + H_2O(l) \rightarrow Ca^{2+}(aq) + Cl^-(aq) + OCl^-(aq) + 2H_2O(l)$$

Hot 'milk of lime' yields *calcium* chloride and *calcium chlorate* (*V*).

$$3Ca(OH)_2(s) + 3H_2O(l) + 3Cl_2(g) \rightarrow 3Ca^{2+}(aq) 5Cl^-(aq) + ClO_3{}^-(aq) + 6H_2O(l)$$

This reaction is similar to that with sodium hydroxide (p. 54).

Uses of calcium hydroxide

(a) In the softening of temporarily hard water (p. 293).
(b) In the building trade in the production of mortar and plaster (p. 99).
(c) In the manufacture of bleaching-powder (p. 363) and in the recovery of ammonia in the Solvay process (p. 56).

Calcium carbonate, $CaCO_3$

Calcium carbonate occurs naturally in two main forms:

(a) *Calcite.* This crystallizes in the hexagonal system and includes (with variable purity) *marble*, *chalk*, and *limestone*, *Iceland spar*, *calcspar*, and *Dog's Tooth spar.* Calcite is the stable form below 303 K.
(b) *Aragonite.* This crystallizes in the rhombic system and occurs in *coral.* Aragonite is formed by crystallization above 303 K and, at room temperature, is metastable.

Laboratory preparation of calcium carbonate

Calcium carbonate is readily prepared as a white precipitate by mixing a hot solution of a calcium salt (usually the chloride) with a hot solution of a carbonate (usually sodium carbonate). The precipitate is filtered, washed with hot distilled water and dried in a steam-oven.

$$Ca^{2+}(aq) + CO_3{}^{2-}(aq) \rightarrow Ca^{2+}CO_3{}^{2-}(s)\downarrow$$

Properties of calcium carbonate

1. *Solubility in water.* Calcium carbonate is almost insoluble in water. For its action with water containing carbon dioxide, see the next section.
2. *Action of heat.* When heated, calcium carbonate decomposes reversibly.

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

This equilibrium is fully discussed in *Advanced Level Physical Chemistry*, pages 201–2. It is enough for our purposes here to note that calcium carbonate is hardly affected by heat at a temperature below 900 K, and needs a temperature of 1200–1300 K to ensure rapid decomposition.
3. *Action of calcium carbonate with acids.* The dilute mineral acids act rapidly in the cold with calcium carbonate; *carbon dioxide* is evolved and the corresponding calcium salt left in solution.

$$CO_3{}^{2-}(s) + 2H^+(aq) \rightarrow H_2O(l) + CO_2(g)$$

In the case of sulphuric acid, however, sparingly soluble calcium sulphate may deposit on the carbonate and stop the action. This is particularly so if the carbonate is in bulk form, e.g., marble chips, and is the reason why hydrochloric acid is preferred for the laboratory preparation of carbon dioxide (p. 148).

Uses of calcium carbonate

Calcium carbonate is used:
(a) In steelmaking and other smelting processes (p. 432).
(b) For the manufacture of 'quicklime' (p. 89) and hence of 'slaked lime'.
(c) When finely powdered and mixed with linseed oil, as putty.
(d) As 'precipitated chalk' in tooth-pastes and cosmetics.

Calcium hydrogencarbonate (calcium bicarbonate), $Ca(HCO_3)_2$

This compound is very unstable and, at ordinary temperature, is known only in solution. If carbon dioxide is passed into lime-water, calcium carbonate (*chalk*) is first precipitated

$$Ca(OH)_2(aq) + CO_2(g) \rightarrow CaCO_3(s) + H_2O(l)$$

If more carbon dioxide is passed, the liquid clears again, leaving *calcium hydrogencarbonate* in solution

$$CaCO_3(s) + H_2O(l) + CO_2(g) \rightleftharpoons Ca(HCO_3)_2(aq)$$

This second reaction, occurring in nature with rain water and atmospheric carbon dioxide, brings calcium hydrogencarbonate into solution in water passing over limestone (or chalk). It may produce caves in limestone. Water containing calcium carbonate is *temporarily hard.* The hardness may be destroyed by boiling the water, which reverses the last equation above and precipitates chalk. This precipitation, occurring slowly in nature at ordinary temperature, produces *stalactites* and *stalagmites* and the deposits in *petrifying wells*. '*Fur*' in kettles and some forms of *boiler-scale* are similar deposits.

Calcium chloride, $CaCl_2$

Preparation

Calcium chloride is usually prepared in the laboratory by dissolving pure calcium carbonate in dilute hydrochloric acid until the calcium carbonate is in slight excess, and filtering off the liquid. By evaporation to a syrupy consistency and cooling, it can be crystallized to the hydrate, $CaCl_2.6H_2O$; or it can be evaporated to dryness and heated to give the anhydrous salt (usually with slight hydrolysis so that it contains a little calcium hydroxide or oxide).

$$CaCO_3(s) + 2H^+(aq) + 2Cl^-(aq) \rightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$$

In industry, calcium chloride is produced in very large amounts (mostly wasted for lack of markets) as a by-product in the Solvay process (p. 56).

Properties and uses of calcium chloride

1. *Solubility.* Calcium chloride is very soluble in water (63 g as $CaCl_2$ in 100 g water at 283 K). It is very deliquescent and the anhydrous solid rapidly turns to a pool of solution in damp air.
2. *As a drying agent.* Calcium chloride (anhydrous) is much used as a drying agent, especially for organic liquids. It cannot be used to dry ethanol, in which it is quite soluble and with which it combines to form the compound, $CaCl_2.2C_2H_5OH$. Nor can it be used to dry ammonia gas, with which it combines.
3. When heated to 470 K, the hydrate, $CaCl_2.6H_2O$, is converted to $CaCl_2.2H_2O$. This dihydrate can be dissolved in water to form the circulating liquid in large-scale refrigeration.
4. Calcium chloride is used as a source of calcium metal (p. 87).

Calcium bromide, $CaBr_2$, and *calcium iodide*, CaI_2, closely resemble the chloride.

Calcium fluoride, CaF_2, differs markedly from the other halides of calcium. It is almost insoluble in water and is not deliquescent. It occurs in nature as *fluorspar*, e.g. in Derbyshire. Samples containing traces of metallic oxides may be coloured; *Blue john* is an example. Fluorspar is used (after fusion) as an enamel, and in the manufacture of glass and glazes. It is also used as a flux in metallurgy and is the chief source of fluorine compounds.

Calcium sulphate, $CaSO_4$

Calcium sulphate occurs naturally, in large deposits, as *anhydrite*. $CaSO_4$, and *gypsum*, $CaSO_4.2H_2O$. *Alabaster* is a decorative form of it.

Preparation

Calcium sulphate is only sparingly soluble in water (0.18 g as $CaSO_4$ in

100 g water at 273 K). It is prepared, as a white precipitate, by mixing moderately concentrated, hot solutions of a calcium salt and a sulphate, usually calcium chloride and sodium sulphate. The precipitate is filtered off, washed and dried in a steam-oven.

$$Ca^{2+}(aq) + SO_4{}^{2-}(aq) + 2H_2O(l) \rightarrow CaSO_4.2H_2O(s)\downarrow$$

Properties and uses of calcium sulphate

1. *Solubility in water.* The solubility of calcium sulphate in water is never more than slight (see above), but it shows the unusual feature of rising to a maximum at 313 K (0.28 g in 100 g of water) and then falling again. For this reason, calcium sulphate in natural water may deposit as a boiler scale.

2. *Action of heat.* If heated to about 400 K, gypsum, $CaSO_4.2H_2O$, loses three-quarters of its water of crystallization to form a hemihydrate, $(CaSO_4)_2.H_2O$. This hydrate is known as *plaster of Paris.* If mixed with water (usually about one-third of its mass), plaster of Paris remains liquid for a time. It can be poured into a mould and then sets. The setting (re-hydration to gypsum) is accompanied by slight expansion, which ensures good reproduction of the detail of the mould, such as a statuette, footprint or tyre-mark. Plaster of Paris is also used (in plaster-casts) to support broken bones while healing, and it gives a smooth surface to plastered walls.

If heated to 470 K, gypsum loses *all* its water of crystallization and forms *anhydrous* calcium sulphate.

3. *Action with ammonium sulphate.* Calcium sulphate dissolves in a concentrated solution of ammonium sulphate, probably by complex ion formation.

$$2NH_4{}^+(aq) + SO_4{}^{2-}(aq) + CaSO_4(s) \rightleftharpoons 2NH_4{}^+(aq) + Ca(SO_4)^{2-}(aq)$$

The sulphates of the two heavier metals of Group II, Ba and Sr, do not dissolve in ammonium sulphate solution.

Calcium nitrate, $Ca(NO_3)_2$

Calcium nitrate can be formed in solution by the action of calcium hydroxide or carbonate with dilute nitric acid, e.g.

$$CaCO_3(s) + 2H^+(aq) + 2NO_3{}^-(aq) \rightarrow Ca(NO_3)_2(aq) + H_2O(l) \\ + CO_2(g)$$

It can be crystallized as the hydrate, $Ca(NO_3)_2.4H_2O$. As a product from the obsolete Birkeland and Eyde process for fixation of atmospheric nitrogen, it was known as *Norwegian saltpetre* and (as a basic nitrate) used as a fertilizer.

Calcium dicarbide (calcium carbide), CaC_2

Manufacture

Calcium dicarbide is manufactured by an *electrothermal* process. The furnace is made of steel and lined with carbon, which acts as one of the electrodes. The other electrode is a vertical carbon rod. *Coke* and *quicklime* are present in the furnace. Alternating current is used. Arcing produces a temperature of 2100–2300 K, and calcium dicarbide is produced by the reaction:

$$CaO(s) + 3C(s) \rightarrow CaC_2(s) + CO(g)$$

It is molten at the temperature employed, solidifies on cooling and is broken up and graded in an atmosphere of nitrogen to avoid possible explosions between ethyne (acetylene—see below) and air.

Properties and uses of calcium dicarbide

1. *With water.* Calcium dicarbide is a white solid when pure, but commercial samples are usually dark grey because of impurities present. It reacts rapidly with cold water to produce *ethyne* and *calcium hydroxide* (not calcium oxide).

$$CaC_2(s) + 2H_2O(l) \rightarrow Ca(OH)_2(s) + C_2H_2(g)$$

The ethyne is used in welding and cutting up steel plate by means of the 'oxyacetylene' flame. Through the ethyne, calcium dicarbide is now an important source of organic chemicals.

2. *With nitrogen.* Finely powdered calcium dicarbide will react with nitrogen to form *calcium cyanamide.*

$$CaC_2(s) + N_2(g) \rightarrow CaCN_2(s) + C(s)$$

Cylindrical steel containers are used, with an electrically heated carbon rod down the middle, which raises the temperature to red heat. Nitrogen is supplied at about 2 atm ($\sim 200\,000$ N m^{-2}) pressure. Calcium cyanamide is used as a nitrogenous fertilizer, *nitrolim.*

Structure of calcium dicarbide

X-ray analysis shows that calcium dicarbide is an electrovalent compound with ions Ca^{2+} and $(C{\equiv}C)^{2-}$.

Phosphate(V) salts of calcium

The chemistry of the phosphates(V) of calcium is complex, though the details are relatively unimportant for practical purposes.

The normal salt, *tricalcium phosphate(V)*, $Ca_3(PO_4)_2$, has probably never been obtained pure. A white precipitate is obtained by addition of disodium hydrogen phosphate(V) solution to calcium chloride solution. This precipitate is mainly tricalcium phosphate(V), but the action of water on it can produce an insoluble basic salt as impurity. The main reaction is:

$$3Ca^{2+}(aq) + 2HPO_4{}^{2-}(aq) + 2OH^- \rightarrow Ca_3(PO_4)_2(s) + 2H_2O(l)$$

This salt occurs in *apatite*, $Ca_3(PO_4)_2.CaF_2$, in rock phosphates as *phosphorite*, in *basic slag*, *guano*, and *bone meal*. It is used as a phosphatic fertilizer, but is very slow in action because of its very low solubility in water (about 0.005 g in 100 g water at 293 K).

For greater solubility and more rapid action, it is converted to *superphosphate of lime*, which contains the soluble acid salt, $Ca^{2+}(H_2PO_4{}^-)_2$. For this conversion, finely ground tricalcium phosphate(V) is mixed thoroughly with the necessary mass of 70 per cent sulphuric acid for the reaction:

$$Ca_3(PO_4)_2(s) + 2H_2SO_4(aq) \rightarrow Ca(H_2PO_4)_2(s) + 2CaSO_4(s)$$

The process may require up to fourteen days at ordinary temperature.

The material *triple superphosphate* is made by the action of phosphoric(V) acid on phosphate rock by a reaction of the type:

$$Ca_3(PO_4)_2(s) + 2H_3PO_4(l) \rightarrow 2Ca(H_2PO_4)_2(s)$$

It has the advantage (in freight charges) of not containing a dead-weight of calcium sulphate, as superphosphate does.

Calcium hydrogensulphite (calcium bisulphite), $Ca(HSO_3)_2$

Calcium hydrogensulphite is prepared, in solution, when milk of lime is saturated with sulphur dioxide.

$$Ca(OH)_2(s) + 2SO_2(g) \rightarrow Ca(HSO_3)_2(aq)$$

It is used in large amounts to remove lignin from wood-pulp, leaving cellulose suitable for paper-making.

Calcium sulphide, CaS

Calcium sulphide can be made by heating calcium sulphate (gypsum) with charcoal at red heat:

$$CaSO_4(s) + 4C(s) \rightarrow CaS(s) + 4CO(g)$$

It is soluble in water but is hydrolysed.

$$2S^{2-}(aq) + 2H_2O(l) \rightleftharpoons 2OH^-(aq) + 2SH^-(aq)$$

If slightly impure, containing a trace of alkali and bismuth, calcium sulphide is *phosphorescent*, i.e. after exposure to light it will continue to glow for a time.

Calcium hydrogensulphide (*calcium hydrosulphide*), $Ca(SH)_2$, is made by passing hydrogen sulphide into milk of lime.

$$OH^-(aq) + H_2S(g) \rightarrow SH^-(aq) + H_2O(l)$$

It is used in removing hair from hides in tanning. Calcium polysulphides, CaS_n where n may be 2, 3, 4, or 5, also exist.

Detection and estimation of calcium

Calcium salts impart a *brick red* colour to the bunsen flame; the colour is easily confused with that of strontium compounds (crimson) and easily obscured by the brilliant yellow of sodium compounds.

In tables of qualitative analysis, calcium, barium and strontium carbonates are precipitated (Group V) by ammonium carbonate in the presence of ammonia. For a separation, see p. 106.

A convenient way of estimating calcium is to precipitate it as calcium ethanedioate (calcium oxalate) by ammonium ethanedioate solution in the presence of ammonium chloride and ammonia. After filtration and washing, the precipitate can be made up to a known volume (usually 250 cm^3) in excess dilute sulphuric acid. The ethanedioic acid so formed can be titrated by standard potassium manganate(VII) solution at about 330 K.

Mortar and cement

Mortar is made by mixing slaked lime (1 part) with sand (4 parts) and enough water to form a suitable paste. After use between bricks, it first *sets*, losing water by evaporation and by absorption into the brickwork. It then *hardens* slowly by absorbing carbon dioxide from the air and forming an interlaced mass of crystals of calcium carbonate.

$$Ca(OH)_2(s) + CO_2(g) \rightarrow CaCO_3(s) + H_2O(l)$$

The sand is present to secure porosity and to prevent cracking of the mortar.

Portland Cement is made by strongly heating limestone and clay. This is done by passing ground limestone and clay (mixed with water to make it flow as a sludge) down a sloping, rotating cylinder. The cylinder is heated internally by a blast of burning coal-dust and air. The resulting clinker is allowed to cool and ground to a fine powder. When mixed with sand and water, it sets in a few hours to a solid mass, which slowly becomes harder over a long period.

Concrete is made by mixing cement, sand and water with gravel or broken brick. When freshly made, it can be poured into moulds, usually of wood, and sets to a rock-like mass in a day or so. The mould is then removed. For additional strength, concrete may be poured round steel girders or rods and is then said to be *reinforced concrete*. The chemistry of cement is very complex.

Strontium

Atomic number 38
Electron arrangement 2.8.18.8.2 ($1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 5s^2$)
Isotopic mass numbers, in order of abundance, 88, 86, 87, 84;
relative atomic mass 87.62

Occurrence and extraction

Strontium occurs as the carbonate, $SrCO_3$, *strontianite*, in Westphalia, and as the sulphate, $SrSO_4$, *celestine*, in Gloucestershire.

There is no large scale use of strontium and it is extracted (in small amounts only) by the electrolysis of the fused chloride. The process resembles that for the extraction of calcium.

At the cathode	*At the anode*
$Sr^{2+} + 2e^- \rightarrow Sr(s)$	$2Cl^- - 2e^- \rightarrow Cl_2(g)$

Properties of strontium

Strontium, when pure, is a white metal, m.p. 1041 K, density 2.6 g cm^{-3}.

It resembles calcium in its general properties but is more reactive, e.g.:

With water $Sr(s) + 2H_2O(l) \rightarrow Sr(OH)_2(s) + H_2(g)$

Heated in air
$$\begin{cases} 2Sr(s) + O_2(g) \rightarrow 2SrO(s) \\ 3Sr(s) + N_2(g) \rightarrow Sr_3N_2(s) \end{cases}$$

The nitride is decomposed by water.

$$Sr_3N_2(s) + 6H_2O(l) \rightarrow 3Sr(OH)_2(s) + 2NH_3(g)$$

Heated in hydrogen

$$Sr(s) + H_2(g) \rightarrow SrH_2(s)$$

This hydride is decomposed by water

$$SrH_2(s) + 2H_2O(l) \rightarrow Sr(OH)_2(s) + H_2(g)$$

Strontium oxide, SrO

Strontium oxide is most conveniently prepared on the laboratory scale by heating strontium nitrate. (The decomposition temperature of the carbonate is very high.)

$$2Sr(NO_3)_2(s) \rightarrow 2SrO(s) + 4NO_2(g) + O_2(g)$$

Strontium oxide is very similar to calcium oxide (quicklime) and has a similar, violent slaking action with water to form the hydroxide.

$$SrO(s) + H_2O(l) \rightarrow Sr(OH)_2(s)$$

If heated to about 1000 K with oxygen under high pressure, strontium oxide yields *strontium peroxide*, SrO_2.

Strontium hydroxide, $Sr^{2+}(OH^-)_2$

Strontium hydroxide resembles calcium hydroxide (slaked lime) but, at ordinary temperature, is about five times more soluble in water (0.81 g in 100 g water at 293 K). Its solubility *increases* as temperature rises. (The solubility of slaked lime *decreases* with rise of temperature.)

Use of strontium hydroxide

Strontium hydroxide forms, with cane sugar, an insoluble *saccharate*, $C_{12}H_{22}O_{11}.2SrO$. In sugar refining, the liquor, *molasses*, left after crystallizing sugar will yield a precipitate of this saccharate if treated with strontium hydroxide. If the precipitate is put into water through which carbon dioxide is then passed, sugar is formed and strontium carbonate precipitates.

$$C_{12}H_{22}O_{11}.2SrO(s) + 2CO_2(g) \rightarrow C_{12}H_{22}O_{11}(aq) + 2SrCO_3(s)$$

The carbonate is filtered off, converted to the hydroxide and used again. Sugar is crystallized from the filtered solution.

Strontium carbonate, $SrCO_3$

Strontium carbonate can be precipitated (white) by mixing solutions of strontium chloride (or nitrate) and sodium carbonate.

$$Sr^{2+}(aq) + CO_3{}^{2-}(aq) \rightarrow Sr^{2+}CO_3{}^{2-}(s)$$

It closely resembles chalk, but is less soluble in water and more difficult to decompose by heat.

Strontium sulphate, $SrSO_4$

Strontium sulphate can be obtained as a white precipitate by mixing solutions of strontium chloride (or nitrate) and sodium sulphate.

$$Sr^{2+}(aq) + SO_4{}^{2-}(aq) \rightarrow SrSO_4(s)$$

It is less soluble in water than calcium sulphate and does *not* dissolve in ammonium sulphate solution (as calcium sulphate does, p. 96). It forms no hydrate.

Detection of strontium

Strontium compounds impart a *crimson* colour to the bunsen flame, but it is easily confused with the *brick-red* of calcium compounds.

Strontium is precipitated, with calcium and barium, as carbonate by ammonium carbonate solution in the presence of ammonium chloride and ammonia (Tables of Qualitative Analysis, Group V). For a separation, see p. 106.

Barium

Atomic number 56; electron arrangement 2.8.18.18.8.2
($1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 6s^2$)
Barium has *seven* isotopes of mass number, in order of abundance, 138, 137, 136, 135, 134, 130, 132.
The relative atomic mass of barium is 137.3.

Occurrence and preparation

The sulphate, $BaSO_4$, is found as *barytes* (or *heavy spar*) in Derbyshire and the carbonate, $BaCO_3$, as *witherite*, in Northumberland.

Barium metal is difficult to prepare because of its great chemical activity. It is usually made by a thermit method in which barium oxide is heated with aluminium powder at white heat (about 1500 K) at very low pressure.

$$3BaO(s) + 2Al(s) \rightarrow Al_2O_3(s) + 3Ba(s)$$

Properties of barium

Barium is a soft, silvery-white metal, m.p. 987 K and density 3.5 g cm^{-3}. It resembles strontium (p. 100) very closely but is more reactive, e.g. it burns spontaneously in air if finely divided. It has only minor uses in industry, e.g. in bearing alloys with lead and calcium.

Barium oxide, BaO

Preparation

Barium carbonate may be used but its decomposition temperature is so high (about 1700 K) that carbon (lamp-black) is added to lower the temperature required and give the reaction:

$$BaCO_3(s) + C(s) \rightarrow BaO(s) + 2CO(g)$$

In the laboratory, barium nitrate may be heated to red heat.

$$2Ba(NO_3)_2(s) \rightarrow 2(BaO)(s) + 4NO_2(g) + O_2(g)$$

Barium oxide slakes with water, even more vigorously than quicklime, to form barium hydroxide.

$$BaO(s) + H_2O(l) \rightarrow Ba(OH)_2(s)$$

Towards dilute mineral acids, it has the usual properties of a basic oxide; it does *not* react well with dilute sulphuric acid because barium sulphate is insoluble and precipitates.

Barium peroxide, BaO_2 ($Ba^{2+}O_2^{\,2-}$)

Barium peroxide is formed if barium oxide is heated to about 800 K in air. The action is reversible, and oxygen is liberated again if the pressure is lowered, or if the temperature is raised to about 1100 K.

This follows from Le Chatelier's Principle (see *Advanced Level Physical Chemistry*, p. 204) since the reaction from left to right (as written below) is *exothermic* and accompanied by *decrease* in volume.

$$2BaO(s) + O_2(g) \rightleftharpoons 2BaO_2(s) \qquad \Delta H = -100\,kJ\,mol^{-1}$$

This reaction was the basis of the obsolete *Brin's process* for manufacture of oxygen from the air.

The hydrate, $BaO_2.8H_2O$, crystallizes out if hydrogen peroxide is added to a cold, saturated solution of barium hydroxide. This hydrate gives a solution of *hydrogen peroxide* if stirred slowly into the calculated amount of *ice-cooled* dilute sulphuric acid. Precipitated barium sulphate can then be filtered off. See also p. 299

$$BaO_2(s) + 2H^+(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s) + H_2O_2(aq)$$

Barium hydroxide, $Ba(OH)_2$

Preparation

On the industrial scale, the native carbonate, *witherite*, can be treated with super-heated steam, leaving barium hydroxide.

$$BaCO_3(s) + H_2O(g) \rightarrow Ba(OH)_2(s) + CO_2(g)$$

In the laboratory, slaking of the oxide is employed.

$$BaO(s) + H_2O(l) \rightarrow Ba(OH)_2(s)$$

Barium hydroxide is a white solid; it has a much higher solubility in water than the hydroxides of calcium or strontium (3.23 g in 100 g water at 288 K). The solution is known as *baryta water*. It is alkaline and is used in titration of weak acids if a carbonate-free alkali is needed. It never contains dissolved carbonate because barium carbonate is insoluble in water.

Barium carbonate, $BaCO_3$

Barium carbonate is almost insoluble in water; it can be precipitated by adding sodium carbonate solution to barium chloride solution.

$$Ba^{2+}(aq) + CO_3^{2-}(aq) \rightarrow BaCO_3(s)$$

It closely resembles chalk, but has a much higher temperature of rapid decomposition (at least 1700 K).

$$BaCO_3(s) \rightarrow BaO(s) + CO_2(g)$$

Barium chloride, $BaCl_2$

Barium chloride can be made in the laboratory by standard methods, e.g. dissolving barium carbonate in dilute hydrochloric acid. It crystallizes as the *di*hydrate, $BaCl_2.2H_2O$ (compare $CaCl_2.6H_2O$ and $SrCl_2.6H_2O$) and is not deliquescent. The other two chlorides shown are both deliquescent.

Barium chloride is readily soluble in water (35.7 g as $BaCl_2$ in 100 g water at 293 K). The solution is much used as a qualitative test for the sulphate ion, $SO_4{}^{2-}$, in solution. The liquid to be tested should contain no metallic radicals other than Na^+, K^+, and $NH_4{}^+$. (This can be arranged by first boiling with excess sodium carbonate and filtering off any precipitated carbonates.) It is acidified by dilute hydrochloric acid. A fine, white precipitate (barium sulphate), appearing on the addition of barium chloride solution, proves sulphate ion present.

Barium sulphate, $BaSO_4$

Barium sulphate occurs in nature as *barytes*; it can be obtained as a white precipitate as above by adding a solution of any soluble sulphate (usually dilute sulphuric acid) to barium chloride solution.

$$Ba^{2+}(aq) + SO_4{}^{2-}(aq) \rightarrow BaSO_4(s)$$

It is, however, difficult to purify because it adsorbs barium chloride (and many other salts if present). These impurities do not readily wash out. Barium sulphate has a very low solubility (0.0023 g per 100 g water at 291 K). It is converted almost entirely to barium carbonate if fused with potassium carbonate in the proportion $BaSO_4 : 9K_2CO_3$. The soluble salts (K_2CO_3 and K_2SO_4) can be removed by hot water, and barium carbonate can be brought into solution again by dilute hydrochloric acid.

Uses of barium sulphate

Use is made of the high density and whiteness of barium sulphate in the manufacture of paint and in 'loading' paper, rubber, and linoleum. It is also a constituent of the pigment, 'lithopone'. It is also used in medical X-ray photography, often in the form of a barium meal, being relatively opaque to the rays.

Barium sulphide, BaS

Barium sulphide is made by roasting barytes, $BaSO_4$, with coke.

$$BaSO_4(s) + 4C(s) \rightarrow BaS(s) + 4CO(g)$$

It is soluble in water but is considerably hydrolysed.

$$S^{2-}(s) + 2H_2O(l) \rightleftharpoons 2OH^-(aq) + 2SH^-(aq)$$

It is chiefly important because it reacts with zinc sulphate to precipitate a mixture of barium sulphate and zinc sulphide.

$$BaS(aq) + ZnSO_4(aq) \rightarrow BaSO_4(s) + ZnS(s)$$

The mixture is known as *lithopone.* It is used as a pigment, and as a 'filler' in making paper, oil-cloth, and linoleum. Impure barium sulphide, containing traces of heavy metals (e.g. bismuth), is phosphorescent.

Barium nitrate, $Ba(NO_3)_2$

Barium nitrate is less soluble than most nitrates (5 g in 100 g water at 273 K) and can be precipitated by mixing concentrated solutions of barium chloride and sodium nitrate.

$$Ba^{2+}(aq) + 2NO_3^-(aq) \rightarrow Ba(NO_3)_2(s)\downarrow$$

It is used to produce 'green fire' in fireworks.

Detection and estimation of barium

Barium compounds impart a *lime green* colour to the bunsen flame.

Barium is usually estimated by precipitating it as barium sulphate by a solution of soluble sulphate. Barium sulphate is filtered, washed and dried to constant mass at red heat; then weighed. The proportion $Ba/BaSO_4$, i.e. 137.4/233.4, of the precipitate is barium.

Identification of calcium, strontium, and barium

Barium is precipitated as carbonate by ammonium carbonate solution in the presence of ammonium chloride and ammonia (Analysis Tables, Group V). It is accompanied by calcium and strontium as carbonates. After washing, the precipitate is dissolved in warm dilute ethanoic acid. Addition of potassium chromate(VI) solution precipitates *barium as chromate*(VI); calcium and strontium remain dissolved.

Barium chromate(VI) is filtered off. The filtrate is divided into two parts.

(a) At least equal bulk of saturated calcium sulphate solution is added and the mixture boiled. A white precipitate (*strontium sulphate*) proves *strontium* present.

(b) The liquid is *boiled* with dilute sulphuric acid. The precipitate (strontium sulphate with, perhaps, some calcium sulphate) is filtered off. Enough *calcium* remains in solution to be detected as *calcium ethanedioate* on the addition of excess ammonia followed by ammonium ethanedioate solution (perhaps after heating).

Questions

1. Mention *two* chemically different forms in which magnesium occurs in nature and give their formulae. State, in essential outline, the extraction of magnesium from sea water. Starting from magnesium, how would you prepare in the laboratory reasonably pure samples of (a) anhydrous magnesium chloride, (b) normal magnesium carbonate? Explain why the product of burning magnesium in air gives a smell of ammonia when damped and warmed.

2. Mention, giving their formulae, *three* chemically different forms in which calcium occurs in nature. Describe briefly the extraction of calcium on the large scale. How, and under what conditions, does calcium react with (a) hydrogen, (b), water, (c) nitrogen?

3. Starting from calcium carbonate (marble), how would you prepare reasonably pure samples of (a) 'quicklime', (b) 'slaked lime', (c) calcium sulphate, (d) calcium hydrogen carbonate solution? Give a brief account of the common forms of calcium sulphate and their uses.

4. Outline the manufacture of (i) calcium dicarbide, (ii) calcium 'superphosphate'. How, and in what conditions, does calcium dicarbide react with water? Discuss the agricultural importance of calcium compounds.

5. Write a concise account of the chemistry of the metals Ca, Sr, and Ba, and of their oxides, hydroxides, chlorides and hydrides, to justify their inclusion together in Group II of the Periodic Table. Mention any differences you know in the chemistry of these metals which serve to differentiate them experimentally.

6. Outline the main factors responsible for the observed trends and gradations in physical and chemical properties of elements, and their compounds, in the same group of the Periodic Table. The elements in Group II of the Periodic Table are, in order of increasing atomic number, beryllium, magnesium, calcium, strontium, barium and radium (chemical symbol: Ra). In the light of your knowledge of the chemistry of the first five of these elements, make predictions concerning the following points: (a) the reaction of radium with water, (b) the solubility of radium salts in water, (c) the acid/base behaviour of the oxide and hydroxide of radium, (d) the type of bonding present in radium compounds and the physical properties of these compounds, (e) methods that could be used to obtain pure radium from its compounds. (L.)

7. Give what explanation you can in terms of structure and bonding for the following:

(a) magnesium chloride and aluminium chloride differ greatly in volatility,
(b) magnesium sulphate is much more soluble in water than is barium sulphate,
(c) beryllium oxide is amphoteric in contrast to the oxides of other Group II elements,
(d) the elements of Group II are all conductors of electricity. (C.)

8. This question concerns the elements barium, calcium, magnesium and strontium.

(a) Give the electronic structures of *two* of the elements.

(b) Illustrate, with examples, the types of bonds which the elements form.
(c) Place the elements in order of metallic character, putting the *least* metallic first.
(d) Place the elements in order of atomic radius, putting the element with the *smallest* atomic radius first.
(e) Helium contains the same number of electrons in its outer shell as the elements above. Explain why the electrons in helium are stable but the outer electrons in the above elements are not.
(f) In some ways, magnesium is not typical of the group. Illustrate this with *two* examples.
(g) A white powder is the carbonate of calcium, strontium or barium. Without using a flame test, how would you determine conclusively which one it is? (A.E.B.)

9. This question concerns the elements barium, calcium, magnesium and strontium.

(a) Which metal could be most easily produced by reduction of its oxide? Explain your reasoning.
(b) Explain why barium reacts more vigorously with water than does magnesium.
(c) Write equations for the action of heat on $BaCl_2.2H_2O$ and $MgCl_2.6H_2O$ and explain any differences.
(d) Place the sulphates of the metals in order of increasing ionic character, i.e. the least ionic first. Explain your reasoning.
(e) Place the sulphates of the metals in order of increasing solubility in water at 20° C, i.e. the least soluble first. Explain your reasoning.
(f) Place the carbonates of the metals in order of increasing ease of dissociation, i.e. the the one which dissociates most easily, first. Explain your reasoning. (A.E.B.)

6

Elements of Group III

The most common elements in Group III are boron and aluminium. Only these two will be considered here.

Boron

Atomic number 5; electron arrangement 2.3($1s^2 2s^2 2p^1$)
Boron has two isotopes of mass number, in order of abundance, 11, 10.
Relative atomic mass 10.81.

Occurrence and extraction

Boron does not occur free in nature. Free trioxoboric acid (*boric acid*), H_3BO_3, occurs with steam in volcanic jets (*soffioni*) in Tuscany. Various *borates* also occur as *kernite*, $Na,_2B_4O_7.4H_2O$, *tincal* or *crude borax*, $Na_2B_4O_7.10H_2O$, in California and Tibet, and *colemanite*, $Ca_2B_6O_{11}.5H_2O$, in California and Asia Minor.

Amorphous boron has been prepared, though probably not completely pure, by very vigorous reducing methods, such as heating diboron trioxide in a closed crucible (to exclude atmospheric oxygen) with a strongly electropositive metal, such as sodium, potassium or magnesium. Some borate of the metal is formed as well as boron, e.g.

$$B_2O_3(s) + 3Mg(s) \rightarrow 2B(s) + 3MgO(s)$$
$$3MgO(s) + B_2O_3(s) \rightarrow Mg_3(BO_3)_2(s)$$

The cooled mass is heated with dilute hydrochloric acid, leaving boron as a brown powder.

A fused mixture of boric oxide and sodium fluoride has been electrolysed with cathode of iron and anode of carbon. Sodium is liberated at the cathode and reduces the oxide of boron.

$$6Na^+ + 6e^- \rightarrow 6Na$$
$$B_2O_3(s) + 6Na(l) \rightarrow 2B(s) + 3Na_2O(s)$$

A crystalline form of boron has been prepared by reducing boron tribromide with hydrogen at a very high temperature.

$$2BBr_3(g) + 3H_2(g) \rightarrow 2B(s) + 6HBr(g)$$

Properties of boron

Crystalline boron is a very hard black powder. It has a metallic appearance but is a poor conductor of electricity.

Amorphous boron (a brown powder) has the following properties.

1. *With oxygen and air.* It burns readily when heated in oxygen forming *diboron trioxide.*

$$4B(s) + 3O_2(g) \rightarrow 2B_2O_3(s)$$

It also burns when heated in air to bright red heat, forming the oxide above and also some nitride.

$$2B(s) + N_2(g) \rightarrow 2BN(s)$$

2. *With other non-metals.* Boron combines with fluorine in the cold and with chlorine, sulphur, and nitrogen when heated, forming BCl_3, BF_3, B_2S_3, and BN.

3. *With acids.* Boron reacts only with *oxidizing* acids, i.e. nitric and sulphuric, when hot and concentrated. The product is *trioxoboric acid,* e.g.

$$2B(s) + 6HNO_3(conc.aq) \rightarrow 2H_3BO_3(s) + 6NO_2(g)$$

4. *With caustic alkali.* With *fused* sodium or potassium hydroxide, boron forms the corresponding *borate* (strictly, trioxoborate(III)). e.g.

$$2B(s) + 6KOH(l) \rightarrow 2K_3BO_3(l) + 3H_2(g)$$

5. *As a reducing agent.* When strongly heated, boron reduces silica or carbon dioxide, e.g.

$$3SiO_2(s) + 4B(s) \rightarrow 3Si(s) + 2B_2O_3(s)$$

Uses of boron

Boron, in small proportion, acts as a deoxidizer in steel; in larger amounts (0.5–2%), it forms boron steels of great strength.

Diboron trioxide, B_2O_3; 'boric', 'borax'

Diboron trioxide is formed when boron burns in air, but is more easily obtained by heating trioxoboric acid to red heat.

$$2H_3BO_3(s) \rightarrow B_2O_3(s) + 3H_2O(g)$$

It is a solid of glassy appearance, hygroscopic, and combining slowly with water to form trioxoboric acid.

$$B_2O_3(s) + 3H_2O(l) \rightarrow 2H_3BO_3(s)$$

It forms various salts, e.g. 'borax', and has, consequently, *acidic* characteristics, boron acting here as a non-metal. It has, also, feebly *basic* properties, forming an acid sulphate, $B(HSO_4)_3$, and a phosphate, BPO_4. The oxide is, therefore, *amphoteric* with the acidic character predominating. In amphoteric nature, diboron trioxide resembles the oxide of aluminium but, in aluminium oxide, the basic characteristics are the stronger.

Several 'boric acids' exist. Ordinary boric acid, *orthoboric acid* (properly trioxoboric acid), H_3BO_3, is the most important as such, but its salts are not common. Salts of the other boric acids occur more frequently. The more important of these acids are related to trioxoboric acid as products of dehydration in the following way:

$$H_3BO_3(s) \xrightarrow{373\text{ K}} H_2O(l) + HBO_2(s) \quad \text{dioxoboric acid (metaboric acid)}$$

$$4H_3BO_3(s) \xrightarrow{430\text{ K}} 5H_2O(l) + H_2B_4O_7(s) \quad \text{heptaoxotetraboric acid (tetraboric acid)}$$

Trioxoboric acid (orthoboric acid, boric acid), H_3BO_3

Preparation

(a) The acid is volatile in steam and occurs in *soffioni*, the volcanic steam-jets of Tuscany. The condensed liquid is collected in shallow pools (or *lagoons*) round the jets and concentrated by heat from the jets.

When sufficiently concentrated and cooled, the liquid gives crystalline trioxoboric acid in good yield because of the great difference in solubility in cold and hot water (3.60 g at 283 K, 39.7 g at 373 K in 100 g water).

(b) In the laboratory, trioxaboric acid is made by acidifying a hot, concentrated solution of 'borax' with hydrochloric acid and crystallizing out the acid by cooling.

$$Na_2B_4O_7(aq) + 2HCl(aq) + 5H_2O(l) \rightarrow 2NaCl(aq) + 4H_3BO_3(s)$$

Properties of trioxoboric acid

The dehydration of this acid to '*metaboric acid*' and '*tetraboric acid*' was stated above. When heated to red heat, it forms a glassy mass of diboron trioxide.

$$2H_3BO_3(s) \rightarrow 3H_2O(l) + B_2O_3(s)$$

It is a *very weak* acid (weaker even than carbonic acid) and does not turn blue litmus fully red. Using *methyl orange* as indicator (change-point about pH 3–5), a borate can be titrated directly by standard hydrochloric acid, like an alkali-metal carbonate.

Trioxoboric acid is so weak that it cannot be directly titrated by alkali in the usual way. If propane-1,2,3-triol (glycerol) is added, however, a complex is formed between molecules of boric acid and glycerol (with elimination of $2H_2O$).

$$C_3H_8O_3(l) + H_3BO_3(s) \rightarrow C_3H_7BO_4(aq) + 2H_2O(l)$$

This complex acts as a *stronger*, *monobasic acid*, which can be titrated by caustic alkali solution, using phenolphthalein as indicator.

$$C_3H_7BO_4(aq) \rightleftharpoons H^+(aq) + C_3H_6BO_4^-(aq)$$

Uses of trioxoboric acid

(a) 'Boric acid' or 'boracic acid' is used medicinally as a mild antiseptic, e.g. in solution as an eye-lotion.
(b) It was formerly employed widely as a food preservative, but many countries have prohibited such use.
(c) It is used in glazing, especially for enamels on metallic surfaces.

Disodium heptaoxotetraborate (sodium tetraborate, borax), $Na_2B_4O_7.10H_2O$

Preparation

Borax is now made almost entirely from *kernite* (also called *rasorite*),

$Na_2B_4O_7.4H_2O$, found in California. The material is extracted with hot water and sandy impurities are filtered out. After treatment to remove colour and further filtration, borax crystallizes on cooling. Above 333 K, a pentahydrate separates; below this temperature the decahydrate, borax, is given.

In the laboratory, the action between sodium hydroxide and trioxoboric acid, both in hot solution, and in the proportions required by the equation, is a suitable method of preparing borax.

$$4H_3BO_3(s) + 2NaOH(aq) \rightarrow Na_2B_4O_7(aq) + 7H_2O(l)$$

It can be crystallized out by cooling, and being filtered, washed with cold, distilled water, and allowed to dry.

Properties of borax

Borax is a crystalline solid, readily soluble in hot water but only sparingly in cold water (99.3 g at 373 K, 3 g at 283 K in 100 g water). Borax is the salt of a very weak acid and a strong base and, consequently, is considerably hydrolysed in solution (see *Advanced Level Physical Chemistry*, p. 223 ff.).

The borax bead test

If borax is heated on a looped platinum wire, it swells a great deal as it loses water of crystallization and then collapses into a colourless, molten bead. The bead contains sodium dioxoborate.

$$Na_2B_4O_7(s) \rightarrow 2NaBO_2(l) + B_2O_3(l)$$

If fused at high temperature with certain metallic compounds, the bead becomes coloured by producing coloured 'metaborates', e.g.:

$$CuSO_4(s) + 2NaBO_2(l) \rightarrow Cu(BO_2)_2(l) + Na_2SO_4(l)$$

The colours produced in the oxidizing bunsen flame are given in the table.

Metal	*Colour of bead*
Copper	Green (hot); blue (cold)
Iron	Brown (hot); yellow (cold)
Chromium	Green
Manganese	Amethyst
Cobalt	Blue
Nickel	Brown

Uses of borax

(a) As with boric acid (p. 112) in glazing enamel on metal, and as a flux for soldering as welding.
(b) Borax and boric acid are used in making low-expansion heat-resisting glass, such as *Pyrex*, for kitchen and laboratory use.
(c) In laundering, borax stiffens and glazes the laundered material. It similarly glazes paper and playing cards.

Sodium dioxoborate (sodium metaborate), $NaBO_2.4H_2O$

This salt can be crystallized out after treating borax, in solution, with the correct amount of sodium hydroxide solution for the reaction:

$$Na_2B_4O_7(s) + 2NaOH(aq) \rightarrow 4NaBO_2(s) + H_2O(l)$$

Being more soluble than borax and more alkaline by hydrolysis, it is sometimes used to replace borax where these properties are desirable.

Sodium dioxoborate peroxohydrate ('sodium perborate'), $NaBO_2.H_2O_2.3H_2O$

This material can be made by the action of hydrogen peroxide on a solution containing the required amounts of sodium hydroxide and borax.

$$Na_2B_4O_7 + 2NaOH + 4H_2O_2 + 11H_2O \rightarrow 4(NaBO_2.H_2O_2.3H_2O)$$

It is a strong oxidizing agent, and is used in bleaching actions, and in toothpastes, mouth washes, etc., for its antiseptic properties. It is also used in washing powders.

Boron nitride, BN

Boron nitride is formed by direct combination of the two elements when heated, or by reacting ammonia with boron trichloride. It is a white powder. Water has no action on it, but it is decomposed by steam.

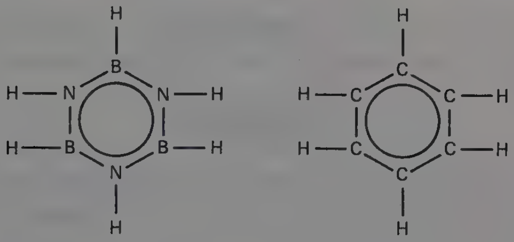
$$BN(s) + 3H_2O(g) \rightarrow H_3BO_3(s) + NH_3(g)$$

Boron nitride has a giant covalent structure similar to that of graphite (see p. 134). Under high pressure and temperature this can be changed into a diamond-type structure. The resulting material is known as *borazon*, and is in fact harder than diamond.

It is worth noting that the B—N bond is isoelectronic with the C—C bond.

Borazine (borazole), $B_3N_3H_6$

Reaction between ammonia and diborane (see below) in the molar proportions 2:1 gives a most interesting compound, *borazine*. The structure and physical properties of borazine are similar to those of benzene, but the B—N bonds are much less stable than those in benzene.



Borazine Benzene

Boron carbide, CB_4

This compound is made by heating diboron trioxide and carbon in the electric furnace.

$$2B_2O_3(s) + 7C(s) \rightarrow CB_4(s) + 6CO(g)$$

It is an extremely hard material, but is less hard than diamond.

Boron trifluoride, BF_3

Boron trifluoride is made by heating a mixture of diboron trioxide, calcium fluoride and concentrated sulphuric acid.

$$3CaF_2(s) + 3H_2SO_4(l) + B_2O_3(s) \rightarrow 2BF_3(g) + 3CaSO_4(s) + 3H_2O(l)$$

It passes off as a colourless, fuming gas. It reacts with water to form *dioxoboric acid* and *tetrafluoboric acid*.

$$4BF_3(g) + 2H_2O(l) \rightarrow HBO_2(s) + 3HBF_4(aq)$$

The molecule of boron trifluoride is a planar triangle in shape. It will be noted that boron, when exercising its usual covalency of three, has only six electrons in its outer shell. It therefore readily receives a lone pair from a suitable donor molecule. For example, boron trifluoride forms an addition compound with ammonia:

$$BF_3(g) + NH_3(g) \rightarrow H_3N.BF_3(s)$$

Species capable of receiving a pair of electrons in this way are known as *Lewis acids*, after G. N. Lewis. Species which can donate a pair of electrons are known as *Lewis bases*. In the above example, BF_3 acts as the 'acid' and NH_3 as the 'base'.

Boron trichloride, BCl_3

Boron trichloride is made by heating boron in a current of *dry* chlorine, or (more usually) by passing *dry* chlorine through an intimate mixture of diboron trioxide and carbon at red heat.

$$B_2O_3(s) + 3C(s) + 3Cl_2(g) \rightarrow 2BCl_3(g) + 3CO(g)$$

It is a fuming liquid, boiling point 286 K, and can be condensed in a freezing-mixture. It shows typical behaviour of a non-metallic chloride in being rapidly hydrolysed by water.

$$BCl_3(g) + 3H_2O(l) \rightarrow 3HCl(g) + H_3BO_3(s)$$

It acts as a Lewis acid towards ammonia and other donor species.

Hydrides of boron

Magnesium boride can be obtained by heating diboron trioxide and magnesium powder in a stream of hydrogen.

$$B_2O_3(s) + 6Mg(s) \rightarrow 3MgO(s) + Mg_3B_2(s)$$

If the boride is treated with a dilute acid, e.g. hydrochloric or phosphoric(V), the gaseous product contains mainly hydrogen, but also various hydrides of boron. They can be condensed out by passage through liquid air and purified by distillation under reduced pressure. Several hydrides have been isolated, e.g. B_4H_{10}, B_5H_9, B_5H_{11}, B_6H_{10}, B_6H_{12}, and $B_{10}H_{14}$. The simple hydride, BH_3, does not appear and has, in fact, not yet been prepared. B_2H_6, *diborane*, has, however, been prepared by passing an electric discharge through boron trichloride and hydrogen, under reduced pressure.

$$2BCl_3(g) + 6H_2(g) \rightarrow B_2H_6(g) + 6HCl(g)$$

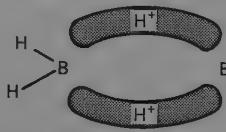
Another method of preparation is by reduction of an ethereal solution of boron trichloride using lithium tetrahydridoaluminate(III) (lithium aluminium hydride).

$$4BCl_3 + 3LiAlH_4 \xrightarrow{\text{ether}} 2B_2H_6(g) + 3LiCl(s) + 3AlCl_3(s)$$

Diborane is a dangerously flammable gas, and is rapidly decomposed by water.

$$B_2H_6(g) + 6H_2O(l) \rightarrow 2H_3BO_3(s) + 6H_2(g)$$

Diborane is an *electron-deficient* compound, and its electronic structure cannot adequately be represented using conventional covalent and ionic bonds. The structure is believed to contain a 'proton bridge', thus:



The structure of the other boron hydrides are complicated, containing similar unconventional bonding.

Detection of boron as a 'borate'

(a) The test material is mixed with concentrated sulphuric acid, and ethanol is added. The mixture is ignited. If a borate is present, the flame will have a *green·edge*. The colour is caused by a volatile borate ester. For example, with borax,

$$Na_2B_4O_7(s) + H_2SO_4(l) + 5H_2O(l) \rightarrow Na_2SO_4(s) + 4H_3BO_3(s)$$
$$H_3BO_3(s) + 3C_2H_5OH(l) \rightarrow B(OC_2H_5)_3(l) + 3H_2O(l)$$

Copper and barium salts may interfere, since both can produce green colour in a bunsen flame. The following test is free from this possibility.
(b) The test material is mixed with calcium fluoride and concentrated sulphuric acid to form a stiff paste. It is caught up on a platinum wire and brought *close* to a bunsen flame, but not actually into it. A *green* coloration in the flame indicates boron present. The colour is produced by the volatile *boron trifluoride*. Barium or copper salts do not colour the flame in these conditions.

Aluminium

Atomic number 13; electron arrangement 2.8.3 ($1s^2 2s^2 2p^6 3s^2 3p^1$).
Aluminium has only one isotope, of mass number 27.
Relative atomic mass 26.98.

Occurrence

Aluminium is the most abundant metal in the Earth's crust (7.8 per cent). It is exceeded in abundance only by two non-metals, oxygen and silicon. Aluminium does not occur free in nature. The following are forms in which it appears:

Oxide	*Corundum*, Al_2O_3
Hydrated oxide	*Bauxite*, $Al_2O_3.2H_2O$
	Gibbsite, $Al_2O_3.2H_2O$
	Diaspore, $Al_2O_3.H_2O$
Fluoride	*Cryolite*, Na_3AlF_6
Silicate	Aluminium occurs in many forms of clay, e.g. *kaolin*, $Al_2Si_2O_7.2H_2O$, in *felspar* and *mica*, $K_2Al_2Si_6O_{15}$

Several gems are transparent forms of aluminium oxide coloured by the presence of other metals, e.g. *ruby* (red; coloured by iron and titanium), *sapphire* (blue; coloured by cobalt or titanium), *amethyst* (violet; coloured by manganese).

Extraction of aluminium. Method of Hall and Héroult, 1886

The metal is obtained from *bauxite*, $Al_2O_3.2H_2O$. The material requires purification, its principal impurities being silica, oxides of iron and titanium oxide.

Purification of bauxite

The bauxite is first roasted at a low temperature to convert all iron oxide to the +3 state. The finely powdered product is then heated to about 430 K in autoclaves with sodium hydroxide solution under pressure. Iron(III) oxide and titanium(IV) oxide remain undissolved; so does most of the silica, though some may dissolve as sodium silicate.

$$SiO_2(s) + 2OH^-(aq) \rightarrow SiO_3{}^{2-}(aq) + H_2O(l)$$

Aluminium oxide reacts to form sodium aluminate(III) in solution.

$$Al_2O_3(s) + 6OH^-(aq) + 3H_2O(l) \rightarrow 2[Al(OH)_6]^{3-}(aq)$$

The undissolved impurities are filtered off. The *diluted* liquid is then 'seeded' with freshly precipitated aluminium hydroxide and agitated. This induces hydrolysis of the dissolved aluminate(III), and aluminium hydroxide precipitates out. (Any silicate present is unaffected and remains in solution.)

$$[Al(OH)_6]^{3-}(aq) \rightarrow Al(OH)_3(s)\downarrow + 3OH^-(aq)$$

The hydroxide is filtered off, washed, dried, and heated strongly to leave pure aluminium oxide, which is then electrolysed.

$$2Al(OH)_3(s) \rightarrow Al_2O_3(s) + 3H_2O(g)$$

Electrolysis of aluminium oxide

Aluminium oxide is electrolysed (Figure 6.1) in a molten mixture of *cryolite*, Na_3AlF_6, and *fluorspar*, CaF_2. If the concentration of oxide is kept above a certain level, the fluorides are unchanged and only the oxide is decomposed. Notice that the steel container is lined with sheets of *carbon* acting as the *cathode*, and that the *anode* is also composed of *carbon* rods. (It is rare in electrolysis to find both electrodes made of carbon.) Aluminium collects on the floor of the cell and is tapped off at intervals. The anode product is oxygen. It tends to oxidize the carbon anodes which require regular renewal.

The reactions occurring during the electrolysis are probably complex but the total result is equivalent to the electrolysis of Al_2O_3, as:

At the cathode	*At the anode*
$2Al^{3+} + 6e^- \rightarrow 2Al(l)$	$3O^{2-} - 6e^- \rightarrow 1\frac{1}{2}O_2(g)$
(This is *reduction* of aluminium ion by electron gain.)	

The aluminium produced is about 99 per cent pure.

It will be noted that each mole of aluminium requires three moles of electrons, i.e. three Faradays (= 289 500 C), for its production. Since one mole of aluminium has a mass of only 27 g, it will be seen that aluminium production is usually performed where electricity is compara-

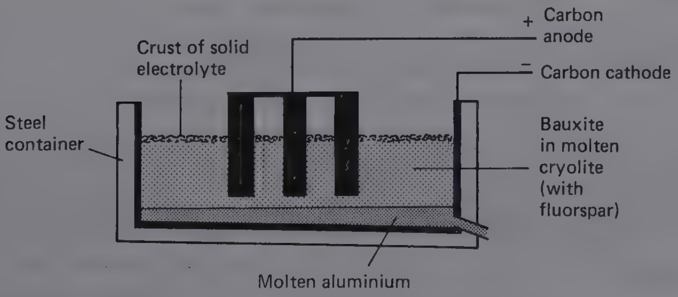


Figure 6.1 *Extraction of aluminium*

tively cheap. Many plants are sited in hilly areas, and use hydro-electric power.

Before the above method was developed in 1886, aluminium was only obtainable by heating the anhydrous chloride with sodium. As a result, aluminium was so expensive that it was used in jewellery.

Uses of aluminium

1. *In door and window frames.* Aluminium is increasingly used for this purpose as it does not rot, corrode, or warp.
2. *As domestic cooking utensil.* For this purpose, aluminium has the advantages of bright appearance, lightness, reasonable cost, resistance to attack by solutions used in cooking and non-poisonous nature. It has the disadvantage of being attacked by alkaline solutions.
3. *In over-head high tension cables for distribution of electrical power.* Aluminium has a high electrical conductivity and its low density enables thicker cable to be used. The cable is strengthened by a steel core.
4. *In light alloys.* Aluminium does not show a very high tensile strength when pure but, when alloyed with other metals, the breaking strain may be increased as much as six times. Some of these *light alloys* combine high tensile strength with low density, and are valuable in the construction of aircraft. Among the best known are *magnalium* (Al 90%; Mg 10%), and *duralumin* (94.4% Al; 4.5% Cu; 0.95% Mg; 0.76% Mn).
5. *In thermit processes.* Powdered aluminium will reduce the powdered oxides of many other metals in very strongly exothermic reactions. These *thermit* processes have been used in welding steel *in situ*. In this case, the reaction is initiated in a mixture of iron(III) oxide and aluminium powder by burning magnesium ribbon in contact with it. A violent reaction follows, leaving white-hot molten iron (used in the welding) and a slag of alumina.

$$2\text{Al(s)} + \text{Fe}_2\text{O}_3\text{(s)} \rightarrow 2\text{Fe(l)} + \text{Al}_2\text{O}_3\text{(s)}$$

A similar process will produce metallic chromium.

$$2\text{Al(s)} + \text{Cr}_2\text{O}_3\text{(s)} \rightarrow 2\text{Cr(l)} + \text{Al}_2\text{O}_3\text{(s)}$$

6. Other uses of aluminium are: as a *packaging material* for sweets, biscuits and cigarettes; as a powder mixed with oil in *aluminium paint*; as a *de-oxidizer* in casting steel. A major use is as *aluminium foil*.

Anodizing

In contact with the atmosphere, aluminium acquires a very thin, coherent layer of its oxide, which then protects it from further attack. It is the existence of this oxide layer which prevents aluminium from reacting with air and many aqueous solutions, and which makes it commercially so valuable.

Anodizing is a process for thickening the layer to provide better protection, especially to alloys. In a typical process, the metal is made the *anode* in a 3 per cent solution of chromic(VI) acid (with a steel cathode). The oxide layer produced on the aluminium is about 0.000 25 cm thick. When freshly produced, it is absorbent and will take up brightly coloured dyes, which make the finish attractive as well as protective.

Physical properties of aluminium

Aluminium is a bluish-white metal, which can be very highly polished, but is usually dulled by a thin layer of oxide. It has a low density (2.69 g cm^{-3}). It melts at 932 K and conducts heat and electricity well. It is malleable and ductile, so that aluminium sheet (or foil) and wire are easily produced.

Chemical properties of aluminium

1. *With air and oxygen.* Aluminium acquires a very thin layer of oxide when exposed to air and this protects it from further attack. It is little changed by heating in air up to about 1000 K, but, at about 1300 K, takes fire and forms its oxide, with some nitride.

$$4Al(s) + 3O_2(g) \rightarrow 2Al_2O_3(s)$$
$$2Al(s) + N_2(g) \rightarrow 2AlN(s)$$

The nitride liberates ammonia when acted upon by water:

$$AlN(s) + 3H_2O(l) \rightarrow Al(OH)_3(s) + NH_3(g)$$

The metal burns readily if heated in oxygen and gives a brilliant, white light. This was formerly used in flashlight photography; aluminium foil in a bulb containing oxygen was ignited by electrical heating.

If aluminium is alloyed with mercury (e.g. by dipping it into mercury(II) chloride solution), a superficial oxide layer cannot cohere. Aluminium will then oxidize rapidly and exothermically in air, forming thin flakes of the oxide at ordinary temperature. This alloy will also attack water with liberation of hydrogen. Normally, the oxide layer protects aluminium from reaction with water. Its removal permits aluminium to show its proper reactivity as an electropositive metal.

Spillage of mercury from broken instruments can cause rapid structural failure in aluminium components. Some aircraft crashes have been attributed to this cause.

2. *With acids.* Aluminium is attacked by *hydrochloric acid*; the action is the more vigorous as the acid becomes hotter and more concentrated. *Hydrogen* is evolved and *aluminium chloride* is left in solution.

$$2Al(s) + 6H^+(aq) \rightarrow 2Al^{3+}(aq) + 3H_2(g)$$

Dilute sulphuric acid does *not* attack aluminium. This rather surprising difference probably arises from the insolubility of the oxide layer in this acid.

Hot, concentrated sulphuric acid reacts with the metal with liberation of *sulphur dioxide* and formation of *aluminium sulphate.*

$$2Al(s) + 6H_2SO_4(aq) \rightarrow Al_2(SO_4)_3(aq) + 6H_2O(l) + 3SO_2(g)$$

Nitric acid is almost without action on aluminium at any concentration, and even when heated. This, again, is surprising in such an electropositive metal, and is in marked contrast to the vigorous reaction of nitric acid with magnesium and zinc. It is probably explained by the insolubility of the oxide layer in this acid.

3. *With aqueous caustic alkalis.* Bench sodium hydroxide solution (2 mol dm^{-3}), added (cold) to aluminium *powder*, reacts violently and exothermically. Aluminium *foil* gives a similar, but much milder, reaction and will probably require heat to start it. *Hydrogen* is evolved and *sodium aluminate*(III) left in solution.

$$2Al(s) + 2OH^-(aq) + 10H_2O(l) \rightarrow 2[Al(OH)_4(H_2O)_2]^-(aq) + 3H_2(g)$$

Potassium hydroxide solution behaves similarly.

4. *With non-metals.* Aluminium will combine, when heated, with chlorine, nitrogen, sulphur and carbon, forming $AlCl_3$, AlN, Al_2S_3, and Al_4C_3.

Aluminium hydroxide, $Al(OH)_3$, and aluminium oxide, alumina, Al_2O_3

Laboratory preparation

Aluminium hydroxide is deposited as a gelatinous precipitate when ammonia is added to a solution of an aluminium salt; 'potash alum' (p. 127) would generally be used.

$$Al^{3+}(aq) + 3OH^-(aq) \rightarrow Al(OH)_3(s)$$

If the mixture is heated, the hydroxide becomes amorphous. It can be filtered, washed with hot water and dried.

When heated, the hydroxide is converted to aluminium oxide. To ensure complete reaction, it should be heated to constant mass.

$$2Al(OH)_3(s) \rightarrow Al_2O_3(s) + 3H_2O(l)$$

Amphoteric nature of aluminium hydroxide

The fresh gelatinous precipitate contains water and can be formulated as $[Al(OH)_3(H_2O)_3]$. This can dissolve in both acids and alkalis.

In solution, the Al^{3+} ion becomes hydrated, forming the octahedral complex ion $[Al(H_2O)_6]^{3+}$. Some hydrolysis occurs, so that a solution of an aluminium salt contains excess $H^+(aq)$ and is acidic.

$$[Al(H_2O)_6]^{3+} \rightleftharpoons [Al(OH)_3(H_2O)_3] \rightleftharpoons [Al(OH)_6]^{3-}$$

$$\xrightarrow[\text{alkali}]{\hspace{10em}}$$

$$\xleftarrow[\text{acid}]{\hspace{10em}}$$

Addition of any alkaline solution, including sodium carbonate, will cause stepwise replacement of the water molecules by OH^- ions (*via* $[Al(OH)(H_2O)_5]$, etc.) and precipitation of the hydrated hydroxide. Addition of more alkali will displace the solution equilibria further, and eventually all the water molecules will be replaced and the soluble $[Al(OH)_6]^{3-}$ formed. The process can be reversed by the addition of a strong acid; OH^- ions are replaced by water molecules and the soluble $[Al(H_2O)_6]^{3+}$ species eventually obtained. Aluminium oxide also shows amphoteric properties (see below).

As indicated above, all aluminium salts of the mineral acids are hydrolysed to give acidic solutions. This is because aluminium hydroxide is a *very weak* base (see *Advanced Level Physical Chemistry*, pp. 223 ff.). Also as indicated above, aluminium carbonate cannot be prepared. Any attempt to make it always gives aluminium hydroxide and carbon dioxide. The reaction may be formulated as:

$$2[Al(H_2O)_6]^{3+}(aq) + 3CO_3^{2-}(aq) \rightarrow 2[Al(OH)_3(H_2O)_3](s)\downarrow$$
$$+ 3CO_2(g) + 3H_2O(l)$$

Uses of aluminium hydroxide

1. *As a mordant in dyeing.* If aluminium hydroxide is precipitated in a liquid containing coloured material such as litmus or congo red, it carries down the colour with it in the form of what is called a 'lake'. The property is used in 'mordanting' dyes.
2. *In the treatment of sewage.* A similar property is used when aluminium

hydroxide is precipitated in sewage-water to clarify it. Bacteria are carried down in the sludge. Also, the triply-charged aluminium ions are particularly efficient at coagulating the colloidal material in sewage (see *Advanced Level Physical Chemistry*, p. 111).

Aluminium oxide, Al_2O_3

The modes of occurrence of this compound in nature were given on p. 118, and a laboratory preparation was given in the preceding section. Aluminium oxide is a white powder, which is highly refractory (m.p. about 2300 K). If prepared at the lowest temperature possible, it is *amphoteric* (see p. 123) and dissolves in both dilute mineral acids and aqueous caustic alkalis. If heated above 1200 K, however, it changes in relative density from 2.8 to 4.0 and is then almost unaffected by acids. The change is exothermic. Similar properties are shown by some other oxides (Cr_2O_3, Fe_2O_3, MgO).

Uses of aluminium oxide (alumina)

(a) *As a source of aluminium metal.* For this, see p. 118.
(b) *As a constituent of cements.* These cements set quickly and are resistant to sea water. There have, however, been problems associated with sudden structural failure in components made from high-alumina cement.
(c) *In refractories.* Refractories with a substantial content of alumina are used in lining cement kilns, glass furnaces, and similar plant.
(d) *In abrasives.* Fused alumina is used in making abrasives, sold as *alundum* and other trade-products.
(e) *In chromatography.* Certain grades of alumina are powerful *ad*sorbents, and are used in column chromatography with organic eluants.

Aluminium chloride, $AlCl_3$

Preparation

In the laboratory, anhydrous aluminium chloride is made by *heating* the metal in *dry* chlorine or *dry* hydrogen chloride. A full account of this is given on p. 367.

$$2Al(s) + 3Cl_2(g) \rightarrow 2AlCl_3(s)$$
$$2Al(s) + 6HCl(g) \rightarrow 2AlCl_3(s) + 3H_2(g)$$

On the large scale, it is made in the same way (using chlorine) or by passing *dry* chlorine through an intimate mixture of aluminium oxide and carbon at red heat.

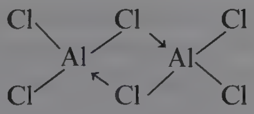
$$Al_2O_3(s) + 3C(s) + 3Cl_2(g) \rightarrow 2AlCl_3(s) + 3CO(g)$$

Properties

This chloride is white when pure, though often appears yellow by containing traces of iron(III) chloride. It fumes in air by hydrolysis, liberating hydrogen chloride.

$$AlCl_3(s) + 3H_2O(l) \rightarrow Al(OH)_3(s) + 3HCl(g)$$

It sublimes at 456 K and, at temperatures little above this value, shows a vapour density relative to hydrogen of about 133, which corresponds to a molecule Al_2Cl_6. The vapour density persists unchanged to 620 K, then begins to decrease and falls to about 67 at 1020 K. This corresponds to the molecule $AlCl_3$. The Al_2Cl_6 dimer is covalently bonded. The 'bridging' chlorine atoms can be thought of as donating a lone pair of electrons to the aluminium atom in the 'other half' of the molecule, so that the octet should be attained in the outer electron shell of each aluminium atom.



At higher temperatures the dimer dissociates into $AlCl_3$ monomers. These molecules are trigonal planar in shape, as are the boron halides; which is as expected for three bonding pairs (see *Advanced Level Physical Chemistry*, p. 79).

Uses

Anhydrous aluminium chloride is in considerable use as a catalyst in organic reactions, e.g. in Friedel–Crafts reactions of the general type:

$$C_6H_6 + R.Cl \rightarrow C_6H_5.R + HCl$$

The reaction is thought to involve interaction of $AlCl_3$ with the halogenoalkane to generate a carbonium ion, R^+. This then reacts with the benzene by electrophilic attack, to give the alkylbenzene and hydrogen chloride and regenerate the aluminium chloride.

$$R.Cl + AlCl_3 \rightarrow R^+ + AlCl_4^-$$
$$C_6H_6 + R^+ \rightarrow C_6H_5R + H^+$$
$$AlCl_4^- + H^+ \rightarrow HCl + AlCl_3$$

Aluminium sulphate, $Al_2(SO_4)_3.18H_2O$

Aluminium sulphate is made on the large scale by the action of sulphuric acid (moderately concentrated, with heat) on bauxite or china clay, e.g.

$$Al_2O_3(s) + 3H_2SO_4(aq) \rightarrow Al_2(SO_4)_3(aq) + 3H_2O(l)$$

In the laboratory, it would be made by dissolving aluminium hydroxide in hot, dilute sulphuric acid,

$$2Al(OH)_3(s) + 3H_2SO_4(aq) \rightarrow Al_2(SO_4)_3(aq) + 6H_2O(l)$$

though 'potash alum' (aluminium potassium sulphate) is a more convenient form of the salt for most purposes.

Uses of aluminium sulphate

(a) As 'alum cake', it is used in purification of water and mordanting dyes (p. 123).
(b) It is used in tanning and in sizing paper.
(c) It is used in 'foam' fire-extinguishers.

If mixed with sodium carbonate or hydrogen carbonate solution, aluminium sulphate solution produces a foam of carbon dioxide, stiffened and stabilized by the accompanying gelatinous precipitate of aluminium hydroxide. (Aluminium forms no carbonate.)

$$2Al^{3+}(aq) + 3CO_3{}^{2-}(aq) + 3H_2O(l) \rightarrow 2Al(OH)_3(s) + 3CO_2(g)$$

The foam is very effective in excluding air from oil fires and so putting them out.

The alums

The alums are a group of compounds of the general formula

$$X^+.Y^{3+}.(SO_4{}^{2-})_2.12H_2O$$

where X represents a unipositive metallic ion and Y represents a tripositive metallic ion. In the common alums, X is Na, K, NH_4; Y is Al, Cr(III), and Fe(III). This combination gives *nine* possible alums of which the best known are:

'*ordinary*' or '*potash alum*'	$K^+.Al^{3+}.(SO_4{}^{2-})_2.12H_2O$
'*iron alum*'	$NH_4{}^+.Fe^{3+}.(SO_4{}^{2-})_2.12H_2O$
'*chrome alum*'	$K^+Cr^{3+}.(SO_4{}^{2-})_2.12H_2O$

(In the rarer alums, X may include Li, Rb, Cs and Y may include In, Ga, Ti, Co, and V.)

All the alums crystallize in the same octahedral form, i.e. they are *isomorphous* (see *Advanced Level Physical Chemistry*, p. 14). Mixed crystals are readily obtained, in which, for example, chromium(III) and iron(III) ions are both contained, and crystals of one alum are readily laid on top of crystals of another. Some typical preparations of alums are given below.

Potash (or ordinary) alum

If there are no conditions laid down about materials, the easiest way to prepare this alum is to dissolve equimolar quantities of potassium and aluminium sulphates separately in the *least possible amount* of almost boiling distilled water (slightly acidified by sulphuric acid for the aluminium compound); the two solutions are then mixed. On cooling, the alum crystallizes out (colourless) and can be filtered off, washed with cold, distilled water and allowed to dry. A purer sample will be obtained by recrystallization.

If aluminium is specified as starting material, the following method is more suitable. Make up a solution of potassium hydroxide (about 0.5 mol dm^{-3}). Dissolve the given aluminium in this solution (cooling in water if necessary to moderate the action). Allow the reaction to continue till metal is left in excess, so that no alkali remains, then filter. This gives a solution of potassium aluminate in which the potassium and aluminium are in the correct proportions for the alum (i.e. K : Al).

$$2Al(s) + 2KOH(aq) + 10H_2O(l) \rightarrow 2K^+[Al(OH)_4(H_2O)_2]^-(aq) + 3H_2(g)$$

With stirring, add dilute sulphuric acid till the mixture is definitely acidic (test by blue litmus paper) and then dilute it with about an equal volume of water.

$$2K^+[Al(OH)_4(H_2O)_2]^-(aq) + 4H_2SO_4(aq) \rightarrow K_2SO_4(aq) + Al_2(SO_4)_3(aq) + 12H_2O$$

Heat the solution and filter off any undissolved material. Evaporate the solution to small bulk, cool and obtain pure alum crystals as stated before.

Iron alum

Here it is convenient to start with iron(II) sulphate crystals and oxidize them to iron(III) during the preparation.

Weigh out iron(II) sulphate crystals and ammonium sulphate in equimolar proportions. Dissolve the iron(II) sulphate, with heat, in dilute sulphuric acid and, in the fume cupboard, carefully add concentrated nitric acid, a little at a time, till no more brown fumes are evolved. The solution will then be brown and will contain iron(III) sulphate by oxidation.

$$6FeSO_4(aq) + 3H_2SO_4(aq) + 2HNO_3(aq) \rightarrow 3Fe_2(SO_4)_3(aq) + 4H_2O(l) + 2NO(g)$$

Stir in the ammonium sulphate till it is dissolved. Filter the liquid if it is not clear, evaporate it to small bulk, cool, etc., to obtain crystals as before. They are *pale purple* in colour, though giving a *brown* solution.

Chrome alum

A convenient way of preparing this alum is to reduce potassium dichromate(VI) solution, containing sulphuric acid, by passage of sulphur dioxide till the solution is fully *green* in colour and shows no brownish tinge from the original dichromate(VI).

$$K_2Cr_2O_7(aq) + 3SO_2(g) + H_2SO_4(aq) \rightarrow K_2SO_4(aq) + Cr_2(SO_4)_3(aq) + H_2O(l)$$

After evaporation and cooling of the solution, the alum can be crystallized as before. It forms dark purple crystals.

Aluminium nitrate, $Al(NO_3)_3 \cdot 9H_2O$

This salt can be made by standard methods, e.g.

$$Al(OH)_3(s) + 3HNO_3(aq) \rightarrow Al(NO_3)_3(aq) + 3H_2O(l)$$

but *not* from aluminium and nitric acid, which do not react appreciably together. It shows the usual behaviour of a heavy-metal nitrate when heated.

$$4Al(NO_3)_3(s) \rightarrow 2Al_2O_3(s) + 12NO_2(g) + 3O_2(g)$$

Aluminium sulphide, Al_2S_3

This compound can be made by heating the two *dry* elements together. The acid and base to which it corresponds are, however, so weak that the sulphide is completely hydrolysed by water, with liberation of hydrogen sulphide (the acid) and precipitation of aluminium hydroxide (the base).

$$\begin{array}{lccc}
\text{From aluminium sulphide:} & 2Al^{3+} & & 3S^{2-} \\
 & + & & + \\
\text{From water:} \quad 6H_2O \rightleftharpoons & 6OH^- & + & 6H^+ \\
 & \uparrow\downarrow & & \uparrow\downarrow \\
 & 2Al(OH)_3\downarrow & & 3H_2S\uparrow
\end{array}$$

Because of this, the addition of a soluble *sulphide* solution (e.g. Na_2S) to a solution of an aluminium salt precipitates aluminium *hydroxide.*

Aluminium tricarbide, Al_4C_3

Aluminium tricarbide can be made by direct combination of the two elements at very high temperature, or by the reaction between aluminium oxide and excess carbon at very high temperature.

$$2Al_2O_3(s) + 9C(s) \rightarrow Al_4C_3(s) + 6CO(g)$$

It is decomposed by water, liberating *methane.*

$$Al_4C_3(s) + 12H_2O(l) \rightarrow 4Al(OH)_3(s) + 3CH_4(g)$$

It will probably have been noticed that boron is not markedly similar in properties to aluminium, though these elements both appear in Group III of the Periodic Table. In fact, boron resembles silicon, the second element of Group IV, more closely than it resembles aluminium. For discussion of this point, see page 9.

Questions

1. By consideration of suitable properties of the element, its oxide, its chloride, and the hydride, B_2H_6, consider whether boron should be classified as a metal or as a non-metal. The chloride, BCl_3, forms a very stable compound, $BCl_3.NH_3$. Explain this fact in electronic terms.

2. Describe one method by which natural bauxite can be purified on the large scale and then used for the extraction of aluminium. Give an account of the use of this metal in thermit reactions and in *two* other important ways. How, and in what conditions, does aluminium react with (a) mineral acids, (b) caustic alkalis?

3. Starting from aluminium foil in all cases, how would you prepare reasonably pure samples of (a) anhydrous aluminium chloride, (b) aluminium oxide, (c) 'potash alum'? Describe and explain what happens if this alum is dissolved in water and then potassium hydroxide solution is added, with shaking, until the alkali is in excess.

4. By considering the properties of the metal, its oxide and chloride, discuss whether aluminium can be regarded as a typical metal.

5. In the extraction of aluminium, the ores are first thoroughly purified and then reduced electrolytically, further refining being unnecessary; whereas for most metals the ores, after some concentration, are reduced thermally, and the metal is *then* refined.

Give an account of the extraction of aluminium, and consider especially why it can and must differ from the extraction of a more typical metal. (L.)

6. State in each case what anion containing aluminium is formed in (a), (b), and (c) below and outline the chemistry of the reactions involved.

- (a) Aqueous sodium hydroxide is added to a solution of an aluminium salt until present in excess.
- (b) Lithium is heated in a stream of hydrogen and the product added in excess to a suspension of aluminium chloride in ethoxyethane.
- (c) A mixture of aluminium fluoride, ammonium fluoride and sodium nitrate is heated.

Draw diagrams to illustrate the electronic structures of the anions containing aluminium formed in (a) and (b).

Would you expect boron to form an anion analogous to that formed by aluminium in (c)? Explain your answer. (C.)

7. Describe briefly the laboratory preparation of anhydrous aluminium chloride starting with the metal. Give *one* use of aluminium chloride in organic chemistry.

How and under what conditions does aluminium chloride react with (a) sodium chloride, (b) lithium hydride, and (c) ammonia? Give the structures of the products.

Explain why the vapour density of aluminium chloride is 132 at 673 K and about 67 at 1073 K. (A.E.B.)

7

Elements of Group IV

Group IV of the Periodic Table contains the elements carbon, silicon, germanium, tin, and lead. They show an interesting gradation of properties from non-metallic to metallic. A summary table is provided at the end of the chapter.

Carbon

Atomic number 6; electron arrangement 2.4($1s^2 2s^2 2p^2$)
Carbon has two isotopes of mass number, in order of abundance, 12 and 13; relative atomic mass 12.01

Allotropy of carbon

Carbon was formerly said to have many allotropes—diamond, graphite, lamp black, soot, animal charcoal, and wood charcoal among them. The analysis of crystal structure by X-ray methods has shown, however, that only two essentially different crystal structures occur—those of *diamond* and *graphite*—and that all other 'allotropes' are only graphitic materials of variable purity.

Diamond and graphite provide an excellent example of how different structures made up of the same atoms can give rise to solids with very different physical properties.

Diamond

The crystal of the diamond allotrope is based upon a tetrahedral structure in which a carbon atom may be considered as situated at the centre of a regular tetrahedron and exercising its four covalencies towards the vertices. This gives a symmetrical arrangement of the valency in three-dimensional space. On this unit, a *giant covalent structure* is built up in which each inner carbon atom is linked covalently to four others. The structure is shown in Figure 7.1. The essential unit is ABCDE. It will be seen that the structure includes a series of inter-lacing hexagons. In this lattice, all the bonding is *covalent*, and between *atoms*. There are no weak van der Waals' forces involved, such as hold together *molecules* in crystals of compounds such as ethanedioic acid or cane sugar. The C—C bond distance in the diamond crystal is 0.154 nm throughout. Its giant structure may become relatively enormous. The Cullinan diamond, for example, weighed about 600 g and consisted of a single crystal. Diamonds weighing more than 30 g are, however, quite rare. This structure explains some of the most striking properties of the diamond—its hardness, its resistance to melting and its extreme lack of volatility. The hardness results from the strength and uniformity of the bonding. There are no planes of weakness in the crystal structure. Diamond is the hardest natural material known. Similarly, as the temperature rises, the vibrational energy of the atoms is not great enough to break down the strong, covalent bonding and the diamond does not melt. At about 3800 K, however, the vibrational energy of the atoms is so great that they begin to break away and the diamond vaporizes.

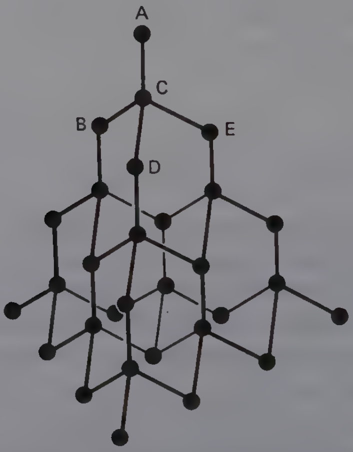


Figure 7.1 *Crystal structure of diamond*

The constant bond length in diamond is rather short compared with the average bond length in graphite, so that diamond has a considerably higher density (3.51 g cm^{-3}; graphite 2.25). Diamond is transparent to X-rays, whereas glass is almost opaque; this provides a ready means of distinguishing the two. Diamond also has a very high refractive index, 2.4. This is the factor which produces its much prized flashing effect as a gem.

Occurrence and chemical properties of diamonds

Diamonds are found in southern Africa, Brazil, the Urals, India, Australia, and Borneo. The principal source of them is South Africa, where they occur in a rock called *blue ground*, which is believed to be the vents of extinct volcanoes. When exposed to air, it weathers to a powder from which the diamonds are extracted by washing or hand-picking.

The natural diamond resembles a rounded pebble and has to be cut and polished for use as a gem. The most valued diamonds (*of the first water*) are clear and free from colour. Diamonds also occur coloured (yellow, red, green, pink) but are much less valued, and grey or black diamonds (*carbonado*) are used only for industrial purposes, as in rock-drilling and in grinding, cutting and polishing processes.

Diamond is chemically unreactive. It burns in air (at about 1200 K) but only with difficulty, and more readily in oxygen, in both cases to *carbon dioxide*, CO_2. It is not attacked by any acid or aqueous alkali, and only very slowly by fused sodium carbonate.

$$Na_2CO_3(l) + C(s) \rightarrow Na_2O(s) + 2CO(g)$$

A mixture of concentrated sulphuric acid and potassium dichromate(VI) at 470 K oxidizes diamond to carbon dioxide, and diamond combines with fluorine (to give CF_4) at red heat.

The possibility that a few pence worth of graphite might be converted to some thousands of pounds worth of diamond has stimulated many efforts to bring about this change. Moissan claimed some success by the use of the then newly discovered electric furnace. He allowed iron to dissolve carbon at very high temperatures (about 3800 K) and then plunged the container into molten lead with the idea that the sudden cooling would solidify the outer layers of metal and crystallize the carbon to diamond in the interior, under great heat and pressure. Desch (1928) was, however, unable to repeat Moissan's work with success. Hershey (1936) produced a diamond about the size of a wheat grain. More recently, the General Electric Company in America and others have made small industrial diamonds by subjecting graphite to very high temperature and pressure, in the presence of an accelerator such as tantalum carbide.

Graphite

The graphite structure is in marked contrast to that of diamond. In graphite, the carbon atoms lie in *parallel planes*, in which the atoms are *covalently* combined in a network of regular hexagons. The sheets, however, are not held together by true covalent bonding, but only by *weak* forces of the van der Waals' type, which hold molecules together in crystals of some compounds. The arrangement is seen in Figure 7.2.

The bonding between the parallel planes is so weak that they can slide readily on each other (a *shearing* effect) and so produce the characteristic softness of graphite.

It is found that in the planes the C to C distance is constant at 0.142 nm. This compares with the usual C—C bond length of 0.154 nm, and the usual C=C value of 0.134 nm. The intermediate figure suggests delocalization of electrons. The carbon-to-carbon bond length in benzene, a fully delocalized six-membered ring molecule, is 0.139 nm. It has been suggested that graphite may be thought of as consisting of planes of polybenzene. The distance between the planes of atoms in graphite is 0.335 nm, which is too great for any form of true covalent C to C bond and suggests that forces of the van der Waals type are in operation.

A rather unexpected observation is that the heat of combustion of graphite is less than that for diamond, from which it is apparent that graphite is thermodynamically the more stable allotrope.

$$\text{C(diamond)} \rightarrow \text{C(graphite)} \qquad \Delta H = -1.9\ \text{kJ mol}^{-1}$$

This is presumably connected with the stability conferred by electron delocalization in the planes of graphite. The rate at which diamond spontaneously converts to graphite is unobservably slow: so many

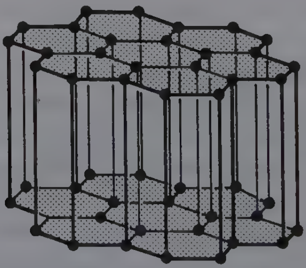


Figure 7.2 *Crystal structure of graphite*

strong covalent bonds would have to be broken that the *activation energy* of the reaction (see *Advanced Level Physical Chemistry*, p. 261) would be extremely high.

Occurrence, manufacture, and uses of graphite

Graphite was once mined in Cumbria (UK), and is still found in important deposits in Korea, Ceylon, Mexico, and elsewhere. Various grades are known as *graphite*, *plumbago*, and *black lead*.

Graphite is manufactured from coke (by Acheson's process) where electric power is cheap. An electric furnace of fire-brick is supplied with carbon electrodes between which is placed a conducting core of carbon. The rest of the furnace is filled with petroleum coke containing some sand and a binding agent, such as coal-tar. By alternating current, a very high temperature is maintained for about thirty hours and graphite is left. The following changes are probably involved:

$$\underset{\text{(sand)}}{SiO_2(s)} + \underset{\text{(coke)}}{3C(s)} \rightarrow SiC(s) + 2CO(g)$$

$$SiC(s) \rightarrow Si(g) + \underset{\text{(graphite)}}{C(s)}$$

The silicon is vaporized at the temperature used.

The Acheson process produces a material with randomly-oriented small crystals. Single crystals, called 'whiskers', can be made by striking an arc between carbon rods. 'Carbon fibres' can be produced by controlled pyrolysis of arcylic polymer fibres. Both the whiskers and fibres have high tensile strength. 'Pyrographite' can be made by heating hydrocarbons above 2300 K. The thermal conductivity of pyrographite is 100 times greater along the planes of atoms than it is perpendicular to them; the electrical conductivity is 1000 times greater. This *anisotropy* is the expected consequence of the structure of near-perfect crystals of graphite.

Graphite has the following *uses*:

(a) Graphite (usually the natural variety) is mixed with clay and water, extruded into thin cylinders and baked. This is the *lead* of a lead pencil and is cased in wood for convenience in use.

(b) Graphite is an important *lubricant*. It may be carried in aqueous tannin solution (the tannin stabilizes the colloidal mixture) or in oil. These varieties are *aquadag* and *oildag*. Graphite is non-volatile and is particularly useful for lubricating parts of machinery which may run hot. Uses (a) and (b) both exploit the softness of graphite.

(c) Graphite is a good conductor of electricity and is used in making battery plates and electrodes, and in *electrotyping* to produce a conducting surface on wood or plastic so that a metal may be deposited on it.

(d) Mixed with clay and sand, moulded and baked, graphite is used in crucibles. It is also an ingredient of stove polishes.

(e) Graphite, highly purified, is used in atomic piles and the cores of some nuclear reactors. Under controlled conditions it remains structurally stable in the intense neutron flux.

(f) As indicated above, carbon fibres have high tensile strength. They are increasingly incorporated in materials for which low density and high strength are of paramount importance, e.g. in the aerospace industry.

Properties of graphite

The structure of graphite is more open than the structure of diamond (p.132), so graphite has the lower density. Graphite is a dark grey solid with some lustre like that of a metal; hence its fancied relation with lead and the names *plumbago* and *lead* pencil. It is a good electrical conductor; diamond is a non-conductor. This is because of the delocalization of electrons in the planes of atoms. Each carbon atom can be considered to be covalently combined with only *three* other carbon atoms. Between the planes, only *van der Waals' forces* operate. Consequently, one of the four valency electrons of each carbon atom is relatively free to move under a p.d., producing electrical conductance. As suggested above, in a perfect graphite crystal, conduction should occur *along* the planes of carbon atoms but not perpendicular to them. Unlike metals, graphite *increases* its electrical conductance with rise of temperature. In diamond, each carbon atom is covalently combined with *four* others and free electrons do not occur.

The more open structure of graphite makes it chemically more active than diamond; chemical attack usually occurs first between the planes of carbon atoms. Carbon electrodes are often observed to flake when gases, especially hydrogen, are released during electrolysis. This is a physical rather than a chemical effect, unlike the consumption of the carbon anodes during the production of aluminium (see p. 119). Graphite is not, however, affected by chlorine, dilute acids or alkalis, or by fused alkalis.

1. *With air or oxygen.* Graphite ignites at red heat (with some difficulty) and burns to *carbon dioxide.*

$$C(s) + O_2(g) \rightarrow CO_2(g)$$

2. *With nitric acid and other acids.* The action of graphite with concen-

trated nitric acid appears variable. If moistened with this acid and heated, some varieties swell in the direction perpendicular to the planes of atoms; other varieties are unchanged.

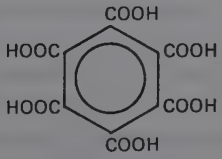
If concentrated nitric acid is used with potassium chlorate(V) (a very vigorous oxidizing mixture) and heated with graphite on a water-bath for a long period, repeated treatment with fresh batches of reagents will produce a product called *graphitic acid*. It is a yellowish solid, almost insoluble in water. The molecular formula of this material is not known with certainty; if heated, it is converted back to graphite. The material is probably formed by the introduction of oxygen and water molecules, in a not very precise chemical way, between the planes of carbon atoms.

In a similar way, so-called *graphite salts* are produced if graphite is acted upon by concentrated sulphuric acid and an oxidizing agent such as chromium(VI) oxide, CrO_3. They are unstable; water converts them back to graphite, in which some oxygen is still retained.

The so-called *amorphous carbon* appears to be a graphitic form, in which the planes of atoms have been broken into minute fragments which lie at random. Prolonged action of fuming nitric acid converts amorphous carbon into '*mellitic acid*', (benzenehexacarboxylic acid), $C_6(COOH)_6$. Distillation with lime converts this acid into *benzene*.

$$C_6(COOH)_6(s) + 6CaO(s) \rightarrow C_6H_6(l) + 6CaCO_3(s)$$

This means that the acid has the structure:



This is obviously derived from the hexagons of carbon atoms in the graphitic planes.

Aqueous chromic(VI) acid in the presence of tannin converts graphite to a form known as *colloidal graphite*. This is the variety used in making *oildag* and *aquadag* lubricants (p. 135). The word *dag* is derived from the initials of *deflocculated Acheson graphite*.

3. *With sodium carbonate*. Like diamond, graphite is slowly attacked by fused sodium carbonate.

$$Na_2CO_3(l) + C(s) \rightarrow Na_2O(s) + 2CO(g)$$

Amorphous carbon

There are several materials which are grouped under this general title

—among them the *charcoals* (from wood, sugar, and bone), *soot*, *lampblack*, *gas carbon*, and *coke*. In all these cases, the carbon content is *graphitic* with the planes of carbon atoms fragmented and lying in random positions. Varying proportions of impurity are also present. The production and uses of the more important ones will be briefly considered.

Wood charcoal

In the ancient process of charcoal-burning, wood (usually the thinner branches from felled trees) is stacked up and covered with turf to reduce the supply of air. The stack is then kindled near the centre: part of the wood burns, distilling the other part, and leaving wood charcoal.

In a more economical and controlled process, wood is distilled in closed retorts. It then yields four products:

(a) wood gas (which can be burnt);
(b) pyroligneous acid (containing water, ethanoic acid, methanol);
(c) wood tar;
(d) charcoal (the solid residue).

Uses of wood charcoal

1. In some countries (where coal is scarce), charcoal is used as a domestic fuel in closed stoves.

2. Charcoal is extremely porous and has a high surface area; it will *adsorb* gases on to its surface, i.e. the gases will become attached to the surface of the charcoal in a layer which is extremely thin, indeed mainly unimolecular. In this way, very large volumes of gas can be adsorbed. Three main factors influence adsorption:

(a) *The nature of the gas.* In a general way, the higher the boiling point of the gas, the more readily it is adsorbed.

(b) *The temperature of adsorption.* The adsorptive power of charcoal *increases* very rapidly as temperature *falls*; at the temperature of liquid air (about 85 K), charcoal adsorbs 230 times its own volume of oxygen, against 18 times at 273 K. Very high vacua can be rapidly produced by adsorbing gases on charcoal at this low temperature.

(c) *The surface of the charcoal.* The surface of charcoal is often contaminated by tarry products of distillation and rendered relatively inactive. The charcoal may be 'activated' so as to clear the surface and so increase porosity and adsorptive power. Among activating processes are:

(i) heating in air at about 800 K, followed by the action of steam at red heat;

(ii) treatment of the wood with phosphoric(V) acid, followed by carbonization at 1300 K. Tarry matter is oxidized away by the phosphoric(V) acid, and the reduction product (phosphorus) also distils off.

Activated charcoal is frequently catalytic to gaseous reactions, because adsorption on to its surface brings the reacting gases into very close association and provides the encounters from which chemical reaction can develop. For example, activated charcoal brings about combination of hydrogen and chlorine in the dark at room temperature. Other reactions catalysed by it are:

$$CO(g) + Cl_2(g) \rightarrow COCl_2(g)$$ Carbon oxide dichloride (carbonyl chloride)

$$SO_2(g) + Cl_2(g) \rightarrow SO_2Cl_2(l)$$ Sulphur dioxide dichloride (sulphuryl chloride)

Bone charcoal or animal charcoal

Bones are treated with benzene to remove grease and steamed to remove gelatine. They are then distilled in closed retorts and the residue is *bone* or *animal charcoal*. It contains only 10–15 per cent of carbon, the remainder being mainly calcium phosphate(V).

This product absorbs colouring matter very effectively from hot aqueous solutions. It is used in removing yellow colour from solutions of raw sugar to produce white sugar crystals.

Sugar charcoal

If pure cane sugar is heated in a covered crucible till all volatile matter is expelled, the residue is *sugar charcoal*. A very pure form of carbon can be obtained from it by the following procedure: (a) heating in a current of chlorine at red heat—this removes any combined hydrogen as hydrogen chloride; (b) washing with hot distilled water to remove any soluble matter, and drying; (c) heating in hydrogen to remove any chlorine.

Sugar charcoal can also be made by the action of concentrated sulphuric acid on moistened sugar. The black mass so obtained is crushed, washed, and dried to give the pure product (see p. 336).

Lamp-black

Lamp-black is made by burning carbonaceous material, usually petroleum gas or ethyne (acetylene), in a very limited air-supply, so that most of the carbon escapes unburnt, e.g.:

$$\underset{\text{ethyne}}{2C_2H_2(g)} + O_2(g) \rightarrow 4C(s) + 2H_2O(g)$$

It is collected on 'blankets' suspended in large chambers. Lamp-black is very finely divided and intensely black. It is used in the production of printers' ink, stove and shoe polishes, black paint, and black rubber tyres.

Soot is a product similar to lamp-black. It is unburnt carbon particles, escaping from coal fires and lodging in chimney flues. It contains potassium and ammonium salts and is applied to gardens as a fertilizer.

Gas carbon

Gas carbon is a very hard deposit, which collects in the retorts when coal is distilled. It conducts electricity well and is used to make carbons for arc lamps, battery plates, and carbon anodes.

Coke

Coke is the residue left after distillation of coal for coal gas. A tonne of typical coal will leave about 700–800 kg of coke, containing 85–90 per cent of carbon.

(a) Coke can be used directly as a fuel.
(b) It is used in the production of the fuel gases, *producer gas* (p. 142) and *water gas* (p. 142) and, hence, as a source of organic chemicals.
(c) Coke is used on a very great scale as an industrial reducing agent, e.g. in the blast furnace for iron (p. 432) and in the reduction of zinc oxide (p. 469).

Chemical properties of amorphous carbon

The term *amorphous carbon* is used rather vaguely to include graphitic forms of carbon other than graphite itself. They vary somewhat in chemical behaviour, but are generally more reactive than graphite or diamond. Their typical behaviour includes the following properties:

1. *With oxygen.* Wood charcoal burns in oxygen at about 620 K, producing *carbon dioxide.*

$$C(s) + O_2(g) \rightarrow CO_2(g)$$

2. *With fluorine.* Heated in fluorine, amorphous carbon combines directly with it to produce tetrafluoromethane.

$$C(s) + 2F_2(g) \rightarrow CF_4(g)$$

The other halogens (Cl_2, Br_2, I_2) do *not* react with carbon.

3. *As a reducing agent.* At a temperature of about 1300 K, amorphous carbon is a powerful reducing agent in many reactions, such as the following:

$$PbO(s) + C(s) \rightarrow Pb(l) + CO(g)$$
$$Fe_2O_3(s) + 3C(s) \rightarrow 2Fe(l) + CO(g)$$

It also reduces concentrated sulphuric and nitric acids when heated with them.

$$C(s) + 2H_2SO_4(l) \rightarrow CO_2(g) + 2SO_2(g) + 2H_2O(g)$$
$$C(s) + 4HNO_3(conc.aq) \rightarrow CO_2(g) + 4NO_2(g) + 2H_2O(g)$$

4. *With other elements at electric furnace temperature.* At the temperature of the electric furnace, carbon combines with many elements, both metallic and non-metallic, to give compounds such as *carbon disulphide*, CS_2, *silcon carbide*, SiC, and the carbides of *aluminium*, Al_4C_3, *calcium*, CaC_2, and *iron*, Fe_3C. Some of these are usually made from the oxide of the element, e.g.

$$CaO(s) + 3C(s) \rightarrow CaC_2(s) + CO(g)$$

Some fuel gases

Natural gas

Natural gas is often found associated with petroleum, or in large 'gas fields' found in underground strata similar to those in which petroleum may occur. The major constituent (about 90 per cent by volume) is methane, with progressively smaller amounts of ethane, propane, and higher alkanes. As with all hydrocarbons, the constituents of natural gas burn in excess air to give carbon dioxide and water with release of a great deal of energy, e.g.

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l) \qquad \Delta H_{298} = -890\ \text{kJ mol}^{-1}$$

In many countries, including Britain, natural gas has replaced coal gas as a convenient piped gaseous fuel. However, supplies of natural gas are limited in extent, and it is also an important feedstock for the organic chemicals industry. It is therefore possible that, within a few decades, natural gas as an energy source may have been replaced once again by gas obtained from the gasification of coal, perhaps while the coal is still underground.

Producer gas and water gas

These gases are obtained by alternately blasting air and superheated steam through a specially-constructed furnace (the 'producer') containing coke at a high temperature.

The *air blow* results in an overall reaction which is *exothermic*. The net reaction is:

$$2C(s) + \underbrace{O_2(g) + 4N_2(g)}_{\text{air}} \rightarrow 2CO(g) + 4N_2(g) \qquad \Delta H = -223\ \text{kJ mol}^{-1}$$

It is necessary to maintain a temperature of at least 1300 K to secure an equilibrium sufficiently favourable to the formation of carbon monoxide in the reversible reaction:

$$C(s) + CO_2(g) \rightleftharpoons 2CO(g)$$

Typical figures are given in the following table.

Temperature (K)	*Percentage by volume of equilibrium*	
	CO_2	CO
723	98.0	2.0
1023	24.0	76.0
1323	0.4	99.6

It will be seen that, since producer gas theoretically contains the proportions $2CO : 4N_2$, two-thirds of it, by volume, is incombustible nitrogen. In practice, producer gas usually contains about 34 per cent CO, 64 per cent N_2 and 2 per cent CO_2 by volume. Its value as a fuel is, therefore, rather low. Producer gas is never stored; it is usually made on an industrial site and delivered at once to a number of local heating points where the gas, still hot from the producer, is burnt with a 'secondary' air-supply to carbon dioxide, in the exothermic reaction:

$$2CO(g) + O_2(g) \rightarrow 2CO_2(g) \qquad \Delta H = -566\ \text{kJ mol}^{-1}$$

In the long run, the whole process simply amounts to the combustion of coke to carbon dioxide. Producer gas was used for heating retorts in coal gas manufacture, and also in the extraction of zinc and in firing glass furnaces.

When the temperature in the furnace is high enough, the air blast is shut off as the *steam blast* is begun. The production of water gas is *endothermic*.

$$C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g) \qquad \Delta H = +121\ \text{kJ mol}^{-1}$$

It will be seen that water gas is, theoretically, a mixture of equal volumes of carbon monoxide and hydrogen. It is, therefore, entirely combustible and a very good fuel. It is used in combustion with 'secondary' air by the exothermic reactions:

$$H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow H_2O(l) \qquad \Delta H = -286\ \text{kJ mol}^{-1}$$
$$CO(g) + \tfrac{1}{2}O_2(g) \rightarrow CO_2(g) \qquad \Delta H = -283\ \text{kJ mol}^{-1}$$

As the water gas reaction proceeds, heat is absorbed from the coke and its temperature falls rapidly. If it falls *below* 1300 K, two adverse factors rapidly develop:

(a) Steam passes unchanged.
(b) The reaction

$$C(s) + 2H_2O(g) \rightarrow CO_2(g) + 2H_2(g)$$

becomes significant, producing non-combustible carbon dioxide. Typical figures are given in the following table.

Temperature (K)	*Percentage of steam decomposed*	*Percentage composition of gas by volume* H_2	CO	CO_2
1398	99.4	50.9	48.5	0.6
1333	98.0	50.7	48.0	1.3
1283	94.0	48.8	49.7	1.5
1228	70.2	53.3	39.9	6.8
1113	41.0	61.9	15.1	22.9

The problem is overcome in the following way. Air is passed through the mass of coke for about two minutes. This raises the coke to incandescence (perhaps 1700–1800 K). Then a *steam blow* (about four minutes) makes water gas, reducing the temperature to about 1300 K. Then the air blow is resumed, and so on alternately, the producer gas and water gas being collected separately.

Uses of water gas

1. *As a fuel gas.* The reactions involved were given above. Water gas was often used to enrich coal gas.
2. *As an industrial source of hydrogen.* The manufacturing process was given on p. 31.
3. *As a source of organic chemicals.* Water gas can be used as a source of organic chemicals. Methanol can be made by enriching water gas with hydrogen and passing it over zinc oxide and chromium(III) oxide

(catalyst) at 720 K and 200 atm.

$$\underbrace{CO(g) + H_2(g)}_{\text{water-gas}} + H_2(g) \rightarrow CH_3OH(l)$$

Coal gas

Coal is a general term describing the complex product of the action of bacterial decay, pressure, temperature and moisture on vegetable matter over a very long period. The vegetable matter probably goes through the following stages, with increasing hardness, decreasing oxygen content and increasing carbon content in the order:

peat → lignite coals → bituminous coal → steam coal → anthracite

In the manufacture of coal gas, a bituminous coal is used. It is distilled, in a continuous process, at about 1300 K out of contact with air. The volatile products pass over leaving coke, which is a valuable material for the extraction of metals and other industrial purposes. The treatment of the volatile products is quite complex, and is not discussed here. Apart from coal gas, the other main products include ammonia, sulphur, and coal tar. The ammonia is used mostly to make ammonium salts for use as fertilizers. The sulphur is largely converted into sulphuric acid. The coal tar is distilled to give a very wide variety of organic materials, which include benzene, methylbenzene (toluene), phenol, and naphthalene. In its early days, the organic chemicals industry was based largely on coal tar products.

Composition of coal gas; its by-products

No *exact* figures can be given for the composition of coal gas, because it may vary with the type of coal used and the temperature of distillation. The following figures are fairly typical:

Constituent	*Percentage by volume*
Hydrogen	50
Methane, CH_4	30
Carbon monoxide	8
Ethene (ethylene), C_2H_4	4
Nitrogen	5
Carbon dioxide	2
Oxygen	1

Combustion and flame

Since carbon and its simple compounds provide much of the World's energy requirements through their combustion, it seems appropriate to consider this topic at this point. The term *combustion* is not absolutely precise in meaning. In a general way, it is taken to indicate a reaction between two substances, one or both being gaseous, the reaction occurring at a high temperature and generating enough heat to maintain itself, once it has been started.

A typical case is that of carbon burning in oxygen gas. The carbon must be heated, to start the reaction, to about 800 K. The process of burning then generates enough heat to maintain itself.

$$C(s) + O_2(g) \rightarrow CO_2(g) \qquad \Delta H = -394\ \mathrm{kJ\ mol^{-1}}$$

On the other hand, lead, for example, will combine with oxygen when heated to form lead(II) oxide, litharge. The reaction is not self-maintaining and, as soon as the source of heat is removed, the system cools and combination between lead and oxygen ceases. It is not regarded as combustion.

The gas involved in the reaction need not be oxygen or air. The combination of yellow phosphorus with chlorine is a case of combustion; so is the burning of magnesium in steam.

$$P_4(s) + 6Cl_2(g) \rightarrow 4PCl_3(l)$$
$$Mg(s) + H_2O(g) \rightarrow MgO(s) + H_2(g)$$

Combustions are usually accompanied by emission of light because the heat generated is enough to raise at least one of the materials involved to a state of incandescence. On the other hand, a flame of hydrogen burning in oxygen, completely dust-free, is almost invisible.

Incandescence does not necessarily bring a reaction within the meaning of the term *combustion*. For example, an intimate mixture of iron filings and sulphur (in the proportions of 56:32) glows when heated and the glow spreads through the mass, once it has started. But both participants are *solid*, so that reaction is outside the usually accepted range of the term *combustion*.

Flame is not necessarily a feature of combustion. Iron wire, for example, burns in oxygen with no discernible flame, but the process is regarded as combustion. Flame appears only when a *gas* or *vapour* is burning. In the combustion of iron in oxygen, the temperature reached is too low to vaporize iron. Phosphorus, however, is vaporized by the heat of its combustion in oxygen and so burns with a flame.

'Combustible substance' and 'supporter of combustion'

These terms are in use as a matter of convenience. In the case of combustions in air, which are so common, the air is generally regarded as the supporter of combustion and the burning substance as the combustible. In other cases, a gas is usually regarded as the supporter of combustion, a liquid or solid as the combustible; for example, chlorine is regarded as supporting the combustion of yellow phosphorus or thin copper foil. That is, to some extent, an arbitrary distinction. In a well-known experiment, air can be made to reverse its usual role and become the combustible, see Figure 7.3.

If the hole at A is covered for a short time and the coal-gas turned on, a flame can be lighted at C. If the cover on A is then removed and the coal gas lighted there, a flame of air (now the combustible) burning in an atmosphere of coal gas (now the supporter of combustion) will appear at B.

Flame

It has already been mentioned that flame is not a necessary accompaniment of combustion. It appears only during the burning of a gas or vapour.

Single-mantled flames

A flame of hydrogen burning in air (or oxygen) is of this simple type.

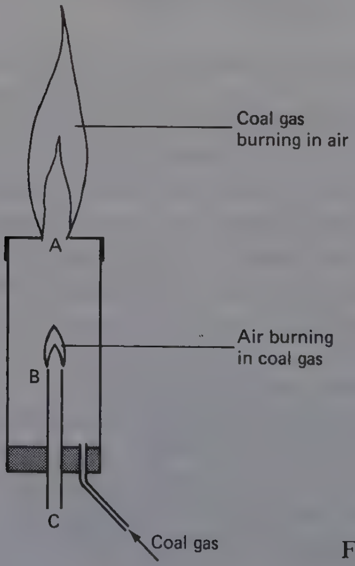


Figure 7.3 *Air as a combustible*

As the hydrogen emerges from a circular jet, it can burn only where it is in contact with air, i.e. in the outer ring of hydrogen. More gas must rise through this ring to obtain air for combustion. This occurs successively, producing a cone-shaped flame.

This flame has two zones. The inner zone is also cone-shaped and consists of unburnt gas not yet in contact with air. The outer zone is a region in which combustion is occurring, producing the total reaction:

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l) \qquad \Delta H = -572\ \text{kJ mol}^{-1}$$

The region of unburnt gas can be demonstrated by holding a piece of card in the flame, removing the card just before it burns. It will show a charred ring, with an uncharred centre corresponding to the region of unburnt gas.

More complex flames

The flames of more complex materials, such as candle-wax or coal gas in air, are much more complex, but similar to each other in general lay-out. They are illustrated in Figure 7.4. The zone so marked contains *unburnt gas* because it is not in contact with a supply of air. The *blue zone* is one of rapid combustion in air. It is comparatively non-luminous, probably because no solid particles appear during the combustion. The *luminous zone* is the zone of most active reaction. The luminosity is caused by particles of carbon. It was at one time thought that these carbon particles were formed by preferential combustion of hydrogen,

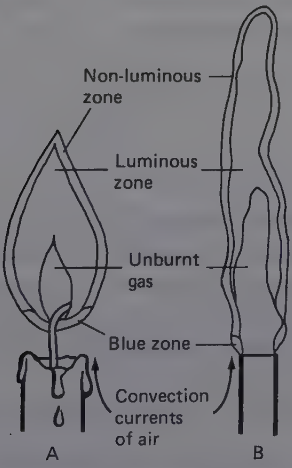


Figure 7.4 *Complex flames*

but it is now known that the process is more complex and that production of hydroxide groups plays a part in it.

The *outer zone* is the zone in which the final stages of oxidation are completed. If not, the flame will smoke.

Luminosity in flames

The cause of luminosity in flames has been much investigated, but is not completely clear. The following facts seem well established:

(a) Solid particles in a flame will cause luminosity, but they are not absolutely necessary to it. The presence of solid particles in the candle flame, or luminous bunsen flame, seems established by the following facts:

(i) The luminous part of the flame casts a shadow if placed between a strong light and a screen; if the flame is made to smoke, the shadow merges with the smoke-shadow.

(ii) Sunlight scattered by the flame is found to be polarized, which is to be expected if minute solid particles are present in the flame. On the other hand, the very luminous flame of phosphorus, by these tests, shows no solid particles.

(b) Increase of pressure increases luminosity in a flame. From this, Frankland deduced that the density of a burning gas is a factor in luminosity and advanced the *dense hydrocarbon theory* of luminosity in hydrocarbon flames.

(c) Luminosity varies with the temperature of the burning materials. If a bunsen burner tube is extended by a silica tube, which is then heated, the bunsen flame becomes more luminous, and luminosity decreases as the silica tube cools.

Carbon dioxide, CO_2

Preparation

Carbon dioxide is usually prepared in the laboratory by the action of dilute hydrochloric acid on marble (calcium carbonate). This combination of materials is chosen because marble, in the form of chips, gives a steady reaction at a convenient rate. The gas is moderately soluble in water, so is usually collected over *warm* water or, if wanted dry, by downward delivery (Figure 7.5).

In general, this reaction is given by any carbonate and any dilute mineral acid.

$$CO_3^{2-}(aq) + 2H^+(aq) \rightarrow CO_2(g) + H_2O(l)$$

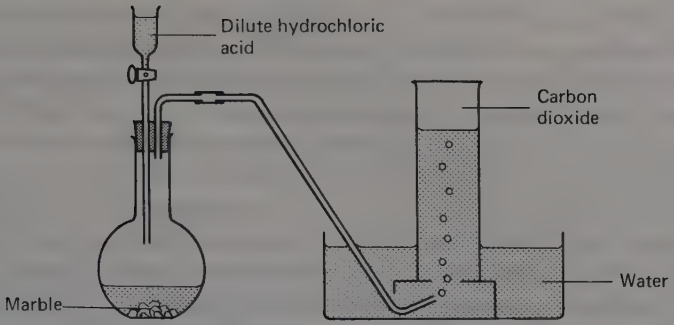


Figure 7.5 *Laboratory preparation of carbon dioxide*

The reaction is, however, unsatisfactory if the metallic salt formed is insoluble in water, or nearly so. For example, marble and dilute sulphuric acid effervesce for a few seconds; then the action stops because the sparingly soluble calcium sulphate forms a coating on the marble and the acid has no further contact with the marble. The reaction between dilute sulphuric acid and lead carbonate or barium carbonate is never satisfactory for the same reason.

Large-scale preparation

(a) A great deal of carbon dioxide is made incidentally during the heating of limestone to produce lime for the building trade.

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$

Carbon dioxide for the ammonia–soda process is made in this way.

(b) Great quantities of the gas are evolved, also, during brewing, or the manufacture of alcohol for industrial purposes. It occurs during the fermentation of glucose by the enzyme, *zymase*, from yeast. The enzyme is an organic catalyst.

$$C_6H_{12}O_6(aq) \rightarrow 2CO_2(g) + 2C_2H_5OH(aq)$$

To concentrate the gas, it is absorbed under pressure in potassium carbonate solution and recovered by reducing the pressure or by heating.

$$CO_3{}^{2-}(aq) + H_2O(l) + CO_2(g) \rightleftharpoons 2HCO_3{}^-(aq)$$

Physical properties of carbon dioxide

Carbon dioxide is a colourless gas with only a slight smell. It is moderately soluble in water (1.75 cm^3 at 273 K, 1 cm^3 at 288 K in 1 cm^3

of water). It reacts with water; see *acidic properties* below. Solid carbon dioxide sublimes at 195 K (at 1 atm). Its critical temperature (304 K) is above room temperature, so it can be liquefied by pressure alone; 5.4×10^6 N m^{-2} (52 atm) pressure are needed to liquefy it at 288 K. It forms a colourless, mobile liquid and will float on water, mixing only slowly.

If liquid carbon dioxide is allowed to evaporate rapidly, heat is absorbed from some of the liquid to evaporate the rest, and it then solidifies as *carbon dioxide snow* or 'dry ice.' This material sublimes to gas, at ordinary pressure, without melting; hence the term *dry ice*. Carbon dioxide is about 1.5 times as dense as air. The gas is not very actively poisonous; 50 per cent of it in air can be breathed *for a short time* without ill-effects to man. Up to 3 per cent of carbon dioxide in air is scarcely noticeable. 10 per cent, however, produces violent panting and more than 20 per cent will be fatal in a few hours.

The atmosphere contains a little more than 0.03 per cent by volume of carbon dioxide. Though the proportion is so small, it is vital for life on Earth (see p. 165), and its presence has important economic and geographical consequences.

Chemical properties of carbon dioxide

Action with water; acidic properties

Carbon dioxide is moderately soluble in cold water (see above), but is completely boiled out if the water is boiled. The solution is *slightly* acidic; it does not turn blue litmus solution fully red, but produces in it a 'claret' colour on the reddish side of purple. Some carbonic acid is presumably formed but in very small amount. The acid has never been isolated.

$$\begin{aligned} H_2O(l) + CO_2(g) \rightleftharpoons H_2CO_3(aq) &\rightleftharpoons H^+(aq) + HCO_3^-(aq) \\ &\rightleftharpoons 2H^+(aq) + CO_3^{2-}(aq) \end{aligned}$$

Solubility of carbon dioxide increases rapidly with pressure.

The acid is *di*basic; consequently it can form two sets of salts, the *normal carbonates* and the *hydrogencarbonates* (formerly *bicarbonates*). For example, if passed into a concentrated solution of sodium hydroxide, carbon dioxide converts it to *sodium carbonate solution* and then to *sodium hydrogencarbonate*, some of which will precipitate.

$$2OH^-(aq) + CO_2(g) \rightarrow CO_3^{2-}(aq) + H_2O(l)$$
$$CO_3^{2-}(aq) + H_2O(l) + CO_2(g) \rightleftharpoons 2HCO_3^-(aq)$$

Potassium hydroxide (caustic potash) gives a similar result, but potassium hydrogencarbonate is more soluble and does not precipitate. This is why 'caustic potash' is preferred to caustic soda as an absorbent for carbon dioxide. Corresponding reactions are given by lime water, producing *calcium carbonate* as a white precipitate, which redissolves as *calcium hydrogencarbonate* when more carbon dioxide is passed. The first stage of this change explains the use of 'milkiness' in lime water as a test for carbon dioxide.

Metallic carbonates are usually insoluble in water, but the carbonates of sodium and potassium are soluble. The insoluble carbonates can be precipitated by adding sodium carbonate solution to a solution of a soluble salt of the metal, e.g.

$$\mathrm{Ca^{2+}(aq) + CO_3{}^{2-}(aq) \rightarrow CaCO_3(s)}$$

Some metals (corresponding to the weaker bases) gives *basic* carbonates by this method, e.g. Mg, Pb and Zn. In these cases, sodium hydrogencarbonate solution precipitates the normal carbonate, e.g.

$$\mathrm{Mg^{2+}(aq) + 2HCO_3{}^{-}(aq) \rightarrow MgCO_3(s) + H_2O(l) + CO_2(g)}$$

Copper, however, forms no normal carbonate.

Very weak bases form no carbonates, so aluminium and iron(III) carbonates are unknown. Any attempt to precipitate them produces the corresponding *hydroxide* and *carbon dioxide* by hydrolysis.

$$\mathrm{2Al^{3+}(aq) + 3CO_3{}^{2-}(aq) + 3H_2O(l) \rightarrow 2Al(OH)_3(s)\downarrow + 3CO_2(g)}$$

Only two common hydrogencarbonates are known as solids, $NaHCO_3$ and $KHCO_3$. Others occur in solution, e.g. $Ca(HCO_3)_2$, $Mg(HCO_3)_2$, and $Pb(HCO_3)_2$, but decompose to carbonate if water is allowed to evaporate. They are all unstable to heat, forming the corresponding *carbonate*. The formation and decomposition of calcium hydrogencarbonate has important geographical and economic consequences (p. 94).

$$\mathrm{2HCO_3{}^{-}(aq) \rightarrow H_2O(l) + CO_2(g) + CO_3{}^{2-}(s)}$$

Most metallic carbonates are decomposed by heat, e.g. $CaCO_3$, $ZnCO_3$, $PbCO_3$, to give the *oxide* and carbon dioxide.

$$\mathrm{CaCO_3(s) \rightarrow CaO(s) + CO_2(g)}$$

Sodium potassium and barium carbonates are, however, unaffected by the highest temperatures available in an ordinary laboratory.

To distinguish between carbonated and hydrogencarbonates

Only two common *solid* hydrogencarbonates are known, $NaHCO_3$ and $KHCO_3$. They are easily distinguished from the corresponding normal carbonates by evolution of *carbon dioxide* (lime water turned 'milky') when heated.

$$2NaHCO_3(s) \rightarrow H_2O(g) + CO_2(g) + Na_2CO_3(s)$$

The normal carbonates are unaffected by heat.

To distinguish between a hydrogencarbonate and a normal carbonate in solution, add magnesium sulphate solution. An *immediate* white precipitate indicates a *normal* carbonate.

$$Mg^{2+}(aq) + CO_3{}^{2-}(aq) \rightarrow MgCO_3(s)$$

A white precipitate *on boiling* indicates a hydrogencarbonate. In the cold, Mg^{2+} and $HCO_3{}^-$ ions are a *soluble* combination. On heating,

$$Mg^{2+}(aq) + 2HCO_3{}^-(aq) \rightarrow MgCO_3(s) + H_2O(g) + CO_2(g)$$

To distinguish a hydrogencarbonate in the presence of a normal carbonate in solution, first add calcium chloride solution in excess to precipitate normal carbonate as chalk. Filter.

$$Ca^{2+}(aq) + CO_3{}^{2-}(aq) \rightarrow CaCO_3(s)\downarrow$$

To the filtrate, add dilute ammonia solution. A white precipitate indicates that hydrogencarbonate is present.

$$HCO_3{}^-(aq) + Ca^{2+}(aq) + OH^-(aq) \rightarrow CaCO_3(s)\downarrow + H_2O(l)$$

Stability of carbon dioxide: combustions in it

Carbon dioxide is very stable to heat; at atmospheric pressure, it shows no appreciable decomposition below 1600 K and, at 1720 K, its degree of dissociation is only about 0.003. Carbon dioxide is difficult to decompose and extinguishes the flames of a candle, wax taper, sulphur and phosphorus. If previously ignited, *magnesium* burns in carbon dioxide for a short time with a spluttering flame, producing *white* particles of its oxide and *black carbon* particles.

$$CO_2(g) + 2Mg(s) \rightarrow 2MgO(s) + C(s)$$

Sodium and potassium burn in the gas, if previously ignited, forming their *carbonates* and *carbon*, e.g.

$$4Na(s) + 3CO_2(g) \rightarrow 2Na_2CO_3(s) + C(s)$$

Uses of carbon dioxide

1. *In the ammonia–soda (Solvay) process for making sodium carbonate.* (See p. 55).

2. *In the production of mineral waters*. Soda-water is a solution of carbon dioxide in water under pressure. If sweetened, suitably flavoured and (possibly) coloured, the liquid is sold as *lemonade* and other fizzy drinks.
3. *As a refrigerant*. Solid carbon dioxide is used in the preservation of ice-cream during transport or sale and, with ethoxyethane (ether), as a powerful freezing mixture.
4. *In fire extinguishers*. The 'water type' fire extinguisher often contains sodium hydrogencarbonate solution and sulphuric acid. When mixed by inversion or by pressing a plunger, the two produce carbon dioxide. The pressure of the gas forces out a stream of liquid. A very convenient form of fire extinguisher contains liquid carbon dioxide under pressure. This is particularly effective for fires involving flammable liquids, such as petrol, which would float on water. A trigger mechanism releases the gas through a nozzle. Carbon dioxide extinguishes fires, except those involving very reactive metals such as magnesium (see above), because it does not take part in combustion and also because, being dense, it 'blankets' the fire. Air cannot therefore get to the burning material.

Volume composition of carbon dioxide

Air is displaced from the bulb by oxygen and the fittings are inserted as shown in Figure 7.6. Mercury levels A and B are equalized; A is marked. The carbon on the spoon is ignited by electrical heating of a fine platinum wire and burns in the oxygen (which should be in excess) forming carbon dioxide. During the combustion, level A falls because of expansion, but, after the apparatus has cooled back to room temperature, A returns to its former mark, i.e. at constant temperature and pressure,

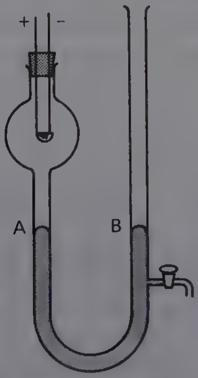


Figure 7.6 *Volume composition of carbon dioxide*

oxygen produces its own volume of carbon dioxide. Using this evidence, the molecular formula of carbon dioxide can be deduced as follows: 1 volume of carbon dioxide contains 1 volume of oxygen (temperature and pressure being constant). Therefore, by Avogadro's Hypothesis,

1 molecule of carbon dioxide contains 1 molecule of oxygen

From this it follows that the molecular formula of carbon dioxide is C_nO_2. The density of carbon dioxide relative to hydrogen is 22, i.e. its molar mass is 44.

From this, $C_nO_2 = 44$

i.e. $12n + 32 = 44$

$$n = 1$$

so the molecular formula of carbon dioxide is CO_2.

Structure of carbon dioxide. Carbon dioxide is a linear molecule, O=C=O.

Carbon monoxide, CO

Preparation

(a) For the small-scale purposes of a laboratory, this gas is conveniently made by the action of *cold, concentrated sulphuric acid* on *sodium methanoate* (sodium formate) Figure 7.7. The alkali removes any carbon dioxide or sulphur dioxide which may be present. The acid first liberates methanoic acid from the salt and then dehydrates it.

$$HCOONa(s) + H_2SO_4(l) \rightarrow HCOOH(l) + NaHSO_4(s)$$

$$HCOOH(l) \xrightarrow{-H_2O} CO(g)$$

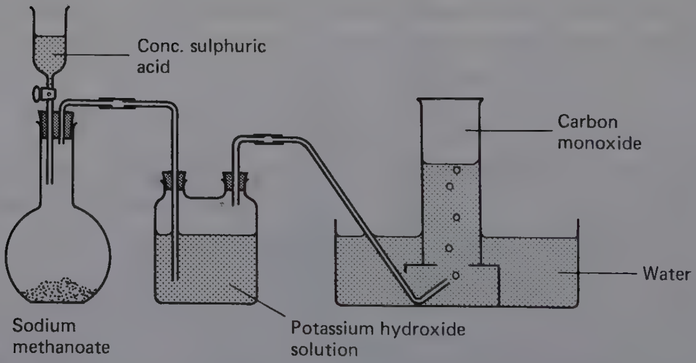


Figure 7.7 *Laboratory preparation of carbon monoxide*

The gas is usually collected over water as shown. If wanted dry, it may be passed through concentrated sulphuric acid and collected by upward delivery (being *less* dense than air) or, in small amounts, over mercury.

(b) Ethanedioic acid crystals may be used in a method similar to the above, but the crystals and *concentrated sulphuric acid* are mixed cold and must be *heated* to about 330 K to bring about a satisfactory evolution of gas. The gas consists of equal volumes of carbon monoxide and dioxide.

$$H_2C_2O_4(s) \xrightarrow{-H_2O} CO(g) + CO_2(g)$$

The dioxide is absorbed by potassium hydroxide solution; two wash bottles of alkali are desirable in view of the large proportion of carbon dioxide.

(c) In a combustion tube, heated carbon reduces carbon dioxide to *carbon monoxide.*

$$CO_2(g) + C(s) \rightleftharpoons 2CO(g)$$

Any carbon dioxide left unchanged is removed by potassium hydroxide solution. This forms a method of preparing carbon monoxide from carbon dioxide. To secure a satisfactory conversion, the temperature of the carbon should be not less than 1300 K.

Properties of carbon monoxide

Carbon monoxide is a colourless gas with very little smell. It is almost insoluble in water and slightly less dense than air (14.0 against 14.4, relative to hydrogen). It is difficult to liquefy, having a low critical temperature, 134 K, and requiring about 3.5×10^6 N m^{-2} ($\sim$ 35 atm) to liquefy it at that temperature. At atmospheric pressure, its boiling point is 81 K.

Poisonous nature of carbon monoxide

Carbon monoxide is poisonous. It exercises its poisoning action by combining with haemoglobin in the red corpuscles of the blood to form a bright red, stable compound, *carboxyhaemoglobin.* In this way, the function of haemoglobin, as a conveyer of oxygen from the lungs to the various organs needing it, is gradually suppressed. Carbon monoxide is particularly dangerous as it has no marked smell and may produce giddiness and fainting as a first symptom of poisoning. In that case, the victim will probably die unless rescued. 0.02 per cent of it in air (by volume) will produce symptoms after a time and 0.13 per cent is fatal to the average adult in about half an hour. First-aid treatment is artificial respiration in the open air and administration of oxygen if possible.

Carbon monoxide is the poisonous constituent of coal gas. It is also the very dangerous *after damp*, which may be present after the partial oxidation of *fire damp* (methane) in mining explosions.

$$2CH_4(g) + 3O_2(g) \rightarrow 2CO(g) + 4H_2O(l)$$

It also occurs in the gases from the exhaust pipes of internal combustion engines. The running of engines in closed garages caused a number of fatalities in the early days of motoring. Combustion of hydrocarbons, gas, or coke in a *limited* supply of air will always produce dangerous concentration of carbon monoxide.

Chemical properties of carbon monoxide

1. *Acidic nature.* Carbon monoxide is almost insoluble in water and produces no appreciable acidity in it. If, however, sodium hydroxide is heated to about 470 K in a stream of carbon monoxide under pressure, *sodium methanoate* is rapidly produced.

$$CO(g) + NaOH^-(l) \rightarrow HCOO^-Na^+(l)$$

Carbon monoxide functions here as *the anhydride of methanoic acid*. (This acid yields carbon monoxide when dehydrated by concentrated sulphuric acid, p. 154.)

2. *Reducing action.* At about red heat, carbon monoxide reduces several metallic oxides, e.g. CuO, PbO, Fe_2O_3 (see p. 433). In combining with their oxygen, it makes electrons available and the metallic ion is *reduced* by accepting them, e.g.

$$O^{2-} + CO(g) \rightarrow CO_2(g) + 2e^- ; \ Cu^{2+} + 2e^- \rightarrow Cu$$

Overall: $$CuO(s) + CO(g) \rightarrow Cu(s) + CO_2(g)$$

(It does *not* reduce aluminium oxide or magnesium oxide.) Carbon monoxide also reduces iodine(V) oxide at about 360 K.

$$I_2O_5(s) + 5CO(g) \rightarrow I_2(s) + 5CO_2(g)$$

This reaction provides a method for estimating the concentration of carbon monoxide in air (see p. 158).

3. *Combustion.* Carbon monoxide burns in air or oxygen, with a characteristic *blue* flame, to form carbon dioxide. The blue flame can often be

seen above a thick layer of glowing coke or coal, as a result of the successive reactions:

$$C(s) + O_2(g) \rightarrow CO_2(g)$$
$$CO_2(g) + C(s) \rightleftharpoons 2CO(g)$$
$$2CO(g) + O_2(g) \rightarrow 2CO_2(g) \qquad \Delta H = -566\,\text{kJ}$$

4. *Addition reactions of carbon monoxide.* Carbon monoxide gives a number of addition reactions, such as:

(a) *With chlorine.* A mixture of carbon monoxide and chlorine exposed to sunlight or passed over charcoal (catalyst) at about 670 K forms *carbon oxide dichloride* (carbonyl chloride) (see p. 139).

$$CO(g) + CI_2(g) \rightarrow COCl_2(g)$$

The product was used as a war gas in World War I, but is now a useful industrial intermediate.

(b) *With sulphur.* A mixture of carbon monoxide and sulphur vapour passed through a heated tube forms *carbon oxide sulphide* (carbonyl sulphide).

$$CO(g) + S(g) \rightarrow COS(q)$$

The compound is a colourless gas, boiling point 223 K at 101 300 N m^{-2} (1 atm).

(c) *With some metals.* Carbon monoxide reacts additively with certain metals to produce *carbonyls*. The most important of these is *tetracarbonyl nickel(O)* (nickel carbony), $Ni(CO)_4$. It is formed when freshly reduced nickel is warmed in carbon monoxide, at atmospheric pressure, to about 320 K.

$$Ni(s) + 4CO(g) \rightleftharpoons Ni(CO)_4(g)$$

As shown, the reaction is reversible; the carbonyl is decomposed, with deposition of metallic nickel, at about 450 K. A process based upon this reaction is used in purifying nickel. The carbonyl is a liquid, boiling point 316 K. It is formed by dative bonding, a lone pair being donated from each of four carbon monoxide molecules to the nickel atom. It will be seen that the oxidation state of the nickel in this compound is zero. (For *oxidation number*, see *advanced Level Physical Chemistry*, p. 246.) The nickel atom is effectively in control of 36 electrons (see p. 399). The molecule is tetrahedral in shape, with the nickel atom at the centre of gravity.

Carbonyls of several other transition metals can also be made, e.g. $Fe(CO)_5$, $Co(CO)_8$.

Uses of carbon monoxide

(a) It is an important constituent of the fuel gases, *coal gas*, *water gas* and *producer gas*.
(b) It is used in the purification of nickel, p. 452.
(c) Methanoates are manufactured from carbon monoxide, p. 156.
(d) It is used in the manufacture of carbon oxide dichloride (phosgene), p. 157.
(e) As a constituent of water gas, carbon monoxide is used in the manufacture of methanol (p. 143) and other compounds.

Detection and estimation of carbon monoxide

In gas analysis, carbon monoxide is usually estimated by absorption in an ammoniacal solution of copper(I) chloride (after acidic gases, such as carbon dioxide, have first been removed). It forms an addition compound, $CuCl.CO.2H_2O$. It can be detected by liberation of iodine from iodine(V) oxide at 360 K.

$$I_2O_5(s) + 5CO(g) \rightarrow I_2(s) + 5CO_2(g)$$

Structure of carbon monoxide

The structure of carbon monoxide has posed problems for chemical theory. Carbon monoxide is isoelectronic with nitrogen, and it is probably best considered as containing a triple bond, $C{\equiv}O$, as in $N{\equiv}N$. Electron diffraction measurements of the bond length in CO agree with this interpretation.

Other oxides of carbon

Several other oxides of carbon are known. The only one of significance for our purposes is tricarbon dioxide (carbon suboxide), C_3O_2. This is prepared by the action of phosphorus(V) oxide on propanedioic acid (malonic acid). It is a choking, colourless gas at room temperature (b.p. 279 K). With water it re-forms the parent acid, so, in common with the two common oxides of carbon, it may be considered as an acid anhydride.

Carbon disulphide, CS_2

Preparation

Carbon disulphide is made by direct combination of its elements at a high temperature. In an electrothermal process (Taylor's), sulphur and coke are fed into an electric furnace heated by an arc maintained by alternating current between carbon electrodes.

In Zahn's process molten sulphur is run from a tank down over shelves in a pre-heater, which vaporizes the sulphur. The vapour is then passed upwards through a mass of coke at about 1300 K. In this case, all the heating is by producer gas and air.

In both cases, $C(s) + 2S(g) \rightarrow CS_2(g)$.

The carbon disulphide is condensed out by passing through pipes immersed in water. It is purified by fractional distillation. It can be further purified by shaking with mercury and distillation over phosphorus(V) oxide.

Physical properties of carbon disulphide

Carbon disulphide is a colourless, mobile, very volatile liquid, density 1.29 g cm^{-3}, boiling point 319 K. It has an endothermic enthalpy of formation.

$$C(s) + 2S(s) \rightarrow CS_2(l) \qquad \Delta H_{298} = +88\ \text{kJ mol}^{-1}$$

It is dangerously flammable because of its combination of great volatility and low ignition temperature, and needs to be handled with the greatest care. When pure, it has a sweetish smell resembling that of trichloromethane, but it soon acquires its usual, rather repulsive, smell when exposed to light and air. Its vapour is poisonous and, in large amounts, fatal to man.

Carbon disulphide mixes only slightly with water (0.210 g in 100 g water at 293 K). It mixes in any proportions with alcohol, ethoxyethane and benzene, and is a good solvent for sulphur, phosphorus, iodine, camphor, waxes, and rubber.

Chemical properties of carbon disulphide

1. *With air or oxygen.* Carbon disulphide ignites in air or oxygen at an unusually low temperature, burning with a blue flame to form *carbon dioxide* and *sulphur dioxide.*

$$CS_2(l) + 3O_2(g) \rightarrow CO_2(g) + 2SO_2(g)$$

Its vapour forms an explosive mixture if sparked with air or oxygen.

2. *With nitrogen oxide* (*nitric oxide*). If a flame is applied to a mixture of nitrogen oxide and carbon disulphide vapour, the mixture burns with a

brilliant light blue flash, in a process resembling an explosion. It was formerly used in flashlight photography. The main reaction is:

$$CS_2(g) + 10NO(g) \rightarrow 2CO(g) + 4SO_2(g) + 5N_2(g)$$

3. *Forming trithiocarbonates.* Carbon disulphide, CS_2, is the sulphur analogue of carbon dioxide, CO_2. It can form *trithiocarbonates*, derived from *trithiocarbonic acid*, H_2CS_3, as carbonates are derived from H_2CO_3. If shaken with sodium sulphide solution, carbon disulphide forms *sodium trithiocarbonate*, an analogue of sodium carbonate, Na_2CO_3.

$$Na_2S(aq) + CS_2(l) \rightarrow Na_2CS_3(aq)$$

4. *Action with chlorine.* This action produces tetrachloromethane, CCl_4. For this, see the next section.

Uses of carbon disulphide

(a) Because of the poisonous nature of its vapour, carbon disulphide has been used in clearing vermin from ships and killing weevil in stored wheat.
(b) Carbon disulphide is used in the manufacture of tetrachloromethane (carbon tetrachloride) and, through this intermediary, of trichloromethane (chloroform) (next section).
(c) Carbon disulphide is a solvent for essential oils, rubber, resins, and gums.
(d) It is used in the *viscose* process of making rayon.

Tetrachloromethane (carbon tetrachloride), CCl_4

Tetrachloromethane is made by chlorinating carbon disulphide, boiling under reflux, in the presence of iodine as catalyst.

$$CS_2(l) + 3Cl_2(g) \rightarrow CCl_4(l) + S_2Cl_2(l)$$

Tetrachloromethane and disulphur dichloride have different boiling points (350 K and 411 K, respectively, at 1 atm.) and are separated by fractional distillation. The tetrachloromethane is purified by washing with dilute sodium hydroxide solution and is then distilled from bleaching powder.

Physical properties of tetrachloromethane

Tetrachloromethane is a colourless liquid, boiling point 350 K and density 1.63 g cm^{-3}. It is a good solvent for fats and has the advantage over certain other common solvents, e.g. benzene, of being non-flammable.

Chemical properties

Tetrachloromethane is chemically rather inert. It is very unusual among non-metallic chlorides in being inert towards water; others usually hydrolyse rapidly, e.g.

$$SiCl_4(l) + 4H_2O(l) \rightarrow Si(OH)_4(s) + 4HCl(g)$$

An explanation for this behaviour is that carbon, like other elements in the period from Li to Ne, is incapable of possessing more than an octet of electrons in its outer electron shell. The silicon atom is larger and can accept electrons into vacant 3d orbitals (see p. 6). Water molecules can donate lone pairs into these orbitals, and this is the first stage in the hydrolysis.

Uses of tetrachloromethane

(a) Because of its good solvent action for fats and its non-flammable nature, tetrachloromethane is used as a de-greasing and dry-cleaning agent, but its toxic nature has led to it being very largely replaced.

(b) As *pyrene*, it is used as a fire-extinguisher, especially for small petrol fires. The very dense vapour (about 5.5 times as dense as air) tends to blanket the fire and put it out by excluding oxygen. Tetrachloromethane has the disadvantage of oxidizing to the very poisonous carbon oxide dichloride, $COCl_2$, at a very hot surface in contact with air.

(c) Tetrachloromethane is reduced, by heating with iron and water, to trichloromethane.

$$CCl_4(l) + Fe(s) + H^+(aq) \rightarrow Fe^{2+}(aq) + Cl^-(aq) + CHCl_3(l)$$

Some dichloromethane, CH_2Cl_2, may also be formed by further reduction of the tetrachloromethane.

Cyanogen, $(CN)_2$

This very poisonous gas can be made by mixing warm concentrated solutions of potassium cyanide and copper(II) sulphate.

$$2Cu^{2+}(aq) + 4CN^-(aq) \rightarrow 2CuCN(s) + (CN)_2(g)$$

The copper(II) ions oxidize the cyanide ions to cyanogen. It will be noted that this reactions is similar to that between iodide ions and Cu^{2+} ions (p. 462). Cyanogen shows other similarities to iodine and other halogens, and is sometimes known as a *pseudohalogen.*

Hydrogen cyanide, (hydrocyanic acid, prussic acid), HCN

Preparation

This compound (and all its soluble salts) are *most dangerous poisons.* They should *never* be handled in any way except under the closest supervision.

Hydrogen cyanide is prepared by distilling *potassium cyanide* with a mixture of *concentrated sulphuric acid and water in equal volumes.*

$$\mathrm{KCN(s) + H_2SO_4(l) \rightarrow KHSO_4(s) + HCN(l)}$$

It may be mentioned that the acid received the name *prussic acid* because of its preparation (by Scheele in 1782) by distilling Prussian blue ($Fe_4[Fe(CN)_6]_3$) with sulphuric acid.

Physical properties of hydrogen cyanide

Hydrocyanic acid is a colourless liquid, boiling point 299 K at 101 300 $N\,m^{-2}$ (1 atm). It solidifies to a white solid at 259 K. It mixes with water in any proportions. It has the odour of bitter almonds and is very poisonous.

The seeds of bitter almonds contain the complex organic compound *amygdalin,* which hydrolyses to liberate hydrogen cyanide.

Chemical properties of hydrogen cyanide

1. *Combustion.* Hydrogen cyanide vapour burns in air with a purple flame.

$$\mathrm{4HCN(g) + 5O_2(g) \rightarrow 2H_2O(l) + 4CO_2(g) + 2N_2(g)}$$

2. *Acidic nature.* Hydrocyanic acid is a *very weak* acid, ionizing very feebly in aqueous solution.

$$\mathrm{HCN(aq) \rightleftharpoons H^+(aq) + CN^{\text{[illegible]}}(aq)}$$

It reacts with aqueous caustic alkalis, producing *cyanides* of the alkali metals, e.g.

$$\mathrm{HCN(aq) + KOH(aq) \rightarrow KCN(aq) + H_2O(l)}$$

It is so weak that these salts are decomposed by carbon dioxide.

$$2CN^-(aq) + CO_2(aq) + H_2O(l) \rightarrow CO_3^{2-}(aq) + 2HCN(aq)$$

They are also considerably hydrolysed in solution and the solutions have the almond smell of the free acid. This issue was fully discussed in connection with potassium cyanide, p. 76.

Many cyanides of the heavier metals are insoluble in water and are produced by precipitation, e.g. AgCN, $Cd(CN)_2$. Complex metallo cyanide ions occur frequently, e.g. the cyanides of *silver*, *copper*(I) and *cadmium* are dissolved by excess potassium cyanide solution because of complex ion formation,

$$AgCN(s) + CN^-(aq) \rightleftharpoons Ag(CN)_2^-(aq)$$
$$CuCN(s) + CN^-(aq) \rightleftharpoons Cu(CN)_2^-(aq)$$
$$Cd(CN)_2(s) + 2CN^-(aq) \rightleftharpoons Cd(CN)_4^{2-}(aq)$$

The *hexacyanoferrate*(II) (*ferrocyanide*) ion $Fe(CN)_6^{4-}$ and *hexacyanoferrate*(III) (*ferricyanide*) ion $Fe(CN)_6^{3-}$ are also well known and important. For these, see p. 447.

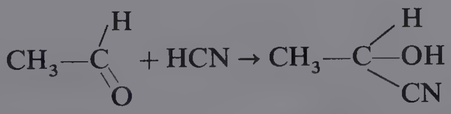
3. *Hydrolysis and reduction.* Hydrogen cyanide is hydrolysed quite readily, even in *cold* water to some extent, to *ammonium methanoate.*

$$HCN(aq) + 2H_2O(l) \rightarrow HCOO^-(aq) + NH_4^+(aq)$$

It is reduced (e.g. by zinc and dilute hydrochloric acid) to *methylamine.*

$$2Zn(s) + 4H^+(aq) + HCN(aq) \rightarrow 2Zn^{2+}(aq) + CN_3NH_2(aq)$$

4. *With aldehydes and ketones.* With aldehydes and ketones, hydrocyanic acid produces important addition products, known as *cyanohydrins.* They are usually produced indirectly; for details, see text-books of organic chemistry.



ethanal
(acetaldehyde)

2-hydroxypropanonitrile
(acetaldehyde cyanohydrin)

Uses of hydrogen cyanide and cyanides

(a) The free acid has been used in fumigating ships, flour mills and other buildings to destroy pests.

(b) Cyanides (especially NaCN and KCN) are used in the extraction of gold and silver; a complex dicyanosilver(I) ion (argentocyanide) is used in electroplating with silver.

Cyanates

Cyanates are produced when cyanides, which are powerful reducing agents, are fused with a number of metallic oxides, e.g. with 'red lead',

$$Pb_3O_4(s) + 4KCN(s) \rightarrow 3Pb(s) + 4KCNO(s)$$

The cyanate is extracted by warm aqueous ethanol. Cyanates are also produced by the action of cyanogen on aqueous caustic alkali (cf. the disproportionation of halogens in dilute alkali, e.g. chlorine, p. 54).

$$2OH^-(aq) + C_2N_2(g) \rightarrow CN^-(aq) + CNO^-(aq) + H_2O(l)$$

Cyanates are not very stable; a solution of potassium cyanate in water (i.e. a neutral solution) decomposes as:

$$CNO^-(aq) + 2H_2O(l) \rightarrow NH_4^+(aq) + CO_3^{2-}(aq)$$

forming the ammonium and carbonate ions.

Cyanic acid, HCNO, is a colourless gas, which can be liquefied in a freezing mixture. On keeping, it soon polymerizes to *cyanuric acid*, $H_3C_3N_3O_3$. Its aqueous solution is rapidly decomposed, as:

$$HCNO(aq) + 2H_2O(l) \rightarrow NH_4(aq) + HCO_3^-(aq)$$

Ammonium cyanate has historical interest. Wöhler (1828) showed that, on heating, it was converted to *urea* (carbamide).

$$NH_4CNO(s) \rightarrow CO(NH_2)_2(s)$$

Previously, urea had been thought to be organic in the old 'vitalistic' sense of being necessarily the product of the activity of a living organism (in this case, mammals). This preparation of urea by ordinary processes of the laboratory played a considerable part in destroying this vitalistic theory of organic chemistry.

Organic chemistry

Carbon is unique in its ability to *catenate* extensively, that is, to form long-chain and ring structures. The immense number of possible skeletal carbon structures gives rise to the millions of carbon-based molecules which have so far been characterized. The study of such molecules is known as *organic chemistry*, and is not included in this book.

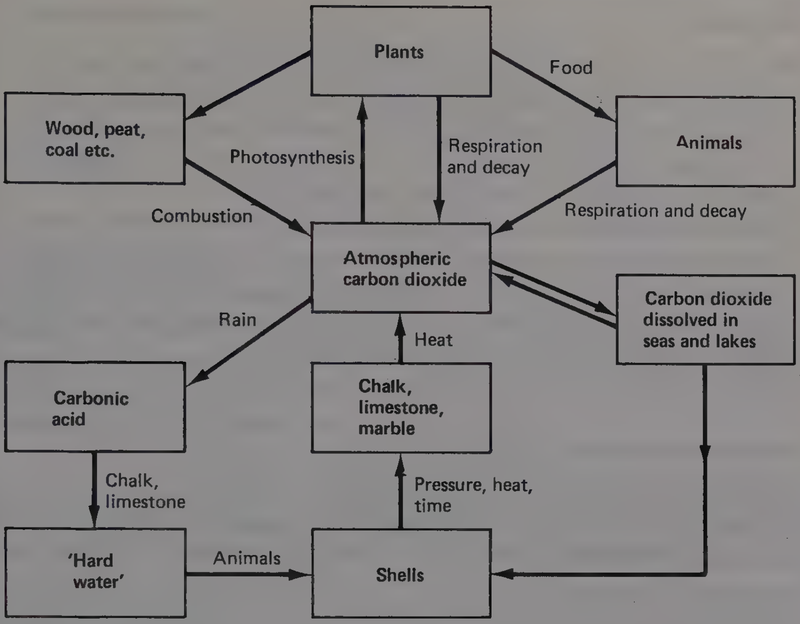


Figure 7.8 *The carbon cycle*

The Carbon Cycle in Nature

Carbon is essential to life, as we know it on Earth. It appears that carbon is the only element capable of providing the skeletons for the often very complex organic molecules which are found in all living cells.

Carbon atoms 'circulate' in Nature. The key compound is carbon dioxide, found to the extent of 0.03 per cent in the atmosphere. The gas is naturally returned to the atmosphere by the process of *respiration*, and removed by the process of *photosynthesis* in plants. These two processes keep the proportion of the gas in air roughly constant. However, combustion of fossil fuels and other activities of industry tend to increase the carbon dioxide concentration. This is compensated, to some extent, by more of the gas dissolving in sea water.

The Cycle is summarized in Figure 7.8.

Silicon

Atomic number 14; electron arrangement 2.8.4 ($1s^2 2s^2 2p^6 3s^2 3p^2$)
Silicon has isotopes of mass number, in order of abundance, 28, 29, 30; relative atomic mass 28.09

Occurrence

Silicon is the second most abundant element in the surface crust of the Earth. (Oxygen is the most abundant.) Silicon occurs principally as:

1. *Silicon dioxide, silica,* SiO_2. This material has *crystalline* forms (often impure) such as quartz, sand and rock crystal and *amorphous* forms such as flint and kieselguhr. See also p. 3.
2. *Metallic silicates.* There are a great many such silicates occurring in rocks and they show great complexity. A few are: *felspar,* $K_2Al_2Si_6O_{16}$, *kaolinite,* $Al_2Si_2O_7.2H_2O$, *anorthite,* $CaAl_2Si_2O_8$, and *olivine,* $Mg_2Fe_2SiO_6$. *Zeolites,* used in softening water, are calcium aluminium silicates, containing some sodium or potassium.

Extraction of silicon

Silicon can be obtained in the *amorphous* or *crystalline* form.

Amorphous silicon

(a) Silica is mixed with magnesium powder (a strong reducing agent) and heated very strongly out of contact with air. Silicon is produced, probably with some magnesium silicide, too.

$$2Mg(s) + SiO_2(s) \rightarrow Si(s) + 2MgO(s)$$
$$4Mg(s) + SiO_2(s) \rightarrow Mg_2Si(s) + 2MgO(s)$$

The oxide and silicide can be removed by hot, dilute hydrochloric acid. Silicon is left as a brown powder.

(b) Silicon is produced when silicon tetrafluoride (or tetrachloride) is heated with potassium (or sodium). Both these compounds of silicon are vapours.

$$SiCl_4(g) + 4Na(l) \rightarrow Si(s) + 4NaCl(s)$$
$$SiF_4(g) + 4K(l) \rightarrow Si(s) + 4KF(s)$$

A variation of this method is to heat potassium hexafluorosilicate(IV) with potassium.

$$K_2SiF_6(s) + 4K(l) \rightarrow Si(s) + 6KF(s)$$

The halides are removed by hot water and the silicon is washed with hydrofluoric acid to remove silica.

(c) On the industrial scale, coke is heated with *excess* of sand in an electric furnace.

$$SiO_2(s) + 2C(s) \rightarrow Si(s) + 2CO(g)$$

Excess of sand is required to avoid the formation of carborundum by the reaction:

$$SiO_2(s) + 3C(s) \rightarrow SiC(s) + 2CO(g)$$

Crystalline silicon

This variety of the element is made by producing it in the presence of excess of a molten metal (e.g. aluminium or zinc). Silicon dissolves in the metal and crystallizes on cooling. For example, aluminium is melted in an atmosphere of hydrogen (to prevent oxidation) and silicon tetrachloride vapour is passed over it.

$$3SiCl_4(g) + 4Al(l) \rightarrow 3Si(s) + 4AlCl_3(g)$$

The aluminium trichloride sublimes away. The cooled aluminium is dissolved by hot, dilute hydrochloric acid, leaving crystalline silicon.

Properties of silicon

Amorphous silicon

This variety of the element is a brown powder of density 2.4 g cm^{-3}. It melts at about 1700 K. It does not conduct electricity.

Chemical properties of amorphous silicon

1. *With oxygen and air.* Amorphous silicon burns readily in oxygen at red heat, but, in air, oxidizes only superficially.

$$Si(s) + O_2(g) \rightarrow SiO_2(s)$$

2. *Formation of halides.* Amorphous silicon ignites spontaneously in fluorine, and at about 720 K in chlorine, forming the corresponding tetrahalide.

$$Si(s) + 2F_2(g) \rightarrow SiF_4(g)$$
$$Si(s) + 2Cl_2(g) \rightarrow SiCl_4(l)$$

Heated in hydrogen chloride, amorphous silicon yields *trichlorosilane* (*silicochloroform*) and hydrogen.

$$Si(s) + 3HCl(g) \rightarrow SiHCl_3(l) + H_2(g)$$

3. *With water.* Amorphous silicon is unaffected by water, but attacks steam slowly at red heat.

$$\mathrm{Si(s) + 2H_2O(g) \rightarrow SiO_2(s) + 2H_2(g)}$$

4. *With acids.* Amorphous silicon is very resistant to the action of acids. It is attacked only by hydrofluoric acid (more rapidly if nitric acid is present).

$$\mathrm{Si(s) + 6HF(l) \rightarrow H_2SiF_6(l) + 2H_2(g)}$$

The product is *hexafluorosilicic acid.*

5. *With alkalis.* Amorphous silicon dissolves readily in hot, concentrated caustic alkali solution, liberating *hydrogen* and forming the corresponding *silicate* in solution.

$$\mathrm{Si(s) + 2OH^-(aq) + H_2O(l) \rightarrow SiO_3{}^{2-}(aq) + 2H_2(g)}$$

6. *With nitrogen.* Amorphous silicon combines with nitrogen when heated to give *silicon nitride.* See also page 213.

$$\mathrm{3Si(s) + 2N_2(g) \rightarrow Si_3N_4(s)}$$

7. *With metals.* Some of the more reactive metals combine with amorphous silicon to form *silicides* when heated out of contact with air, e.g.

$$\mathrm{2Mg(s) + Si(s) \rightarrow Mg_2Si(s)}$$

Crystalline silicon

This form is dark grey, very hard and of variable density, between 2.34 and 3 g cm^{-3}. It has an appreciable conductivity for electricity; *amorphous* silicon is classified as a non-conductor. In chemical behaviour, it resembles amorphous silicon, but is less reactive, e.g. it does not ignite readily in oxygen. Silicon for use in semi-conductor devices is rigorously purified by zone-refining techniques (see p. 181) before trace amounts of impurities are then added to give it the required properties. The silicon is usually used in the form of thin chips.

Silicon hydrides

Magnesium silicide, when treated with 20 per cent hydrochloric acid, gives off a mixture of hydrides of silicon (together with hydrogen). The mixture is spontaneously flammable on contact with air. If dried and condensed by liquid air, it can be fractionated to yield a number of hydrides of silicon, such as *silane*, SiH_4, *disilane* (*silico-ethane*), Si_2H_6, and *trisilane* (*silico-propane*), Si_3H_8. Silane may also be prepared by the action of lithium tetrahydridoaluminate(III) on a silicon tetrahalide.

Silane, SiH_4

The reaction producing this hydride (see above) is:

$$Mg_2Si(s) + 4HCl(aq) \rightarrow 2MgCl_2(aq) + SiH_4(g)$$

Silane is a colourless gas (boiling point 161 K), not spontaneously flammable in air, but burning readily when ignited to produce *silica* and *steam.*

$$SiH_4(g) + 2O_2(g) \rightarrow SiO_2(s) + 2H_2O(g)$$

Methane behaves in a similar way.

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$$

Silane is decomposed by caustic alkali solution:

$$SiH_4(g) + 2OH^-(aq) + H_2O(l) \rightarrow SiO_3{}^{2-}(aq) + 4H_2(g)$$

Methane gives no such reaction; cf. the resistance of CCl_4 to hydrolysis, p. 161.

Silane is a strong reducing agent. It will reduce iron(III) salts to iron(II), and precipitate silver from solutions of its salts:

$$4Fe^{3+}(aq) + SiH_4(g) \rightarrow Si(s) + 4H^+(aq) + 4Fe^{2+}(aq)$$
$$4Ag^+(aq) + SiH_4(g) \rightarrow Si(s) + 4H^+(aq) + 4Ag(s)\downarrow$$

Methane gives no similar reactions, although it shows reducing action with some metallic oxides at red heat, e.g.

$$4CuO(s) + CH_4(g) \rightarrow 4Cu(s) + CO_2(g) + 2H_2O(g)$$

Silane is less stable than methane, decomposing into its elements at 670 K. (Methane is unaffected at this temperature.) It gives similar, but much more vigorous, substitution reactions with chlorine.

$$SiH_4(g) + Cl_2(g) \rightarrow SiH_3Cl(g) + HCl(g)$$
$$CH_4(g) + Cl_2(g) \rightarrow CH_3Cl(g) + HCl(g)$$

The other silicon hydrides mentioned above are spontaneously flammable in air and much less stable than silane, e.g. Si_2H_6 yields its elements at 470 K. They all have higher boiling points than the corresponding hydrides of carbon, are more reactive and less stable. About ten silanes are known. Their low stability is connected with the fact that the Si—Si bond is much weaker than the C—C bond (mean bond energies: C—C, 356 kJ mol^{-1}; Si—Si, 226 kJ mol^{-1}). The higher silanes are so unstable that they decompose slowly at room temperature. This behaviour should be compared with that of the alkanes. Petroleum hydrocarbons may have more than forty carbon atoms in the chain.

Halides of silicon

A number of compounds containing silicon and a halogen element have been described, but only two are important. They are *silicon tetrafluoride*, SiF_4, and *silicon tetrachloride*, $SiCl_4$.

Silicon tetrafluoride, SiF_4

Preparation

In principle, silicon tetrafluoride is made by the action of hydrofluoric acid on silica or a silicate (e.g. powdered glass). In practice, it is usual to generate the required hydrofluoric acid in the course of the preparation by heating calcium fluoride and excess of concentrated sulphuric acid in the presence of silica (or the silicate).

$$CaF_2(s) + H_2SO_4(l) \rightarrow CaSO_4(s) + 2HF(l)$$
$$SiO_2(s) + 4HF(l) \rightarrow SiF_4(g) + 2H_2O(l)$$

The excess of sulphuric acid absorbs the water produced in the reaction. One of the most important chemical reactions of silicon tetrafluoride is its behaviour with water. Consequently, it is not usually collected in quantity, but is passed at once into water, as in Figure 7.9. The layer of mercury prevents stoppage of the end of the delivery tube by gelatinous silicic acid, which is a product of the reaction.

When the silicon tetrafluoride enters the water, it reacts at once with it to produce a colourless gelatinous precipitate of '*silicic acid*', at the same time producing, in solution, *hexafluorosilicic acid*, H_2SiF_6.

$$3SiF_4(g) + 3H_2O(l) \rightarrow H_2SiO_3(s) + 2H_2SiF_6(aq)$$

The liquid should be stirred to break down the channels formed in the gelatinous precipitate by the silicon tetrafluoride bubbles. The liquid can be filtered at the close of the preparation to remove the precipitated silicic acid. It should *not* be heated, as hexafluorosilicic acid is decomposed by heat.

$$H_2SiF_6(aq) \rightarrow SiF_4(g) + 2HF(aq)$$

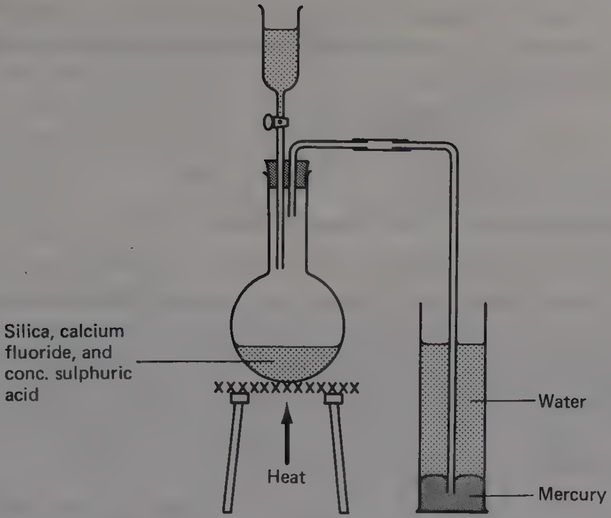


Figure 7.9 *Preparation of SiF_4; its action with water*

Properties of silicon tetrafluoride

Silicon tetrafluoride is a colourless gas with a very pungent smell. At atmospheric pressure, it solidifies at 176 K without liquefying first. Its principal reaction is the one given above with water. It yields silicon if heated with sodium or potassium.

$$SiF_4(g) + 4K(l) \rightarrow Si(s) + 4KF(s)$$

The above reaction can be used as a test for a *fluoride*. The test material is mixed with silica and concentrated sulphuric acid and heated. A glass rod wetted and held in the vapour will be covered with a gelatinous layer of *silicic acid* if a fluoride is present.

$$2F^- + H_2SO_4(l) \rightarrow 2HF(l) + SO_4{}^{2-}$$
$$4HF(l) + SiO_2(s) \rightarrow SiF_4(g) + 2H_2O(l)$$
$$3SiF_4(g) + 3H_2O(l) \rightarrow H_2SiO_3(s) + 2H_2SiF_6(aq)$$

If a fluoride is available, the reaction may be used in the same way as a test for *silica* or a *silicate*, but must not be performed in a glass or porcelain vessel, both of which contain silicate. A leaden dish is suitable.

The experiment also provides a means of preparing silica from a silicate such as powdered glass. The silicate is placed with calcium fluoride and concentrated sulphuric acid in the reaction flask and heated.

$$CaSiO_3(s) + 2CaF_2(s) + 3H_2SO_4(l) \rightarrow SiF_4(g) + 3CaSO_4(s) + 3H_2O(l)$$

The silicon fluoride is passed through mercury into water as before with the same reaction. The 'silicic acid' formed is filtered off, washed, dried and ignited to leave *silica*.

$$H_2SiO_3(s) \rightarrow H_2O(g) + SiO_2(s)$$

Hexafluorosilicic acid, H_2SiF_6, and its salts

Hexafluorosilicic acid, prepared in solution as above, has never been obtained pure, though a crystalline hydrate, $H_2SiF_6.2H_2O$, has been described. The acid is only weak (i.e. slightly ionized), but forms salts, called *hexafluorosilicates*. Potassium hexafluorosilicate, K_2SiF_6, and barium hexafluorosilicate, $BaSiF_6$, are only sparingly soluble in water.

The acid and its salts are used in certain electroplating baths and in producing lead of very high purity. For this, see p. 193.

Silicon tetrachloride, $SiCl_4$

Silicon, when heated, will combine directly with chlorine to form its tetrachloride, but a more convenient preparation is available not requiring the element, silicon. This preparation consists in strongly heating an intimate mixture of silica and carbon in a current of *dry* chlorine.

$$SiO_2(s) + 2C(s) + 2Cl_2(g) \rightarrow SiCl_4(g) + 2CO(g)$$

The vapour of silicon tetrachloride is condensed to a liquid, which contains dissolved chlorine. This can be removed by shaking with mercury and the silicon tetrachloride is then redistilled. It may contain other chlorides such as Si_2Cl_6 and, if so, will require fractionation.

Properties of silicon tetrachloride

This compound is a colourless liquid, boiling point 331 K. Tetrachloromethane (with a considerably *lower* molar mass, 154 against 170) has the *higher* boiling point, 350 K. This is unusual. Silicon tetrachloride fumes in damp air because of its reaction with water mentioned immediately below.

1. *Action with water*. Silicon tetrachloride is hydrolysed rapidly by water in the cold to form *hydrogen chloride* (hence the fuming) and a '*silicic acid*' (usually represented as H_2SiO_3).

$$SiCl_4(l) + 3H_2O(l) \rightarrow H_2SiO_3(s) + 4HCl(g)$$

Other degrees of hydration of silica are possible, e.g. H_4SiO_4 or $SiO_2.2H_2O$, and may occur in the product.

Note the marked contrast here with the behaviour of tetrachloromethane, which is *not* hydrolysed by water (see p. 161).

2. *Action with the alkali metals.* Silicon tetrachloride is decomposed when heated with the alkali metals to form *silicon*, e.g.

$$SiCl_4(l) + 4K(s) \rightarrow Si(s) + 4KCl(s)$$

Silicon dioxide, silica, SiO_2

The physical forms in which silica can occur present considerable complexity. The following is a somewhat simplified account of the situation, which is not, perhaps, very important in a chemical sense, though of much interest to geologists.

Crystalline forms of silica

Silica possesses a giant covalent structure, in which each silicon atom is bonded to four oxygen atoms. The oxygen atoms are arranged at the apices of a tetrahedron, with the silicon atom at the centre of gravity. The detailed structures of the various forms of silica are beyond the scope of this book. This complexity, however, should be contrasted with the simple molecular structure of CO_2.

The best known form of crystalline silica is *quartz*. It is colourless and forms transparent, six-sided crystals, the purest forms of which are known as *rock crystal*. The density of quartz is about 2.64 g cm^{-3}. Impurities produce varieties of quartz, e.g. *smoky quartz* (with organic matter), *milky quartz* (with air bubbles). *Sand* is disintegrated quartz. When pure, it is white, but iron(III) oxide is often present and produces various degrees of yellowish colour. *Sandstone* consists of sandy particles cemented by clay, chalk and (usually) iron(III) oxide. *Cairngorm* and *chalcedony* are decorative varieties of impure quartz.

At about 1140 K, quartz passes into another crystalline variety of silica, *tridymite* (density 2.55 g cm^{-3}). At about 1740 K, a further change occurs, into *cristobalite*. Silica is completely molten at about 1980 K (The melting point is not sharp; liquefaction may begin at about 1870 K.) On cooling, the liquid forms a glassy solid. This solid has an extremely low coefficient of expansion (about 5×10^{-7}; compare that of a typical glass, about 8×10^{-6}). Consequently, vessels made of *fused quartz* can be put red-hot into cold water without breaking, because the strains of sudden contraction are so slight. Quartz glass is transparent to ultraviolet light and is used in making mercury vapour lamps.

Amorphous silica

Amorphous silica occurs naturally as flint, though not pure and associated with some quartz. *Opal* contains amorphous silica, together with combined water and impurities such as organic matter and iron(III) oxide, which may colour it yellow or brown. *Agate* is similar to opal, but with quartz present in addition. *Kieselguhr* is amorphous silica in a very porous form derived from the skeletons of diatoms.

Uses of silica

(a) As *sand*. Enormous amounts of sand are used in *mortar*, *cement*, and *concrete* in the building industry; for the manufacture of *glazes* and *glass* (see p. 178); in *filter beds* for purifying public water supplies.

(b) As *quartz*. Very fine *quartz threads* are relatively very strong and are used as suspensions in electrical instruments. *Quartz glass* is made into tubes, flasks, dishes, etc., for laboratory use. Some varieties of quartz are used as gems.

(c) *Kieselguhr* is used, on account of its absorbent properties, in pharmacy for the making of dry, antiseptic dressings, and for the absorption of liquids such as bromine. Its former use in absorbing nitroglycerine to form dynamite is now out of date. It is, however, often used as the stationary phase in column or thin-layer chromatography.

Chemical properties of silica

On the whole, silica is rather inactive, especially at low temperatures. The amorphous form is more reactive than the crystalline.

1. *Acidic nature*. Silica has no action with water up to its boiling point. It reacts slightly if heated with water under pressure and some silica dissolves.

$$H_2O(l) + SiO_2(s) \rightarrow H_2SiO_3(aq)$$

This probably explains the occurrence of deposits of silica round many hot geysers. It is thrown out of solution when the pressure is released as the geyser spouts at the surface.

Amorphous silica is rapidly attacked by *hot*, *concentrated* caustic alkali solution or by the *fused* alkali.

$$SiO_2(s) + 2OH^-(aq) \rightarrow SiO_3^{2-}(aq) + H_2O(l)$$

The product is the corresponding alkali metal *silicate*.

The above behaviour closely resembles that of carbon dioxide, taking into account the fact that silica is a solid and carbon dioxide a gas.

2. *Behaviour with acids.* Silica is unaffected by any of the mineral acids under any usual conditions of use. Its only important reaction under this heading is with *hydrofluoric acid*, forming *silicon tetrafluoride.*

$$SiO_2(s) + 4HF(l) \rightarrow SiF_4(g) + 2H_2O(l)$$

3. *Behaviour as an acidic anhydride.* At ordinary temperature, silica acts as a very weak acidic compound; at high temperatures, however, it can displace most other acidic anhydrides from their salts to form silicates. This arises because silica is non-volatile at the temperatures used (say red heat), while the other anhydrides are vapours. Consequently, these anhydrides tend to escape as soon as they are produced, their effective concentration tends to zero and there is no reversal of the forward reaction induced by the silica. Examples of this behaviour at high temperatures are:

$$Na_2SO_4(s) + SiO_2(s) \rightarrow Na_2SiO_3(l) + SO_3(g)\uparrow$$
$$Na_2CO_3(s) + SiO_2(s) \rightarrow Na_2SiO_3(l) + CO_2(g)\uparrow$$
$$2Ca_3(PO_4)_2(s) + 6SiO_2(s) \rightarrow 6CaSiO_3(l) + P_4O_{10}(g)\uparrow$$

This last reaction is used in the manufacture of phosphorus (see p. 252). Competing on equal terms, SO_3 and P_4O_{10} are certainly stronger acidic compounds than silica.

4. *With carbon.* Silica reacts with excess coke at the temperature of the electric furnace and produces *silicon carbide* or *carborundum.*

$$SiO_2(s) + 3C(s) \rightarrow SiC(s) + 2CO(g)$$

5. *With magnesium.* Silica is reduced when strongly heated with powdered magnesium (air being excluded) and forms *amorphous silicon.*

$$SiO_2(s) + 2Mg(s) \rightarrow Si(s) + 2MgO(s)$$

Excess of magnesium may produce some magnesium silicide, Mg_2Si.

Silicon monoxide

An unstable lower oxide of silicon may be obtained by heating silica very strongly with silicon. A brown powder is produced, which disproportionates rapidly on cooling.

$$2SiO(s) \rightarrow SiO_2(s) + Si(s)$$

'Silicic acids'

Many silicates are known, the majority of them being very complex.

Two *simple* acids may exist from which silicates could be derived. They can be named:

tetraoxosilicic acid (orthosilicic acid)	$Si(OH)_4$ or H_4SiO_4
trioxosilicic acid (metasilicic acid)	$O{=}Si(OH)_2$ or H_2SiO_3

The 'meta-acid' is derived from the 'ortho-' by loss of one H_2O molecule between two of the (OH) groups of the 'ortho-acid.'

The nearest approximation to '*orthosilicic acid*' is obtained by the action of silicon tetrachloride with water. This produces a gelatinous precipitate, which, if filtered, washed with ethoxyethane (ether) and benzene and allowed to dry without heat, gives a product with a composition corresponding roughly to H_4SiO_4. This does not, however, guarantee the structure $Si(OH)_4$; a hydrated silica, $SiO_2.2H_2O$, would have the same composition.

In a similar way, acidification of a concentrated solution of sodium silicate gives a gelatinous precipitate which, when dried without heat, corresponds in composition to '*metasilicic acid*', H_2SiO_3. Again, a hydrated silica, $SiO_2.H_2O$, would have the same composition.

If hydrated silica is dried slowly, the vapour pressure curve of the material is said to show definite breaks at the compositions corresponding to H_4SiO_4 and H_2SiO_3, which points to the existence of definite compounds at these points, but not necessarily the structures $Si(OH)_4$ and $O{=}Si(OH)_2$. On the whole, the existence of these two silicic acids must be taken as probable, but not certainly proved.

Colloidal silicic acid

If a *dilute* solution of sodium silicate is acidified by dilute hydrochloric acid, no precipitation of silicic acid occurs. This compound is formed, but remains in *colloidal suspension* in the liquid. (For a treatment of colloids, see *Advanced Level Physical Chemistry*, p. 105ff.) A clear, colourless *hydrosol* is formed, containing the acid. (When silicic acid separates as a gelatinous mass from a more concentrated solution of sodium silicate on acidification, the precipitated material is known as a *hydrogel*.)

$$Na_2SiO_3(aq) + 2HCl(aq) \rightarrow 2NaCl(aq) + H_2SiO_3(s)$$

The hydrosol can be dialysed and, in this way, the dissolved electrolytes, HCl and NaCl, are removed. After dialysis, the solution can be concentrated by evaporation till it contains about 14 per cent of silicic acid. After cooling, it slowly sets to a hydrogel.

Any form of silicic acid, or hydrated silica, is finally converted by heat into anhydrous silica, SiO_2.

Silica gel

The product known as *silica gel* is precipitated from concentrated sodium silicate solution at about 373 K by the addition of hydrochloric acid. It usually contains about 5–7% of water and is regarded as a partially hydrated silica. It has marked absorbent powers for moisture and is used in large-scale drying of gases, e.g. in drying air for the blast in a blast furnace. When spent, the gel can be re-activated by heating it suitably.

Silica gel is also used in absorbing volatile solvents, which would otherwise be lost in effluent, e.g. propanone and carbon disulphide. The liquids are recovered by heating the gel. It has also been used in freeing petroleum from sulphur compounds.

Silicates

Sodium silicate

Sodium silicate is made by fusing together a mixture of sand and anhydrous sodium carbonate (Na_2CO_3) or sodium sulphate (Na_2SO_4).

$$Na_2CO_3(s) + SiO_2(s) \rightarrow Na_2SiO_3(l) + CO_2(g)$$
$$Na_2SO_4(s) + SiO_2(s) \rightarrow Na_2SiO_3(l) + SO_3(g)$$

When cool, it forms a glassy solid. It is broken up and heated with water under pressure. The sodium silicate then passes into solution. After concentration and cooling, the material forms a colourless, treacly liquid known as *water glass*. It is sold in this form in tins.

Uses of water glass

(a) *In the preservation of eggs.* The eggs (which must not be cracked) are immersed in a suitably diluted solution of water glass. Reaction between sodium silicate and the calcium carbonate of the egg shell precipitates calcium silicate, which seals the pores of the shell and prevents the entry of bacteria. A cracked egg probably contains bacteria already, so will go rotten anyway. This use of sodium silicate is now much diminished.

(b) Water glass is used in fire-proofing wood and in manufacturing cements for fireclay.

(c) Water glass may be an ingredient of cheap soap.

Glass

There are many forms of glass, suitable for differing purposes (as mentioned below), but, in principle, their manufacture is quite similar. The glass used for ordinary windows, milk bottles and similar containers, and glass connection tubing, is a *lime-soda* glass. The essential ingredients for its manufacture are *sodium carbonate* (or sodium sulphate; or both), *calcium carbonate* and *sand* (i.e. silica). To assist in the fusion of these materials, some broken glass (*cullet*) is usually added, and a little carbon, acting as a reducing agent. This mixture is heated in a tank lined with fire-brick. A fused mixture of calcium silicate and sodium silicate, containing some unchanged silica, is eventually formed, by reactions usually represented as:

$$CaCO_3(s) + SiO_2(s) \rightarrow CaSiO_3(l) + CO_2(g)$$

$$Na_2CO_3(s) + SiO_2(s) \rightarrow Na_2SiO_3(l) + CO_2(g)$$

or

$$Na_2SO_4(s) + SiO_2(s) \rightarrow Na_2SiO_3(l) + SO_3(g)$$

Bohemian glass or *hard glass* is a *potash-lime* glass, made as above but using potassium carbonate instead of sodium carbonate. It contains K_2SiO_3 instead of Na_2SiO_3. It fuses at a higher temperature than lime-soda glass and is suitable for making combustion tubes and similar uses. *Jena glass* is another variety of hard glass; it contains some alumina and borate.

Flint glass is a potash-lead glass. The lead is supplied as one or more of the lead oxides. It has a high refractive index, is used in making prisms, lenses, and other optical devices, but is very soft and scratches easily. *Cut glass* is a variety of flint glass.

In recent years, varieties of glass have been introduced which have considerable percentages of borate and a high silica content, e.g. Pyrex contains about 12 per cent of B_2O_3 and 80 per cent of SiO_2. Such glasses have a low coefficient of expansion and are used for oven ware and scientific apparatus.

Coloured glass is produced by introducing various metallic oxides into the glass, or, sometimes, other materials, e.g. cobalt(II) oxide for blue glass, copper(I) oxide for ruby glass, calcium phosphate (or fluoride) for opaque, milky glass.

Safety glass consists of a layer of glass cemented to each side of a tough transparent polymeric organic material. It does not splinter if struck forcibly.

Nature of glass

Glass is not a true solid. It is best considered as a supercooled liquid.

It is essentially a solution of silica in a mixture of other silicates, which has not crystallized on cooling, but has acquired some of the outward characteristics of the solid state by a great increase of viscosity with fall of temperature.

Not being a true solid, glass has no definite melting point. It softens at a certain temperature, gradually becomes less and less viscous as temperature rises, until it reaches the point of free flow at which it is recognizable as a liquid. The process may cover 150 K or so. This property is very valuable. The glass can be caught in its semi-solid state and blown in a mould, or on the end of a glass-blower's tube, into a desired shape which it will retain permanently when cold. It can also be bent (as tubing) and joined into quite complicated apparatus while in the softened state. After such treatment, it requires *annealing*, i.e. slow cooling from a high temperature so that there are no internal stresses set up by uneven contraction.

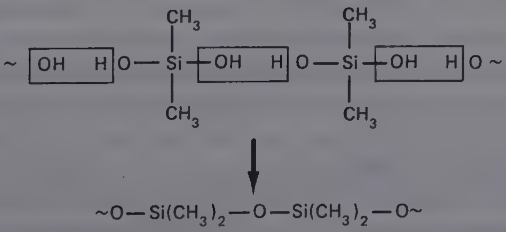
If heated for a long time at about its softening point, or if cooled very slowly, glass may actually crystallize. In that case, it becomes opaque because the small crystals scatter light, and is said to *devitrify*. The same process may also occur if glass is subject to great temperature changes between summer and winter. In extreme cases, the glass may collapse into powder.

Silicones

Silicon and oxygen provide the basis for an important group of polymeric materials known as *silicones*. Several methods can be used to make the starting materials, which are *alkylchlorosilanes*, e.g. dimethyldichlorosilane $(CH_3)_2SiCl_2$. These are then hydrolysed as, for example:

$$(CH_3)_2SiCl_2(l) + 2H_2O(l) \rightarrow (CH_3)_2Si(OH)_2(l) + 2HCl(g)$$

The resulting molecule has two functional groups which can interact with other molecules, which is an essential condition for any type of *condensation polymerization*. In this case, loss of water occurs each time a link is formed.

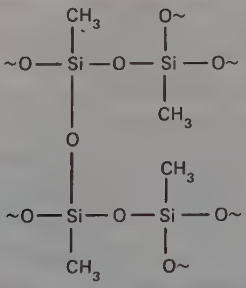


$$\sim\boxed{\mathrm{OH\quad H}}\mathrm{O}-\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{Si}}}-\boxed{\mathrm{OH\quad H}}\mathrm{O}-\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{Si}}}-\boxed{\mathrm{OH\quad H}}\mathrm{O}\sim$$

$$\downarrow$$

$$\sim O-Si(CH_3)_2-O-Si(CH_3)_2-O\sim$$

Monoalyltrichlorosilanes, e.g. CH_3SiCl_3, can form a three-dimensional cross-linked polymer:



The proportions of the monomers, and the conditions of hydrolysis, can be controlled to produce materials ranging from non-volatile oils and greases to rubber-like solids.

The relation between silicon and boron

Though boron appears in Group III and silicon in Group IV of the Periodic Table, there is quite a marked resemblance between the two. The following are the chief points of similarity:

(a) Their oxides, B_2O_3 and SiO_2, are both strongly acidic in type. Consequently, both elements form oxyacids, H_3BO_3 and H_2SiO_3, and the corresponding salts, borates and silicates.

(b) Both elements form volatile fluorides, BF_3 and SiF_4, which are hydrolysed by water in a corresponding way, to produce HBO_2 and HBF_4 from boron, and H_2SiO_3 and H_2SiF_6 from silicon.

(c) They form metallic borides and silicides, which have corresponding reactions with dilute mineral acid, producing hydrides of boron and silicon.

(d) Both elements form a complex series of hydrides.

(e) Boron and silicon form similar glassy materials and associate similarly in borosilicate glasses.

On the whole, boron resembles silicon more closely than it resembles aluminium which is a fellow member of Group III. Aluminium is much more metallic in type than boron, its oxide has definite basic properties and forms a series of stable salts with the mineral acids. There is no compound of aluminium corresponding to trioxoboric acid, because aluminium hydroxide has only very feeble acidic properties and the aluminates are much hydrolysed, and decomposed by carbon dioxide.

This boron–silicon similarity is one of a series of diagonal relations in the Periodic Table, by which the first element of a group tends to resemble the second element of the next higher group (see p. 9).

Germanium

Atomic number 32.
Electron arrangement 2.8.18.4 ($1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^2$).
Germanium has isotopes of mass number, in order of abundance, 74, 72, 70, 73, 76; relative atomic mass 72.59.

Occurrence

Germanium is quite rare. The mineral *germanite*, containing up to 5 per cent germanium, is found in S.W. Africa. In Britain it is extracted mostly from flue dusts and the ashes of certain coals, in which it can be present up to one per cent. Only a few aspects of its chemistry will be considered here.

Extraction of germanium

If materials containing germanium are heated strongly with hydrogen chloride, germanium(IV) chloride, $GeCl_4$, distils off. This is then hydrolysed to germanium(IV) oxide, GeO_2. The element is obtained by heating the oxide in hydrogen or with carbon. For use in semi-conductor devices, it is further purified by *zone-refining*. In this technique, a molten zone is made to move slowly along a long bar of the material. Impurities are concentrated in the molten region. The process can be repeated many times until virtually all the impurities are concentrated in a short portion at the end of the bar, which can then be cut off.

Properties of germanium

Germanium is a grey, brittle solid, density 5.36 g cm^{-3}. It melts at 1210 K and boils at 3100 K. It has semi-conductor properties, and is used in transistors. Within Group IV, germanium shows properties intermediate between those of the non-metals carbon and silicon and the metals tin and lead. Whereas the $+2$ oxidation states of carbon and silicon are very rare and unstable, germanium can form stable compounds in which it is in the $+2$ state as well as those in which it is in the normal $+4$ state.

Some chemical properties of germanium and its compounds

1. *Action of alkali on germanium.* Like silicon, germanium reacts with

even dilute alkalis.

$$Ge(s) + 2OH^-(aq) + H_2O(l) \rightarrow GeO_3{}^{2-}(aq) + 2H_2(g)$$

2. *Hydrides of germanium. Germane*, GeH_4, may be prepared by the action of lithium tetrahydridoaluminate(III) on germanium(IV) chloride in dry ethoxyethane (ether).

$$GeCl_4 + LiAlH_4 \xrightarrow{\text{dry ether}} GeH_4(g) + LiAlCl_4$$

Several of the series of germanes, Ge_nH_{2n+2}, are known, although all are unstable. They resemble the corresponding silanes, except that they are less reactive towards hydrolysis.

3. *Oxides of germanium.*

(a) *Germanium*(II) *oxide* (*germanium monoxide*), GeO. This can be made by the action of water on germanium(II) chloride.

$$GeCl_2(s) + H_2O(l) \rightarrow GeO(s) + 2HCl(aq)$$

When made in this way, it is a yellow hydrated solid. It is amphoteric; it dissolves in acids, and also dissolves in caustic alkalis. It is rather more acidic than either SnO or PbO. However, it is more stable than SiO, which shows that germanium is more metallic than silicon. When heated out of contact with air at 800 K germanium(II) oxide disproportionates:

$$2GeO(s) \rightarrow Ge(s) + GeO_2(s)$$

Anhydrous germanium(II) oxide is a black powder.

(b) *Germanium*(IV) *oxide* (*germanium dioxide*), GeO_2. This compound may be prepared by the hydrolysis of germanium(IV) chloride.

$$GeCl_4(l) + 2H_2O(l) \rightarrow GeO_2(s) + 4HCl(aq)$$

It can also be made by the action of concentrated nitric acid on germanium.

$$Ge(s) + 4HNO_3(\text{conc. aq.}) \rightarrow GeO_2(s) + 4NO_2(g) + 2H_2O(l)$$

Germanium(IV) oxide is essentially acidic in character, whereas tin(IV) oxide and lead(IV) oxide are both amphoteric. However, GeO_2 is less acidic than SiO_2.

4. *Chlorides of germanium.*

(a) *Germanium*(II) *chloride.* This compound is a pale yellow solid, and may be prepared by passing the vapour of germanium(IV) chloride over hot germanium. The reaction is, however, reversible. The germanium(II) chloride completely disproportionates at about 720 K.

$$GeCl_4(g) + Ge(s) \rightleftharpoons 2GeCl_2(s)$$

Germanium(II) chloride is readily hydrolysed by water (see above).

(b) *Germanium*(IV) *chloride*. This compound may be prepared by passing chlorine over germanium at 370–450 K.

$$Ge(s) + 2Cl_2(g) \rightarrow GeCl_4(g)$$

The vapour is condensed to a colourless liquid. It is a covalent compound. It is easily and irreversibly hydrolysed by water (see above). The hydrolysis is slower than for silicon tetrachloride, but is faster than for tin(IV) chloride and lead(IV) chloride. Hydrolysis of these last two compounds may be prevented by the presence of dilute hydrochloric acid; this is not possible with germanium(IV) chloride.

Tin

Atomic number 50; electron arrangement 2.8.18.18.4 ($1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^2$).
Tin has isotopes of mass number, in order of abundance, 120, 118, 116, 119, 117, 124, 122, 112, 114, and 115 (this is the maximum number of stable isotopes shown by any element); relative atomic mass 118.70.

Occurrence and extraction of tin

The only important source of tin is *cassiterite* or *tinstone*, SnO_2. It may occur in *lodes* or *veins*, or in *alluvial deposits*, from which it is dredged. Tin occurs in Malaya (which produces about one-third of total world output), in Bolivia, Nigeria, China, East Indies, and, in comparatively small amount, in Cornwall.

The *extraction* of tin falls into three main parts: (1) *concentration* of the oxide, (2) *smelting* for the metal, (3) *purification.*

1. *Concentration of the oxide.* The ore from lodes is crushed and the lighter, earthy materials are removed from the dense tinstone by washing with water. It is then roasted to remove arsenic and sulphur as volatile oxides, and iron compounds are removed by an electromagnetic separator.

The treatment of alluvial tin is not essentially different, though varying in detail.

2. *Smelting.* The concentrated tin(IV) oxide is heated with carbon (anthracite or coke) in a reverberatory furnace at about 1500 K. The oxide is reduced to metal, which runs to the bottom of the furnace and

is tapped off.

$$SnO_2(s) + 2C(s) \rightarrow Sn(l) + 2CO(g)$$

3. *Purification of the metal.* The tin is first *liquated*, i.e. it is heated to a temperature a little above its low melting-point (505 K) when the molten tin runs away from less fusible impurities. It is then stirred in contact with air. Most remaining metal impurities oxidize preferentially, and form a scum which can be skimmed off.

Properties of tin

Ordinary tin is a white metal. It has a low melting point, 505 K, but a high boiling point, 2543 K. It is rather soft and very ductile, forming tin foil readily by rolling. It can also be easily extruded into tubes. It can be drawn into wire, most easily at about 370 K, but, at a higher temperature (about 470 K), it can be powdered.

When a bar of tin is bent, it gives out a crackling sound, the 'cry' of tin, which is caused by the rubbing of crystal faces against each other.

Allotropy of tin

The allotropy of tin can be summarized in the form:

Grey tin	$\rightleftharpoons$	White tin	$\rightleftharpoons$	Rhombic tin
(cubic) Stable below 286.4 K		(tetragonal) Stable 286.4 K to 434 K		Stable 434 K to 505 K (m.p.)

The ordinary form of tin is *white tin*. It will be seen that the transition point between white and grey tin (286.4 K) is about room temperature. If (as in winter) temperature falls below this value, white tin becomes metastable and tends to pass into the grey form. A considerable fall of temperature is, however, necessary to cause appreciable change; the change is most rapid at about 220 K. It is accelerated by contact with grey tin or 'pink salt', $(NH_4)_2SnCl_6$. When the change occurs, white tin develops grey, wart-like formations. The effect is known as *tin disease* and, if fully developed, causes the tin to crumble to a grey powder. White tin is considerably denser than grey tin (7.29 against 5.80 g cm^{-3}).

Chemical properties of tin

1. *With air.* Tin is not affected by air at ordinary temperature, but burns to tin(IV) oxide, SnO_2, at about 1750 K.

2. *With acids.*

(a) *Hydrochloric acid.* The hot dilute acid attacks tin slowly. The reaction is more rapid at higher concentrations. *Tin*(II) *chloride* is formed in solution and *hydrogen* evolved.

$$Sn(s) + 2H^+(aq) \rightarrow Sn^{2+}(aq) + H_2(g)$$

(b) *Sulphuric acid.* Dilute sulphuric acid has little (if any) action on tin. The *hot, concentrated* acid reacts to give mainly *tin*(IV) *sulphate*, with some basic sulphate and sulphur. The gas *sulphur dioxide* is evolved. The main reaction is:

$$Sn(s) + 4H_2SO_4(l) \rightarrow Sn(SO_4)_2(aq) + 4H_2O(l) + 2SO_2(g)$$

(c) *Nitric acid.* The action of dilute nitric acid on tin is slight; it produces the usual mixed products—tin(II) nitrate, oxides of nitrogen and ammonium nitrate.

Much more important is the behaviour of concentrated nitric acid (which contains some water). It reacts violently with tin, especially if heated, giving off copious *reddish-brown fumes* (*nitrogen dioxide*) and leaving a *white* precipitate of a hydrated oxide (sometimes called *metastannic acid*). The essential reaction is:

$$Sn(s) + 4HNO_3(\text{conc. aq.}) \rightarrow SnO_2(s) + 4NO_2(g) + 2H_2O(l)$$

Notice that *tin*(IV) *nitrate is not formed* in any significant amount; this is the only case of a common metal reacting with nitric acid to form a precipitate. All other common reacting metals give their nitrates in solution.

3. *With caustic alkalis.* Tin reacts with *hot, concentrated* aqueous sodium or potassium hydroxide solution to liberate *hydrogen* and form the *hexahydroxostannate*(IV) (*stannate*) in solution. The action is slow.

$$Sn(s) + 2OH^-(aq) + 4H_2O(l) \rightarrow [Sn(OH)_6]^{2-}(aq) + 2H_2(g)$$

4. *Forming chlorides.* Tin, when *heated*, reacts with *dry* hydrogen chloride to form anhydrous tin(II) chloride (a white solid) or with *dry* chlorine to form tin(IV) chloride (a fuming liquid).

$$Sn(s) + 2HCl(g) \rightarrow SnCl_2(s) + H_2(g)$$
$$Sn(s) + 2Cl_2(g) \rightarrow SnCl_4(l)$$

These preparations are fully considered on p. 368.

Uses of tin

1. In *tin plate.* Tin is resistant to corrosion and imparts no taste to

food products; consequently, it is employed as a cover for mild steel in *tin plate* and the product is used in canning fruit, meat and fish. Thin sheets of mild steel are cleaned in dilute acid, washed and dried. They are then passed through molten tin covered with a flux, such as zinc chloride. Excess tin is squeezed off between rollers.

The protection is, unlike that afforded by zinc, destroyed when the tin layer is pierced or scratched. Because tin is *less* electropositive than iron, the iron will lose electrons to it and so oxidize more easily.

2. *In alloys.* Tin is a constituent of many useful alloys, among which are:

Common solder	tin, 50%; lead, 50%
Fine solder	tin, 67%; lead, 33%
Pewter	tin, 75%; lead, 22%; antimony, 3%
Type-metal	tin, 5%; lead, 75%; antimony, 20%
Bearing metal	tin, 82%; copper, 4%; antimony, 14%
Coinage bronze	copper, 95.5%; tin, 3%; zinc, 1.5%

Tin also occurs in gun-metal, bell-metal and phosphor bronze.

3. *In glass making.* The modern method for making plate glass involves floating molten glass on a bath of molten tin. The glass solidifies while the tin is still liquid, so ensuring a perfectly flat surface for the glass.

Compounds of tin

The common oxidation states of tin in its compounds are + 2 and + 4 (formerly known as *stannous* and *stannic* respectively).

Tin(II) (*stannous*) *compounds*	*Tin*(IV) (*stannic*) *compounds*
SnO	SnO_2
$Sn(OH)_2$	$Sn(OH)_4$
$SnCl_2$	$SnCl_4$
$SnSO_4$	$Sn(SO_4)_2$
SnS	SnS_2

In a general way, when in the + 2 oxidation state, tin tends to react as a *metallic* element and its compounds are largely *ionic*; when in the + 4 oxidation state, tin resembles the early, *non-metallic* members of Group IV (C and Si), and its compounds are mainly *covalent*.

Tin(II) oxide, SnO, and 'tin(II) hydroxide,' $Sn(OH)_2$

Tin(II) oxide is most easily made by heating tin(II) ethanedioate (stannous oxalate).

$$SnC_2O_4(s) \rightarrow SnO(s) + CO(g) + CO_2(g)$$

The gases evolved protect the oxide from the oxidizing action of the air. This oxide is a dark grey or brown powder. It is rarely seen (except as an exhibit in a sealed tube), because it oxidizes rapidly if exposed to air, even at room temperature, forming tin(IV) oxide.

$$2SnO(s) + O_2(g) \rightarrow 2SnO_2(s)$$

It is seen to glow as the action proceeds; it is said to be *pyrophoric*.

'Tin(II) hydroxide' is formed as a gelatinous, white precipitate by *cautious* addition of alkali solution to a solution of a tin(II) salt, usually the chloride. (Excess alkali redissolves the hydroxide.) The material has no definite composition.

$$Sn^{2+}(aq) + 2OH^-(aq) \rightarrow Sn(OH)_2(s)\downarrow$$

It acts as an *amphoteric hydroxide.*

It dissolves in acids to give tin(II) salts.

$$Sn(OH)_2(s) + 2H^+(aq) \rightarrow Sn^{2+}(aq) + H_2O(l)$$

It dissolves in excess aqueous alkali to form a *hydroxostannate*(II) (stannite) in solution.

$$SnO(s) + H_2O(l) + OH^-(aq) \rightarrow [Sn(OH)_3]^-(aq)$$

Because of this, aqueous alkali first *precipitates tin*(II) *hydroxide* from tin(II) chloride solution and *then redissolves it* as the alkali passes into excess.

Tin(II) oxide acts similarly as an amphoteric compound.

Tin(II) chloride, $SnCl_2$

Tin(II) chloride can be obtained in solution by heating tin with moderately concentrated hydrochloric acid, and crystallizes as the dihydrate, $SnCl_2.2H_2O$, known as *tin salt.*

$$Sn(s) + 2H^+(aq) \rightarrow Sn^{2+}(aq) + H_2(g)$$

It hydrolyses readily, so that the anhydrous salt is best obtained by *heating* tin in a current of *dry* hydrogen chloride.

$$Sn(s) + 2HCl(g) \rightarrow SnCl_2(s) + H_2(g)$$

Tin(II) chloride does not dissolve satisfactorily in water; it precipitates a basic chloride, or even tin(II) hydroxide if the water is hot and in large excess.

$$SnCl_2(s) + H_2O(l) \rightleftharpoons Sn(OH)Cl(s) + HCl(aq)$$
$$SnCl_2(s) + 2H_2O(l) \rightleftharpoons Sn(OH)_2(s) + 2HCl(aq)$$

Because of this, it is better to dissolve it (with heat) in moderately concentrated hydrochloric acid. Bottles of the laboratory reagent usually contain fairly concentrated hydrochloric acid. Metallic tin is sometimes added to maintain the stability of the tin(II) chloride.

Notice that tin(II) chloride, in which the oxidation state of tin is + 2, is a chloride of the *metallic* type—a solid, an electrolyte in solution and non-volatile. Contrast this with the *non-metallic* nature of tin(IV) chloride, $SnCl_4$ (p. 190).

Tin(II) chloride as a reducing agent

Tin(II) chloride, usually in solution in moderately concentrated hydrochloric acid, is a powerful reducing agent. Like all reducing agents, the tin(II) ion acts as an electron-donor, parting with *two* electrons per ion, to produce the tin(IV) ion.

$$Sn^{2+}(aq) \rightarrow Sn^{4+}(aq) + 2e^-$$

The electrons are accepted by the oxidizing agent involved. The tin(IV) ion probably exists only in a complex (e.g. hydrated) but this fact does not affect the essentials of the change as stated above.

1. *With an iron*(III) *salt.* Tin(II) chloride reduces an iron(III) salt in solution to the corresponding *iron*(II) *salt*, the solution changing from *yellow* (or brown) to *pale green.*

$$Sn^{2+}(aq) + 2Fe^{3+}(aq) \rightarrow Sn^{4+}(aq) + 2Fe^{2+}(aq)$$

2. *With iodine.* Tin(II) chloride reduces iodine, usually dissolved in potassium iodide solution, to the *iodide ion.* The solution turns from *dark brown to colourless.*

$$Sn^{2+}(aq) + I_2\,(\text{in KI}(aq)) \rightarrow Sn^{4+}(aq) + 2I^-(aq)$$

3. *With potassium manganate*(VII). Potassium manganate(VII) (usually in acidified solution) is rapidly decolorized by tin(II) chloride solution, producing the *manganese*(II) *ion* as principal product.

$$2MnO_4^-(aq) + 5Sn^{2+}(aq) + 16H^+(aq) \rightarrow 2Mn^{2+}(aq) + 5Sn^{4+}(aq) + 8H_2O(l)$$

4. *With potassium dichromate*(VI). Potassium dichromate(VI) (usually in acidified solution) is reduced by tin(II) chloride, the *golden yellow* solution changing to a *green* solution containing the *chromium*(III) ion.

$$Cr_2O_7^{2-}(aq) + 3Sn^{2+}(aq) + 14H^+(aq) \rightarrow 2Cr^{3+}(aq) + 3Sn^{4+}(aq) + 7H_2O(l)$$

5. *With mercury*(II) *chloride.* Mercury(II) chloride, in solution, is reduced by tin(II) chloride in two distinct stages:

(a) with *little* tin(II) chloride, a *white precipitate* of mercury(I) chloride appears.

$$2Hg^{2+}(aq) + Sn^{2+}(aq) + 2Cl^-(aq) \rightarrow Hg_2Cl_2(s) + Sn^{4+}(aq)$$

(b) with *excess* of tin(II) chloride, the precipitate turns *dark grey* (or black) and is *metallic mercury.*

$$Hg_2^{2+}(s) + Sn^{2+}(aq) \rightarrow 2Hg(l) + Sn^{4+}(aq)$$

6. *With organic nitro-compounds.* Tin(II) chloride is often used in reducing nitro-compounds to *primary amines.* The best known case is that of nitrobenzene to phenylamine (aniline), which occurs rapidly at a temperature just short of the boiling point of the liquid.

$$C_6H_5.NO_2(l) + 3Sn^{2+}(aq) + 6H^+(aq) \rightarrow C_6H_5.NH_2(l) + 3Sn^{4+}(aq) + 2H_2O(l)$$

Tin(II) sulphide is described with tin(IV) sulphide a little later. Other tin(II) compounds (e.g. sulphate and nitrate) are of little importance.

Tin(IV) oxide, SnO_2

A white gelatinous precipitate is thrown down by the action of ammonia on tin(IV) chloride solution and is '*stannic hydroxide*,' a hydrated tin(IV) oxide.

$$Sn^{4+}(aq) + 4OH^-(aq) \rightarrow SnO_2.2H_2O(s)$$

The composition is not definite.
The same precipitate is obtained with aqueous caustic alkali, but is dissolved by *excess* of the alkali forming a hexahydroxostannate(IV) (stannate).

$$SnO_2.2H_2O(s) + 2OH^-(aq) \rightarrow [Sn(OH)_6]^{2-}(aq)$$

This indicates the *acidic* properties of the material; it has no appreciable basic properties and forms no salts with dilute acids. Here tin is clearly acting with *non-metallic* behaviour.

Tin(IV) oxide occurs as the important natural product, *cassiterite* or *tinstone*, from which tin is extracted. A convenient way of preparing tin(IV) oxide is to heat tin with concentrated nitric acid, having the acid in excess. Copious brown fumes (nitrogen dioxide) appear, and a hydrated tin(IV) oxide (or *metastannic acid*) precipitates. When the action is over, the mixture is diluted, boiled and filtered. The precipitate is well washed with hot, distilled water, dried and heated to constant weight.

$$Sn(s) + 4HNO_3(conc.aq.) \rightarrow SnO_2(s) + 4NO_2(g) + 2H_2O(l)$$

This oxide is *acidic* in nature, showing tin acting with *non-metallic* properties. Tin(IV) oxide forms no salts with dilute acids (i.e. shows no *basic* character) but forms hydroxostannates(IV) when heated with aqueous caustic alkali (see above). This is analogous to the behaviour of the acidic oxides of carbon and silicon, e.g.

$$CO_2(g) + 2OH^-(aq) \rightarrow CO_3{}^{2-}(aq) + H_2O(l)$$

The oxide is said to show very feebly basic characteristics if mixed with concentrated sulphuric acid by forming tin(IV) sulphate, $Sn(SO_4)_2$; this salt is, however, immediately and fully hydrolysed on dilution with water, re-forming the oxide.

The oxide is readily reduced when heated with carbon or carbon monoxide.

$$SnO_2(s) + 2C(s) \rightarrow Sn(s) + 2CO(g)$$
$$SnO_2(s) + 2CO(g) \rightarrow Sn(s) + 2CO_2(g)$$

Tin(IV) oxide is used in glazing white tiles and in producing opaque milk-glass.

Tin(IV) chloride, $SnCl_4$

Tin(IV) chloride is made by *heating* metallic tin in a stream of *dry* chlorine. The apparatus is fully described on p. 367.

$$Sn(s) + 2Cl_2(g) \rightarrow SnCl_4(l)$$

Tin(IV) chloride is a volatile liquid, boiling point 387 K, and a non-electrolyte when water-free. It is *covalent*. It is rapidly hydrolysed by excess water, especially if heated, to form ‘stannic hydroxide’, hydrated tin(IV) oxide.

$$SnCl_4(l) + 4H_2O(l) \rightarrow SnO_2.2H_2O(s) + 4HCl(aq)$$

The reaction causes it to fume in air. All these are the characteristics of a chloride of a *non-metal*, and show tin acting like carbon and silicon, the earlier members of the group.

Tin(II) sulphide, SnS, and tin(IV) sulphide, SnS_2

Tin(II) *sulphide* is usually prepared by passing hydrogen sulphide through a hot solution of tin(II) chloride (acidified with dilute hydrochloric acid). A *brown* precipitate appears (probably the hydrogensulphide). If filtered, washed and dried, it turns to *black* tin(II) sulphide.

$$Sn^{2+}(aq) + S^{2-}(aq) \rightarrow SnS(s)$$

It can also be made by heating tin in sulphur vapour.

The sulphide is soluble in yellow ammonium sulphide which puts tin into Group IIB of the usual tables for Qualitative Analysis. It is *oxidized* in the process by disulphide ion, $S_2{}^{2-}$, contained in the ammonium sulphide, and forms the trithiostannate(IV) ion, $SnS_3{}^{2-}$.

$$SnS(s) + S_2{}^{2-}(aq) \rightarrow SnS_3{}^{2-}(aq)$$

Consequently, on acidification, the *yellow* tin(IV) sulphide is precipitated, not the original black tin(II) sulphide.

$$SnS_3{}^{2-}(aq) + 2H^+(aq) \rightarrow SnS_2(s) + H_2S(g)$$

Tin(IV) *sulphide* is precipitated as a yellow solid when hydrogen sulphide is passed through a hot solution of tin(IV) chloride in dilute hydrochloric acid.

$$SnCl_4(aq) + 2H_2S(g) \rightarrow SnS_2(s)\downarrow + 4HCl(aq)$$

It is soluble in yellow ammonium sulphide, forming the trithiostannate(IV) ion, like tin(II) sulphide above.

$$SnS_2(s) + S^{2-}(aq) \rightarrow SnS_3{}^{2-}(aq)$$

It also dissolves in excess aqueous caustic alkali, forming the *hydroxostannate*(IV) and *trithiostannate*(IV) ions.

$$3SnS_2(s) + 6OH^-(aq) \rightarrow [Sn(OH)_6]^{2-}(aq) + 2SnS_3{}^{2-}(aq)$$

Tin tetrahydride, SnH_4

As a heavy metal, tin would not be expected to form a salt-like hydride resembling NaH. By analogy with CH_4 and SiH_4, it might, however, be expected to form a covalent hydride, SnH_4. This compound does exist. It is a gas, boiling point 221 K. It decomposes slowly at room temperature, and rapidly at 420 K, to its elements. It is therefore much less stable than CH_4 and SiH_4, as would be expected from the more metallic nature of tin.

The hydride is given (with much hydrogen) by the action of dilute sulphuric acid on an alloy of magnesium and tin.

$$2Mg(s) + Sn(s) + 4H^+(aq) \rightarrow 2Mg^{2+}(aq) + SnH_4(g)$$

A recent method produces the hydride much more satisfactorily by the action of lithium tetrahydridoaluminate(III) on tin(IV) chloride,

$$SnCl_4(l) + LiAlH_4(s) \rightarrow SnH_4(g) + LiAlCl_4(s)$$

Detection of tin

As explained in the preceding section, tin appears in Group IIB of the usual Qualitative Analysis tables, as its sulphide SnS or SnS_2. It is accompanied in this group by the sulphides of arsenic and antimony. For details of their identification, analytical tables should be consulted.

Lead

Atomic number 82; electron arrangement 2.8.18.32.18.4
($1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 5d^{10} 6s^2 6p^2$
Lead has isotopes of mass number, in order of abundance, 208, 206, 207, 204. It also has radioactive isotopes 210, 211, 212, 214.
Relative atomic mass 207.2

Occurrence and extraction

The most important ore of lead is its sulphide, *galena*, PbS. It is usually accompanied by zinc sulphide and by silver sulphide. Other lead ores (of little industrial importance) are *cerussite*, $PbCO_3$, *anglesite*, $PbSO_4$, and *wulfenite*, $PbMoO_4$. Lead occurs principally in the USA, Germany Spain, Mexico, and New South Wales. Much was formerly mined in Wales and N. England.

The extraction of lead occurs in four stages: (1) *concentration* of the ore, (2) *roasting*, (3) *smelting*, (4) *refining*.

1. *Concentration of the ore*. This is done by *flotation*, the technical details of which are rather complex. The powdered ore is agitated with water in which certain chemicals (among which are slaked lime, potassium cyanide and pine oil) are contained. Galena particles are removed in the froth.

2. *Roasting*. The concentrated ore is roasted in a reverberatory furnace with plenty of air available, and is oxidized to lead(II) oxide. Sulphur dioxide is evolved.

$$2PbS(s) + 3O_2(g) \rightarrow 2PbO(s) + 2SO_2(g)$$

3. *Smelting*. The lead(II) oxide is heated with coke in a small blast furnace and is reduced to lead.

$$PbO(s) + C(s) \rightarrow Pb(l) + CO(g)$$

Iron is also introduced into the furnace to act as a reducing agent for any remaining lead(II) sulphide.

$$PbS(s) + Fe(s) \rightarrow Pb(l) + FeS(s)$$

Limestone is also present to act as a flux, converting sandy materials into fusible calcium silicate.

$$CaCO_3(s) + SiO_2(s) \rightarrow CaSiO_3(l) + CO_2(g)$$

The iron(II) sulphide and calcium silicate form a molten slag which is tapped off separately from the lead.

4. *Refining*. Lead for ordinary uses is refined by heating it in a shallow reverberatory furnace or by blowing air through the molten metal. Impurities oxidize before the lead and are skimmed from the surface. Very pure lead can be prepared by electrolysis. Cathodes of pure lead are suspended in an electrolyte containing hexafluorosilicic acid, H_2SiF_6, and its lead salt, $PbSiF_6$ (with some glue or gelatine). Impure lead is made the anode. When current is passed:

At the cathode	*At the anode*
$Pb^{2+} + 2e^- \rightarrow Pb(s)$	$Pb - 2e^- \rightarrow Pb^{2+}(aq)$ Au and Ag precipitate as anode mud

Uses of lead

(a) Lead is extensively used in the building industry as sheet lead for roofing and, sometimes, for damp-coursing. It is also used for water pipes of small size. Lead has considerable advantages for this purpose; it is soft, easily bent and repaired and not attacked by water which is slightly hard. Soft water can be dangerous in contact with lead piping (see p. 195). Lead for piping is being replaced by copper and plastic. Some lead pipes installed in Roman times are still in use.

(b) Lead finds considerable use in chemical works, being fairly resistant to attack by sulphuric acid. It is used in evaporation vessels, and the linings of lead chambers employed in the manufacture of the acid.

(c) Lead is used in accumulator plates.

(d) Several alloys contain lead, e.g.

Common solder	lead, 50%; tin, 50%
Fine solder	lead, 33%; tin, 67%
Pewter	lead, 22%; tin, 75%; antimony, 3%
Type-metal	lead, 75%; tin, 5%; antimony, 20%

(e) Lead is used in making many of its compounds, e.g. 'red lead oxide' and 'white lead' in paints, lead azide as a detonator, tetraethyllead as a petrol additive.

(f) The high density of lead has found a use in clock pendulums and weights, plumb bobs, fishing tackle, etc. It is also opaque to radiations and is used as a shield for operators of X-ray equipment, etc.

Properties of lead

Physical properties

Lead is bluish-grey, lustrous when newly cut but tarnishing rapidly in air. It melts at 600 K. The density of lead varies somewhat according to the way it has been treated; a representative figure is 11.3 g cm^{-3}. It is a soft metal, easily cut with a knife and making a mark on paper; it easily forms foil and can be extruded as rod and piping. It breaks too easily to form wire readily. Lead is, by metallic standards, rather a poor conductor of heat and electricity.

Chemical properties

1. *With air.* Lead tarnishes quickly in air by acquiring a thin layer of hydroxide and carbonate. This protects it from further attack, so that the change remains superficial.

If heated just above its melting-point (600 K), lead oxidizes to a yellow form of its oxide, PbO, known as *massicot*. At a higher temperature, 670–720 K, it forms '*red lead oxide*' Pb_3O_4(see p. 197).

$$2Pb(l) + O_2(g) \rightarrow 2PbO(s)$$
$$6PbO(s) + O_2(g) \rightarrow 2Pb_3O_4(s)$$

2. *With water.* Pure water, free from air, does not attack lead; the presence of air, however, produces the very sparingly soluble '*lead

hydroxide'.

$$2Pb(s) + 2H_2O(l) + O_2(g) \rightarrow 2Pb(OH)_2(s)$$

If carbonate or sulphate is present in the water, insoluble lead carbonate or sulphate is precipitated, forming a protective layer, so that further attack is inhibited. From this it follows that very soft water may be unsafe when carried in lead pipes; its continuous use may produce lead poisoning. Certain farm houses in the Pennines, where the water is not only soft but slightly acid from the peat, were notorious for the incidence of lead-induced insanity in their inhabitants. Lead piping is far safer in 'hard' water areas.

3. *With acids.*

(a) *Hydrochloric acid.* This acid attacks lead only if *hot* and *concentrated*. Lead(II) chloride is insoluble in the cold. The action is rather slow unless the lead is in powder form, when it is quite rapid. The products are *hydrogen* and *lead chloride*.

$$Pb(s) + 2H^+(aq) \rightarrow Pb^{2+}(aq) + H_2(g)$$

(b) *Sulphuric acid.* This acid attacks lead only if *hot* and *concentrated* to form *lead*(II) *sulphate* and liberate *sulphur dioxide*.

$$Pb(s) + 2H_2SO_4(l) \rightarrow PbSO_4(s) + 2H_2O(l) + SO_2(g)$$

(c) *Nitric acid.* Very pure nitric acid (almost water-free) is said not to attack lead. Any other concentration of the acid attacks the metal, more vigorously with rise of temperature and increase of concentration. The products are *lead*(II) *nitrate* and *oxides of nitrogen*. No single equation can be written for the reaction. Lead is also attacked by organic acids, such as ethanoic acid, especially in the presence of air, e.g.

$$Pb(s) + 2CH_3COOH(l) + \tfrac{1}{2}O_2(g) \rightarrow Pb(CH_3COO)_2(aq) + H_2O(l)$$

4. *With alkalis.* Lead is attacked by alkalis only very slowly in hot concentrated solution to give hexahydroxoplumbate(II).

$$Pb(s) + 4OH^-(aq) + 2H_2O(l) \rightarrow [Pb(OH)_6]^{4-}(aq) + H_2(g)$$

Compounds of lead

Lead forms two sets of compounds, the lead(II) series (usually called simply *lead* compounds) in which the oxidation state of lead is +2, and the *lead*(IV) series in which the oxidation state of lead is +4.

In the lead(II) series, lead acts as a typical *metal* and the compounds are ionic, e.g. $PbSO_4$, $PbCl_2$.

In the lead(IV) series, lead shows *non-metallic* behaviour, resembling that of the earlier members of Group IV, carbon and silicon. Lead(IV) compounds are usually *covalent*, e.g. PbO_2, $PbCl_4$.

Lead(II) oxide, (plumbous oxide), PbO, and 'lead(II) hydroxide', $Pb(OH)_2$

Lead(II) hydroxide is precipitated when ammonia or aqueous caustic alkali (not in excess) is added to a solution of a lead(II) salt, such as lead(II) nitrate or lead(II) ethanoate.

$$Pb^{2+}(aq) + 2OH^-(aq) \rightarrow Pb(OH)_2(s)$$

It is a white, gelatinous solid, most probably a hydrated oxide, which decomposes if heated to about 420 K, leaving the yellow solid, *lead*(II) *oxide* or *litharge*. Lead(II) oxide is more basic than any other oxide of a Group IV element but is still amphoteric. It dissolves readily in those acids which give a soluble lead salt (e.g. nitric acid). It slowly dissolves in alkalis to give hydroxoplumbates(II).

$$PbO(s) + 2H^+(aq) \rightarrow Pb^{2+}(aq) + H_2O(l)$$
$$PbO(s) + 4OH^-(aq) + H_2O(l) \rightarrow [Pb(OH)_6]^{4-}(aq)$$

Preparation

If lead is heated to a temperature not much above its melting-point (601 K), it oxidizes to the *massicot* form of lead(II) oxide. This is yellow. If heated to fusion and then cooled and ground, the more orange-coloured *litharge* is formed.

The above methods are quite unsuitable for laboratory use. In the laboratory, litharge is formed by the general methods given on p. 282.

Litharge is slightly soluble in water, giving a faintly alkaline reaction to it by the reaction: $PbO(s) + H_2O(l) \rightleftharpoons Pb^{2+}(aq) + 2OH^-(aq)$. Because of this equilibrium, litharge shows the *amphoteric* characteristics of 'lead hydroxide' considered above.

Reduction of litharge

Litharge is readily reduced to metallic lead if *heated* with a variety of reducing agents, as below:

$$PbO(s) + H_2(g) \rightarrow Pb(s) + H_2O(l)$$
$$PbO(s) + C(s) \rightarrow Pb(s) + CO(g)$$
$$PbO(s) + CO(g) \rightarrow Pb(s) + CO_2(g)$$

Uses of litharge

Litharge has quite a variety of uses, among them being:
(a) The manufacture of optical glass.
(b) As a drier for paint and varnish.
(c) Filling the grids in the lead accumulator.

Dilead(II) lead(IV) oxide (red lead oxide), Pb_3O_4

Red lead oxide is also known as *triplumbic tetraoxide*, *minium*, or simple *red lead.*

Manufacture

Red lead oxide is made by heating the *massicot* form of lead(II) oxide (not litharge) in air for some hours at a temperature of 670–720 K. The product finally turns black while hot, but cools to a brilliant scarlet colour, as red lead.

$$6PbO(s) + O_2(g) \rightleftharpoons 2Pb_3O_4(s)$$

If heated to a higher temperature, the red lead oxide is decomposed and *litharge* is left. This material does *not* readily convert to red lead oxide again.

Red lead oxide is probably not a true oxide, but a salt. It operates, for most purposes, as a mixture of lead(II) oxide and lead(IV) oxide, $2PbO.PbO_2$. This suggests that it is the *lead*(II) salt of '*ortho-plumbic acid*', H_4PbO_4, i.e. the compound $Pb_2.PbO_4$. It is, in fact, formed by mixing a lead(II) salt and a plumbate(IV) in solution.

By the action of warm, dilute nitric acid, red lead oxide is converted to lead(IV) oxide, PbO_2. It resembles this compound so closely in its reactions that it is convenient to take them together. For this, see p. 201.

Uses of red lead oxide

(a) Red lead oxide is used in making glazes and optical glass.
(b) It is used in cementing joints in pipes.
(c) It is used as the oxidizing agent in matches and in driers (i.e. oxidizing agents) for varnish.
(d) Red lead oxide is used in pasting the plates of lead accumulators.
(e) It is used as a constituent of protective paint, especially for iron and steel.

Insoluble salts of lead

Lead is well known for the insolubility of most of its salts. If a high concentration of lead ion is wanted in solution, *lead ethanoate* is the only common compound which can provide it (solubility 46 g in 100 g water at 288 K).

The insoluble salts shown below are precipitated by mixing a *solution* of lead(II) nitrate or ethanoate with a *solution* of a compound containing the other ion shown in each case.

Lead(II) chloride

e.g.

$$Pb(NO_3)_2(aq) + 2HCl(aq) \rightarrow PbCl_2(s)\downarrow + 2HNO_3(aq)$$

In the simplest ionic terms, this becomes:

$$Pb^{2+}(aq) + 2Cl^-(aq) \rightarrow PbCl_2(s)$$

The precipitated lead(II) chloride is white. It is sparingly soluble in cold water (0.67 g in 100 g water at 273 K) and considerably more soluble in boiling water (3.34 g in 100 g of water at 373 K). When the hot solution cools, fine needle-like crystals are formed.

Lead(II) chloride is more soluble in concentrated hydrochloric acid than in water. This arises from the formation of a complex ion.

$$PbCl_2(s) + 2Cl^-(aq) \rightleftharpoons PbCl_4{}^{2-}(aq)$$

Lead(II) chloride is not a reducing agent and so shows a marked difference from tin(II) chloride. This can be accounted for in terms of the inert pair effect (see p. 9). Lead(II) chloride is essentially ionic in character.

Lead(II) sulphate

e.g.

$$Pb(NO_3)_2(aq) + H_2SO_4(aq) \rightarrow PbSO_4(s) + 2HNO_3(aq)$$

The precipitated lead(II) sulphate is white. It is insoluble in both hot and cold water.

Lead(II) chromate

e.g.

$$Pb(NO_3)_2(aq) + \underset{\substack{\text{potassium}\\\text{chromate(VI)}}}{K_2CrO_4(aq)} \rightarrow PbCrO_4(s) + 2KNO_3(aq)$$

Lead(II) chromate(VI) is a bright yellow solid. It is used in identifying lead in Group I of the usual tables for Qualitative Analysis. Lead chromate(VI) is used as the yellow pigment, *chrome yellow*; if boiled with caustic alkali solution, it is converted to a basic chromate(VI), $Pb_2(OH)_2CO_4$, used as *chrome red*.

Lead(II) iodide

e.g.

$$Pb(NO_3)_2(aq) + 2KI(aq) \rightarrow PbI_2(s) + 2KNO_3(aq)$$

The precipitate of lead(II) iodide is bright yellow in colour. Like lead(II) chloride, it is considerably more soluble in hot water than in cold. When crystallizing slowly from cooling solutions of suitable concentration, it forms very thin, crystalline plates, which appear as coloured spangles by optical interference effects. Though bright yellow in colour as solid, lead iodide forms a colourless solution.

Lead(II) carbonate

If the *normal* carbonate is wanted, sodium hydrogencarbonate is used as precipitating agent in solution. With lead(II) nitrate solution:

$$Pb^{2+}(aq) + 2HCO_3^-(aq) \rightarrow PbCO_3(s) + H_2O(l) + CO_2(g)$$

Sodium carbonate solution precipitates a *basic* carbonate. '*White lead*' is the usual product.

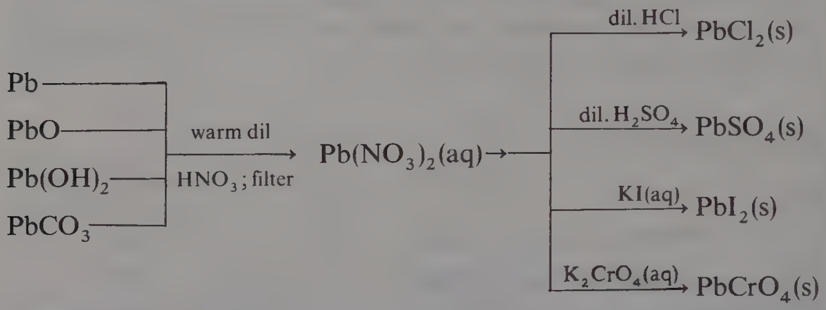
$$3Pb^{2+}(aq) + 2OH^-(aq) + CO_3^{2-}(aq) \rightarrow Pb_3(OH)_2(CO_3)_2(s)$$

A considerable OH^- concentration is available by hydrolysis of the sodium carbonate in solution.

In all cases, the product precipitated may be filtered off, washed with cold distilled water and dried.

In connection with these preparations, it should be noted that, if an *insoluble* starting material is to be converted into an *insoluble* product, the conversion should not be attempted in one stage. The reason is that the insoluble product will usually precipitate on to the starting material and prevent completion of the reaction. Instead, the starting material should be converted to a *soluble* intermediary (usually a nitrate), and from this, in solution, the final product can be precipitated.

For example, to prepare lead(II) sulphate (insoluble) from lead(II) carbonate (insoluble), the direct action of dilute sulphuric acid is quite unsatisfactory. The lead(II) sulphate would precipitate on the carbonate and stop the action. Instead the following scheme, generalized to include other cases, should be followed:



A similar case is:

$$CaCO_3(s) \xrightarrow{\text{as above}} Ca(NO_3)_2(aq) \xrightarrow{\text{dil. } H_2SO_4} CaSO_4(s)$$

Basic lead(II) carbonate, 'white lead', $Pb(OH)_2.2PbCO_3$

This material is an important white pigment in the paint trade. It has good covering power when applied to a surface and can be used with coloured materials. It has the disadvantages of being poisonous, especially to children, and of turning brown in a town atmosphere containing traces of hydrogen sulphide; dark brown lead(II) sulphide is formed.

'White lead' can be precipitated by the action of sodium carbonate solution on a solution of a soluble lead(II) salt such as the nitrate. Its manufacture as a pigment is a complex process, and will not be considered here.

Lead(II) nitrate, $Pb(NO_3)_2$

Lead(II) nitrate can be made by standard methods, e.g. by the action of lead, its oxide, hydroxide or carbonate with hot, dilute nitric acid. Excess of the solid reagent is filtered off, the liquid concentrated by evaporation and cooled. The white crystals which separate are filtered, washed with cold distilled water and dried, e.g.

$$PbCO_3(s) + 2HNO_3(aq) \rightarrow Pb(NO_3)_2(aq) + H_2O(l) + CO_2(g)$$

Lead(II) nitrate is less soluble in water than most nitrates (39 g in 100 g water at 273 K). It crystallizes anhydrous. This is why it is often used to make nitrogen dioxide by the action of heat.

$$2Pb(NO_3)_2(s) \rightarrow 2PbO(s) + 4NO_2(g) + O_2(g)$$

Other heavy metal nitrates behave similarly, but the products would contain the water of crystallization present in most of them.

Lead(II) sulphide, PbS

Lead(II) sulphide occurs as the important ore, *galena*. In the laboratory, it is usually precipitated by passing hydrogen sulphide through a hot solution of lead(II) chloride, acidified with dilute hydrochloric acid. An intermediate precipitate of composition $PbS.PbCl_2$ may be formed, but is converted to dark brown lead(II) sulphide by more hydrogen sulphide.

$$H_2S(aq) \rightleftharpoons 2H^+(aq) + S^{2-}(aq)$$
$$Pb^{2+}(aq) + S^{2-}(aq) \rightarrow PbS(s)$$

Lead(II) sulphide differs from tin(II) sulphide in being insoluble in yellow ammonium sulphide solution.

Lead(II) sulphide is oxidized by hydrogen peroxide solution to *lead*(II) *sulphate* and so turns from dark brown to white.

$$PbS(s) + 4H_2O_2(aq) \rightarrow PbSO_4(s) + 4H_2O(l)$$

This is the reaction used in the restoration of paintings turned dingy by the action of hydrogen sulphide in town atmospheres.

Lead(IV) oxide (lead dioxide), PbO_2

Preparation

(a) Red lead oxide is shaken into hot, dilute nitric acid with excess of the acid always present so that red lead oxide cannot be left in the precipitate. A dark brown precipitate of lead(IV) oxide is formed.

$$Pb_3O_4(s) + 4HNO_3(aq) \rightarrow PbO_2(s) + 2Pb(NO_3)_2(aq) + 2H_2O(l)$$

It is filtered off, washed well with hot, distilled water and allowed to dry.

(Notice that *nitric* acid is the only one of the mineral acids that is suitable for use in this preparation. The reason is that, if hydrochloric or sulphuric acid is used, lead(II) chloride or sulphate will *precipitate* with lead(IV) oxide and be difficult to remove.)

(b) Bleaching powder is shaken with water for a time and the mixture is filtered. The clear liquid contains *calcium chlorate*(I) (*hypochlorite*) and *lime*. This liquid is added to a solution of lead ethanoate (or nitrate) and the mixture is heated. Lead(IV) oxide precipitates as a dark brown powder. It is purified as before.

$$Pb^{2+}(aq) + 2OH^-(aq) + OCl^-(aq) \rightarrow PbO_2(s) + H_2O(l) + Cl^-(aq)$$

If lead (or lead(II) oxide) is specified as starting material for making lead(IV) oxide, it should be converted to lead(II) nitrate (p. 200) and the nitrate used as above.

Properties of lead(IV) oxide and red lead oxide

Red lead, Pb_3O_4, usually reacts as if it had the composition $PbO_2.2PbO$. A systematic name is *dilead*(II) *lead*(IV) *oxide*. Consequently, it resembles lead(IV) oxide closely in its reactions and the two are conveniently considered together, as below.

1. *With hydrochloric acid. If warmed* with *concentrated* hydrochloric acid, lead(IV) oxide oxidizes the acid to *chlorine* and leaves a *white precipitate* of *lead*(II) *chloride.*

$$PbO_2(s) + 4HCl(conc.aq.) \rightarrow PbCl_2(s) + 2H_2O(l) + Cl_2(g)$$

Red lead oxide behaves similarly.

$$Pb_3O_4(s) + 8HCl(conc.aq.) \rightarrow 3PbCl_2(s) + 4H_2O(l) + Cl_2(g)$$

2. *With sulphuric acid.* If *heated* with *concentrated* sulphuric acid, lead(VI) oxide evolves *oxygen* and turns to a *white* solid, *lead sulphate.*

$$2PbO_2(s) + 2H_2SO_4(l) \rightarrow 2PbSO_4(s) + 2H_2O(l) + O_2(g)$$

Red lead oxide behaves similarly.

$$2Pb_3O_4(s) + 6H_2SO_4(l) \rightarrow 6PbSO_4(s) + 6H_2O(l) + O_2(g)$$

3. *The action of heat.* When heated, lead(IV) oxide evolves *oxygen* and leaves *lead*(II) *oxide* (*litharge*).
The litharge is dark brown while hot but turns *yellow* when cold.

$$2PbO_2(s) \rightarrow 2PbO(s) + O_2(g)$$

Red lead oxide behaves similarly, turning black before decomposing.

$$2Pb_3O_4(s) \rightarrow 6PbO(s) + O_2(g)$$

Lead(IV) oxide is a *covalent* compound, O═Pb═O. It is not a salt of hydrogen peroxide (like $Ba^{2+}.O_2^{2-}$) and does not yield hydrogen peroxide by the action of a dilute acid.

Acidic properties of lead(IV) oxide

Lead(IV) oxide is insoluble in water and gives no acidic reaction when mixed with it. It shows acidic tendencies, however, by forming *potassium* *hydroxoplumbate*(IV) in solution when heated with fused potassium hydroxide. The reaction can be approximately represented as:

$$PbO_2(s) + 2OH^-(aq) + 2H_2O(l) \rightarrow [Pb(OH)_6]^{2-}(aq)$$

Here, lead, when in the +4 oxidation state, is shown acting as a *non-metal* with an *acidic* oxide. Lead(IV) oxide is also soluble to a slight extent in concentrated nitric or sulphuric acid. The oxide is therefore somewhat amphoteric; but it does not react readily with either acids or alkalis.

Lead(IV) oxide as an oxidizing agent

The reaction quoted above in which chlorine is liberated from hot, concentrated hydrochloric acid is an oxidizing action of lead(IV) oxide.

Sulphur dioxide combines with warm lead(IV) oxide, causing it to glow with the energy of the reaction and leave a *white* deposit of *lead*(II) *sulphate*.

$$PbO_2(s) + SO_2(g) \rightarrow PbSO_4(s)$$

This is equivalent to the oxidation of SO_2 to SO_3 and the subsequent combination of the trioxide with lead(II) oxide, as:

$$PbO_2(s) + SO_2(g) \rightarrow PbO(s) + SO_3(g)$$
$$PbO(s) + SO_3(g) \rightarrow PbSO_4(s)$$

Lead(IV) oxide can be used as the oxidizing agent in matches. Lead(IV) oxide will ignite a jet of hydrogen sulphide gas. This behaviour should be contrasted with that of tin(IV) oxide. The difference is attributed to the inert pair effect (see p. 9).

The lead accumulator

The lead accumulator contains an anode and a cathode, both of which are grids made of lead or a lead antimony alloy. The interstices of the grids contain lead compounds varying in composition according to the state of charge of the cell, as indicated below. The electrolyte is sulphuric acid.

At the state of *discharge*, the anode and cathode grids are both impregnated with *lead sulphate*, $PbSO_4$. To charge the accumulator, direct current is passed at a suitable rate.

The following changes occur:

At the cathode

$$\left\{\begin{array}{l} Pb^{2+}(aq) + 2e^- \rightarrow Pb(s) \\ \quad SO_4{}^{2-} \rightarrow \text{into solution} \end{array}\right.$$

At the anode

$$\left\{\begin{array}{l} Pb^{2+} + 2H_2O(l) - 2e^- \rightarrow PbO_2(s) \\ \qquad\qquad\qquad\qquad\qquad + 4H^+(aq) \\ SO_4{}^{2-} \rightarrow \text{into solution} \end{array}\right.$$

Thus, during charge, the *cathode* acquires a deposit of *spongy lead* and the *anode* one of *lead*(IV) *oxide*. The passage of ions in the ratio of $4H^+ : 2SO_4^{2-}$ into solution increases the concentration and density of the sulphuric acid. At full charge, the accumulator constitutes a storage battery of e.m.f. slightly exceeding 2 V. The acid density is 1.25 g cm^{-3}.

It will discharge, yielding electrical energy, by the changes:

At the cathode	*At the anode*
$Pb(s) \rightarrow Pb^{2+}(aq) + 2e^-$	$PbO_2(s) + 4H^+(aq) + 2e^- \rightarrow Pb^{2+}(aq) + 2H_2O(l)$
From solution $SO_4^{2-}(aq)$	From solution $SO_4^{2-}(aq)$
$PbSO_4(s)$ deposits	$PbSO_4(s)$ deposits

Electrons discharged from lead atoms at the cathode pass round the external circuit, doing the useful electrical work required, and are absorbed at the anode. Absorption of ions in the proportion of $4H^+ : 2SO_4^{2-}$ from the solution decreases the concentration and density of the acid. The e.m.f. should become 2 V shortly after discharge begins, and remain steady for almost the whole discharge period. When it falls quickly to 1.8 V, recharge is necessary. In practice, the state of charge can be conveniently assessed by observing the density of the acid by a small hydrometer. Too full a discharge is undesirable; lead(II) sulphate then forms in so dense a mass on the plates that recharge is difficult and the cell is said to be 'sulphated'.

Lead(IV) chloride (plumbic chloride), $PbCl_4$

If concentrated hydrochloric acid is cooled in ice-salt, lead(IV) oxide slowly stirred into it, and the liquid then filtered, a bright yellow liquid will be obtained. This liquid is formed by the production of lead(IV) chloride, which then enters a complex *hexachloroplumbate*(IV) *ion* with the chloride ion of the acid.

$$PbO_2(s) + 4HCl(\text{conc.aq.}) \rightarrow PbCl_4(l) + 2H_2O(l)$$
$$PbCl_4(l) + 2Cl^-(aq) \rightarrow PbCl_6^{2-}(aq)$$

A similar solution is formed by passing chlorine into a mixture of lead(II) chloride and concentrated hydrochloric acid, immersed in ice-salt.

$$PbCl_2(s) + Cl_2(g) + 2Cl^-(\text{conc.aq.}) \rightarrow PbCl_6^{2-}(aq)$$

The liquid behaves like lead(IV) chloride by liberating *chlorine* when gently warmed and precipitating *lead*(II) *chloride* as a white solid.

$$PbCl_4(l) \rightarrow PbCl_2(s) + Cl_2(g)$$

If a concentrated solution of ammonium chloride is added to it, it gives an immediate pale yellow precipitate of *ammonium hexachloroplumbate*(IV).

$$2NH_4^+(\text{conc.aq.}) + PbCl_6^{2-}(aq) \rightarrow (NH_4)_2PbCl_6(s)$$

This compound, cooled in ice-salt, and treated gradually with concentrated sulphuric acid, yields *lead*(IV) *chloride* as a heavy *yellow* liquid, rather oily in appearance.

$$PbCl_6^{2-} + 2H^+(\text{conc.aq.}) \rightarrow PbCl_4(l) + 2HCl(g)$$

Lead(IV) chloride is *covalent*. It is a non-electrolyte when pure and is hydrolysed by water.

$$PbCl_4(l) + 2H_2O(l) \rightarrow PbO_2(s) + 4HCl(g)$$

Having these properties, it is a non-metallic chloride and shows lead behaving as a *non metal* when it is in an oxidation state of +4. The chloride shows a general resemblance to $SiCl_4$. The properties of lead(IV) chloride should be compared with those of lead(II) chloride (p. 198).

Lead hydride and its derivatives

In the direction C → Si → Ge → Sn → Pb, the non-metallic nature of the elements of Group IV is decreasing. Lead is, therefore, the least likely of these elements to form a stable hydride. Only one hydride of lead is known—*plumbane*, PbH_4. It is extremely unstable and decomposes to its elements very rapidly. Organic derivatives of lead hydride are, however, known. The most important of them is *tetraethyllead*(IV), $Pb(C_2H_5)_4$, which is used as a petrol additive. The compound can be made by heating an alloy of lead and sodium in chloroethane vapour.

$$Pb(s) + 4Na(s) + 4C_2H_5Cl(g) \rightarrow Pb(C_2H_5)_4(l) + 4NaCl(s)$$

It is a liquid (boiling point 471 K) and is poisonous. It is added to petrol to control the explosion of petrol vapour and air. It corrects any tendency to pre-ignition and 'knocking' in the engine, but the emission of lead compounds into the environment in exhaust fumes may cause pollution problems. In many countries, the amounts of lead in petrol is controlled by law, and there is considerable pressure from environmental groups to reduce the quantity further.

A covalent compound of this type illustrates again the tendency of lead in its +4 oxidation state to show non-metallic characteristics.

Detection of lead

Lead is precipitated as its sparingly soluble chloride and so appears in Group I of the usual tables of Qualitative Analysis. This chloride is separated from accompanying silver chloride and mercury(I) chloride by its considerable solubility in boiling water, and lead is then identified by precipitation of its *yellow chromate*(VI) with potassium chromate(VI) solution.

Lead is usually determined by precipitation and weighing of its insoluble sulphate.

Comparison and summary of properties of the elements of Group IV

Element	C	Si	Ge	Sn	Pb
Relative atomic mass	12.01	28.09	72.59	118.7	20.72
Melting point (K)	4000 (sublimes) as graphite	1680	1210	505	600
Boiling point (K)	5100 (graphite)	2630	3100	2540	2017
Density (g cm^{-3})	2.25 (graphite) 3.51 (diamond)	2.33	5.35	7.28 (white) 5.75 (grey)	11.3
Electronegativity (Pauling scale)	2.5	2.0	1.8	1.8	1.8
Oxidation states (less common in brackets)	(2), 4	(2), 4	2, 4	2, 4	2, 4
Hydrides	CH_4 and many other hydrocarbons	SiH_4 and several other silanes, Si_nH_{2n+2}	GeH_4 and several other germanes, Ge_nH_{2n+2}	SnH_4 stannane	PbH_4 plumbane
Thermal stability of hydride, XH_4	Very stable	Moderately stable	Decomposes on heating	Decomposes on gentle heating	Very unstable at room temperature
Oxides, and nature of oxides	CO CO_2 } gaseous; acidic C_3O_2 + several others	SiO solid; unstable SiO_2 solid; acidic	GeO solid; amphoteric GeO_2 solid; acidic	SnO solid; amphoteric; oxidizes in air. SnO_2 solid; amphoteric	PbO solid; amphoteric but predominantly basic. PbO_2 solid; amphoteric; powerful oxidizing agent Pb_3O_4 solid; a 'mixed' oxide
Chlorides, and nature of chlorides	CCl_4 liquid; unaffected by water. + other chlorocarbons	$SiCl_4$ liquid; rapidly hydrolysed by water	$GeCl_2$ solid; hydrolysed by water. $GeCl_4$ liquid; hydrolysed by water	$SnCl_2$ solid; partly ionic; slowly hydrolysed by water. $SnCl_4$ liquid; fumes in moist air; soluble in organic solvents	$PbCl_2$ solid; ionic; insoluble in cold water, soluble in hot water. $PbCl_4$ liquid; hydrolysed by water

Questions

1. Give a brief account of *two* methods for the laboratory perparation of carbon monoxide. How, and in what conditions, does this gas react with (a) chlorine, (b) nickel, (c) oxygen, and (d) in a reducing action? Can this gas be considered to be an acidic anhydride? Give your reasons.

2. State in outline *one* method by which amorphous silicon may be prepared. Compare the behaviour of silicon and carbon (graphite) with (a) oxygen, (b) chlorine, (c) hydrogen chloride, (d) caustic alkali.

3. Outline the extraction of lead from galena. Starting from metallic lead, how would you prepare (a) lead(II) nitrate, (b) lead(II) iodide, both in a state of reasonable purity?

4. By considering the behaviour of the elements, their oxides, chlorides and hydrides (if any), examine the statement that in Group IV of the Periodic Table (C, Si, Ge, Sn and Pb), increase of atomic mass brings a change from non-metallic to metallic nature in the elements.

5. Write an account of the common oxides of the Group IV elements carbon, silicon, tin, and lead, referring especially to their structure, physical properties and acid-base behaviour.
Mention *two* characteristics which you would expect germanium dioxide, GeO_2, to possess, remembering that germanium comes between silicon and tin in Group IV. (L.)

6. This question concerns the elements carbon, silicon, tin, and lead.
(a) Give one method in each case for the preparation of the monoxides of *two* of the elements and the dioxides of the other *two* elements.
(b) Explain why (i) silicon tetrachloride is readily hydrolysed by water, but carbon tetrachloride is not, (ii) lead forms the Pb^{2+} ion but carbon does not form the C^{2+} ion.
(c) Compare the reactions of (i) tin and lead with chlorine, (ii) carbon and lead with nitric acid. (A.E.B.)

7. Give *one* method in each case for the preparation of the tetrachlorides of carbon and lead. Compare and explain the reactions of these compounds with water.
Give the structures of the dioxides of carbon and lead.
Explain why
(a) carbon will form chain compounds but lead will not;
(b) carbon is more electronegative than lead;
(c) the principal valency of carbon is 4 but that of lead is 2. (A.E.B.)

8. (a) *Outline* the preparation of
  (i) the dioxides of carbon and silicon,
  (ii) the tetrachlorides of carbon and silicon.
(b) How do the electronic structures of the elements carbon and silicon (atomic numbers C = 6, Si = 14) and the structures of the dioxides and tetrachlorides help to explain that, at ordinary temperature and pressure,
  (i) carbon dioxide is a gas, whilst silicon (IV) oxide (silicon dioxide) is a solid of high melting point,
  (ii) Tetrachloromethane (carbon tetrachloride) does not react with water, whilst silicon tetrachloride reacts vigorously with cold water giving steamy fumes and a gelatinous precipitate?

(c) For the systems

$$\mathrm{Sn^{4+}(aq) + 2e^- \rightleftharpoons Sn^{2+}(aq)}; \quad E^\ominus = +0.15\ \mathrm{V}$$

and

$$\mathrm{PbO_2(s) + 4H^+(aq) + 2e^- \rightleftharpoons Pb^{2+}(aq) + 2H_2O(l)}; \quad E^\ominus = +1.46\ \mathrm{V}$$

state, with an explanation, which of the following reactions is more likely to occur,

(i) $\mathrm{PbO_2(s) + 4H^+(aq) + Sn^{2+}(aq) \rightarrow Pb^{2+}(aq) + Sn^{4+}(aq) + 2H_2O(l)}$
(ii) $\mathrm{Sn^{4+}(aq) + Pb^{2+}(aq) + 2H_2O(l) \rightarrow Sn^{2+}(aq) + PbO_2(s) + 4H^+(aq)}$
(A.E.B.)

8

Elements of Group V

Group V of the Periodic Table contains the elements nitrogen, phosphorus, arsenic, antimony, and bismuth. Nitrogen and phosphorus are strongly non-metallic in type; as relative atomic masses increase, there is the usual development by which metallic tendencies increase, too. These tendencies appear only slightly in arsenic and more strongly in antimony, while bismuth is almost as metallic as lead. The principal oxidation numbers of all elements of the group are *three* and *five*.

Nitrogen

Atomic number 7; electron arrangement 2.5($1s^2 2s^2 2p^3$)
Nitrogen has isotopes of mass number in order of abundance, 14 and 15; relative atomic mass 14.01

Occurrence of nitrogen

Nitrogen occurs in vast quantities near the surface of the Earth. As the *free element*, it comprises almost four-fifths of the atmosphere by volume. This represents a mass of nitrogen of about 4×10^{15} tonnes.

Nitrogen occurs combined in Chile saltpetre, $NaNO_3$, and in all living organisms, being a constituent of proteins.

Preparation of nitrogen

(1) *From the atmosphere*

A preparation of what is usually called *atmospheric nitrogen* can be made by the apparatus shown in Figure 8.1. Air is forced out of the bottle by a stream of tap water; sodium hydroxide solution absorbs carbon dioxide

$$2OH^-(aq) + CO_2(g) \rightarrow CO_3{}^{2-}(aq) + H_2O(l)$$

and red-hot copper in the combustion tube absorbs oxygen.

$$2Cu(s) + O_2(g) \rightarrow 2CuO(s)$$

In Figure 8.1, the residual nitrogen is collected over water. If required dry, it could be passed through a U-tube of anhydrous calcium chloride after leaving the combustion tube and collected, on a small scale, over mercury.

The gas prepared in this way still contains about 1 per cent by volume of the noble gases, principally argon. If wanted free from noble gases, the nitrogen prepared as above could be absorbed by heated magnesium to form magnesium nitride, Mg_3N_2. Ammonia could be liberated from the nitride by the action of water.

$$Mg_3N_2(s) + 6H_2O(l) \rightarrow 3Mg(OH)_2(s) + 2NH_3(g)$$

The ammonia could then be oxidized to nitrogen by passage over red-hot copper(II) oxide. For a suitable apparatus, see *ammonia* later in the present chapter.

$$3CuO(s) + 2NH_3(g) \rightarrow 3Cu(s) + 3H_2O(g) + N_2(g)$$

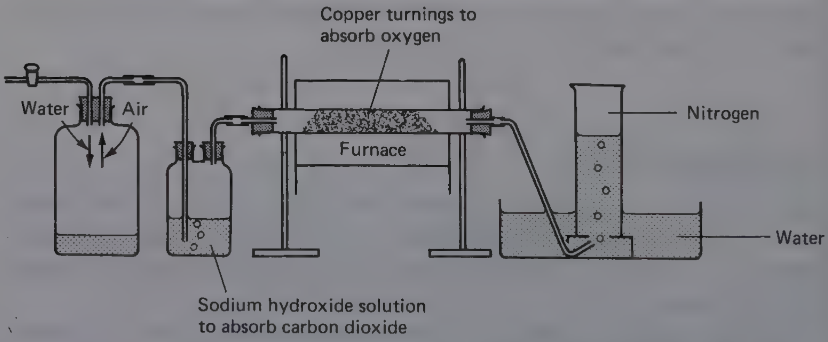


Figure 8.1 *Preparation of atmospheric nitrogen*

(2) *Preparation of nitrogen from chemical sources*

(a) In the laboratory, nitrogen is usually prepared by heating an aqueous solution of *ammonium nitrite.*

$$NH_4^+(aq) + NO_2^-(aq) \rightarrow N_2(g) + 2H_2O(l)$$

In practice, *sodium nitrite* and *ammonium chloride* are used in approximately equimolar proportions.

17 g sodium nitrite and 14 g ammonium chloride in 350 cm^3 water is a suitable solution, used in the apparatus of Figure 8.2.

The reaction is started by slight warming and then usually increases, without further heating, to a very rapid rate. If wanted purer, the gas should be passed in turn through (i) strong alkali solution to remove any acidic gas or chlorine; (ii) through concentrated sulphuric acid to remove ammonia (and water vapour); (iii) over heated copper to decompose any oxides of nitrogen, e.g.

$$2Cu(s) + 2NO(g) \rightarrow 2CuO(s) + N_2(g)$$

It should then be dried by concentrated sulphuric acid and collected by upward delivery, or, on a small scale, over mercury.

(b) *Ammonium dichromate*(VI) decomposes almost explosively when heated to liberate nitrogen, leaving a green solid residue of chromium(III) oxide.

$$(NH_4)_2Cr_2O_7(s) \rightarrow Cr_2O_3(s) + 4H_2O(g) + N_2(g)$$

In a preparation, the ammonium dichromate(VI) should be diluted with three or four times its bulk of dry sand (to moderate the action) and heated in the apparatus above. The gas can be purified, if required, on the same lines as in the earlier preparation. Ammonium

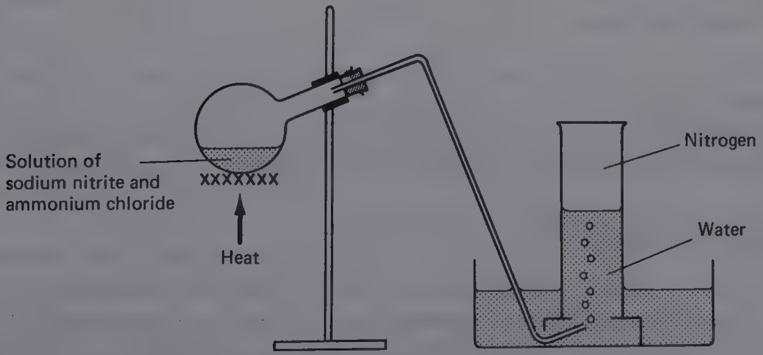


Figure 8.2 *Preparation of nitrogen*

dichromate(VI) is, however, much more expensive than the materials used in the previous method.

Other reactions which yield nitrogen, but are much less suitable for laboratory use, are:

(c) The action of ammonia with copper(II) oxide at red heat.

$$3CuO(s) + 2NH_3(g) \rightarrow 3Cu(s) + 3H_2O(g) + N_2(g)$$

(d) The action of chlorine with ammonia solution.

$$8NH_3(aq) + 3Cl_2(g) \rightarrow 6NH_4Cl(aq) + N_2(g)$$

In this reaction, *excess of chlorine can be very dangerous*, producing the violently explosive nitrogen trichloride by the further reaction:

$$NH_4Cl(aq) + 3Cl_2(g) \rightarrow NCl_3(l) + 4HCl(g)$$

(e) The action of copper at red heat with an oxide of nitrogen, e.g.

$$Cu(s) + N_2O(g) \rightarrow CuO(s) + N_2(g)$$

Industrial preparation of nitrogen

Nitrogen is extracted by the fractional distillation of liquid air. Oxygen and nitrogen differ in boiling point by about 13 K (oxygen 90 K, nitrogen 77 K). Nitrogen is the more volatile of the two and, with efficient fractionating columns, the two gases can both be obtained in reasonable purity. They are stored under pressure in steel cylinders.

A great deal of nitrogen is used in the manufacture of ammonia by Haber's process. See later in the present chapter for an account of this.

Properties of nitrogen

Physical properties

Nitrogen is a colourless gas with no smell. It is only slightly soluble in water (about 0.02 cm^3 in 1 cm^3 water at room temperature). Its boiling point is 77 K at 1 atm. Nitrogen is not actively poisonous, but, if mixed with insufficient oxygen, causes death of animals by suffocation.

Chemical properties

Nitrogen is usually described as an *inert* element, but this adjective can be properly applied to its character only in the neighbourhood of room temperature. At high temperature, it gives quite a variety of reactions as shown below. Before it can react, the gas probably has to dissociate into single atoms. This requires the disruption of three covalent bonds per molecule, a process in which considerable absorption of heat occurs, as:

$$N{\equiv}N(g) \rightarrow 2N(g) \qquad \Delta H = +944 \text{ kJ mol}^{-1}$$

Consequently, the nitrogen molecule shows a high order of stability unless the necessary thermal energy is supplied.

Unlike the other elements in Group V, nitrogen cannot have more than eight electrons in its outer energy level. (This is a property common to the first element in any Group of the Periodic Table.) As a result, the maximum number of covalent bonds which can be formed by nitrogen is four, e.g. in NH_4^+.

1. *With metals.* Nitrogen combines with many metals at red heat or higher temperature, forming the corresponding *nitride*, e.g.

$$3Mg(s) + N_2(g) \rightarrow Mg_3N_2(s)$$
$$3Ca(s) + N_2(g) \rightarrow Ca_3N_2(s)$$
$$2Al(s) + N_2(g) \rightarrow 2AlN(s)$$
$$6Li(s) + N_2(g) \rightarrow 2Li_3N(s)$$

Consequently, all these metals form an oxide–nitride mixture when burnt in air; this mixture yields *ammonia* when wetted and warmed, e.g.

$$Mg_3N_2(s) + 6H_2O(l) \rightarrow 3Mg(OH)_2(s) + 2NH_3(g)$$

2. *With non-metals.* Nitrogen combines with a number of non-metals, at red heat or higher temperature, to produce a *nitride*, e.g. with silicon and boron.

$$2B(s) + N_2(g) \rightarrow 2BN(s)$$
$$6Si(s) + 4N_2(g) \rightarrow 2Si_3N_4(s)$$

Similarly, above 1300 K, nitrogen combines with oxygen to give *nitrogen oxide* (*nitric oxide*).

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$$

At 3300 K, the equilibrium mixture contains about 5 per cent of nitrogen oxide by volume. This was the basis of the (now obsolete) arc processes of manufacture of nitric acid.

3. *With calcium dicarbide.* At red heat, under about 2 atm. pressure, nitrogen reacts with calcium dicarbide to produce *calcium cyanamide* $CaCN_2$.

$$CaC_2(s) + N_2(g) \rightarrow CaCN_2(s) + C(s)$$

This is an important fertilizer (*nitrolim*).

The Nitrogen Cycle

Nitrogen, in combined form, is necessary to the life of both plants and animals. They participate, together with natural phenomena, in a complicated inter-relationship called the *Nitrogen Cycle*. The following are the essentials of it.

Consider a piece of land on which vegetable matter grows, with no interference from man or animals. In a given season, the plants grow, extracting nitrogen from the soil as nitrate, and incorporating it into their tissues. At the end of the season, they die and decay. Bacterial action puts back much of the nitrogen into the soil as *ammonium* compounds. Bacteria in the soil use oxygen of the air to convert these to *nitrates* for use by the next generation of plants. Some nitrogen is lost by escaping into the air as free nitrogen. This loss may be compensated by electrical effects in the atmosphere (lightning, auroral discharges), which combine the oxygen and nitrogen of the air into compounds which are later washed into the soil. Further, certain plants, such as peas, beans, clover, lupins, vetches (i.e. the leguminosae), enrich the soil in nitrogen compounds. They do this by harbouring, on their roots, colonies of bacteria which can 'fix' the free nitrogen of the air as nitrogen compounds, which spread into the soil after the death of the plants. The balance of these processes is such that the land will probably be slowly enriched, season by season, in combined nitrogen. Such, more or less, was the condition of the North American prairie before the advent of Europeans.

Animals may intervene by consuming the plants. This denudes the soil of nitrogen, but the excreta of the animals, and their ultimate death and decay, restore the nitrogen to the soil.

Man may interfere in a much more serious way by removing crops and consuming them, perhaps thousands of miles from their source. Further, human excreta is disposed of by sanitation in such a way that, in many of the more industrialized areas at least, little of its nitrogen is returned to the soil. Since the average human adult excretes nitrogen to the extent of about 30 g of carbamide (urea), CON_2H_4, per day, it will be seen that the loss is enormous, all of it being derived, in the last resort, from the soil. If this nitrogen is not replaced, the soil will slowly lose fertility and produce poorer crops.

The principal sources of replenishment of nitrogen are:

(a) ammonium sulphate (see p. 217);
(b) natural deposits, e.g. Chile saltpetre, $NaNO_3$;
(c) 'fixation' of atmospheric nitrogen in compounds by manufacture, e.g. (i) Haber's process for ammonia (see p. 216), (ii) the manufacture of calcium cynamide (p. 213);
(d) animal excreta.

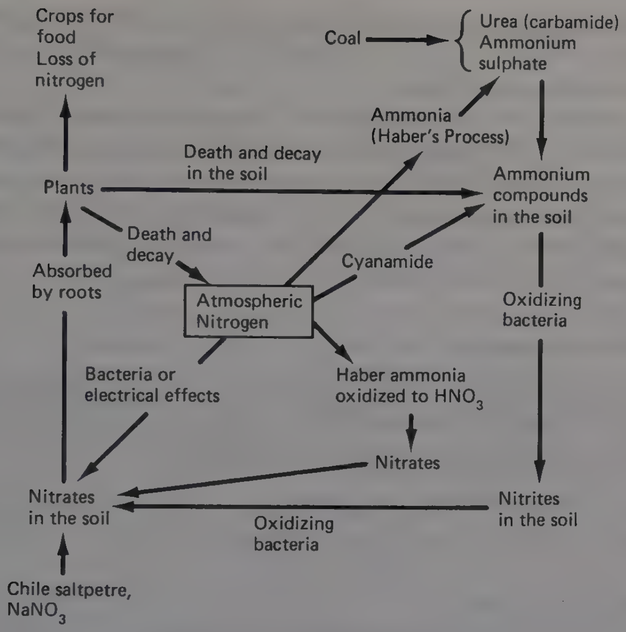


Figure 8.3 *The nitrogen cycle*

The third of these sources has outgrown all the others in the course of the present century.

It will be noticed that *free* nitrogen cannot be utilized by plants, except in the indirect and limited way mentioned above for the leguminous plants. Almost any form of nitrogen compound (provided it is not actually poisonous) can, however, be made use of by plants, e.g. ammonium compounds, carbamide (urea), cyanamides, nitrates, nitrites. This is because a variety of bacteria in the soil can operate on these compounds and convert them, usually by hydrolysis or oxidation, or a combination of these, to nitrates, which the plant can then absorb in solution by its roots. The process of converting atmospheric nitrogen into such compounds by manufacturing process is called *fixation of nitrogen.*

The scheme just described is usually expressed by a diagram, of which Figure 8.3 is a simplified form.

Fixation of nitrogen

(1) *The cyanamide process*

The manufacture of calcium cyanamide was described on p. 213. The nitrogen used in the process is obtained from the air by fractional distillation of liquid air and so is 'fixed' by being brought into combination as calcium cyanamide.

The product has been widely used as a nitrogenous fertilizer under the name of *nitrolim.* Its utilization by plants depends on a complex set of reactions occurring in the soil, catalysed by bacterial action, in which ammonium ions are produced from cyanamide by the action of carbon dioxide and water. The ammonium ion is then oxidized to nitrite and nitrate, and the nitrate is taken up by the plants.

(2) *Haber's process*

Here the reaction used is direct combination of nitrogen of the air with hydrogen to produce ammonia. The production of ammonia is exothermic and accompanied by a reduction in volume

$$\begin{array}{llll} & N_2(g) + 3H_2(g) & \rightleftharpoons 2NH_3(g) & \Delta H = -92\,\text{kJ mol}^{-1} \\ \text{Volumes} & 22.4 \quad 3 \times 22.4 & \quad 2 \times 22.4\,\text{dm}^3 \text{ at s.t.p.} & \end{array}$$

Conditions

1. *Pressure.* Ammonia is formed with reduction in volume. By Le Chatelier's Principle, an increase of pressure applied to an equilibrium mixture of nitrogen, hydrogen and ammonia must shift the equilibrium in such a way that pressure tends to be reduced again, i.e. the volume will tend to decrease by formation of more ammonia. That is, *high pressure is favourable to the production of ammonia.* The usual pressure employed is at least 2×10^7 N m^{-2} (200 atm) and in some modern plants may be as high as 10^8 N m^{-2} (1000 atm).
2. *Temperature.* The production of ammonia from its elements is an exothermic reaction. By Le Chatelier's Principle, lowering of temperature of a nitrogen–hydrogen–ammonia system in equilibrium must shift the equilibrium in such a way that the temperature tends to be raised again, i.e. the system will tend to produce more ammonia and so liberate heat. That is, *low temperature is favourable to the production of ammonia.* But lowering of temperature tends to slow down the reaction and a compromise temperature must be chosen at which the equilibrium is sufficiently favourable and the reaction sufficiently rapid, when aided by a catalyst. The usual temperature used is about 720 K.

It is worth noting that in processes of this kind *true equilibrium is never actually reached*—since it would take too long to attain it. The so-called *contact time* between the reactants and the catalyst is critical. The aim is to hit the correct balance between the yield of ammonia and the time needed to achieve it, so that the production of ammonia over a given period is maximized.

3. *The catalyst.* The usual catalyst on the large scale is finely divided reduced iron, promoted by alkali or alumina.

In the more recent versions of the Haber process, nitrogen and oxygen are obtained by fractional distillation of liquid air. Some of the oxygen is fed, with natural gas (methane, CH_4) and steam, into a partial combustion furnace. In controlled conditions, a gas containing carbon monoxide, hydrogen and carbon dioxide is obtained. A carbon monoxide–hydrogen mixture can also be obtained by passing a mixture of the gaseous naphtha fraction from petroleum refining, together with superheated steam, over a nickel-chromium catalyst at about $10^6\,N\,m^{-2}$ (10 atm) and 1000 K. In older versions of the process, the carbon monoxide–hydrogen mixture was provided by *water gas* (see p. 142).

The monoxide is then oxidized by passage with more steam over a heated catalyst (iron(III) oxide promoted by chromium(III) oxide).

$$CO(g) + H_2O(g) \rightarrow CO_2(g) + H_2(g)$$

The total carbon dioxide is then absorbed by caustic alkali solution. The hydrogen is dried and freed from hydrocarbon by liquid nitrogen. It is then mixed with gaseous nitrogen, compressed to the required pressure (200–1000 atm) and, by heat exchangers, raised to the required temperature (720 K) for the catalyst chambers. The ammonia formed is then removed by solution in water, or by cooling to form the liquid. Much of it is converted to nitric acid or ammonium sulphate.

Conversion of ammonia to ammonium sulphate

Anhydrite ($CaSO_4$) is placed in water which is steam-heated and forms a suspension. Ammonia and carbon dioxide are blown into it. Chalk is formed and precipitated, while ammonium sulphate forms in solution.

$$2NH_3(g) + H_2O(l) + CO_2(g) + CaSO_4(s) \rightarrow CaCO_3(s) + (NH_4)_2SO_4(aq)$$

After settling, the solution can be filtered or decanted and the ammonium sulphate obtained by crystallization. It is a very important nitrogenous fertilizer. In this process, the anhydrite acts as a cheap source of sulphate ion.

Conversion of ammonia to nitric acid

Ammonia gas (10 per cent) and air (90 per cent by volume) are passed through a platinum gauze catalyst kept at red heat (about 1120 K). The ammonia is oxidized to nitrogen oxide (nitric oxide). In modern plants, the platinum is often alloyed with rhodium (10 per cent).

$$4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g) \qquad \Delta H = -906 \text{ kJ mol}^{-1}$$

The gauze catalyst is heated at the start, but the exothermic reaction then maintain it at red heat. *After cooling*, the nitrogen oxide is allowed to pass slowly with excess of air through an oxidizing chamber where it is converted to nitrogen dioxide.

$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$$

If heated, nitrogen dioxide dissociates into nitrogen oxide and oxygen (beginning at 420 K under atmospheric pressure), so that maximum yield of nitrogen dioxide can only be obtained at low temperature.

The nitrogen dioxide, in the presence of excess air, is then absorbed in water at about 350 K. This avoids formation of nitrous acid (unstable to heat) and enforces the final reaction:

$$4NO_2(g) + O_2(g) + 2H_2O(l) \rightarrow 4HNO_3(aq)$$

Acid of about 60 per cent concentration, to a yield of 93 per cent of theoretical, can be obtained. A pressure of about 700 000 $N\ m^{-2}$ (7 atm) is used, not in order to alter the position of equilibrium (since there is little diminution of volume in the oxidation of the ammonia), but to ensure a reasonable rate of gas flow through the plant.

Ammonia and its compounds

Ammonia, NH_3

Laboratory preparation

Ammonia is a gaseous compound, which is readily prepared by heating an ammonium salt with any solid alkali and water. The unusual combination of materials employed in practice is *ammonium chloride* and calcium hydroxide (*slaked lime*). The apparatus of Figure 8.4 is suitable.

$$2NH_4Cl(s) + Ca(OH)_2(s) \rightarrow CaCl_2(s) + 2H_2O(g) + 2NH_3(g)$$

Notice that the ammonia is dried by *calcium oxide* (*quicklime*). This is an unusual drying agent and is employed because the usual drying agents, calcium chloride, concentrated sulphuric acid and phosphorus(V) oxide, are all unsuitable. The last two are both *acidic* and the alkaline ammonia

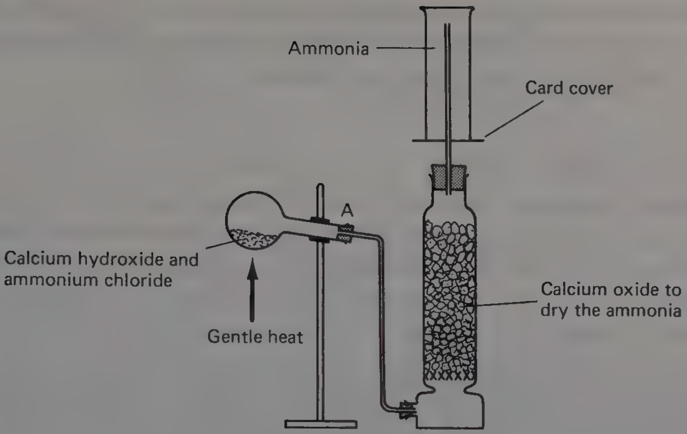


Figure 8.4 *Preparation of ammonia*

would form salts with them; ammonia also combines with calcium chloride to give the addition compound, $CaCl_2.4NH_3$. The gas is collected by upward delivery, being less dense than air.

Ammonia can also be generated by the action of water on the nitrides of calcium, magnesium and aluminium (and other metals), e.g.

$$Mg_3N_2(s) + 6H_2O(l) \rightarrow 3Mg(OH)_2(s) + 2NH_3(g)$$

Calcium cyanamide yields ammonia when treated with superheated steam.

$$CaCN_2(s) + 3H_2O(g) \rightarrow CaCO_3(s) + 2NH_3(g)$$

Large scale preparation of ammonia

This preparation is Haber's process, described in recent pages of this chapter.

Ammonia was obtained from the 'ammonia liquor' produced during the distillation of coal for coal gas. It was usually converted to ammonium sulphate and used as a fertilizer.

Properties of ammonia

Ammonia is a colourless gas. Its boiling point is 240 K. Its critical temperature is rather high (405.6 K) so that, at room temperature, it is easily liquefied by a pressure of about nine atmospheres.

The gas has a characteristic pungent, choking smell. The choking effect is caused by a temporary paralysis of muscles connected with respiration; in large or sudden doses, ammonia may cause death by asphyxiation or by vagal reflex. Concentrated solutions of ammonia should always be treated with great respect.

(a) Behaviour with water

Ammonia is extremely soluble in water (710 cm^3 in 1 cm^3 of water at 273 K and 1 atm). This solubility can be demonstrated by the *fountain experiment*. One of several suitable arrangements of apparatus is shown in Figure 8.5. A round, thick-walled, dry flask is filled with dry ammonia, clipped at A and B, and placed in position as shown. Clip A is removed and the flask is gently warmed. On cooling and contraction, a few drops of water enter the flask at A. These drops dissolve a substantial fraction of the ammonia in the flask and so pressure falls considerably inside it. Air pressure from outside then forces water into the flask as a fountain, as shown, and the flask will fill with water to the extent to which it was formerly filled with ammonia. The effect of the demonstration can be heighted by adding a few drops of dilute acid to the water, together with an indicator such as methyl orange. As in such cases generally, this high solubility is explained by chemical reaction between the gas and the water. This is usually represented as producing ammonium ions. The extent of ionization is small, and so ammonia solution acts as a weak base.

$$NH_3(g) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

At a concentration of 1 mol dm^{-3}, about 4 molecules per thousand are ionized, i.e. the degree of ionization is 0.4 per cent. In consequence of this,

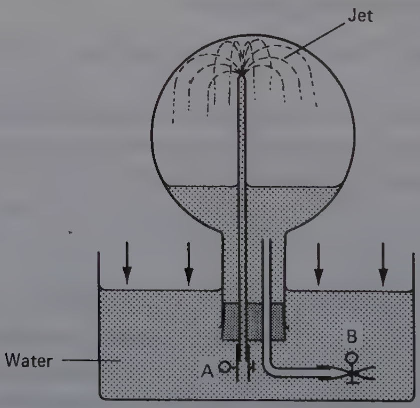
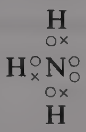


Figure 8.5 *The fountain experiment*

the solution is an electrolyte, turns red litmus paper blue, and precipitates many metallic hydroxides from solutions of their salts, e.g.

$$Fe^{3+}(aq) + 3OH^-(aq) \rightarrow Fe(OH)_3(s)$$
$$Al^{3+}(aq) + 3OH^-(aq) \rightarrow Al(OH)_3(s)$$

The ammonia molecule, NH_3, has the electronic structure



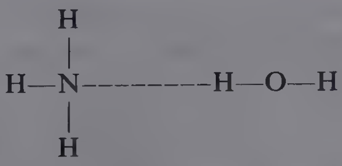
in which a lone pair of electrons is present. The ammonium ion is formed when this molecule utilizes the lone pair to combine with a proton (hydrogen ion) derived from an acid or, as above, from water. This proton conveys a positive charge to the group as a whole; the group cannot exist separately but is always associated with a univalent negative ion in an electrovalent relation, e.g.

$$NH_3(g) + HCl(g) \rightarrow NH_4{}^+Cl^-(s)$$

In this way, ammonia forms stable *salts* with all the mineral acids and many weaker acids, too. The ammonium ion, $NH_4{}^+$, acts like the univalent alkali metal ions and forms similar salts. The ion $NH_4{}^+$ is *isoelectronic* with (i.e. it contains the same number of electrons as) the ion Na^+. Compare the following:

Na^+Cl^-	$NH_4{}^+Cl^-$
$Na^+NO_3{}^-$	$NH_4{}^+NO_3{}^-$
$(Na^+)_2SO_4{}^{2-}$	$(NH_4{}^+)_2SO_4{}^{2-}$

In ammonia solution, ionization is only slight because there is a large amount of combination by *hydrogen bonding* (*Advanced Level Physical Chemistry*, p. 98), indicated by the dotted line in the structure:



$$\begin{array}{c} \mathrm{H} \\ | \\ \mathrm{H{-}N{-}{-}{-}{-}{-}{-}{-}{-}H{-}O{-}H} \\ | \\ \mathrm{H} \end{array}$$

In the relation $NH_3(g) + H_2O(l) \rightleftharpoons NH_4{}^+(aq) + OH^-(aq)$, the position of equilibrium lies strongly to the left in ordinary working solutions of ammonia. If all four hydrogen atoms of the group $NH_4{}^+$ are replaced by organic groups such as CH_3, there is no hydrogen atom left to which such hydrogen bonding can occur. Then ionization is almost complete, and the compound $N(CH_2)_4{}^+OH^-$ (tetramethylammonium hydroxide) is a very strong base.

By using its lone pair electrons for combination by dative bonds, ammonia can associate with metallic ions in complexes such as $Cu(NH_3)_4{}^{2+}$ and $Co(NH_3)_6{}^{3+}$. The compounds in which such complexes occur are called *ammines*. The shape of the ammonia molecule is pyramidal. It is discussed in *Advanced Level Physical Chemistry*, p. 79. The shape of the $NH_4{}^+$ ion is, as expected, tetrahedral with four completely equivalent N—H bonds.

(b) Oxidation of ammonia

1. *By air or oxygen.* Ammonia will not burn in air; it may give a slight greenish flicker if a flame is applied to it, but will not continue to burn. It will, however, burn in an atmosphere containing at least 25 per cent of oxygen by volume and mixtures of ammonia and oxygen (between certain limits) are explosive if sparked. The main reaction is:

$$4NH_3(g) + 3O_2(g) \rightarrow 6H_2O(g) + 2N_2(g)$$

If passed with excess of air over red hot platinum as catalyst, ammonia oxidizes readily to *nitrogen oxide* and *steam.*

$$4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g)$$

This is the basis of the conversion of ammonia to nitric acid on the industrial scale. The process was considered in full earlier in the present chapter.

2. *By copper*(II) *oxide.* Ammonia is also oxidized to *nitrogen* and

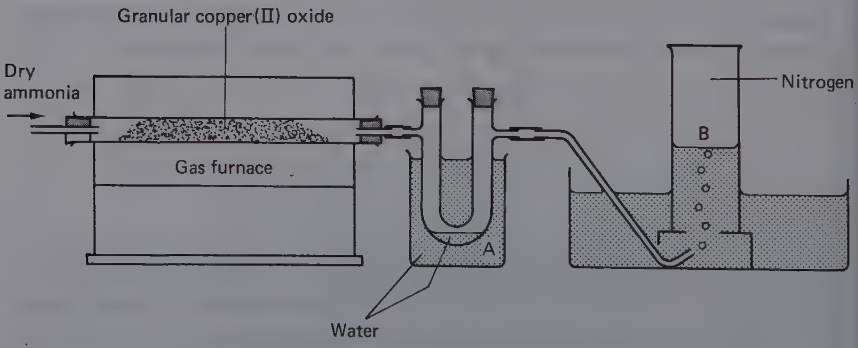


Figure 8.6 *Oxidation of ammonia*

steam by passage over red hot copper(II) oxide.

$$3CuO(s) + 2NH_3(g) \rightarrow 3Cu(s) + 3H_2O(g) + N_2(g)$$

A suitable apparatus for demonstrating this is given in Figure 8.6 as shown. Nitrogen collects at B and steam is condensed to water at A.

3. *By chlorine*. Ammonia is readily oxidized by chlorine. To demonstrate this, allow *concentrated* ammonia to fall drop by drop into an atmosphere of chlorine. Each drop will burst into a greenish flame, showing the vigour of the reaction, and dense *white fumes* of *ammonium chloride* appear in addition to *nitrogen*.

$$8NH_3(g) + 3Cl_2(g) \rightarrow 6NH_4Cl(s) + N_2(g)$$

The reaction probably occurs in the two stages:

$$2NH_3(g) + 3Cl_2(g) \rightarrow 6HCl(g) + N_2(g)$$
$$6NH_3(g) + 6HCl(g) \rightarrow 6NH_4Cl(s)$$

Remember, however, that, in the presence of excess of chlorine, the dangerously explosive oil, NCl_3, may be produced.

$$NH_3(g) + 3Cl_2(g) \rightarrow NCl_3(l) + 3HCl(g)$$

(c) Action of ammonia with metals

Sodium reacts with *dry* ammonia at about 670 K to produce *sodamide*. Potassium gives a similar reaction.

$$2Na(l) + 2NH_3(g) \rightarrow 2NaNH_2(s) + H_2(g)$$

Magnesium heated in dry ammonia, however, produces its *nitride*, liberating hydrogen.

$$3Mg(s) + 2NH_3(g) \rightarrow Mg_3N_2(s) + 3H_2(g)$$

Both products liberate *ammonia* by the action of water

$$NaNH_2(s) + H_2O(l) \rightarrow NaOH(aq) + NH_3(g)$$
$$Mg_3N_2(s) + 6H_2O(l) \rightarrow 3Mg(OH)_2(s) + 2NH_3(g)$$

(d) Action of ammonia with carbon dioxide

Large amounts of *urea* (*carbamide*) have been manufactured by combination between ammonia and carbon dioxide. The conditions required are about 460 K and 10^7 N m^{-2} (100 atm).

$$CO_2(g) + 2NH_3(g) \rightarrow CO(NH_2)_2(s) + H_2O(l)$$

Urea is an important nitrogenous fertilizer and valuable in the production of urea–methanal (urea-formaldehyde) plastics.

Uses of ammonia

(a) Ammonia is used industrially in the manufacture of urea, of nitric acid, and of ammonium sulphate. All these have been considered in the present chapter. Ammonia is also an important participant in the Solvay ammonia–soda process.

(b) Liquid ammonia has been used in refrigeration because of its volatility and its high molar enthalpy of vaporization (23.4 kJ mol^{-1}). The gas is liquefied by compression and the heat liberated is dissipated by water flowing over the condensing coils. The liquid is then passed, through a valve, into expansion coils. It vaporizes and takes the heat required from the brine in which the coils are immersed. The refrigerated brine can be circulated as a coolant. Ammonia is no longer used in domestic refrigerators, as it is too toxic and corrosive.

(c) Ammonia is used in the manufacture of certain man-made fibres for textiles, e.g. Nylon.

(d) Ammonia is used (in solution) for domestic purposes, especially in the laundering of woollens. It is a constituent of silver polishes and smelling salts.

General properties of ammonium compounds

1. *Action of heat.* All ammonium compounds decompose when heated; some of them undergo sublimation as well, though not all.
Examples of the action of heat are:

$$NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g) \text{ (with sublimation)}$$
$$(NH_4)_2SO_4(s) \rightarrow 2NH_3(g) + H_2O(g) + SO_3(g) \text{ (with sublimation)}$$
$$NH_4NO_3(s) \rightarrow N_2O(g) + 2H_2O(g)$$
$$(NH_4)_2Cr_2O_7(s) \rightarrow N_2(g) + 4H_2O(g) + Cr_2O_3(s)$$
$$NH_4^+(aq) + NO_2^-(aq) \rightarrow N_2(g) + 2H_2O(l)$$

2. *Action of strong alkalis and heat.* All ammonium salts liberate *ammonia* gas if *heated* with a strong alkali such as sodium or potassium hydroxides or calcium hydroxide (slaked lime) with water present (e.g. in the laboratory preparation of ammonia, p. 218). The ammonia can be detected by its choking smell and by the turning of damp red litmus paper blue.

$$NH_4^+ + OH^- \rightarrow NH_3(g) + H_2O(g)$$

3. *Action with Nessler's reagent.* Nessler's reagent is prepared by adding potassium iodide solution to mercury(II) chloride solution till the scarlet precipitate of mercury(II) iodide is just redissolved *and then making the liquid alkaline with potassium hydroxide solution.* That is, Nessler's reagent is an alkaline solution of potassium tetraiodomercury(II).

$$\mathrm{Hg^{2+}(aq) + 2I^-(aq) \rightarrow HgI_2(s)\downarrow}$$
$$\mathrm{HgI_2(s) + 2I^-(aq) \rightarrow HgI_4{}^{2-}(aq)}$$

If added in excess to a solution containing the ion, $NH_4{}^+$, Nessler's reagent gives a *yellowish-brown precipitate* of formula $(OHg_2)NH_2I$. If the $NH_4{}^+$ is present in very small concentration, there may be only a brownish coloration and no precipitate. This is a very sensitive test for the ammonium ion and is used in the analysis of water. For this, see p. 295.

Ammonium chloride, NH_4Cl

Preparation

In the laboratory, ammonium chloride is conveniently made by careful addition of hydrochloric acid to ammonia (both dilute) until the liquid is faintly acidic.

$$\mathrm{NH_3(aq) + HCl(aq) \rightarrow NH_4Cl(aq)}$$

The solid can then be obtained by the usual procedure of careful evaporation, cooling, etc. It can also be made on the large scale by heating sodium chloride with ammonium sulphate, when ammonium chloride is obtained as a sublimate.

$$\mathrm{(NH_4)_2SO_4(s) + 2NaCl(s) \rightarrow Na_2SO_4(s) + 2NH_4Cl(s)}$$

It is also made by direct combination of hydrogen chloride and ammonia at about 520 K.

$$\mathrm{NH_3(g) + HCl(g) \rightleftharpoons NH_4Cl(s)}$$

Ammonium chloride is a white crystalline solid.

Dissociation of ammonium chloride

Ammonium chloride vaporizes at about 620 K without liquefying at all, i.e. it *sublimes.* Just above its vaporizing temperature, ammonium chloride has a vapour density relative to hydrogen of 14.5. In its molecular form as NH_4Cl (molar mass 53.5), the salt would have a vapour density of 53.5/2, i.e. 26.75. The low actual vapour density is ascribed to dissociation of the chloride in the vapour, as: $NH_4Cl(g) \rightleftharpoons NH_3(g) + HCl(g)$. This, by producing two molecules for one, doubles the volume for no change in mass, and so lowers the vapour density.

If the degree of dissociation of ammonium chloride is taken to be α, the situation will be:

$$NH_4Cl \rightleftharpoons NH_3 + HCl$$

Before dissociation	1 mol	—	—
At equilibrium	$(1-\alpha)$ mol	α	α mol

Assuming no dissociation, the volume occupied is proportional to 1; at equilibrium as shown, the volume occupied is proportional to $(1-\alpha)+2\alpha$. Since the mass of the material is unchanged, the relative vapour densities are inversely proportional to the volumes, i.e.

$$\frac{(1-\alpha)+2\alpha}{1} = \frac{\frac{1}{2}NH_4Cl(\text{or } 26.75)}{\text{Observed relative vapour density}}$$

At about 620 K, this relation is:

$$\frac{(1-\alpha)+2\alpha}{1} = \frac{26.75}{14.5}$$

i.e.

$$(1+\alpha) = 1.85$$

From this, $\alpha = 0.85$; that is, the ammonium chloride appears to be about 85 per cent dissociated at 620 K. Baker claimed that intensively dried ammonium chloride does not dissociate, but there is some doubt about this. Evidence of the dissociation of ammonium chloride is also given by the experiment shown in Figure 8.7. When the ammonium chloride is heated, the red litmus paper at A turns blue; the blue litmus paper at B turns red. These changes are explained in the following way. Dissociation of ammonium chloride gives an atmosphere of ammonia gas and hydrogen chloride near the ceramic wool.

$$NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$$

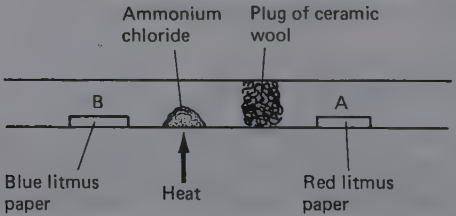


Figure 8.7 *Thermal dissociation of ammonium chloride*

In accordance with Graham's Law of Diffusion (see *Advanced Level Physical Chemistry*, p. 32), the much less dense ammonia diffuses more rapidly through the plug. Consequently, ammonia is put into excess near A and the litmus turns to its *alkaline* colour. The more rapid diffusion of ammonia leaves hydrogen chloride in excess near B; this turns the litmus to its *acidic* colour.

Ammonium chloride is used in Leclanché batteries and as a constituent of fluxes for soldering.

Ammonium sulphate, $(NH_4)_2SO_4$

The preparation of ammonium sulphate was described on p. 217. It is a very important nitrogenous fertilizer.

Ammonium nitrate, NH_4NO_3

On the large scale, ammonium nitrate is made by the action of ammonia *gas* with concentrated nitric acid. Ammonium nitrate is left fused.

$$NH_3(g) + HNO_3(\text{conc. aq.}) \rightarrow NH_4NO_3(s)$$

It can also be made by mixing concentrated solutions of ammonium sulphate and calcium nitrate, when the sparingly soluble calcium sulphate precipitates and ammonium nitrate can be crystallized from the solution.

$$(NH_4)_2SO_4(aq) + Ca(NO_3)_2(aq) \rightarrow 2NH_4NO_3(aq) + CaSO_4(s)\downarrow$$

Ammonium nitrate is used as a fertilizer, sometimes in mixtures with ammonium sulphate or chalk. Since it is so soluble in water, ammonium nitrate as normally prepared would wash rapidly through soil and cause pollution of waterways, etc. It is therefore made into *prills*. The prilling process involves allowing droplets of a mixture of molten ammonium nitrate with a little water to fall down a tower. The resulting glassy granules dissolve at a rate slow enough for efficient utilization by the soil microorganisms to occur. It is also an ingredient of the explosives *amatol* (80 per cent ammonium nitrate, 20 per cent TNT) and *ammonal* (ammonium nitrate and aluminium powder). Ammonium nitrate dissolves in water with great absorption of heat, i.e. the process is highly *endothermic*. A freshly made concentrated solution of it can be used as a freezing mixture.

Ammonium carbonate

The material sold as 'ammonium carbonate' is made by first subliming a mixture of calcium carbonate (as chalk) and ammonium sulphate and then re-subliming the product in the presence of a little water. Its main constituent is actually ammonium carbamate, $(NH_2COO^-)NH_4^+$, i.e. the ammonium salt of carbamic acid, NH_2COOH. A little ammonium hydrogencarbonate, $NH_4^+HCO_3^-$, is also present, especially on the surface. The material is usually used in solution in water, with some ammonia added. In these conditions, the solution contains ammonium carbonate.

$$NH_2COO^-(aq) + NH_4^+(aq) + H_2O(l) \rightleftharpoons 2NH_4^+(aq) + CO_3^{2-}(aq)$$

Ammonium sulphide

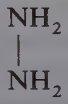
The chemistry associated with sulphides of ammonia is complex. If hydrogen sulphide is passed through concentrated aqueous ammonia, a liquid is obtained containing the *hydrogen sulphide*, NH_4HS, and the *normal sulphide*, $(NH_4)_2S$. The liquid rapidly turns yellow in air by oxidation and formation of *ammonium polysulphides*.

$$2NH_4HS(aq) + O_2(g) \rightarrow 2NH_3(aq) + 2H_2O(l)$$
$$(NH_4)_2S(aq) + nS(s) \rightarrow (NH_4)_2S_{n+1}(aq)$$

The pentasulphide, $(NH_4)_2S_5$, is prominent among them. The laboratory product, *yellow ammonium sulphide*, contains polysulphides of this kind.

Hydrazine

N_2H_4 or, structurally,



$$\begin{array}{c} NH_2 \\ | \\ NH_2 \end{array}$$

Hydrazine is a hydride of nitrogen. It can be prepared as its sulphate, in the following way.

Aqueous ammonia and a freshly made sodium chlorate(I) (hypochlorite) solution are boiled together, with a little glue present. (The glue is present to inhibit catalytic decomposition caused by heavy metal ions.) The reaction proceeds by the intermediate formation of chloramine, NH_2Cl, as:

$$NH_3(aq) + NaOCl(aq) \rightarrow NH_2Cl(aq) + NaOH(aq)$$
$$NH_3(aq) + NH_2Cl(aq) \rightarrow NH_2NH_2(aq) + HCl(aq)$$
$$NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l)$$

On addition of these equations, the total change can be represented as:

$$2NH_3(aq) + NaOCl(aq) \rightarrow NH_2NH_2(aq) + NaCl(aq) + H_2O(l)$$

When the reaction is finished, the liquid is cooled, acidified with dilute sulphuric acid and then cooled in ice. Colourless crystals of hydrazine sulphate separate out. Pure hydrazine is difficult to obtain. Distillation of the sulphate with aqueous caustic alkali under reduced pressure gives a liquid of composition, $N_2H_4.H_2O$. This liquid, when distilled with barium oxide under reduced pressure, yields anhydrous hydrazine.

$$BaO(s) + N_2H_4.H_2O(l) \rightarrow Ba(OH)_2(s) + N_2H_4(l)$$

It is a colourless liquid, poisonous and boiling (with decomposition) at 387 K under atmospheric pressure. It dissolves readily in water and alcohol.

Hydrazine hydrate can be used as a rocket fuel (with 15 per cent methanol) in association with nitric acid or hydrogen peroxide.

An alternative method of production of hydrazine is by glow discharge electrolysis of liquid ammonia which contains a little ammonium chloride. The electrodes are of platinum. The product is anhydrous.

Properties of hydrazine

1. *Basic properties.* In aqueous solution, hydrazine acts as a weak, di-acid base. It can form two series of salts, which are considerably hydrolysed in solution. The chlorides correspond to the compositions $N_2H_4.HCl$ and $N_2H_4.2HCl$. The ordinary sulphate corresponds to the composition $N_2H_4.H_2SO_4$. There is also a sulphate $(N_2H_4)_2.H_2SO_4$.

2. *Reducing properties.* Hydrazine and its sulphate are very *vigorous reducing agents*, e.g.:

(a) Iron(III) salts in solution are reduced to iron(II) salts.

$$4Fe^{3+}(aq) + N_2H_4(aq) \rightarrow 4Fe^{2+}(aq) + 4H^+(aq) + N_2(g)$$

(b) *Iodine* (in solution in potassium iodide solution) is reduced to *iodide ion.*

$$2I_2(aq) + N_2H_4(aq) \rightarrow 4H^+(aq) + 4I^-(aq) + N_2(g)$$

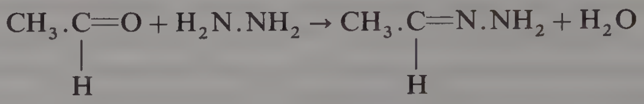
(c) Acidified potassium manganate(VII) solution is decolorized.

$$4MnO_4{}^-(aq) + 12H^+(aq) + 5N_2H_4(aq) \rightarrow 4Mn^{2+}(aq) + 16H_2O(l) + 5N_2(g)$$

This reaction can be used to estimate hydrazine.

3. *Behaviour with certain organic compounds.* Aldehydes and ketones

(containing the *carbonyl group*, $>C{=}O$) form condensation products with hydrazine, called *hydrazones*. For example, with ethanal (acetaldehyde),



$$CH_3.\underset{\substack{|\\H}}{C}{=}O + H_2N.NH_2 \rightarrow CH_3.\underset{\substack{|\\H}}{C}{=}N.NH_2 + H_2O$$

The hydrazones are crystalline and easily purified. They were used to characterize the aldehyde (or ketone) by their melting points. A derivative of hydrazine (2,4-dinitrophenylhydrazine, $C_6H_3(NO_2)_2NHNH_2$) is now usually used as more satisfactory for the purpose.

Hydroxylamine, NH_2OH

Preparation

Hydroxylamine can be prepared, as its sulphate, by electrolytic reduction of nitric acid. A lead anode is contained in a porous pot and 50 per cent sulphuric acid is electrolysed with a mercury (or amalgamated lead) cathode outside the porous pot. 50 per cent nitric acid is added to the cathode region drop by drop and the whole is cooled in ice. The cathode acts as a reducing agent, i.e. an electron-donor in the reaction:

$$HNO_3(aq) + 6H^+(aq) + 6e^- \rightarrow NH_2OH(aq) + 2H_2O(l)$$

Hydroxylamine sulphate can be crystallized, as $(NH_3OH^+)_2SO_4^{2-}$, from the cathode liquid.

Hydroxylamine (as its chloride) can also be obtained by reducing nitric acid, or nitrogen oxide (nitric oxide) by tin and concentrated hydrochloric acid.

$$HNO_3(aq) + 3Sn(s) + 6H^+(aq) \rightarrow NH_2OH(aq) + 3Sn^{2+}(aq) + 2H_2O(l)$$
$$2NO(g) + 3Sn(s) + 6H^+(aq) \rightarrow 2NH_2OH(aq) + 3Sn^{2+}(aq)$$

Properties of hydroxylamine

The pure compound is a colourless solid, melting point 306 K. It is rarely prepared because the salts serve satisfactorily for most purposes.

Hydroxylamine decomposes explosively if heated.

$$3NH_2OH(s) \rightarrow NH_3(g) + 3H_2O(l) + N_2(g)$$

1. *Basic properties*. Hydroxylamine is readily soluble in water and is a *weak* base.

$$NH_2OH(s) + H_2O(l) \rightleftharpoons NH_3OH^+(aq) + OH^-(aq)$$

It forms a chloride, $NH_3OH^+Cl^-$, and a sulphate, $(NH_3OH^+)_2SO_4{}^{2-}$, both of which are considerably hydrolysed in solution.

2. *Reducing action.* Hydroxylamine has marked reducing properties, e.g.

(a) Reduction of a copper(II) salt in the presence of alkali (Fehling's solution) to *copper*(I) *oxide* (a reddish-brown precipitate).

$$2NH_2OH(aq) + 4Cu^{2+}(aq) + 8OH^-(aq) \rightarrow N_2O(g) + 2Cu_2O(s) + 7H_2O(l)$$

(b) Reduction of mercury(II) chloride in solution to *mercury*(I) *chloride* (white precipitate).

$$4Hg^{2+}(aq) + 4Cl^-(aq) + 2NH_2OH(aq) \rightarrow N_2O(g) + H_2O(l) + 4H^+(aq) + 2Hg_2Cl_2(s)$$

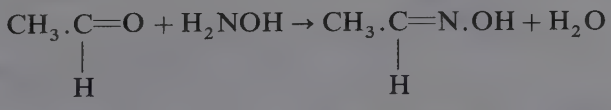
Hydroxylamine shows unusual behaviour with compounds of iron. In the presence of *alkali*, it *oxidizes* iron(II) compounds to iron(III); for example, it converts freshly precipitated iron(II) hydroxide (green) to iron(III) hydroxide (brown).

$$2Fe(OH)_2(s) + NH_2OH(aq) + H_2O(l) \rightarrow 2Fe(OH)_3(s) + NH_3(g)$$

In *acidic* solution, however, it *reduces iron*(III) salts (yellow) to iron(II) salts

$$4Fe^{3+}(aq) + 2NH_2OH(aq) \rightarrow N_2O(g) + H_2O(l) + 4H^+(aq) + 4Fe^{2+}(aq)$$

3. *Condensation reactions of hydroxylamine.* Hydroxylamine reacts with both aldehydes and ketones (which contain the carbonyl group, >C=O), eliminating water and producing the corresponding *oxime*, e.g.



$$CH_3.\underset{\underset{\displaystyle H}{|}}{C}{=}O + H_2NOH \rightarrow CH_3.\underset{\underset{\displaystyle H}{|}}{C}{=}N.OH + H_2O$$

ethanal (acetaldehyde) ethanal oxime (acetaldoxime)

The oximes are crystalline solids, which serve to characterize the corresponding aldehyde or ketone by their melting points.

Oxides and oxy-acids of nitrogen

There are four stable oxides of nitrogen:
(1) Dinitrogen oxide (nitrous oxide), N_2O; (2) Nitrogen oxide (nitric

oxide), NO; (3) Nitrogen dioxide, NO_2, dinitrogen tetraoxide, N_2O_4; (4) Dinitrogen pentoxide, N_2O_5.

The tetroxide, N_2O_4, dissociates with rise of temperature to yield NO_2 molecules (p. 238). Dinitrogen trioxide, N_2O_3, is known but is not stable at room temperature.

Dinitrogen oxide (nitrous oxide), N_2O

Preparation from ammonium nitrate

This is the usual laboratory method of preparing the gas, using the apparatus of Figure 8.8. Well-mixed equimolar quantities of potassium nitrate and ammonium chloride are placed in the flask and gently heated. The ammonium and nitrate ions interact and decompose.

$$NH_4{}^+Cl^-(s) + K^+NO_3{}^-(s) \rightarrow K^+Cl(s) + 2H_2O(l) + N_2O(g)$$

The gas is usually collected over warm water, being appreciably soluble in cold water. Ammonium nitrate can be used by itself, but when much of it has reacted the remainder may decompose with dangerously explosive violence.

$$NH_4NO_3(s) \rightarrow N_2O(g) + 2H_2O(l)$$

If wanted purer, the gas should be passed through *iron*(II) *sulphate* solution (to remove nitrogen oxide), through *caustic alkali* solution (to remove chlorine, derived from ammonium chloride impurity in the

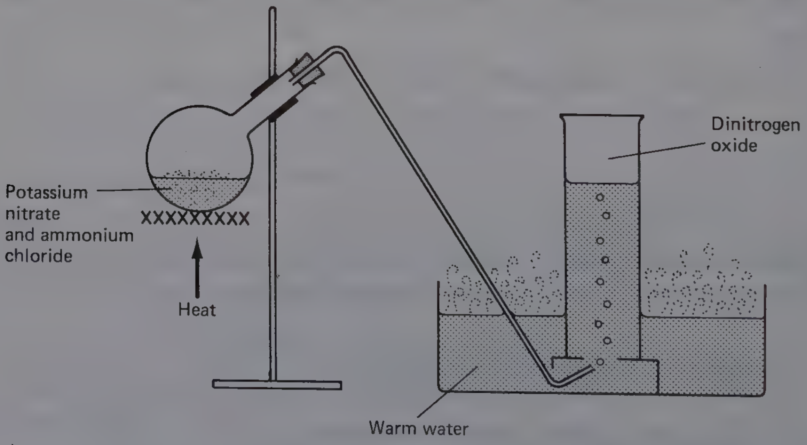


Figure 8.8 *Preparation of dinitrogen oxide*

nitrate). If required dry, it may be passed through calcium chloride and collected (in small amounts) over mercury.

Alternative preparations

(a) Reduction of nitric acid by tin(II) chloride in hydrochloric acid, with heat.

$$4Sn^{2+}(aq) + 2HNO_3(aq) + 8H^+(aq) \rightarrow N_2O(g) + 4Sn^{4+}(aq) + 5H_2O(l)$$

(b) Heating an equimolecular mixture of sodium nitrite and hydroxylammonium chloride in solution.

$$NO_2^-(aq) + H^+(aq) + NH_2OH(aq) \rightarrow N_2O(g) + 2H_2O(l)$$

Properties of dinitrogen oxide

Dinitrogen oxide is a colourless gas (boiling point 183 K) with a slight, sweetish smell. It has anaesthetic action, and is used in dentistry. Patients recovering from it are occasionally slightly hysterical; hence the name *laughing gas* applied to it. Dinitrogen oxide is fairly soluble in water (130 cm^3 in 100 cm^3 water at 273 K). The solution is *neutral*. It does not contain nitric(I) acid (hyponitrous acid), though dinitrogen oxide is given, with water, by the action of heat on this acid.

$$H_2N_2O_2(s) \rightarrow H_2O(l) + N_2O(g)$$

The decomposition is irreversible.

Combustions in dinitrogen oxide

Dinitrogen oxide dissociates into nitrogen and oxygen at a rather low temperature (about 870 K).

$$2N_2O(g) \rightarrow 2N_2(g) + O_2(g) \qquad \Delta H = -170\,\text{kJ mol}^{-1}$$

The resulting mixture contains 33 per cent of oxygen by volume (against the ordinary atmosphere 21 per cent). Consequently dinitrogen oxide readily supports the combustion of any burning material of which the flame is hot enough to start its dissociation. The material then burns in the oxygen produced. The following are typical cases:

Magnesium burns with a brilliant, bluish-white flame, leaving magnesium oxide (white powder) and nitrogen.

$$Mg(s) + N_2O(g) \rightarrow MgO(s) + N_2(g)$$

Phosphorus burns with a bright yellow flame, leaving phosphorus(V) oxide (white fumes) and nitrogen.

$$P_4(s) + 10N_2O(g) \rightarrow P_4O_{10}(s) + 10N_2(g)$$

Sulphur is extinguished if burning feebly. The temperature of the flame is too low to dissociate the dinitrogen oxide.

Vigorously burning sulphur continues to burn with a bright purple flame to form sulphur dioxide and nitrogen.

$$S(s) + 2N_2O(g) \rightarrow SO_2(g) + 2N_2(g)$$

A candle continues to burn with a small, very bright flame, forming carbon dioxide and water vapour, and leaving nitrogen.

A *glowing splint* is rekindled by dinitrogen oxide. The glowing end is hot enough to dissociate some of the gas and the wood burns in the 33 per cent oxygen–67 per cent nitrogen mixture made available.

Dinitrogen oxide can be distinguished from oxygen because (a) dinitrogen oxide is unaffected by nitrogen oxide. Oxygen turns it to *brown* nitrogen dioxide;

$$2NO(g) + O_2 \rightleftharpoons 2NO_2(g)$$

(b) oxygen is absorbed by an alkaline solution of pyrogallol (benzene-1, 2, 3-triol). Dinitrogen oxide is not.

Copper, at red heat, decomposes dinitrogen oxide to produce *copper*(II) *oxide* and *nitrogen*. All the gaseous oxides of nitrogen behave in this way.

$$Cu(s) + N_2O(g) \rightarrow CuO(s) + N_2(g)$$

Structure of dinitrogen oxide

The structure of dinitrogen oxide is linear. It is probably a 'resonance hybrid' of the two forms:

$$N^+{=}N^-{=}O \leftrightarrow N{\equiv}N^+{-}O^-$$

Nitrogen oxide (nitric oxide), NO

Preparation

1. *From nitric acid and copper.* This is the usually laboratory preparation, using the apparatus of Figure 8.9.

Concentrated nitric acid should be diluted with its own volume of water and added to the copper turnings in the flask.

$$3Cu(s) + 8HNO_3(aq) \rightarrow 3Cu(NO_3)_2(aq) + 4H_2O(l) + 2NO(g)$$

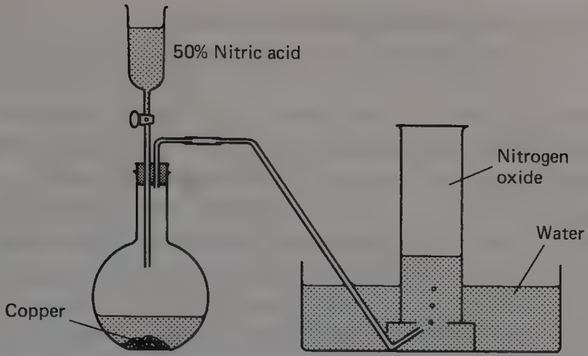


Figure 8.9 *Preparation of nitrogen oxide*

In redox terms, $Cu^0 \rightarrow Cu^{+2}$ and $N^{+5} \rightarrow N^{+2}$.
So

$$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$$
$$NO_3^-(aq) + 3e^- + 4H^+(aq) \rightarrow NO(g) + 2H_2O(l)$$

Balancing electron loss and electron gain:

$$3Cu(s) + 2NO_3^-(aq) + 8H^+(aq) \rightarrow 3Cu^{2+}(aq) + 2NO(g) + 4H_2O(l)$$

At first, the flask is filled with brown fumes by the reaction:

$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$$

but the brown fumes dissolve in water. They tend to disappear as the air in the flask is exhausted. As the action proceeds and the acid becomes more dilute, dinitrogen oxide and nitrogen may appear in the gas. It can be purified by absorption in *cold* iron(II) sulphate solution and expulsion by heat (see p. 441).

Other methods of preparing nitrogen oxide are:

2. *Heating a mixture of iron*(II) *sulphate, dilute sulphuric acid and potassium nitrate* (*or nitric acid*).

$$3Fe^{2+}(aq) + NO_3^-(aq) + 4H^+(aq) \rightarrow 3Fe^{3+}(aq) + 2H_2O(l) + NO(g)$$

3. *Dropping* 50 *per cent sulphuric acid on to a solution containing potassium iodide and sodium nitrite*. (This is equivalent to the oxidation of hydriodic acid by nitrous acid, p. 251).

$$2I^-(aq) + 2NO_2^-(aq) + 4H^+(aq) \rightarrow I_2(s) + 2H_2O(l) + 2NO(g)$$

Properties of nitrogen oxide

Nitrogen oxide is a colourless gas; it forms brown fumes of nitrogen dioxide instantaneously on contact with air.

$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$$

Consequently, its smell is unknown. It is difficult to liquefy (critical temperature, 177 K). Its boiling point is 122 K. Nitrogen oxide is only slightly soluble in water (5 cm^3 in 100 cm^3 water at 288 K).

1. *Combustion in nitrogen oxide.* Nitrogen oxide is much more stable than dinitrogen oxide and does not dissociate appreciably into its elements until about 1300 K is reached. Consequently, it extinguishes all burning materials except those with very hot flames, which can dissociate the gas sufficiently to obtain oxygen to support continued combustion. A *glowing splint*, *candle* or *taper*, and *sulphur* are all extinguished.

Phosphorus may be extinguished if burning feebly; if burning vigorously, it will continue to burn with a very bright, yellow flame, leaving *phosphorus*(V) *oxide* (white fumes) and *nitrogen.*

$$P_4(s) + 10NO(g) \rightarrow P_4O_{10}(s) + 5N_2(g)$$

Magnesium continues to burn with a dazzling bluish-white flame leaving *magnesium oxide* (white powder) and *nitrogen.*

$$2Mg(s) + 2NO(g) \rightarrow 2(Mg^{2+}.O^{2-})(s) + N_2(g)$$

Carbon disulphide vapour and nitrogen oxide will burn if a light is applied to the mixture (see p. 159).

Copper, when red hot, reduces nitrogen oxide to nitrogen.

$$2Cu(s) + 2NO(g) \rightarrow 2(Cu^{2+}O^{2-})(s) + N_2(g)$$

2. *Addition reactions of nitrogen oxide.* Nitrogen oxide participates in a number of addition reactions as below:

(a) With *oxygen* at ordinary temperature to form brown fumes of *nitrogen dioxide.* The reaction is instantaneous.

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

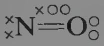
(b) With *chlorine* slowly at ordinary temperature, to form *nitrosyl chloride.*

$$2NO(g) + Cl_2(g) \rightarrow 2NOCl(g)$$

The reaction is catalysed by finely divided charcoal.

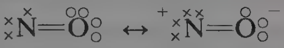
(c) With *iron*(II) *sulphate solution* at ordinary temperature. This is the familiar 'brown ring' reaction (see p. 247). In aqueous solution, the Fe^{2+} ion is usually surrounded by six water molecules as *ligands* (see p. 398). If a molecule of nitrogen oxide replaces one of these water molecules, the unstable brown-coloured complex ion $[Fe(H_2O)_5NO]^{2+}$ is obtained. This decomposes rapidly if the temperature is raised.

These addition reactions point to some unusual structure in the molecule, NO. The molecule contains eleven valency electrons, so that one of them must be unpaired. The compound is paramagnetic. These *odd electron molecules* are very rare, and the only examples commonly encountered are NO and NO_2. Nitrogen oxide can be represented as containing a three electron bond,



$$ {}^{\times}_{\times}N\overset{\times\circ\circ}{=}O^{\circ}_{\circ} $$

or as a resonance hybrid of:



$$ {}^{\times}_{\times}\overset{\times}{N}=\overset{\circ\circ}{O}{}^{\circ}_{\circ} \leftrightarrow {}^{+}\,{}^{\times}_{\times}\overset{\times\times}{N}=\overset{\circ}{O}{}^{\circ}_{\circ}{}^{-} $$

Nitrogen oxide dimerizes in the solid state to N_2O_2. This possibly involves pairing of the odd electrons, since the resulting compound is no longer paramagnetic, indicating that no unpaired electrons are present.

3. *Behaviour of nitrogen oxide with oxidizing agents and reducing agents.* As we have already seen, oxygen oxidizes nitrogen oxide on contact at ordinary temperature to form nitrogen dioxide; other oxidizing agents usually convert nitrogen oxide to the nitrate ion, e.g.:

(a) *Iodine* in potassium iodide solution.

$$2NO(g) + 3I_2(aq) + 4H_2O(aq) \rightarrow 2NO_3^-(aq) + 8H^+(aq) + 6I^-(aq)$$

(b) Acidified potassium manganate(VII) solution.

$$3MnO_4^-(aq) + 5NO(g) + 4H^+(aq) \rightarrow 3Mn^{2+}(aq) + 5NO_3^-(aq) + 2H_2O(l)$$

These reactions are rather slow, probably because of the small solubility of nitrogen oxide in water.

Nitrogen oxide will also react with reducing agents, to yield nitrogen as a rule, but sometimes ammonia or dinitrogen oxide, as in examples below.

(i) If sparked with hydrogen, nitric oxide is reduced to nitrogen.

$$2NO(g) + 2H_2(g) \rightarrow N_2(g) + 2H_2O(l)$$

(ii) If the mixture is passed over heated platinum black, hydrogen reduces nitrogen oxide to ammonia.

$$2NO(g) + 5H_2(g) \rightarrow 2NH_3(g) + 2H_2O(l)$$

(iii) With sulphur dioxide in the presence of water, nitrogen oxide is reduced to dinitrogen oxide.

$$2NO(g) + SO_2(g) + H_2O(l) \rightarrow N_2O(g) + H_2SO_4(aq)$$

Dinitrogen trioxide, N_2O_3

If a mixture of nitrogen oxide, NO, and nitrogen dioxide, NO_2, in equal volumes is cooled to 240 K, a bluish liquid condenses. This is *dinitrogen trioxide*, though not completely pure, with an empirical formula N_2O_3. It dissociates completely at room temperature: $N_2O_3(g) \rightleftharpoons NO(g) + NO_2(g)$. Nitrogen trioxide is the anhydride of nitrous acid.

$$2HNO_2(aq) \rightleftharpoons H_2O(l) + N_2O_3(g)$$

The blue colour which appears on acidification of a nitrite solution by mineral acid is probably caused by the presence of some N_2O_3.

Since NO and NO_2 are 'odd-electron molecules' possessing an unpaired electron each, it is possible that N_2O_3 is formed (cf. N_2O_4) by the pairing of one electron each from NO and NO_2.

The oxide NO_2 or N_2O_4

As will be seen below, an oxide of nitrogen exists (and is well known) which is mostly in the molecular form, N_2O_4, just above its boiling point (295 K). It gradually dissociates with rise of temperature until, at 420 K, it is entirely in the molecular form, NO_2. That is, just above 295 K, it is mainly *dinitrogen tetraoxide*; at 420 K, it is *nitrogen dioxide*; at intermediate temperatures, it is a mixture of the two forms. The latter name is usually employed in referring descriptively to the gas.

Preparation of nitrogen dioxide

1. *From lead*(II) *nitrate by the action of heat*. This is the usual laboratory preparation, using the apparatus of Figure 8.10, in which the accompanying oxygen is also collected. In this case, the oxide of nitrogen is collected as a dark *green liquid* (mainly N_2O_4) by condensation in the freezing mixture. The *pure* liquid is *pale yellow*; the green colour is caused by impurity, probably N_2O_3. The equation for the decomposition is:

$$2Pb(NO_3)_2(s) \rightarrow 2PbO(s) + 4NO_2(g) + O_2(g)$$

Then, on cooling,

$$2NO_2(g) \rightarrow N_2O_4(l)$$

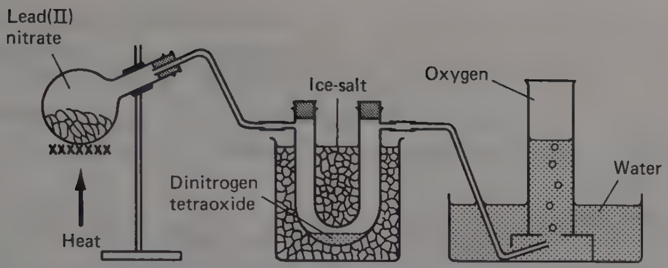


Figure 8.10 *Preparation of dinitrogen tetraoxide*

2. Nitrogen dioxide is also the product of reactions such as those between:

Copper and concentrated nitric acid (in the cold).

$$Cu(s) + 4HNO_3(conc.aq.) \rightarrow Cu(NO_3)_2(aq) + 2H_2O(l) + 2NO_2(g)$$

Tin and concentrated nitric acid (usually heated).

$$Sn(s) + 4HNO_3(conc.aq.) \rightarrow SnO_2(s) + 2H_2O(l) + 4NO_2(g)$$

Properties of nitrogen dioxide

1. *Action of heat*; *dissociation.* The *solid* form of this oxide of nitrogen is *colourless* and melts at 264 K to a pale yellow liquid. As the temperature rises, the liquid deepens in colour; before it boils (at 295 K) it is orange in colour and, on boiling, gives off a reddish-brown vapour. If this vapour were entirely composed of N_2O_4 molecules, its vapour density relative to hydrogen would be $\frac{1}{2}$ N_2O_4, i.e. 46. At about 300 K its vapour density is actually 38. This corresponds to a mixture of about 20 per cent NO_2 and 80 per cent N_2O_4 (by mass).

As the temperature rises, the colour of the gas darkens to chocolate-brown at about 310 K, and almost black at 420 K. At the same time, the vapour density gradually falls, reaching the value of 23 at 420 K. This corresponds to a gas completely composed of molecules of the type NO_2.

With further rise of temperature, the colour begins to lighten and the vapour density to fall further still. This is explained by a dissociation of NO_2 molecules into the *colourless* gases, oxygen and nitrogen oxide, which occupy one and a half times the volume of the nitrogen dioxide from which they are formed. This dissociation is complete at 900 K, at which temperature the mixture is colourless and its density relative to hydrogen is 15.3. The process can be summarized in the relations:

	N_2O_4	$\rightleftharpoons 2NO_2$	$\rightleftharpoons 2NO + O_2$
	b.p. 295 K	complete at 420 K	complete at 900 K
Colour	pale yellow, as liquid	almost black	colourless
vapour density relative to hydrogen	46	23	15.3

(pressure constant throughout.)

From this it will be seen that nitrogen dioxide cannot be formed at all from oxygen and nitrogen oxide if the temperature is above 900 K; it cannot be *fully* formed unless the temperature is below 420 K.

The relation $N_2O_4 \rightleftharpoons 2NO_2$ can be followed by observing the density of the mixture. The following is a typical calculation. Let the degree of dissociation of N_2O_4 at, say, 373 K be α. The situation then is:

	N_2O_4	$\rightleftharpoons 2NO_2$
If undissociated	1 mol.	
At equilibrium	$(1-\alpha)$ mol.	2α mol.

If undissociated, N_2O_4 has a vapour density relative to hydrogen of $\frac{1}{2}\,N_2O_4$, i.e. 46. The number of moles present is *one*, and the volume is proportional to this figure. At equilibrium at 373 K, the number of moles present is $(1-\alpha)+2\alpha$. The volume is proportional to this figure. Since there is no change of mass during dissociation, the density is inversely proportional to the volume. The relative vapour density of the gas at 373 K being 24.3:

$$\frac{(1-\alpha)+2\alpha}{1} = \frac{46}{24.3}$$

From this,

$$(1+\alpha) = 1.89$$
$$\alpha = 0.89$$

This means that, at 373 K, 89 per cent *by mass* of the gas is NO_2 and 11 per cent is N_2O_4.

The percentage of NO_2 *by volume* is

$$\frac{2\alpha}{(1-\alpha)+2\alpha} \times 100, \quad \text{or} \; \frac{2 \times 0.89}{1.89} \times 100 = 94 \text{ per cent}$$

2. *Behaviour of nitrogen dioxide with water.* Nitrogen dioxide reacts rapidly with water in the cold forming an *acidic* liquid containing both

nitric acid and *nitrous acid.*

$$2NO_2(g) + H_2O(l) \rightarrow HNO_3(aq) + HNO_2(aq)$$

The gas acts, therefore, as a *mixed anhydride.* In aqueous caustic alkali, nitrogen dioxide gives a mixture of the *nitrite* and *nitrate* of the alkali metal.

$$2OH^-(aq) + 2NO_2(g) \rightarrow NO_2^-(aq) + NO_3^-(aq) + H_2O(l)$$

3. *Combustions in nitrogen dioxide.* This gas will support the combustion of any material burning vigorously enough to dissociate it into nitrogen and oxygen. Combustion then continues in the oxygen liberated. Vigorously burning phosphorus and magnesium continue to burn in nitrogen dioxide.

$$4Mg(s) + 2NO_2(g) \rightarrow 4MgO(s) + N_2(g)$$

$$2P_4(s) + 10NO_2(g) \rightarrow 2P_4O_{10}(s) + 5N_2(g)$$

The gas is decomposed by copper at red heat.

$$4Cu(s) + 2NO_2(g) \rightarrow 4CuO(s) + N_2(g)$$

4. *Nitrogen dioxide in sulphuric acid manufacture.* Nitrogen dioxide will oxidize sulphur dioxide in the presence of water and form sulphuric acid.

$$SO_2(g) + H_2O(l) + NO_2(g) \rightarrow H_2SO_4(l) + NO(g)$$

It occurs in the catalytic process usually quoted for the now obsolescent Lead Chamber manufacture of sulphuric acid. Nitrogen oxide is the catalyst and *intermediate compound catalysis* operates by the repeated cycle:

$$NO(g) + \underset{\text{from air}}{\tfrac{1}{2}O_2(g)} \rightarrow NO_2(g)$$

$$SO_2(g) + H_2O(g) + NO_2(g) \rightarrow H_2SO_4(l) + NO(g)$$

In the absence of water, it combines with sulphuric acid to form *nitrosyl hydrogensulphate.*

$$H_2SO_4(l) + 2NO_2(g) \rightarrow NO.HSO_4(s) + HNO_3(l)$$

This compound may occur as 'chamber crystals' in sulphuric acid manufacture if the water supply is deficient.

Like nitrogen oxide, nitrogen dioxide is an *odd-electron* molecule. It is paramagnetic. The N_2O_4 molecule presumably results from pairing of the previously unpaired electrons in each of two NO_2 molecules.

Nitric acid, HNO_3

Preparation of nitric acid

In the laboratory, nitric acid is usually prepared by distilling a mixture of potassium nitrate and *concentrated* sulphuric acid, Figure 8.11.

$$KNO_3(s) + H_2SO_4(l) \rightleftharpoons KHSO_4(s) + HNO_3(l)$$

A *retort* is used for the distillation because it is made entirely of glass. Hot nitric acid vapour rapidly attacks cork or rubber stoppers. The acid decomposes slightly while distilling, giving rise to brown fumes of nitrogen dioxide.

$$4HNO_3(l) \rightarrow 2H_2O(l) + 4NO_2(g) + O_2(g)$$

These fumes dissolve in the condensed nitric acid, giving it a yellow colour. The acid may be decolorized by bubbling air through it, so driving out the nitrogen dioxide.

The reaction is a general one for nitrates. Potassium nitrate is usually used, being readily available and containing no water of crystallization.

Manufacture of nitric acid

Almost all nitric acid is now manufactured by the catalytic oxidation of ammonia. This process was described in connection with Haber's process, p. 217. Formerly, the acid was also manufactured by a process similar to the laboratory preparation described above.

Ordinary concentrated nitric acid (density 1.42 g cm^{-3}) contains 68 per cent of the acid and 32 per cent of water. It is a constant boiling

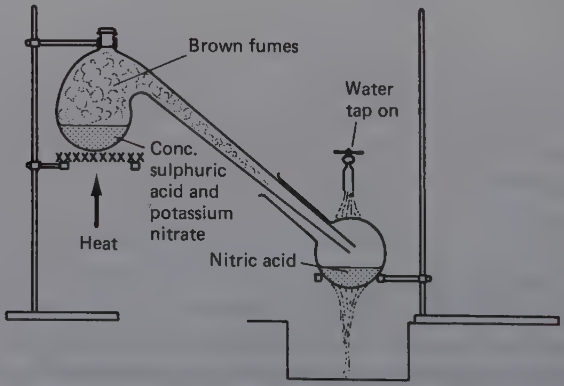


Figure 8.11 *Laboratory preparation of nitric acid*

mixture, boiling point 394 K. *Fuming nitric acid* contains about 95 per cent of the acid (density 1.5 g cm^{-3}) and can be obtained by distillation of the concentrated acid with concentrated sulphuric acid. Pure nitric acid boils, with some decomposition, at 359 K.

Properties of nitric acid

The chemical properties of nitric acid can be classified as:
(1) *acidic properties*, (2) *oxidizing action*, (3) *ester formation*, (4) *nitration.*

(1) Acidic properties

The acidic properties depend on the ionization of the acid in water to produce hydrated protons.

$$HNO_3(l) + aq. \rightleftharpoons H^+(aq) + NO_3{}^-(aq)$$

Completely anhydrous nitric acid is covalent, has no acidic properties, and does not, for example, attack dry chalk. The acidic properties are:

(a) *Blue litmus turned red.*

(b) *Formation of salts with bases.*

$$KOH(aq) + HNO_3(aq) \rightarrow KNO_3(aq) + H_2O(l)$$
$$PbO(s) + 2HNO_3(aq) \rightarrow Pb(NO_3)_2(aq) + H_2O(l)$$

Essentially in ionic terms, these are neutralizations, based on the types:

$$O^{2-} + H_2O(l) \rightleftharpoons 2OH^-(aq); \quad OH^-(aq) + H^+(aq) \rightleftharpoons H_2O(l)$$

(c) *Liberation of carbon dioxide from carbonates and hydrogen carbonates.*

$$CO_3{}^{2-} + 2H^+(aq) \rightarrow H_2O(l) + CO_2(g)$$
$$HCO_3{}^- + H^+(aq) \rightarrow H_2O(l) + CO_3(g)$$

Notice that, at no usual laboratory concentration, does nitric acid liberate hydrogen by the action of any metal. Its oxidizing action is too strong to allow hydrogen to escape. The products of the action of metals on nitric acid are metallic nitrates, oxides of nitrogen, possibly nitrogen and ammonium compounds.

(2) Oxidizing action of nitric acid

(a) *With metals.* Nitric acid is a powerful and much used oxidizing agent, and this is shown by its reaction with most metals. Metals are reducing agents, readily losing their valency electrons to become cations.

The *oxidation state*, or *oxidation number* (see *Advanced Level Physical Chemistry*, p. 246) of nitrogen in nitric acid is + 5. An oxidizing agent is an *acceptor* of electrons. When nitric acid, or the nitrate ion, accept electrons, the oxidation state of the nitrogen is reduced. The most common reduction products are NO_2, nitrogen dioxide (nitrogen in the + 4 state); NO, nitrogen oxide (+ 2 state); and NH_4^+, the ammonium ion (− 3 state). It will be seen that the change $NO_3^- \rightarrow NO_2$ involves a diminution in the oxidation state of nitrogen from + 5 to + 4, corresponding to the acceptance of one electron. At the opposite extreme, the change $NO_3^- \rightarrow NH_4^+$ involves acceptance of eight electrons.

The essential reactions are:

(i) $NO_3^-(aq) + e^- + 2H^+(aq) \rightarrow NO_2(g) + H_2O(l)$
(ii) $NO_3^-(aq) + 3e^- + 4H^+(aq) \rightarrow NO(g) + 2H_2O(l)$
(iii) $NO_3^-(aq) + 8e^- + 10H^+(aq) \rightarrow NH_4^+(aq) + 3H_2O(l)$

It is rare for one reaction to occur to the total exclusion of the others. However, conditions may be adjusted so that one reaction predominates.

The stage to which reduction will be taken in a given case depends on three main factors: (a) the concentration of the acid, (b) the temperature, (c) the nature of the reducing agent. Reaction (i) is prominent when concentrated nitric acid reacts with copper. The metal is the reducing agent, i.e. the electron donor.

$$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$$

Combining this equation with (i) so that the electrons lost and gained balance, we have:

$$2NO_3^-(aq) + 4H^+(aq) + Cu(s) \rightarrow Cu^{2+}(aq) + 2H_2O(l) + 2NO_2(g)$$

Reaction (ii) is prominent when copper acts upon a mixture of equal volumes of concentrated nitric acid and water at ordinary temperature. As before, copper is the reducing agent:

$$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$$

Combining this with equation (ii) and balancing, we obtain the equation:

$$2NO_3^-(aq) + 8H^+(aq) + 3Cu(s) \rightarrow 3Cu^{2+}(aq) + 4H_2O(l) + 2NO(g)$$

This is the common laboratory preparation of nitrogen oxide.

Reaction (iii) occurs when zinc acts upon dilute nitric acid. Some ammonium salt occurs in the product. Zinc is the reducing agent:

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$$

Combining this with equation (iii) and balancing, we obtain the equation:

$$NO_3^-(aq) + 10H^+(aq) + 4Zn(s) \rightarrow 4Zn^{2+}(aq) + 3H_2O(l) + NH_4^+(aq)$$

Notice also the exceptional behaviour of *tin* in forming tin(IV) oxide when heated with concentrated nitric acid (p. 185), of *iron* in becoming 'passive' (p. 436) and of *aluminium* in resisting attack by nitric acid (p. 122).

(b) *With non-metals.* Several non-metals are oxidized by *hot, concentrated* nitric acid to the most highly oxidized stable acid containing the non-metal. Brown fumes of nitrogen dioxide are evolved. In such vigorously oxidizing conditions, the system of non-metal and water (from the acid) operates as a reducing system, making electrons available. These are accepted by the nitric acid (oxidizing agent). For example:

$$P_4(s) + 16H_2O(l) \rightarrow 4H_3PO_4(l) + 20H^+(aq) + 20e^-$$
$$5HNO_3(\text{conc.aq.}) + 5H^+(aq) + 5e^- \rightarrow 5H_2O(l) + 5NO_2(g)$$

Adding and balancing these,

$$P_4(s) + 20HNO_3(\text{conc.aq.}) \rightarrow 4H_2O(l) + 20NO_2(g) + 4H_3PO_4(l)$$

The *phosphoric*(V) *acid* is made from red phosphorus, white being too violent in this reaction. Other examples are the following.

$$S(s) + 6HNO_3(\text{conc.aq.}) \rightarrow 2H_2O(l) + 6NO_2(g) + \underset{(\textit{sulphuric acid})}{H_2SO_4(l)}$$

$$I_2(s) + 10HNO_3(\text{conc.aq.}) \rightarrow 4H_2O(l) + 10NO_2(g) + \underset{(\textit{iodic}(V)\ \textit{acid})}{2HIO_3(aq)}$$

The sulphur reaction is catalysed by *bromine*. Iodine should be boiled under reflux with concentrated nitric acid while a current of carbon dioxide is passing to sweep out oxides of nitrogen. See p. 386.

(c) *With some compounds*

(i) *Iron*(II) *sulphate*. This compound is dissolved in dilute sulphuric acid and heated with concentrated nitric acid. It oxidizes to *iron*(III) *sulphate*, the solution turning from pale green to yellow or brown, with evolution of *nitrogen oxide* (forming brown fumes in air).

$$Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-$$
$$NO_3^-(aq) + 3e^- + 4H^+(aq) \rightarrow NO(g) + 2H_2O(l)$$

Combining and balancing the equations:

$$3Fe^{2+}(aq) + 4H^+(aq) + NO_3^-(aq) \rightarrow 3Fe^{3+}(aq) + 2H_2O(l) + NO(g)$$

(ii) *Sulphur dioxide, sulphurous acid or a soluble sulphite*. These materials are oxidized in solution by heating with concentrated nitric acid to give *sulphuric acid* or a *sulphate*. Brown fumes (nitrogen dioxide) are evolved. Sulphur is oxidized from the +4 state to +6.

$$SO_3^{2-}(aq) + 2H^+(aq) + 2NO_3^-(aq) \rightarrow SO_4^{2-}(aq) + H_2O(l) + 2NO_2(g)$$

(iii) *Hydrogen sulphide.* When hydrogen sulphide is passed into cold concentrated nitric acid, considerable heat is developed, a little *sulphur* precipitates and *sulphuric acid* is formed. Brown fumes (nitrogen dioxide) are evolved.

$$H_2S(g) + 2HNO_3(\text{conc.aq.}) \rightarrow 2H_2O(l) + 2NO_2(g) + S(s)$$
$$H_2S(g) + 8HNO_3(\text{conc.aq.}) \rightarrow 4H_2O(l) + 8NO_2(g) + H_2SO_4(l)$$

(d) *With organic compounds.* Concentrated nitric acid will oxidize many organic compounds, often with great violence, and much evolution of nitrogen dioxide, e.g. dry sawdust, or sugar, yields ethanedioic acid. If the sawdust is slightly warmed, it will ignite when *fuming* nitric acid is poured on it.

Ethanol is also oxidized by concentrated nitric acid (in a dangerously violent and erratic reaction), mainly to ethanedioic acid.

$$C_2H_5OH(l) + 10HNO_3(\text{conc.aq.}) \rightarrow H_2C_2O_4(s) + 7H_2O(l) + 10NO_2(g)$$

(3) Ester formation by nitric acid

Nitric acid can form esters by reacting with alcohols.

$$R.OH(l) + HNO_3(\text{conc.aq.}) \rightleftharpoons R.NO_3(l) + H_2O(l)$$

Only one nitric ester is important, the so-called *nitroglycerine*, which is not a nitro-compound and would be better named '*glyceryl trinitrate*.' It is made by spraying propane-1,2,3-triol (glycerol) into a mixture of concentrated nitric acid and concentrated sulphuric acid at a temperature not exceeding 295 K. The sulphuric acid acts as dehydrating agent.

$$C_3H_5(OH)_3(l) + 3HNO_3(l) \rightarrow C_3H_5(NO_3)_3(l) + 3H_2O(l)$$

The compound is violently explosive. It is usually absorbed in porous material for greater safety and used as 'dynamite'.

(4) Formation of nitro-compounds by nitric acid

Nitro-compounds are mainly important in the aromatic series of organic compounds. A typical nitration is that of benzene (1 part by weight) by a mixture of concentrated nitric acid (2 parts) and concentrated sulphuric acid (3 parts) at a temperature not exceeding 330 K. The yellow oil produced is *nitrobenzene.*

$$C_6H_6(l) + HO.NO_2(conc.aq.) \rightarrow C_6H_5.NO_2(l) + H_2O(l)$$

Some properties of metallic nitrates

(a) *Solubility.* All metallic nitrates are soluble in water. In some cases, however, metallic nitrates are hydrolysed to insoluble *basic* salts. In these cases, water acidified with nitric acid should be used as solvent, e.g. with mercurous nitrate.

(b) *Action of heat.* With regard to this property, metallic nitrates fall into four classes:

(i) *Ammonium nitrate.* This compound melts and effervesces, giving off *dinitrogen oxide* and *steam.* If heated rapidly, it may explode when the amount left is small. No residue remains.

$$NH_4NO_3(s) \rightarrow N_2O(g) + 2H_2O(l)$$

(ii) *Sodium nitrate and potassium nitrate.* These nitrates melt and efferversce, liberating *oxygen* and leaving the corresponding *nitrite* as a very pale yellow solid on cooling, e.g.

$$2KNO_3(s) \rightarrow 2KNO_2(s) + O_2(g)$$

(iii) *Other nitrates,* e.g. those of lead, magnesium, copper, zinc and aluminium, decompose to give off *nitrogen dioxide* and *oxygen* and to leave the corresponding metallic oxide, e.g.

$$2Pb(NO_3)_2(s) \rightarrow 2PbO(s) + 4NO_2(g) + O_2(g)$$
$$4Al(NO_3)_3(s) \rightarrow 2Al_2O_3(s) + 12NO_2(g) + 3O_2(g)$$

This corresponds to the decomposition of nitric acid when heated. This mode of decomposition is the common one. Notice that the mole ratio of nitrogen dioxide to oxygen is always 4:1.

(iv) *Nitrates* of metals such as *silver* and *mercury,* which have unstable oxides, give a reaction similar to the above, but the oxide decomposes too, leaving the *metal.* In the case of mercury, the metal may vaporize, leaving no residue.

$$2AgNO_3(s) \rightarrow 2Ag(s) + 2NO_2(g) + O_2(g)$$
$$Hg(NO_3)_2(s) \rightarrow Hg(l) + 2NO_2(g) + O_2(g)$$

Detection and estimation of nitrate

1. *The 'brown ring' test.* To the test material in aqueous solution is added a solution of iron(II) sulphate. Then concentrated sulphuric

acid is poured in, slowly down the side of the test tube, to form a lower layer of the acid. A *brown ring* at the junction of the liquids indicates a *nitrate* present.

$$6Fe^{2+}(aq) + 8H^+(aq) + 2NO_3^-(aq) \rightarrow 6Fe^{3+}(aq) + 4H_2O(l) + 2NO(g)$$

$$[Fe(H_2O)_6]^{2+}(aq) + NO(g) \rightarrow \underset{\text{brown}}{[Fe(H_2O)_5NO]^{2+}}(aq) + H_2O(l)$$

2. A safer method is to warm gently a small amount of the test solid with a few drops of concentrated sulphuric acid. A few copper turnings are then added to the mixture. If a brown gas is produced which gives no precipitate with silver nitrate solution, a nitrate is present.

$$NO_3^- + H_2SO_4(l) \rightarrow HSO_4^- + HNO_3(l)$$

$$Cu(s) + 4HNO_3(l) \rightarrow Cu(NO_3)_2(g) + 2H_2O(l) + 2NO_2(g)$$

3. Provided that *nitrites* and *ammonium compounds* are known to be *absent*, nitrate can be detected and estimated by the use of caustic alkali solution and Devarda's alloy (which contains Cu, 50 per cent; Al, 45 per cent; Zn, 5 per cent). When heated with aqueous caustic alkali, this alloy will reduce nitrate (and nitrite) to *ammonia gas*. Taking aluminium as the reactive element in the alloy, the reaction is:

$$8Al(s) + 5OH^-(aq) + 34H_2O(l) + 3NO_3^-(aq) \rightarrow 8[Al(OH)_4(H_2O)_2]^-(aq) + 3NH_3(g)$$

The ammonia can be detected by its choking smell and alkaline action on red litmus paper. The estimation can be made quantitative by absorbing the ammonia in a known excess volume of standard dilute sulphuric acid and back-titrating by standard alkali to determine the excess.

Dinitrogen pentoxide, N_2O_5

Preparation

Pure nitric acid (freshly distilled from concentrated sulphuric acid) is cooled by ice in a retort. To it is added, a little at a time, twice its mass of phosphorus(V) oxide. When distilled at 330–340 K, the product in the cooled receiver contains dinitrogen pentoxide in an upper layer. This layer will solidify if cooled in ice-salt.

$$4HNO_3(l) + P_4O_{10}(s) \rightarrow 2N_2O_5(s) + 4HPO_3(s)$$

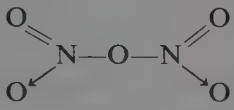
Dinitrogen pentoxide is a colourless solid, which melts (with decomposition) at 303 K. It is very hygroscopic. It decomposes slowly at ordinary temperature and explosively if heated suddenly.

$$2N_2O_5(s) \rightarrow 2N_2O_4(g) + O_2(g)$$

The crystals hiss on contact with cold water (like phosphorus(V) oxide) and form *nitric acid*.

$$N_2O_5(s) + H_2O(l) \rightarrow 2HNO_3(l)$$

That is, dinitrogen pentoxide is the anhydride of nitric acid.
The structural formula of nitrogen pentoxide can be written as:



Nitrous acid (nitric(III) acid), HNO_2

This acid is said to exist as a gas, but otherwise has never been obtained free from water. The most concentrated solution of it that is stable at 273 K contains about 9 g dm^{-3}.

Preparation

The acid is usually prepared by the action of dilute hydrochloric or dilute sulphuric acid on a solution of sodium (or potassium) nitrite in the cold (preferably at 273 K). The liquid is pale blue. The pale blue colour is probably caused by the presence of some N_2O_3, the anhydride of the acid.

$$NaNO_2(s) + HCl(aq) \rightarrow HNO_2(aq) + NaCl(aq)$$

If the acid is required free from sodium or potassium salts, barium nitrite is used with a calculated volume of dilute sulphuric acid. Barium sulphate precipitates and can be filtered off.

$$Ba(NO_2)_2(aq) + H_2SO_4(aq) \rightarrow BaSO_4(s) + 2HNO_2(aq)$$

Properties of nitrous acid

Action of heat

Nitrous acid decomposes rapidly if its solution is boiled, giving off brown fumes in air and leaving nitric acid. The main reaction is:

$$3HNO_2(aq) \rightarrow HNO_3(aq) + H_2O(l) + 2NO(g)$$
$$2NO(g) + \underset{\text{from air}}{O_2(g)} \rightleftharpoons 2NO_2(g)$$

Nitrous acid as oxidizing agent and reducing agent

In electronic terms, the oxidizing action of the acid can be written as:

$$2H^+(aq) + 2HNO_2(aq) + 2e^- \rightarrow 2H_2O(l) + 2NO(g)$$

(i.e. the acid is an electron acceptor) while its reducing action can be written as:

$$H_2O(l) + HNO_2(aq) \rightarrow HNO_3(aq) + 2H^+(aq) + 2e^-$$

(i.e. the acid is an electron donor).

(a) *As a reducing agent*

(i) *With acidified potassium manganate*(VII) *solution.* This solution is rapidly decolorized by nitrous acid at ordinary temperature.

$$2MnO_4^-(aq) + 6H^+(aq) + 5NO_2^-(aq) \rightarrow 5NO_3^-(aq) + 3H_2O(l) + 2Mn^{2+}(aq)$$

At first sight this looks a complicated equation, but notice the changes in oxidation state. Five nitrogen atoms are oxidized from the +3 state to +5, while two manganese atoms are reduced from +7 to +2. As always in a redox reaction, the number of electrons lost is balanced by the number gained.

(ii) *With acidified potassium dichromate*(VI) *solution.* This solution is turned green by reduction, but rather slowly, at ordinary temperature.

$$Cr_2O_7^{2-}(aq) + 8H^+(aq) + 3NO_2^-(aq) \rightarrow 2Cr^{3+}(aq) + 4H_2O(l) + 3NO_3^-(aq)$$

(iii) *With bromine water.* This reagent is decolorized.

$$Br^2(aq) + H_2O(l) + NO_2^-(aq) \rightarrow NO_3^-(aq) + 2H^+(aq) + 2Br^-(aq)$$

In all these cases, the nitrous acid is oxidized to nitric acid.

(b) *As an oxidizing agent*

(i) *With iron*(II) *sulphate in acidic solution.* The iron(II) sulphate is oxidized to iron(III) sulphate, the solution turning from pale green to yellow or brown. Brown fumes of nitrogen dioxide are evolved.

$$2Fe^{2+}(aq) + 4H^{+}(aq) + 2NO_2^{-}(aq) \rightarrow 2Fe^{3+}(aq) + 2H_2O(l) + 2NO(g)$$
$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

(ii) *With acidified potassium iodide solution* (*or hydriodic acid*). This reagent is oxidized to free iodine, which forms a brown solution (or possibly a black precipitate). Brown fumes of nitrogen dioxide are evolved.

$$2I^{-}(aq) + 4H^{+}(aq) + 2NO_2^{-}(aq) \rightarrow 2H_2O\,(l) + 2NO(g) + I_2(s)$$
$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

(iii) *With sulphurous acid.* This acid is oxidized to sulphuric acid with evolution of brown fumes of nitrogen dioxide.

$$SO_3^{2-}(aq) + 2H^{+}(aq) + 2NO_2^{-}(aq) \rightarrow SO_4^{2-}(aq) + 2NO(g) + H_2O(l)$$
$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

In similar, less important reactions, *tin*(II) *chloride* and *hydrogen sulphide* are oxidized, as:

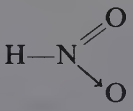
$$Sn^{2+}(aq) + 4H^{+}(aq) + 2NO_2^{-}(aq) \rightarrow Sn^{4+}(aq) + 2H_2O(l) + 2NO(g)$$
$$H_2S(g) + 2H^{+}(aq) + 2NO_2^{-}(aq) \rightarrow S(s) + 2H_2O(l) + 2NO(g)$$

For the important reactions between nitrous acid and organic compounds containing the amino group, NH_2, a text-book of organic chemistry should be consulted.

Formula of nitrous acid

Two possible formulae for nitrous acid are:

$H{-}O{-}N{=}O$ and

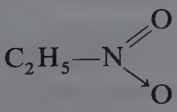


$$H{-}N\begin{matrix}{=}O\\ \rightarrow O\end{matrix}$$

Organic derivatives of both are known, e.g. ethyl nitrite,

$$C_2H_5{-}O{-}N{=}O$$

and nitroethane,



$$C_2H_5{-}N\begin{matrix}{=}O\\ \rightarrow O\end{matrix}$$

The free acid is mainly of the type H—O—N=O. It is a *weak* acid, ionizing only slightly, as:

$$\text{H—O—N=O} + H_2O \rightleftharpoons H_3O^+ + (\text{O=N} \rightarrow \text{O})^-$$

'Hyponitrous' acid (nitric(I) acid, $H_2N_2O_2$

This acid is made by the action of nitrous acid on hydroxylamine.

$$HNO_2(aq) + NH_2OH(s) \rightarrow H_2N_2O_2(s) + H_2O(l)$$

It is a solid. As an acid it is weak and dibasic. Its structure can be represented as HON=NOH. The acid and its salts are reducing agents, being readily oxidized to compounds containing nitrogen in the +3 or +5 states.

Phosphorus

Atomic number 15; electron arrangement 2.8.5 ($1s^2 2s^2 2p^6 3s^2 3p^3$)
Phosphorus has only one species of atom of mass number 31.
Relative atomic mass 30.97

Phosphorus occurs as calcium phosphate(V), $Ca_3(PO_4)_2$, in mineral phosphates and in animal bones. The chief minerals in which it occurs are: *Fluorapatite*, $Ca_3(PO_4)_2.CaF_2$, *Chlorapatite*, $Ca_3(PO_4)_2.CaCl_2$. It also occurs, as aluminium phosphate in *Wavellite*, $2Al(PO_4).2Al(OH)_3.9H_2O$.

Extraction

Calcium phosphate(V), coke and silica (sand) are fed into an electric furnace, fitted with carbon electrodes, as in Figure 8.12. At the high temperature of the furnace, silica, being a *non-volatile, acidic oxide*, displaces the more volatile phosphorus(V) oxide from combination.

$$2Ca_3(PO_4)_2(s) + 3SiO_2(s) \rightarrow 6CaSiO_3(l) + P_4O_{10}(g)$$

The oxide is then reduced by the coke.

$$P_4O_{10}(g) + 10C(s) \rightarrow P_4(g) + 10CO(g)$$

At A, calcium silicate is run off as molten slag and the phosphorus is

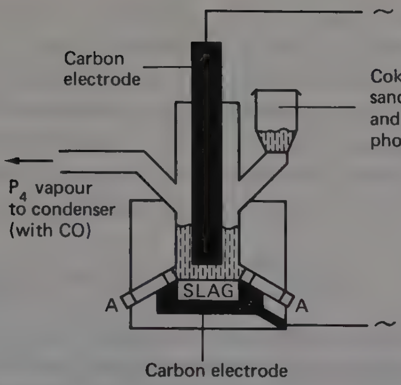
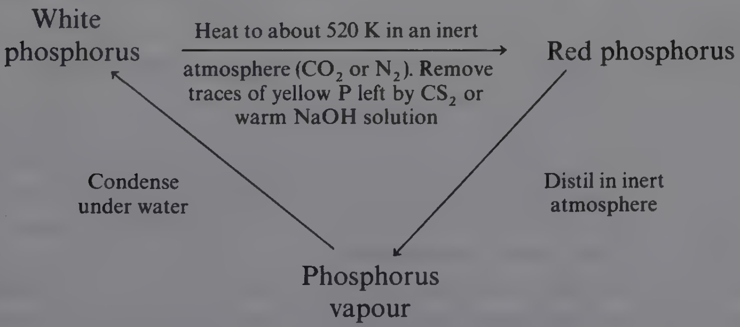


Figure 8.12 *Extraction of phosphorus*

condensed under water to form *white phosphorus*. For purification, the phosphorus may be stirred with warm chromic(VI) acid, filtered through canvas and cast into sticks. Note that the above process is purely electrothermal, and does not involve electrolysis. Electric current is used solely for the production of high temperature.

Allotropy of phosphorus

There are two principal allotropes of phosphorus—*white* (or *yellow*) *phosphorus* and *red phosphorus*. Their inter-conversion can be expressed in diagrammatic form as:



In industry, red phosphorus is prepared by heating yellow phosphorus to about 520 K in cast-iron vessels. A long, narrow, vertical tube suffices to exclude air sufficiently and to act as safety valve. Iodine may be added in small amounts to accelerate the change. Remaining yellow phosphorus is removed by heating with aqueous sodium hydroxide (with which red phosphorus has no action).

White phosphorus is the unstable form, of higher vapour pressure, in all conditions, and is slowly changing to the red form at room temperature. It is said to be *metastable*. This type of allotropy is called *monotropy*, i.e. direct conversion of one allotrope to the other is possible in only one direction (white to red). In the other direction, a vapour phase must intervene. Contrast the *enantiotropy* of sulphur where direct conversion is possible in both directions by mere temperature change.

$$\text{Rhombic sulphur} \underset{\text{cool below 369 K}}{\overset{\text{heat above 369 K}}{\rightleftharpoons}} \text{Monoclinic sulphur}$$

The structure of white phosphorus consists of P_4 units in which the phosphorus atoms are at the apices of a tetrahedron. The bond angle between the atoms in only 60°, which leads to considerable strain. It is this strain which is thought to be largely responsible for the high reactivity of white phosphorus. The red allotrope is essentially polymeric in nature (but see *violet phosphorus*, below).

Comparison of the allotropes

Observe that white phosphorus is the more reactive and the more soluble throughout.

Property	*White phosphorus*	*Red phosphorus*
Solubility in water	Appreciably soluble; very poisonous	Insoluble; non-poisonous
Solubility in carbon disulphide	Readily soluble	Insoluble
With oxygen	Ignites at about 313 K	Ignites at about 570 K
	$P_4(s) + 5O_2(g) \rightarrow P_4O_{10}(s)$	Same equation
With chlorine	Ignites spontaneously at room temperature	Combines when heated
	$P_4(s) + 6Cl_2(g) \rightarrow 4PCl_3(l)$	Same equations
	If excess chlorine present,	
	$PCl_3(l) + Cl_2(g) \rightarrow PCl_5(s)$	
With hot, aq. caustic alkali	Liberates phosphine, PH_3 $3NaOH(aq) + P_4(s) + 3H_2O(l)$ $\rightarrow PH_3(g) + 3NaH_2PO_2(aq)$	No reaction

An allotrope of phosphorus also exists known as *black phosphorus*. It is obtained by the action of heat and very high pressure on white phosphorus. It consists of corrugated sheets of atoms. The bonding forces between the sheets are weak, and the material conducts electricity. This behaviour is reminiscent of that of graphite (p. 134).

Also, it is found that when red phosphorus is heated for a long period to about 770 K in a vacuum, it gives a *violet* variety of the element. This may be the true allotrope and red phosphorus a mixture (or solid solution) of white and violet. For practical purposes, however, red phosphorus is the effective allotrope.

Use of phosphorus in matches

1. *Ordinary, 'strike anywhere' type.* The essential constituents of the match head are tetraphosphorus trisulphide, P_4S_3, and a solid oxidizing agent such as potassium chlorate(V). Glue is present to hold the mixture together and a filler (iron(III) or zinc oxide) to delay the burning. Friction on a rough surface generates heat enough to ignite the mixture.
2. *Safety type.* The match-head contains solid oxidizing agents such as potassium chlorate(V) and manganese(IV) oxide, sulphur, fillers as above, and glue. The side of the match-box is coated with a paste containing red phosphorus, antimony(III) sulphide, fillers, and glue. When the match is struck on the box, phosphorus from it ignites and the flame passes to the match head.

Phosphorus is also employed in making fireworks, smoke bombs, phosphor bronze and rat poison.

Properties of white phosphorus

White phosphorus is a solid, almost colourless when pure, but darkening rapidly if exposed to light. Most samples are yellow in colour. At ordinary temperature, it can be cut with a knife, but is much harder at 273 K. It melts at 317 K, and boils at 553 K in an inert atmosphere. White phosphorus is only very slightly soluble in water (about 3 parts per million at room temperature) and is usually stored under water as a precaution against ignition. It is readily soluble in carbon disulphide and appreciably soluble in trichloromethane (chloroform), turpentine, benzene, and ethanol. White phosphorus is very poisonous. Continual exposure to its fumes may set up 'phossy jaw'—an extremely painful disease causing rotting of the bones of the jaw and nose, which afflicted workers in the early match industry.

1. *Combustion of white phosphorus.* It is said that, if both are *perfectly dry*, white phosphorus can be melted and distilled in oxygen without ignition. Under ordinary conditions, however, white phosphorus ignities in air at about 303 K, or higher temperatures as the air becomes drier.

It produces white fumes of *phosphorus*(V) *oxide* (phosphoric oxide).

$$P_4(s) + 5O_2(g) \rightarrow P_4O_{10}(s)$$

The ignition temperature is so low that white phosphorus should never be handled. Body temperature may ignite it and produce bad burns.

White phosphorus oxidizes slowly in air at ordinary temperature (say 283–288 K) without igniting. It gives off white fumes with a smell of garlic, and is covered with a greenish glow which is clearly visible in the dark.

2. *With metals.* In an inert atmosphere, white phosphorus combines with many metals to form the corresponding *phosphide*, e.g.

$$P_4(s) + 12Na(s) \rightarrow 4Na_3P(s)$$
$$P_4(s) + 6Ca(s) \rightarrow 2Ca_3P_2(s)$$

3. *With non-metals.* White phosphorus reacts with many non-metals, usually when heated, e.g.

$$P_4(s) + 5O_2(g) \rightarrow P_4O_{10}(s)$$
$$P_4(s) + 6Cl_2(g) \rightarrow 4PCl_3(l)$$
$$P_4(s) + 6S(s) \rightarrow 2P_2S_3(s)$$

4. *As a reducing agent.* White phosphorus is a vigorous reducing agent. It precipitates copper from copper(II) sulphate solution.

$$P_4(s) + 10Cu^{2+}(aq) + 12H_2O(l) \rightarrow 10Cu(s)\downarrow + 20H^+(aq) + 4HPO_3(aq)$$

Phosphorus also acts vigorously in the reduction of nitric acid. Red phosphorus is usually preferred as being milder in action. For this, see the preparation of phosphoric(V) acid later in this chapter.

Phosphine, phosphorus trihydride, PH_3

This gas is usually prepared by heating white phosphorus in aqueous caustic alkali in a flask from which air has been displaced by coal gas, Figure 8.13. If coal gas is not available, the preparation is not recommended (see below).

$$P_4(s) + 3NaOH(aq) + 3H_2O(l) \rightarrow PH_3(g) + \underset{\substack{\text{sodium phosphinate} \\ \text{(hypophosphite)}}}{3NaH_2PO_2(aq)}$$

Prepared this way, the gas is spontaneously flammable through the presence of the compound P_2H_4, the phosphorus analogue of hydrazine (which may be removed by a freezing mixture), and, because of this and the extremely poisonous nature of phosphine, it is not usually collected in bulk. It is allowed to burn and produce the well known effect of vortex

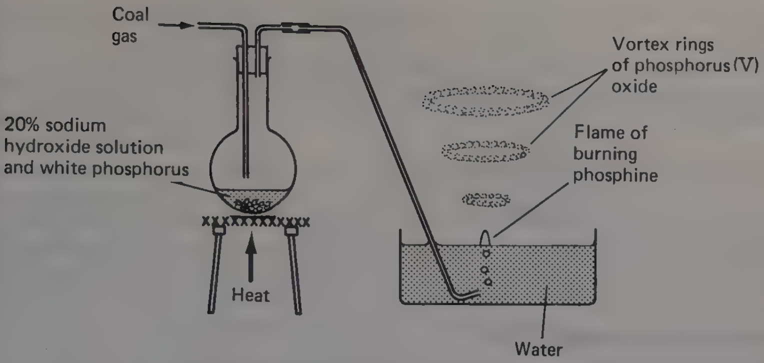


Figure 8.13 *Preparation of phosphine*

rings of phosphorus(V) oxide.

$$4PH_3(g) + 8O_2(g) \rightarrow P_4O_{10}(s) + 6H_2O(l)$$

If collection in bulk is desired, it may be collected over water. Phosphine may also be prepared by the action of water on certain metallic phosphides. The one usually employed is calcium phosphide, Ca_3P_2.

$$Ca_3P_2(s) + 6H_2O(l) \rightarrow 3Ca(OH)_2(s) + 2PH_3(g)$$

See also *phosphonium iodide*, below.

Phosphine is the phosphoric analogue of the nitrogen compound, ammonia, NH_3. Their properties are compared below.

Comparison of phosphine, PH_3, and ammonia, NH_3

Property	*Phosphine*	*Ammonia*
Solubility in water; basic character	Almost insoluble; shows no alkalinity, but forms very unstable *phosphonium* salts, e.g. PH_4I dissociating at 303 K $PH_4I(s) \rightleftharpoons PH_3(g) + HI(g)$	Very soluble; shows marked alkalinity $NH_3(g) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$ Forms much more stable *ammonium* salts, e.g. NH_4Cl, which dissociates at about 570 K $NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$
Reducing action	Very strong, e.g. precipitates Cu and Ag from solutions of their salts $4Cu^{2+}(aq) + PH_3(g) + 4H_2O(g) \rightarrow 4Cu(s) + H_3PO_4(aq) + 8H^+(aq)$	Slight; reduces copper(II) oxide at red heat $3CuO(s) + 2NH_3(g) \rightarrow 3Cu(s) + N_2(g) + 3H_2O(l)$

(continued)

Property	*Phosphine*	*Ammonia*
Poisonous character	Very poisonous	Not poisonous in the usual sense, but large doses may kill by asphyxiation
Combustion	Burns readily in air $4PH_3(g) + 8O_2(g) \rightarrow P_4O_{10}(s) + 6H_2O(l)$	Burns if oxygen percentage is 25% by volume or more $4NH_3(g) + 3O_2(g) \rightarrow 2N_2(g) + 12H_2O(l)$

Phosphonium iodide, PH_4I

This compound is the most important of phosphonium salts. It is prepared as follows. Equimolar amounts of white phosphorus and iodine (i.e. in the proportion of P:I, 31:127 by mass) are dissolved in carbon disulphide. The solvent is then distilled off by steam heat in a retort and condensed. The residual mixture of iodine and phosphorus is then treated, drop by drop with the mass of cold water required by the equation:

$$10I_2(s) + 9P_4(s) + 64H_2O(l) \rightarrow 20PH_4I(s) + 16H_3PO_4(l)$$

The phosphonium iodide can be sublimed off in a stream of dry carbon dioxide. The compound dissociates readily, beginning at 303 K.

$$PH_4I(s) \rightleftharpoons PH_3(g) + HI(g)$$

If heated with aqueous caustic alkali, it liberates *phosphine.*

$$PH_4I(s) + KOH(aq) \rightarrow PH_3(g) + H_2O(l) + KI(aq)$$

Compare the reaction:

$$NH_4Cl(s) + KOH(aq) \rightarrow NH_3(g) + H_2O(l) + KCl(aq)$$

Oxides and oxyacids of phosphorus

Phosphorus(V) oxide, tetraphosphorus decaoxide (phosphorus pentoxide), P_4O_{10}

There is no very satisfactory way of making this oxide in the laboratory. Small amounts may be made by burning yellow phosphorus in a large bell-jar of air over a glass plate. The oxide will settle on the plate and may be subsequently heated in oxygen to oxidize any phosphorus(III) oxide present.

$$P_4(s) + 5O_2(g) \rightarrow P_4O_{10}(s)$$

Properties of phosphorus(V) oxide

1. *With water.* Phosphorus(V) oxide reacts with hissing on contact with cold water and gives *trioxophosphoric*(V) *acid* (*metaphosphoric acid*).

$$P_4O_{10}(s) + 2H_2O(l) \rightarrow 4HPO_3(s)$$

(This product is also given if the oxide is left exposed to air.) On boiling with excess water for about half an hour, it is converted to *tetraoxophosphoric*(V) *acid* (*orthophosphoric acid*).

$$HPO_3(s) + H_2O(l) \rightarrow H_3PO_4(aq)$$

2. *As a dehydrating agent.* Phosphorus(V) oxide is an extremely vigorous dehydrating agent. In two typical reactions, it dehydrates concentrated sulphuric acid and pure nitric acid, when *heated* with them, to form the corresponding anhydrides (sulphur trioxide and dinitrogen pentoxide).

$$2H_2SO_4(l) + P_4O_{10}(s) \rightarrow 2SO_3(s) + 4HPO_3(s)$$
$$4HNO_3(l) + P_4O_{10}(s) \rightarrow 2N_2O_5(s) + 4HPO_3(s)$$

It also dehydrates organic compounds, e.g. when distilled with an *amide* it produces the corresponding *nitrile.*

$$2RCONH_2(s) + P_4O_{10}(s) \rightarrow 2RCN(l) + 4HPO_3(s)$$

The structures of the two oxides P_4O_{10} and P_4O_6 are based on the P_4 tetrahedron. In P_4O_6, there is an oxygen atom between any two phosphorus atoms, so that each phosphorus atom still has three covalent bonds to it. The structure of P_4O_{10} is the same, except that each phosphorus atom has an additional oxygen atom attached to it by a double bond. The structures are shown in Figure 8.14.

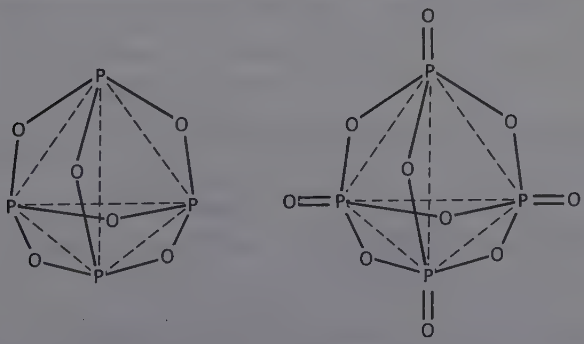


Figure 8.14 *Structures of* P_4O_6 *and* P_4O_{10}

There are three acids of phosphorus derived from phosphorus(V) oxide. They are: *tetraoxophosphoric*(V) *acid* (*orthophosphoric acid*), H_3PO_4; *trioxophosphoric*(V) *acid* (*metaphosphoric acid*), HPO_3; *heptaoxodiphosphoric*(V) *acid* (*pyrophosphoric acid*), $H_4P_2O_7$.

Tetraoxophosphoric(V) acid (orthophosphoric acid), H_3PO_4

This acid is best made from phosphorus in one of the following two ways.

1. Red phosphorus is warmed with concentrated nitric acid as oxidizing agent. A violent reaction follows, with evolution of clouds of nitrogen dioxide fumes, so a good fume-cupboard is essential. Further red phosphorus is added when the reaction moderates, till finally, excess red phosphorus is left. The mixture is diluted with distilled water, filtered and evaporated (to remove water and nitric acid) till its temperature reaches 450 K when a syrupy liquid is left.

$$P_4(s) + 20HNO_3(\text{conc. aq.}) \rightarrow 4H_3PO_4(l) + 4H_2O(l) + 20NO_2(g)$$

2. White phosphorus is burnt in excess of air (to avoid production of phosphorus(III) oxide). The phosphorus(V) oxide produced is added to excess of cold water and boiled for half an hour.

$$P_4(s) + 5O_2(g) \rightarrow P_4O_{10}(s); P_4O_{10}(s) + 2H_2O(l) \rightarrow 4HPO_3(aq)\,(\text{cold})$$
$$HPO_3(aq) + H_2O(l) \rightarrow H_3PO_4(aq)\,(\text{hot})$$

The liquid is then evaporated, etc., as above.

Sodium salts of tetraoxophosphoric(V) acid, H_3PO_4 ('phosphoric (V) acid')

This acid is *tri*basic and forms three sodium salts by the reactions:

(a) $$H_3PO_4(aq) + NaOH(aq) \rightarrow \underset{\substack{\text{sodium dihydrogen}\\ \text{phosphate(V)}}}{NaH_2PO_4(aq)} + H_2O(l)$$

(b) $$H_3PO_4(aq) + 2NaOH(aq) \rightarrow \underset{\substack{\text{disodium hydrogen}\\ \text{phosphate(V)}}}{Na_2HPO_4(aq)} + 2H_2O(l)$$

(c) $$H_3PO_4(aq) + 3NaOH(aq) \rightarrow \underset{\substack{\text{trisodium}\\ \text{phosphate(V)}}}{Na_3PO_4(aq)} + 3H_2O(l)$$

The first two of these are *acid* salts, still containing replaceable hydrogen; the third is a *normal* salt. Stage (b) is reached when the indicator, phenolphthalein, shows neutrality. This allows the following technique of preparation. 25.0 cm^3 of a suitable solution of sodium hydroxide are titrated by a tetraoxophosphoric(V) acid solution until neutral, with *phenolphthalein* as indicator. Say x cm^3 of the acid are required. Then: for reaction (b), mix the sodium hydroxide solution and the phosphoric(V) acid in the proportion of 25 cm^3 to x cm^3 to any desired bulk. For reaction (a), the equation shows that *half* the above proportion of sodium hydroxide is needed, i.e. the proportion of 12.5 cm^3 of the sodium hydroxide solution to x cm^3 of the acid to give any desired bulk. For reaction (c), the equation shows that *one and a half times* as much sodium hydroxide is required for the same bulk of acid as in (b), i.e. the proportion of 37.5 cm^3 of sodium hydroxide solution to x cm^3 of the acid to give any desired bulk.

In all cases, crystals may be obtained by evaporation to small bulk and cooling. They are then filtered off, washed with cold distilled water and dried. The ordinary 'sodium phosphate' is the hydrate, $Na_2HPO_4.12H_2O$.

Microcosmic salt

This compound is *sodium ammonium hydrogenphosphate*(V), $Na.NH_4.HPO_4.4H_2O$. It can be made by mixing 'sodium phosphate' and ammonium chloride (in the correct amounts for the equation below), both in hot, concentrated solution. Common salt precipitates and is filtered off. Microcosmic salt can then be crystallized out.

$$Na_2HPO_4(\text{conc.aq.}) + NH_4Cl(\text{conc.aq.}) \rightarrow NaCl(s) + Na.NH_4.HPO_4(aq)$$

When heated, this salt leaves sodium trioxophosphate(V) (sodium metaphosphate) and was used formerely in producing coloured beads from certain metals, similar to the borax beads still used.

$$Na.NH_4.HPO_4(s) \rightarrow NaPO_3(s) + H_2O(l) + NH_3(g)$$

The action of heat on the sodium tetraoxophosphates(V)

The salt Na_3PO_4 is unchanged by heat. The other sodium salts behave as below:

$$2Na_2HPO_4(s) \rightarrow Na_4P_2O_7(s) + H_2O(l)$$

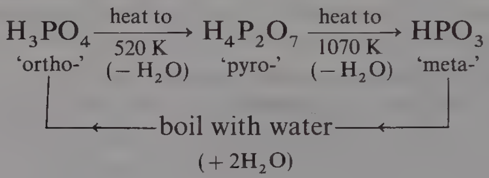
tetrasodium hepta-
oxodiphosphate(V)
(sodium pyrophosphate)

$$NaH_2PO_4(s) \rightarrow NaPO_3(s) + H_2O(l)$$

sodium trioxo-
phosphate(V)
(sodium metaphosphate)

Other acids from phosphorus(V) oxide

In addition to tetraoxophosphoric(V) acid (orthophosphoric acid), phosphorus(V) oxide yields the heptaoxodiphosphoric(V) (pyrophosphoric) and trioxophosphoric(V) (metaphosphoric) acids. 'Metaphosphoric acid' is, in fact, *poly*trioxophosphoric(V) acid, but we will use the usual formula HPO_3. It will be noted that both the 'pyro' and 'meta' acids are *condensed* forms of the 'ortho' acid, i.e. they are derived from the 'ortho' form by loss of water. There are many other condensed forms. The interrelations of the three common phosphoric(V) acids are:

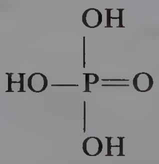


$$\underset{\text{'ortho-'}}{H_3PO_4} \xrightarrow[\substack{520\ K\\(-H_2O)}]{\text{heat to}} \underset{\text{'pyro-'}}{H_4P_2O_7} \xrightarrow[\substack{1070\ K\\(-H_2O)}]{\text{heat to}} \underset{\text{'meta-'}}{HPO_3}$$

$$HPO_3 \xrightarrow[(+2H_2O)]{\text{boil with water}} H_3PO_4$$

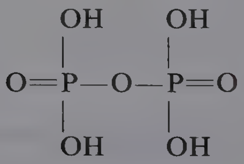
Structures of the phosphoric(V) acids

It may be noticed that, theoretically, an acid $P(OH)_5$ or H_5PO_5 is possible, if phosphorus exerts its maximum covalency of 5 towards hydroxyl groups. This acid does not exist.



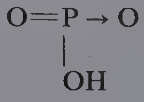
Tetraoxophosphoric(V) acid
(orthophosphoric acid), H_3PO_4
(three OH groups; a *tri*basic acid)

If a molecule of water is eliminated between two hydroxyl groups in *different* molecules of this acid, the following structure is given:



Heptaoxodiphosphoric(V) acid
(pyrophosphoric acid), $H_4P_2O_7$
(four OH groups; a *tetra*basic acid)

If a molecule of water is eliminated between two hydroxyl groups in the *same* molecule of H_3PO_4 the following structure may be obtained. The material is usually polymeric, however (see above.)



Trioxophosphoric(V) acid
(metaphosphoric acid), HPO_3
(one OH group; a *mono*basic acid)

The molybdate(V) test for phosphates(V)

Tetraoxophosphoric(V) acid and its soluble salts give the molybdate(VI) test. The test substance is acidified with nitric acid and then warmed with an *excess* of ammonium molybdate(VI) solution. A yellow coloration or precipitate indicates the presence of the phosphate(V). 'Meta-' and 'pyro-'phosphates(V) also give the test. They hydrolyse to the 'orthophosphate' stage first. The yellow precipitate is variable in composition and is known as '*ammonium phosphomolybdate*'. Arsenates(V) also give the molybdate(VI) test, but not until the mixture is boiling.

Phosphorus(III) oxide, tetraphosphorus hexaoxide (phosphorus trioxide), P_4O_6

This compound is relatively unimportant. It can be prepared as follows. White phosphorus is heated in a slow stream of air. The main product is phosphorus(III) oxide with some phosphorus(V) oxide. The P_4O_{10} is filtered out as solid by a cotton wool plug in a tube surrounded by a water bath kept close to 330 K. The phosphorus(III) oxide is a vapour at this temperature. It passes on and is condensed in a U-tube immersed in a freezing mixture of ice–salt. The U-tube should be protected from atmospheric moisture by an anhydrous calcium chloride guard tube.

$$P_4(s) + 3O_2(g) \rightarrow P_4O_6(s)$$

The structure of P_4O_6 is given on p. 259.
This oxide produces phosphoric acid (*phosphorous acid*) when combined with water.

$$P_4O_6(s) + 6H_2O(l) \rightarrow 4H_3PO_3(s)$$

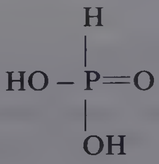
This acid is also produced by the action of phosphorus trichloride with water.

$$PCl_3(l) + 3H_2O(l) \rightarrow H_3PO_3(s) + 3HCl(g)$$

The pure acid melts at 347 K. It is a very vigorous reducing agent. It precipitates metals such as copper and silver from solutions of their salts.

$$Cu^{2+}(aq) + H_3PO_3(aq) + H_2O(l) \rightarrow Cu(s)\downarrow + 2H^+(aq) + H_3PO_4(aq)$$

Phosphoric acid acts as a *di*basic acid.



$$\begin{array}{c} \phantom{HO-{}}H \\ \phantom{HO-{}}| \\ HO-P{=}O \\ \phantom{HO-{}}| \\ \phantom{HO-{}}OH \end{array}$$

Only the hydrogen atoms of the (OH) groups are capable of ionization. The hydrogen atom combined directly with the phosphorus atom does not ionize.

When heated, phosphoric acid decomposes to form *tetraoxophosphoric*(V) *acid* and liberate *phosphine.* This is an example of *disproportionation* (see e.g. p. 382). The four phosphorus atoms in the + 3 oxidation state are converted to three in the + 5 state and one in the − 3 state.

$$4H_3PO_3(s) \rightarrow 3H_3PO_4(l) + PH_3(g)$$

Phosphinic acid (hypophosphorous acid) , H_3PO_2

Salts of this acid are produced when white phosphorus is heated with an alkaline solution, as in the phosphine preparation, p. 256.

$$P_4(s) + 3OH^-(aq) + 3H_2O(l) \rightarrow PH_3(g) + 3H_2PO_2{}^-(aq)$$

If the free acid is wanted, it is best to use a solution of barium hydroxide as the alkali. This gives *barium phosphinate* in solution. If the salt is decomposed by the calculated amount of dilute sulphuric acid, barium sulphate is precipitated and can be filtered off, leaving phosphinic acid in solution.

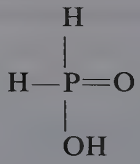
$$Ba(H_2PO_2)_2(aq) + H_2SO_4(aq) \rightarrow BaSO_4(s) \rightarrow + 2H_3PO_2(aq)$$

The pure acid is a crystalline solid, melting at 300 K.

Phosphoric acid is a very strong reducing agent. With copper(II) sulphate solution, it gives a red precipitate of copper(I) hydride.

$$\begin{aligned} 3H_3PO_2(aq) + 3H_2O(l) + 2Cu^{2+}(aq) \rightarrow {} & 3H_3PO_3(aq) + 4H^+(aq) \\ & + 2CuH(s) \end{aligned}$$

The acid is only *mono*basic. This is because only one of its hydrogen atoms is part of a hydroxide group and capable of ionizing; the other two are covalently combined with phosphorus and cannot ionize.



$$\begin{array}{ccc} & \mathrm{H} & \\ & | & \\ \mathrm{H}- & \mathrm{P} & =\mathrm{O} \\ & | & \\ & \mathrm{OH} & \end{array}$$

The chlorides of phosphorus

Phosphorus forms two chlorides: *phosphorus trichloride*, PCl_3 (a colourless liquid); *phosphorus pentachloride*, PCl_5 (a pale yellow solid).

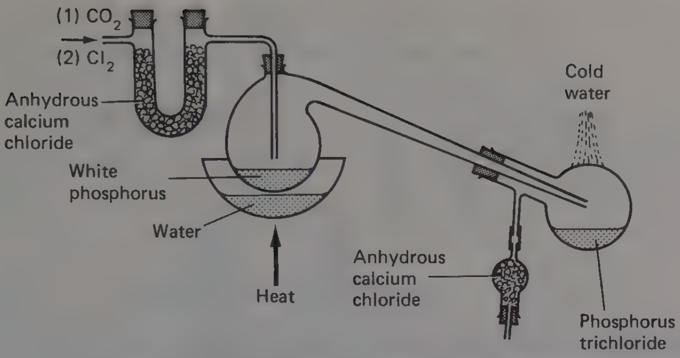


Figure 8.15 *Preparation of phosphorus trichloride*

Phosphorus trichloride, PCl_3

This is prepared as in Figure 8.15. The carbon dioxide expels air. After this, the water-bath may be heated and chlorine passed. Adjustment of supply will maintain steady combination without distillation of unchanged phosphorus.

$$P_4(s) + 6Cl_2(g) \rightarrow 4PCl_3(l)$$

The trichloride can be purified by redistillation over white phosphorus, which reduces any pentachloride which may have been formed. Phosphorus trichloride is a colourless liquid. Its boiling point is 347 K. It is rapidly hydrolysed by cold water to form *phosphonic acid* and *hydrogen chloride.*

$$PCl_3(l) + 3H_2O(l) \rightarrow H_3PO_3(s) + 3HCl(g)$$

This reaction with water vapour causes it to fume in air.

Phosphorus pentachloride, PCl_5

This chloride cannot be prepared in a satisfactory way from phosphorus directly. It is prepared from the trichloride by the apparatus of Figure 8.16.

Rather wide tubes should be used for the chlorine inlet and outlet, because phosphorus pentachloride is a solid and tends to block them. The trichloride is allowed to drip into the bottle as soon as the colour of chlorine is seen in it.

$$PCl_3(l) + Cl_2(g) \rightarrow PCl_5(s)$$

X-ray crystallographic studies have shown that solid phosphorus pentachloride consists of PCl_4^+ and PCl_6^- units.

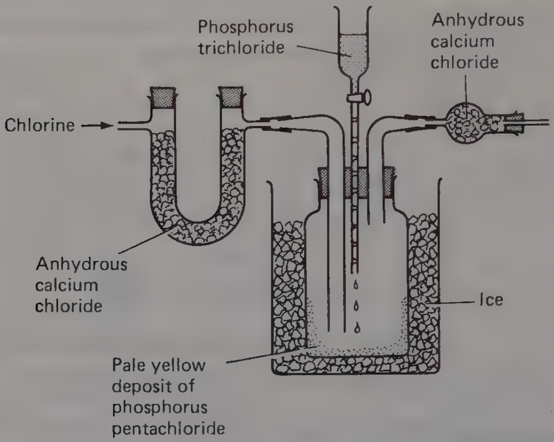


Figure 8.16 *Preparation of phosphorus pentachloride*

Reactions of the chlorides of phosphorus

The chief action of these chlorides is with compounds containing the hydroxyl group—OH, of which water is one example.

1. *With water.* Both chlorides react violently with water at ordinary temperature, liberating 'steamy' fumes of hydrogen chloride.

$$PCl_3(l) + 3H_2O(l) \rightarrow \underset{\text{phosphoric acid}}{H_3PO_3(s)} + 3HCl(g)$$

With the pentachloride, the reaction may occur in two stages:

(a) With a *calculated mass* of water:

$$PCl_5(s) + H_2O(l) \rightarrow \underset{\substack{\text{phosphorus trichloride oxide} \\ \text{(phosphoryl chloride)}}}{POCl_3(l)} + 2HCl(g)$$

(b) With *excess* water, the further reaction occurs:

$$POCl_3(l) + 3H_2O(l) \rightarrow H_3PO_4(aq) + 3HCl(aq)$$

or, in all,

$$PCl_5(s) + 4H_2O(l) \rightarrow \underset{\substack{\text{tetraoxophosphoric(V)} \\ \text{acid}}}{H_3PO_4(aq)} + 5HCl(aq)$$

2. *With alcohols.* With simple alcohols, both compounds react violently at ordinary temperature, liberating 'steamy' fumes of hydrogen chloride and giving the corresponding *chloroalkanes*, e.g. with ethanol,

$$C_2H_5OH(l) + PCl_5(s) \rightarrow C_2H_5Cl(g) + POCl_3(l) + HCl(g)$$
$$6C_2H_5OH(l) + 4PCl_3(l) \rightarrow 6C_2H_5Cl(g) + P_4O_6(s) + 6HCl(g)$$

3. *With carboxylic acids.* The reactions are like those with the alcohols but less vigorous. In the case of the trichloride, heat is usually required. The organic product is the corresponding *acyl chloride*, e.g.

$$CH_3COOH(l) + PCl_5(s) \rightarrow CH_3COCl(l) + POCl_3(l) + HCl(g)$$

$$6CH_3COOH(l) + 4PCl_3(l) \rightarrow 6CH_3COCl(l) + P_4O_6(s) + 6HCl(g)$$

ethanoic acid ethanoyl chloride

Dissociation of phosphorus pentachloride

In the vapour state, phosphorus pentachloride shows abnormal vapour density effects. Up to about 450 K its vapour density relative to hydrogen is normal and is equal to $PCl_5/2$, or about 104. At 570 K the vapour density is equal to $PCl_5/4$, or about 52. At intermediate temperatures, values between 104 and 52 are shown. This behaviour is explained by the dissociation of the compound. At lower temperatures, the molecule is PCl_5, so the relative vapour density is $PCl_5/2$. As the temperature rises, the chloride dissociates, as:

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

This has the effect of doubling the volume with no change of mass; consequently, when dissociation is complete, the relative vapour density is half of its initial value, or $PCl_5/4$. The degree of dissociation at intermediate temperatures can be calculated in the following way. Suppose, at a certain temperature t K, the relative vapour density of phosphorus pentachloride is 70. Let the degree of dissociation at this temperature be x.

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

Initially	1 mol	—	—	(no dissociation; relative vapour density is 104.25)
At t K,	$(1-x)$ mol	x mol	x mol	(relative vapour density is 70)

Since the mass of the phosphorus pentachloride is constant, the density must be inversely proportional to the volume occupied at constant pressure, i.e.

$$\frac{(1-x)+2x}{1} = \frac{104.25}{70}$$

or

$$(1+x) = 1.49$$

and

$$x = 0.49$$

i.e. the degree of dissociation is 0.49 or 49 per cent.

Shapes of the molecules of the phosphorus chlorides

The shape of the phosphorus trichloride molecule is essentially that of a trigonal pyramid. The pentachloride has a regular trigonal bipyramid structure (see *Advanced Level Physical Chemistry*, p. 80).

It will be noticed that in PCl_5 the phosphorus atom has exceeded the octet of electrons in the outer quantum shell. This can happen because, unlike nitrogen, phosphorus has 3d orbitals available for bonding (see *Advanced Level Physical Chemistry*, p. 77).

Phosphorus trichloride oxide (phosphoryl chloride or phosphorus oxychloride), $POCl_3$

This compound is most conveniently made by distilling phosphorus trichloride with potassium chlorate(V).

$$3PCl_3(l) + KClO_3(s) \rightarrow 3POCl_3(l) + 3KCl(s)$$

Phosphorus trichloride oxide is manufactured by heating a mixture of calcium phosphate(V) and charcoal in chlorine at about 670 K.

$$Ca_3(PO_4)_2(s) + 6Cl_2(g) + 6C(s) \rightarrow 2POCl_3(l) + 3CaCl_2(s) + 6CO(g)$$

It is a liquid of higher boiling point (380 K) than the trichloride (347 K). Its principal reaction is its hydrolysis by water to tetraoxophosphoric(V) acid.

$$POCl_3(l) + 3H_2O(l) \rightarrow H_3PO_4(aq) + 3HCl(g)$$

Phosphorus tribromide, PBr_3, and pentabromide, PBr_5

The tribromide can be made by mixing bromine and white phosphorus, both in solution in carbon disulphide. The carbon disulphide is distilled away and the phosphorus tribromide (boiling point, 446 K) is distilled. It resembles the trichloride in properties but is less reactive. It combines directly with bromine to form the pentabromide, a yellow solid.

$$PBr_3(l) + Br_2(l) \rightarrow PBr_5(s)$$

The pentabromide is similar to the pentachloride in its reactions but less vigorous.

Phosphorus tri-iodide, PI_3

This compound can be made by mixing white phosphorus and iodine (in calculated masses), both in solution in carbon disulphide. After evaporation of the solvent, the iodide is left as a reddish solid, melting point 334 K.

$$P_4(\text{in } CS_2) + 6I_2(\text{in } CS_2) \rightarrow 4PI_3(\text{in } CS_2)$$

If iodine is brought into contact with white phosphorus in air, the reaction is usually vigorous enough to inflame the mixture. Phosphorus forms no penta-iodide.

Sulphides of phosphorus

Phosphorus forms several sulphides. They can be made by heating *red* phosphorus with sulphur, in the appropriate amounts, in an inert atmosphere. (White phosphorus will react, but is dangerously violent.) The following sulphides are known: P_2S_5, P_4S_3, P_4S_7. Ordinary matches usually contain a sulphide of phosphorus. The pentasulphide is hydrolysed by water.

$$P_2S_5(s) + 8H_2O(l) \rightarrow 2H_3PO_4(aq) + 5H_2S(g)$$

Arsenic

Atomic number 33.
Electron arrangement 2.8.18.5($1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^3$)
Arsenic has only one isotope, of mass number 75.
Relative atomic mass 74.92

Antimony

Atomic number 51.
Electrons 2.8.18.18.5($1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^3$)
Antimony has isotopes of mass number, in order of abundance, 121 and 123.
Relative atomic mass 121.8

Bismuth

Atomic number 83; electron arrangement
2.8.18.32.18.5 ($1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 5d^{10} 6s^2 6p^3$)
Bismuth has only one stable isotope, of mass number 209.
Radioactive isotopes exist, of mass numbers 210, 211, 212, 214.
Relative atomic mass 209.0

A detailed knowledge of the chemistry of arsenic, antimony and bismuth is not necessary at this level. However, comparison of their properties with those of nitrogen and phosphorus illustrates the gradation of properties, from non-metallic to essentially metallic, down Group V of the Periodic Table. These comparisons are summarized below.

Element	N	P	As	Sb	Bi
Relative atomic mass	14.01	30.97	74.92	121.8	209.0
Melting point (K)	63	317 (white) 863 (red)	Sublimes	903	544
Boiling point (K)	77	553 (white)	Sublimes	1650	1830
Density($\mathrm{g\,cm^{-3}}$)	0.808 (at 77 K)	1.82 (white) 2.34 (red)	5.72 (grey)	6.62	9.80
Electronegativity (Pauling scale)	3.0	2.1	2.0	1.9	1.9
Oxidation states (less common in brackets)	(1), (2), 3, (4), 5	3, 5	3, 5	3, 5	3, (5)
Hydrides	NH_3, ammonia N_2H_4, hydrazine HN_3, hydrazoic acid	PH_3, phosphine P_2H_4	AsH_3 arsine	SbH_3 stibine	BiH_3 bismuthine
Thermal stability of hydride, XH_3	Quite stable	Decomposes on heating	Decomposes on heating	Unstable at room temperature	Unstable at room temperature
Oxides, and nature of oxides	$\left.\begin{matrix}N_2O\\NO\end{matrix}\right\}$ neutral $\left.\begin{matrix}N_2O_3\\N_2O_4(NO_2)\\N_2O_5\end{matrix}\right\}$ acidic	$\left.\begin{matrix}P_4O_6\\P_4O_{10}\end{matrix}\right\}$ acidic	$\left.\begin{matrix}As_4O_6\\As_4O_{10}\end{matrix}\right\}$ acidic	Sb_2O_3 amphoteric Sb_2O_5 acidic	Bi_2O_3 basic Bi_2O_5 unstable; acidic
Chlorides, and nature of chlorides	NCl_3 dangerously unstable liquid	PCl_3 liquid; PCl_5 solid. Both fume in moist air	$AsCl_3$ liquid; fumes in most air	$SbCl_3$ solid; dissolves in water with partial hydrolysis	$BiCl_3$ solid; dissolves in water with partial hydrolysis

Arsine—Arsine, AsH_3, is made by the action of zinc and dilute hydrochloric acid on arsenic or any compound containing arsenic. This is the basis of Marsh's test for arsenic, which was used for many years in murder cases involving arsenic. The gases produced in the reaction were passed through a heated glass tube; the unstable arsine decomposed to form a black mirror of arsenic, which could be dissolved in sodium chlorate(I) (sodium hypochlorite) solution. (An antimony mirror does not so dissolve.)

Questions

1. Give an account of the preparation of nitrogen from the atmosphere; also, briefly, of the preparation of nitrogen from *two* chemical sources. What important difference of composition is there between the product from the atmosphere and from chemical sources? Comment, with appropriate examples, on the statement that nitrogen is *inert*.

2. Write a concise account of the Nitrogen Cycle in Nature. How, and why, do the activities of man interfere with this cycle?

3. What is meant by *fixation of nitrogen*? Give a *full* account of a process for fixation of nitrogen on the industrial scale.

4. Give a concise account of the large-scale production of nitric acid by oxidation of ammonia. This acid is said to show *oxidizing* properties. Justify this statement by a concise account of appropriate examples, *two* in each case, referring to (i) metals, (ii) non-metals, (iii) inorganic compounds. Specify reaction conditions throughout.

5. Give a general account, with appropriate examples, of the action of heat on metallic nitrates.

6. How would you prepare a sample of phosphoric(V) acid (H_3PO_4) from red phosphorus? Explain why this acid can form three sodium salts and outline the preparation of the three from the acid. Why does the acid H_3PO_3 act as only *di*basic?

7. By reference to the properties and reactions of the elements, their oxides, chlorides and hydrides (if any), discuss the statement that metallic nature increases in the direction As → Sb → Bi.

8. Four common oxidation states of nitrogen are -3, $+3$, $+4$ and $+5$. Give the names and formulae of *four* compounds containing nitrogen, one in each of these oxidation states.

Describe briefly how *three* of the compounds you mention could be conveniently prepared in the laboratory.

Describe how you could obtain a specimen of nitrogen from one of the compounds you have discussed. (L.)

9. Describe the manufacture of nitric acid from ammonia. Give careful attention to the physico-chemical principles including the importance of the catalyst.

Discuss the importance of the acid in industry today. (L.)

Describe and explain the action of nitric acid in varying concentrations on copper.

10. (a) Describe the Haber process for the manufacture of ammonia, explaining carefully the reasons for the physical and chemical conditions under which the process is carried out, but omitting details of industrial plant.

(b) How does ammonia react with chlorine?

(c) By means of a clearly labelled schematic diagram *only*, describe the nitrogen cycle. Your diagram should give the principal classes of compounds involved and show how they are interconverted. (O.)

11. Outline the chemical reactions involved in the synthesis of ammonia and of nitric acid starting from nitrogen.

State and explain the variation in the action of water on the trichlorides of the elements of Group V. Why does nitrogen not form a pentachloride? (C.)

12. (a) The reduction of nitrate ions in acid solution may result in the formation of five different nitrogenous products, depending on the conditions. Write ion-electron equations to show the formation of *any four* and describe the structure of *any two*.

(b) Nitrite ion may be determined by oxidation to nitrate ion by an acidic solution of potassium permanganate. In a typical determination 25.00 cm^3 of a solution, in molar sulphuric acid, containing 3.16 g cm^{-3} of potassium manganate(VII) were heated to 310–320 K and titrated with nitrite solution of which 27.50 cm^3 were required.
  (i) Write ion–electron equations for the reactions involved.
  (ii) Calculate the concentration in grammes dm^{-3} of the nitrite solution.
  (iii) Explain why the nitrite solution is added to the potassium manganate(VII) rather than the other way round. (A.E.B.)

13. This question concerns the elements nitrogen, phosphorus, and arsenic.
  (a) Give the electronic configurations of the elements.
  (b) Give a different type of reaction in each case for the formation of the trihydrides of the elements.
  (c) Explain why ammonia has a higher dissociation constant than phosphine.
  (d) Give the structures of nitrogen and phosphorus and relate them to the physical states and stabilities of the elements. (A.E.B.)

14. (a) By writing equations for suitable reactions, illustrate the behaviour of ammonia as (i) a base, (ii) a reducing agent (reductant), (iii) a ligand.
  (b) For the elements, nitrogen, phosphorus, and arsenic,
  (i) give the formulae of their characteristic hydrides;
  (ii) state how the thermal stability of the characteristic hydride varies from nitrogen to phosphorus to arsenic.
  (c) (i) Give the oxidation number (state) of nitrogen in the following compounds: nitric acid; nitrous acid; ammonia.
  (ii) Explain why nitric acid can be reduced but cannot be oxidized; give an example of its reduction.
  (iii) Explain, giving one example in each case, why nitrous acid can act both as a reducing agent and as an oxidizing agent. (A.E.B.)

15. This question concerns the elements arsenic (atomic number 33), nitrogen (atomic number 7) and phosphorus (atomic number 15).
  (a) For what reason are the elements placed in the same group of the Periodic Table?
  (b) Distinguishing between s, p, and d electrons, give the electronic configuration of the elements.
  (c) Place the elements in order of decreasing electronegativity (i.e. putting the most electronegative element first). Name one other element which is more electronegative than all three.
  (d) Give the structures of
  (i) the tetraamminezinc(II) ion;
  (ii) dinitrogen tetraoxide;
  (iii) solid phosphorus pentachloride.
  Outline the preparation of (iii).
  (e) Explain why
  (i) phosphorus forms a trichloride and a pentachloride but nitrogen forms only a trichloride;
  (ii) ammonia is more basic than phosphine;
  (iii) nitrogen is more inert than phosphorus. (A.E.B.)

16. Describe the chemistry of the extraction of phosphorus from calcium tetraoxophosphate(V) (orthophosphate) and state which allotrope is formed.

Give the reaction conditions and an equation for the formation of phosphine from white phosphorus.

Explain why ammonia (a) is more basic, (b) has a higher boiling point, (c) has a greater bond angle than phosphine.

Give the structure of tetraoxophosphoric(V) acid (orthophosphoric acid) and state briefly how it could be formed from phosphorus pentachloride. (A.E.B.)

9

Elements of Group VI

Group VI of the Periodic Table contains the elements oxygen, sulphur, selenium, tellurium, and polonium. Of these, only oxygen and sulphur will be considered here.

Oxygen

Atomic number 8.
Electron arrangement 2.6 ($1s^2 2s^2 2p^4$)
Oxygen has isotopes of mass number, in order of abundance, 16, 18 and 17.
Relative atomic mass 16.00

Oxygen is the most abundant of all elements in the Earth's crust. It comprises almost one-quarter of the atmosphere by mass and eight-ninths of the water of the oceans. It also occurs in many natural rocks, which may contain calcium carbonate (oxygen, 48 per cent) and silica (oxygen, 53.3 per cent), silicates and oxides, as well as less common oxysalts.

Preparation of oxygen

1. *From hydrogen peroxide.* A quick and convenient method for the preparation of small quantities of oxygen is to drop hydrogen peroxide solution at room temperature on to manganese(IV) oxide (Figure 9.1). The manganese(IV) oxide catalyses the decomposition of the hydrogen

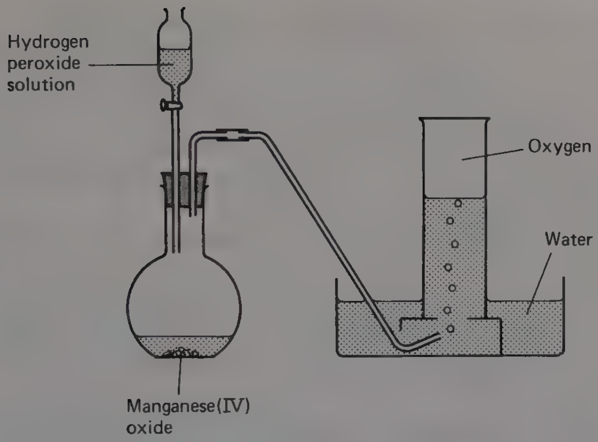


Figure 9.1 *Preparation of oxygen*

peroxide to water and oxygen. Reaction is immediate, and the quantity of gas is easily controlled.

$$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$$

The gas may be collected over water, in which it is only slightly soluble.

2. *From potassium chlorate*(V). When heated alone, potassium chlorate(V) liberates all its oxygen at about 900 K. To reduce the temperature required, it is usual to grind the chlorate(V) with about one quarter of its mass of manganese(IV) oxide which acts as *catalyst* and enables the oxygen to be released at a much lower temperature (about 500 K). Oxygen prepared in this way usually contains chlorine (see below) and carbon dioxide (derived from the combustion of traces of organic matter in the manganese(IV) oxide). Both these impurities can be removed by sodalime and the oxygen is usually collected over water.

$$2KClO_3(s) \rightarrow 2KCl(s) + 3O_2(g)$$

This is regarded as a case of *intermediate compound catalysis*. McLeod postulated the following sequence:

$$\left.\begin{array}{r} 2MnO_2(s) + 2KClO_3(s) \rightarrow 2KMnO_4(s) + Cl_2(g) + O_2(g) \\ 2KMnO_4(s) \rightarrow K_2MnO_4(s) + MnO_2(s) + O_2(g) \\ K_2MnO_4(s) + Cl_2(g) \rightarrow 2KCl(s) + MnO_2(s) + O_2(g) \end{array}\right\}$$

$$\text{Total result: } 2KClO_3(s) \rightarrow 2KCl(s) + 3O_2(g)$$

It will be seen that the manganese(IV) oxide is recovered. Three observations provide evidence for this mechanism.

(a) The presence of a little chlorine in the oxygen produced.
(b) If potassium chlorate(V) is heated strongly with manganese(IV) oxide in the approximate proportions 5000:1, the strong purple colour of the manganate(VII) ion develops in the molten mass. The colour remains if the material is allowed to cool and solidify.
(c) If this purple mixture is heated even more strongly, the green coloration of the manganate(VI) ion is seen.

Certain other oxysalts also liberate oxygen when heated, but are much less convenient than potassium chlorate(V) for practical use, e.g.

Potassium (or sodium) nitrate $2KNO_3(s) \rightarrow 2KNO_2(s) + O_2(g)$
Potassium manganate(VII) (potassium permanganate) $2KMnO_4(s) \rightarrow K_2MnO_4(s) + MnO_2(s) + O_2(g)$

3. *From oxides.* A number of oxides will yield oxygen when heated. Examples are:

Lead(IV) oxide	$2PbO_2(s) \rightarrow 2PbO(s) + O_2(g)$
Red lead oxide	$2Pb_3O_4(s) \rightarrow 6PbO(s) + O_2(g)$
Barium peroxide	$2BaO_2(s) \rightarrow 2BaO(s) + O_2(g)$
Silver oxide	$2Ag_2O(s) \rightarrow 4Ag(s) + O_2(g)$
Mercury(II) oxide	$2HgO(s) \rightarrow 2Hg(l) + O_2(g)$

Industrial preparation of oxygen

Most of the oxygen (and nitrogen) used in industry is obtained by the fractional distillation of liquid air. (For the liquefaction of air see *Advanced Level Physical Chemistry*, p. 123.) Nitrogen has a lower boiling point (77 K) than oxygen (90 K). This difference of 13 K between the boiling points of the two gases enables them to be almost completely separated by a careful fractionation. The boiling points of all mixtures of oxygen and nitrogen lie between the boiling points of the two pure gases. Since nitrogen is the more volatile of the two gases, the vapour in equilibrium with a given liquid must contain a higher proportion of nitrogen than the liquid itself. The dotted curve (Figure 9.2) shows the composition of vapour in equilibrium with liquid mixtures of nitrogen and oxygen.

Thus a liquid of composition A will yield a vapour of composition B. This will condense to a liquid C, which will distil giving a vapour D. D will condense to a liquid E, distilling to vapour F and so on. As the progression along the graph shows, a large number of distillations tend, in this way, to yield comparatively pure gaseous nitrogen as the final vapour, and leave behind comparatively pure liquid oxygen.

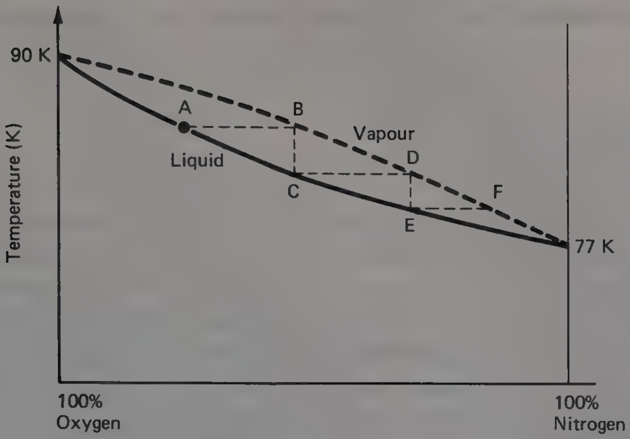


Figure 9.2 *Boiling points, at 1 atm, of oxygen–nitrogen mixtures*

In industry, an elaborate apparatus simulates a large number of such distillations. A lengthy, vertical rectifying column is used, with perforated shelves at frequent intervals. Incoming air is liquefied in *two stages* so that the first liquid fraction is comparatively rich in the more easily liquefied oxygen, while the second fraction is rich in nitrogen. The nitrogen-rich fraction is pumped to the top of the rectifying column. As it descends, almost pure nitrogen evaporates from it and is collected and compressed into cylinders for use. The oxygen-rich fraction enters the column lower down. As it descends, nitrogen evaporates from it and oxygen condenses into it, so that it becomes progressively richer in oxygen until it contains about 96 per cent of oxygen. The gas evaporating from this liquid is collected and stored in steel cylinders under high pressure.

Uses of oxygen

(a) Oxygen is now used for making steel by the L.D. and Kaldo processes (see p. 434).
(b) Oxygen is used in the 'oxyhydrogen' and 'oxyacetylene' flames, the latter for cutting steel plate and for welding.
(c) Oxygen has medical uses, particularly in the treatment of persons who have been exposed to carbon monoxide poisoning, near-suffocation or similar situations. It is also used by climbers and fliers at high altitudes.
(d) Oxygen is used in thickening (by oxidation) oils for use in the making of linoleum and varnish.

(e) Liquid oxygen can be used in explosive cartridges employed in mining, and as the oxidant in rocket propellant system.

Properties of oxygen

Physical properties

Oxygen is a colourless, odourless gas. It is slightly soluble in water (about 4 cm^3 of the gas in 100 cm^3 of water at room temperature). This is important for the maintenance of fish life, which depends on this dissolved oxygen for respiration. The critical temperature of oxygen is 154 K and its boiling point is 90 K. It has a melting point of 54 K. Both liquid and solid oxygen are pale blue.

Chemical properties

Oxygen has a diatomic molecule, O_2. This molecule is fairly stable and oxygen is not very reactive at ordinary temperature. If, however, the temperature is raised so that a certain amount of dissociation into *separate atoms* of oxygen occurs, the gas then becomes very reactive. As it reacts, more heat is liberated, which produces further dissocation, and a rapid and complete reaction usually occurs. Thus, when heated, oxygen combines vigorously with all the more electropositive *metals*, causing them to vaporize and burn rapidly to an *oxide* of the metal, e.g.

$$2Mg(s) + O_2(g) \rightarrow 2MgO(s)$$
$$2Ca(s) + O_2(g) \rightarrow 2CaO(s)$$

Sodium (and potassium) may form a mixture of the *monoxide*, Na_2O, and *peroxide*, Na_2O_2; excess oxygen will produce peroxide only. Iron produces its *black* oxide, Fe_3O_4. The less electropositive metals, such as lead, copper and mercury, combine slowly when heated with oxygen, e.g.

$$2Cu(s) + O_2(g) \rightarrow 2CuO(s)$$
$$2Pb(s) + O_2(g) \rightarrow 2PbO(s)$$

Platinum and gold remain unchanged.

Many *non-metals* burn rapidly if heated with oxygen, producing an *oxide* of the non-metal, e.g. P_2O_5, SO_2, CO_2. Oxygen also reacts with many *compounds*. Sulphides are usually oxidized by oxygen (of the air) when heated, a fact which is frequently used in the extraction of metals from their ores, e.g.

$$2ZnS(s) + 3O_2(g) \rightarrow 2ZnO(s) + 2SO_2(g)$$
$$2PbS(s) + 3O_2(g) \rightarrow 2PbO(s) + 2SO_2(g)$$

Hydrogen sulphide and carbon disulphide burn if ignited in air or oxygen.

$$CS_2(l) + 3O_2(g) \rightarrow CO_2(g) + 2SO_2(g)$$
$$2H_2S(g) + 3O_2(g) \rightarrow 2H_2O(g) + 2SO_2(g)$$

Nitrogen oxide combines rapidly with oxygen at ordinary temperature to form *nitrogen dioxide* as brown furmes.

$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$$

Oxygen and oxidation

The close association of the two names *oxygen* and *oxidation* tends to convey the impression that the phenomenon of oxidation is more closely associated with oxygen than with any other element. In the modern view, this is not so. When acting as an oxidizing agent, oxygen operates, as do all oxidizing agents, as an electron acceptor, but does not differ in function from other elements when they, too, operate as oxidizing agents. It is obvious that oxygen, sulphur and chlorine are all behaving similarly in the reactions shown below. They are all *reduced* to ions by electron gain and the zinc atom is *oxidized* to its ion by electron loss.

$$Zn(s) + \tfrac{1}{2}O_2(g) \rightarrow Zn^{2+}.O^{2-}(s)$$
$$Zn(s) + Cl_2(g) \rightarrow Zn^{2+}.2Cl^{-}(s)$$
$$Zn(s) + S(s) \rightarrow Zn^{2+}.S^{2-}(s)$$

The phenomenon of oxidation was closely associated with oxygen in the early days of chemistry simply because oxygen was readily available as a constituent of air and information about it was easily accessible. Oxygen is now recognized to be merely one of many elements which, as electron acceptors, exercise oxidizing properties. (See also *Advanced Level Physical Chemistry*, p. 243 ff.)

Classification of oxides

Oxides, i.e. compounds containing oxygen and *one* other element, vary widely in properties and can be classified into the following groups. It should be emphasized that many oxides cannot easily be classified under a single heading.

(1) *Acidic oxides*

Acidic oxides are oxides of *non-metals.* When combined with the elements of water, they produce *acids*, though in some cases the acids are very unstable (e.g. H_2CO_3) or ill-defined (e.g. the acids corresponding to SiO_2). Because of this behaviour, they are sometimes known as the *anhydrides* of the corresponding acids, e.g. sulphur dioxide is the anhydride of sulphurous acid.

$$SO_2(g) + H_2O(l) \rightleftharpoons H_2SO_3(aq)$$

Carbon dioxide is the anhydride of carbonic acid.

$$CO_2(g) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$$

Such oxides also react with bases to form *salts*, e.g.

$$SO_2(g) + 2NaOH(aq) \rightarrow Na_2SO_3(aq) + H_2O(l)$$
$$CO_2(g) + CaO(s) \rightleftharpoons CaCO_3(s)$$

Some non-metal oxides are insoluble in water, but still react with concentrated or fused alkalis to give salts, e.g.

$$SiO_2(s) + 2NaOH(l) \rightarrow Na_2SiO_3(l) + 2H_2O(g)$$

(2) *Basic oxides*

Basic oxides are oxides of *metals* (though not all oxides of metals are basic). The characteristic property of a basic oxide is to react with an *acid* to form a salt and water only, e.g.

$$CuO(s) + H_2SO_4(aq) \rightarrow CuSO_4(aq) + H_2O(l)$$
$$MgO(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2O(l)$$

The ionic interpretation of this behaviour is that the oxide is an electrovalent compound containing the ion, O^{2-}. This ion participates in an equilibrium with water.

$$O^{2-} + H_2O(l) \rightleftharpoons 2OH^-(aq)$$

and the OH^- so produced enters into a reaction of neutralization with the H^+ ion of the acid:

$$OH^-(aq) + H^+(aq) \rightleftharpoons H_2O(l)$$

If the equilibrium, $O^{2-} + H_2O(l) \rightleftharpoons 2OH^-(aq)$, lies much to the right, the oxide dissolves and forms an alkali, e.g.

$$Na_2O(s) + H_2O(l) \rightleftharpoons 2NaOH(aq)$$

If it lies much to the left, the oxide is an 'insoluble' base, e.g. CuO.

(3) *Amphoteric oxides*

An amphoteric oxide is a metallic oxide which can exert *basic* properties by reacting with an acid to form a salt and water only, and *acidic* properties by reacting with an alkali to form a salt and water only, e.g. with zinc oxide (see p. 472) and aluminium oxide (see p. 123).

Basic
$$ZnO(s) + H_2SO_4(aq) \rightarrow ZnSO_4(aq) + H_2O(l)$$
$$Al_2O_3(s) + 6HCl(aq) \rightarrow 2AlCl_3(aq) + 3H_2O(l)$$

Acidic
$$ZnO(s) + 2OH^-(aq) + 3H_2O(l) \rightarrow [Zn(OH)_4(H_2O)_2]^{2-}(aq)$$
$$Al_2O_3(s) + 2OH^-(aq) + 7H_2O(l) \rightarrow 2[Al(OH)_4(H_2O)_2]^-(aq)$$

(4) *Neutral oxides*

These are oxides which show neither acidic nor basic properties, e.g. dinitrogen oxide. Carbon monoxide is often said to be a neutral oxide, but it can be made to act as the anhydride of methanoic acid (formic acid) (see p. 156).

(5) *Peroxides*

A peroxide is a metallic oxide containing a higher proportion of oxygen than the corresponding basic oxide and *capable of yielding hydrogen peroxide by the action of dilute mineral acid.* Examples are sodium, potassium, calcium, and barium peroxides. Peroxides are *electrovalent* and act as *salts* of hydrogen peroxide, which is a very weak acid. They contain the peroxide ion, O_2^{2-}. Their reactions with dilute mineral acid are of the type:

$$BaO_2(s) + H_2SO_4(aq) \rightarrow BaSO_4(s) + H_2O_2(aq)$$

Certain other oxides, such as PbO_2 and MnO_2, have molecular formulae resembling those of peroxides. These oxides are, however, *covalent* (e.g. $O{=}Pb{=}O$) and do not yield hydrogen peroxide with dilute mineral acids. They are usually classified as *acidic oxides.* For example, on heating with concentrated or fused caustic alkali, lead(IV) oxide yields the hexahydroxoplumbate(IV) ion.

$$PbO_2(s) + 2OH^-(aq) + 2H_2O(l) \rightarrow [Pb(OH)_6]^{2-}(aq)$$

(6) *Compound oxides*

Compound oxides are metallic oxides which behave as if they are compounds of *lower* and *higher* oxides of the same metal. Examples are:

Red lead oxide, Pb_3O_4, behaving as $PbO_2.2PbO$.
'Black iron oxide', Fe_3O_4, behaving as $Fe_2O_3.FeO$.

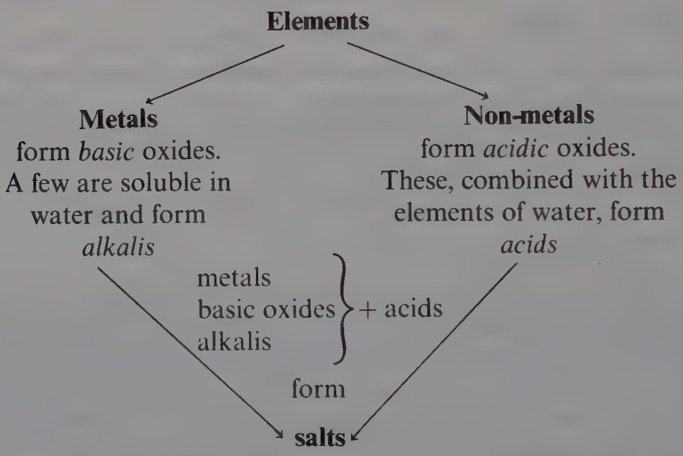
An example of mixed behaviour is:

$$Fe_3O_4(s) + 8HCl(aq) \rightarrow 2FeCl_3(aq) + FeCl_2(aq) + 4H_2O(l)$$

This is equivalent to:

$$\left\{ \begin{array}{l} Fe_2O_3(s) + 6HCl(aq) \rightarrow 2FeCl_3(aq) + 3H_2O(l) \\ \quad FeO(s) + 2HCl(aq) \rightarrow FeCl_2(aq) + H_2O(l) \end{array} \right.$$

The relations summarized in tabular form below are important and should be thoroughly appreciated.



Where a metal can form more than one oxide, the general rule is that the higher the oxidation state of the metal, the more acidic (or less basic!) is the corresponding oxide. See, for example, the oxides of lead (pp. 196 and 202) and of chromium (pp. 414 and 416).

General methods of preparing oxides of heavy metals

This is a convenient point at which to consider these general methods. The heating of a heavy metal in any gas (e.g. air, oxygen, dinitrogen oxide) is never entirely satisfactory as a method of preparing its oxide. The reason is that oxidation tends to be superficial, because the initial layer of oxide cuts off contact between remaining metal and the oxidizing gas. The following methods are satisfactory and fairly general. Zinc is used as the example.

To the zinc, add moderately concentrated nitric acid and warm the mixture. Effervescence will occur with evolution of oxides of nitrogen (brown fumes). Zinc will dissolve to form zinc nitrate in solution. Allow the reaction to continue, with zinc always present, till it is visibly slackening, showing that the acid is almost used up. Then filter off the excess of zinc and divide the zinc nitrate solution into three parts.

Part 1. Evaporate the solution to dryness in a crucible till solid zinc nitrate is left. Then heat it more strongly. Brown fumes will be evolved, leaving a solid which is yellow when hot and white when cold, zinc oxide. As an assurance of complete decomposition of the nitrate, heat the oxide to constant mass.

$$2Zn(NO_3)_2(s) \rightarrow 2ZnO(s) + 4NO_2(g) + O_2(g)$$

Part 2. Add *sodium carbonate solution* to the solution of zinc nitrate to precipitate zinc carbonate (basic) as a white solid. Ignoring the basic character:

$$Zn(NO_3)_2(aq) + Na_2CO_3(aq) \rightarrow ZnCO_3(s) + 2NaNO_3(aq)$$

Filter off the zinc carbonate, wash it well with hot, distilled water and dry it in a steam oven. Then heat it to constant mass, leaving zinc oxide as before.

$$ZnCO_3(s) \rightarrow ZnO(s) + CO_2(g)$$

Part 3. Proceed exactly as in Part 2, but using *sodium hydroxide solution*. The precipitate is zinc hydroxide; *excess sodium hydroxide solution must be avoided* because it will redissolve the precipitate.

$$Zn(NO_3)_2(aq) + 2NaOH(aq \rightarrow Zn(OH)_2(s) + 2NaNO_3(aq)$$

Treat the precipitate exactly as in Part 2. On heating,

$$Zn(OH)_2(s) \rightarrow ZnO(s) + H_2O(g)$$

These methods are suitable for preparing the oxides of *zinc*, *copper*(II), *lead*(II), and *magnesium* from the corresponding metals. The equations are the same as for zinc above, substituting the appropriate symbol. Colours involved are:

	Colour of nitrate solution	*Colour of carbonate*	*Colour of hydroxide (or hydrated oxide) precipitate*	*Colour of oxide*
Zn	colourless	white	white	yellow—hot white—cold
Cu	blue	green	blue	black
Pb	colourless	white	white	yellow
Mg	colourless	white	white	white

Aluminium oxide cannot be prepared quite as above, because nitric acid does not attack aluminium. Instead, the aluminium metal should be dissolved, with heat, in moderately concentrated hydrochloric acid, filtering off the excess of metal as the reaction slackens.

$$2Al(s) + 6HCl(aq) \rightarrow 2AlCl_3(aq) + 3H_2(g)$$

The filtrate can then be treated as in Part 2 or Part 3 above. Aluminium forms no carbonate so, in either case, the precipitate is the *hydroxide* (colourless, gelatinous). Again, the precipitate will dissolve if excess sodium hydroxide solution is added.

$$AlCl_3(aq) + 3NaOH(aq) \rightarrow Al(OH)_3(s) + 3NaCl(aq)$$

Heating: $$2Al(OH)_3(s) \rightarrow \underset{\text{white}}{Al_2O_3(s)} + 3H_2O(g)$$

Iron(III) *oxide.* Reaction of iron with dilute nitric acid gives a mixture of Fe^{2+} and Fe^{3+} ions in solution, while iron is *passive* to concentrated nitric acid. In this case, the best method is to convert iron to iron(III) chloride (black sublimate) by heating it in dry chlorine (p. 368).

$$2Fe(s) + 3Cl_2(g) \rightarrow 2FeCl_3(s)$$

The iron(III) chloride can then be dissolved in distilled water (yellow solution) and treated as in Part 3 above.

$$FeCl_3(aq) + 3NaOH(aq) \rightarrow Fe(OH)_3(s) + 3NaCl(aq)$$

Heating: $$2Fe(OH)_3(s) \rightarrow \underset{\text{reddish brown}}{Fe_2O_3(s)} + 3H_2O(g)$$

Silver oxide can be made from silver by first producing silver nitrate solution as described for zinc.

$$Ag(s) + 2HNO_3(aq) \rightarrow AgNO_3(aq) + NO_2(g) + H_2O(l)$$

Then add sodium hydroxide solution. This precipitates silver oxide (dark brown); silver hydroxide is unknown.

$$2AgNO_3(aq) + 2NaOH(aq) \rightarrow Ag_2O(s) + H_2O(l) + 2NaNO_3(aq)$$

The oxide should be filtered off, washed with hot distilled water and dried in a steam oven. (Evaporation and heating of the nitrate, or precipitation and heating of the carbonate, would produce *silver metal*, because the oxide decomposes at about 570 K.)

Mercury(II) *oxide* is best made by first heating mercury in dry chlorine to produce mercury(II) chloride (p. 368). This is a white solid.

$$Hg(l) + Cl_2(g) \rightarrow HgCl_2(s)$$

To make the *yellow* variety of mercury(II) oxide, mix *cold* solutions of mercury(II) chloride and sodium hydroxide solution. Yellow mercury(II) oxide precipitates; mercury forms no hydroxide.

$$HgCl_2(aq) + 2NaOH(aq) \rightarrow HgO(s) + H_2O(l) + 2NaCl(aq)$$

Filter the precipitate, wash it with cold distilled water and allow it to dry.

To make the *red* variety of mercury(II) oxide, mix *boiling* solutions of mercury(II) chloride and sodium carbonate. The red oxide precipitates; mercury forms no carbonate.

$$HgCl_2(aq) + Na_2CO_3(aq) \rightarrow HgO(s) + CO_2(g) + NaCl(aq)$$

Filter the precipitate, wash it with hot, distilled water and dry it in a steam oven.

Ozone (trioxygen), O_3

Ozone (more systematically, *trioxygen*) is an allotropic form of oxygen. The usual molecule, O_2, could be called dioxygen. The names *ozone* and *oxygen* will be used in this discussion.

Preparation of ozone

Ozone is usually prepared, mixed with unchanged oxygen, by the effect of a silent electrical discharge on dry oxygen. Two alternative forms of ozonizer are shown in Figure 9.3. They are essentially similar, differing only in the use of tin foil in one case, and dilute sulphuric acid in the other, as conductors. The voltage from the induction coil should

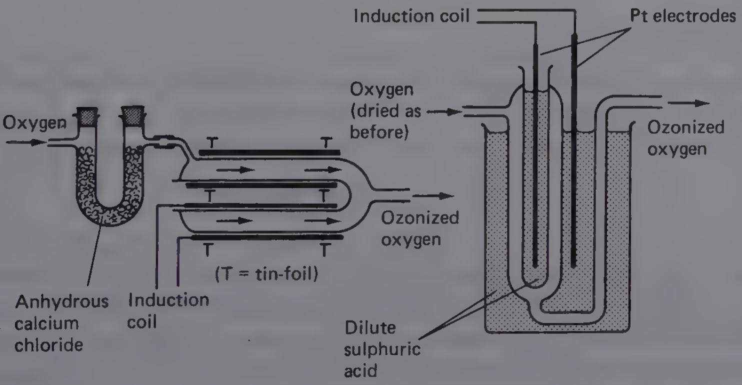


Figure 9.3 *Preparation of ionized oxygen*

be about 15000 V. Notice that the tin foil must be on the side of the glass *away* from the gases in all cases; otherwise the metal will be oxidized by the ozone. The issuing gas may contain up to 8 per cent of ozone by volume.

$$3O_2(g) \rightarrow 2O_3(g)$$

Passage of ozonized oxygen through a tube immersed in liquid oxygen will condense out a mixture of liquid ozone and liquid oxygen. Fractional distillation of this gives liquid ozone, which is dark blue in colour; pure gaseous ozone can be obtained by careful evaporation. The liquid is liable to explode.

Ozone occurs, in traces, as a product of many chemical changes. Among them are the following: the electrolysis of dilute sulphuric acid, especially with a small, platinum anode; the slow oxidation of phosphorus; the heating of manganese(IV) dioxide with concentrated sulphuric acid. The action of fluorine on water may produce a gas containing up to 14 per cent of ozone by volume.

$$3F_2(g) + 3H_2O(l) \rightarrow 3H_2F_2(aq) + O_3(g)$$
$$2F_2(g) + 2H_2O(l) \rightarrow 2H_2F_2(aq) + O_2(g)$$

It is also formed when oxygen is exposed to ultraviolet radiation, as in the rarefied upper atmosphere and by electrical discharges in the atmosphere. This 'ozone layer' in the upper atmosphere plays an important part in filtering out potentially harmful ultra-violet radiation from the Sun. There is some controversy as to whether the use of fluorochlorohydrocarbons as aerosol propellants will diminish the amount of ozone and its protective effect. The exhaust fumes of supersonic aircraft are thought by some workers to have a similar effect.

Properties of ozone

Ozone is a colourless, very poisonous gas with a distinctive smell resembling that of much diluted chlorine. It is slightly soluble in water. Ozone boils at 161 K. Its chemical properties can be summarized as follows:

(1) Action of heat

Ozone is an *endothermic* compound; the conversion of 3 mol of oxygen to 2 mol of ozone ($3O_2(g) \rightarrow 2O_3(g)$) is accompanied by the *absorption* of 284 kJ. Ozone is unstable at room temperature. Heating accelerates its decomposition, if the proportion of ozone present is greater than the equilibrium concentration for the particular temperature. However, high temperatures increase (in accordance with Le Chatelier's Principle) the proportion of ozone in the equilibrium mixture: less than 0.01 per cent at 600 K, about 0.1 per cent at 2500 K, and 1 per cent at 3500 K.

The decomposition of ozone to oxygen is catalysed by many materials, including powdered platinum, manganese(IV) oxide, lead(IV) oxide, copper(II) oxide, and silver oxide.

(2) Oxidizing action

Ozone is a very powerful oxidizing agent. Among its oxidizing actions are the following.

(a) *With potassium iodide solution (acidified). Iodine* is liberated, giving a *brown* coloration.

$$2I^-(aq) + 2H^+(aq) + O_3(g) \rightarrow H_2O(l) + O_2(g) + I_2(s)$$

(b) *With acidified solutions of iron*(II) *salts.* Ozone oxidizes these to solutions of iron(III) ions, the colour changing from green to yellow.

$$2Fe^{2+}(aq) + 2H^+(aq) + O_3(g) \rightarrow 2Fe^{3+}(aq) + H_2O(l) + O_2(g)$$

(c) *With sulphides of metals.* Ozone oxidizes lead(II) sulphide to the *sulphate* with a change in colour from dark brown to white.

$$PbS(s) + 4O_3(g) \rightarrow PbSO_4(s) + 4O_2(g)$$

Sulphides of copper, cadmium and zinc are oxidized similarly.

It will be observed that, in the reactions in aqueous solution, the ozone acts as an electron acceptor (i.e. oxidizing agent) by one of the reactions:

$$O_3(g) + H_2O(l) + 2e^- \rightarrow O_2(g) + 2OH^-(aq)$$
$$O_3(g) + 2H^+(aq) + 2e^- \rightarrow O_2(g) + H_2O(l)$$

Molecular oxygen is liberated. Ozone also shows two reactions in which no oxygen is liberated; all the ozone is absorbed into combination. These are:

With sulphur dioxide

$$3SO_2(g) + O_3(g) \rightarrow 3SO_3(s)$$

With acidified tin(II) chloride solution

$$3Sn^{2+}(aq) + 6H^+(aq) + O_3(g) \rightarrow 3Sn^{4+}(aq) + 3H_2O(l)$$

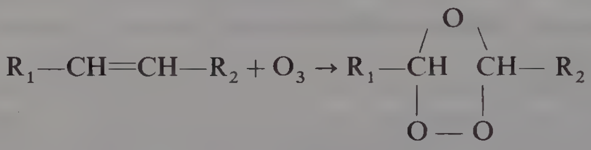
In the second of these, ozone acts as an electron acceptor by the essential change:

$$6H^+(aq) + O_3(g) + 6e^- \rightarrow 3H_2O(l)$$

By its oxidizing action, ozone is very destructive of many kinds of organic matter, e.g. cork and rubber. It can also act as a bleaching agent. It oxidizes all the common metals except gold and platinum.

(3) Reaction with alkenes

Ozone is rapidly absorbed by alkenes (i.e. organic compounds containing the structure —CH=CH—) to form *ozonides.*



$$R_1\text{—CH=CH—}R_2 + O_3 \rightarrow \begin{array}{ccc} & \text{O} & \\ & / \quad \backslash & \\ R_1\text{—CH} & & \text{CH—}R_2 \\ | & & | \\ \text{O} & \text{—} & \text{O} \end{array}$$

where R_1 and R_2 are univalent organic groups. Ozonides can be dangerously explosive.

Detection of ozone

The best test for ozone is its action upon mercury. The metal becomes dull in appearance and sticks to glass (instead of flowing freely over it leaving no traces, as the pure metal does). This sticking effect is called 'tailing' of mercury. It is probably caused by oxidation which alters the surface tension of the metal.

Uses of ozone

The chief use of ozone has been in ventilation of the premises of underground railways to which fresh air has little access. It is used at a very low concentration, and rapidly oxidizes the organic materials responsible for stuffiness. It has also been used in sterilizing water and in bleaching wax.

Water

The composition of water

(1) Composition of steam by volume; its molecular formula

The composition of steam by volume can be demonstrated by the apparatus of Figure 9.4. By raising the funnel E and opening tap C, the tube CD can be filled with mercury. If C is then attached to an appropriate supply, a mixture of hydrogen (2 volumes) and oxygen (1 volume)

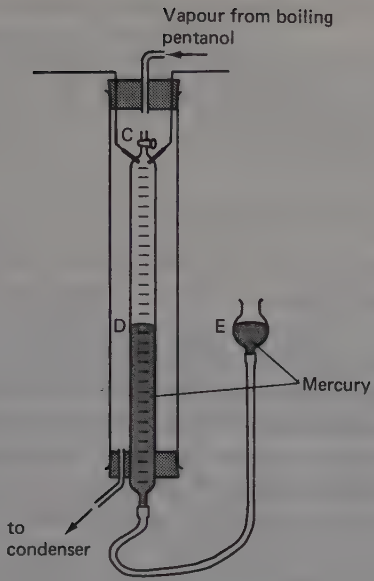


Figure 9.4 *Volume composition of steam*

can be drawn into CD as the funnel is lowered. Tap C is then closed. The vapour from boiling pentanol is passed into the outer jacket and time is allowed for the contents of the tube CD to reach the corresponding steady temperature, 403 K. Levels E and D are equalized (giving atmospheric pressure in CD). The level D is read off. E is then lowered as much as possible to reduce the pressure in CD and the gases are sparked by connecting the electrical leads to an induction coil. The tube CD is allowed time to return to the steady temperature of pentanol vapour. It will then be found that the level D has risen and, if this new level is equalized with the mercury in the funnel, E, by raising E, it will be found that the remaining volume of vapour is two-thirds of the volume of mixed gases used. On cooling, it is found that all this vapour condenses, leaving only a minute drop of water. From these observations,

2 volumes of hydrogen and 1 volume of oxygen combine to form 2 volumes of steam (temperature and pressure constant).

The molecular formula of steam can be deduced as follows. Applying Avogadro's Hypothesis to the above volume relations,

2 molecules of hydrogen and 1 molecule of oxygen give 2 molecules of steam

Given that both hydrogen and oxygen have diatomic molecules,

4 atoms of hydrogen and 2 atoms of oxygen yield 2 molecules of steam, i.e. 2 atoms of hydrogen and 1 atom of oxygen yield 1 molecule of steam. That is, the molecular formula of steam is H_2O

(2) Gravimetric composition of water

The gravimetric composition of water states the proportions by mass in which hydrogen and oxygen combine. A classical determination was made by Dumas in 1842, but it is now mainly of historical interest. In principle, the method consisted of passing pure dry hydrogen over pure heated copper(II) oxide, then absorbing the water formed by condensation and absorption in potassium hydroxide solution and phosphorus(V) oxide. The mass of water, w_1, was given by the increase in mass of the absorption apparatus; the mass of oxygen, w_2, was given by the loss in mass of the copper(II) oxide. The mass of the hydrogen was then $(w_1 - w_2)$.

Hydrogen was generated by the action of dilute sulphuric acid on zinc and purified by passage over:

(a) Lead(II) nitrate solution to remove hydrogen sulphide.
(b) Silver sulphate solution to remove arsine and phosphine.
(c) Solid potassium hydroxide to remove acidic gases.
(d) Phosphorus(V) oxide in a freezing-mixture to remove water vapour.

A guard tube of phosphorus(V) oxide was placed immediately before the copper(II) oxide and was required to remain constant in mass throughout a determination as a guarantee of the dryness of the hydrogen. The absorption apparatus was protected from atmospheric moisture by concentrated sulphuric acid and phosphorus(V) oxide. Dumas' method is subject to several sources of error, such as:

(a) Retention of occluded hydrogen in the copper formed so that its mass is greater than it should be.
(b) Interference by air swept out of sulphuric acid as the hydrogen is evolved.
(c) Occlusion of atmospheric nitrogen into the copper(II) oxide.
(d) Difficulty in sweeping the apparatus free of hydrogen at the end for weighing.

As an average of about twenty determinations, Dumas obtained the ratio, oxygen 16.000 to hydrogen 2.004. The proportion of hydrogen in this result is actually too low by about one part in 200.

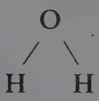
Other more accurate methods for determining the gravimetric composition of water were later developed.

One difficulty of these determinations (not recognized at the time) is that ordinary hydrogen contains a small proportion of its heavy isotope, deuterium (about one part in 6500). If the methods of purification involve any change in the proportion of this isotope, the results of the experiments may vary slightly from one investigator to another. The figure accepted today for the mass ratio of oxygen to hydrogen in water is 16.000:2.016.

The molecular formula and structure of water

The above results of analysis show that the empirical formula of water is undoubtedly H_2O. Except at temperatures only a little higher than 373 K, where a certain amount of association occurs, steam has the molecular formula, H_2O, as is shown by its vapour density (relative to hydrogen) of 9 and molar mass of 18. The molecular situation in water and in ice is, however, very much more complex.

The water molecule has the following structure:



The molecule is *polar*, and the properties are much influenced by *hydrogen bonding*. This topic is discussed in detail in *Advanced Level Physical Chemistry*, p. 98ff.

Some impurities in water; their effects and estimation

Ordinary water, as supplied for domestic consumption, is never pure in the chemical sense of that term. Recently distilled or deionized water is, in fact, so tasteless as to be unpalatable. Water has very great solvent power. It dissolves measurable proportions of all salts and relatively large quantities of a very great number of materials. Consequently, natural and domestic water, in its contacts with the earth and with water pipes, acquires a considerable range of soluble impurities. The most important of these are:

(a) Salts of calcium and magnesium, which are responsible for hardness in water.
(b) Chlorides.
(c) Ammonium salts and their oxidation products, nitrites and nitrates.

(d) Traces of heavy metals, such as Pb and Cu.
These impurities are considered below.

(1) Hardness of water

A hard water is one which will not lather readily with soap. The general cause of hardness is the presence in water of the calcium ion, Ca^{2+}, or the magnesium ion, Mg^{2+}, derived from a *soluble* calcium or magnesium compound. A typical soap is *sodium octadecanoate* (sodium stearate), $C_{17}H_{35}COO^-Na^+$. When this compound is added to water containing a dissolved calcium compound, there is precipitation of a curdy deposit in the water (or a scum on its surface) which is the *insoluble* salt, *calcium octadecanoate.*

$$Ca^{2+}(aq) + 2C_{17}H_{35}COO^-(aq) \rightarrow (C_{17}H_{35}COO^-)_2Ca^{2+}(s)$$

No lather can occur until this precipitation has been completed and some extra soap has been dissolved to form lather. The amount of soap needed for the precipitation makes the water appear hard. A corresponding precipitation occurs with the Mg^{2+} ion.

Two kinds of hardness are recognized—*temporary* and *permanent* hardness. Temporary hardness is destroyed by boiling the water; permanent hardness is not affected by boiling. In England, *temporary hardness* is caused by *calcium hydrogencarbonate* in the water. It is produced in the following way. Rain water dissolves carbon dioxide during its contact with the air and forms dilute carbonic acid (a very weak acid).

$$H_2O(l) + CO_2(g) \rightleftharpoons H_2CO_3(aq) \rightleftharpoons 2H^+(aq) + CO_3{}^{2-}(aq)$$

If the water then encounters chalk or limestone in its passage through the earth, the insoluble calcium carbonate of these materials is converted to hydrogencarbonate which is appreciably soluble and is taken into solution.

$$CaCO_3(s) + H_2CO_3(aq) \rightleftharpoons Ca(HCO_3)_2(aq)$$

This reaction, continued over many years in a limited area, may cause *caves* in limestone rock. Indeed, the reaction is the dominant factor in determining the physical geography of many areas of the Earth's surface. In Britain, such features as Cheddar Gorge, Malham Cove, and the clints, pot-holes, and limestone pavements of the Dales depend on the action of rain water on limestone.

Corresponding reactions can occur with magnesium carbonate.

Temporary hardness is softened by the general ion-exchange methods mentioned below and also by the two following methods:

(a) *By boiling the water.* In this case, calcium hydrogencarbonate is decomposed to form calcium carbonate, which, being insoluble in water, precipitates and no longer causes hardness. Carbon dioxide is evolved.

$$Ca(HCO_3)_2(aq) \rightarrow CaCO_3(s) + H_2O(l) + CO_2(g)$$

This precipitate of calcium carbonate appears in ordinary experience as the chief constituent of *fur* in kettles and of *boiler scale*. The same decomposition, occurring at ordinary temperature, is responsible for the deposition of *stalactites* and *stalagmites* in limestone caves and for the stony deposits laid down over objects in *petrifying wells*. Hardness caused by magnesium hydrogencarbonate is not satisfactorily destroyed by boiling because magnesium carbonate is appreciably soluble in water (nearly 1 g dm^{-3} at room temperature).

(b) *By the addition of calcium hydroxide* (*slaked lime*). The addition of calcium hydroxide (or lime water) to a temporarily hard water precipitates calcium carbonate, which, being insoluble, does not produce hardness. If the exact calculated quantity of calcium hydroxide is added, the *whole* of the calcium is precipitated.

$$Ca(HCO_3)_2(aq) + Ca(OH)_2(aq.suspension) \rightarrow 2CaCO_3(s) + 2H_2O(l)$$

This is known as *Clark's method* of softening. Slaked lime removes hardness caused by magnesium hydrogencarbonate, but mainly by precipitation of magnesium hydroxide, which has only a very low solubility (about 0.01 g dm^{-3} at room temperature).

Permanent hardness is produced by any soluble calcium compound in the water except calcium hydrogencarbonate (and correspondingly for magnesium compounds). In natural waters, *calcium sulphate* is the usual cause of permanent hardness. It occurs very frequently in soils and is dissolved out as the water passes through the soil. No chemical action is involved.

Permanent hardness is removed by the ion-exchange methods given below and also by *washing soda* (sodium carbonate). This precipitates calcium carbonate, so removing the ion Ca^{2+} from solution and softening the water.

$$Ca^{2+}(aq) + CO_3{}^{2-}(aq) \rightarrow CaCO_3(s)$$

This explains the use of washing soda as a domestic softening agent.

Softening by ion exchange

Materials capable of performing *cation exchange* possess a giant three-dimensional structure carrying negative charges, with the cations able to move freely through the open lattice. Certain natural aluminosilicates, known as '*zeolites*', have been used, as have synthetic aluminosilicates, e.g. 'Permutit'. The exchange material may also be a cross-linked organic polymer, such as sulphonated polystyrene. The cations on the solid material, whether that material is inorganic or organic, are usually sodium. The material is used in the form of granules packed in a column. As hard water trickles down the column, calcium and magnesium ions in the water are 'exchanged' for sodium ions from the solid. This removes both temporary and permanent hardness, since the calcium and magnesium ions in the water are replaced by sodium ions; and sodium compounds cannot cause hardness.

When the capacity of the column is exhausted, it can be recharged by disconnecting the water supply and pouring a concentrated solution of sodium chloride down the column. The concentration of sodium ions is high enough to displace the calcium and magnesium ions from the solid lattice of the exchange material.

It is also possible to make *anion exchange* materials. If hydrogen ions are used instead of sodium ions on the cation exchanger, and hydroxyl ions are used on the anion exchanger, the ions present in impure water can be replaced by hydrogen and hydroxide ions. These combine to form water. Thus, if water containing dissolved salts is passed through both types of ion exchanger, it emerges relatively pure. Such water is said to be *deionized.*

Estimation of hardness in water

The concentration of calcium and magnesium ions in a given sample of water can be determined by a number of titrimetric methods. These include: (i) titration using a soap solution which has been standardized against known concentrations of calcium ions; (ii) complexometric titration using EDTA ('ethylenediaminetetraacetic acid', a hexadentate ligand—see p. 399). Details of these and other methods will be found in textbooks of quantitative analysis.

(2) Chloride in tap-water

Chloride in tap-water is estimated by titration with silver nitrate solution, using potassium chromate(VI) solution as indicator. The standard methods will be found in textbooks of quantitative analysis.

In general, except near the sea where salt spray may blow in, water should contain less than 20 parts per million of Cl^-. A chloride content greater than this probably indicates contamination by sewage.

(3) Ammonium salts, nitrites, and nitrates in water

Ammonium salts in water usually result from the decomposition of nitrogenous animal refuse, and, therefore, usually indicate contamination by sewage. If so, dangerous bacteria may have entered the water. The ammonium salts oxidize to nitrites and then to nitrates, so that concentrations, above certain limits, of these ions probably indicate remoter contamination.

Determination of ammonium involves use of *Nessler's reagent* (see p. 225). Methods for the determination of ammonium, nitrite, and nitrate in samples of water will be found in textbooks of quantitative analysis.

Ammonia can be estimated as both *free* and *albuminoid* ammonia; it is generally taken that the state of a water for human consumption is undesirable if the content of free ammonia exceeds 0.1 parts per million and albuminoid ammonia 0.08 parts per million.

In upland surface water the total nitrogen present as nitrite and nitrate should not exceed 0.3 parts per million, though it may be considerably more in cultivated areas, where there is run-off of nitrate fertilizers from the soil. High concentrations of nitrate in drinking water can be especially harmful to very young children.

(4) Heavy metals in water

Because of the extensive use of lead pipes and, more recently, copper pipes in the conveyance of domestic water supplies, these are two of the metals most likely to occur in such supplies. Their concentrations may be estimated by standard analytical methods. Metal pipes are being replaced for many purposes by pipes made from plastic.

In drinking water, one part of copper per million of water is the greatest permissible concentration. Such a proportion of lead, however, has proved fatal because lead is a cumulative poison. It is desirable to have not more than 0.2 parts per million for safety, and much less is preferred.

Town water supplies are usually purified in the following way. The water is filtered through beds of gravel and sand of increasing fineness. Any remaining suspended or colloidal material is then removed by the addition of aluminium sulphate which causes precipitation of aluminium hydroxide which carries the material, including bacteria, with it. The water is then usually chlorinated before it passes to consumers. About three parts of chlorine per million is adequate to destroy any remaining bacteria. In some areas, sodium fluoride (about one part per million) is added in order to inhibit dental caries.

Chemical reactions of water

1. *Action of heat.* Water is extremely stable. It shows no appreciable decomposition below 1300 K and, at 2300 K, the degree of dissociation into hydrogen and oxygen is still less than 1 per cent.

2. *Behaviour with metals.* The most electropositive of the common metals (Li, Na, K, and Ca) react with cold water to liberate *hydrogen* and leave the metallic *hydroxide* in a solution which is highly alkaline, e.g.

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$$
$$2Na(s) + 2H^+(aq) \rightarrow 2Na^+(aq) + H_2(g)$$

The reactions with lithium and calcium are slow, with sodium rapid, and with potassium violent enough to inflame the hydrogen.

Magnesium will attack hot water (especially as powder) and burns with vigour if heated in steam.

$$Mg(s) + H_2O(l) \rightarrow MgO(s) + H_2(g)$$

Zinc reacts similarly but less rapidly if heated in steam, and *iron* at red heat gives a reversible reaction in which its black oxide iron(II) diiron(III) oxide (ferrosoferric oxide) is the product.

$$3Fe(s) + 4H_2O(l) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$$

Aluminium attacks water (with liberation of hydrogen) if amalgamated with mercury; in ordinary condition as foil, however, it is protected by a layer of oxide and does not attack water.

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$$
$$2Al(s) + 6H^+(aq) \rightarrow 2Al^{3+}(aq) + 3H_2(g)$$

3. *Behaviour with non-metals.* Most of the non-metals show no reaction with water. *Carbon*, however, decomposes steam at 1300 K or higher temperature to yield a mixture of *carbon monoxide* and *hydrogen*, known as water gas (see p. 142).

$$C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$$

Below 1300 K, the reaction $C(s) + 2H_2O(g) \rightleftharpoons CO_2(g) + 2H_2(g)$ becomes appreciable.

Silicon attacks steam at white heat but more slowly then carbon, forming *silica.*

$$Si(s) + 2H_2O(g) \rightarrow SiO_2(s) + 2H_2(g)$$

Chlorine reacts with water in the cold to give a liquid containing *hydrochloric acid* and *chloric*(I) *acid* (*hypochlorous acid*).

$$H_2O(l) + Cl_2(g) \rightleftharpoons HCl(aq) + HOCl(aq)$$

Sunlight decomposes the chloric(I) acid and *oxygen* is evolved, to give a total reaction:

$$2Cl_2(g) + 2H_2O(l) \rightarrow 4HCl(aq) + O_2(g)$$

Fluorine attacks water rapidly in the cold to liberate *oxygen* containing a considerable proportion of *ozone.*

$$2F_2(g) + 2H_2O(l) \rightarrow 4HF(aq) + O_2(g)$$
$$3F_2(g) + 3H_2O(l) \rightarrow 6HF(aq) + O_3(g)$$

4. *Water as a hydrolysing agent.* Water gives a great many reactions which are grouped loosely together as reactions of *hydrolysis.* They occur with both organic and inorganic compounds. It is not possible in this book to give an exhaustive account of them, but the following examples are representative for inorganic materials.

(a) Most *chlorides of non-metals* are hydrolysed rapidly by cold water, usually with liberation of *hydrogen chloride* and *an oxyacid* of the non-metal, e.g.

$$PCl_3(l) + 3H_2O(l) \rightarrow 3HCl(aq) + H_3PO_3(aq)$$
$$PCl_5(s) + 4H_2O(l) \rightarrow 5HCl(aq) + H_3PO_4(aq)$$
$$SiCl_4(l) + 4H_2O(l) \rightarrow 4HCl(aq) + H_4SiO_4 \text{ or } SiO_2.2H_2O(s)$$

Nitrogen trichloride hydrolyses with unusual products (*ammonia* and *chloric*(I) *acid*),

$$NCl_3(l) + 3H_2O(l) \rightarrow NH_3(g) + 3HOCl(aq)$$

while tetrachloromethane does not hydrolyse at all. For discussion of this, see p. 161.

(b) *Chlorides of metals.* The chlorides of the most electropositive metals (e.g. NaCl, KCl) are not attacked by water, but other metallic chlorides usually hydrolyse to some extent in solution, especially during evaporation. The chlorides of aluminium and iron(III) are almost completely hydrolysed during evaporation to dryness. Some examples of hydrolysis are:

$$ZnCl_2(s) + H_2O(l) \rightleftharpoons Zn(OH)Cl(s) + HCl(g)$$
$$SnCl_2(s) + 2H_2O(l) \rightleftharpoons Sn(OH)_2(s) + 2HCl(g)$$
$$AlCl_3(s) + 3H_2O(l) \rightleftharpoons Al(OH)_3(s) + 3HCl(g)$$

The trichlorides of antimony and bismuth can be hydrolysed by excess water to the chloride oxides (*oxychlorides*), which appear as white precipitates.

The reaction can be reversed by addition of hydrochloric acid.

$$BiCl_3(aq) + H_2O(l) \rightleftharpoons BiOCl(s) + 2HCl(aq)$$

5. *Additive reactions of water*. Water will combine directly with the oxides of the more electropositive metals to produce *hydroxides*, which, with excess of water, pass into solution which is then alkaline. The essential reaction is:

$$O^{2-} + H_2O(l) \rightarrow 2OH^-(aq)$$

Examples of these reactions are:

$$Na_2O(s) + H_2O(l) \rightarrow 2NaOH(aq)$$
$$CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(s)$$

Water will also form many *hydrates* by combining as water of crystallization, usually with metallic salts. Well-known examples of such hydrates include $Na_2CO_3.10H_2O$ (*washing soda*), $CuSO_4.5H_2O$, $FeSO_4.7H_2O$, $Na_2SO_4.10H_2O$.

Self-ionization of water; pH; acidity and alkalinity

These topics are discussed in detail in *Advanced Level Physical Chemistry*, pp. 211–220.

Water in Nature

Water is found in all living cells. It provides the medium in which the many complex biochemical reactions can occur. There is evidence that, thanks to its ability to hydrogen bond and the polar nature of the cell constituents, water molecules in a living cell are more ordered than in ordinary liquid water. The great majority of plant and animal species perish quite rapidly in the absence of water, although some have adapted to drought conditions. Certain seeds and microorganisms appear capable of an indefinite dormant existence without water.

The effect of rainwater on limestone and chalk has been noted above (p. 292). The weathering and denudation of upland areas is effected largely by water. Rock is broken up by chemical action, by abrasion due to glaciers, or by the action of frost and ice. Water has the almost unique property of expanding when solidifying, so that water freezing in a crack in the rock will tend to split the rock apart. Debris from weathering is carried down by streams and deposited when the water velocity drops. Colloid-sized particles may be deposited to form deltas by contact with the charged ions in sea water (see *Advanced Level Physical Chemistry*, p. 112).

Water is also an immensely important factor in many of Man's activities, including transport, manufacturing industry, production of electric power, and recreation.

Further discussion of the biological, geographical, and social aspects of water is outside the scope of this book, but every student of chemistry should be aware of these aspects of this fascinating substance.

Hydrogen peroxide, H_2O_2

Laboratory preparation of hydrogen peroxide

Hydrogen peroxide is usually prepared by the gradual addition of the calculated weight of *hydrated* barium peroxide to *ice-cooled* dilute sulphuric acid.

$$BaO_2.8H_2O(s) + H_2SO_4(aq) \rightarrow BaSO_4(s) + H_2O_2(aq) + 8H_2O(l)$$

Ratio: 313 g 98 g (in dilute solution)

Good stirring (mechanical if possible) is desirable to avoid local excesses of barium peroxide, which tends to decompose the hydrogen peroxide. The barium sulphate can be filtered off, leaving a dilute solution of hydrogen peroxide. For its purification, see later. A similar method can be used substituting dilute phosphoric(V) acid for sulphuric acid.

$$3BaO_2(s) + 2H_3PO_4(aq) \rightarrow Ba_3(PO_4)_2(s) + 3H_2O_2(aq)$$

Alternatively, hydrated barium peroxide may be stirred slowly into ice-cooled water into which a stream of carbon dioxide is passing.

$$BaO_2(s) + CO_2(g) + H_2O(l) \rightarrow BaCO_3(s) + H_2O_2(aq)$$

The barium carbonate is removed by filtration.

If dissolved electrolyte is tolerable in the product, a rapid and convenient method of producing hydrogen peroxide solution is the gradual addition of sodium peroxide to cold (preferably ice-cooled) dilute hydrochloric or sulphuric acid.

$$Na_2O_2(s) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + H_2O_2(aq)$$

(Nitric acid should not be used. Its oxidizing properties could interfere with those of the hydrogen peroxide.)

Purification of hydrogen peroxide

Hydrogen peroxide solution may be concentrated up to about 60 per cent H_2O_2 by evaporation on a water bath at a temperature not exceeding 340 K. Further concentration to over 90 per cent H_2O_2 can be brought about by distillation *under reduced pressure* so that the lower temperature required does not decompose the hydrogen peroxide. This leaves a colourless syrupy liquid, which is usually stabilized by phosphoric(V) acid. A sample of this syrupy liquid will solidify in a freezing-mixture of solid carbon dioxide and ethoxyethane (ether). Some of the solid, used to 'seed' the rest of the liquid cooled to about 263 K in ice-salt, will induce crystallization of pure hydrogen peroxide.

Manufacture of hydrogen peroxide

A great deal of hydrogen peroxide has been manufactured in recent years from peroxodisulphuric acid (persulphuric acid). In one of these processes, a solution of ammonium sulphate acidified with sulphuric acid (i.e. ammonium hydrogensulphate solution) is electrolysed, producing peroxodisulphate ions at the anode.

$$2HSO_4^-(aq) - 2e^- \rightarrow 2H^+(aq) + S_2O_8^{2-}(aq)$$

In the Kurfstein process, the solution is then steam-distilled.

$$S_2O_8^{2-}(aq) + 2H_2O(l) \rightarrow H_2O_2(aq) + 2HSO_4^-(aq)$$

In a variation of this process, the product of the electrolysis is treated with potassium hydrogensulphate solution to precipitate potassium peroxodisulphate.

$$2K^+(aq) + S_2O_8^{2-}(aq) \rightarrow K_2S_2O_8(s)$$

This is acidified by sulphuric acid and steam-distilled as before.

$$S_2O_8^{2-}(aq) + 2H_2O(l) \rightarrow H_2O_2(aq) + 2HSO_4^-(aq)$$

An alternative process for making hydrogen peroxide is now replacing electrolytic methods. Certain organic hydroxyl compounds can be oxidized by molecular oxygen to yield hydrogen peroxide and an oxidation product of the organic compound, usually a ketone. The hydrogen peroxide is then extracted and the ketone is reduced, usually by hydrogen in the presence of a catalyst such as nickel or palladium, to the original hydroxyl compound. Such a process can be carried on continuously with the same organic material for a long time. Essentially it uses a cycle such as:

$$X(OH)_2 + O_2 \rightarrow XO_2 + H_2O_2$$
$$XO_2 + H_2 \rightarrow X(OH)_2$$

where X represents an organic structure, which is usually complex. The net reaction is simply: $H_2 + O_2 \rightarrow H_2O_2$. The most successful processes seem to be those involving substituted benzene-1,4-diols (hydroquinones) as the initial hydroxyl compounds.

Properties of hydrogen peroxide

Hydrogen peroxide is a syrupy liquid of density 1.4 g cm^{-3} at room temperature and pressure. It has a slight bluish colour when viewed in thick layers. It forms colourless, prismatic crystals, melting point 271 K. Liquid hydrogen peroxide mixes with water in all proportions. The chemical properties of its aqueous solution are as follows.

(1) Decomposition

Dilute solutions of hydrogen peroxide decompose rapidly when heated to temperatures approaching 373 K. *Oxygen* is liberated in a disproportionation reaction.

$$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$$

This decomposition is catalysed by many materials, including finely divided platinum, copper and gold, manganese(IV) oxide, dust particles, such as occur in ordinary air, and powdered glass. The reaction with manganese(IV) oxide is used in the laboratory preparation of small amounts of oxygen (see p. 274). Hydrogen peroxide solution keeps badly in a glass bottle with a rough inner surface. In the absence of impurities, even very concentrated solutions of hydrogen peroxide keep quite well. Various stabilizers can be added, such as phosphoric acid or N-phenylethanamide (acetanilide), but purity is the best guarantee of stability.

(2) Oxidizing action

Hydrogen peroxide is a powerful oxidizing agent. Like all oxidizing agents, it functions as an *electron acceptor*; in this case, the essential half-reaction is:

$$H_2O_2(aq) + 2H^+(aq) + 2e^- \rightarrow 2H_2O(l)$$

The electrons are supplied by the reducing agent present. Examples of oxidizing behaviour are:

(a) *With iron*(II) *sulphate in dilute sulphuric acid*. The *pale green iron*(II) solution becomes *yellow* by oxidation to *iron*(III) *sulphate*.
The two half reactions are:

$$H_2O_2(aq) + 2H^+(aq) + 2e^- \rightarrow 2H_2O(l)$$
$$2Fe^{2+}(aq) \rightarrow 2Fe^{3+}(aq) + 2e^-$$

$$\text{Overall: } 2Fe^{2+}(aq) + 2H^+(aq) + H_2O_2(aq) \rightarrow 2Fe^{3+}(aq) + 2H_2O(l)$$

(b) *With hydriodic acid (acidified potassium iodide solution)*. *Iodine* is produced, giving a *brown* coloration.

$$2I^-(aq) + 2H^+(aq) + H_2O_2(aq) \rightarrow 2H_2O(l) + I_2(s)$$

In this and the subsequent examples, the reader may wish to write the separate half-reactions.

(c) *With sulphurous acid (or a sulphite in solution)*. Oxidation occurs to *sulphuric acid* (or a *sulphate*).

$$SO_3{}^{2-}(aq) + H_2O_2(aq) \rightarrow SO_4{}^{2-}(aq) + H_2O(l)$$

(d) *With lead*(II) *sulphide*. The *black* lead(II) sulphide is oxidized to *white* lead(II) sulphate.

$$S^{2-}(s) + 4H_2O_2(aq) \rightarrow SO_4{}^{2-}(aq) + 4H_2O(l)$$

Reaction (d) is used in restoring paintings in which white lead pigment has been blackened by hydrogen sulphide from the air.

(e) *With chromium*(III) *hydroxide*. This is usually done by heating the hydroxide, in suspension in sodium hydroxide solution, with hydrogen peroxide. This reaction is used as a test for chromium in Qualitative Analysis. A *yellow* solution is obtained, containing *sodium chromate*(VI).

$$2Cr^{3+}(aq) + 10OH^-(aq) + 3H_2O_2(aq) \rightarrow 2CrO_4{}^{2-}(aq) + 8H_2O(l)$$

The oxidizing action of hydrogen peroxide causes it to act as a *bleaching agent* (for hair, wax, silk, and feathers) and as an *antiseptic*.

(3) Hydrogen peroxide as a reducing agent

Hydrogen peroxide can act as a reducing agent (electron donor) towards several materials which are relatively stronger oxidizing agents, as listed below. It makes electrons available by the change:

$$H_2O_2(aq) \rightarrow 2H^+(aq) + O_2(g) + 2e^-$$

and the electrons are accepted by the other participating substance, acting as oxidizing agent. Examples are:

(a) *With silver oxide.* Effervescence occurs with *oxygen* evolved, and a *black precipitate* of finely divided *silver* is left.

$$\left.\begin{aligned} H_2O_2(aq) &\rightarrow 2H^+(aq) + O_2(g) + 2e^- \\ Ag_2O(s) + 2H^+(aq) + 2e^- &\rightarrow 2Ag(s) + H_2O(l) \end{aligned}\right\}$$

Adding these,

$$Ag_2O(s) + H_2O_2(aq) \rightarrow 2Ag(s) + H_2O(l) + O_2(g)$$

(b) *With lead*(IV) *oxide.* Effervescence occurs with *oxygen* evolved, and the *litharge* form of lead(II) oxide is left as a *yellow precipitate.*

$$PbO_2(s) + H_2O_2(aq) \rightarrow PbO(s) + H_2O(l) + O_2(g)$$

(c) *With acidified potassium manganate*(VII) *solution.* The solution is rapidly turned from *purple* to *colourless* with evolution of *oxygen.*

$$2MnO_4^-(aq) + 6H^+(aq) + 5H_2O_2(aq) \rightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 5O_2(g)$$

(d) *With manganese*(IV) *oxide in dilute sulphuric acid.* Manganese(IV) oxide (a black solid) dissolves with evolution of *oxygen.* A pale *pink* solution of manganese(II) sulphate remains.

$$MnO_2(s) + H_2O_2(aq) + 2H^+(aq) \rightarrow Mn^{2+}(aq) + 2H_2O(l) + O_2(g)$$

(e) *With ozone.* Hydrogen peroxide reacts with ozone to liberate *oxygen.* Water is the other product.

$$O_3(g) + H_2O_2(aq) \rightarrow H_2O(l) + 2O_2(g)$$

(4) Acidity of hydrogen peroxide

Hydrogen peroxide is appreciably acidic.

$$H_2O_2(aq) \rightleftharpoons 2H^+(aq) + O_2^{2-}(aq)$$

With a saturated solution of barium hydroxide, it precipitates barium peroxide (hydrated), which appears here as a *salt* of hydrogen peroxide.

$$\underset{\text{base}}{Ba(OH)_2(aq)} + \underset{\text{acid}}{H_2O_2(aq)} \rightarrow \underset{\text{a salt}}{BaO_2(s)} + \underset{\text{water}}{2H_2O(l)}$$

Test for hydrogen peroxide

With acidified potassium dichromate(VI) *solution* (chromic acid). To the dichromate(VI) solution in a test-tube is added about one centimetre depth of ethoxyethane (ether). The test liquid is added and the whole is *well shaken.* A *blue* colour in the ethoxyethane layer (after settling) proves hydrogen peroxide present. The blue colour is ascribed to 'peroxochromic acid', CrO_5. It is covalent and soluble in ethoxyethane, which serves to concentrate and stabilize it; it is unstable in aqueous solution.

$$CrO_4^{2-}(aq) + 2H^+(aq) + 2H_2O_2(aq) \rightarrow CrO_5(aq) + 3H_2O(l)$$

Estimation of hydrogen peroxide. The concentrations of its commercial solutions

Accurately diluted hydrogen peroxide can be titrated (in solution acidified by dilute sulphuric acid) by potassium manganate(VII) solution of concentration 0.02 mol dm^{-3}. It is necessary to titrate a small amount of the hydrogen peroxide solution approximately with the manganate(VII) solution to ascertain a suitable dilution factor. (For a fresh '20-volume' solution of hydrogen peroxide, this factor is 40.) The diluted solution can then be made up and titrated in approximate equality with the manganate(VII) solution. The calculation is based on the essential reaction:

$$2MnO_4^-(aq) + 6H^+(aq) + 5H_2O_2(aq) \rightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 5O_2(g)$$

'Volume' solutions of hydrogen peroxide

Hydrogen peroxide is sold retail in '20 volume' and '10 volume' solutions. (It is also obtainable commercially in '100 volume' solution; this contains about 30 per cent of hydrogen peroxide.) A 20 volume solution of hydrogen peroxide is one which liberates 20 *times its own volume of oxygen when heated* (and correspondingly for the other concentrations). The conditions of measurement of the oxygen never seem to be exactly specified. Assuming standard conditions, the situation is:

$$\underset{\substack{2\ \text{mol} \\ 2 \times 34\,\text{g}}}{2H_2O_2(aq)} \rightarrow 2H_2O(l) + \underset{\substack{1\ \text{mol} \\ 22.4\ \text{dm}^3\ \text{at s.t.p.}}}{O_2(g)}$$

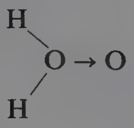
It therefore follows that 68 g of hydrogen peroxide in one dm^3 of solution gives 22.4 dm^3 of oxygen, measured at s.t.p. For '20 volume' hydrogen peroxide, the concentration must be $(20/22.4) \times 68 = 60.7$ g of hydrogen peroxide in one dm^3 of solution. This is approximately a 6 per cent solution. Correspondingly, a 10 volume solution is approximately 3 per cent.

Formula of hydrogen peroxide

Experiment shows that a mass of hydrogen peroxide proportional to 34 decomposes into a mass of oxygen proportional to 16 and a mass of water proportional to 18. There are no other products. This indicates an empirical formula of HO for hydrogen peroxide. At 363 K the vapour density relative to hydrogen of hydrogen peroxide is 17, indicating a relative molecular mass of 34, and a molecular formula of H_2O_2. This is supported by molecular mass determination using the freezing point depression of water.

The two possible structural formulae are:

H—O—O—H and



I II

Anhydrous hydrogen peroxide corresponds to formula I. This is known from its dipole moment and infra-red spectrum. The molecule is, however, not linear or planar; it is arranged as in Figure 9.5.

Hydrogen peroxide as a propellant

The decomposition of hydrogen peroxide is strongly *exothermic:*

$$2H_2O_2(l) \rightarrow 2H_2O(l) + O_2(g) \qquad \Delta H^{\ominus} = -196\ \text{kJ mol}^{-1}$$

If this heat is retained and allowed to vaporize the water and then

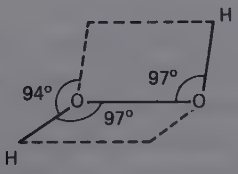


Figure 9.5 *Structure of hydrogen peroxide*

expand the steam and gaseous oxygen, the total volume of product is about 5000 times the volume of the liquid hydrogen peroxide. If generated rapidly by a decomposition catalyst (e.g. MnO_2), this stream of gas can be made to drive a gas-turbine engine. If a fuel such as alcohol is injected into the stream of gas, it vaporizes and burns. This generates more heat and a greater volume of gas. The German V-2 rockets of World War II were propelled in this way.

The atmosphere and combustion

Composition of the atmosphere

The atmosphere is a very complex gaseous mixture, containing a large number of substances, most of them only in small traces. The substances (other than water vapour) which are regarded as 'normal' constituents of the atmosphere are stated below, together with their proportions in a typical sample of *dry* air:

	Percentage	
	by volume	*by mass*
Nitrogen	78.03	75.51
Oxygen	20.99	23.15
Noble gases	0.95	1.30
Carbon dioxide	0.03	0.04

The water vapour content of the air is, of course, variable. It is usually about one per cent by volume, but is sometimes four times as high in hot, humid districts. On the other hand, in desert areas the water vapour content is under 0.1 per cent by volume. Among the substances usually present in air in small proportions, and regarded as impurities, are the following:

1. *Ammonia.* This gas is a product of decomposition of organic compounds. It is returned to the soil, in solution in rain water, as ammonium salts.
2. *Sulphur compounds.* These are produced mainly by the combustion of coal and coke containing traces of sulphur compounds, such as iron pyrites. Sulphur dioxide, sulphuric acid, and hydrogen sulphide are the chief of them and they occur most obviously in industrial areas. They are responsible for much corrosion of buildings and for respiratory diseases.

3. *Hydrogen and hydrocarbons.* These are produced mainly by the use of raw coal, and escape from it, by distillation, during burning. Small proportions of hydrogen, methane, benzene, and methylbenzene have been detected in the air. Small amounts of other carbon compounds also occur, e.g. carbon monoxide from the exhausts of internal combustion engines.

4. *Oxides of nitrogen, ozone (trioxygen), and hydrogen peroxide.* These are grouped together because they are all believed to be products of electrical discharges in the atmosphere. The nitrogen compounds are the most important. In England, probably about 5 kg per hectare per year of combined nitrogen reaches the soil from the atmosphere.

(5) *Chlorides.* Hydrogen chloride may occur in the atmosphere of towns in which chemical operations occur, and salt spray blows in from coastal areas, carrying droplets of brine.

Nature of air as a mixture

There is no doubt that air is a mixture, not a compound. Two pieces of evidence which are decisive on this point are:

(a) Air shows small, but quite definite, variations in composition in samples from different areas. The volume percentage of oxygen in air, for example, has been found to vary from 21.00 to 20.80. A compound would be *constant* in composition.

(b) The constituents of air can be separated by *physical* methods, in which *no chemical reactions* are involved. Examples of such separations are:

   (i) If air is liquefied by cooling and pressure, and fractionally distilled, almost pure nitrogen and oxygen can be obtained from it.

   (ii) If air is dissolved in water and boiled out again, the oxygen content in the air rises from about one-fifth to about one-third by volume.

   Other evidence, less decisive but contributory, is the following.

(c) If air were a compound, it would be expected to have a molecular formula. No such formula can be found. The ratio of nitrogen to oxygen in air approximates to N_4O, but the density relative to hydrogen of N_4O would be 36. The relative density of air is about 14.4, corresponding to that of a *mixture* of about four-fifths nitrogen (relative density 14) and one-fifth oxygen (relative density 16) by volume.

(d) If nitrogen, oxygen, noble gases, etc., are mixed in appropriate proportions, there is no explosion, heat change, volume change or other usual accompaniment of chemical action, but the product resembles air in every way. It is a process of mere mechanical mixing.

(e) The general properties of air such as would be expected for a *mixture* of its constituents, e.g. the oxygen can be dissolved out by alkaline benzene-1,2,3-triol (pyrogallol), leaving the nitrogen unchanged. The properties of a compound are usually very different from those of its constituent elements.

Determination of the percentage of oxygen in air by volume

Probably the most accurate method for this determination is to explode a sample of air with hydrogen (Figure 9.6). By raising the levelling tube, L, the endiometer tube, E, can be filled with mercury. By lowering L again with the tap, T, open, air can be admitted to E. The mercury levels in E and L are equalized and the volume of air is read off. Hydrogen is then admitted to E and the total volume is read off in similar conditions. The volume of hydrogen should be at least half the volume of the air. The open end of L is tightly stoppered and the air–hydrogen mixture is sparked, when it explodes forming water. The stopper is then removed from L and, when the tube has *cooled back to room temperature*, the residual volume of nitrogen (and noble gases) and hydrogen is read off, with mercury levels again equalized. From the equation:

$$\underset{\text{2 volumes}}{2H_2(g)} + \underset{\text{1 volume}}{O_2(g)} \rightarrow \underset{\text{volume negligible as water}}{2H_2O(l)}$$

one-third of the diminution of volume caused by the explosion is the

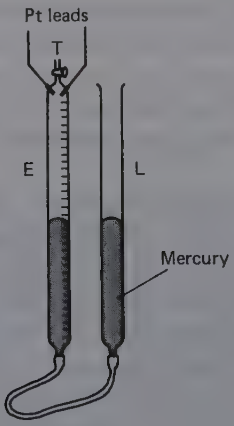


Figure 9.6

volume of oxygen present in the sample of air. That is, if x cm^3 of air were mixed with y cm^3 of hydrogen, and the residual volume of gases after explosion was z cm^3:

$$\text{Percentage of oxygen in air by volume} = \frac{\frac{1}{3}(x+y-z)}{x} \times 100$$

Factors influencing the proportion of carbon dioxide in the air

Carbon dioxide is delivered to the atmosphere mainly from two sources:

(a) The *combustion of fossil* (*carbonaceuous*) *fuels* such as coal, coke, and hydrocarbons (gasoline, kerosene and natural gas). The amount of carbon dioxide thrown into the air from this source is very great. For example, about 110 million tonnes of coal are mined in Great Britain annually; if reckoned as 90 per cent carbon and all burnt directly or indirectly, this coal would deliver about 360 million tonnes of carbon dioxide to the air. To this must be added that produced by the burning of petroleum products, gas, and wood. Other industrial activities, such as the roasting of limestone in the manufacture of cement, also release carbon dioxide into the atmosphere.

(b) *Respiration* by animals and plants. In respiration, animals absorb oxygen from their lungs, combine it with haemoglobin in the red corpuscles of the blood and distribute it to the various bodily organs by the blood circulation. Energy is supplied by the oxidation of carbohydrate, such as glucose, which is available from the digestion of starchy foods. This produces carbon dioxide which is eliminated as the circulation carries the blood through the lungs again.

$$\underset{\text{glucose}}{C_6H_{12}O_6(aq)} + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l)$$

Plants carry on some similar, though much slighter, respiratory activity.

(c) A third source of atmospheric carbon dioxide is the activity of volcanoes. Many of them emit the gas.

These processes tend to raise the proportion of carbon dioxide in the air, and it has risen significantly this century (from about 300 parts per million to about 330). The counteractivities, which tend to reduce the carbon dioxide content of the air, are:

1. *Photosynthesis by plants.* In photosynthesis, plants combine carbon dioxide and water to form starch (or other carbohydrate), liberating oxygen at the same time. To do this, they employ energy derived from the Sun's radiation and the catalytic activity of chlorophyll, their green

colouring matter.

$$6n\text{CO}_2(\text{g}) + 5n\text{H}_2\text{O}(\text{l}) \rightarrow \underset{\text{starch}}{(\text{C}_6\text{H}_{10}\text{O}_5)_n(\text{s})} + 6n\text{O}_2(\text{g})$$

This process extracts carbon dioxide from the air and restores oxygen to it, thus reversing the effect produced by respiration and by combustion of carbon and carbon-containing compounds.

2. *Solution in water.* Carbon dioxide is soluble in water. It must, therefore, set up an equilibrium between dissolved gas in the seas, rivers and lakes and the carbon dioxide of the air. An increase of the partial pressure of carbon dioxide in the air increases the amount dissolved.

3. *Weathering of rocks.* The weathering of igneous rocks is believed to absorb quite large amounts of atmospheric carbon dioxide, by reactions of the following type:

$$\underset{\text{a felspar}}{2\text{KAlSi}_3\text{O}_8(\text{s})} + 2\text{H}_2\text{O}(\text{l}) + \text{CO}_2(\text{g}) \rightarrow \text{K}_2\text{CO}_3(\text{s}) + 4\text{SiO}_2(\text{s}) + \text{Al}_2\text{Si}_2\text{O}_7.2\text{H}_2\text{O}(\text{s})$$

In addition, carbon dioxide is also taken up from the air in the formation of soluble calcium and magnesium hydrogencarbonates from the corresponding carbonates, occurring as rocks.

$$\text{CO}_3{}^{2-}(\text{aq}) + \text{H}_2\text{O}(\text{l}) + \text{CO}_2(\text{g}) \rightleftharpoons 2\text{HCO}_3{}^-(\text{aq})$$

The reaction is, however, reversible, and some at least of the carbon dioxide is restored to the air in the formation, by the reverse process, of stalactites and stalagmites, boiler scale, kettle fur, and the deposits in petrifying wells. All these deposits contain calcium (or magnesium) carbonate.

Sulphur

Atomic number 16.
Electron arrangement 2.8.6 ($1s^2 2s^2 2p^6 3s^2 3p^4$)
Sulphur has isotopes of mass number, in order of abundance, 32, 34, 33 and 36.
Relative atomic mass 32.06.

Occurrence, extraction and uses

Sulphur occurs as the *element* in the USA (Texas and Louisiana) and in Sicily. Other small producers are Japan, Chile and France.

Combined sulphur occurs in many forms; among them are galena, PbS, iron pyrites, FeS_2, zinc blende, ZnS, which are *sulphides*. Gypsum,

$CaSO_4.2H_2O$, anhydrate, $CaSO_4$, and barytes, $BaSO_4$, contain sulphur as *sulphate*. Sulphur is extracted as follows.

(1) *From the American deposits*

The states of Texas and Louisiana in the USA are the world's biggest producers of elemental sulphur.

The sulphur is deposited in porous limestone which averages about 40 m in thickness and lies at a depth of about 150 m below the surface. Ordinary mining for the sulphur is not practicable, partly because of the nature of the strata above the sulphur and partly because of poisonous gases (H_2S and SO_2) associated with it. The sulphur is extracted by the Frasch process. A boring is made down to the sulphur-bearing layer and lined with a steel casing. Down the boring is lowered the Frasch sulphur pump. It consists of three (or, in some cases, four) concentric tubes of which the widest is usually about 15 cm in diameter (Figure 9.7). Water, superheated *under pressure* to about 450 K is forced down the widest tube and out into the sulphur-bearing rock as shown. Sulphur is melted by this hot water. It forms a pool of molten sulphur round the base of the pump and flows into it, rising up the middle tube. Compressed air is forced down the second tube, as shown. It lifts an emulsion of water, sulphur and air to the surface, where it flows into vats and the sulphur solidifies. It requires no purification, being normally about 99.8 per cent pure. (The fourth tube of the pump, when present, is used

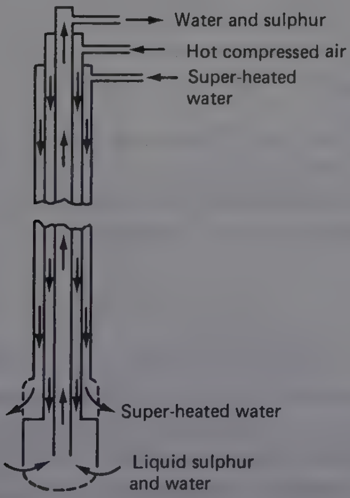


Figure 9.7 *Frasch sulphur pump*

to carry extra water.) A modern boring will produce up to 6000 tonnes of sulphur per day, and a total of over 500 000 tonnes.

2. *Sulphur from petroleum gases.* An important example of this process has been worked at Lacq in southern France since 1957. Gas associated with petroleum deposits in this area contains 15 per cent of hydrogen sulphide (with carbon dioxide and methane). It is passed, at about 7×10^6 N m^{-2} (70 atm), over an amine solution which absorbs the acidic hydrogen sulphide and carbon dioxide. The gases are released again by heating at atmospheric pressure.

After mixing with controlled supplies of air, the hydrogen sulphide of the mixture is oxidized in three stages, the last two being oxidations in contact with heated *bauxite* as a catalyst:

$$2H_2S(s) + O_2(g) \rightarrow 2H_2O(l) + 2S(s)$$

The sulphur is condensed as liquid, cooled to solid and ground, yielding a product which is 99.95 per cent pure.

Uses of sulphur

Sulphur is used mainly in the following ways:

(a) To manufacture sulphuric acid (the chief use).
(b) In vulcanizing rubber.
(c) In the manufacture of gunpowder, fireworks, and matches.
(d) In the manufacture of calcium hydrogen sulphite for use in preparing wood pulp for the manufacture of paper.

The allotropy of sulphur

Many varieties of sulphur have been described at various times (at least a dozen), but those of importance appear to be:

rhombic sulphur (*octahedral* or α-sulphur); *monoclinic* sulphur (*prismatic* or β-sulphur); *amorphous* sulphur; *plastic* sulphur.

Rhombic sulphur

Rhombic sulphur is made by first shaking powdered sulphur with carbon disulphide for some time (*not* with heat; carbon disulphide is very flammable). The mixture is then filtered and placed in a small beaker covered with filter paper, which is held in place by a rubber band. The carbon disulphide will slowly evaporate away, leaving some large crystals of rhombic sulphur. Their approximate shape is shown

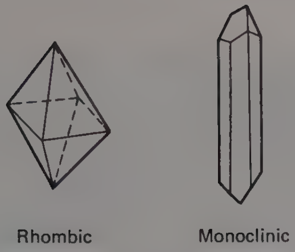


Figure 9.8 *Sulphur crystals*

in Figure 9.8. The crystals are produced at room temperature. Rhombic sulphur is soluble in carbon disulphide and melts at 386 K. Its density is 2.06 g cm^3.

Monoclinic sulphur

In an evaporating dish (preferably of porcelain), sulphur is heated *gently* (to avoid burning) until the dish is almost full of molten sulphur. It is then allowed to cool. As it does so, a crust of solid forms over the surface. As soon as this crust is continuous, it is pierced in two points at opposite ends of a diameter and the molten sulphur still left is poured out. The crust can then be cut round and lifted off. It will reveal long needle-shaped crystals of monoclinic sulphur attached to the undersurface of the crust and to the bottom of the evaporating dish. Their approximate shape is shown in Figure 9.8. Monoclinic sulphur is formed in close contact with *molten* sulphur, i.e. at high temperature. Monoclinic sulphur has a density of 1.96 g cm^3 and melts at 392 K.

Alternatively, monoclinic sulphur crystals can be formed by crystallization from solution in hot dimethylbenzene.

Amorphous sulphur

This is a non-crystalline variety of sulphur, which is often almost white. It is usually produced by chemical action between materials in aqueous solution, as:

Acidification of a sodium thiosulphate solution,

$$S_2O_3{}^{2-}(aq) + 2H^+(aq) \rightarrow H_2O(l) + SO_2(g) + S(s)$$

Action between hydrogen sulphide and sulphurous acid,

$$2H_2S(g) + SO_2(aq) \rightarrow 2H_2O(l) + 3S(s)$$

Amorphous sulphur is usually very finely divided and difficult to filter. It may form a colloidal 'solution' in water, known as *milk of sulphur*.

Plastic sulphur

Plastic sulphur is formed by pouring a thin stream of sulphur, at (or close to) its boiling point, into cold water. It forms yellow rubbery ribbons of sulphur, which are soft and stretch readily. This state lasts for only a few minutes, after which plastic sulphur is slowly converted to rhombic sulphur. The plastic variety is not soluble in carbon disulphide. For a consideration of the nature of plastic sulphur, see p. 316.

Relations between rhombic and monoclinic sulphur

Both these allotropes of sulphur are stable in appropriate conditions. *Rhombic* sulphur is the stable variety *below* 369 K; *monoclinic* is the stable variety *above* 369 K. If rhombic sulphur is kept for some time above 369 K (and below its melting-point, 386 K), it will pass into monoclinic sulphur; if the latter variety is kept below 369 K for some time, it will pass into rhombic sulphur. This temperature of 369 K is known as the *transition point* between the two forms, and a mixture of the two is in equilibrium only at this temperature.

$$\text{rhombic} \xrightleftharpoons[\text{below } 369\text{K}]{\text{above } 369\text{K}} \text{monoclinic}$$

This kind of allotropy, in which the two allotropes are directly convertible into each other by mere temperature change and each has its own temperature range of stability, is known as *enantiotropy*. It is distinguished from *monotropy* in which one of the allotropes is always the stable variety and the other is *metastable*, i.e. existing only because the rate of change at room temperature is so slow. In monotropy, direct conversion is possible in one direction only—from the metastable to the stable allotrope. A case of this is the relation between white phosphorus (metastable) and red phosphorus. White is convertible to red by raising the temperature (in the absence of air) to about 570 K. The reverse change is not *directly* possible; red phosphorus must be vaporized as an intermediate stage and the vapour cooled under water to give white phosphorus.

If rhombic sulphur is heated *rapidly*, it will melt at 386 K. This is its true melting point and is shown because no appreciable time is allowed for the transition to monoclinic sulphur. Rhombic is metastable as soon as 369 K is passed. If, however, rhombic sulphur is heated *slowly*, it will change to monoclinic sulphur as soon as 369 K is passed; this variety will then melt at 392 K. These relations are expressed in diagrammatic form in Figure 9.9. Rhombic sulphur is metastable over the region AB. A is the transition point between rhombic and monoclinic

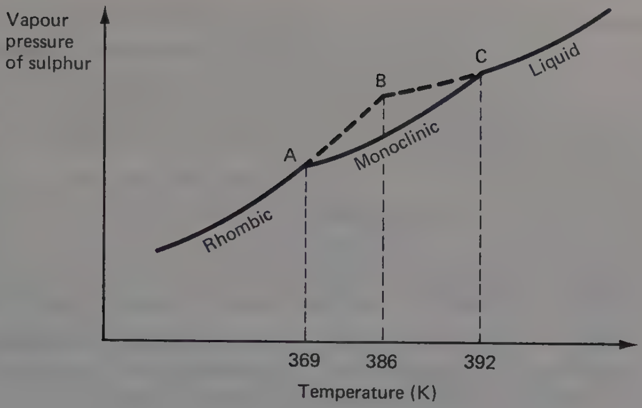


Figure 9.9

sulphur; B is the melting point of rhombic; C is the melting point of monoclinic sulphur.

Behaviour of sulphur when heated out of contact with air

Sulphur undergoes the following changes when heated:

(a) It melts at 386 K (when rapidly heated) to form an amber, mobile liquid.
(b) At about 450 K, it becomes very viscous and will not pour; it darkens considerably in colour.
(c) When heated further, it becomes mobile again, but almost black in colour.
(d) It boils at 718 K, and gives off a dark red vapour.

An explanation of these changes of viscosity is as follows. Rhombic sulphur has a molecule, S_8, in which the eight sulphur atoms form a ring which is not planar (Figure 9.10). When it melts, these rings are little affected. As the temperature rises, however, the rings are subject to vibration arising from increased energy in the molecule. They break and form open chains of sulphur atoms arranged in zig-zag fashion. The chains polymerize and become entangled, giving a liquid of very high viscosity. With further rise of temperature and greater vibration,

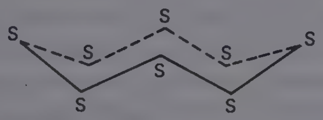


Figure 9.10 *Sulphur molecule*, S_8

the chains break up until the prevailing molecule becomes S_2 near the boiling point. These particles interfere less with each other. This causes a decrease of viscosity, and the liquid sulphur becomes quite mobile. This is a case of *dynamic allotropy.* This type of allotropy resembles enantiotropy (p. 314) in that the forms involved can be converted directly into each other. It differs from enantiotropy in that there is no fixed transition point. For a given pressure, the change takes place over a range of temperature.

If the almost boiling sulphur is poured into cold water, cooling is so rapid that true molecules S_8 have no time to form. Open chains of sulphur atoms are produced which, entangled together, form the soft, elastic material, *plastic sulphur.* In a few minutes, the molecular rings S_8 are formed and the true solid, rhombic sulphur, is given.

Chemical properties of sulphur

In the following pages, sulphur should really be written in the molecular form, S_8, in equations. Since this would lead to rather cumbersome expressions, the symbol S will be used.

1. *With non-metals.* Sulphur combines with a number of non-metals. If heated in air or oxygen, it melts and takes fire, burning with a blue flame to form mainly *sulphur dioxide.* A trace of sulphur trioxide is also formed, which gives a misty appearance to the gas.

$$S(s) + O_2(g) \rightarrow SO_2(g)$$

Heated in a current of dry *chlorine*, sulphur forms *disulphur dichloride*, S_2Cl_2. See also p. 366. Sulphur combines with *carbon* at the temperature of the electric furnace and forms carbon *disulphide.*

$$C(s) + 2S(g) \xrightarrow{\text{very high temp.}} CS_2(g)$$

2. *With metals.* Sulphur combines with most of the common metals when heated with them out of contact with air. The reactions are usually performed by heating two reagents, mixed in powder form and in calculated masses.

$$Fe(s) + S(l) \rightarrow FeS(s)$$
$$2Cu(s) + S(l) \rightarrow Cu_2S(s)$$

3. *With acids.* Sulphur is unaffected by hydrochloric acid at any concentration and by dilute sulphuric and nitric acids, because none of these acids has powerful oxidizing action. It reacts with hot, concentrated sulphuric acid to liberate *sulphur dioxide* (rather slowly) and with hot, concentrated nitric acid to form *sulphuric acid.* Bromine

catalyses this reaction. Both of these are oxidizing actions of the respective acids.

$$S(s) + 2H_2SO_4(l) \rightarrow 2H_2O(l) + 3SO_2(g)$$
$$S(s) + 6HNO_3(\text{conc.aq.}) \rightarrow H_2SO_4(l) + 6NO_2(g) + 2H_2O(l)$$

4. *With aqueous alkalis.* Sulphur gives a slow and rather complex reaction with hot, concentrated sodium hydroxide solution. The *thiosulphate* and *sulphide* of the metal are probably the initial products:

$$6OH^-(aq) + 4S(s) \rightarrow S_2O_3{}^{2-}(aq) + 2S^{2-}(aq) + 3H_2O(l)$$

but the sulphide combines with more sulphur to form the *pentasulphide*.

$$S^{2-}(aq) + 4S(s) \rightarrow S_5{}^{2-}(aq)$$

Potassium hydroxide gives a corresponding reaction.

Hydrogen sulphide

Preparation

1. *From iron*(II) *sulphide.* This is the usual laboratory preparation of the gas, by apparatus shown in Figure 9.11. Dilute hydrochloric acid or dilute sulphuric acid may be used. Hydrogen sulphide is usually collected over warm water, being fairly soluble in cold water.

$$FeS(s) + 2H^+(aq) \rightarrow H_2S(g) + Fe^{2+}(aq)$$

Prepared in this way, hydrogen sulphide contains two principal impurities—acid spray and hydrogen, the latter appearing because the

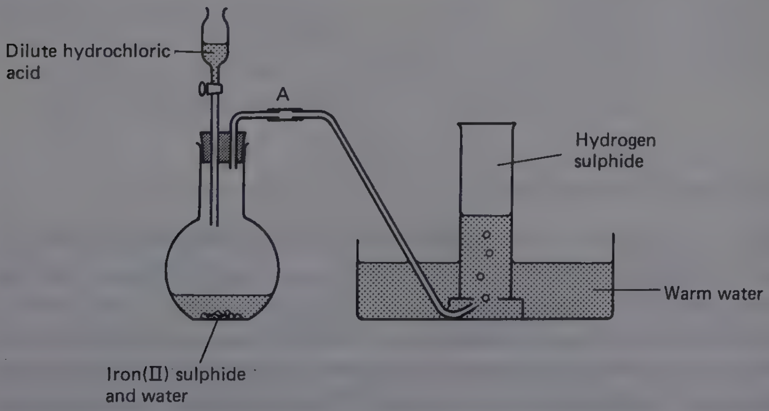


Figure 9.11 *Preparation of hydrogen sulphide*

iron(II) sulphide contains free iron, which reacts with the acid. To purify the gas, it can be passed into sodium hydroxide solution (connected at A), which absorbs hydrogen sulphide and acid spray, and allows hydrogen to pass through it and escape.

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$$
$$H_2S(g) + OH^-(aq) \rightarrow HS^-(aq) + H_2O(l)$$

Acidification of the solution will then yield purer hydrogen sulphide.

$$HS^-(aq) + H^+(aq) \rightarrow H_2S(g)$$

It may be dried over phosphorus(V) oxide (or over anhydrous calcium chloride, though hydrogen sulphide attacks this drying agent to some extent) and collected by downward delivery. Hydrogen sulphide must *not* be dried by concentrated sulphuric acid. This reagent slowly oxides it.

$$H_2SO_4(l) + 3H_2S(g) \rightarrow 4H_2O(l) + 4S(s)$$

In practice, the pure gas is usually prepared by one of the following methods.
2. *From antimony*(III) *sulphide*, Sb_2S_3. Fairly pure hydrogen sulphide can be prepared by *heating* antimony(III) sulphide with concentrated hydrochloric acid (or, better, a mixture of this acid, and water in a volume ratio of 2 :1).

$$Sb_2S_3(s) + 6HCl(aq) \rightleftharpoons 2SbCl_3(aq) + 3H_2S(g)$$

The gas is passed through water, to remove HCl fumes, and through phosphorus(V) oxide on glass wool to dry it. It is collected by upward displacement of air.

The action of water on aluminium sulphide also yields hydrogen sulphide. Heat is unnecessary in this case.

$$Al_2S_3(s) + 6H_2O(l) \rightarrow 2Al(OH)_3(s) + 3H_2S(g)$$

Properties of hydrogen sulphide

Hydrogen sulphide is a colourless gas. It has a well-known 'rotten egg' smell. The gas emitted by a rotten egg does contain hydrogen sulphide, derived from the decomposition of organic sulphur compounds in the egg yolk. Hydrogen sulphide is extremely poisonous, but the strong smell of the gas becomes very unpleasant much before a dangerously poisonous concentration is reached. (This behaviour contrasts with that of carbon monoxide, see p. 155). Hydrogen sulphide boils at 212 K and freezes at 190 K under atmospheric pressure. Water dissolves about three times its own volume of the gas at room temperature.

The chemical properties of the gas are as follows.

(1) Combustion

In a plentiful supply of air, hydrogen sulphide burns with a *blue* flame and the products are *sulphur dioxide* and *steam.*

$$2H_2S(g) + 3O_2(g) \rightarrow 2H_2O(g) + 2S_2(g)$$

In a limited air supply, sulphur tends to remain unoxidized and will deposit on any cold object in contact with the flame, e.g. a crucible lid or the walls of a gas jar.

$$2H_2S(g) + O_2(g) \rightarrow 2H_2O(g) + 2S(s)$$

(2) Hydrogen sulphide as a reducing agent

Hydrogen sulphide is a powerful reducing agent. *Like all reducing agents, it operates by acting as an electron donor*; in most cases, the hydrogen sulphide is oxidized to *sulphur* (which precipitates) by the essential reactions:

$$\begin{aligned} H_2S(aq) &\rightleftharpoons 2H^+(aq) + S^{2-}(aq) \\ S^{2-}(aq) &\rightarrow S(s) + 2e^- \text{ to oxidizing agent} \end{aligned}$$

Occasionally, oxidation of the H_2S may go as far as H_2SO_4. Important examples of the reducing action of hydrogen sulphide are:

(a) *With halogen elements,* Cl_2, Br_2, *and* I_2. Hydrogen sulphide is passed through water containing the halogen element. In all cases, the halogen colour is discharged, *sulphur* is precipitated and the solution contains the corresponding *halogen acid*; e.g.

$$\begin{aligned} H_2S(aq) &\rightleftharpoons 2H^+(aq) + S^{2-}(aq) \\ 2H^+(aq) + S^{2-}(aq) + Cl_2(g) &\rightarrow 2HCl(aq) + S(s) \end{aligned}$$

The two redox half-equations here are:

$$\begin{aligned} S^{2-}(aq) &\rightarrow S(s) + 2e^- \\ Cl_2(g) + 2e^- &\rightarrow 2Cl^-(aq) \end{aligned}$$

The reader may wish to write the appropriate half-equations for the other examples.

(b) *With an iron*(III) *salt in aqueous solution. Sulphur* is precipitated and the colour of the solution changes from yellow to green by formation of the corresponding *iron*(II) *salt.*

$$2Fe^{3+}(aq) + S^{2-}(aq) \rightarrow 2Fe^{2+}(aq) + S(s)$$

(c) *With acidified potassium manganate*(VII) *solution.* The purple colour of this solution is discharged and *sulphur* is precipitated.

$$5S^{2-}(aq) + 2MnO_4{}^{-}(aq) + 16H^{+}(aq) \rightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 5S(s)$$

(d) *With acidified potassium dichromate*(VI) *solution.* The orange colour of the solution is changed to green and *sulphur* is precipitated.

$$\underset{\text{orange}}{Cr_2O_7{}^{2-}(aq)} + 14H^{+}(aq) + 3S^{2-}(aq) \rightarrow \underset{\text{green}}{2Cr^{3+}(aq)} + 7H_2O(l) + 3S(s)$$

(c) *With hydrogen peroxide. Sulphur* is precipitated.

$$2H^{+}(aq) + S^{2-}(aq) + H_2O_2(aq) \rightarrow S(s) + 2H_2O(l)$$

(f) *With concentrated nitric acid.* When hydrogen sulphide is passed into concentrated nitric acid, the acid heats up considerably. Some *sulphur* is deposited and *sulphuric acid* is formed in solution.

$$H_2S(aq) \rightleftharpoons 2H^{+}(aq) + S^{2-}(aq)$$
$$2H^{+}(aq) + S^{2-}(aq) + 2HNO_3\,(conc.aq.) \rightarrow 2H_2O + 2NO_2 + S$$
$$2H^{+}(aq) + S^{2-}(aq) + 8HNO_3\,(conc.aq.) \rightarrow 4H_2O(l) + 8NO_2(g) + H_2SO_4(aq)$$

(g) *With sulphur dioxide.* If sulphur dioxide and hydrogen sulphide are mixed *with liquid water present* (not merely water vapour), sulphur is deposited. Liquid water is a necessary catalyst here, and, without it, there is no reaction.

$$2H_2S(aq) \rightleftharpoons 4H^{+}(aq) + 2S^{2-}(aq)$$
$$SO_2(g) + H_2O(l) \rightleftharpoons 2H^{+}(aq) + SO_3{}^{2-}(aq)$$

Adding the right-hand sides of these equations,

$$4H^{+}(aq) + 2S^{2-}(aq) + 2H^{+}(aq) + SO_3{}^{2-}(aq) \rightarrow 3H_2O(l) + 3S(s)$$

In effect, sulphur dioxide is *reduced* to sulphur and hydrogen sulphide is *oxidized* to sulphur.

(h) *With lead*(IV) *oxide.* A stream of hydrogen sulphide is ignited by contact with lead(IV) oxide to give a mixture of solid products, including lead(II) sulphide and lead(II) sulphate.

(3) Hydrogen sulphide as a precipitant of metallic sulphides

Almost all metallic sulphides are 'insoluble' in water, in the loose sense in which this term is usually employed. The sulphides of sodium, potassium and ammonium are soluble, but hydrolyse rapidly with release of hydrogen sulphide gas. An important aspect of sulphide precipitation is its application in Qualitative Analysis. For this, see *Advanced Level Physical Chemistry*, p. 238.

(4) Hydrogen sulphide as an acid

Hydrogen sulphide is moderately soluble in water and ionizes very slightly in the form:

$$H_2S(aq) \rightleftharpoons H^+(aq) + HS^-(aq) \rightleftharpoons 2H^+(aq) + S^{2-}(aq)$$

It behaves, therefore, as a very weak *dibasic* acid. It forms normal and acid salts with the caustic alkalis and with ammonia, a typical reaction being:

$$H_2S(aq) \rightleftharpoons H^+(aq) + HS^-(aq) \rightleftharpoons 2H^+(aq) + S^{2-}(aq)$$
$$2NaOH(aq) + 2H^+(aq) + S^{2-}(aq) \rightarrow Na_2S(aq) + 2H_2O(l)$$
$$NaOH(aq) + H^+(aq) + HS^-(aq) \rightarrow NaHS(aq) + H_2O(l)$$

For fuller accounts of these reactions, see the chemistry of *sodium*, *potassium*, and *ammonium sulphides*.

Detection of hydrogen sulphide

Hydrogen sulphide is readily detected by the fact that it turns damp lead(II) ethanoate paper brown, then black.

$$H_2S(aq) \rightleftharpoons 2H^+(aq) + S^{2-}(aq)$$
$$Pb^{2+}(aq) + S^{2-}(aq) \rightarrow \underset{\text{black}}{PbS(s)}$$

Sulphur dioxide, SO_2

Laboratory preparation

Most of the common metals (except gold and platinum) react with hot, concentrated sulphuric acid to liberate sulphur dioxide. To prepare the gas on the laboratory scale, *copper* is the metal used because the reaction is rapid enough to be convenient without any danger of its

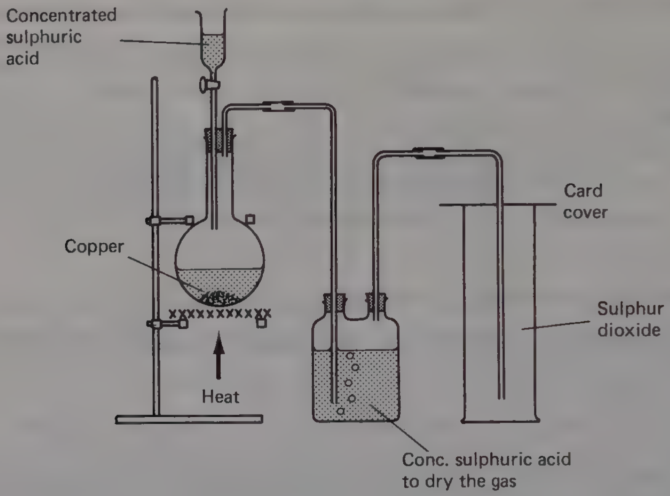


Figure 9.12 *Preparation of sulphur dioxide*

getting out of hand. The apparatus used is shown in Figure 9.12. The principal reaction is:

$$Cu(s) + 2H_2SO_4(l) \rightarrow CuSO_4(aq) + 2H_2O(l) + SO_2(g)$$

Some sulphide of copper is also produced, which makes the residual solid black.

Sulphur dioxide can also be made by the action of dilute hydrochloric (or sulphuric) acid on sodium sulphite crystals. The apparatus of Figure 9.12 can be used but only gentle warming is needed.

$$SO_3^{2-}(s) + 2H^+(aq) \rightarrow H_2O(l) + SO_2(g)$$

Liquefaction of sulphur dioxide. If *dry* sulphur dioxide is passed through a coil of glass tubing surrounded by an efficient ice–salt freezing mixture, liquid sulphur dioxide is produced, boiling point 263 K. Sulphur dioxide is obtainable in liquid form in metal canisters. At room temperature, the liquid exists under the pressure of its own vapour at about 2.5 atm. The gas can be obtained as required by opening a valve fitted to the canister. The large-scale preparation of sulphur dioxide is considered later in connection with the manufacture of sulphuric acid.

Properties of sulphur dioxide

Sulphur dioxide is a colourless gas with an unpleasant smell and a rather metallic taste. It is nearly two and a half times as dense as air. It has high solubility in water (80 cm^3 in 1 cm^3 of water at 273 K), but can be entirely expelled by boiling the liquid. It forms a colourless liquid, boiling point 263 K. The gas is quite poisonous.

The chemical properties of sulphur dioxide may be summarized as: (1) *acidic*, (2) *reducing*, (3) *oxidizing*, (4) *additive*.

(1) Acidic properties

The acidic properties of sulphur dioxide are exercised in solution in water, presumably by the formation, and ionization, of *sulphurous acid*, The liquid smells strongly of sulphur dioxide. For its preparation, see Figure 9.13.

$$SO_2(g) + H_2O(l) \rightleftharpoons H_2SO_3(aq)$$
$$H_2SO_3(aq) + 2H_2O(l) \rightleftharpoons 2H_3O^+(aq) + SO_3{}^{2-}(aq)$$

This acid has never been isolated. Its formation is presumed because:

(a) The solubility of sulphur dioxide departs to a very marked extent from the requirements of Henry's Law; this state of affairs almost always accompanies chemical action between solvent and gas.
(b) The solution shows acidic properties with indicators and forms salts with metals and bases.
(c) The electrical conductivity of the solution is much greater than that of water. This requires the formation of ions.

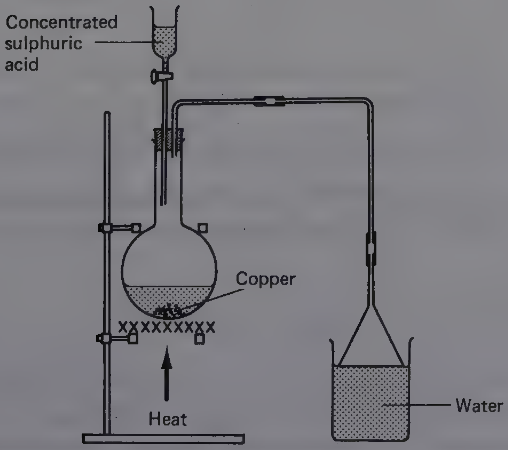


Figure 9.13 *Preparation of sulphurous acid*

Sulphurous acid is *dibasic* and forms both *normal* and *acid* salts.

$$\underset{}{H_2SO_3(aq) \rightleftharpoons H^+(aq) + \underset{\text{hydrogensulphite ion}}{HSO_3^-(aq)}};\ H_2SO_3(aq) \rightleftharpoons 2H^+(aq) + \underset{\text{sulphite ion}}{SO_3^{2-}}$$

The SO_3^{2-} ion is that of the normal salts; the HSO_3^- ion is that of the acid salts. Typical examples of these salts are *sodium sulphite* and *sodium hydrogensulphite*, prepared as below.

Sodium hydrogensulphite (*sodium bisulphite*), $NaHSO_3$. Sulphur dioxide is passed through a *cold* concentrated solution of sodium hydroxide (or sodium carbonate) until no more is absorbed and the liquid smells of sulphur dioxide. The hydrogensulphite is formed; the liquid is usually pale greenish-yellow.

$$OH^-(aq) + SO_2(g) \rightarrow HSO_3^-(aq)$$
$$CO_3^{2-}(aq) + H_2O(l) + 2SO_2(g) \rightarrow 2HSO_3^-(aq) + CO_2(g)$$

The liquid must *not* be heated because the hydrogensulphite will decompose:

$$4HSO_3^-(aq) \rightarrow 2SO_4^{2-}(aq) + 2H_2O(l) + SO_2(g) + S(s)$$

Powdered sodium hydrogensulphite can be precipitated by the addition of alcohol, then filtered, washed with a little *cold*, distilled water and dried.

Sodium sulphate, $Na_2SO_3.7H_2O$. A quantity of sodium hydroxide solution is divided into two equal parts. One is saturated with sulphur dioxide to form the hydrogensulphite in solution as above.

$$OH^-(aq) + SO_2(g) \rightarrow HSO_3^-(aq)$$

The other half of the sodium hydroxide solution is then added, converting the whole to a solution of sodium sulphite.

$$HSO_3^-(aq) + OH^-(aq) \rightarrow SO_3^{2-}(aq) + H_2O(l)$$

The solution is then evaporated to crystallizing point and cooled. The crystals are filtered off, washed with a little cold, distilled water and dried.

(2) Sulphur dioxide as a reducing agent

The reducing actions of sulphur dioxide are usually exercised in solution and are, in that sense, reducing actions of sulphurous acid. *Like all other reducing agents, sulphurous acid operates as an electron donor*, in this case in conjunction with water, by the essential reactions:

$$H_2O(l) + SO_2(g) \rightleftharpoons 2H^+(aq) + SO_3^{2-}(aq)$$
$$SO_3^{2-}(aq) + H_2O(l) \rightarrow SO_4^{2-}(aq) + 2H^+(aq) + 2e^-$$

The sulphite ion is oxidized to the sulphate ion, SO_4^{2-}. Some important reducing actions of sulphur dioxide in water, or of sulphurous acid, are:

(a) *With iron*(III) *salts in solution.* The *brown* (or yellow) iron(III) solution will turn *green* by conversion to an iron(II) salt.

$$H_2O(l) + SO_2(g) \rightleftharpoons H_2SO_3(aq) \rightleftharpoons 2H^+(aq) + SO_3^{2-}(aq)$$

Overall: $$2Fe^{3+}(aq) + H_2O(l) + SO_3^{2-}(aq) \rightarrow 2Fe^{2+}(aq) + 2H^+(aq) + SO_4^{2-}(aq)$$

The two redox half-equations are:

$$SO_3^{2-}(aq) + H_2O(l) \rightarrow SO_4^{2-}(aq) + 2H^+(aq) + 2e^-$$
$$2Fe^{3+}(aq) + 2e^- \rightarrow 2Fe^{2+}(aq)$$

The reader may wish to write the appropriate half-equations for the other examples.

(b) *With acidified potassium manganate*(VII) *solution.* The solution is rapidly turned from *purple* to *colourless.*

$$2MnO_4^-(aq) + 6H^+(aq) + 5SO_3^{2-}(aq) \rightarrow 2Mn^{2+}(aq) + 3H_2O(l) + 5SO_4^{2-}(aq)$$

(c) *With acidified potassium dichromate*(VI) *solution.* The solution is rapidly turned from *orange-yellow* to *green.* The green colour is caused by the hydrated chromium(III) ion.

$$Cr_2O_7^{2-}(aq) + 8H^+(aq) + 3SO_3^{2-}(aq) \rightarrow 2Cr^{3+}(aq) + 4H_2O(l) + 3SO_4^{2-}(aq)$$

(d) *Chlorine and bromine.* These halogens are *decolorized* in water with formation of the corresponding *halogen acid*, e.g:

$$Cl_2(aq) + H_2O(l) + SO_3^{2-}(aq) \rightarrow SO_4^{2-}(aq) + 2H^+(aq) + 2Cl^-(aq)$$

Iodine gives a similar reaction but it is appreciably reversible unless the sulphur dioxide concentration is very low (limit about 0.05 per cent).

$$SO_3^{2-}(aq) + H_2O(l) + I_2(s) \rightleftharpoons SO_4^{2-}(aq) + 2H^+(aq) + 2I^-(aq)$$

(e) *Iodates*(V). Iodates(V) are reduced in solution to *iodine* (brown coloration).

$$2IO_3^-(aq) + 4H^+(aq) + 5SO_3^{2-}(aq) \rightarrow 2HSO_4^-(aq) + 3SO_4^{2-}(aq) + H_2O(l) + I_2(s)$$

Bleaching action of sulphur dioxide. In association with water, sulphur dioxide is a useful bleaching agent and is used in the bleaching of wool, silk, straw, and sponges. The coloured material forms a reduced *leuco*-compound, which is colourless.

$$SO_3^{2-}(aq) + H_2O(l) + X \rightarrow SO_4^{2-}(aq) + XH_2$$

where X is the coloured molecule. The action may be reversed by the action of air and light; this can account for the gradual yellowing of straw hats, white flannel trousers, and newsprint.

(3) Sulphur dioxide as an oxidizing agent

The oxidizing actions of sulphur dioxide are few and relatively unimportant. Sulphur dioxide will support the combustion of burning magnesium, oxidizing the magnesium to its ion, Mg^{2+}.

$$3Mg(s) + SO_2(g) \rightarrow MgS(s) + 2MgO(s)$$

Some sulphur may also be observed.

Potassium, calcium, iron and arsenic will also burn if finely divided and heated strongly in the gas. The products may be quite complex, e.g. potassium forms a mixture of its *sulphite* and *thiosulphate*.

$$4K(s) + 3SO_2(g) \rightarrow K_2SO_3(s) + K_2S_2O_3(s)$$

Sulphur dioxide is also reduced if passed over carbon at about 1400 K. The carbon is oxidized.

$$C(s) + SO_2(g) \rightarrow CO_2(g) + S(s)$$

(4) Additive reactions of sulphur dioxide

(a) *With lead*(IV) *oxide.* If warm lead(IV) oxide is introduced into a gas jar of sulphur dioxide, the lead(IV) oxide glows brightly and turns *white* by formation of *lead sulphate.*

$$PbO_2(s) + SO_2(g) \rightarrow PbSO_4(s)$$

(b) *With halogen elements.* Sulphur dioxide will combine directly with chlorine to form *sulphur dichloride dioxide* (*sulphuryl chloride*), SO_2Cl_2, a colourless liquid.

$$SO_2(g) + Cl_2(g) \rightarrow SO_2Cl_2(l)$$

The reaction is catalysed by sunlight and (more effectively) by camphor.

(c) *With oxygen.* Sulphur dioxide can be made to combine directly with oxygen in the presence of a catalyst and when heated. In laboratory conditions, *platinized asbestos* is often used at about 720 K. In industry the cheaper vanadium(V) oxide, V_2O_5, is used. The product is *sulphur trioxide.*

This is the main reaction in the Contact Process for making sulphuric acid (see p. 331).

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(s)$$

Molecular formula of sulphur dioxide

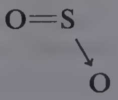
When sulphur is burnt in oxygen, the volume of sulphur dioxide produced is *equal* to that of the oxygen used, all measurements being made at the same temperature and pressure. The experimental work to prove this is exactly the same as that described for carbon dioxide on p. 153, using sulphur instead of carbon. From this:

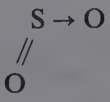
1 volume of sulphur dioxide contains 1 volume of oxygen at constant temperature and pressure.

By Avogadro's Hypothesis, 1 molecule of sulphur dioxide contains 1 molecule of oxygen, i.e. assuming the diatomicity of oxygen, the molecular formula of sulphur dioxide is S_nO_2. The relative vapour density of sulphur dioxide is 32; its relative molecular mass is, therefore, 64. From this,

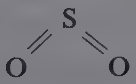
$$\begin{aligned} S_nO_2 &= 64 \\ \text{i.e.} \quad (32n + 32) &= 64 \\ \text{or} \quad n &= 1 \end{aligned}$$

The molecular formula of sulphur dioxide is SO_2. The molecule of sulphur dioxide is not linear. The structure can be written as a resonance hybrid between the two forms:





Since sulphur can have more than eight electrons in its outer quantum level, it is possible that the atoms are joined by double bonds:



Detection of sulphur dioxide

The best test for sulphur dioxide is a combination of the following:

(a) it rapidly decolorizes a dilute neutral solution of potassium manganate(VII);

(b) the decolorized liquid gives a white precipitate (of barium sulphate) on the addition of dilute hydrochloric acid and barium chloride solution. The second part of the test distinguishes sulphur dioxide from other reagents which decolorize manganate(VII).

$$SO_2(g) + H_2O(l) \rightleftharpoons H_2SO_3(aq) \rightleftharpoons 2H^+(aq) + SO_3^{2-}(aq)$$

$$5SO_3^{2-}(aq) + 2MnO_4^-(aq) + 6H^+(aq) \rightarrow 5SO_4^{2-}(aq) + 2Mn^{2+}(aq) + 3H_2O(l)$$

$$SO_4^{2-}(aq) + Ba^{2+}(aq) \rightarrow BaSO_4(s)$$

Uses of sulphur dioxide

(a) By far the most important use of sulphur dioxide is for the manufacture of sulphuric acid, for which see later in this chapter.

(b) Sulphur dioxide is used in the manufacture of sulphites and hydrogensulphites, especially calcium hydrogensulphite used in the manufacture of paper from wood-pulp.

(c) Sulphur dioxide is used in bleaching wool, straw, silk, and other materials.

Sulphur dioxide is formed when the sulphur-containing impurities in coal and oil are burnt. It is one of the most important causes of atmospheric pollution.

Sulphur trioxide (sulphuric anhydride), SO_3

Under laboratory conditions, sulphur trioxide is usually prepared by the apparatus of Figure 9.14. The freezing mixture is ice–water. Platinized asbestos is the usual catalyst. Sulphur trioxide appears as white needles.

$$2SO_2(g) + O_2(g) \rightarrow 2SO_3(s)$$

Sulphur trioxide is mainly important in industry as an intermediate in the manufacture of sulphuric acid by the Contact process. In this case, *vanadium*(V) *oxide*, V_2O_5, is the usual catalyst.

Sulphur trioxide is a product of decomposition of a number of compounds by heat, e.g.

$$2NaHSO_4(s) \rightarrow Na_2SO_4(s) + H_2O(g) + SO_3(g)$$

$$2FeSO_4(s) \rightarrow Fe_2O_3(s) + SO_2(g) + SO_3(g)$$

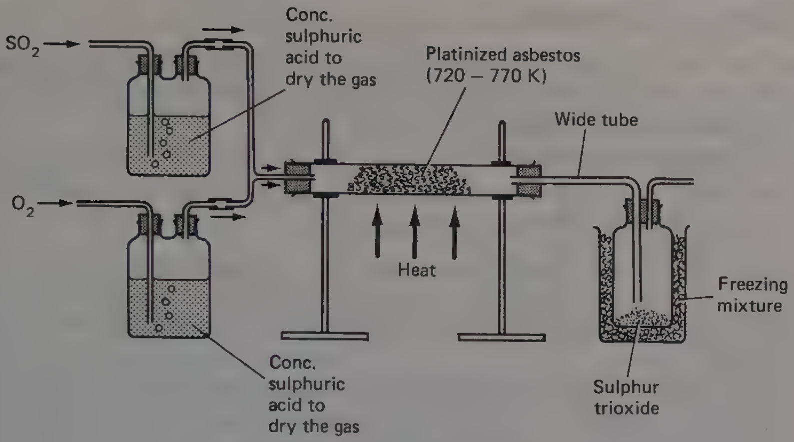


Figure 9.14 *Preparation of sulphur trioxide*

Properties of sulphur trioxide

Sulphur trioxide exists in two forms. *α-sulphur trioxide* is a colourless liquid, boiling point 318 K. It can be solidified in ice–salt and the solid melts at 290 K. The vapour density of this form is about 40, corresponding to a molecule, SO_3, but the solid consists of a trimer, S_3O_9. *β-sulphur trioxide* is formed if the α-variety is kept at about room temperature for a time, in contact with moist air. It turns back to the α-form if sublimed at about 320 K. It melts at 306 K. The β-form occurs as needle-shaped crystals and is a chain-like polymer. The two forms are very similar in chemical behaviour with the β-form rather less reactive.

1. *With cold water.* A violent reaction occurs with a hissing sound and much heat evolved. The product is *sulphuric acid*, hence the name *sulphuric anhydride* for this oxide.

$$H_2O(l) + SO_3(s) \rightarrow H_2SO_4(l) \qquad \Delta H = -88\ \text{kJ mol}^{-1}$$

2. *With metallic oxides.* Sulphur trioxide reacts vigorously if passed over many heated metallic oxides, the solid usually becoming incandescent, forming the *sulphate*. The oxides of magnesium, calcium and barium behave in this way, as:

$$BaO(s) + SO_3(g) \rightarrow BaSO_4(s)$$

3. *When heated.* Sulphur trioxide decomposes when heated, decomposition being almost complete at 1300 K.

$$2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$$

Formula of sulphur trioxide

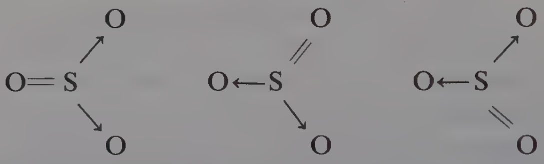
In the reaction mentioned immediately above, two volumes of sulphur trioxide produce two volumes of sulphur dioxide and one volume of oxygen at constant temperature and pressure.

By Avogadro's Hypothesis, the same *molecular* proportions must hold. Writing sulphur trioxide as S_nO_m, and accepting SO_2 and O_2 as the other molecular formulae, we have:

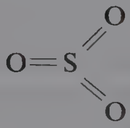
$$2S_nO_m(s) \rightarrow 2SO_2(g) + O_2(g)$$

That is, $n = 1$ and $m = 3$, so that sulphur trioxide has the molecular formula SO_3.

It has a planar molecule, which can be written as a resonance hybrid of the three forms:



Again, as sulphur may have up to 12 electrons in its outer quantum shell, the structure may be written simply as:



Sulphuric acid, H_2SO_4

There is no really convenient way of making sulphuric acid on the small scale. It is made on the industrial scale, in very large amounts, by the *Contact process* and the now largely obsolete *Lead Chamber process*. For both processes, sulphur dioxide is required as raw material. It is available from the following sources.

Sources of sulphur dioxide

1. *The burning of sulphur.* A number of different sulphur burners are used, the details of which are mainly of technical interest. In one of them, molten sulphur is pumped in at the top of a tower packed with spaced brickwork, and a current of air flows with the sulphur.

$$S(s) + O_2(g) \rightarrow SO_2(g)$$

This method has the advantage of producing sulphur dioxide free from troublesome impurities.

2. *The burning of iron pyrites*, FeS_2. One of the ways of burning pyrites is in a sloping, rotary kiln in which it meets a current of air. The kiln is made of steel, lined with fire-brick. Iron(III) oxide is discharged from the kiln.

$$4FeS_2(s) + 11O_2(g) \rightarrow 2Fe_2O_3(s) + 8SO_2(g)$$

The gas given off from the burning pyrites contains about 7 per cent of sulphur dioxide. It is accompanied by oxygen and nitrogen (from the air), and by dust particles, which usually include arsenic(III) oxide as well as compounds of iron.

3. *From anhydrite*, $CaSO_4$. The production of sulphur dioxide from anhydrite is combined with the manufacture of cement. The anhydrite is ground with coke and shale (silica). The mixture is heated by powdered coal in a rotary kiln. The principal reactions which take place are:

$$2CaSO_4(s) + C(s) \rightarrow 2CaO(s) + 2SO_2(g) + CO_2(g)$$
$$CaO(s) + SiO_2(s) \rightarrow CaSiO_3(s)$$

The temperature is eventually raised to 1700 K and the solid product can be ground and sold as a cement. The gas leaving the kiln contains about 9 per cent of sulphur dioxide. It contains impurities comparable with those in the gas from pyrites.

The Lead Chamber process

This process is now largely obsolete. It depends on the catalytic oxidation of sulphur dioxide by oxygen of the air in the presence of water at about 363 K. The catalyst is *nitrogen oxide* (*nitric oxide*). The changes involved are usually represented by the cycle of equations given below, though they are known to be considerably more complex:

$$NO(g) + \tfrac{1}{2}O_2(g) \rightarrow NO_2(g)$$
$$NO_2(g) + H_2O(l) + SO_2(g) \rightarrow H_2SO_4(l) + NO(g)$$

Intermediate compounds can be isolated. The most important is *chamber crystals*, nitrosyl hydrogensulphate, $NO.HSO_4$.

The Contact process

This process depends on the following stages:
(1) production of sulphur dioxide and its purification (see later);
(2) catalytic oxidation of sulphur dioxide to sulphur trioxide by oxygen

of the air:

$$2SO_2(g) + O_2(g) \rightarrow 2SO_3(s)$$

(3) combination of sulphur trioxide with the elements of water (not directly; see later).

Conditions for catalytic oxidation of sulphur dioxide

Relative volumes	$2SO_2(g)$ +	$O_2(g) \rightarrow$	$2SO_3(s)$	$\Delta H = -190\,\mathrm{kJ\,mol^{-1}}$
as gases	2×22.4	22.4	$2 \times 22.4\,\mathrm{dm^3}$ at constant temperature and pressure	

(a) *Pressure.* Sulphur trioxide is produced with *reduction* in volume. By Le Chatelier's Principle, raising of the pressure of a system of sulphur dioxide, oxygen, and sulphur trioxide in equilibrium will cause it to produce more sulphur trioxide in the effort to reduce the volume, and so the pressure. That is, *high pressure is favourable to the production of sulphur trioxide.* In practice, however, almost complete conversion of sulphur dioxide to trioxide can be obtained at ordinary pressure, i.e. the pressures used are sufficient simply to ensure flow of gases through the system.

(b) *Concentration of materials.* By Le Chatelier's Principle, increase of concentration of oxygen in a system of sulphur dioxide, oxygen and sulphur trioxide in equilibrium will cause increased production of sulphur trioxide in the effort to reduce the raised concentration of oxygen. In practice, sufficient air is used to raise the volume ratio of oxygen to sulphur dioxide from the theoretical requirement of 1:2 to 3:2. This favours the conversion of sulphur dioxide to trioxide. Further addition of air would make the sulphur dioxide too dilute to give an adequate yield of sulphuric acid in a given time.

(c) *Temperature.* The production of sulphur trioxide is exothermic. By Le Chatelier's Principle, lowering of the temperature of an equilibrium mixture containing sulphur dioxide, sulphur trioxide and oxygen will cause it to produce more sulphur trioxide in the effort to liberate heat and raise the temperature to its former level. That is, *low temperature is favourable to the production of sulphur trioxide.* But, as temperature falls, rate of reaction falls and *it is necessary to use a compromise temperature* (an *optimum* temperature) at which the equilibrium is sufficiently favourable and the reaction rapid enough *with a catalyst present.* This temperature is about 720 K.

(d) *Catalyst.* The process was originally worked with platinum (as platinized asbestos) but this is now abandoned as too expensive, and too easily 'poisoned' by impurities. The catalyst then used was *vanadium*(V) *oxide*, V_2O_5, which is cheaper and not so easily poisoned, though it is valueless after use.

The catalyst now in use consists of silica grains covered with a complex organometallic material containing vanadium. It is known as *promoted* vanadium. The oxidation state of the vanadium is + 4 or + 5. The operating conditions are essentially unchanged.

Catalyst poisoning occurs very readily in this process (especially by As_2O_3) and the gases must be thoroughly purified before they reach the catalyst chamber to prevent poisoning. Sulphur dioxide produced from sulphur needs little purification. From other sources (spent oxide, pyrites, and anhydrite), it needs elaborate and thorough purification on the following lines:

(i) Deposition of the heavier dust particles by gravity in a settling chamber.
(ii) Electrostatic precipitation of fine dust particles. The gases pass between electrodes with a potential difference of 50 000 V. The dust particles acquire electric charges. They are attracted to oppositely charged plates, lose their charges and fall into collectors.
(iii) The gases are cooled and washed in vertical towers. Some impurities condense out.
(iv) Wet electrostatic precipitators remove remaining dust particles which have acted as centres of condensation.
(v) The gas is dried by concentrated sulphuric acid.

The mixture, containing sulphur dioxide and air, is then passed through a heat exchanger to adjust its temperature to 670–720 K and into the catalyst (or *converter*). It is cylindrical, made of steel and carries the catalyst on perforated shelves. To give the maximum surface area, the catalyst is distributed on an inert carrier, such as silica gel. Oxidation of sulphur dioxide occurs here.

$$2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$$

The temperature of the gas is raised, by this exothermic reaction, to about 850 K. The gas passes through a heat-exchanger to lower it again to about 720 K, then into a second converter; and so on to, possibly, four stages, by which time about 98 per cent of the possible yield of sulphur trioxide has been attained.

Direct combination of this with water is not practicable because a spray of particles of dilute sulphuric acid forms and escapes. The sulphur trioxide is absorbed by cold 98 per cent sulphuric acid flowing down a tower packed with inert material. This forms 'oleum', or 'fuming sulphuric acid', containing up to 60 per cent of dissolved sulphur trioxide.

$$H_2SO_4(l) + SO_3(g) \rightarrow H_2S_2O_7(l)$$

This product finds a market as an oxidizing and sulphonating agent for organic compounds. It is converted to concentrated sulphuric acid by combining with the calculated weight of water.

$$H_2S_2O_7(l) + H_2O(l) \rightarrow 2H_2SO_4(l)$$

It is not possible to produce impure Contact acid because the catalyst is rapidly poisoned by impurities in the gases. The only considerable impurity in the acid is a small percentage of water.

Uses of sulphuric acid

Sulphuric acid is probably the World's most important manufactured chemical. The total World production is about 25 million tonnes per year. Its main use is the production of fertilizers ('superphosphate', see p. 98, and ammonium sulphate, see p. 217). Other uses include the 'pickling' (pre-treatment to remove oxide film) of metals before galvanizing, tinning, or electroplating; the manufacture of explosives, dyes, drugs, and many fine chemicals; the sulphonation of oils in the manufacture of detergents; the preliminary purification of crude petroleum; and in lead–acid accumulators.

Properties of sulphuric acid

Sulphuric acid is a colourless, viscous liquid with no smell. The high viscosity is due to strong intermolecular hydrogen bonding. At 288 K, its density is 1.84 g cm^{-3} and it freezes at 283.5 K. The highest quality commercial acid contains about 2 per cent of water and has a much lower freezing point. Sulphuric acid boils at about 603 K with some decomposition, giving off very irritating and poisonous white fumes. The distillate is a constant-boiling mixture containing about 2 per cent water.

$$H_2SO_4(l) \rightarrow H_2O(g) + SO_3(g)$$

If allowed to fall on a red-hot, inert surface, it decomposes according to the equation

$$2H_2SO_4(l) \rightarrow 2H_2O(g) + 2SO_2(g) + O_2(g)$$

The chemical properties of sulphuric acid can be classified under the following headings: (1) *acidic properties*, (2) *dehydrating action*, (3) *oxidizing action*, (4) *sulphonating action.*

(1) Acidic properties

It is probable that perfectly water-free sulphuric acid is completely *covalent*, a non-electrolyte with no acidic properties. Such a situation is very difficult to attain in ordinary practice, because the acid is extremely hygroscopic. In 'dilute' solution it acts as a strong (i.e. highly ionized), dibasic acid by ionizing:

$$H_2SO_4(aq) \rightleftharpoons 2H^+(aq) + SO_4{}^{2-}(aq)$$

It is weaker, i.e. less fully ionized, than hydrochloric acid or nitric acid in 'bench' dilutions. Being ionized in this way, sulphuric acid in *dilute solution* shows typical acidic properties:

(a) It gives their acidic colours to indicators, e.g. methyl orange, pink; litmus, red.

(b) It reacts with the more electropositive metals with liberation of hydrogen, e.g.

$$Zn(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g)$$
$$Mg(s) + 2H^+(aq) \rightarrow Mg^{2+}(aq) + H_2(g)$$

Mercury, lead, copper, bismuth and the noble metals are not attacked by the dilute acid. Aluminium, nickel and chromium are usually protected by an oxide layer, but are reactive if it is removed, e.g. aluminium is quite rapidly attacked if amalgamated with mercury.

(c) It reacts with bases and alkalies to form both *normal* and *acid* sulphates, e.g.

$$2NaOH(aq) + H_2SO_4(aq) \rightarrow \underset{\substack{\text{sodiumsulphate}\\ \text{(normal)}}}{Na_2SO_4(aq)} + 2H_2O(l)$$

$$NaOH(aq) + H_2SO_4(aq) \rightarrow \underset{\substack{\text{sodium hydrogensulphate}\\ \text{(acid)}}}{NaHSO_4(aq)} + H_2O(l)$$

(d) It reacts with *carbonates* (or hydrogencarbonates) liberating *carbon dioxide.*

$$CO_3{}^{2-} + 2H^+(aq) \rightarrow H_2O(l) + CO_2(g)$$

(2) Dehydrating action

Concentrated sulphuric acid has a very great affinity for water. Dilution is very exothermic, and the acid must *always* be added to water. In this way the much higher heat capacity of the water acts as a restraint. If water is added to the acid, the temperature attained may be high enough to vaporize instantaneously the small quantity of water added at first and eject it, together with acid, from the apparatus. Many serious accidents have occurred in this way. Concentrated sulphuric acid will readily dehydrate certain materials by removing from them the elements of water. Important cases of dehydration are:

(a) *Methanoic acid* (*formic acid*) *and methanoates.* These are dehydrated by *cold, concentrated* sulphuric acid with effervescence and liberation of *carbon monoxide* (test: burns with a blue flame; product turns lime water 'milky'); e.g. with sodium methanoate:

$$HCOONa(s) + H_2SO_4(l) \rightarrow H.COOH(l) + NaHSO_4(s)$$

$$HCOOH(l) \xrightarrow{-H_2O} CO(g)$$

(b) *Ethanedioic* (*oxalic acid*) *and ethanedioates.* These are dehydrated by *concentrated* sulphuric acid *at about* 330 K. Effervescence occurs and the products are *carbon monoxide* (test above) and *carbon dioxide* (turns lime water 'milky') in equal volumes; e.g. with sodium ethanedioate:

$$Na_2C_2O_4(s) + H_2SO_4(l) \rightarrow H_2C_2O_4(s) + Na_2SO_4(s)$$

$$H_2C_2O_4(s) \xrightarrow{-H_2O} CO(g) + CO_2(g)$$

(c) *Sugar* (*sucrose*). To a cold, very concentrated syrup of sugar and water, concentrated sulphuric acid is added in excess. There is a violent action, much heat generated and steam evolved, leaving a swollen black mass of *carbon.*

$$C_{12}H_{22}O_{11}(s) \xrightarrow{-11H_2O} 12C(s)$$

This mass, when crushed, washed well with water and dried, provides a very pure form of carbon—'sugar charcoal'.

(d) *Copper*(II) *sulphate crystals.* These crystals are dehydrated by cold, concentrated sulphuric acid. They turn from blue to white and crumble to anhydrous copper sulphate powder.

$$CuSO_4.5H_2O(s) \xrightarrow{-5H_2O} CuSO_4(s)$$

Concentrated sulphuric acid can itself be dehydrated by heating with phosphorus(V) oxide: $H_2SO_4(l) \xrightarrow{-H_2O} SO_3(g)$. Sulphuric acid is known to form definite hydrates. $H_2SO_4.4H_2O$ and $H_2SO_4.H_2O$ occur below 273 K and have been isolated as crystals.

(3) Oxidizing action of sulphuric acid

The action of dilute sulphuric acid on the more electropositive metals, e.g.

$$Zn(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g)$$

is a case of oxidation of the metal by hydrated hydrogen ion, but the acid has a more powerful oxidizing action when it is both *hot and concentrated.* Like all oxidizing agents, it operates by accepting electrons (provided by a reducing agent). The principal oxidizing action of the acid, in these conditions, is:

$$2H_2SO_4(l) + 2e^- \rightarrow SO_4{}^{2-}(aq) + 2H_2O(l) + SO_2(g)$$

with the production of *sulphur dioxide.* Most of the common metals (not gold or platinum) react in this way. Examples are:

$$Cu(s) + 2H_2SO_4(l) \rightarrow CuSO_4(aq) + 2H_2O(l) + SO_2(g)$$
$$2Al(s) + 6H_2SO_4(l) \rightarrow Al_2(SO_4)_3(aq) + 6H_2O(l) + 3SO_2(g)$$

During these reactions, further reduction of the acid may occur to *sulphide, free sulphur,* or *hydrogen sulphide* in minor reactions such as:

$$6H^+(aq) + H_2SO_4(l) + 8e^- \rightarrow S^{2-}(aq) + 4H_2O(l)$$
$$6H^+(aq) + H_2SO_4(l) + 6e^- \rightarrow S(s) + 4H_2O(l)$$
$$8H^+(aq) + H_2SO_4(l) + 8e^- \rightarrow H_2S(g) + 4H_2O(l)$$

Some non-metals are also oxidized by *hot, concentrated* sulphuric acid. For example, powdered *carbon* is oxidized to *carbon dioxide*; sulphur dioxide is also evolved as the reduction product of the acid.

$$C(s) + 2H_2SO_4(l) \rightarrow CO_2(g) + 2SO_2(g) + 2H_2O(l)$$

A similar reaction occurs with *sulphur.* Here the oxidation product of sulphur, and the reduction product of the acid, are both *sulphur dioxide.*

$$S(s) + 2H_2SO_4(l) \rightarrow 3SO_2(g) + 2H_2O(l)$$

The *hot, concentrated* acid can also oxidize iron(II) sulphate to iron(III) sulphate.

$$2Fe^{2+} + 2H_2SO_4(l) \rightarrow 2Fe^3(aq) + 2H_2O(l) + SO_2(g) + SO_4{}^{2-}(aq)$$

For this reason, the acid (in these conditions) oxidizes iron to the iron(III) state.

$$2Fe(s) + 6H_2SO_4(l) \rightarrow Fe_2(SO_4)_3(aq) + 6H_2O(l) + 3SO_2(g)$$

Dilute sulphuric acid oxidizes iron to the iron(II) state only.

$$Fe(s) + 2H^+(aq) \rightarrow Fe^{2+}(aq) + H_2(g)$$

Having a relatively high boiling point (i.e. low volatility), concentrated sulphuric acid is used in preparing more volatile acids, such as *hydrogen chloride* (and hydrochloric acid) from chlorides, and *nitric acid* from nitrates:

$$NaCl(s) + H_2SO_4(l) \rightarrow NaHSO_4(s) + HCl(g)$$
$$KNO_3(s) + H_2SO_4(l) \rightarrow KHSO_4(s) + HNO_3(l)$$

In the second case, the nitric acid is distilled off. This does not mean that sulphuric acid is the strongest of the three. The volatility of the other two acids tends to reduce their effective concentration to zero. Consequently, the reactions tend to go to completion from left to right as written above. Corresponding reactions *cannot* be used satisfactorily to prepare *hydrobromic or hydriodic acid.* These acids are stronger reducing agents than hydrochloric acid and, when produced, react with concentrated sulphuric acid as an oxidizing agent. For example, addition of *concentrated* sulphuric acid to potassium bromide gives the sequence of reactions:

$$KBr(s) + H_2SO_4(l) \rightarrow KHSO_4(s) + HBr(g)$$
$$2HBr(g) + H_2SO_4(l) \rightarrow 2H_2O(l) + SO_2(g) + Br_2(l)$$

That is, the gaseous product contains *brown fumes of bromine* vapour, *hydrogen bromide* and *sulphur dioxide.*

Hydrogen iodide is a more powerful reducing agent. Addition of *concentrated* sulphuric acid to potassium iodide may give the following sequence of reactions:

$$KI(s) + H_2SO_4(l) \rightarrow KHSO_4(s) + HI(g)$$
$$2HI(g) + H_2SO_4(l) \rightarrow 2H_2O(l) + SO_2(g) + I_2(s)$$
$$8HI(g) + H_2SO_4(l) \rightarrow 4H_2O(l) + H_2S(g) + 4I_2(s)$$
$$2H_2S(g) + SO_2(g) \rightarrow 3S(s)\downarrow + 2H_2O(l)$$

Possible products are:

Hydrogen iodide—steamy fumes.
Sulphur dioxide—decolorizes acidified potassium manganate(VII) solution.
Hydrogen sulphide—turns lead(II) ethanoate paper black.
Iodine—black sublimate; purple vapour if warmed.
Sulphur—yellow precipitate.

(4) Sulphonating action of sulphuric acid

This property is exercised towards organic compounds, chiefly aromatic. A typical case is the sulphonation of benzene to *benzenesulphonic* *acid* by concentrated sulphuric acid at 450 K.

$$C_6H_6(l) + H_2SO_4(l) \rightarrow C_6H_5.SO_3H(s) + H_2O(l)$$

Fuming sulphuric acid ('oleum'; see p. 334) is much more effective as a sulphonating agent than is the ordinary 'concentrated' sulphuric acid.

Acid chlorides of sulphuric acid

Sulphuric acid can be thought of as a dihydroxy-compound, $SO_2(OH)_2$. Theoretically, it may produce two acid chlorides, in which Cl replaces one, or two, of the hydroxyl groups. Both these compounds exist.

1. *Chlorosulphonic acid*, $Cl.SO_2.OH$ (liquid; b.p. 424 K). This compound is made by passing dry hydrogen chloride into sulphuric acid containing dissolved sulphur trioxide, i.e. fuming sulphuric acid.

$$HCl(g) + SO_3 \xrightarrow{\text{in oleum}} Cl.SO_2.OH(l)$$

The product is then distilled. It is rapidly hydrolysed by water.

$$HO.H(l) + Cl.SO_2.OH(l) \rightarrow HCl(g) + HO.SO_2.OH(l)$$

2. *Sulphur dichloride dioxide* (*sulphuryl chloride*), SO_2Cl_2 (liquid; b.p. 342 K at 1 atm). This compound can be made by reaction between concentrated sulphuric acid and phosphorus pentachloride,

$$SO_2(OH)_2(l) + 2PCl_5(s) \rightarrow SO_2Cl_2(l) + 2POCl_3(l) + 2HCl(g)$$

but the process is slow. A better method is direct combination of sulphur dioxide and chlorine, catalysed by sunlight, by activated charcoal or by camphor.

$$SO_2(g) + Cl_2(g) \rightarrow SO_2Cl_2(l)$$

Sulphur dichloride dioxide is hydrolysed by cold water but rather slowly.

$$SO_2Cl_2(l) + 2H.OH(l) \rightarrow 2HCl(g) + SO_2(OH)_2(l)$$

In both cases, the product of hydrolysis is sulphuric acid.

Structural formula of sulphuric acid

(1) As stated immediately above, two acid chlorides of sulphuric acid exist and are converted to the acid by the action of water in standard reactions of the type:

$$—Cl + H.OH \rightarrow \quad —OH + HCl$$

This behaviour points clearly to the presence of *two hydroxyl groups* in a molecule of the acid, which can be written $SO_2(OH)_2$. This deduction is supported by the *dibasicity* of the acid.

(2) Organometallic derivatives of sulphuric acid can be produced of the general type, $RO.SO_2.OK$, where R is an alkyl group, CH_3, C_2H_5, etc. There is only *one* form of such compounds. This means that the (OH) groups are related to the rest of the molecule in a symmetrical way. If they were not, *two* forms of these compounds would exist, $RO.SO.OK$ and $KO.SO_2.OR$.

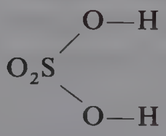
(3) By replacement reactions of the type:

$$SO_2(OH)_2 \rightarrow SO_2(OH)Cl \rightarrow SO_2(OH)R$$

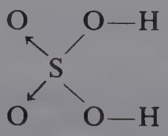
organic derivatives of sulphuric acid can be produced. These compounds are identical with those obtained by oxidizing thiols which are known to have structures of the type R—S—H. The oxidation is likely to be:

$$R—S—H + 3(O) \rightarrow R—SO_3H$$

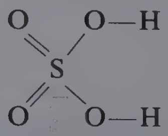
That is, the group R is directly combined with the sulphur atom; consequently, arguing from the replacement reactions above, the OH group substituted by R is likely to be directly combined with the sulphur atom. This gives a structure



The bonding from the S to the two O atoms is often represented as dative covalent bonding, as:



Since sulphur can accommodate more than eight electrons in its outer quantum shell, the structure could equally well be written:



The molecule is covalent though with polar bonds. In aqueous solution, the acid ionizes.

$$H_2SO_4(aq) \rightarrow 2H^+(aq) + SO_4^{2-}(aq)$$

In the ion, SO_4^{2-}, all four bonds are known to be identical and to have a bond distance of 0.151 nm. This is almost as short as the normal sulphur–oxygen double bond length, suggesting that the bonds in the ion are largely double in character. The shape of the ion is tetrahedral.

Detection and estimation of sulphuric acid and sulphates

Detection

The test material is dissolved in water and acidified with dilute hydrochloric acid. Barium chloride solution is added. A white precipitate occurs (barium sulphate) if a sulphate is present.

$$SO_4^{2-}(aq) + Ba^{2+}(aq) \rightarrow BaSO_4(s)$$

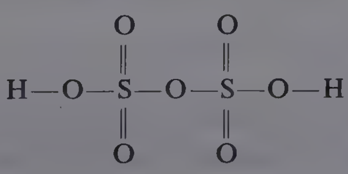
The hydrochloric acid must be present to prevent precipitation of certain other barium salts, such as the sulphite, carbonate, or phosphate.

Estimation of sulphate

A known mass of the sulphate is dissolved in water, acidified by dilute hydrochloric acid and precipitated, in hot solution, by a slight excess of barium chloride solution. The precipitated barium sulphate is filtered off, washed, dried, heated to constant mass and weighed. The mass of the SO_4^{2-} radical is the proportion $SO_4/BaSO_4$ or 96/233 of the mass of the barium sulphate. It is usually expressed as a percentage of the mass of metallic sulphate used.

Heptaoxodisulphuric acid (pyrosulphuric acid; fuming sulphuric acid; oleum), $H_2S_2O_7$

This acid is formed by the action of sulphur trioxide on concentrated sulphuric acid. It is a solid, melting at 308 K. It is also known as *Nordhausen sulphuric acid*. The structure of the acid is:



$$\begin{array}{ccccccccccccc} & & & & \mathrm{O} & & & & \mathrm{O} & & & & \\ & & & & \| & & & & \| & & & & \\ \mathrm{H} & - & \mathrm{O} & - & \mathrm{S} & - & \mathrm{O} & - & \mathrm{S} & - & \mathrm{O} & - & \mathrm{H} \\ & & & & \| & & & & \| & & & & \\ & & & & \mathrm{O} & & & & \mathrm{O} & & & & \end{array}$$

Peroxodisulphuric acid, $H_2S_2O_8$

Peroxodisulphuric acid can be formed at the anode by electrolysis of sulphuric acid (about 50 per cent with water), cooled by ice and with a high current density. At the anode, the effect is:

$$2HSO_4^-(aq) - 2e^- \rightarrow H_2S_2O_8(aq)$$

The acid contains a peroxide linkage, —O—O—, and is unstable, decomposing finally to sulphuric acid and hydrogen peroxide. This provides a method for manufacturing hydrogen peroxide (see p. 300).

$$2H_2O(l) + H_2S_2O_8(aq) \rightarrow H_2O_2(aq) + 2H_2SO_4(aq)$$

Potassium peroxodisulphate is only sparingly soluble in water and can be precipitated at the anode by electrolysis, at a high current density, of an ice-cold solution of potassium hydrogensulphate. The anode compartment should be separated by a porous partition.

$$2HSO_4^-(aq) - 2e^- \rightarrow H_2S_2O_8(aq) \rightleftharpoons 2H^+(aq) + S_2O_8^{2-}(aq)$$
$$2K^+(aq) + S_2O_8^{2-}(aq) \rightleftharpoons K_2S_2O_8(s)$$

This salt is a powerful oxidizing agent; the following are examples of this:

$$2Fe^{2+}(aq) + S_2O_8^{2-}(aq) \rightarrow 2Fe^{3+}(aq) + 2SO_4^{2-}(aq)$$
$$2I^-(aq) + S_2O_8^{2-}(aq) \rightarrow I_2(s) + 2SO_4^{2-}(aq)$$

Some other compounds of sulphur

Disulphur dichloride (sulphur monochloride), S_2Cl_2

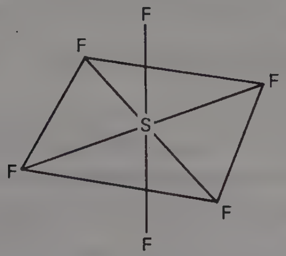
Sulphur monochloride can be formed by direct combination between two elements. *Dry* chlorine is passed over molten sulphur; the apparatus given for the preparation of phosphorus trichloride (p. 265) is suitable. Disulphur dichloride is a yellow liquid with a pungent smell. It fumes in moist air because of hydrolysis with water according to the equation:

$$2S_2Cl_2(l) + 3H_2O(l) \rightarrow 4HCl(g) + H_2SO_3(aq) + 3S(s)$$

Disulphur dichloride has some industrial use in the vulcanization of rubber.

Sulphur hexafluoride, SF_6

Sulphur hexafluoride is prepared by direct combination of the elements. It is an unreactive gas: so unreactive that it is not attacked even by fused alkalis. The molecule is highly symmetrical, and octahedral in shape:



The ability of elements in the period Na → Ar and below to accommodate more than eight electrons in the outer quantum shell is discussed in *Advanced Level Physical Chemistry*, p. 77.

Sulphur dichloride oxide (thionyl chloride), $SOCl_2$

Sulphur dichloride oxide is made in industry by the action of sulphur trioxide on disulphur dichloride.

$$SO_3(s) + S_2Cl_2(l) \rightarrow SOCl_2(l) + SO_2(g) + S(s)$$

It can also be made by the action of phosphorus pentachloride on *dry* sulphur dioxide.

$$SO_2(g) + PCl_5(s) \rightarrow SOCl_2(l) + POCl_3(l)$$

Sulphur dichloride oxide is a colourless liquid, boiling point 352 K at 1 atm. It is hydrolysed by water to *sulphurous acid* and so acts as the acid chloride of this acid.

$$SOCl_2(l) + 2H_2O(l) \rightarrow 2HCl(g) + H_2SO_3(aq)$$

Thionyl chloride is used in preparing the acid chlorides of organic acids.

Thiosulphates

Sodium thiosulphate is the only important example. For details, see p. 67.

Aminosulphonic acid (sulphamic acid), NH_2SO_3H

This acid is also an amide, derived from H_2SO_4 when OH is replaced by NH_2.

Preparation. Industrially, urea (carbamide) is dissolved in concentrated sulphuric acid and treated with oleum of high SO_3 content. Heating to

370 K is needed; later, cooling is required to maintain this temperature, the reaction being exothermic. Aminosulphonic acid separates at room temperature and is recrystallized from hot water.

$$CO(NH_2)_2(s) + H_2S_2O_7(l) \rightarrow CO_2(g) + 2NH_2.SO_3H(s)$$

Aminosulphonic acid is a white, crystalline solid, m.p. 478 K, soluble in water and ethanol. In dilute aqueous solution, aminosulphonic acid is a *strong* acid, almost as strong as hydrochloric acid. Being easily purified and stable, aminosulphonic acid can be used as a standard acid in analysis.

$$NH_2.SO_3H(aq) \rightleftharpoons NH_2.SO_3^-(aq) + H^+(aq)$$

The pure acid forms ions internally, $NH_3^+.SO_3^-$. All its known salts are soluble in water except a basic salt of mercury. Aminosulphonic acid is slowly hydrolysed by hot water, but cold water has negligible action.

$$NH_2.SO_3H(aq) + H_2O(l) \rightarrow NH_4^+.HSO_4^-(aq)$$

Nitrous acid replaces the NH_2 group of aminosulphonic acid by OH, producing sulphuric acid and nitrogen; concentrated nitric acid behaves correspondingly, liberating dinitrogen oxide.

$$HNO_2(aq) + H_2N.SO_3H(s) \rightarrow HO.SO_3H(aq) + N_2(g) + H_2O(l)$$
$$HNO_3(\text{conc. aq.}) + H_2N.SO_3H(s) \rightarrow HO.SO_3H(aq) + N_2O(g) + H_2O(l)$$

Questions

1. Briefly review the methods available for preparing oxygen in the laboratory. Describe in detail the one you consider most suitable for practical purposes. In outline only, state the principles involved in the production of oxygen and nitrogen from liquid air and indicate briefly how the two gases are separated.
2. Give an account of the various kinds of oxides which exist, illustrating each type by *two* examples.
3. Mention *three* common inpurities (other than those producing hardness) in ordinary domestic water supplies. Discuss the sources and significance of these impurities and outline methods (one in each case) by which they may be estimated.
4. Give an account of the chemical behaviour of water under the headings: (a) reactions with metal, (b) reactions with non-metals, (c) hydrolysis, (d) catalysis. Water is often said to show anomalous behaviour. What does this mean and what are the reasons for it?
5. Outline the process by which sulphur is extracted from the deposits in the south of the USA. How would you prepare in the laboratory samples of (a) rhombic sulphur, (b) monoclinic sulphur, starting in both cases from ordinary roll sulphur?

Explain why (a) may show two different melting points depending on whether it is heated rapidly or very slowly. What are the effects of heating roll sulphur from room temperature to about 720 K out of contact with air? Can you explain the changes in molecular terms?

6. An important reaction involved in the Contact process for the manufacture of sulphuric acid is:

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \qquad \Delta H = -190\ \text{kJ mol}^{-1}$$

In the light of Le Chatelier's Principle, deduce the conditions required for successful industrial operation of this reaction. Outline the general course of the manufacture of the acid by this process.

7. Illustrate by *three* reactions in each case the behaviour of sulphuric acid as (a) an oxidizing agent, (b) a dehydrating agent. The acid can also behave as a sulphonating agent. Give *one* example of this. What are the general acidic properties of this acid? Illustrate by examples.

8. The principal oxidation states of sulphur are -2, $+2$, $+4$ and $+6$. Give the names and formulae of *four* compounds containing sulphur, one in each of these oxidation states.

Describe briefly how *three* of the compounds you mention can be obtained from elemental sulphur.

Outline how a named compound with sulphur in its lowest oxidation state may be converted to one with sulphur in its highest oxidation state. (L.)

9. Describe the manufacture of sulphuric acid from sulphur. Give careful attention to the physicochemical principles, including the importance of the catalyst.

Discuss the importance of the acid in industry today.

Describe and explain the action of concentrated sulphuric acid on copper, and the subsequent dilution of the product. (L.)

10. (a) Water is often described as an abnormal liquid. Give *three* properties which you regard as justifying this description and say how these properties may be explained.
(b) Distinguish between *hydration and hydrolysis.* What happens when water is added to tetrachloromethane, CCl_4, and phosphorus trichloride, PCl_3? How may the differences in behaviour be explained?
(c) Discuss briefly the acid-base properties of water. How should water be classified? (O.)

11. (a) Give *one* reaction in each case to distinguish between (i) Na_2O and Na_2O_2, (ii) PbO and PbO_2, (iii) N_2O and NO_2.
How would you classify the above oxides?
(b) Compare the structures of (i) CO_2 and SiO_2, (ii) H_2O and H_2O_2, (iii) CaO and PbO. (A.E.B.)

12. Sulphuric acid is one of the most versatile reagents used in the laboratory. Discuss this statement by referring to reactions which illustrate its behaviour
(a) as an acid,
(b) in the displacement of other acids from their salts,
(c) as a sulphonating agent,
(d) as an oxidizing agent,
(e) as a dehydrating agent. (J.M.B.)

13. (a) Name two substances containing sulphur from which sulphur dioxide is prepared industrially. *Outline* the method of production in each case.
(b) Compare the bleaching action of sulphur dioxide with that of chlorine.

(c) Give examples, and explanations, of the following properties of concentrated sulphuric acid:
 (i) its dehydrating properties;
 (ii) its use as a sulphonating agent.

(d) Why has sulphuric acid a higher boiling point (657 K) than would be expected for a covalent compound of formula H_2SO_4? (A.E.B.)

10

Elements of Group VII

Group VII of the Periodic Table contains the elements *fluorine*, *chlorine*, *bromine*, and *iodine*. Together, these elements form the very important *halogen group*. The very rare radioactive element *astatine* has more recently been added to the halogen group. It is not considered here, but it may be useful for the reader to know that examiners at all levels from CSE to Honours Degree seem to be very fond of asking candidates to predict the properties of astatine by extrapolation from the known properties of the common halogens.

The word *halogen* was coined by Berzelius in the early nineteenth century from two Greek words meaning *salt producer*, and alludes to the fact that all the halogen elements (as then known) formed compounds with the alkali metals which closely resemble common salt. The chemical behaviour of the individual elements will be examined. A comparison summary will be found on p. 388.

Fluorine

Atomic number 9; electron arrangement 2.7 ($1s^2 2s^2 2p^5$).
Fluorine possesses only one species of atom, mass number 19, and has no isotopes.
Relative atomic mass 19.00.

Occurrence and extraction of fluorine

Fluorine occurs principally in the minerals *fluorspar*, CaF_2, *cryolite*, Na_3AlF_6, and *fluorapatite*, $CaF_2.3Ca_3(PO_4)_2$.

The element, fluorine, was recognized as existing quite early in chemical history through its various salts, but proved very difficult to isolate. This was because of the very great chemical activity of the element. The difficulties were overcome by Moissan (1886) in a process of which the details are now of historical interest only, but which was essentially similar to the process now used for the industrial production of fluorine. The essentials of a modern electrolytic cell are shown in Figure 10.1.

The electrolyte contains *anhydrous hydrofluoric acid, potassium hydrogen fluoride,* and *lithium fluoride.* (The best proportions by mass are given as 14 :83 :3 respectively.) The hydrofluoric acid acts as an ionizing solvent for the potassium salt. The lithium fluoride lowers the melting point of the electrolyte and enables electrolysis to be carried out at a lower temperature and with a smaller proportion of hydrofluoric acid. The working temperature of the electrolyte is about 370 K: the cell is often heated by steam. As will be seen from Figure 10.1, the *anodes* are of *carbon.* These are prepared from amorphous carbon, and are only slowly attacked by fluorine. The *cathodes* consist of *sheet steel* in the form of cylinders. They are separated from the anodes by a diaphragm of Monel metal. This is an alloy of nickel (60–70 per cent) and copper (25–35 per cent), together with small amounts of iron, manganese, silicon, and carbon. It is resistant to attack by fluorine and hydrogen fluoride up to about 520 K. The part of the diaphragm which is immersed in the electrolyte is perforated to allow electrolysis to occur; the upper part is a continuous sheet.

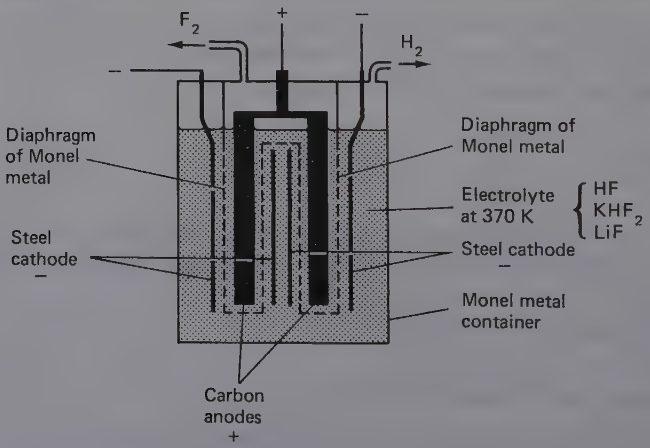


Figure 10.1 *Preparation of fluorine*

Potassium hydrogen fluoride ionizes as:

K^+	$HF_2^- \rightleftharpoons H^+ + 2F^-$
At cathode	*At anode*
$2H^+ + 2e^- \rightarrow H_2(g)$	$2F^- - 2e^- \rightarrow F_2(g)$

Fluorine can be stored safely, at pressures of up to 200 atm (2×10^7 N m^{-2}), in containers made of a Cu–Ni alloy containing over 60 per cent of Cu. The alloy becomes coated with a coherent, protective layer of metallic fluoride.

Properties of fluorine

Fluorine is a pale yellow gas in ordinary conditions. It has an irritating smell resembling that of chlorine. It is dangerous to breathe. It liquefies at 85 K at 1 atm.

Fluorine is the most electronegative element known and is extremely reactive. Its chemical properties are as follows:

1. *With hydrogen.* At low temperature and with pure gases, hydrogen and fluorine show little reaction. At room temperature with impure gases, violent explosion occurs, forming *hydrogen fluoride.*

$$H_2(g) + F_2(g) \rightarrow 2HF(g)$$

Because of this, fluorine reacts rapidly with many compounds of hydrogen. For example, fluorine reacts rapidly with water to produce *oxygen*, which is usually considerably ozonized.

$$2H_2O(l) + 2F_2(g) \rightarrow 4HF(g) + O_2(g)$$
$$3H_2O(l) + 3F_2(g) \rightarrow 6HF(g) + O_3(g)$$

Many hydrocarbons burn spontaneously in fluorine, e.g.

methane $CH_4(g) + 4F_2(g) \rightarrow CF_4(g) + 4HF(g)$
ethyne $C_2H_2(g) + 5F_2(g) \rightarrow 2CF_4(g) + 2HF(g)$

2. *With metals.* All metals react with fluorine, but the rate and extent attack vary greatly with the metal and the temperature employed. In general, the metal tends to attain its highest state of oxidation when combining with fluorine. The following are typical cases:

Potassium, rubidium, and *caesium* react with fluorine at 410–90 K. The materials formed contain more fluorine than is indicated by the formulae KF, RbF and CsF.

Iron, zinc, magnesium, aluminium, copper, and *silver* burn in fluorine if gently heated.

Gold and *platinum* are attacked only at very high temperatures.

Certain nickel and copper alloys (for examples see above) become coated with a coherent layer of fluoride which prevents further attack. These alloys, together with *Teflon* (see p. 351), are used for the transport and storage of fluorine and hydrogen fluoride.

3. *With non-metals.* Fluorine combines directly and vigorously with most of the non-metals, though not with oxygen, nitrogen and most of the noble gases. Xenon, however, can be made to react with fluorine (see p. 25).

Powdered charcoal, phosphorus and sulphur ignite spontaneously in fluorine at room temperature, giving mainly the highest fluoride.

$$C(s) + 2F_2(g) \rightarrow CF_4(g)$$
$$P_4(s) + 10F_2(g) \rightarrow 4PF_5(g)$$
$$S(s) + 3F_2(g) \rightarrow SF_6(g)$$

Notice, however, that carbon anodes can be used successfully in the electrolytic production of fluorine. They are in block form and graphitized. Silicon and boron also combine readily with fluorine to give the tetrafluoride, SiF_4, and the trifluoride, BF_3. Both bromine and iodine burn in fluorine. A variety of compounds can be formed, such as BrF, BrF_3 and BrF_5; IF_5 and IF_7. Chlorine reacts with fluorine with much more difficulty. At 520 K, it forms chlorine monofluoride, ClF; excess of fluorine may produce ClF_3.

4. *Displacement reactions.* Fluorine displaces chlorine readily from its compounds, forming the corresponding fluorides, e.g.

$$2Cl^-(s) + F_2(g) \rightarrow 2F^-(s) + Cl_2(g)$$
$$CCl_4(l) + 2F_2(g) \rightarrow CF_4(g) + 2Cl_2(g)$$

Free chlorine is liberated. Similar reactions occur with other halogen compounds, but are complicated by the marked tendency of fluorine to combine with the liberated bromine and iodine.

Organic compounds of fluorine

Organic compounds of fluorine are becoming increasingly important in industry. *Freons* are chlorofluorocarbons and chlorofluorohydrocarbons, which have become important recently as refrigerants and aerosol propellants. (See also p. 286). *Freon*-12 is *dichlorodifluoromethane* (b.p. 243 K) and can be made by reaction between the vapours of tetrachloromethane and hydrogen fluoride.

$$CCl_4(g) + 2HF(g) \rightarrow CCl_2F_2(g) + 2HCl(g)$$

Freon-22 is CHF_2Cl, a liquid of boiling point 314 K.

Organic fluorocompounds have also entered the field of plastics. *Telflon* is *polytetrafluoroethene*, i.e. the compound C_2F_4 polymerized to a substance of very long chain length. It has very high electrical resistance and is used as in insulating material in cables, and in related electrical uses. It also has the remarkable property that almost nothing will stick to it. This makes it useful on conveyor belts carrying sticky materials, in bread-making machinery, and for lightly-loaded bearings, e.g. for skateboards and model cars. *KEL-F* is a similar material and is *polychlorotrifluoroethene*, i.e. a polymer of C_2ClF_3. *Teflon* is the trade-mark of the du Pont Company and *KEL-F* of the M. W. Kellog Company. Both materials are more resistant to chemicals and heat than earlier plastic polymers, such as polyethene.

Hydrogen fluoride, HF

Preparation

Hydrogen fluoride can be made in two forms—as a solution in water (known as *hydrofluoric acid*) or anhydrous. To make the aqueous solution, calcium fluoride is distilled with 90 per cent sulphuric acid in a cast-iron retort.

$$CaF_2(s) + H_2SO_4(l) \rightarrow CaSO_4(s) + 2HF(g)\uparrow$$

The vapour is absorbed in water contained in boxes made of lead. They are cooled in water. The commercial acid usually contains about 50 per cent of hydrogen fluoride. This acid attacks glass and is stored and sold in containers made of polyethene or lead. The anhydrous acid can be made similarly by using anhydrous sulphuric acid.

The anhydrous acid can also be made (on laboratory scale) by distilling anhydrous potassium hydrogen difluoride, KHF_2. A copper or platinum retort may be used and the acid condensed in a copper flask immersed in a freezing mixture.

$$KHF_2(s) \rightarrow KF(s) + HF(g)$$

The *anhydrous* acid does not attack copper appreciably, though the aqueous acid does.

Properties of hydrogen fluoride

Anhydrous hydrogen fluoride is a colourless, fuming liquid, boiling point 293 K at 101 300 N m^{-2} (1 atm). The 50 per cent aqueous solution also fumes. The vapour of the acid is very poisonous.

Nature of the hydrogen fluoride molecule

At about 360 K, the relative density of hydrogen fluoride is close to 10. This corresponds to a molar mass of 20 and a molecule, HF. As the temperature falls, however, the relative density rises and, just above the boiling point (293 K) of the acid, it approaches the value of 26, corresponding to a molar mass of 52. This indicates association of the acid mainly into molecules, H_3F_3, though molecules from H_2F_2 to H_5F_5 probably occur also. Freezing point determinations in water indicate mainly H_2F_2 molecules, but, since the degree of association is very varied, the formula is given in this book simply as HF. The dimer H_2F_2 gives rise to acid salts, e.g. KHF_2. This salt gives an ion, HF_2^-. This ion is believed to be formed by hydrogen bonding and is written as $(F{-}H\ldots F)^-$, the dotted line representing the hydrogen bond. The associated nature of hydrogen fluoride accounts for its unexpectedly high boiling point. All the other halogen acids are *gaseous* at room temperature and pressure. The association also accounts for the fact that hydrogen fluoride is an ionizing solvent. Water shows similar association, unexpectedly high boiling point (compare H_2S, which is gaseous) and ionizing behaviour.

Chemical properties

1. *As an acid.* Anhydrous hydrofluoric acid is unionized, a non-electrolyte with negligible acidic properties. In aqueous solution, hydrofluoric acid is a rather *weak* acid, i.e. it is not greatly ionized (about 15 per cent at a concentration of 0.1 mol dm^{-3}). It is stronger than organic acids, such as ethanoic acid, but very much weaker than hydrochloric acid.

$$2HF(aq) \rightleftharpoons H^+(aq) + HF_2^-(aq)$$

Hydrofluoric acid attacks many metals, e.g. iron, copper, and silver, liberating hydrogen, e.g.

$$Fe(s) + 2HF(aq) \rightarrow FeF_2(aq) + H_2(g)$$

Hydrofluoric acid reacts with sodium or potassium hydroxide solution to form a *normal* and an *acid fluoride.*

$$KOH(aq) + HF(aq) \rightarrow KF(aq) + H_2O(l)$$
$$KF(aq) + HF(aq) \rightarrow KHF_2(aq)$$

It differs in this respect from all the other halogen acids which produce only normal salts, such as KCl.

2. *Behaviour with silica and glass.* The *anhydrous* acid does not attack silica or glass. Concentrated hydrofluoric acid attacks silica to form *silicon tetrafluoride*, SiF_4. If excess of the acid is available, it combines with silicon tetrafluoride, producing *hexafluorosilicic acid*, H_2SiF_6.

$$SiO_2(s) + 4HF(aq) \rightarrow 2H_2O(l) + SiF_4(g)$$
$$SiF_4(g) + 2HF(aq) \rightarrow H_2SiF_6(aq)$$

Hydrofluoric acid reacts in a corresponding way on glass. Any silica in the glass reacts as above. Other constituents of ordinary glass are calcium silicate and sodium silicate. Both of these react with hydrofluoric acid to produce *hexafluorosilicates.*

e.g. $$CaSiO_3(s) + 6HF(aq) \rightarrow CaSiF_6(aq) + 3H_2O(l)$$

The reactions are used in etching glass. The glass is covered with etching varnish (or wax). The required lettering or design is traced through the varnish with a sharp point, exposing the glass. Exposure to hydrofluoric acid then etches the design on to the glass and the varnish is removed.

3. *Constant boiling mixture of hydrofluoric acid.* Hydrogen fluoride resembles all the other halogen acids in forming a constant boiling mixture with water. This mixture contains 36 per cent of hydrogen fluoride and boils at 293 K.

Uses of hydrofluoric acid

Among the uses of this acid are the following:

(a) The production of chlorofluorocarbons, etc., for refrigeration and as aerosol propellants.
(b) The etching of measuring scales on to glass and the production of 'frosted' glass.
(c) The manufacture of artificial cryolite, Na_3AlF_6, for use in the electrolytic extraction of aluminium.
(d) As an antiseptic in brewing. It has marked action on certain organisms, but little action on yeast.
(e) It is used for making uranium(VI) fluoride, UF_6, which is a key compound in the process of enriching natural uranium for use as a nuclear fuel.

A test for fluorides

The underside of a watch glass is waxed. Through the wax a design is scratched. The test material is then warmed in a leaden crucible with concentrated sulphuric acid and the watch glass is exposed to the vapour evolved. If, after removal of the wax, the design is etched on the glass, a fluoride was present.

Fluorine as an atypical halogen element

Fluorine, atomically the simplest of the halogens, differs to quite a marked extent from the other members of the group. The following are among the important differences:

(a) Calcium fluoride is insoluble in water. The chloride, bromide, and iodide of calcium are very soluble and deliquescent.

(b) Silver fluoride is soluble in water. The chloride, bromide, and iodide of silver are insoluble.

(c) The hydrogen compound of fluorine is associated (H_2F_2 to H_5F_5) and is a *liquid* in room conditions. It is a rather weak acid and can form both *acid* salts, (ion HF_2^-), and *normal* salts, (ion F^-). The hydrides of chlorine, bromine, and iodine are all *gaseous* in room conditions; they are strong acids in solution and form *normal* salts only. They are not associated.

(d) Fluorine reacts with cold, very dilute aqueous sodium hydroxide to give oxygen difluoride.

$$2F_2(g) + 2OH^-(aq) \rightarrow 2F^-(aq) + F_2O(g) + H_2O(l)$$

Chlorine and bromine, with the same reagent, give the halide and halate(I) (hypohalite) as:

$$X_2 + 2OH^-(aq) \rightarrow X^-(aq) + OX^-(aq) + H_2O(l) \text{ (where } X = \text{Cl or Br)}$$

Chlorine, bromine, and iodine

These halogen elements resemble each other so closely in general chemical behaviour that it is convenient to consider them together. The chemical similarity arises from the similarity of their electron structures which are:

Chlorine	2.8.7
Bromine	2.8.18.7
Iodine	2.8.18.18.7

Chlorine, Cl_2

Atomic number 17; electron arrangement 2.8.7 ($1s^2 2s^2 2p^6 3s^2 3p^5$);

chlorine has isotopes of mass number, in order of abundance, 35 and 37. relative atomic mass 35.45.

Bromine, Br_2

Atomic number 35; electron arrangement 2.8.18.7 ($1s^22s^22p^63s^23p^6 3d^{10}4s^24p^5$); bromine has isotopes of mass number, in order of abundance, 79 and 81; relative atomic mass 79.90.

Iodine, I_2

Atomic number 53; electron arrangement 2.8.18.18.7 ($1s^22s^2sp^63s^23p^6 3d^{10}4s^24p^64d^{10}5s^25p^5$); iodine has only one kind of atom, of mass number 127; relative atomic mass 126.9.
The physical properties of these elements are summarized on p. 388.

Laboratory preparation of chlorine, bromine, and iodine

These three elements can all be prepared by the same fundamental method, as below:

$$\textit{Heat}\begin{cases}\text{a \textit{chloride} (NaCl) or a \textit{bromide} (KBr) or an \textit{iodide} (KI)}\\ \textit{concentrated sulphuric acid}\\ \textit{manganese}\text{(IV) }\textit{oxide}\end{cases}$$

The general equation would then be:

$$2X^-(s) + 4H^+ + MnO_2(s) \rightarrow Mn^{2+}(aq) + 2H_2O(l) + X_2$$

where X represents the halogen atom, Cl or Br or I. The practical method used depends on the physical state of the halogen in question, chlorine being gaseous, bromine liquid and iodine solid. *For chlorine only*, the concentrated acid, in this case hydrochloric acid, can be used as a source of the element. This material is *heated* with manganese(IV) oxide, or, much more conveniently, dripped on to *solid* potassium manganate(VII) in the cold. The apparatus for chlorine in Figure 10.2 is suitable. If the gas is not required dry, chlorine may be conveniently collected over brine. (It is too soluble in water.)

$$MnO_2(s) + 4H^+(aq) + 2Cl^-(aq) \rightarrow Mn^{2+}(aq) + 2H_2O(l) + Cl_2(g)$$

$$2MnO_4{}^-(aq) + 16H^+(aq) + 10Cl^-(aq) \rightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 5Cl_2(g)$$

Methods for preparing bromine and iodine are shown in Figure 10.3.

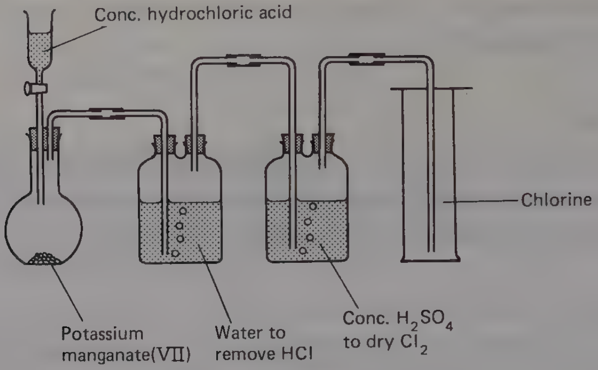


Figure 10.2 *Preparation of chlorine*

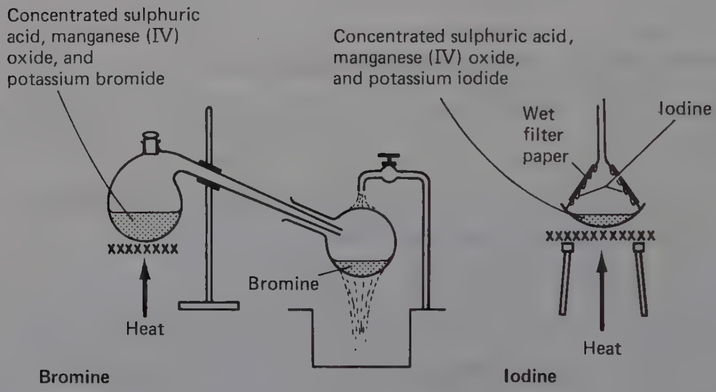


Figure 10.3 *Preparation of bromine and iodine*

The appropriate equations are given below.

$$MnO_2(s) + 4H^+(aq) + 2KBr(s) \xrightarrow{\text{heat}} Mn^{2+}(aq) + 2K^+(aq) + 2H_2O(l) + Br_2(g)$$

$$MnO_2(s) + 4H^+(aq) + 2KI(s) \xrightarrow{\text{heat}} Mn^{2+}(aq) + 2K^+(aq) + 2H_2O(l) + I_2(g)$$

Liquid bromine and solid iodine are obtained by condensation.

Chemical properties of the halogens

These three halogen elements resemble each other very closely in chemical behaviour. In general, as expected from their atomic radii and electronegativities, chlorine is the most reactive of the three and iodine the least, with bromine intermediate.

(1) *The silver salts of the halogens*

Silver chloride, bromide, and iodide are all insoluble in water and can be precipitated by reactions summarized below:

$$\mathrm{AgNO_3(aq) + NaCl(aq) \rightarrow \underset{\text{white ppt.}}{AgCl(s)} + NaNO_3(aq)}$$

$$\mathrm{AgNO_3(aq) + KBr(aq) \rightarrow \underset{\text{pale yellow ppt.}}{AgBr(s)} + KNO_3(aq)}$$

$$\mathrm{AgNO_3(aq) + KI(aq) \rightarrow \underset{\text{yellow ppt.}}{AgI(s)} + KNO_3(aq)}$$

All the precipitates may be filtered, washed with hot distilled water, and dried to purify them, but all require protection from light.

The term 'insoluble' is not absolute and, in fact, these compounds show typical halogen gradation, the chloride being the most soluble and the iodide the least, though all three solubilities are very low. Similarly, in aqueous ammonia, the chloride is readily soluble, the bromide sparingly soluble and the iodide insoluble. The high solubility of silver chloride in ammonia is explained by complex cation formation:

$$\mathrm{AgCl(s) + 2NH_3(aq) \rightarrow [Ag(NH_3)_2]^+(aq) + Cl^-(aq)}$$

Silver iodide is appreciably covalent in character, which is reflected in its insolubility in aqueous ammonia.

(2) *Displacement reactions of halogens*

Written in the order $\mathrm{Cl_2}$—$\mathrm{Br_2}$—$\mathrm{I_2}$, each halogen displaces those to the right of it from simple salts, e.g. if chlorine is passed into potassium iodide solution, a *brown* coloration is produced by liberation of *iodine*. More chlorine may produce a black precipitate of iodine.

$$\mathrm{2I^-(aq) + Cl_2(g) \rightarrow 2Cl^-(aq) + I_2(s)}$$

Similarly, chlorine displaces bromine from a bromide in aqueous solution and bromine displaces iodine from an aqueous solution of an iodide. Free bromine colours the liquid reddish-brown.

$$\mathrm{2Br^-(aq) + Cl_2(g) \rightarrow 2Cl^-(aq) + Br_2(aq);}$$
$$\mathrm{2I^-(aq) + Br_2(l) \rightarrow 2Br^-(aq) + I_2(s)}$$

Taking the first ionic equation as the example, the iodide ion is oxidized by electron loss and the chlorine molecule is reduced by electron gain; and correspondingly for the other equations.

(3) *Halogens as oxidizing agents*

As electronegative elements and, therefore, ready acceptors of electrons, the halogens act as oxidizing agents. The essential reaction is:

$$X_2 + 2e^- \rightarrow 2X^-, \text{ where } X = \text{Cl, Br, or I}$$

The electrons are supplied by the reducing agent involved. Chlorine is the most powerful, iodine the least, in oxidizing behaviour.

The relevant standard redox potentials (See *Advanced Level Physical Chemistry*, p. 250) are as follows:

$$\begin{array}{ll} Cl_2(aq) + 2e^- \rightarrow 2Cl^-(aq) & E^\ominus = +1.36\text{ V} \\ Br_2(aq) + 2e^- \rightarrow 2Br^-(aq) & E^\ominus = +1.09\text{ V} \\ I_2(aq) + 2e^- \rightarrow 2I^-(aq) & E^\ominus = +0.54\text{ V} \end{array}$$

The following are typical oxidizing actions.

(a) Iron (II) to iron (III)

If chlorine water or bromine water is added to a (pale green) solution of iron(II) sulphate in dilute sulphuric acid, the colour of the halogen is discharged and the yellow colour of a iron(III) solution develops.

$$2Fe^{2+}(aq) + Cl_2(aq) \text{ or } Br_2(aq) \rightarrow 2Fe^{3+}(aq) + 2Cl^-(aq) \text{ or } 2Br^-(aq)$$

The iron(II) ion is oxidized by electron loss; the halogen is reduced by electron gain. The standard reduction potential of iron(III) is 0.77 V:

$$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq) \qquad E^\ominus = +0.77\text{ V}$$

From this it will be seen that $Fe^{2+}(aq)$ can be oxidized by chlorine and bromine, but not iodine. Indeed, $Fe^{3+}(aq)$ will oxidize potassium iodide.

(b) Hydrogen sulphide

If chlorine and hydrogen sulphide are mixed, or if hydrogen sulphide is passed into water containing chlorine, bromine, or iodine, the halogen colour is discharged in each case, and the corresponding halogen acid is produced, together with a yellow precipitate of sulphur.

$$H_2S(g) + Cl_2(aq) \rightarrow 2HCl(aq) + S(s); \text{ or}$$
$$S^{2-}(aq) + Cl_2(g) \rightarrow S(s) + 2Cl^-(aq)$$

with corresponding equations for the other halogens. Here again, the sulphur ion is oxidized by electron loss and the halogen reduced by electron gain.

(c) Sulphur dioxide, sulphurous acid or a soluble sulphite

Each of these reagents is oxidized in aqueous solution by chlorine water or bromine water. There is no visible evidence of reaction except discharge of halogen colour, but the production of sulphate ion may be proved by subsequent addition of dilute hydrochloric acid and barium chloride solution, when a white precipitate of barium sulphate is formed.

$$SO_2(g) + H_2O(l) \rightleftharpoons H_2SO_3(aq) \rightleftharpoons 2H^+(aq) + SO_3{}^{2-}(aq)$$
$$SO_3{}^{2-}(aq) + Cl_2(aq) + H_2O(l) \rightarrow SO_4{}^{2-}(aq) + 2H^+(aq) + 2Cl^-(aq)$$

Corresponding equations apply for bromine. Note the occurrence of water as a reagent in the equation. The $SO_3{}^{2-}$ ion is oxidized to $SO_4{}^{2-}$, as the oxidation state of sulphur increases from +4 to +6. The halogen is reduced by electron gain as it forms the ion.

(d) Sodium thiosulphate

Iodine, usually dissolved in potassium iodide solution, oxidizes sodium thiosulphate in solution. The brown iodine colour is discharged. Sodium tetrathionate is left in solution.

$$2S_2O_3{}^{2-}(aq) + I_2 \text{ (in KI aq)} \rightarrow S_4O_6{}^{2-}(aq) + 2I^-(aq)$$

The ion $S_2O_3{}^{2-}$ is oxidized to $S_4O_6{}^{2-}$ as the average oxidation state of the sulphur atoms increases from +2 to +2.5. The iodine is reduced by electron gain as it forms the ion.

Chlorine in water also oxidizes sodium thiosulphate but to different products. With a moderate amount of the halogen, the thiosulphate ion is oxidized to sulphate ion, $SO_4{}^{2-}$, with precipitation of some sulphur; with chlorine in large excess, all the sulphur is converted to sulphate ion, as:

$$S_2O_3{}^{2-}(aq) + Cl_2(aq) + H_2O(l) \rightarrow SO_4{}^{2-}(aq) + 2Cl^-(aq) + 2H^+(aq) + S(s)$$

With excess chlorine:

$$S_2O_3^{2-}(aq) + 4Cl_2(aq) + 5H_2O(l) \rightarrow 2SO_4^{2-}(aq) + 10H^+(aq) + 8Cl^-(aq)$$

This explains the use of sodium thiosulphate as an *antichlor* to remove chlorine from a bleached fabric. Bromine water behaves correspondingly.

The *bleaching action* of chlorine is an oxidizing action, through the intermediary of chloric(I) acid (hypochlorous acid).

$$Cl_2(aq) + H_2O(l) \rightleftharpoons HCl(aq) + HClO(aq)$$
$$HClO(aq) + \text{dyestuff} \rightarrow HCl(aq) + \text{oxidized dyestuff}$$

The oxidized dyestuff is colourless. Loss of colour is caused by a structural change in the organic molecule. Since water is required for the above changes, *dry chlorine does not bleach.* Nor does chlorine bleach printers' ink which consists of carbon particles upon which chloric(I) acid has no action. It bleaches ordinary inks which are solutions of dyes. Bromine has a similar but much less vigorous bleaching action.

(4) *Halogens in reaction with alkalis*

(a) Cold dilute caustic alkali solution

Chlorine and bromine react with cold, dilute caustic alkali solution to produce pale yellow solutions of *sodium* (or *potassium*) *chloride* and chlorate(I), or *bromide* and bromate(I).

$$2OH^-(aq) + X_2 \rightarrow X^-(aq) + OX^-(aq) + H_2O(l), \text{where X is Cl or Br}$$

The behaviour of iodine is less certain. (Iodic(I) acid, HOI, appears to have some basic character, as I^+OH^-.) Sodium chlorate(I) is the most important of these products. It is a vigorous oxidizing agent, in general domestic use as a bleaching and antiseptic agent.

Commercial chlorate(I) (hypochlorite) solutions usually contain common salt and sodium hydroxide as impurities. The mixed halide and halate(I) solutions regenerate the halogen if acidified, as:

$$X^-(aq) + OX^-(aq) + 2H^+(aq) \rightarrow H_2O(l) + X_2, \text{where X is Cl or Br}$$

Manufacture of sodium chlorate(I) *solution.* A cold solution of common salt is caused to flow between *carbon anodes* and *iron cathodes* set close together to force the products at the two poles into contact.

At cathode	*At anode*
$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$ H^+ discharges, inducing more ionization of water, putting OH^- into excess. This with incoming Na^+, from sodium chloride, is equivalent to the production of sodium hydroxide Na^+OH^-. Hydrogen is liberated. $2H^+(aq) + 2e^- \rightarrow H_2(g)$	Cl^- discharges and the chlorine atoms combine in pairs to give molecular chlorine. $Cl^-(aq) - e^- \rightarrow (Cl)$ $(Cl) + (Cl) \rightarrow Cl_2(g)$

The anode and cathode products then react as:

$$2NaOH(aq) + Cl_2(g) \rightarrow NaCl(aq) + NaOCl(aq) + H_2O(l)$$

(b) Hot, concentrated caustic alkali solutions

Chlorine, bromine, and iodine react with hot, concentrated solutions of caustic alkali to produce colourless solutions of *sodium* (or *potassium*) *chloride* and *chlorate*(V), *bromide* and *bromate*(V), or *iodide* and *iodate*(V).

$$6OH^-(aq) + 3X_2 \rightarrow 5X^-(aq) + XO_3{}^-(aq) + 3H_2O(l),$$

where X is Cl, Br, or I

Essentially, the halate(I) is produced at first, and then disproportionates.

$$X_2 + OH^-(aq) \rightarrow X^-(aq) + OX^-(aq)$$
$$3OX^-(aq) \rightarrow 2X^-(aq) + XO_3{}^-(aq)$$

The most important case is the production of potassium chlorate(V) by the reaction:

$$6KOH(aq) + 3Cl_2(g) \rightarrow 5KCl(aq) + KClO_3(aq) + 3H_2O(l)$$

Laboratory preparation of potassium chlorate(V). The inverted funnel (Figure 10.4) is used to prevent 'sucking back'. The preparation must be carried on in a fume cupboard. Chlorine is passed into the solution until the liquid bleaches blue litmus paper, i.e. the potassium hydroxide is all used up and chlorine has gone into excess. On cooling, perhaps after some evaporation, the solution will deposit crystals of potassium

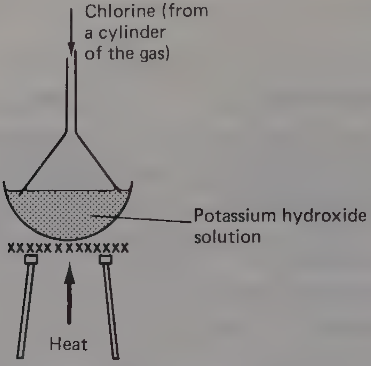


Figure 10.4 *Preparation of potassium chlorate*

chlorate(V), which is much less soluble at room temperature than the chloride. The chlorate(V) may be filtered off, washed, and recrystallized to remove any accompanying potassium chloride.

Manufacture of potassium chlorate(V). A hot, concentrated solution of potassium chloride is passed between *carbon anodes* and *iron cathodes* set close together to force the anode and cathode products into contact.

At cathode	*At anode*
$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$ H^+ discharges, inducing more ionization of water, putting OH^- into excess. This, with incoming K^+ from potassium chloride, is equivalent to the production of potassium hydroxide, K^+OH^-. Hydrogen is liberated. $2H^+(aq) + 2e^- \rightarrow H_2(g)$	Cl^- discharges and the chlorine atoms combine in pairs to give molecular chlorine. $Cl^-(aq) - e^- \rightarrow (Cl)$ $(Cl) + (Cl) \rightarrow Cl_2(g)$

The cathode and anode products then react as:

$$6KOH(aq) + 3Cl_2(g) \rightarrow 5KCl(aq) + KClO_3(aq) + 3H_2O(l)$$

The potassium chlorate(V) may be separated and purified as in the preceding preparation. An important use of it is as the oxidizing agent in matches, p. 255. *Sodium chlorate*(V) is now being manufactured in a similar way from common salt and used as a weed-killer.

Laboratory preparation of potassium iodide and iodate(V). Take a hot, concentrated solution of potassium hydroxide and stir into it solid iodine until the liquid becomes permanently brown, i.e. iodine has gone into excess of the requirement for the reaction:

$$6KOH(aq) + 3I_2(s) \rightarrow 5KI(aq) + KIO_3(aq) + 3H_2O(l)$$

This ensures no excess potassium hydroxide. Then carefully add more potassium hydroxide solution (almost drop by drop) till the brown colour is just discharged and the liquid is colourless.

For potassium iodate(V). Cool the liquid, perhaps after some concentration, and the less soluble iodate(V) will crystallize out. Filter it, wash with a little cold, distilled water and recrystallize to purify it.

For potassium iodide. Evaporate the liquid to dryness and heat the solid cautiously till effervescence stops. This converts potassium iodate(V) to iodide so that the whole product is now iodide.

$$2KIO_3(s) \rightarrow 2KI(s) + 3O_2(g)$$

Dissolve the solid in as little, almost boiling, distilled water as possible, filter if it is not clear, and allow it to cool and crystallize. Filter the crystals, wash them with a very little cold, distilled water and allow them to dry.

The mixture of potassium iodide and iodate(V) produced by the action of iodine on hot, potassium hydroxide solution liberates the whole of the iodine again if acidified.

$$5I^-(aq) + IO_3^-(aq) + 6H^+(aq) \rightarrow 3I_2(s) + 3H_2O(l)$$

This is used in the laboratory to estimate potassium iodate(V) by mixing a measured volume of potassium iodate solution with *excess* of acidified potassium iodide so that the iodate(V) determines the amount of iodine liberated. The iodine is then titrated by a standard solution of sodium thiosulphate.

(c) Calcium hydroxide (slaked lime)

Chlorine reacts with solid 'slaked lime' at ordinary temperature to produce bleaching powder. An approximate equation is usually written as:

$$Ca(OH)_2(s) + Cl_2(g) \rightarrow \text{‘}CaOCl_2.H_2O\text{’}(s)$$

but it does not accurately represent the change. In a modern plant, slaked lime is driven through horizontal cylinders by Archimedean screws and meets a counter-flow of chlorine. Alternatively, slaked lime may descend from floor to floor of a vertical tower, being stirred continually by rakes which expose fresh surfaces of the lime. A stream of chlorine flows up the tower. (Bromine also forms a bleaching powder, though it has no practical value. Iodine does not.)

The following is a brief summary of the properties of bleaching powder.

(i) With dilute acids, chlorine is evolved.

$$\text{`}CaOCl_2\text{'}(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + H_2O(l) + Cl_2(g)$$

(ii) With a cobalt salt (catalyst) and heat, oxygen is evolved.

$$2\text{`}CaOCl_2\text{'}(s) \rightarrow 2CaCl_2(s) + O_2(g)$$

(iii) Oxidizing actions. Bleaching powder, usually in association with dilute sulphuric or hydrochloric acid, shows oxidizing actions resembling those of chlorine, e.g.:

$$2FeSO_4(aq) + \text{`}CaOCl_2\text{'}(s) + H_2SO_4(aq) \rightarrow CaCl_2(aq) + Fe_2(SO_4)_3(aq) + H_2O(l)$$

$$2KI(aq) + \text{`}CaOCl_2\text{'}(s) + H_2SO_4(aq) \rightarrow CaCl_2(aq) + K_2SO_4(aq) + H_2O(l) + I_2(s)$$

Bleaching powder deteriorates on keeping for two reasons:

(a) It reacts with carbon dioxide of the air.

$$\text{`}CaOCl_2\text{'}(s) + CO_2(g) \rightarrow CaCO_3(s) + Cl_2(g)$$

(b) It undergoes 'auto-oxidation'.

$$5\text{`}CaOCl_2\text{'}(s) + \text{`}CaOCl_2\text{'}(s) \rightarrow 5CaCl_2(s) + Ca(ClO_3)_2(s)$$

Both these changes reduce the 'available' chlorine content, i.e. the chlorine liberated by dilute acid.

Though bleaching powder has been known since the late eighteenth century, its formula posed many problems. Information based on X-ray work suggests that the chlorination of slaked lime occurs in two stages. In the earlier stage, a basic chloride and a basic chlorate(I) of calcium are formed. These can be formulated as $CaCl_2.Ca(OH)_2.H_2O$ and $Ca(OCl)_2.Ca(OH)_2$. In the later stage, the basic chlorate(I) is converted to the normal salt, $Ca(OCl)_2$, and a greater proportion of the basic chloride is produced. Fresh bleaching powder contains about 35 per cent of 'available' chlorine.

(5) *Reactions of halogens with non-metals*

(a) Hydrogen

Chlorine reacts with hydrogen in the following conditions: (i) slowly in diffused daylight, (ii) explosively if exposed to sunlight, (iii) by combustion of a jet of either gas in the other, (iv) explosively if sparked. In all cases, the product is *hydrogen chloride.*

$$H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$$

This affinity of chlorine for hydrogen gives rise to reactions of the following kind.

(i) *With turpentine.* If a filter paper soaked in warm turpentine is dropped into chlorine, spontaneous combustion occurs with the formation of a black smoke ring of *carbon* particles. *Hydrogen chloride* is also formed.

$$C_{10}H_{16}(l) + 8Cl_2(g) \rightarrow 10C(s) + 16HCl(g)$$

(ii) *With ammonia.* If *concentrated* aqueous ammonia falls drop by drop into chlorine, each drop inflames and burns with a greenish flame. White fumes of *ammonium chloride* are produced together with *nitrogen.*

$$8NH_3(\text{conc.aq.}) + 3Cl_2(g) \rightarrow 6NH_4Cl(s) + N_2(g)$$

The action of chlorine in excess on ammonia, or on ammonium chloride, may produce the dangerously explosive yellow oil, *nitrogen chloride.*

$$NH_3(\text{conc.aq.}) + 3Cl_2(g) \rightarrow NCl_3(l) + 3HCl(g)$$
$$NH_4Cl(s) + 3Cl_2(g) \rightarrow NCl_3(l) + 4HCl(g)$$

With concentrated ammonia in excess, bromine behaves like chlorine, giving the reaction

$$8NH_3(\text{conc.aq.}) + 3Br_2(l) \rightarrow 6NH_4Br(s) + N_2(g)$$

but the action of bromine on ammonium bromide gives *ammonium tribromide,* $NH_4{}^+(Br_3),^-$ not NBr_3.

The action of iodine with excess of aqueous ammonia precipitates a brown compound, $NI_3.nNH_3$ known as *nitrogen triiodide.*

$$(4+n)NH_3(\text{conc.aq.}) + 3I_2(s) \rightarrow 3NH_4I(aq) + NI_3.nNH_3(s)$$

The compound is dangerously explosive when dry.

Bromine combines slowly with hydrogen in sunlight. The two elements combine when heated or if led over a platinum spiral (catalyst), heated to red heat. The product is *hydrogen bromide.*

$$H_2(g) + Br_2(g) \rightleftharpoons 2HBr(g)$$

Iodine is the least energetic in combining with hydrogen, but can be made to do so by passing iodine vapour and hydrogen over heated platinized asbestos. The reaction is reversible, hydrogen iodide being about 18 per cent dissociated at 550 K and 25 per cent at 800 K.

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

(b) Sulphur

If sulphur is heated in a current of dry chlorine, *disulphur dichloride* is formed.

$$2S(s) + Cl_2(g) \rightarrow S_2Cl_2(l)$$

Bromine vapour and sulphur will combine similarly when heated, but no compounds of iodine and sulphur are known.

(c) Phosphorus

White phosphorus burns spontaneously in chlorine at room temperature and red phosphorus combines with chlorine when heated. In both cases, the primary product is *phosphorus trichloride* (a liquid), but, if excess chlorine is available, *phosphorus pentachloride* (a solid) may also be formed.

$$P_4(s) + 6Cl_2(g) \rightarrow 4PCl_3(l)$$
$$PCl_3(l) + Cl_2(g) \rightarrow PCl_5(s)$$

Liquid bromine inflames if dropped on to red phosphorus. A controlled reaction can be obtained by gradually mixing solutions of white phosphorus and bromine in carbon disulphide. *Phosphorus tribromide* is formed. Carbon disulphide can be distilled off and the tribromide distilled.

$$P_4(s) + 6Br_2(l) \rightarrow 4PBr_3(l)$$

The tribromide reacts with bromine to give the pentabromide, PBr_5. Phosphorus triiodide can be made by the method used for the tribromide above. It is a reddish crystalline solid, melting at 334 K. A diiodide, P_2I_4, is known, but no pentaiodide of phosphorus exists.

Chlorine, bromine and iodine do not combine directly with oxygen, nitrogen or carbon. This explains the frequent use of carbon anodes in electrolysis in which chlorine is the anodic product.

(6) *Reactions of halogens with metals*

Chlorine combines with most metals, usually when heated. The most highly oxidized chloride is usually formed, unless it is unstable at the temperature used, e.g.:

$$2Fe(s) + 3Cl_2(g) \rightarrow 2FeCl_3(s)$$
$$Sn(s) + 2Cl_2(g) \rightarrow SnCl_4(l)$$

A thin leaf of Dutch metal (80% Cu, 20% Zn) ignites spontaneously in chlorine. Finely divided antimony or arsenic also ignites.

Bromine and iodine usually react in a way similar to chlorine, but require higher temperatures. Iron filings, however, react with bromine at ordinary temperature and are used to trap escaping bromine vapour in its manufacture. Mercury, too, reacts with iodine if the two are merely rubbed together in a mortar. Red mercury(II) iodide, HgI_2, or green mercury(I) iodide, Hg_2I_2, are formed according to the proportions used.

Preparation of anhydrous chlorides of some metals

It is rarely possible to obtain a chloride of a heavy metal in a pure, anhydrous state by any method involving its crystallization from water. This is because such chlorides usually crystallize hydrated, e.g. $AlCl_3.6H_2O$, $ZnCl_2.H_2O$, and basic salts or hydroxides are formed if an attempt is made to dehydrate them by heat, e.g.

$$ZnCl_2(s) + H_2O(l) \rightleftharpoons Zn(OH)Cl(s) + HCl(g)$$
$$AlCl_3(s) + 3H_2O(l) \rightleftharpoons Al(OH)_3(s) + 3HCl(g)$$

The following methods are available.

Methods (1) and (2). By heating the metal in a current of dry chlorine or dry hydrogen chloride

These are conveniently taken together because the apparatus used is

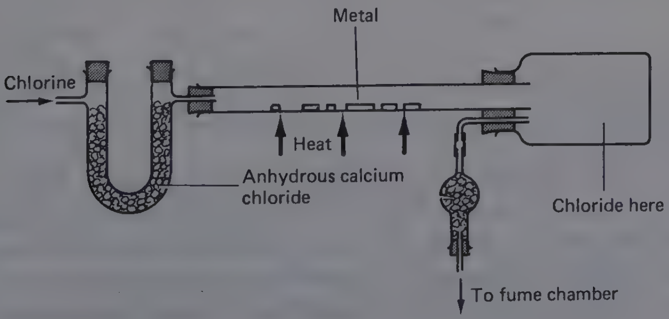


Figure 10.5 *Preparation of some anhydrous metallic chlorides*

similar for both. In the case of solid metallic chlorides (the great majority), it is shown in Figure 10.5.

In a general way, a metal which shows a constant oxidation number and forms only one chloride will produce it with either chlorine or hydrogen chloride, e.g.

$$\mathrm{Mg(s) + 2HCl(g) \rightarrow \underset{\text{white}}{MgCl_2(s)} + H_2(g);}$$

$$\mathrm{2Al(s) + 6HCl(g) \rightarrow \underset{\text{white}}{2AlCl_3(s)} + 3H_2(g);}$$

$$\mathrm{Mg(s) + Cl_2(g) \rightarrow MgCl_2(s)}$$

$$\mathrm{2Al(s) + 3Cl_2(g) \rightarrow 2AlCl_3(s)}$$

Chlorine is usually more convenient, being available in cylinders, and more rapid in action.

If the metal has variable oxidation number, the *lower* chloride may sometimes be given by hydrogen chloride and the *higher* chloride by chlorine, e.g.

$$\mathrm{Fe(s) + 2HCl(g) \rightarrow \underset{\substack{\text{iron(II)}\\ \text{chloride;}\\ \text{white}}}{FeCl_2(s)} + H_2(g)}$$

$$\mathrm{Sn(s) + 2HCl(g) \rightarrow \underset{\substack{\text{iron(II)}\\ \text{chloride;}\\ \text{white}}}{SnCl_2(s)} + H_2(g)}$$

$$\mathrm{2Fe(s) + 3Cl_2(g) \rightarrow \underset{\substack{\text{iron(III)}\\ \text{chloride;}\\ \text{black}}}{2FeCl_3(s)}}$$

$$\mathrm{Sn(s) + 2Cl_2(g) \rightarrow \underset{\substack{\text{tin (IV) chloride;}\\ \text{a liquid. See special}\\ \text{apparatus below}}}{SnCl_4(l)}}$$

If hydrogen chloride is used, the apparatus should be swept clear of air before heating to avoid production of explosive air–hydrogen mixtures in the apparatus.

Mercury(II) chloride, $HgCl_2$, and copper(II) chloride, $CuCl_2$, can both be prepared by heating the metal in chlorine as above. For mercury, a *liquid* metal, use a porcelain boat or a bulb-tube. The lower chlorides of these metals are not prepared by the use of hydrogen chloride. They are insoluble in water and are produced by methods described later.

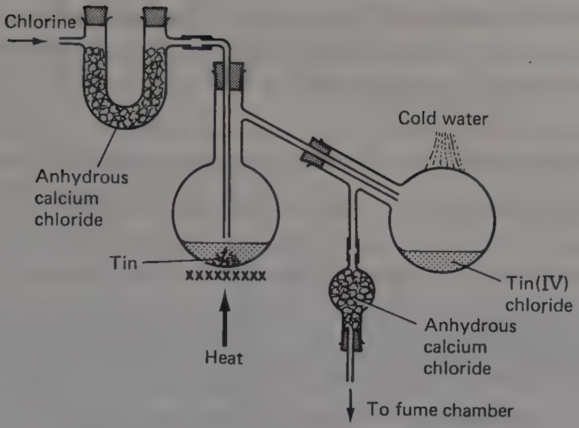


Figure 10.6 *Preparation of tin(IV) chloride*

Method 3. Preparation of insoluble chlorides

(a) *Lead*(II) *chloride, mercury*(I) *chloride and silver chloride from the metals.* For lead and silver, heat the metal with moderately concentrated nitric acid, keeping excess metal present, till the reaction is moderating, i.e. acid is almost used up. The filter from excess metal and insoluble impurities.

$$3Pb(s) + 8HNO_3(conc.aq.) \rightarrow 3Pb(NO_3)_2(aq) + 4H_2O(l) + 2NO(g)$$
$$Ag(s) + 2HNO_3(conc.aq.) \rightarrow AgNO_3(aq) + H_2O(l) + NO_2(g)$$

In the case of mercury, warm the metal with dilute nitric acid, keeping excess metal present. These conditions of moderate oxidation are designed to oxidize the metal to mercury(I) nitrate only. (Concentrated nitric acid, heated, would give rapid oxidation to mercury(II) nitrate.)

$$6Hg(l) + 8HNO_3(conc.aq.) \rightarrow 3Hg_2(NO_3)_2(aq) + 4H_2O(l) + 2NO(g)$$

Filter the liquid from excess metal and insoluble impurities.

To the filtrate in each case, add dilute hydrochloric acid. The respective chlorides are precipitated as white solids. In each case, filter, wash with distilled water and allow the precipitate to dry. Lead(II) chloride is quite soluble in hot water, so must be washed with cold; the other two may be washed with hot distilled water.

$$Pb(NO_3)_2(aq) + 2HCl(aq) \rightarrow PbCl_2(s) + 2HNO_3(aq)$$
$$AgNO_3(aq) + HCl(aq) \rightarrow AgCl(s) + HNO_3(aq)$$
$$Hg_2(NO_3)_2(aq) + 2HCl(aq) \rightarrow Hg_2Cl_2(s) + 2HNO_3(aq)$$

(b) *Copper*(I) *chloride*, CuCl. (See p. 461.)

The common chlorides not covered by the above preparations are the alkali metal chlorides, ammonium chloride, and calcium chloride.

Method 4. *The method of neutralization* (*for* NaCl, KCl *and* NH_4Cl)

To prepare sodium chloride, use sodium hydroxide solution. To it add a little litmus. Then, cautiously, with stirring add dilute hydrochloric acid till the litmus is purple or only just red. Add animal charcoal to adsorb the colouring matter, boil and filter to remove litmus. Evaporate the filtrate to small bulk and cool it. Filter off the crystals, wash with cold distilled water cautiously and allow the crystals to dry.

$$NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l)$$

Prepare potassium chloride and ammonium chloride in a similar way using potassium hydroxide solution and ammonia. All these chlorides crystallize anhydrous.

Method 5. *The action of hydrochloric acid on a metal carbonate*

This is suitable for preparing calcium chloride. Add calcium carbonate to dilute hydrochloric acid, with stirring, till the calcium carbonate remains in excess.

$$CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$$

Boil the mixture and filter off the excess chalk. Evaporate the filtrate to dryness. The product may be slightly hydrolysed to a basic chloride:

SUMMARY

Methods for preparing metallic chlorides

(1) Heating the metal in dry hydrogen chloride
 —for $MgCl_2$, $ZnCl_2$, $AlCl_3$, $SnCl_2$, $FeCl_2$

(2) Heating the metal in dry chlorine
 —for $MgCl_2$, $ZnCl_2$, $AlCl_3$, $FeCl_3$, $SnCl_4$, $HgCl_2$, $CuCl_2$

(3) Precipitation method (double decomposition)
 —for *insoluble* chlorides, i.e. $PbCl_2$, AgCl, Hg_2Cl_2
 A special case of this for CuCl

(4) Neutralization of alkali by dilute hydrochloric acid
 —for NaCl, KCl, NH_4Cl

(5) Action of carbonate of metal on dilute hydrochloric acid
 —for $CaCl_2$

Industrial manufacture of chlorine, bromine, and iodine

(1) *Chlorine*

Chlorine is made industrially as a by-product of the electrolysis of brine to produce sodium hydroxide. A full account of typical cells in use for this purpose was given on pp. 50–51.

Uses

(a) Chlorine is extensively used as a bleaching agent and in the manufacture of bleaching agents, such as bleaching powder and sodium chlorate(I); also in the manufacture of chlorates(V) and hydrogen chloride.
(b) It is also used in the manufacture of organic chemicals, such as tetrachloromethane, chloroethene (vinyl chloride) for PVC, fluorochloroalkanes as aerosol propellants, and many others.
(c) It is used in sterilizing water supplies for domestic and industrial use, and for swimming-baths.

(2) *Bromine*

Bromine occurs associated with the *carnallite*, $KCl.MgCl_2.6H_2O$, of the Stassfurt deposits and can be considered to be present as *magnesium bromide*. It also occurs in sea water as *bromide ion*, Br^-, associated with various metallic ions (Na^+, Mg^{2+} and others). It is now mainly extracted from sea water.

Extraction of bromine from sea water. Sea water, containing more than 100000 tonnes of bromine per cubic kilometre, is acidified by sulphuric acid to the point (pH 3.5) at which the equilibrium:

$$Br_2(aq) + H_2O(l) \rightleftharpoons H^+(aq) + Br^-(aq) + HBrO(aq)$$

is most favourable to the yield of free bromine. The sea water is then chlorinated.

$$2Br^-(aq) + Cl_2(aq) \rightarrow Br_2(aq) + 2Cl^-(aq)$$

Bromine is swept out by air and mixed with sulphur dioxide. Water is added, giving the reaction:

$$SO_2(g) + 2H_2O(l) + Br_2(l) \rightarrow 4H^+(aq) + 2Br^-(aq) + SO_4{}^{2-}(aq)$$

Chlorine and steam are then blown into the solution, expelling bromine which is now sufficiently concentrated to be condensed out by cooling.

$$Cl_2(g) + 2Br^-(aq) \rightarrow Br_2(l) + 2Cl^-(aq)$$

It can be purified by drying with concentrated sulphuric acid, and then distilling over potassium bromide to remove any chlorine present.

Uses of bromine

(a) A great deal of bromine is used in making 1,2-dibromoethane, $BrCH_2.CH_2Br$. This is added to petrol together with tetraethyllead(IV), $Pb(C_2H_5)_4$ (see p. 205). The lead compound inhibits pre-ignition ('knocking') in high compression engines. The 1,2-dibromoethane is present so that the lead can be eliminated from the engine as relatively volatile lead bromide. There is controversy as to whether this use can give rise to serious pollution problems.

(b) Bromine is used in making certain dyestuffs and drugs, and in black-and-white photography (as silver bromide).

(3) *Iodine*

(a) *Extraction of iodine from Chile saltpetre.* Iodine occurs as sodium iodate(V), $NaIO_3$, in Chile saltpetre (which is mostly sodium nitrate) and is left in solution after crystallization of the saltpetre. Iodate(V) is reduced by blowing sulphur dioxide up a tower down which sodium iodate(V) is trickling.

$$IO_3^-(aq) + SO_3^{2-}(aq) \rightarrow I^-(aq) + 3SO_4^{2-}(aq)$$

Any iodide formed reacts immediately, in these acid conditions, with remaining iodate(V) to liberate iodine.

$$IO_3^-(aq) + 5I^-(aq) + 6H^+(aq) \rightarrow 3H_2O(l) + 3I_2(s)$$

The iodine is filtered, washed, and pressed dry, then purified by sublimation.

(b) *Extraction of iodine from seaweed.* This provides an example of how a living organism may concentrate a particular element out of high dilution in its environment. Seaweed is dried and burned to remove organic matter. The ash is extracted with water. After concentration and cooling, the solution deposits the less soluble salts of the alkali metals, leaving the iodides in solution. After removal of the crystals, the concentrated liquor is heated with manganese(IV) oxide and concentrated sulphuric acid. Iodine distils off and is condensed, and purified by sublimation.

$$2I^-(aq) + MnO_2(s) + 4H^+(aq) \rightarrow 2H_2O(l) + Mn^{2+}(aq) + I_2(s)$$

Uses of iodine

Iodine has been widely used as an antiseptic, in solution in alcohol (*tincture of iodine*) or in potassium iodide solution. It is also a constituent of other antiseptics such as triodomethane (iodoform), CHI_3. Silver iodide is used in photography.

The halogen hydrides

Hydrogen chloride, HCl, and hydrochloric acid

Preparation

These two materials may be readily prepared as in Figure 10.7.

$$NaCl(s) + H_2SO_4(l) \rightarrow NaHSO_4(s) + HCl(g)$$

The preparation is made possible at room temperature by the high volatility of hydrogen chloride. In the comparable reaction with potassium nitrate, which is used in the preparation of nitric acid, heat has to be used to distil off the nitric acid as it is formed (p. 242).

Any given chloride (e.g. KCl, NH_4Cl) may be substituted for common salt. Note that under normal laboratory conditions the hydrogensulphate, $NaHSO_4$, is formed and *not* the normal sulphate, Na_2SO_4.

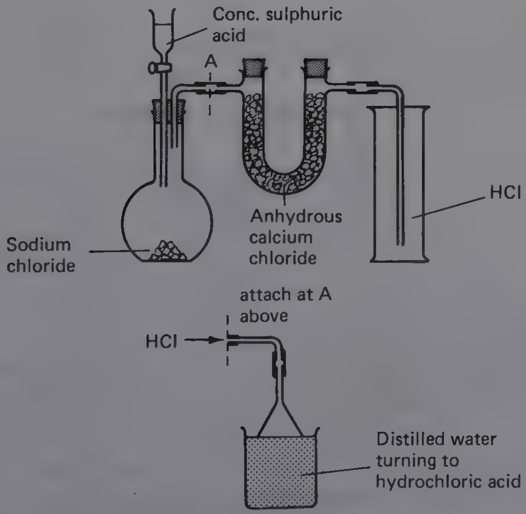


Figure 10.7 *Preparation of hydrogen chloride*

Manufacture of hydrochloric acid

The acid is now manufactured by direct combination of hydrogen and chlorine in the presence of activated charcoal with subsequent absorption of the hydrogen chloride in water.

$$H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$$

It is important to notice, however, that the above laboratory method is not suitable for preparing hydrogen bromide or iodide. The reason is that these compounds are reducing agents. Though produced at first by the reaction between concentrated sulphuric acid and a bromide or iodide, they are at once partially or wholly oxidized by excess acid to bromine or iodine, with other products as stated in detail on p. 338.

Hydrogen bromide, HBr, and hydrogen iodide, HI

Hydrobromic acid and hydriodic acid

Hydrogen bromide and hydrobromic acid are usually prepared as in Figure 10.8, the experiment being performed in a fume cupboard. Hydrogen bromide and hydrogen iodide cannot be prepared by methods similar to that used for hydrogen chloride, because, unlike hydrogen chloride, these compounds are oxidized by concentrated sulphuric

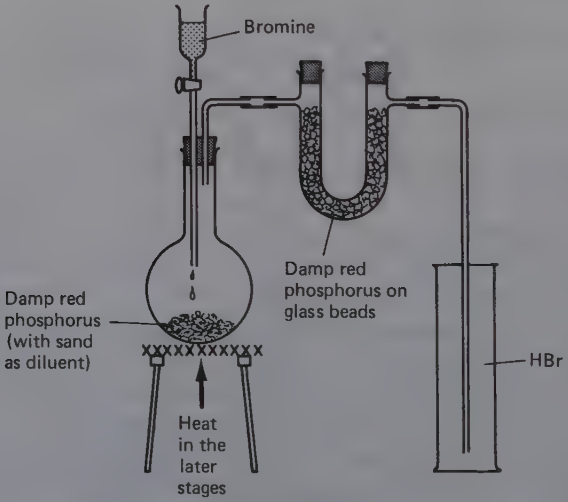


Figure 10.8 *Preparation of hydrogen bromide*

acid (see p. 338). As each drop of bromine touches the damp red phosphorus in the early stages, there is flash of light. The U-tube is inserted to trap bromine vapour and is, in effect, a second reaction vessel.

$$P_4(s) + 6Br_2(l) \rightarrow 4PBr_3(l); PBr_3(l) + 3H_2O(l) \rightarrow 3HBr(g) + H_3PO_3(s)$$

To obtain the acid, absorb hydrogen bromide in water as in Figure 10.7.

Hydrogen iodide can be prepared correspondingly by putting *iodine* and *red phosphorus* in the flask and dripping *water* on to the mixture. The equations are similar, with I instead of Br.

Hydrogen bromide and hydrogen iodide may also be made by warming the appropriate metal halide with solid 100 per cent phosphoric(V) acid. Although phosphoric(V) acid is only a weak acid, the reaction proceeds because the hydrogen halides are gases and can escape from the reaction mixture.

e.g. $$2NaCl(s) + H_3PO_4(s) \rightarrow Na_2HPO_4(s) + 2HCl(g)$$

If the aqueous acids are wanted (not the dry gases), they can be made by passing hydrogen sulphide into distilled water containing bromine or iodine until the halogen colour is discharged.

$$H_2S(g) + Br_2(aq)\,(\text{or } I_2(aq)) \rightarrow 2HBr(aq)\,(\text{or } 2HI(aq)) + S(s)$$

The mixture can then be boiled to expel hydrogen sulphide and filtered free from sulphur. Sulphur dioxide may be used instead of hydrogen sulphide, after which the halogen acid may be distilled off. Sulphuric acid is non-volatile.

$$\begin{aligned}2H_2O(l) + SO_2(g) + Br_2(aq)\,(\text{or } I_2(aq)) \rightarrow H_2SO_4(aq) + 2HBr(aq)\\ (\text{or } 2HI(aq))\end{aligned}$$

General properties of the halogen acids

(1) *Acidic behaviour*

This arises from the ionization:

$$HCl(g) + aq \rightleftharpoons H^+(aq) + Cl^-(aq)$$

and correspondingly for HBr and HI. All the acids are *strong*, i.e. highly ionized. They show the following properties:

(a) They turn blue litmus solution to red.

(b) They liberate hydrogen with the more electropositive metals.

$$Mg(s) + 2H^+(aq) \rightarrow Mg^{2+}(aq) + H_2(g)$$

(c) They form salts with bases, e.g.

$$NaOH(aq) + HBr(aq) \rightarrow NaBr(aq) + H_2O(l)$$

(d) They liberate carbon dioxide from carbonates, e.g.

$$CaCO_3(s) + 2H^+(aq) \rightarrow Ca^{2+}(aq) + H_2O(l) + CO_2(g)$$

(2) *Reducing action*

Hydrochloric acid is not a reducing agent in the ordinary sense but, when concentrated, it can be oxidized to chlorine by vigorous oxidizing agents such as potassium manganate(VII) (cold), or manganese(IV) oxide (with heat).

$$2MnO_4^-(aq) + 10Cl^-(aq) + 8H^+(aq) \rightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 5Cl_2(g)$$
$$MnO_2(s) + 4H^+(aq) + 2Cl^-(aq) \rightarrow Mn^{2+}(aq) + 2H_2O(l) + Cl_2(g)$$

Hydriodic acid (usually used as *acidified potassium iodide solution*) is a very vigorous reducing agent. It liberates iodine quantitatively with many oxidizing agents, e.g.

Potassium manganate(VII)

$$2MnO_4^-(aq) + 10I^-(aq) + 16H^+(aq) \rightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 5I_2(s)$$

Hydrogen peroxide

$$H_2O_2(aq) + 2I^-(aq) + 2H^+(aq) \rightarrow 2H_2O(l) + I_2(s)$$

The acid quickly turns brown by liberation of iodine when exposed to air.

$$4HI(aq) + O_2(g) \rightarrow 2H_2O(l) + 2I_2(s)$$

Hydrobromic acid is intermediate between the other two, but has no particularly important reducing actions. The oxidation of hydrogen bromide and hydrogen iodide by concentrated sulphuric acid is considered on p. 338.

(3) *Stability towards heat*

The three halogen hydrides show the usual halogen gradation in their their stability towards heat. Hydrogen chloride shows no appreciable decomposition below 1800 K; hydrogen bromide begins to decompose at about 1070 K and hydrogen iodide at about 450 K.

$$2HBr(g) \rightleftharpoons H_2(g) + Br_2(g); \; 2HI(g) \rightleftharpoons H_2(g) + I_2(g)$$

(4) *Behaviour when distilled*

The continuous line of the graph (Figure 10.9) shows approximately the relation between boiling point and composition for hydrochloric acid of various concentrations. The dotted line represents the composition of vapour in equilibrium with the liquid, e.g. point B represents the composition of vapour in equilibrium with liquid of composition A. It will be observed that a liquid containing 20.2 per cent HCl has a maximum boiling point of 383 K. All other solutions of HCl have a lower boiling point, i.e. a higher vapour pressure.

There are here four important types of liquid to be considered for distillation.

(a) *Pure water.* This distils unchanged at the constant boiling point of 373 K.

(b) *Liquid of composition A, i.e. between pure water and* 20.2 per cent HCl. The first vapour given off from A must have composition B, and would condense to liquid C. This in turn would evolve vapour D, condensing to liquid E, and so on. The condensing surfaces of an effective fractioning column are intended to provide the equivalent of a series of distillations of this kind as vapour rises over the condensed liquids and tends to reach equilibrium with them. It is obvious that the liquid finally delivered by the column will be more dilute than A and will, in fact, tend towards the composition of

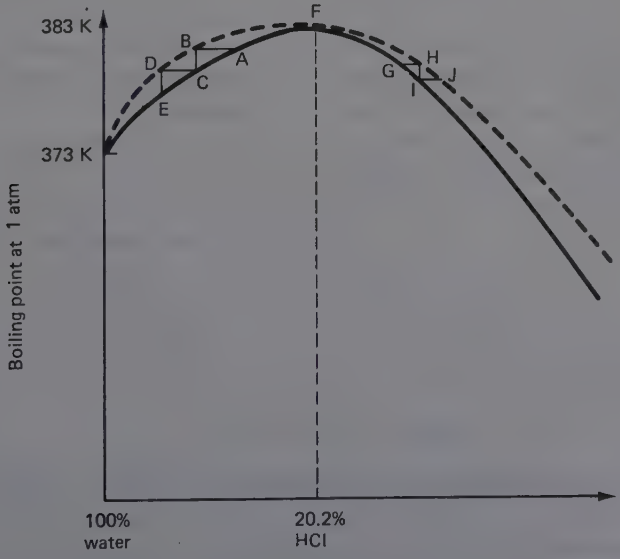


Figure 10.9 *Boiling points of hydrochloric acids of varying concentration*

pure water. As it is boiled off, the *residual* liquid concentrates, follows the composition and boiling points represented by the continuous curve and finally reaches 20.2% HCl. This mixture is then delivered unchanged in composition and at the constant boiling point of 383 K.

(c) *Liquid of composition G, i.e. more than* 20.2 *per cent* HCl. Here liquid G yields vapour H, which condenses to liquid I, giving vapour J, and so on. The fractionating column delivers a liquid with a greater percentage of HCl than 20.2 per cent. The *residual* liquid gradually becomes more dilute, follows the compositions and boiling points of the continuous curve, and finally reaches 20.2 per cent HCl. It then distils unchanged at the constant boiling point of 383 K.

(d) *Liquid F.* This is the maximum boiling point mixture itself. It is in equilibrium with vapour of exactly its own composition and distils unchanged at the constant boiling point of 383 K. Such a liquid is known as an *azeotropic mixture.*

Thus it will be seen that hydrochloric acid of any composition whatever will, if distilled long enough at 101 300 N m^{-2} (1 atm) leave a residual liquid containing 20.2 per cent HCl with a boiling point of 383 K. It will then distil unchanged in boiling point and composition. The composition, 20.2 per cent HCl, 79.8 per cent water, corresponds very closely to that of a compound, $HCl.8H_2O$, and it was once thought that the liquid of maximum boiling point might be a compound of this formula. In fact, however, its composition varies with pressure, which is unlikely for a true compound. It is a mixture, and the composition conforms only accidently to that of a compound.

Hydrobromic acid and hydriodic acid behave like hydrochloric acid, but with different quantitative relations as:

	b.p. at 101 300 *N* m^{-2} (1 *atm*)	*Mixture of maximum b.p. composition*
Hydrobromic acid	398 K	48.2% HBr
Hydriodic acid	399 K	57.8% HI

Detection and estimation of chlorine, bromine, and iodine and their ions

Chlorine and Cl$^-$

In fairly high concentrations, chlorine can be detected by its greenish-yellow colour and bleaching of damp litmus paper. Chlorine can be estimated by absorption in excess of potassium iodide solution. The iodine liberated is titrated by standard sodium thiosulphate solution.

Chloride ion can be detected in solution by the addition of excess of dilute nitric acid and silver nitrate solution. A white, curdy precipitate of silver chloride, readily soluble in ammonia, is produced.

$$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$$
$$AgCl(s) + 2NH_3(aq) \rightarrow [Ag(NH_3)_2]^+Cl^-(aq)$$

Chloride ion is usually estimated by titration with standard silver nitrate solution, in the presence of potassium chromate(VI) as indicator.

Bromine and Br^-

Free bromine can be recognized by the reddish-brown vapour it gives off when heated. Nitrogen dioxide and chromium(VI) dichloride dioxide (chromyl chloride) are gases with a very similar colour. Bromine can be distinguished by the following facts:

(a) Bromine vapour in water gives a yellow-brown solution. If this solution is shaken with a little trichloromethane, the colour concentrates into the trichloromethane layer.

(b) Chromium(VI) dichloride dioxide gives with water a yellow solution containing the chromate(VI) ion, $CrO_4{}^{2-}$. It gives no colour in trichloromethane.

Nitrogen dioxide gives a colourless solution in water (nitrous and nitric acid). It may be pale blue if N_2O_3 is present.

In the absence of chlorine, bromine can be estimated (as chlorine above) by liberation of iodine from excess of potassium iodide solution. Bromide ion can be detected by adding chlorine water to the acidified solution. Bromine is released. If the solution is shaken with a little trichloromethane, the brown colour of the bromine is concentrated in the trichloromethane layer.

$$2Br^-(aq) + Cl_2(aq) \rightarrow 2Cl^-(aq) + Br_2(aq)$$

With an excess of dilute nitric acid and silver nitrate solution, a pale yellow, curdy precipitate of silver bromide is formed, sparingly soluble in ammonia.

$$Ag^+(aq) + Br^-(aq) \rightarrow AgBr(s)$$

To confirm, add to the *solid* test material some manganese(IV) oxide and concentrated sulphuric acid and warm the mixture. Reddish-brown fumes of bromine are evolved, which give a pale yellow precipitate with dilute nitric acid and silver nitrate solution.

$$2Br^-(s) + MnO_2(s) + 4H^+(conc.aq.) \rightarrow Mn^{2+}(aq) + 2H_2O(l) + Br_2(g)$$

Bromide ion is estimated by titration with silver nitrate solution (see chloride ion above).

Iodine and I^-

Free iodine is readily detected by the dark blue coloration it gives with starch solution in the cold. The colour disappears at about 350 K, but returns when the material is cooled. Iodine is estimated, usually in solution in excess of potassium iodide solution, with standard sodium thiosulphate solution. Starch solution, added near the end of the titration, is the indicator.

$$2S_2O_3{}^{2-}(aq) + I_2\,(\text{in KI}(aq)) \rightarrow S_4O_6{}^{2-}(aq) + 2I^-(aq)$$

Iodide ion can be detected in acidified solution by adding chlorine water. The solution can be shaken with a little trichloromethane. The purple colour of the iodine appears in the trichloromethane layer.

$$2I^-(aq) + Cl_2(aq) \rightarrow I_2(aq) + 2Cl^-(aq)$$

With an excess of dilute nitric acid and silver nitrate solution, a curdy, yellow precipitate of silver iodide, insoluble in ammonia, shows the presence of iodide ion.

$$I^-(aq) + Ag^+(aq) \rightarrow AgI(s)$$

To confirm, heat the *solid* test substance with manganese(IV) oxide and concentrated sulphuric acid. The purple vapour of iodine evolved confirms the presence of iodide.

$$2I^-(s) + MnO_2(s) + 4H^+(\text{conc.aq.}) \rightarrow 2H_2O(l) + 2Mn^{2+}(aq) + I_2(s)$$

Iodides may be precipitated as silver iodide (above) and weighed in this form.

Oxides and oxyacids of the halogens

Chlorine forms six oxides, but only the following three have any considerable importance. All six oxides are unstable.

Dichlorine oxide (chlorine monoxide), Cl_2O

Dichlorine oxide can be made by passing *dry chlorine* over freshly precipitated *mercury*(II) *oxide* which has been dried at 670 K. The reaction tube should be cooled by water. Dichlorine oxide can be condensed in a U-tube immersed in ice–salt.

$$2HgO(s) + 2Cl_2(g) \rightarrow \underset{\substack{\text{basic mercuric(II)}\\ \text{chloride}}}{HgO.HgCl_2(s)} + Cl_2O(g)$$

Chlorine monoxide is a yellow gas, which condenses to a reddish-brown liquid, which boils at 277 K at 1 atm. The liquid is very explosive. It may explode by mere contact with materials like turpentine, phosphorus and sulphur, and when subjected to very slight mechanical shock.

The gas reacts with water forming *chloric*(I) *acid* (*hypochlorous acid*), so acting as the anhydride of this acid.

$$Cl_2O(g) + H_2O(l) \rightarrow 2HOCl(aq)$$

Chlorine dioxide, ClO_2

Chlorine dioxide is a very explosive gas which is best known as the product of reaction between potassium chlorate(V) and concentrated sulphuric acid. If *very small* amounts of these two are mixed and warmed in a dry test tube, a series of sharp cracks indicates the formation and explosive decomposition of chlorine dioxide. It is very dangerous to mix anything but *small* quantities of these two reagents.

$$\underset{\text{chlorate(V) ion}}{3ClO_3^-(s)} + 2H^+(\text{conc.aq.}) \rightarrow 2ClO_2(g) + \underset{\text{chlorate(VII) ion}}{ClO_4^-(aq)} + H_2O(l)$$

The gas is best prepared by the action of dry chlorine on silver chlorate(V) at about 360 K.

$$2ClO_3^-(s) + Cl_2(g) \rightarrow 2ClO_2(g) + 2Cl^-(\text{conc.aq.}) + O_2(g)$$

By passing through a condensing apparatus immersed in solid carbon dioxide and ethoxyethane, oxygen remains gaseous while chlorine dioxide solidifies.

Chlorine dioxide is a reddish-yellow gas, which condenses to a dark red liquid of boiling point 284 K. The gas is readily exploded by sparking or by a hot wire. The liquid may explode without any obvious exciting agent, other than impurity. The gas is a very vigorous oxidizing agent and ignites materials like white phosphorus and sugar spontaneously.

Chlorine dioxide reacts with water as a mixed acidic anhydride, forming *chloric*(III) *acid* (*chlorous acid*) and *chloric*(V) *acid* (*chloric acid*).

$$2ClO_2(g) + H_2O(l) \rightarrow \underset{\text{chloric(V) acid}}{HClO_3(aq)} + \underset{\text{chloric(III) acid}}{HClO_2(aq)}$$

Dichlorine heptoxide, Cl_2O_7

Dichlorine heptoxide is a colourless oil, boiling point 355 K. It is principally interesting as the acidic oxide of the non-metal, chlorine, in which the characteristic group oxidation number of 7 is shown. It is the acidic anhydride of chloric(VII) acid (perchloric acid), $HClO_4$.

$$Cl_2O_7(l) + H_2O(l) \rightarrow 2HClO_4(l)$$

It is typical of a non-metal to produce an acidic oxide of this kind when showing the characteristic group oxidation number. The oxide is usually prepared by dehydration of chloric(VII) acid. The acid is added gradually to phosphorus(V) oxide cooled in ice–salt. After an interval in which dehydration occurs, dichlorine heptoxide can be distilled off.

$$2HClO_4(l) \xrightarrow{-H_2O} Cl_2O_7(l)$$

Chloric(I) acid (hypochlorous acid), HClO

This acid is known only in dilute aqueous solution. It is usually prepared by passing chlorine through a suspension of freshly prepared yellow mercury(II) oxide in water.

$$HgO(s) + 2Cl_2(g) + H_2O(l) \rightarrow HgCl_2(aq) + 2HClO(aq)$$

Distillation under reduced pressure yields chloric(I) acid. Both the acid and its salts have powerful oxidizing properties and are used as bleaching agents and antiseptics. Examples of their oxidizing action in solution are:

$$2Fe^{2+}(aq) + 2H^+(aq) + ClO^-(aq) \rightarrow 2Fe^{3+}(aq) + H_2O(l) + Cl^-(aq)$$

$$\underbrace{2I^-(aq) + 2H^+(aq)}_{\text{acidified KI solution}} + ClO^-(aq) \rightarrow H_2O(l) + Cl^-(aq) + \underset{\text{iodine}}{I_2(s)}$$

$$SO_3{}^{2-}(aq) + ClO^-(aq) \rightarrow SO_4{}^{2-}(aq) + Cl^-(aq)$$

Sodium chlorate(I) solution is made as described on p. 360, and is sold as a bleaching agent for household use under various trade names. The solution decomposes when heated, giving *sodium chloride* and *chlorate*(V) as products.

$$3ClO^-(aq) \rightarrow 2Cl^-(aq) + ClO_3{}^-(aq)$$

This is an example of *disproportionation*. Three chlorine atoms in the + 1 oxidation state become two in the − 1 state and one in the + 5 state. Chloric(I) acid is only a weak acid. It liberates oxygen under the action of sunlight

$$2HClO(aq) \rightarrow 2HCl(aq) + O_2(g)$$

and is decomposed by heat.

$$3HClO(aq) \rightarrow 2HCl(aq) + HClO_3(aq)$$

The acid and its salts liberate oxygen when warmed with a cobalt(II) salt present as catalyst.

$$2ClO^-(aq) \rightarrow 2Cl^-(aq) + O_2(g)$$

A solution of chlorine in water contains chloric(I) acid and yields oxygen on exposure to sunlight.

$$\left\{\begin{array}{r} Cl_2(g) + H_2O(l) \rightleftharpoons HCl(aq) + HOCl(aq) \\ 2HOCl(aq) \rightarrow 2HCl(aq) + O_2(g) \end{array}\right.$$

Chloric(V) acid and chlorates(V)

The two most important chlorates(V) are the sodium and potassium salts, $NaClO_3$ and $KClO_3$. Their preparation by electrolysis of hot solutions of the corresponding chlorides has been described earlier (p. 362). Both are very powerful oxidizing agents. A mixture of powdered carbon or sulphur with potassium chlorate(V) explodes violently when heated; so much so that the mixing of potassium chlorate(V) and sulphur or other easily oxidizable materials is prohibited by law.

$$2KClO_3(s) + 3C(s) \rightarrow 2KCl(s) + 3CO_2(g)$$
$$2KClO_3(s) + 3S(s) \rightarrow 2KCl(s) + 3SO_2(g)$$

The chlorates(V) are also vigorous oxidizing agents in solution, e.g. in the following reactions:

$$6Fe^{2+}(aq) + 6H^+(aq) + ClO_3^-(aq) \rightarrow 6Fe^{3+}(aq) + 3H_2O(l) + Cl^-(aq)$$
$$3SO_3^{2-}(aq) + ClO_3^-(aq) \rightarrow 3SO_4^{2-}(aq) + Cl^-(aq)$$
$$\underbrace{6I^-(aq) + 6H^+(aq)}_{\text{acidified KI solution}} + ClO_3^-(aq) \rightarrow 3H_2O(l) + Cl^-(aq) + 3I_2(s)$$

Like all other oxidizing agents, the chlorates(V) act as electron acceptors, the essential change being:

$$ClO_3^-(aq) + 6H^+(aq) + 6e^- \rightarrow Cl^-(aq) + 3H_2O(l)$$

When heated with concentrated hydrochloric acid, potassium chlorate(V) oxidizes it to yield a mixture of *chlorine* and *chlorine dioxide*, a dangerously explosive bright yellow gaseous mixture.

$$8ClO_3^-(s) + 24H^+(conc.aq.) + 16Cl^-(conc.aq.) \rightarrow 9Cl_2(g) + 6ClO_2(g) + 12H_2O(l)$$

For the reaction between potassium chlorate(V) and concentrated sulphuric acid, see *chlorine dioxide*, p. 381.

If heated carefully at 620 K, potassium chlorate(V) first melts and then forms *chloride* and *chlorate*(VII) by disproportionation. Four chlorine atoms in the + 5 oxidation state become one in the − 1 state and three in the + 7 state.

$$4ClO_2^-(s) \rightarrow Cl^-(s) + 3ClO_4^-(s)$$

At higher temperature, *oxygen* is evolved.

$$3ClO_4^-(s) \rightarrow 3Cl^-(s) + 6O_2(g)$$

The whole of this change corresponds to the reaction:

$$2ClO_3^-(s) \rightarrow 2Cl^-(s) + 3O_2(g)$$

This used to be the usual laboratory preparation of oxygen (p. 275). The reaction is catalysed by manganese(IV) oxide and occurs rapidly at about 500 K.

Sodium chlorate(V) is manufactured for use as a weed-killer on garden paths. It operates by sterilizing the soil. In the absence of soil bacteria, weeds cannot grow.

Chloric(V) acid can be prepared in aqueous solution by the action of barium chlorate(V) with an equimolar proportion of sulphuric acid in dilute solution.

$$Ba(ClO_3)_2(aq) + H_2SO_4(aq) \rightarrow BaSO_4(s)\downarrow + 2HClO_3(aq)$$

Above 40 per cent concentration (and at any concentration if heated), the acid decomposes by the reaction:

$$3HClO_3(aq) \rightarrow HClO_4(aq) + 2ClO_2(g) + H_2O(l)$$

Chloric(VII) acid (perchloric acid) and chlorates(VII)

If potassium chlorate(V) is heated for some time at 620 K, it will be substantially converted to the *chloride* and *chlorate*(VII).

$$4ClO_2^-(s) \rightarrow Cl^-(s) + 3ClO_4^-(s)$$

The product is then boiled with about ten times its mass of water. On cooling, potassium chlorate(VII) separates, being only sparingly soluble in water. When purified and distilled *under reduced pressure* (2000 N m^{-2}, about 15 mm Hg) with concentrated sulphuric acid, potassium chlorate(VII) yields a hydrate of chloric(VII) acid, $HClO_4.H_2O$, as distillate. The pure acid is a colourless, fuming liquid. It decomposes explosively when heated and, sometimes, merely after standing for some days. It ignites wood, paper and charcoal on contact.

Potassium chlorate(VII), $KClO_4$, is manufactured in the following way. Sodium chlorate(V) solution is electrolysed and undergoes anodic oxidation.

$$ClO_3^-(aq) + H_2O(l) - 2e^- \rightarrow ClO_4^-(aq) + 2H^+(aq)$$

The solution is then treated with potassium chloride which precipitates the sparingly soluble potassium chlorate(VII). It is used in the explosives industry. So is ammonium chlorate(VII), which is made in a corresponding way. The chlorate(VII) ion is much more stable than the chlorate(V) ion.

Chloric(VII) *acid as a test for the potassium ion,* K^+

Potassium chlorate(VII) is only sparingly soluble in water and practically insoluble in 50 per cent aqueous ethanol. To detect the potassium ion, K^+, in a solution in the presence of sodium ion, Na^+, alcohol is added, followed by some 20 per cent chloric(VII) acid. If K^+ is present, a white crystalline precipitate of potassium chlorate(VII) separates out. This test is reliable only if NH_4^+, Rb^+, and Cs^+ are absent, because the chlorates(VII) of these cations are also sparingly soluble.

Bromic(I) acid (hypobromous acid), HBrO, and its salts

A solution containing bromic(I) acid can be made by the action of cold bromine water on mercury(II) oxide.

$$HgO(s) + H_2O(l) + 2Br_2(aq) \rightarrow HgBr_2(s) + 2HOBr(aq)$$

The acid is unstable. A solution containing bromate(I) can be made by the addition of bromine water to cold, aqueous caustic alkali.

$$2OH^-(aq) + Br_2(l) \rightarrow Br^-(aq) + OBr^-(aq) + H_2O(l)$$

Bromic(V) acid, $HBrO_3$, and bromates(V) are made by methods corresponding to those used for chloric(V) acids and chlorates(V). Bromic (VII) acid (perbromic acid) and bromates(VII) have only very recently been prepared.

Three extremely unstable oxides of bromine have been prepared. They are not important materials.

Iodic(V) acid, HIO_3, and iodine(V) oxide (iodine pentoxide), I_2O_5

Iodic(V) acid is usually prepared by heating iodine under reflux with concentrated nitric acid, preferably with a current of carbon dioxide passing to carry off oxides of nitrogen.

$$I_2(s) + 10HNO_3(\text{conc.aq.}) \rightarrow 2HIO_3(aq) + 10NO_2(g) + 4H_2O(l)$$

On cooling, iodic(V) acid crystallizes as a white solid and can be filtered off, washed and dried. When heated to red heat, it loses the elements of water and leaves iodine(V) oxide, a white solid.

$$2HIO_3(s) \rightarrow H_2O(l) + I_2O_5(s)$$

This is the only stable halogen oxide. Iodic(V) acid is also made by the action of chlorine on a suspension of iodine in water.

$$I_2(s) + 5Cl_2(g) + 6H_2O(l) \rightarrow 2HIO_3(aq) + 10HCl(aq)$$

Iodic(V) acid is a strong oxidizing agent. The following are examples of it oxidizing behaviour:

(1) *With hydrogen sulphide.*

$$H_2S(g) \rightleftharpoons 2H^+(aq) + S^{2-}(aq)$$
$$5S^{2-}(aq) + 12H^+(aq) + 2IO_3^-(aq) \rightarrow 5S(s) + 6H_2O(l) + I_2(s)$$

(2) *With sulphur dioxide.*

$$SO_2(g) + H_2O(l) \rightleftharpoons H_2SO_3(aq) \rightleftharpoons 2H^+(aq) + SO_3^{2-}(aq)$$
$$2H^+(aq) + 5SO_3^{2-}(aq) + 2IO_3^-(aq) \rightarrow 5SO_4^{2-}(aq) + H_2O(l) + I_2(s)$$

(3) *With hydriodic acid (acidified* KI *solution).*

$$5I^-(aq) + IO_3^-(aq) + 6H^+(aq) \rightarrow 3H_2O(l) + 3I_2(s)$$

The constitution of iodic(V) acid is uncertain. If forms a series of acid iodates(V) such as $KIO_3.HIO_3$ and $KIO_3.2HIO_3$. The iodates(V) resemble the chlorates(V) in a general way, but have higher decomposition temperatures. The preparation of potassium iodide and iodate(V) was described on p. 362.

Metallic characteristics in iodine

The compound, HIO, which would correspond to chloric(I) acid, appears to operate also as *iodine hydroxide*, IOH. It is a weak electrolyte, amphoteric in character. This corresponds to the general tendency of the heavier atoms of a given group to become more electropositive.

Iodine appears able to ionize partially to two positive ions, I^+ and I^{3+}. The former produces salts such as ICI and INO_3. The latter produces salts such as IPO_4, $I(C_2H_3O_2)_3$ and $I(NO_3)_3$. The 'oxides' of iodine, I_2O_4 and I_4O_9, appear to be salt-like in character. I_2O_4 may be considered as *basic iodine iodate*(V), $IO^+.IO_3^-$, while I_4O_9 is *normal iodine iodate*(V), $I^{3+}.(IO_3^-)_3$. In solution in ethanol iodine appears to ionize as:

$$2I_2 \rightleftharpoons 3I^- + I^{3+}$$

The addition of ethanolic silver nitrate solution to this precipitates silver iodide and leaves a solution of iodine trinitrate.

$$3AgNO_3 + I^{3+}.3I^- \rightarrow 3AgI + I^{3+}.(NO_3^-)_3$$

Interhalogen compounds

About a dozen interhalogen compounds are known. They fall into four groups, with molecular formulae AB, AB_3, AB_5 and AB_7, where A represents one atom of the less electronegative, and B one atom of the more electronegative, halogen present. Type AB includes *iodine monochloride* ICl, and IBr, BrCl, ClF, and BrF (all of which are named correspondingly). Iodine monochloride can be produced by mixing equimolecular proportions of the two halogens and this method is general for the type, though the reactions may be incomplete. Iodine monochloride can also be produced (in solution) by mixing potassium iodide and iodate(V) in concentrated hydrochloric acid. This provides a method for estimating iodide ion.

$$IO_3^-(aq) + 6H^+ + 3Cl^-(aq) + 2I^-(aq) \rightarrow 3ICl(aq) + 3H_2O(l)$$

Type AB_3 includes *chlorine trifluoride*, ClF_3, and BrF_3, and ICl_3. Chlorine trifluoride is prepared by mixing fluorine with chlorine in appropriate volumes.

$$7F_2(g) + 5Cl_2(g) \rightarrow 8ClF(g) + 2ClF_3(g)$$

The product is cooled to about 190 K when the trifluoride (boiling point 284 K) condenses and the monofluoride (boiling point 172 K) remains gaseous. Liquid chlorine trifluoride is pale green and extremely reactive.

Iodine trichloride, ICl_3, can be made by the direct combination of its elements; or, in solution in concentrated hydrochloric acid, by mixing potassium iodide and iodate(V) in that solvent.

$$I^-(aq) + 2IO_3^-(aq) + 12H^+(\text{conc.aq.}) + 12Cl^-(aq) \rightarrow 3ICl_3(aq) + 3Cl^-(aq) + 6H_2O(l)$$

It forms yellow crystals, which sublime below 273 K yielding the monochloride and chlorine.

The type AB_5 includes the pentahalides, BrF_5 and IF_5. The former is prepared (with BrF_3) by passing bromine and fluorine through a copper tube at 470 K. The two can be separated by fractional distillation under reduced pressure. BrF_5 is a liquid, boiling at 314 K at 1 atm. Iodine pentafluoride is best prepared by the action between silver fluoride and iodine at red heat.

$$5AgF(s) + 3I_2(g) \rightarrow IF_5(g) + 5AgI(s)$$

The type AB_7 has only one representative, IF_7. This is the only binary compound in which a co-ordination number of 7 is shown. The small size of the fluorine atom is an important factor in its formation. Iodine heptafluoride is formed by direct action between the pentafluoride and fluorine at 550–560 K. It is normally a colourless gas, which forms crystals melting (under slight pressure) at 278 K.

Polyhalides

Iodine is well known to be almost insoluble in water, but readily soluble in a concentrated solution of potassium iodide. This occurs because the iodine participates in a complex triiodide ion.

$$I^-(aq) + I_2(s) \rightleftharpoons I_3^-(aq)$$

The iodine is so loosely held as to operate, for purposes of reaction, as free iodine, e.g. it can be titrated by sodium thiosulphate solution. Other polyiodide ions are known up to I_9^-. Mixed halogen anions are also formed, as in compounds such as $K^+.ICl_2^-$, $NH_4^+.IBr_2^-$, $K^+.(ClIBr)^-$ and $Cs^+.(FIBr)^-$.

Comparison of the properties of the commoner halogens

	Chlorine	*Bromine*	*Iodine*
Relative atomic mass	35.45	79.90	126.9
State	Gas	Liquid	Solid
Colour of vapour	Yellowish-green	Reddish-brown	Violet
Melting point	172 K	266 K	387 K
Boiling point	238 K	332 K	457 K
Density ($g\ cm^{-3}$)	1.33 (liquid)	3.12 (liquid)	4.93 (solid)
Solubility at 288 K (g/100 g water)	0.82	3.5	0.015

(*continued*)

	Chlorine	*Bromine*	*Iodine*
Combination with hydrogen	Explosive in sunlight	Combines on heating	Does not combine readily
Bleaching action	Vigorous bleacher	Mild bleacher	Will not bleach
Preparation	Action of concentrated hydrochloric acid on crystalline potassium manganate(VII)	By heating a bromide with manganese(IV) oxide and concentrated sulphuric acid	In a manner similar to bromine, using an iodide
Silver salt	White Insoluble in water and nitric acid Soluble in ammonia	Very pale yellow Insoluble in water and nitric acid Slightly soluble in ammonia	Yellow Insoluble in water and nitric acid Insoluble in ammonia
Displacing action on halides in aqueous solution	Displaces bromine and iodine	Displaces iodine	Does not displace the other halogens

Questions

1. Give labelled sketch and equation to show the laboratory preparation, from sodium chloride, of reasonably pure, dry chlorine gas. Briefly mention the chief industrial source and mode of storage of this gas. How, and in what conditions, does chlorine react with (a) the element hydrogen, (b) turpentine, (c) potassium hydroxide, (d) copper, (e) water?

2. How is bromine usually prepared in the laboratory? Outline the industrial extraction of this element from sea water. How, and in what conditions, does bromine react with (a) hydrogen, (b) sodium hydroxide, (c) hydrogen sulphide, (d) potassium iodide?

3. How may iodine be prepared in the laboratory from potassium iodide? Give an account of the chemistry involved in the extraction of iodine as a by-product from Chile saltpetre. How is the element purified? How, and in what conditions, does iodine react with (a) hydrogen, (b) potassium hydroxide, (c) sodium thiosulphate?

4. Demonstrate that the elements chlorine, bromine and iodine show close chemical resemblance by giving an account of their behaviour (a) with hydrogen, (b) in producing silver salts, (c) as oxidizing agents, (d) with caustic alkalis. In what respects is fluorine not a typical halogen element?

5. Explain the following: (a) if a few grams of iodine are added to a moderate amount of water, most of the iodine is left undissolved; addition of potassium iodide will produce a brown solution, (b) the addition of a little acidified bleaching powder to starch-KI solution produces an intense blue coloration, (c) passage of hydrogen sulphide through bromine water produces a colourless solution containing a white or pale yellow precipitate, (d) addition of silver nitrate solution to common salt solution produces a curdy white precipitate; excess of ammonia causes the liquid to become clear.

6. Write an essay on the chlorides of the elements sodium, magnesium, aluminium, silicon, phosphorus and sulphur. You may like to consider their composition, preparation, physical nature and their reactions with water. You should also try to relate these considerations to such properties of the atoms as size and electronic structure.

Describe how you would determine the formula of one of these chlorides in the laboratory, if you were given the relative atomic mass of the parent element. (L.)

7. (a) Fluorine and its compounds often have properties noticeably different from those of chlorine and other halogens. Discuss the following, relating the differences where possible to the data given below.

(i) Chlorine gas can be prepared from chlorides by 'chemical' methods but fluorine gas has to be prepared by electrolysis.

(ii) The vapour pressures of aluminium fluoride, chloride, and bromide reach a value of one atmosphere at 1564 K, 696 K, and 530 K respectively.

(iii) The pH of an aqueous solution of sodium fluoride is greater than 7 while that of a similar solution of sodium chloride is 7.

Size of ions/nm F^- 0.133; Cl^- 0.181; Br^- 0.196

Standard electrode potentials/V $F_2(g)\,2F^-(aq)$ $+2.87$

$Cl_2(aq)\,2Cl^-(aq)$ $+1.36$

$Br_2(aq)\,2Br^-(aq)$ $+1.09$

The dissociation constant of hydrofluoric acid is 5.6×10^{-4} mol dm^{-3}.

(b) Aqueous copper(II) sulphate solution is blue in colour; when aqueous potassium fluoride is added, a green *precipitate* is formed but, when aqueous potassium chloride is added instead, a bright green *solution* is formed. What do you think is happening in the two cases? (L.)

8. Comment on the following statements.

(a) The hydrides of chlorine, bromine, and iodine dissolved in water are strong acids, and each forms only one potassium salt; hydrogen fluoride forms a weaker acid, and forms both potassium fluoride and potassium hydrogen difluoride (KHF_2).

(b) When chlorine is dissolved in cold sodium hydroxide solution and acidified silver nitrate solution added, only one half of the chlorine which has dissolved is precipitated as silver chloride. When the sodium hydroxide solution is hot, up to five-sixths of the chlorine can be thus precipitated.

(c) Sulphuric acid is a weaker acid than hydrochloric acid, but hydrogen chloride is evolved when concentrated sulphuric acid is added to sodium chloride.

(d) Bromine reacts rapidly with hex-1-ene (C_6H_{12}) in the dark, but light is necessary for its reaction with the isomer cyclohexane. (L.)

9. It is said that the chemistry of fluorine and its compounds differs markedly from that of the other halogens. Discuss this statement by reference to:

(a) the reactions of the halogens with hydrogen and with sodium hydroxide solutions,

(b) the acidity of aqueous solutions of the hydrogen halides,

(c) the solubility of the halides,

(d) the oxidizing properties of the halogens. (J.M.B.)

10. *Outline* the chemistry of an industrial process in which chlorine is one of the important products. (N.B. Detailed diagrams of industrial plant are not required.) Describe the action of the reagents listed below on (i) sodium chloride, (ii) sodium bromide, and (iii) sodium iodide, giving equations and explanations.

(a) Concentrated sulphuric acid is added separately to each of the solids (i), (ii), and (iii) and the mixture warmed.
(b) To aqueous solutions of (i), (ii) and (iii) aqueous silver nitrate is added, followed by aqueous ammonia.
(c) To aqueous solutions of (i), (ii) and (iii) chlorine water is added followed by tetrachloromethane (carbon tetrachloride); the mixture is then shaken and allowed to settle. (A.E.B.)

11

The d-block elements

This chapter deals with a group of elements which are both vitally important for all our industrial activities and of very great interest from the point of view of theory.

The chapter is divided into three sections. The first (which is very brief) consists of summaries of the main properties of the first 'transition series', Sc → Zn; the second section deals with complexes; and the third gives details of the chemistry of the first transition series and also of the elements silver, cadmium, and mercury.

Section 1 Properties of the d-block elements summarized

One definition of a transition element is *an element which forms some compounds in which there is an incomplete sub-level of d-electrons*. This definition would exclude scandium and zinc. These two elements differ from the others in the first row of the d-block in possessing only one common oxidation state. However, they are included here in order to complete the series of ten elements which corresponds to the filling of the 3d sub-level.

The d-block elements are all metals, and generally have the usual physical properties of metals. They are often called the *transition metals*. Many of their ions are coloured (see p. 402) and/or paramagnetic (see p. 401). A large number of transition elements and their compounds are used as catalysts in industrial processes (see e.g. p. 216 and p. 331). Whether the catalytic action occurs through surface adsorption or by formation of unstable intermediates, the ability of d-block elements to change their oxidation states is presumably involved. (For theories of catalysis, see *Advanced Level Physical Chemistry*, p. 265.)

General properties of the first transition series, Sc → Zn

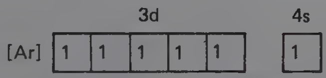
(1) *Electronic configurations*

[Only the 3d and 4s sub-levels are shown in the table; all these elements possess the *argon core*: $1s^22s^22p^63s^23p^6$.]

Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Configuration (for unexcited atoms)	$3d^14s^2$	$3d^24s^2$	$3d^34s^2$	$3d^54s^1$	$3d^54s^2$	$3d^64s^2$	$3d^74s^2$	$3d^84s^2$	$3d^{10}4s^1$	$3d^{10}4s^2$

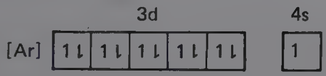
Notice the anomalous behaviour of chromium and copper. This is caused by the extra stability of the 3d sub-level (with its *five* orbitals) when it is either exactly half full or when it is completely full.

So, for chromium, the configuration in the *ground state* (i.e. when the atom is unexcited) is:

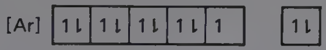


and not:

For copper, the configuration is:



rather than



(2) *Atomic radii*

Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Atomic radius (nm)	0.144	0.132	0.122	0.117	0.117	0.116	0.116	0.115	0.117	0.125

Because no new electron levels are being occupied as the series is traversed from Sc → Zn, the atomic radii only vary slightly, particularly after titanium. Because the atoms are so similar in size, these elements form many alloys with one another: e.g. brass (p. 457), 'cupronickel' (p. 458), and steels with different properties and uses (p. 435).

These elements also form many *interstitial* 'compounds'. These are *non-stoichiometric*, i.e. there is no fixed whole number ratio between the numbers of each kind of atom in the substance. Such materials are formed when elements with small atoms, e.g. H, B, C, and N, occupy the *interstices* in the crystal lattice of a metal (see *Advanced Level Physical Chemistry*, p. 90). Many of these materials are important in industry; all steels, for example, contain interstitial carbon.

(3) *Oxidation states*

Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Oxidation states (other than zero). The important ones are in bold type.					**+7**					
				+6	+6	+6				
			+5	+5	+5	+5				
		+4	+4	+4	**+4**	+4	+4	+4		
	+3	+3	+3	**+3**	+3	**+3**	**+3**	**+3**	+3	
		+2	+2	+2	**+2**	**+2**	**+2**	+2	**+2**	**+2**
				+1					**+1**	

It is important to know the common oxidation states of the more frequently met with elements, such as iron, copper, chromium and manganese. The detailed chemistry of their oxidation states is discussed in the final section of this chapter. The zero oxidation state in compounds is encountered in the carbonyls (p. 157), e.g. $Ni(CO)_4$.

In general, the compounds of these metals in their higher oxidation states are *covalent*, and act as *oxidizing agents*. The higher oxides are *acidic*. For example, chromium(III) oxide (p. 414) is an ordinary, basic metal oxide; chromium(VI) oxide (p. 416) melts at a low temperature, is soluble in propanone (acetone), ignites ethanol on contact, and reacts with sodium hydroxide to form sodium chromate(VI).

(4) *Melting and boiling points*

Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Melting, point (K)	1813	1948	2173	2163	1513	1808	1765	1726	1356	693
Boiling point (K)	3000	3530	3270	2755	2370	3270	3170	3000	2868	1180

The melting and boiling points of the transition elements are generally much higher than those of the s-block elements. When the d sub-level is completely filled, the boiling points and melting points are low. The elements Zn, Cd, and Hg are much more volatile than the other members of their transition series.

(5) *Ionization energies*

Ionization energies ($kJ\ mol^{-1}$)					*(All values positive)*					
Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
First	632	661	648	653	716	762	757	736	745	908
Second	1240	1310	1370	1590	1510	1560	1640	1750	1960	1730
Third	2390	2720	2870	2990	3250	2960	3230	3390	3550	3828

Nuclear charge increases across a period. The outer electrons of the d-block elements are therefore more firmly attracted to the nucleus than are those of the s-block; the first ionization energies are therefore higher. Nonetheless the ionization energies are relatively low, so that these elements form cations fairly easily.

A and B sub-Groups

Earlier forms of the Periodic Table linked the s-block and p-block elements with the d-block elements as A and B sub-Groups. For example, the alkali metals were Group IA, and the coinage metals (Cu, Ag, Au) Group IB; Cr, Mo, W were Group VIA, and O, S, Se, Te, and Po were Group VIB. For a brief discussion of these relationships, see p. 15.

Section 2 Complexes

The compounds considered in this section will mostly be discussed in more detail under the heading of the appropriate metal later in the chapter.

Complexes should not be confused with *double salts*. Double salts, such as the *alums* (see p. 126) and ammonium iron(II) sulphate, show all the reactions of their constituent ions when in solution. For example, a solution of ammonium iron(II) sulphate shows the reactions characteristic of NH_4^+, Fe^{2+}, and SO_4^{2-} ions. Double salts can normally be made by mixing hot, concentrated solutions of the individual salts (e.g. $FeSO_4$ and $(NH_4)_2SO_4$) in the appropriate molar ratios and allowing crystals to form on cooling, perhaps after some evaporation.

Complexes, on the other hand, dissociate in water into a *complex ion* together with, normally, a simple ion; e.g. potassium hexacyanoferrate(II):

$$K_4[Fe(CN)_6](s) + aq \longrightarrow 4K^+(aq) + [Fe(CN)_6]^{4-}(aq)$$

Complexes may be *anionic*, e.g. hexacyanoferrate(II), or *cationic*, e.g. the familiar royal blue diaquatetraamminecopper(II) ion, $[(Cu(NH_3)_4(H_2O)_2]^{2+}$.

Some complex ions are very unstable with respect to their constituents, so that there is no clear dividing line between complexes and double salts. Most of the complexes which are commonly met with at this level are sufficiently stable to leave no doubt of their nature.

Detection of complex ion formation

It will be seen from the example of potassium hexacyanoferrate(II) above that, in solution, it will contain a lower concentration of ions overall than if it contained free and uncomplexed iron(II) and cyanide ions. Formation of complexes may therefore be detected by methods in which the results depend on the number of particles in solution, e.g. boiling point elevation and freezing point depression (see *Advanced Level Physical Chemistry*, pp. 133–40). The conductance of solutions depends on the concentration of free ions present; formation of a complex reduces the ionic concentration, so that conductance measurements can also give information about the presence of complexes.

Other methods of determining whether complex ion formation has occurred make use of (a) the Distribution Law (e.g. *Advanced Level Physical Chemistry* p. 177 for the copper-ammonia complex); (b) e.m.f. measurements (*Advanced Level Physical Chemistry*, p. 251), since the formation of a complex ion changes the ionic concentration in an electrochemical cell and so changes the voltage of the cell.

Stability constants

A *stability constant* is a special case of an equilibrium constant (see *Advanced Level Physical Chemistry*, p. 194 ff.) as applied to the formation of complex ions.

Consider the equilibrium:

$$M^{n+}(aq) + 2X(aq) \rightarrow [MX_2]^{n+}(aq)$$

Unfortunately, the usual symbol [ ] for a complex ion also denotes 'concentration in mol dm^{-3}' in equilibrium constant expressions. Bearing this in mind, the stability constant for the above reaction can be written:

$$K_{stab} = \frac{[MX_2{}^{n+}]}{[M^{n+}][X]^2}\ mol^{-2}\,dm^6$$

Notice that the overall units depend on the various powers attained in the numerator and denominator.

So, for example, for the tetraamminecopper(II) complex (ignoring the water molecules—strictly, the complex is $[Cu(NH_3)_4(H_2O)_2]^{2+}$):

$$Cu^{2+}(aq) + 4NH_3(aq) \rightleftharpoons [Cu(NH_3)_4]^{2+}(aq)$$

$$K_{stab} = \frac{[Cu(NH_3)_4{}^{2+}]}{[Cu^{2+}][NH_3]^4}$$

$$= 1.4 \times 10^{13}\ mol^{-4}\ dm^{12}\ at\ 298\ K$$

(The units '$mol^{-4}\ dm^{12}$' arise thus:

$$\frac{(mol\ dm^{-3})}{(mol\ dm^{-3})(mol^4\ dm^{-12})} = mol^{-4}\ dm^{12})$$

For complexes of similar structure, the greater the value of K_{stab} the more stable the complex. It is apparent from the figures below that tetracyanocopper(I) is more stable than tetraamminecopper(II), and that hexaamminecobalt(III) is more stable than hexaamminecobalt(II).

Complex ion	*Stability constant, K_{stab} at 298 K*	*Units*	$\log_{10} K_{stab}$
$[Cu(CN)_4]^{3-}$	2.0×10^{27}	$mol^{-4} dm^{12}$	27.3
$[Cu(NH_3)_4]^{2+}$	1.4×10^{13}	$mol^{-4} dm^{12}$	13.1
$[Co(NH_3)_6]^{3+}$	4.5×10^{33}	$mol^{-6} dm^{18}$	33.7
$[Co(NH_3)_6]^{2+}$	7.7×10^{4}	$mol^{-6} dm^{18}$	4.9

It is, however, difficult to compare the relative stabilities of, for example, $[Cu(CN)_4]^{3-}$ and $[Co(NH_3)_6]^{3+}$, as the concentrations of the components are raised to different powers in the equilibrium constant expression.

Two more points need to be made.

(a) If, by addition of a complexing agent to a solution of an existing complex ion, a more stable complex may be formed, the existing *ligands* (see below) will be displaced.

e.g. $[Ag(CN)_2]^-$ $K_{stab} = 1.0 \times 10^{21}\ mol^{-1}\ dm^3$
$[Ag(NH_3)_2]^+$ $K_{stab} = 1.7 \times 10^{7}\ mol^{-1}\ dm^3$

From these data it may be deduced that addition of a solution of potassium cyanide to a solution of diamminesilver(I) will result in the formation of the dicyanoargentate(I) complex, with the ammonia being displaced as ligand by the cyanide.

(b) Where the overall reaction can occur in steps, the product of the equilibrium constants for the individual steps is equal to the overall stability constant.

For example:

(i) $[Cu(H_2O)_6]^{2+}(aq) + NH_3(aq) \rightleftharpoons [Cu(NH_3)(H_2O)]^{2+}(aq)$

$K_1 = 2.0 \times 10^4\ mol^{-1}\ dm^3\ (\log_{10} K_1 = 4.3)$

(ii) $[Cu(NH_3)(H_2O)_5]^{2+}(aq) + NH_3(aq) \rightleftharpoons [Cu(NH_3)_2 \cdot (H_2O)_4]^{2+}(aq)$

$K_2 = 4.2 \times 10^3\ mol^{-1}\ dm^3\ (\log_{10} K_2 = 3.6)$

(iii) $[Cu(NH_3)_2(H_2O)_4]^{2+}(aq) + NH_3(aq) \rightleftharpoons [Cu(NH_3)_3 \cdot (H_2O)_3]^{2+}(aq)$

$K_3 = 1.0 \times 10^3\ mol^{-1}\ dm^3\ (\log_{10} K_3 = 3.0)$

(iv) $[Cu(NH_3)_3(H_2O)_3]^{2+}(aq) + NH_3(aq) \rightleftharpoons [Cu(NH_3)_4 \cdot (H_2O)_2]^{2+}(aq)$

$K_4 = 1.7 \times 10^2\ mol^{-1}\ dm^3\ (\log_{10} K_4 = 2.2)$

Overall: $[Cu(H_2O)_6]^{2+}(aq) + 4NH_3(aq) \rightleftharpoons [Cu(NH_3)_4 \cdot (H_2O)_2]^{2+}(aq)$

$$K_{stab} = K_1 \times K_2 \times K_3 \times K_4 = 1.4 \times 10^{13}\ mol^{-4}\ dm^{12}$$

$$(\log_{10} K_{stab} = \log_{10} K_1 + \log_{10} K_2 + \log_{10} K_3 + \log_{10} K_4 = 4.3 + 3.6 + 3.0 + 2.2 = 13.1)$$

Structure of complexes

A complex always contains a central metal atom or ion surrounded by oppositely charged ions or neutral molecules, which are called *ligands*. These ligands possess *lone pairs* of electrons which can be donated into the vacant orbitals of the metal atom or ion. Most common examples of complexes contain transition metals, since many of these already possess partially filled energy levels into which lone pairs may be donated. For the first transition series (Sc → Zn) it is the small difference in energy between the 3d and 4s and 4p sub-levels in the atom of the transition metal which enables easy excitation of the 3d electrons for use in bonding.

The total number of donations of lone pairs from ligands in a complex is known as the *coordination number* of the metal atom or ion.

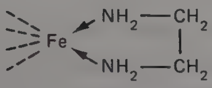
For example:

hexacyanoferrate(II) $[Fe(CN)_6]^{4-}$ coordination number 6

But also:

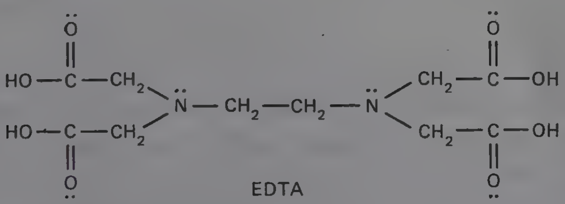
tris (ethane-1, 2-diamine) iron(II)
$[Fe(NH_2{-}CH_2CH_2{-}NH_2)_3]^{2+}$ coordination number 6

It will be noted in the second example above that the ligand ethane-1, 2-diamine can donate *two* lone pairs, so that three of these ligands attached to a metal ion still mean that it has a coordination number of six. Such ligands give extra stability to the complexes. The structures produced contain rings, e.g.



These ring structures are known as *chelates*, from the Greek word meaning 'a claw'. The ligands responsible for *chelation* are described as *polydentate*; ethane-1,2-diamine is a *bidentate* ligand (because its 'claw' has two 'teeth').

A most powerful and important chelating agent is bis[di(carboxylmethyl)amino] ethane, better known by its old name of 'ethylenediaminetetraacetic acid', EDTA. It is a *hexadentate* ligand, and can wrap itself entirely round a metal ion to form a very stable octahedrally-shaped complex. The available lone pairs are shown in the molecular structure below.



EDTA

For the first transition series (Sc → Zn), a 36-electron rule was once proposed. It will be remembered that the noble gas krypton possesses 36 electrons. Many stable complexes (e.g. $[Fe(CN)_6]^{4-}$, $Ni(CO)_4$, $[Co(NH_3)_6]^{3+}$) are found to have 36 electrons associated with the central metal atom. However, there are so many exceptions to the rule that it can be no more than an occasionally useful rule of thumb.

Naming of complexes

The International Union of Pure and Applied Chemistry (IUPAC) has developed a systematic nomenclature for complex compounds. The rules may be summarized thus:

1 The cation is always named before the anion.
2 The names of ligands precede the name of the central ion or atom.
3 The oxidation state of the central ion or atom is shown in Roman numerals in brackets immediately after its name.

4 Metals forming complex anions are given the word-ending *-ate*, whereas complex cations and neutral molecules are given their usual names.

5 The order for naming ligands is: anions, neutral molecules, cations. Within each category, if there is more than one type of ligand, they are named in alphabetical order.

The names of *anionic ligands* end in *– o*, e.g. CN^- *cyano-*, Cl^- *chloro-*, etc. Neutral ligands usually possess their normal names; important exceptions are H_2O *aqua*, NH_3 *ammine*, CO *carbonyl*. Cationic ligands end in *-ium*, e.g. $NH_2—NH_3{}^+$ *hydrazinium*.

6 When a number prefix (e.g. di-, tri-) is already included in the name of the ligand, the name of the ligand is placed in a bracket with the prefix *bis-*, *tris-*, *tetrakis-*, instead of di-, tri-, tetra-.

Examples:

$[Cu(NH_3)_4(H_2O)_2]SO_4$	Diaquatetraamminecopper(II) sulphate
$[Cr(H_2O)_6]Cl_3$	Hexaaquachromium(III) chloride
$[Co(NH_2CH_2CH_2NH_2)_3]Cl_3$	Tris (ethane-1,2-diamine)cobalt(III) chloride
$[Cu(CN)_4]^{3-}$	Tetracyanocuprate(I) ion

Metal carbonyls may be considered as complexes, with carbon monoxide molecules as the ligands and the metal atom in the oxidation state zero. The important compound nickel cabonyl, $Ni(CO)_4$ (see p. 455), may therefore be named as tetracarbonylnickel(0).

Coordination number and the shapes of complexes

Some common complexes and their shapes are shown below.

Coordination number	*Shape*	*Examples*
2	Linear	$[Ag(NH_3)_2]^+$ $[Ag(CN)_2]^-$
4	Square planar	$[Ni(CN)_4]^{2-}$ $[Pt(NH_3)_4]^{2+}$
4	Tetrahedral	$[Cd(CN)_4]^{2-}$ $[Ni(CO)_4]$

(*continued*)

Coordination number	*Shape*	*Examples*
6	Octahedral	$[Cr(H_2O)_6]^{3+}$ $[Co(NH_3)_6]^{3+}$ $[Fe(CN)_6]^{3-}$ $[Fe(CN)_6]^{4-}$
6	Distorted octahedral	$[Cu(NH_3)_4(H_2O)_2]^{2+}$

The shapes of these complexes can be discussed in terms of either *hybridization* of atomic orbitals (see *Advanced Level Physical Chemistry*, p. 81) or the mutual repulsion of electron pairs (see *Advanced Level Physical Chemistry*, p. 79). In order to explain the existence of *unpaired electrons* and hence paramagnetism in some complexes and not in others, and to account for distortions from regular shapes, the *crystal field* and *ligand field* theories have been developed. A detailed discussion of these theories is beyond the scope of this book. It is enough for our purposes to accept that ligands vary in the 'strength' of their 'field', that is, the influence that they exert on the energy levels in the complex. The order of decreasing 'field strength' for some common ligands is:

$$CN^- > NO_2^- > NH_3 \text{ and amines} > H_2O > F^- > OH^- > Cl^- > Br^- > I^-$$

Magnetic properties and colour

Before embarking on a short discussion of the more common types of complex ion, it is necessary to stress that if all the electrons in an ion or molecule are *paired*, the material is *diamagnetic*—i.e. it is essentially unresponsive to a magnetic field. If any electrons in the ion or molecule are *unpaired*, the material is *paramagnetic*—it is weakly attracted by a magnet. (*Ferromagnetic* materials respond much more strongly.) The extent of the response of a paramagnetic material to a magnetic field is proportional to the number of unpaired electrons in its molecule or ion. Measurement of the number of unpaired electrons in a particular species is, in principle, quite simple and makes use of a *Goüy balance*, which is basically a balance adapted so that the material being weighed is exposed to a strong magnetic field. Apparatus and experimental methods suitable for A Level are described in *Transition Element Chemistry* by J. N. King and P. McManus, Experimental Chemistry Series, Book 4 (London: Heinemann, 1976).

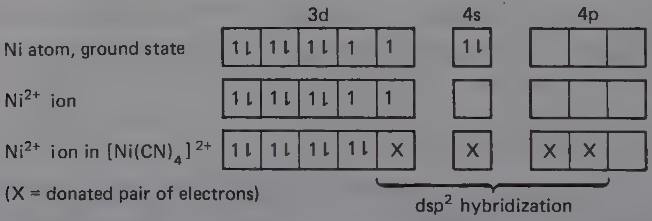
It is easy to observe that many of the complexes which contain transition metals are coloured. This is a consequence of the comparatively small differences in energy between the energy levels in the complex. The comparatively low energy radiation which is associated with visible light is sufficient to excite electrons to higher energy levels. The difference in energy between any two levels, ΔE, is equal to $h\nu$, where h is Planck's constant and ν is the frequency of radiation absorbed when electrons are excited into the upper energy level. When white light is shone on to many complexes, therefore, visible frequencies are absorbed, so that the material appears coloured.

The more common types of complex

Square planar, tetrahedral, and octahedral complexes, together with nickel carbonyl, will be briefly discussed.

Square planar complexes

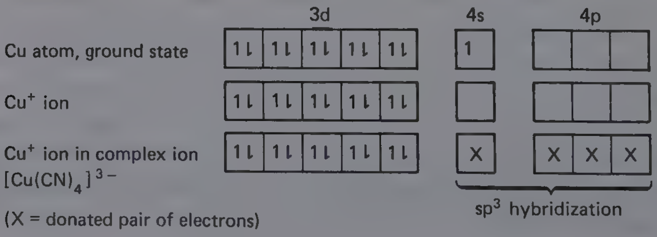
These complexes result from dsp^2 hybridization (i.e. hybridization involving one *d*, one *s*, and two *p* orbitals). An example is tetracyanonickelate(II), $[Ni(CN)_4]^{2-}$.



As there are no unpaired electrons, this complex ion is diamagnetic.

Tetrahedral complexes

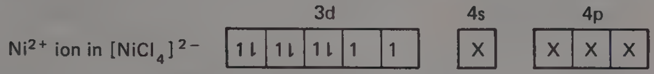
An examples is tetracyanocuprate(I), $[Cu(CN)_4]^{3-}$.



This complex has no unpaired electrons and is therefore diamagnetic.

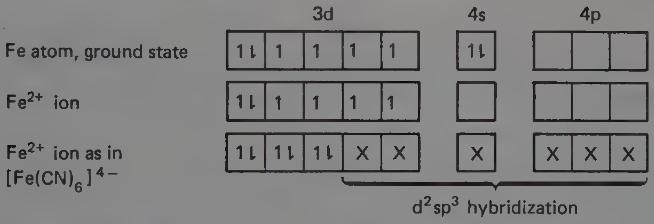
Weak ligands such as Cl^- can give paramagnetic tetrahedral complexes:

e.g.



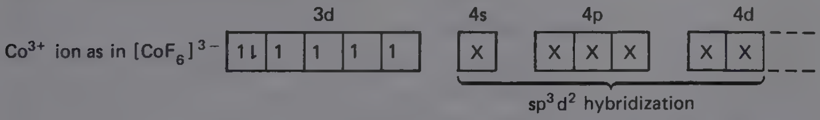
Octahedral complexes

An example is hexacyanoferrate(II), $[Fe(CN)_6]^{4-}$.



Pairing of electrons in the Fe^{2+} ion is caused by the 'strong' cyanide ligands. Only inner d orbitals are used here, so this is an *inner orbital complex*, and the hybridization is described as d^2sp^3. All six bonds in the octahedral are equivalent, and the complex has no unpaired electrons and is therefore diamagnetic. Notice that, like $[Cu(CN)_4]^{3-}$ above, this complex obeys the 36 electron 'rule' (see p. 399).

Less powerful ligands have a greater tendency to leave the electrons in the metal ion unpaired, e.g. as in $[CoF_6]^{3-}$:

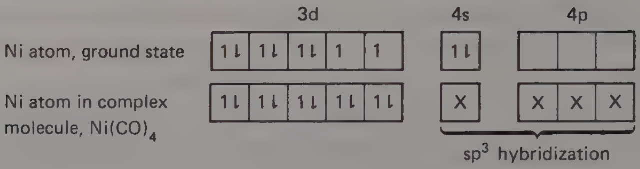


This is an sp^3d^2 or *outer orbital complex*. The unpaired electrons cause it to be paramagnetic. Measurements using a Goüy balance confirm four unpaired electrons per complex ion.

Other paramagnetic octahedral complexes include $[Ni(H_2O)_6]^{2+}$ (two unpaired electrons) and $[Fe(H_2O)_6]^{2+}$ (four unpaired electrons).

Metal carbonyls

An example of a simple metal carbonyl is tetracarbonylnickel(0), nickel carbonyl, $NI(CO)_4$ (see p. 455).



The molecule is therefore tetrahedral and diamagnetic. Notice that the 36 electron 'rule' applies here. However, the actual bonding in the molecule is not as simple as this picture would suggest. There is probably some delocalization involving the carbon monoxide molecules.

Isomerism

Isomerism occurs when the same molecular formula can represent more than one compound. It is often (and mistakenly) thought to apply to organic compounds only, but, as shown below, it is frequently met within inorganic chemistry also.

Only the main types of isomerism found in complexes are discussed here.

Hydrate isomerism

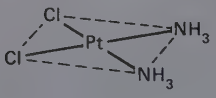
For example, there are three salts with the formula $Cr(H_2O)_6Cl_3$. They are:

$[Cr(H_2O)_6]Cl_3$	violet
$[Cr(H_2O)_5Cl]Cl_2.H_2O$	green
$[Cr(H_2O)_4Cl_2]Cl.2H_2O$	green

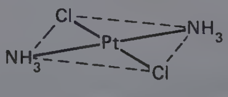
Although all three salts correspond to the same formula, they differ in their properties. The violet salt will give, when excess silver nitrate solution is added, three moles of silver chloride precipitate for each mole of the salt. The salt therefore acts as $[Cr(H_2O)_6]^{3+} + 3Cl^-$. The other salts will give either two moles or one mole of silver chloride per mole of salt, depending on how many chloride ions are free and not bonded as ligands to the chromium(III) ion.

Geometrical isomerism

This can occur in square planar or octahedral complexes. For example:



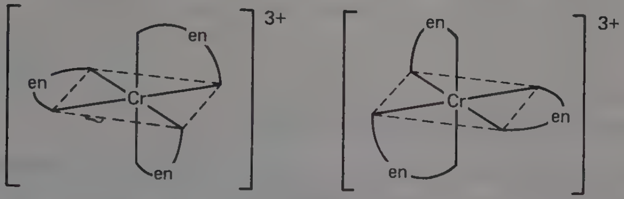
cis



trans

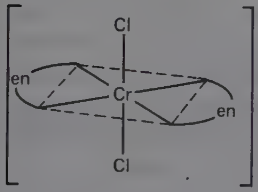
Optical isomerism

This is usually met in octahedral structures which contain bidentate ligands, e.g. tris(ethane-1, 2-diamine) chromium(III). (Ethane-1, 2-diamine is usually written *en*.)

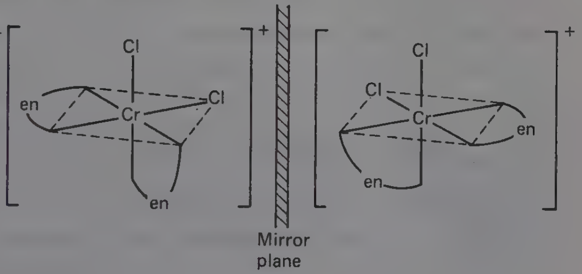


These two isomers are non-superimposable mirror images, and are therefore optically active.

An interesting combination of both optical and cis-trans isomerism is met with in the ion $[Cr(en)_2Cl_2]^+$.



trans (inactive)



Optically active *cis* isomers

Section 3 Details of the chemistry of some d-block elements

Scandium

Atomic number 21.
Electron arrangement 2.8.9.2 $(1s^2 2s^2 2p^6 3s^2 3p^6 3d^1 4s^2)$.
Scandium has only one nuclide, of mass number 45.
Relative atomic mass 44.96.
Scandium is difficult to obtain pure. In combination it is invariably in the +3 oxidation state. It possesses few of the usual properties of a transition element, and resembles aluminium and even the lanthanides rather than the other d-block elements.

Titanium

Atomic number 22.
Electron arrangement 2.8.10.2 ($1s^2 2s^2 sp^6 3s^2 3p^6 3d^2 4s^2$).
Titanium has isotopes of mass number, in order of abundance, 48, 46, 47, 49, 50.
Relative atomic mass 47.90.

Occurrence, extraction, and uses of titanium

Titanium is, after iron, the most abundant transition element in the Earth's crust (0.58 per cent). It occurs as *rutile*, a form of TiO_2, and *ilmenite*, $FeTiO_3$.

The metal is difficult and expensive to extract. Direct reduction of TiO_2 with carbon or carbon monoxide is not possible. The usual commercial process is the *Kroll method*. The rutile ore is crushed and purified and mixed with powdered coke. The mixture is heated to red heat and a stream of chlorine is passed through a fluidized bed of the material. Under these conditions titanium(IV) chloride is formed. This is a volatile liquid (b.p. 409 K at 1 atm) and can be purified by fractional distillation. Reduction of the chloride to the metal is carried out using molten magnesium at about 1100 K in a specially-constructed steel crucible. An atmosphere of argon surrounds the reactants.

$$TiCl_4(g) + 2Mg(l) \longrightarrow Ti(s) + 2MgCl_2(l) \quad \Delta H = -540\ \mathrm{kJ\ mol^{-1}}$$

As the reduction occurs at a temperature well below the melting point of titanium, a spongy mass of the metal is obtained. Magnesium and magnesium chloride are volatilized off *in vacuo* at about 1300 K. The pure metal is made by heating the powdered titanium sponge in an arc furnace under an atmosphere of argon or helium. The arc is struck between the metal powder and a consumable compressed titanium sponge cathode.

Titanium is more difficult to use than is steel, because it readily takes up oxygen and nitrogen. These harden the metal but also make it much more brittle. Its strength, low density, low thermal expansion and resistance to corrosion have meant that it is used in supersonic aircraft, and in various military applications where expense is no object.

Properties of titanium

Titanium has the usual silvery metallic appearance. Its density is 4.54 g cm^{-3}, and it melts at 1948 K. Heating with non-metals possessing small atoms (B, C, N, O) tends to give non-stoichiometric interstitial compounds. Titanium is most unusual in that when a piece is fractured at room temperature in oxygen at high pressure, the metal ignites and even ingots will burn completely.

Titanium is generally quite resistant to chemical attack, but dissolves readily in cold, moderately concentrated sulphuric acid to give titanium(III) sulphate.

$$2Ti(s) + 6H_2SO_4(aq) \rightarrow Ti_2(SO_4)_3(aq) + 3H_2O(l) + 6SO_2(g)$$

Compounds of titanium

Titanium forms compounds in which it shows oxidation states of +2, +3, and +4, of which the +2 state is uncommon and unstable. In the +4 state, the titanium atom has lost the two 3d and two 4s electrons; it therefore has no unpaired electrons, and the compounds are neither coloured nor paramagnetic. Titanium in the +3 state still has one electron in the 3d sub-level, and because of this unpaired electron the compounds of titanium(III) are coloured and paramagnetic.

Compounds of titanium in the +2 oxidation state.

Titanium(II) chloride can be made by heating titanium(IV) chloride with titanium metal at about 1200 K. It disproportionates on standing to re-form $TiCl_4$ and the metal.

$$TiCl_4(l) + Ti(s) \rightleftharpoons 2TiCl_2(s)$$

A few other titanium(II) compounds, including TiO, are known. Titanium(II) is oxidized at once by water, so it has no aqueous solution chemistry.

Compounds of titanium in the +3 oxidation state

Anhydrous titanium(III) chloride can be made by reduction of $TiCl_4$ with hydrogen at about 800 K. There are violet and brown forms. The violet solid $TiCl_3.6H_2O$ can be crystallized from aqueous solution. Titanium(III) ions can also be formed by reaction of the metal with dilute acid in the absence of air, or by reduction of aqueous titanium salts, e.g. by zinc and hydrochloric acid. Aqueous solutions of titanium(III) are mildly reducing; $Ti^{3+}(aq)$ is rapidly oxidized by air, and the solutions must be kept in an inert atmosphere. It has been used in redox volumetric analysis, and to reduce organic nitro-compounds (RNO_2) to primary amines (RNH_2).

Compounds of titanium in the +4 oxidation state

As stated above, titanium(IV) compounds do not show the usual properties of compounds of the transition metals; they resemble compounds of the heavier elements in Group IV. In earlier forms of the Periodic Table, titanium is placed in Group IVA (see *Advanced Level Physical Chemistry*, p. 60).

Titanium(IV) oxide (titanium dioxide), TiO_2

The most common of the three crystalline forms of TiO_2 which are found in nature is *rutile*. Titanium(IV) oxide is exceptionally stable, non-toxic, opaque, and brilliantly white. It is therefore much used in white paint.

The ion $Ti^{4+}(aq)$ does not exist. Evidence for the 'titanyl' ion TiO^{2+} is limited, and it is probable that structurally more complicated ions are present. Anhydrous TiO_2 dissolves with difficulty in hot concentrated sulphuric acid. It is not soluble in aqueous alkali, but gives the so-called 'titanates' with fused alkalis. The anion formed is not $TiO_3{}^{2-}$; its structure is in doubt. These reactions show the amphoteric nature of TiO_2.

Titanium(IV) chloride, $TiCl_4$

This compound is made as described above in the method for extracting titanium from rutile. It is a covalent colourless liquid, b.p. 409 K at 1 atm. It is rapidly hydrolysed by water and fumes in air.

$$TiCl_4(l) + 2H_2O(l) \longrightarrow TiO_2(s) + 4H_2O(l)$$

It dissolves in concentrated hydrochloric acid to give the complex hexachlorotitanate(IV), $[TiCl_6]^{2-}$ (cf. the behaviour of lead(IV) chloride, p. 204).

$$TiCl_4(l) + 2Cl^-(\text{conc. aq.}) \longrightarrow [TiCl_6]^{2-}(aq)$$

A mixture of trimethylaluminium, $(CH_3)_3Al$, and titanium(IV) chloride was developed by Ziegler and Natta as a catalyst for the low-pressure polymerization of ethene, propene, and other alkenes to give materials such as high-density Polythene.

The other titanium(IV) halides, TiF_4, $TiBr_4$, and TiI_4 are known.

Vanadium

Atomic number 23.
Electron arrangement 2.8.11.2 ($1s^2 2s^2 2p^6 3s^2 3p^6 3d^3 4s^2$).
Vanadium has isotopes of mass number, in order of abundance, 51 (present to 99.8 per cent) and 50.
Relative atomic mass 50.94.

Occurrence, extraction, and uses of vanadium

Although vanadium is found widely distributed in the Earth's crust there are few commercially useful ores. *Vanadinite*, $Pb_5(VO_4)_3Cl$, is mined in Peru. The ore is treated in a complex series of reactions to give vanadium(V) oxide, V_2O_5. This is then reduced by heating with calcium, using calcium as a flux.

$$V_2O_5(s) + 5Ca(l) \longrightarrow 5CaO(s) + 2V(l)$$

The pure metal is very difficult to obtain; it is normally produced as *ferrovanadium*, which contains 40–90 per cent of vanadium. The main use of vanadium is making steels for high-speed machine tools.

Properties of vanadium

Vanadium is a silvery metal, density 5.96 g cm^{-3}, m.p. about 2170 K at 1 atm. It combines rather more readily with small-atomed elements than does titanium (see above). It dissolves in oxidizing acids, but is otherwise fairly resistant to corrosion.

Compounds of vanadium

The +4 oxidation state of vanadium is the most stable under normal conditions. The +5 state is also important, and the +2 and +3 states can also be obtained fairly readily. As usual with transition elements, the covalent character of the compounds increases with increasing oxidation number. Vanadium(II) oxide, VO, is ionic and basic; vanadium(III) oxide, V_2O_3, shows mainly ionic and basic properties; vanadium(IV) oxide, VO_2, is largely covalent with amphoteric properties; vanadium(V) oxide, V_2O_5, is covalent and essentially acidic in nature.

All four oxidation states of vanadium can be observed in the aqueous species formed when a solution of ammonium vanadate(V) is treated with dilute sulphuric acid and zinc metal.

Species	$VO_2^+(aq) \rightarrow$	$VO^{2+}(aq) \rightarrow$	$[V(H_2O)_6]^{3+}(aq) \rightarrow$	$[V(H_2O)_6]^{2+}(aq)$
Oxidation state	$+5$	$+4$	$+3$	$+2$
Colour	colourless	blue	green	lilac

The rather delightful sequence of colour changes in this reaction can be used as an analytical test for vanadium, if the metal is present in the $+5$ oxidation state.

Vanadium in the +2 and +3 oxidation states

These oxidation states do not give rise to important compounds. Vanadium(II) ions can be obtained in aqueous solution as above, by reduction of the higher oxidation states with zinc and acid. Vanadium(II) is easily oxidized by air. Vanadium(III) ion in aqueous solution is also a reducing agent and is oxidized by air to the $+4$ state. Both VO and V_2O_3 are black solids with basic properties.

Vanadium in the +4 oxidation state

Under normal conditions this is the most stable oxidation state of vanadium. It is formed by oxidation of vanadium(III) or reduction of vanadium(V). The blue vanadium(IV) species in aqueous solution is often written as $VO^{2+}(aq)$ for simplicity, but is more probably $[VO(H_2O)_5]^{2+}(aq)$, an essentially octahedral complex with oxygen as one of the ligands. The oxide, VO_2, is a dark blue solid. It is amphoteric. The reaction with alkalis is complicated. Vanadium(IV) chloride, VCl_4, is a red-brown covalent liquid. The molecule has a tetrahedral structure.

Vanadium in the +5 oxidation state

Vanadium(V) is a strong oxidizing agent. The characteristic cationic vanadium(V) species in aqueous solution is VO_2^+, usually in acid solution. The equation for its reduction to vanadium(IV), as VO^{2+}, is given below.

$$VO_2^+(aq) + 2H^+(aq) + e^- \rightarrow VO^{2+}(aq) + H_2O(l) \quad E^\ominus = +1.0\ V$$

The reader should appreciate that a positive $E^\ominus$ value indicates that the equation as written proceeds from left to right; the more positive the value the more the equilibrium position favours the right hand side. A discussion of redox potentials will be found in *Advanced Level Physical Chemistry*, p. 251 ff.

The only important compound of vanadium(V) is vanadium(V) oxide (vanadium pentoxide), V_2O_5. It is a red brown solid. It is amphoteric, but with definite acidic properties. It can be made by heating vanadium in oxygen (although the reaction is not complete) or by heating ammonium vanadate(V):

$$2NH_4VO_3(s) \rightarrow V_2O_5(s) + 2NH_3(g) + H_2O(g)$$

Vanadium(V) oxide was widely used as a catalyst in the manufacture of sulphuric acid (see p. 333). Because vanadium(V) is so strongly oxidizing, the only stable vanadium(V) halide is VF_5. It is a white solid, which melts and boils easily and is easily hydrolysed.

Chromium

Atomic number 24.
Electron arrangement 2.8.13.1 ($1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$).
Chromium has isotopes of mass numbers, in order of abundance, 52, 53, 50, 54.
Relative atomic mass 52.00.

Occurrence, extraction, and uses of chromium

The only important ore of chromium is *chromite* or *chrome iron ore*, $FeCr_2O_4$ or $FeO.Cr_2O_3$. Some lead chromate(VI), $PbCrO_4$, also occurs in nature as *crocoisite*.

Chromium is extracted as follows.

(1) *The thermit process with aluminium*

Chromium(III) oxide, Cr_2O_3, is mixed with powdered aluminium (in the proportion of 3 parts of Cr_2O_3 to 1 part of Al). The mixture is 'fired' by a piece of burning magnesium ribbon inserted into sodium peroxide. This is hot enough to start the reaction at one point. It is exothermic enough to spread through the material in a violent process.

$$Cr_2O_3(s) + 2Al(s) \rightarrow Al_2O_3(s) + 2Cr(l) \qquad \Delta H = -470\ \text{kJ mol}^{-1}$$

If done in a crucible of suitable size, the reaction yields molten chromium at the bottom of the crucible. As used in industry, this is known as the Goldschmit process and yields chromium of about 99 per cent purity.

(2) *The electrolytic process*

This process is used chiefly in electroplating of steel parts to improve their appearance and to protect them from rusting. The steel is plated first with copper or nickel (or both), as chromium does not deposit well directly on to steel. The object to be plated is then made the cathode in a plating bath which usually contains chromium in the + 6 and + 3 states, e.g. CrO_3 and $Cr_2(SO_4)_3$, with sulphuric acid present. The temperature (usually about 310 K) and current density have to be carefully controlled. Chromium is then deposited in a coherent, hard layer with a bright, bluish-white appearance. Lead anodes are usual.

At the cathode: $Cr^{3+}(aq) + 3e^- \rightarrow Cr(s)\downarrow$

(3) *Carbon reduction process*

This process is used to prepare alloys of iron and chromium which can be applied to metallurgical uses. Chromite is heated with carbon in the electric furance, giving the reaction:

$$FeCr_2O_4(s) + 4C(s) \rightarrow Fe(l) + 2Cr(l) + 4CO(g)$$

The product is known as *ferrochrome*, and contains chromium (about 70 per cent), iron and a certain proportion of carbon.

Uses of chromium

(a) *In electroplating.* This use of chromium has already been mentioned in (2) above.

(b) *As a constituent of alloys.* Alloys of nickel and chromium, containing about 20 per cent of chromium, are used as electrical resistances in electric fires, heaters, etc. They resist oxidation to a marked extent even at red heat. Chromium is also a constituent of acid-resisting alloys. Chromium is an important constituent of *stainless steel*, which usually contains about 13 per cent of chromium and 1 per cent of nickel, in addition to iron. It also occurs, with tungsten, vanadium, and iron, in high-speed cutting tools.

Properties of chromium

Chromium is a bluish-white metal, which can be highly polished. It is hard; if containing carbon, it can be almost as hard as diamond.

The melting-point of chromium is 2163 K. Its chemical properties are as follows.

1. *With air.* Chromium is unaffected by air at ordinary temperature. If heated, it oxidizes superficially to green *chromium*(III) *oxide*, Cr_2O_3. It burns well in oxygen but only if the temperature reaches about 2300 K.

2. *With acids.* Chromium is attacked by dilute hydrochloric and sulphuric acids, slowly in the cold and more rapidly when heated. It forms *blue* solutions of the corresponding chromium(II) salts.

$$Cr(s) + 2H^+(aq) \rightarrow Cr^{2+}(aq) + 2H_2O(l) + H_2(g)$$

These turn to *green* chromium(III) salts in air by oxidation.

$$4Cr^{2+}(aq) + 4H^+(aq) + O_2(g) \rightarrow 4Cr^{3+}(aq) + 2H_2O(l)$$

Hot, concentrated sulphuric acid attacks chromium in the usual way. to give chromium(III) sulphate and *sulphur dioxide.*

$$2Cr(s) + 6H_2SO_4(l) \rightarrow Cr_2(SO_4)_3(aq) + 6H_2O(l) + 3SO_2(g)$$

Dilute nitric acid does not attack pure chromium; concentrated nitric acid renders chromium *passive.*

3. *With chlorine.* Chromium combines with dry chlorine when heated to produce *chromium*(III) *chloride.*

$$2Cr(s) + 3Cl_2(g) \rightarrow 2CrCl_3(s)$$

Compounds of Chromium

The three common oxidation states of chromium are + 2, + 3, and + 6. The + 3 state is normally the most stable. As with the other transition elements, the covalent nature of the compounds and the acidity of the oxides increases with increasing oxidation number.

Chromium in the +2 oxidation state

These compounds are not particularly important. Chromium(II) oxide, CrO, is a black solid. The corresponding hydroxide is yellow and is precipitated by the action of aqueous caustic alkali on a chromium(II) salt (chloride or sulphate) in solution.

$$Cr^{2+}(aq) + 2OH^-(aq) \rightarrow Cr(OH)_2(s)$$

Chromium(II) chloride can be prepared by heating chromium in dry hydrogen chloride.

$$Cr(s) + 2HCl(g) \rightarrow Cr(Cl)_2(s) + H_2(g)$$

Chromium(II) compounds are vigorous reducing agents, i.e. electron donors, by the change:

$$Cr^{2+}(aq) - e^- \rightarrow Cr^{3+}(aq) \qquad E^\ominus = +0.41\ V$$

Chromium(III) compounds are formed. Oxygen of the air and all the common oxidizing agents bring about this oxidation, e.g.:

$$2Cr^{2+}(aq) + Cl_2(g) \rightarrow 2Cr^{3+}(aq) + 2Cl^-(aq)$$

Chromium in the +3 oxidation state

In aqueous solution, chromium(III) is the most stable oxidation state of chromium: it also forms the most stable of the tripositive ions given by the transition elements. The ion $[Cr(H_2O)_6]^{3+}$ is violet in colour and octahedral in shape; it is often green because of partial replacement of water molecules by other ligands. Stable octahedral complexes of Cr(III), both cations and anions, are common (e.g. $[Cr(NH_3)_6]^{3+}$, $[CrCl_6]^{3-}$).

Chromium(III) oxide (chromic oxide), Cr_2O_3

Chromium(III) oxide may be made by heating ammonium dichromate(VI).

$$(NH_4)_2Cr_2O_7(s) \rightarrow Cr_2O_3(s) + N_2(g) + 4H_2O(g)$$

The reaction is quite violent and spreads rapidly through the material. Chromium(III) oxide is a bulky, green powder. It is unusually stable and resists reduction by both hydrogen and carbon monoxide. It is *amphoteric*, with basic character predominating. The basic character is shown by the reaction of the oxide with acids to form *chromium*(III) salts, though, after heating, the oxide dissolves only slowly in dilute acids.

$$Cr_2O_3(s) + 6HCl(aq) \rightarrow 2CrCl_3(aq) + 3H_2O(l)$$

Acidic character is shown when the oxide forms *chromates*(III) with excess caustic alkali.

$$Cr_2O_3(s) + 3H_2O(l) + 6OH^-(aq) \rightarrow 2[Cr(OH)_6]^{3-}(aq)$$

Chromium(III) oxide is used industrially as a pigment and as an abrasive.

‘Chromium(III) hydroxide’, hydrated chromium(III) oxide, $Cr_2O_3.xH_2O$

This compound can be obtained as a green, gelatinous precipitate by the addition of ammonium chloride solution and ammonia to a solution of a chromium(III) salt. This precipitation puts chromium into Group III of the usual analytical tables, with Al and Fe.

The fresh precipitate reacts readily with dilute acids to form the hydrated chromium(III) cation.

$$Cr_2O_3.xH_2O(s) \underset{OH^-(aq)}{\overset{H^+(aq)}{\rightleftharpoons}} [Cr(H_2O)_6]^{3+}(aq)$$

In concentrated alkali, the soluble hydroxo-complex $[Cr(OH)_6]^{3-}$ is formed (see above). In the presence of caustic alkali, hydrated chromium(III) oxide is oxidized by chlorine, bromine, or hydrogen peroxide to the corresponding chromate(VI). The solution turns yellow as chromium(VI) is formed. This reaction is used to identify chromium in Group III of the analysis tables. The presence of both alkali and hydrogen peroxide can be ensured by adding sodium peroxide to the chromium(III) solution. A further test is to add hydrogen peroxide to the acidified dichromate(VI) solution. The blue colour of the highly unstable ‘peroxochromic acid’ is seen. This material is often formulated as CrO_5. It is stabilized by solution in an ether layer placed on top of the aqueous reaction mixture.

Chromium(III) chloride, $CrCl_3$

Chromium(III) chloride can be prepared anhydrous by passing *dry* chlorine over heated chromium metal, or over an intimate mixture of chromium(III) oxide and carbon at red heat.

$$Cr_2O_3(s) + 3C(s) + 3Cl_2(g) \rightarrow 2CrCl_3(s) + 3CO(g)$$

Hydrated chromium(III) chloride exists in three isomeric forms (see p. 404).

Chromium in the +6 oxidation state

The configuration of chromium in the ground state shows the stability of the half-filled d sub-shell: $[Ar]3d^54s^1$. Chromium(VI) is formed when all six outer electrons are lost. It is, however, so strong an oxidizing agent that it can only be found combined with the two most electronegative elements, fluorine and oxygen.

Chromium(VI) oxide (chromium trioxide, chromic anhydride), CrO_3

Chromium(VI) oxide forms dark red crystals. They are precipitated in long needles when a saturated solution of potassium dichromate(VI) is acidified by concentrated sulphuric acid and then cooled.

$$Cr_2O_7^{2-}(\text{sat. aq.}) + 2H^+(\text{conc. aq.}) \rightarrow 2CrO_3(s) + H_2O(l)$$

The crystals can be filtered using glass wool (not paper because the acid would attack it). To purify, the crystals are washed with concentrated nitric acid, which removes sulphates and non-volatile sulphuric acid, and dried in a current of warm air. Chromium(VI) oxide melts at 463 K and decomposes at about 520 K.

$$4CrO_3(l) \rightarrow 2Cr_2O_3(s) + 3O_2(g)$$

It is soluble in propanone or ethanoic acid. This solution is used as an oxidizing agent in organic chemistry. Its volatility and solubility in organic solvents show chromium(VI) oxide to be a covalent compound.

It is a very vigorous oxidizing agent. Ethanol burns on contact with it at ordinary temperature and it chars paper. As an oxidizing reagent, chromium(VI) oxide is usually used in the form of a solution of potassium dichromate(VI) acidified by sulphuric acid. Its reactions are considered in connection with potassium dichromate(VI) a little later.

Chromium(VI) oxide is deliquescent and very soluble in water, with which it forms several *chromic*(VI) *acids*. The two most important of these are chromic(VI) acid, H_2CrO_4, and dichromic(VI) acid, $H_2Cr_2O_7$. Salts corresponding to the acids $H_2Cr_3O_{10}$ and $H_2Cr_4O_{13}$ are also known. All these 'polychromic acids' are converted to H_2CrO_4 by alkali,

e.g. $$Cr_2O_7^{2-}(aq) + 2OH^-(aq) \rightarrow 2CrO_4^{2-}(aq) + H_2O(l)$$

The CrO_4^{2-} ion is tetrahedral in shape. The $Cr_2O_7^{2-}$ ion is essentially a double tetrahedron, joined by a shared oxygen atom. In aqueous solution a low pH favours the orange dichromate(VI) ion, and a high pH the yellow chromate(VI) ion.

$$2CrO_4^{2-}(aq) + 2H^+(aq) \underset{OH^-(aq)}{\overset{H^+(aq)}{\rightleftharpoons}} Cr_2O_7^{2-}(aq) + H_2O(l)$$

Chromic(VI) acid has never been isolated but many salts of it are known. They are usually *yellow* in colour. The chromates(VI) of the alkali metals and calcium and magnesium are soluble; the rest are insoluble. They are usually *yellow* in colour.

Sodium chromate(VI), $Na_2CrO_4 . 10H_2O$

Sodium chromate(VI) is made by roasting powdered chromite with anhydrous sodium carbonate and calcium oxide in good contact with air.

$$\begin{aligned}4Fe(CrO_2)_2(s) + 8Na_2CO_3(s) + 7O_2(g) \rightarrow 2Fe_2O_3(s) &+ 8Na_2CrO_4(s)\\ &+ 8CO_2(g)\end{aligned}$$

The calcium oxide prevents fusion of the mass. The sodium chromate(VI) is extracted by hot water and crystallized. Sodium chromate(VI) is deliquescent. Addition of acid gives the dichromate(VI).

Potassium chromate(VI), K_2CrO_4

Potassium chromate(VI) is made by using potassium carbonate, instead of sodium carbonate, in the process described immediately above. It is non-deliquescent, so is preferred to the sodium salt as a laboratory reagent. Potassium chromate(VI) crystallizes in lemon-yellow crystals. It is quite soluble in water (57.1 g in 100 g water at 273 K.)

There are several insoluble chromates(VI), which can be precipitated by adding potassium chromate(VI) solution to a solution of a salt of the corresponding metal. Examples are:

$$\begin{aligned}Ba^{2+}(aq) + CrO_4{}^{2-}(aq) &\rightarrow BaCrO_4(s)\\ Sr^{2+}(aq) + CrO_4{}^{2-}(aq) &\rightarrow SrCrO_4(s)\\ Pb^{2+}(aq) + CrO_4{}^{2-}(aq) &\rightarrow PbCrO_4(s)\end{aligned}$$

All the above chromates(VI) are yellow in colour; lead chromate(VI) is known as *chrome yellow*. Silver chromate(VI) is, however, brick red and is precipitated by the addition of potassium chromate(VI) solution to silver nitrate solution.

$$2Ag^+(aq) + CrO_4{}^{2-}(aq) \rightarrow Ag_2CrO_4(s)$$

The precipitation of a trace of this salt, *after* completion of the precipitation of white silver chloride, explains the use of potassium chromate(VI) as an indicator in titration of chloride by silver nitrate. The solubility product of silver chloride at room temperature is $[Ag^+][Cl^-] = 1 \times 10^{-10}\ mol^2\ dm^{-6}$. That is, at the moment when chloride precipitation is complete, $[Ag^+] = 1 \times 10^{-5}\ mol\ dm^{-3}$. This concentration of silver ion should be just at the point of precipitating silver chromate(VI). Since the solubility product of this salt is $1 \times 10^{-12}\ mol^2\ dm^{-6}$, the position should be:

$$[Ag^+]^2[CrO_4{}^{2-}] = 1 \times 10^{-12}\,mol^2\,dm^{-6} \text{ at the end-point.}$$

i.e. $(1 \times 10^{-5})^2[CrO_4{}^{2-}] = 1 \times 10^{-12}$

i.e. $[CrO_4{}^{2-}] = 1 \times 10^{-2}\,mol\,dm^{-3}$

That is, at the end point, the concentration of potassium chromate(VI) should be about 0.01 mol dm^{-3}.

The dichromates(VI)

Sodium dichromate(VI), $Na_2Cr_2O_7.2H_2O$

Sodium dichromate(VI) is prepared by first making a solution of sodium chromate(VI) as described above. The solution is then acidified by sulphuric acid. This produces the dichromate(VI):

$$2CrO_4{}^{2-}(aq) + 2H^+(aq) \rightarrow Cr_2O_7{}^{2-}(aq) + H_2O(l)$$

At the concentrations employed, sodium sulphate crystallizes out (as the decahydrate) and the solution is decanted away from it and concentrated by evaporation. After filtration (from more crystallized sodium sulphate) and cooling, sodium dichromate(VI) crystallizes out. It forms reddish, deliquescent crystals, which are very soluble in water (109 g in 100 g water at 288 K).

Potassium dichromate(VI) $K_2Cr_2O_7$

Potassium dichromate(VI) can be made by mixing hot, almost saturated solutions of sodium dichromate(VI) and potassium chloride. Sodium chloride precipitates from the hot liquid, is filtered off and potassium dichromate(VI) crystallizes as the solution cools.

$$2KCl(conc.aq.) + Na_2Cr_2O_7(conc.aq.) \rightarrow 2NaCl(s) + K_2Cr_2O_7(conc.aq.)$$

It forms reddish crystals which are much less soluble than the sodium salt (10 g in 100 g water at 288 K).

(1) *Oxidizing actions of the dichromates*(VI)

The dichromates(VI) act as powerful oxidizing agents. They are usually used in solution, acidified by sulphuric acid, which is equivalent to the use of *chromic acid*(VI). Like all oxidizing agents, the dichromates(VI) act as electron acceptors, by the essential reaction:

$$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$$

The electrons are supplied by a reducing agent. The *orange colour* (of the ion, $Cr_2O_7^{2-}$) is replaced by the *green* of the hydrated chromium(III) ion.

Examples of the oxidizing actions are:

(a) *Conversion of iron*(II), *in acidified solution, to iron*(III).

$$6Fe^{2+}(aq) + Cr_2O_7^{2-}(aq) + 14H^+(aq) \rightarrow 6Fe^{3+}(aq) + 2Cr^{3+}(aq) + 7H_2O(l)$$

The green to yellow colour change of iron(II) to iron(III) will not be visible against the more marked colour change of $Cr_2O_7^{2-}$ (orange) to Cr^{3+} (green). This reaction can be used in titration of iron(II) in solution, but it is necessary to use a suitable redox indicator, such as diphenylamine, to give a sharp end point.

(b) *Liberation of iodine from acidified potassium iodide solution.*

$$6I^-(aq) + Cr_2O_7^{2-}(aq) + 14H^+(aq) \rightarrow 2Cr^{3+}(aq) + 7H_2O(l) + 3I_2(s)$$

With excess of potassium iodide present, the solution will be turned *brown*, as the liberated iodine remains dissolved.

(c) *Oxidation of sulphite ion to sulphate ion.*

The sulphite ion is derived from sulphurous acid (i.e. a solution of sulphur dioxide) or from a sulphite.

$$3SO_3^{2-}(aq) + Cr_2O_7^{2-}(aq) + 8H^+(aq) \rightarrow 3SO_4^{2-}(aq) + 4H_2O(l) + 2Cr^{3+}(aq)$$

If sulphur dioxide is bubbled into acidified potassium dichromate(VI) solution, the ions present after reaction are in the correct proportions for 'chrome alum', $K^+Cr^{3+}(SO_4^{2-})_2.12H_2O$, to be crystallized from the resulting solution.

(d) *Oxidation of hydrogen sulphide to sulphur, which precipitates.*

$$H_2S(aq) \rightleftharpoons 2H^+(aq) + S^{2-}(aq)$$

$$3S^{2-}(aq) + Cr_2O_7^{2-}(aq) + 14H^+(aq) \rightarrow 3S(s) + 2Cr^{3+}(aq) + 7H_2O(l)$$

(e) *Oxidation of ethanol to ethanal and ethanoic acid.*

$$\underset{\text{ethanol}}{3CH_3CH_2OH(aq)} + Cr_2O_7^{2-}(aq) + 8H^+(aq) \rightarrow \underset{\text{ethanal}}{3CH_3CHO(aq)} + 2Cr^{3+}(aq) + 7H_2O(l)$$

$$3CH_3CHO(aq) + Cr_2O_7^{2-}(aq) + 8H^+(aq) \rightarrow 3\underset{\text{ethanoic acid}}{CH_3COOH}(aq) + 2Cr^{3+}(aq) + 4H_2O(l)$$

This reaction is characteristic of primary alcohols. If required, the ethanal (acetaldehyde) formed may be distilled off in moderate yield. The green solution may also, after evaporation and crystallization, give chrome alum.

(2) *Action of heat on dichromates*(VI)

The dichromates(VI) of sodium and potassium decompose when strongly heated to produce the corresponding *chromate*(VI), *chromium*(III) *oxide*, and *oxygen.*

$$4Na_2Cr_2O_7 \rightarrow 4Na_2CrO_4(s) + 2Cr_2O_3(s) + 3O_2(g)$$

Ammonium dichromate(VI) gives a violent reaction which spreads rapidly, with sparking, through the mass of solid if started by heat at one point. A bulky green mass of *chromium*(VI) *oxide* is left, with *nitrogen* and *steam* liberated.

$$(NH_4^+)_2.Cr_2O_7^{2-}(s) \rightarrow Cr_2O_3(s) + 4H_2O(l) + N_2(g)$$

Chromium(VI) dichloride dioxide (chromyl chloride), CrO_2Cl_2

Chromium(VI) dichloride dioxide is a dark red liquid, boiling point 389 K at 1 atm. It can be distilled from a mixture of potassium dichromate(VI) concentrated sulphuric acid and sodium chloride.

$$K_2Cr_2O_7(s) + 4NaCl(s) + 3H_2SO_4(l) \rightarrow 2CrO_2Cl_2(g) + 3H_2O(l) + K_2SO_4(aq) + 2Na_2SO_4(aq)$$

A better preparation is obtained by dissolving chromium(VI) oxide in slight excess of concentrated hydrochloric acid and adding concentrated sulphuric acid slowly with cooling. Chromium(VI) dichloride dioxide is obtained as a lower layer and can be separated by a tap-funnel.

$$CrO_3(s) + 2Cl^-(\text{conc. aq.}) + 2H^+(\text{conc. aq.}) \rightarrow CrO_2Cl_2(l) + H_2O(l)$$

Chromium(VI) dichloride dioxide is analogous to sulphur dichloride dioxide (sulphuryl chloride), SO_2Cl_2. It is hydrolysed by water to a *chromic*(VI) *acid* and *hydrochloric acid.*

$$CrO_2Cl_2(l) + 2H_2O(l) \rightarrow H_2CrO_4(aq) + 2HCl(aq), \quad \text{or, possibly,}$$
$$2CrO_2Cl_2(l) + 3H_2O(l) \rightarrow H_2Cr_2O_7(aq) + 4HCl(aq)$$

Uses of chromates(VI) and dichromates(VI)

Although these materials are very toxic, they are widely used as oxidizing agents in industry, e.g. for tanning leather. Some chromates(VI) are used as pigments, e.g. lead chromate(VI), $PbCrO_4$, 'chrome yellow'.

Detection of chromium

A method for this is given on p. 302.

Manganese

Atomic number 25.
Electron arrangement 2.8.13.2($1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^2$).
Manganese has only one kind of atom, of mass number 55.
Relative atomic mass 54.94.

Occurrence, extraction, and uses of manganese

The most important ore of manganese is *pyrolusite*, MnO_2. This contains a theoretical 63.2% of the metal; good samples of the ore contain about 50 per cent. Other oxides occur as *hausmannite*, Mn_3O_4, and *braunite*, Mn_2O_3. The carbonate, *dialogite*, $MnCO_3$, often occurs with siderite, $FeCO_3$. *Manganese blend*, MnS, is also known.

Manganese is extracted as follows.

1. *By a thermit process* (*Goldschmidt*). Manganese(IV) oxide is too violent in this reaction so it is first heated to redness to convert it to the oxide, Mn_3O_4.

$$3MnO_2(s) \rightarrow Mn_3O_4(s) + O_2(g)$$

This oxide is mixed with aluminium powder and the mixture is 'fired' by burning magnesium ribbon in contact with sodium peroxide or barium peroxide.

$$3Mn_3O_4(s) + 8Al(s) \rightarrow 4Al_2O_3(s) + 9Mn(l)$$

The manganese can be purified by distillation *in vacuo*.

(2) *By reduction with carbon.* This method has two disadvantages. It requires very high temperatures and so the use of the electric furnace. Further, the manganese produced is liable to contain a good deal of carbon (up to 7 per cent), though the use of less than the theoretical

amount of carbon reduces this figure.

$$MnO_2(s) + 2C(s) \rightarrow Mn(l) + 2CO(g)$$

As a variation on this method of reduction, mixed manganese and iron ores may be smelted together in a blast furnace process, which then gives an alloy of iron and manganese. A typical ferromanganese alloy may contain about 80 per cent Mn, up to 7 per cent C, and the rest Fe.

Uses of manganese

Manganese is chiefly employed in alloying with steel. Most samples of steel and cast iron contain up to 0.5 per cent of manganese. A 'manganese steel' will contain about 1.5 per cent of manganese or more. Manganese steels with the lower range of manganese content are used in general engineering work. If the percentage of manganese is increased to about 12 per cent, very hard steel is obtained suitable for railway cross-overs and similar uses where severe wear is encountered.

Manganese is also used in non-ferrous alloys, such as alloy for electrical resistance (Cu, 86%; Ni, 4%; Mn, 10%), manganese bronze (3.5% Mn) and light alloys of which aluminium is the chief metal. It increases mechanical strength and resistance to corrosion.

Properties of manganese

Pure manganese is silvery white, but is usually yellowish or reddish in industrial samples. It has a density of 7.4 g cm^{-3} and melts at 1510 K. It is brittle and very hard.

Chemical properties of manganese

1. *With air.* Pure manganese is not attacked by air at room temperature but, if finely divided, burns when heated strongly.

$$3Mn(s) + 2O_2(g) \rightarrow Mn_3O_4(s)$$

2. *With water and dilute acids.* Pure manganese does not attack water or steam up to 770 K. The dilute acids, hydrochloric and sulphuric, are rapidly attacked by manganese to form the corresponding *manganese*(II) *salt* and hydrogen.

$$Mn(s) + 2H^+(aq) \rightarrow Mn^{2+}(aq) + H_2(g)$$

Nitric acid yields oxides of nitrogen. Ordinary concentrated nitric acid gives mainly *nitrogen dioxide.*

3. *With non-metals.* Manganese combines with *nitrogen* at white heat to form *nitrides*, Mn_5N_2 and Mn_3N_2. It also combines with *carbon*, at electric furnace temperatures, to form the *carbide*, Mn_3C. When heated, manganese also combines with chlorine and sulphur.

Compounds of manganese

Manganese can exist in the +2, +3, +4, +5, +6 and +7 oxidation states. In the +2 state, the two 4s electrons are lost, leaving the half-filled 3d sub-shell. This half-filled arrangement possesses some stability, so that Mn(II) is more stable than Ti, V, or Cr in the +2 state. As usual, as the oxidation number of manganese increases, there is an increase in the covalent nature of its compounds and the acidity of its oxides.

Compounds of manganese in the +2 oxidation state

As stated above, manganese(II) compounds are more resistant to oxidation than the corresponding compounds of the earlier transition elements. Manganese(II) is the most stable oxidation state of manganese under normal conditions. Powerful oxidizing agents (e.g. lead(IV) oxide, peroxodisulphate, sodium bismuthate(V)) in acidic solution may oxidize Mn(II) to Mn(VII) in the manganate(VII) (permanganate) ion, MnO_4^-.

Manganese(II) oxide, MnO

Manganese(II) oxide is obtained by heating manganese(II) carbonate, or ethanedioate (oxalate), in the absence of air.

$$MnCO_3(s) \rightarrow MnO(s) + CO_2(g)$$
$$MnC_2O_4(s) \rightarrow MnO(s) + CO(g) + CO_2(g)$$

Manganese(II) oxide is a greenish powder. It is strongly *basic* (showing manganese acting with *metallic* properties), and forms manganese(II) salts with dilute acids in the usual way.

Manganese(II) hydroxide, $Mn(OH)_2$

This compound is precipitated by the addition of aqueous caustic alkali to a solution of any soluble manganese(II) salt. It is white when pure, but rapidly turns dark brown by oxidation on exposure to air.

The brown compound is hydrated Mn_2O_3. Manganese(II) hydroxide is purely *basic*. It is not dissolved by excess caustic alkali solution.

Manganese(II) chloride, sulphate, and nitrate

These manganese(II) salts are all *pink* in colour and are made by standard methods. They are all soluble in water. The chloride and sulphate form hydrates, $MnCl_2.4H_2O$ and $MnSO_4.5H_2O$. The nitrate is unusual in leaving *manganese*(IV) *oxide* as the solid product when heated (to about 470 K):

$$Mn(NO_3)_2(s) \rightarrow MnO_2(s) + 2NO_2(g)$$

Compare $2Zn(NO_3)_2(s) \rightarrow 2ZnO(s) + 4NO_2(g) + O_2(g)$

Manganese(II) carbonate, $MnCO_3$

This compound is an insoluble reddish compound precipitated by the action of a solution of any soluble carbonate on a solution of a manganese(II) salt.

$$Mn^{2+}(aq) + CO_3{}^{2-}(aq) \rightarrow MnCO_3(s)$$

Manganese(II) sulphide, MnS

Manganese(II) sulphide is a flesh-coloured precipitate produced by passing hydrogen sulphide through a solution containing a manganese(II) salt, ammonium chloride and ammonia. This places manganese in Group IV of the usual analytical tables.

$$Mn^{2+}(aq) + S^{2-}(aq) \rightarrow MnS(s)$$

The sulphide is readily soluble in dilute mineral acid; hydrochloric acid is used in analytical tables.

$$MnS(s) + 2H^+(aq) + 2Cl^-(aq) \rightarrow H_2S(g) + Mn^{2+}(aq) + 2Cl^-(aq)$$

Compounds of manganese in the +3 oxidation state

Manganese(III) compounds are relatively uncommon. They tend to disproportionate in aqueous solution, thus:

$$2Mn^{3+}(aq) + 2H_2O(l) \rightarrow Mn^{2+}(aq) + MnO_2(s) + 4H^+(aq)$$

Manganese(III) oxide, Mn_2O_3

Manganese(III) oxide occurs as *braunite*, and can be made in the laboratory by heating manganese(IV) oxide in ammonia gas.

$$6MnO_2(s) + 2NH_3(g) \rightarrow 3Mn_2O_3(s) + 3H_2O(l) + N_2(g)$$

It is also formed by aerial oxidation of manganese(II) hydroxide (see above).

It is feebly *basic*, forming the *manganese*(III) *salts.*

Manganese(II) dimanganese(III) oxide, Mn_3O_4

This red oxide of manganese is obtained by heating any other oxide of the metal strongly in air, e.g.

$$6MnO(s) + O_2(g) \rightarrow 2Mn_3O_4(s)$$
$$3MnO_2(s) \rightarrow Mn_3O_4(s) + O_2(g)$$

It is mixed oxide; cf. Pb_3O_4, Fe_3O_4. For example, in cold, concentrated sulphuric acid, it yields manganese(II) and manganese(III) sulphates.

$$Mn_3O_4(s) + 8H^+(aq) \rightarrow Mn^{2+}(aq) + 2Mn^{3+}(aq) + 4H_2O(l)$$

Hot nitric acid, however, precipitates manganese(IV) oxide, presumably due to disproportionation of Mn(III).

$$Mn_3O_4(s) + 4H^+(aq) \rightarrow MnO_2(s) + 2Mn^{2+}(aq) + 2H_2O(l)$$

Compounds of manganese in the +4 oxidation state

The most important of these compounds is manganese(IV) oxide.

Manganese(IV) oxide, MnO_2

This compound occurs as *pyrolusite.* It is rarely prepared in the laboratory, but can be made by heating manganese(II) nitrate at about 470 K.

$$Mn(NO_3)_2(s) \rightarrow MnO_2(s) + 2NO_2(g)$$

Any remaining nitrate is extracted by boiling with dilute nitric acid and the oxide is filtered, washed and dried. It is a black powder, insoluble in water. It is non-stoichiometric (the formula MnO_2 is not exactly accurate) and amphoteric, although its reactivity towards both acids and alkalis is slight. It is not affected by dilute acids. Cold concentrated hydrochloric acid dissolves it by formation of the unstable octahedral complex $[MnCl_6]^{2-}$.

$$MnO_2(s) + 4H^+(\text{conc.aq.}) + 6Cl^-(\text{conc.aq.}) \rightarrow [MnCl_6]^{2-}(aq) + 2H_2O(l)$$

With *warm, concentrated* hydrochloric acid, manganese(IV) oxide evolves *chlorine* (not oxygen) with possible intermediate formation of $MnCl_3$ or $MnCl_4$, both of which decompose to leave manganese(II) chloride, $MnCl_2$. This is the former laboratory preparation of chlorine. (Manganese(IV) chloride has never been obtained.)

$$MnO_2(s) + 4H^+(\text{conc.aq.}) + 2Cl^-(\text{conc.aq.}) \rightarrow Mn^{2+}(aq) + 2H_2O(l) + Cl_2(g)$$

If warmed with concentrated sulphuric acid, manganese(IV) oxide yields *oxygen* and manganese(II) sulphate.

$$2MnO_2(s) + 4H^+(\text{conc.aq.}) \rightarrow 2Mn^{2+}(aq) + 2H_2O(l) + O_2(g)$$

Manganese(IV) oxide forms manganates(IV) with alkalis. These are of uncertain structure.

1. *Oxidizing action.* The conversion of warm, concentrated hydrochloric acid to chlorine (above) is an example of the oxidizing action of manganese(IV) oxide. It also oxidizes ethanedioic acid (oxalic acid) to carbon dioxide in the presence of dilute sulphuric acid and with boiling.

$$MnO_2(s) + C_2O_4{}^{2-}(aq) + 4H^+(aq) \rightarrow Mn^{2+}(aq) + 2H_2O(l) + 2CO_2(g)$$

2. *Action of heat. Use as a catalyst.* Manganese(IV) oxide liberates oxygen when strongly heated.

$$3MnO_2(s) \rightarrow Mn_3O_4(s) + O_2(g)$$

It is also used as a catalyst for the decomposition of potassium chlorate(V) by heat, and in the usual laboratory preparation of oxygen from hydrogen peroxide. For this, see p. 274.

Uses of manganese(IV) *oxide*

(a) It is used in glass-making. Its purpose is to oxidize green iron(II) silicate (impurity) in the glass to iron(III) silicate, which is much paler. Also, the slight pinkish tint from the manganese content neutralizes the colour caused by the iron salts. In pottery glaze, manganese(IV) oxide gives a purple colour, or, if in excess, black.

(b) It is used to oxidize the polarizing film of hydrogen which may appear on the anode of Leclanché cells.

(c) It is used in the manufacture of manganates(VII) and other manganese compounds. For the oxidation of MnO_2 to potassium manganate(VI), see below.

Compounds of manganese in the +5 oxidation state

These are of little importance. The manganate(V) ion, MnO_4^{3-}, is blue.

Compounds of manganese in the +6 oxidation state

Manganese(VI) oxide, MnO_3, probably does not exist. The green manganate(VI) ion, MnO_4^{2-}, is the only comparatively stable species to contain Mn(VI).

Potassium manganate(VI), K_2MnO_4

Potassium manganate(VI) is produced by fusing manganese(IV) oxide and potassium hydroxide together, with free access of air, or with the addition of a source of oxygen, such as KNO_3 or $KClO_3$. (See preparation of potassium manganate(VII), below.)

$$2MnO_2(s) + 4KOH(l) + O_2(g) \rightarrow 2K_2MnO_4(l) + 2H_2O(g)$$

Extraction of the mass with a little water gives a dark green solution of potassium manganate(VI). Dark green crystals can be obtained by evaporation at room temperature under reduced pressure. Sodium manganate(VI), Na_2MnO_4, can be made correspondingly, or by fusing manganese(IV) oxide with sodium peroxide.

$$MnO_2(s) + Na_2O_2(l) \rightarrow Na_2MnO_4(l)$$

The manganates(VI) are quite powerful oxidizing agents, acting, like all oxidizing agents, as electron acceptors.

$$MnO_4^{2-}(aq) + 2H_2O(l) + 2e^- \rightarrow MnO_2(s)\downarrow + 4OH^-(aq)$$

The manganates are stable in the presence of caustic alkali, but disproportionate in neutral or acid solution. Consequently the solution turns from dark green to purple, with a brown-black precipitate.

$$3MnO_4^{2-}(aq) + 2H_2O(l) \rightarrow 2MnO_4^-(aq) + MnO_2(s) + 4OH^-(aq)$$
$$3MnO_4^{2-}(aq) + 4H^+(aq) \rightarrow 2MnO_4^-(aq) + MnO_2(s) + 2H_2O(l)$$

Only the weakest acidity is needed; even bubbling of carbon dioxide through the solution is enough.

Compounds of manganese in the +7 oxidation state

Potassium manganate(VII) (potassium permanganate), $KMnO_4$

Potassium manganate(VII) is an important oxidizing agent. For its laboratory preparation, the following is suitable. Potassium hydroxide (10 g) and *potassium chlorate*(V) (5 g) are fused in an iron (or nickel) crucible. *Manganese*(IV) *oxide* (10 g) is gradually stirred in, with continuous heating. When the mass goes stiff, it is cooled and boiled with water (200 cm^3). Carbon dioxide (i.e. a weak acid) is passed through the solution until all trace of green colour is gone and only the purple of manganate(VII) is left. It is then filtered through glass wool, evaporated to about one-third bulk and left to cool, when potassium manganate(VII) crystallizes out. It is filtered, washed with a little cold water and allowed to dry. Potassium manganate(VII) is only moderately soluble, 6.45 g in 100 g water at 288 K. It crystallizes readily.

$$2MnO_2(s) + 2KOH(l) + KClO_3(l) \rightarrow 2KMnO_4(l) + H_2O(l) + 2KCl(l)$$

Carbon dioxide in solution serves as an acid to convert any manganate(VI) formed to manganate(VII), by disproportionation.

$$3MnO_4^{2-}(aq) + 4H^+(aq) \rightarrow 2MnO_4^-(aq) + MnO_2(s) + 2H_2O(l)$$

The industrial preparation is similar, except that potassium nitrate and air, instead of potassium chlorate(V), supply the oxygen, and the acidification is by sulphuric acid.

Sodium manganate(VII), $Na^+MnO_4^-$, is made by corresponding means, but is used in solution only, because it is difficult to crystallize. It is a constituent of *Condy's fluid*, a liquid used as a disinfectant.

Properties of potassium manganate(VII)

Potassium manganate(VII) forms dark purple crystals, with a greenish tinge in reflected light.

1. *Action of heat.* When strongly heated, potassium manganate(VII) decomposes to give the *manganate*(VI), *manganese*(IV) *oxide*, and *oxygen*.

$$2KMnO_4(s) \rightarrow K_2MnO_4(s) + MnO_2(s) + O_2(g)$$

2. *Oxidizing action. Solid* potassium manganate(VII) explodes if rubbed,

or heated, with sulphur or red phosphorus, and may ignite organic matter in similar conditions. The crystals burn if heated in hydrogen, giving potassium hydroxide and manganese(II) oxide.

$$2KMnO_4(s) + 5H_2(g) \rightarrow 2KOH(l) + 2MnO(s) + 4H_2O(l)$$

Cold, concentrated hydrochloric acid dripped on to solid potassium manganate(VII) at room temperature is oxidized rapidly to *chlorine* (see p. 355).

$$2KMnO_4(s) + 16H^+(\text{conc.aq.}) + 10Cl^-(\text{conc.aq.}) \rightarrow 2Mn^{2+}(aq) + 2K^+(aq) + 8H_2O(l) + 5Cl_2(g)$$

In solution, it is also a very vigorous oxidizing agent. Like all oxidizing agents, it acts as an electron acceptor, but shows different intensity of oxidation according to the conditions used.

Oxidation by manganate(VII) *in acidic solution*

The acid used is dilute sulphuric, because hydrochloric acid may be oxidized by the manganate(VII), and nitric acid is itself an oxidizing agent which might interfere with the action of the manganate(VII). Most of the following oxidations occur at room temperature. An exception is the oxidation of ethanedioate (oxalate), which requires a temperature of about 330 K. The rates of manganate(VII) oxidation are increased by the presence of $Mn^{2+}(aq)$ ions. Since these are among the products of the reaction in acid solution, this reaction is catalysed by a product. This effect is known as *autocatalysis.*

Potassium manganate(VII) is especially useful in redox titrations for volumetric analysis, as its own purple colour appears at the end point.

The essential behaviour of manganate(VII) in acidic conditions is represented by the equation:

$$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l) \qquad E^\ominus = +1.51\ V$$

Examples of oxidations involving potassium manganate(VII)

1. *Iron*(II) *to iron*(III).

$$Fe^{2+}(aq) \rightleftharpoons Fe^{3+}(aq) + e^-$$

Overall: $5Fe^{2+}(aq) + MnO_4^-(aq) + 8H^+(aq) \rightarrow Mn^{2+}(aq) + 4H_2O(l) + 5Fe^{3+}(aq)$

2. *Ethanedioic acid or an ethanedioate* (*in acidic solution at* 330 *K*) *to*

carbon dioxide.

$$(COO)_2^{2-}(aq) \rightleftharpoons 2CO_2(g) + 2e^-$$

Overall: $$5C_2O_4^{2-}(aq) + 2MnO_4^-(aq) + 16H^+(aq) \rightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 10CO_2(g)$$

3. *Nitrite (in acid solution) to nitrate.*

$$NO_2^-(aq) + H_2O(l) \rightleftharpoons NO_3^-(aq) + 2H^+(aq) + 2e^-$$

Overall: $$5NO_2^-(aq) + 2MnO_4^-(aq) + 6H^+(aq) \rightarrow 2Mn^{2+}(aq) + 3H_2O(aq) + 5NO_3^-(aq)$$

4. *Iodide to iodine.*

$$2I^-(aq) \rightleftharpoons I_2(s) + 2e^-$$

Overall: $$10I^-(aq) + 2MnO_4^-(aq) + 16H^+(aq) \rightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 5I_2(s)$$

5. *Hydrogen peroxide to oxygen.*

$$H_2O_2(aq) \rightleftharpoons O_2(g) + 2H^+(aq) + 2e$$

Overall: $$5H_2O_2(aq) + 2MnO_4^-(aq) + 6H^+(aq) \rightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 5O_2(g)$$

Permanganate(VII) in slightly acid solution slowly decomposes.

$$4MnO_4^-(aq) + 4H^+(aq) \rightarrow 4MnO_2(s) + 3O_2(g) + 2H_2O(l)$$

This reaction is catalysed by light, which is why the reagent is usually kept in brown glass bottles.

Oxidation by manganate(VII) *in neutral or faintly alkaline conditions*

In these conditions, manganese(IV) oxide is precipitated, the essential reaction being:

$$MnO_4^-(aq) + 2H_2O(l) + 3e^- \rightarrow MnO_2(s) + 4OH^-(aq) \qquad E^\ominus = +0.59\ V$$

A notable reaction here is the oxidation of an *iodide* to iodate(V).

$$2MnO_4^-(aq) + H_2O(l) + I^-(aq) \rightarrow 2MnO_2(s) + 2OH^-(aq) + IO_3^-(aq)$$

Contrast this with the oxidation of iodide in acidic solution to free iodine, as in (4) above.

In *strongly* alkaline solution, manganate(VII) may be reduced only to the green manganate(VI).

$$MnO_4^-(aq) + e^- \rightarrow MnO_4^{2-}(aq)$$

Alkaline manganate(VII) solutions are sometimes used in organic chemistry to oxidize alcohols to aldehydes and ketones, and to convert alkenes to 1,2-diols.

Manganic(VII) acid (permanganic acid), $HMnO_4$

Manganic(VII) acid is produced in solution by adding the calculated amount of dilute sulphuric acid to a solution of barium manganate(VII). Barium sulphate may be filtered off.

$$Ba(MnO_4)_2(aq) + 2H^+(aq) + SO_4{}^{2-}(aq) \rightarrow BaSO_4(s) + 2HMnO_4(aq)$$

Manganese(VII) oxide (manganese heptoxide), Mn_2O_7

This oxide is liberated as a reddish-brown oil if potassium manganate(VII) is added to well-cooled sulphuric acid of density 1.78 g cm^{-3}, corresponding to the composition $H_2SO_4.H_2O$.

$$2MnO_4{}^-(aq) + 2H^+(\text{conc. aq.}) \rightarrow Mn_2O_7(l) + H_2O(l)$$

The oxide is unstable and may explode if warmed.

$$2Mn_2O_7(l) \rightarrow 4MnO_2(s) + 3O_2(g)$$

It combines with water, forming manganic(VII) acid.

$$H_2O(l) + Mn_2O_7(l) \rightarrow 2HMnO_4(aq)$$

Manganese(VII) oxide is a powerful oxidizing agent and will ignite dry organic matter (like paper) on contact. The occurrence and acidity of this oxide are the chief points of resemblance manganese and chlorine. Chlorine forms a corresponding oxide, Cl_2O_7, and a corresponding chloric(VII) acid (*perchloric acid*), $HClO_4$.

Detection of manganese

(a) A little of the test material is fused with a little potassium hydroxide and potassium nitrate on porcelain. A *green* residual mass, giving a *green* solution (manganate(VI)) on the addition of a *little* water, turning *purple* (manganate(VII)) on acidification by dilute sulphuric acid, indicates manganese present.

(b) Manganese(II) ions in solution may be detected by adding nitric acid followed by solid sodium bismuthate(V), $NaBiO_3$. The purple manganate(VII) colour is observed.

Iron

Atomic number 26.
Electron arrangement 2.8.14.2 ($1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$).
Iron has isotopes of mass number, in order of abundance, 56, 54, 57, 58.
Relative atomic mass 55.85.

Occurrence

Iron is the most abundant metal, other than aluminium, in the Earth's crust. It is the fourth most abundant element. It occurs in three principal forms.

1. *As iron*(III) *oxide*, Fe_2O_3. These ores are known as *haematites.* The *red* variety, occurring in Spain and North America, is the superior type. *Brown* haematites are less pure. They are usually hydrated and contain phosphorus which is detrimental to the quality of the iron produced. They are found in England, Germany, and the USA.
2. *As the oxide*, Fe_3O_4. This is the black oxide of iron, known as *magnetite.* It is usually almost pure, and is found in Sweden and North America.
3. *As iron*(II) *carbonate*, $FeCO_3$. The purest form of this ore is *siderite* or *spathic iron ore. Clay ironstone* and *Cleveland ironstone* contain iron(II) carbonate and clay.

Iron is very widely distributed and enters, in an important manner into the activities of living organisms. It is constituent of haemoglobin, which has the function of distributing oxygen round the human body.

Extraction

Roasting in air converts hydrated or spathic ore to anhydrous iron(III) oxide. For spathic ore:

$$4FeCO_3(s) + O_2(g) \rightarrow 2Fe_2O_3(s) + 4CO_2(g)$$

Reduction in the blast furnace

The furnace (see Figure 11.1) is charged with the *ore*, *coke*, and *limestone* in weighed proportions suitable to the sample of ore. The blast furnace process is very complex, but the principal reactions are the following. Near the base of the furnace, coke burns in the air blast to produce carbon monoxide, probably by the stages:

$$C(s) + O_2(g) \rightarrow CO_2(g);\ CO_2(g) + C(s) \rightleftharpoons 2CO(g)$$

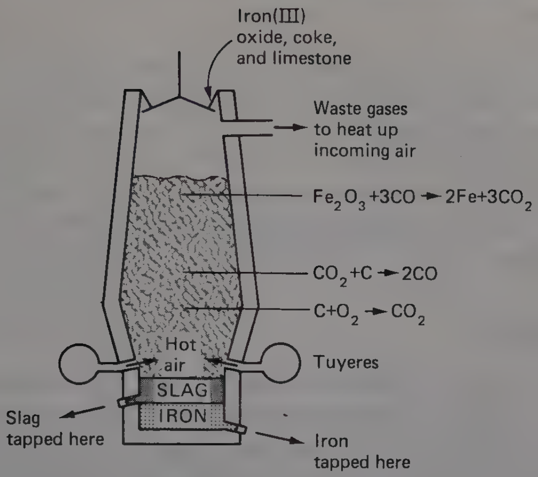


Figure 11.1

This first reaction is strongly exothermic, and the temperature is raised to about 1800 K. Near the top of the furnace, at about 900 K, the iron(III) oxide is reduced to iron as a spongy solid.

$$Fe_2O_3(s) + 3CO(g) \rightarrow 2Fe(s) + 3CO_2(g)$$

Some reduction also takes place directly by carbon.

$$Fe_2O_3(s) + 3C(s) \rightarrow 2Fe(s) + 3CO(g)$$

Function of the limestone

In the furnace, the limestone is decomposed by heat to quicklime:

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

The lime reacts with siliceous earthy materials (which would otherwise silt up the furnace) to form a fusible slag of silicates.

$$CaO(s) + SiO_2(s) \rightarrow CaSiO_3(l)$$

The iron melts as it sinks to the hotter parts of the furnace and collects molten in the well of the furnace with molten slag above it. Iron and slag are tapped off separately at intervals and the iron is allowed to solidify in moulds in wet sand. The product is *cast iron* or *pig iron*. Removal of all products as gases, slag or iron enables the furnace to continue working for many months. A typical output is 500 tonnes of iron daily. Economy of operation is secured by drying and pre-heating the air-blast.

Cast iron

This material is very impure. It may contain up to 4.5 per cent of carbon and some phosphorus, silicon, manganese, and sulphur. It is granular and very brittle, therefore not used in structures where considerable strains occur. But it has a relatively low melting point (about 1450 K) and solidifies with expansion, so can be cast. It is used in casting objects such as gas stoves and gas rings, street lamp standards, manhole covers, and railings.

Wrought iron

This is the purest form of industrial iron. It contains iron with some slag, and traces of carbon, phosphorus, sulphur, etc., from cast iron. It is really a very mild steel. To produce it, cast iron is melted on hearth lined with haematite. The carbon of the cast iron is oxidized away as carbon monoxide gas.

$$Fe_2O_3(s) + 3C(s) \rightarrow 2Fe(l) + 3CO(g)$$

Other impurities, e.g. Mn and Si, oxidize and remain as slag. The iron becomes pasty as its melting point rises with purification. It can be collected on rods and pressed under steam hammers to squeeze out the slag. Subsequent re-heating and rolling produce a characteristic fibrous structure. Wrought iron is fibrous and tough. It is also malleable and ductile, and was formerly much used as sheets and wire, and for ornamental iron work and horse-shoes. It is now replaced to a great extent by mild steel (i.e. steel of low carbon content).

Steel

The essential principle in steelmaking is to melt the iron in contact with materials which will react with and remove the impurities in the iron. The most widely used methods were the *Siemens–Martin open hearth process*, which used producer gas and a hearth lined with a basic material, and the *Bessemer Process*, which used an air blast through the molten iron.

These methods have now been largely replaced by the more efficient oxygen-blast methods, such as the *Linz–Donawitz* (*L.D.*) and *Kaldo* processes. The fundamentals of the *basic oxygen* steelmaking process are as follows.

The converter is a cylindrical vessel which can be rotated about both the horizontal and vertical axes (Figure 11.2). It is charged with

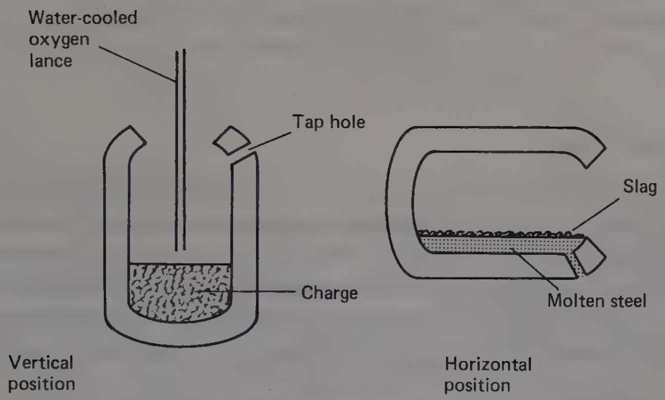


Figure 11.2 *Basic oxygen steelmaking*

scrap steel and molten iron from the blast furnace, and put in the vertical position. A jet of oxygen under pressure is delivered by a water-cooled tube placed about 60 cm above the molten metal. Carbon is oxidized and removed as carbon dioxide gas. During the blow, which lasts about 20 minutes, lime is added to remove the usual silica-based impurities, and also the non-volatile oxides (e.g. of phosphorus), as a slag. Rapid removal of impurities is helped by the convection currents set up in the molten mass. The molten metal is sampled at intervals. When the desired concentration of carbon has been reached, the blast is turned off and the converter tilted into the horizontal position so that the molten steel can be tapped off.

This process is very suitable for making low-carbon steel for rolling into sheet to make motor car bodies. The product is less brittle than basic Bessemer steel because of the absence of nitrogen in the blow.

Properties and uses of steel

The properties of steel depend on its composition and heat treatment. Very soft steel (about 0.15 per cent carbon) resembles wrought iron. As the carbon percentage rises, tensile strength increases up to the limit of 1.5 per cent carbon, and reaches a very high level. Steel of high tensile strength is used in the construction of buildings, bridges, ships, locomotives, and similar structures.

Steel for cutting tools is quenched and then tempered. *Quenching* consists of dropping red-hot steel into cold water. It is then very hard and brittle. In *tempering*, it is re-heated to a temperature between 500 and 590 K, the particular temperature chosen being determined by the intended use of the steel, e.g. 500 K for razor blades.

Many special steels have been brought into use in recent years, e.g. stainless steel for cutlery (Fe, 85%, Cr, 15%).

Properties of iron

Iron is a grey metal when pure. It has a high melting point (about 1800 K). The melting point is much depressed by impurity, e.g. carbon, so that cast iron melts at about 1450 K. The pure metal is quite soft, malleable, and ductile. Iron is highly magnetic, more so than any other element, but it ceases to be magnetic at 1042 K. The density of iron at room temperature is 7.87 g cm^{-3}. Its chemical properties are as follows:

(1) *With air or oxygen*

Iron is not affected by *dry* air or oxygen at room temperature. If heated, it combines with oxygen to give its black oxide, Fe_3O_4, iron(II) diiron(III) oxide (*triferric tetroxide*).

$$3Fe(s) + 2O_2(g) \rightarrow Fe_3O_4(s)$$

For rusting of iron, see later.

(2) *With acids*

Iron is a fairly electropositive metal and liberates hydrogen readily from warm, dilute hydrochloric and sulphuric acid. It produces the corresponding iron(II) *salt* in solution.

$$Fe(s) + 2H^+(aq) \rightarrow Fe^{2+}(aq) + H_2(g)$$

Dilute nitric acid gives a very mixed reaction for which no definite equation can be written. The products may include iron(II) and iron(III) nitrate, oxides of nitrogen, and ammonium salts. *Concentrated nitric acid* renders iron 'passive'. It produces no obvious action, but the iron is no longer attacked by dilute acids as above and does not precipitate copper from solutions of its salts. The cause of the passivity is a thin continuous player of Fe_3O_4, formed by the oxidizing action of the concentrated nitric acid. It can be removed by scratching the surface and by heating in a stream of hydrogen.

Concentrated sulphuric acid, with heat, converts iron to iron(III) *sulphate* (not iron(II) sulphate, because the acid concentrated oxidizes this salt).

$$2Fe(s) + 6H_2SO_4(l) \rightarrow Fe_2(SO_4)_3(aq) + 6H_2O(l) + 3SO_2(g)$$

Because of its comparatively strong electropositive character, iron precipitates copper from solutions of its salts.

$$Fe(s) + Cu^{2+}(aq) \rightarrow Fe^{2+}(aq) + Cu(s)$$

(3) *With non-metals*

(a) *Sulphur*. If mixed with powdered sulphur in the appropriate proportions and heated at one point, iron combines with incandescence, which spreads through the mass, to form *iron*(II) *sulphide* as a dark grey or black solid.

$$Fe(s) + S(s) \rightarrow FeS(s)$$

(b) *With chlorine and bromine*. Iron combines vigorously with dry chlorine, when heated, to form *iron*(III) *chloride* as a black sublimate.

$$2Fe(s) + 3Cl_2(g) \rightarrow 2FeCl_3(s)$$

Hydrogen chloride yields *iron*(II) *chloride* when heated with iron. See also p. 368.

$$Fe(s) + 2HCl(g) \rightarrow FeCl_2(s) + H_2(g)$$

Bromine combines rapidly with damp iron filings at ordinary temperature to form a product called *iron*(III) *bromide*, which is properly $FeBr_3$, though Fe_3Br_8 (or $FeBr_2.2FeBr_3$) is also a product.

(c) *With carbon*. At high temperatures, iron forms a carbide, Fe_3C, known as *cementite*. It plays a very important part in producing the typical properties of steel. Iron also forms compounds with silicon and phosphorus which are significant in the metallurgy of iron.

(4) *With water*

Pure iron has no action with pure water in the cold. At red heat, iron decomposes steam in a reversible reaction forming *iron*(II) *diiron*(III) *oxide* (Fe_3O_4) and *hydrogen*.

$$3Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$$

If steam is passed over red hot iron in an open tube, the hydrogen formed is continually swept away. Its concentration tends to zero; consequently, the reverse action is negligible and iron can be completely converted to its oxide.

If hydrogen is passed over the red hot oxide in an open tube, the position is reversed and the oxide can be completely reduced.

In a closed, heated container of sufficient strength, an equilibrium will be reached (provided all four materials are present). The proportions of hydrogen and steam at equilibrium depend on the temperature used.

The rusting of iron

This is a very complex subject. Important points about it are:

(a) Rusting requires the combined effects of oxygen and liquid water. Water vapour is not enough.
(b) Rusting is accelerated by the presence of most electrolytes, though it is retarded by alkalis.
(c) Completely homogeneous iron does not rust.

Ordinary iron never has a completely uniform surface. The non-uniformity may be due to impurities or to stress. Consequently, in water, it exhibits *cathodic areas* (of low electrode potential) and *anodic areas* (of high electrode potential). This gives, in effect, a shortcircuited cell showing the changes:

At anodic areas	*At cathodic areas*
$Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$	$O_2(g) + H_2O^-(l) + 4e^- \rightleftharpoons 4OH^-(aq)$
	$2H^+(aq) + 2e^- \rightarrow H_2(g)$

The electrons flow through the metal from the anodic points to the cathodic points. Obvously, if an electrolyte such as common salt is present in the water, current will flow more freely in the circuit and corrosion will be more rapid.

Reaction of the iron(II) ions from anodic areas and hydroxide ions from cathodic areas gives insoluble *iron*(II) *hydroxide.* This is oxidized rapidly by air to *hydrated iron*(III) *oxide*, which appears as rust. Rust is therefore formed as a result of a reaction in solution, rather than directly on the surface of the metal.

It will be seen from the equations above that the anodic corrosion of iron is most likely when it is out of contact with oxygen but an adjacent region is exposed to oxygen. If water is placed on clean iron or steel, corrosion will occur fastest under the centre of the drop. Iron covered with paint is out of contact with oxygen. If the paint layer is broken, the great difference in the concentrations of oxygen available to the newly-exposed iron and to the iron under the paint will mean that rusting occurs rapidly under the paint layer.

A supply of electrons to the iron will inhibit corrosion. This can be done either (as with, say, a pipeline) by giving the iron or steel object a small negative potential or, more usually, by coupling the iron with a metal more electropositive than itself. The usual metal used is *zinc*, and the process in which iron or steel objects are coated with zinc by dipping into a bath of the molten metal is known as *galvanizing*. The zinc corrodes preferentially; it acts as a *sacrificial anode*, and provides electrons to the iron, thus inhibiting the iron corrosion reaction. Usually, however, the zinc is not required to corrode in order to protect the iron; a thin coherent layer of basic carbonate forms on the zinc and protects it (see p. 470).

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$$

The protection is maintained even when the zinc layer is scratched or broken, because the zinc is anodic with respect to the iron. This is not the case, however, with *tin plate*. Here the iron or steel is coated with tin, which is less electropositive than iron. When the tin layer is scratched or otherwise penetrated, the iron becomes anodic with respect to the tin, so that the iron corrodes faster than it would if tin were not present. Tin is preferred to zinc for cans containing food and drink because zinc may dissolve to form poisonous compounds.

Other ways of protecting iron and steel depend largely on the exclusion of air by the use of oil, paint, or plastic coatings.

The compounds of iron

The usual oxidation states of iron in its compounds are +2 and +3. The electron arrangements for these states are:

		3d					4s
Iron (ground state)	Ar	↑↓	↑	↑	↑	↑	↑↓
Iron(II)	Ar	↑↓	↑	↑	↑	↑	
Iron(III)	Ar	↑	↑	↑	↑	↑	

It will be noticed that the comparative stability of the iron(III) state is associated with the half-filled 3d sub-shell. Higher, and much less stable, oxidation states of iron have been achieved, but only in anions and only under vigorous conditions. For example, hydrated iron(III) oxide (represented here as iron(III) hydroxide, $Fe(OH)_3$) reacts with chlorate(I) in concentrated alkali to give the deep red ferrate(VI) ion.

$$2Fe(OH)_3(s) + 3ClO^-(aq) + 4OH^-(aq) \rightarrow 2FeO_4{}^{2-}(aq) + 3Cl^-(aq) + 5H_2O(l)$$

Unlike the preceding d-block elements in the period, iron cannot achieve its theoretical maximum oxidation state by losing or sharing all its outer electrons.

Compounds of iron in the +2 oxidation state

Iron(II) compounds are readily oxidized by air or other oxidizing agents, particularly under neutral or alkaline conditions. In water, iron(II) is present as the hexaaquairon(II) ion, $[Fe(H_2O)_6]^{2+}(aq)$.

Iron(II) oxide, FeO

Iron(II) oxide can be made by heating iron(II) ethanedioate (ferrous oxalate) in the absence of air.

$$FeC_2O_4(s) \rightarrow FeO(s) + CO(g) + CO_2(g)$$

It is a black powder, which is rarely encountered because it oxidizes rapidly on exposure to air to give iron(III) oxide. It is a *basic* oxide, reacting readily with dilute acids to give iron(II) salts.

Iron(II) hydroxide, hydrated iron(II) oxide, '$Fe(OH)_2$'

Pure iron(II) hydroxide is white, but, as usually precipitated by the action of aqueous alkali or ammonia on a solution of an iron(II) salt, it is a dark green, gelatinous material.

$$Fe^{2+}(aq) + 2OH^-(aq) \rightarrow Fe(OH)_2(s)$$

It rapidly turns brown on exposure to air by oxidation to 'iron(III) hydroxide', hydrated iron(III) oxide, $Fe_2O_3.xH_2O$. It has *basic* properties corresponding to those of iron(II) oxide and is a strong reducing agent. Iron(II) hydroxide is a stronger base than iron(III) hydroxide. An iron(II) carbonate is formed and is quite ordinarily stable; indeed, it is found as the ore *siderite*. No iron(III) carbonate is known.

Iron(II) sulphate, $FeSO_4.7H_2O$

Iron(II) sulphate is usually prepared in the laboratory by warming iron filings (or, better, iron wire), with dilute sulphuric acid, keeping moderate excess of acid always present to avoid precipitation of basic iron(III) compounds by oxidation and hydrolysis. An atmosphere of hydrogen can be maintained by using a *bunsen valve* connected to the top of the flask: this consists of a short length of thin rubber tube with a vertical slit cut by a sharp razor blade, and blocked at the top by a piece of glass rod. Hydrogen can excape through the slit as it is produced, but air cannot enter. After filtration, the solution can be evaporated to small bulk and will yield crystals when cooled. These can be filtered, washed with slightly acidified water and dried.

$$\mathrm{Fe(s) + H_2SO_4(aq) \rightarrow FeSO_4(aq) + H_2(g)}$$

The crystals are efflorescent and oxidize on exposure to air, with formation of brown patches of basic iron(III) sulphate.

When heated, iron(II) sulphate is completely dehydrated by about 570 K and, in the absence of air, is white. The anhydrous solid decomposes on further heating to yield *sulphur dioxide*, *sulphur trioxide*, and iron(III) *oxide* (a fine reddish-brown powder, known and used as *Jeweller's Rouge*).

$$\mathrm{FeSO_4.7H_2O(s) \rightarrow FeSO_4(s) + 7H_2O(g)}$$
$$\mathrm{2FeSO_4(s) \rightarrow Fe_2O_3(s) + SO_2(g) + SO_3(g)}$$

The cooled sulphur trioxide will combine vigorously with water and form sulphuric acid.

$$\mathrm{H_2O(l) + SO_3(s) \rightarrow H_2SO_4(l)}$$

This was a very early method of making sulphuric acid.

In solution, iron(II) sulphate will absorb nitrogen oxide to form a dark brown compound. This compound is responsible for the colour in the *brown ring test* for nitrates (p. 247).

Ammonium iron(II) sulphate, $\mathrm{FeSO_4.(NH_4)_2SO_4.6H_4O}$

This compound can be made by mixing hot concentrated solutions of equimolar quantities of ammonium sulphate and iron(II) sulphate. In the case of iron(II) sulphate, the water should be first boiled out and acidified slightly by sulphuric acid to avoid oxidation and hydrolysis of the iron(II) salt. After cooling, the double salt deposits as pale green crystals, which can be purified in the usual way. They are better precipitated by adding ethanol to a concentrated aqueous solution and should then be washed with ethanol after filtration.

This salt can be obtained quite pure and has two advantages over iron(II) sulphate: (i) it is not efforescent, (ii) it is resistant to atmospheric oxidation. Consequently, it is used as a redox standard in moderately precise volumetric analysis. It is fairly soluble (20 g in 100 g water at 288 K). In solution, the constituent ions ($\mathrm{Fe^{2+}, NH_4{}^+, SO_4{}^{2-}}$) act independently.

Iron(II) chloride

Iron(II) chloride can be produced anhydrous by heating iron wire in a current of dry hydrogen chloride.

$$Fe(s) + 2HCl(g) \rightarrow FeCl_2(s) + H_2(g)$$

For suitable apparatus, see p. 367. It can be produced in solution by dissolving iron wire in warm, dilute hydrochloric acid. From solution, it can be crystallized as green $FeCl_2.4H_2O$. The anhydrous salt cannot be obtained from this hydrate by heating because of hydrolysis and oxidation. The anhydrous salt is yellow.

Iron(II) sulphide, FeS

Iron(II) sulphide is a black solid. It is manufactured by heating equimolar quantities of iron filings and sulphur. The two elements combine with incandescence and the iron(II) sulphide is usually melted and cast into plates or sticks. It is used (with moderately concentrated hydrochloric acid) as a source of hydrogen sulphide. See also p. 317.

$$FeS(s) + 2H^+(aq) \rightarrow H_2S(g) + Fe^{2+}(aq)$$

Iron(II) sulphide can also be precipitated from an iron(II) salt in solution by ammonium sulphide.

Compounds of iron in the +3 oxidation state

In strongly acidic solution, iron(III) exists as the pale purple ion $[Fe(H_2O)_6]^{3+}$. As the pH increases yellow aqua/hydroxo complexes are formed, and above pH 3 hydrated iron(III) oxide is precipitated. The hydrated Fe^{3+} ion can be considered as a Brønsted acid—i.e. a proton donor.

$$\begin{aligned}[Fe(H_2O)_6]^{3+}(aq) &\rightleftharpoons [Fe(H_2O)_5(OH)]^{2+}(aq) + H^+(aq)\\ &\rightleftharpoons [Fe(H_2O)_4(OH)_2]^+(aq) + 2H^+(aq)\\ &\rightleftharpoons [Fe(H_2O)_3(OH)_3](s) + 3H^+(aq)\end{aligned}$$

Iron(III) Compound

Iron(III) oxide, Fe_2O_3

Iron(III) oxide occurs as the very important *haematite* iron ores, some of which are hydrated. In the laboratory, it can be made by strong heating of iron(II) sulphate crystals.

$$FeSO_4.7H_2O(s) \rightarrow Fe_2SO_4(s) + 7H_2O(g)$$
$$2FeSO_4(s) \rightarrow Fe_2O_3(s) + SO_2(g) + SO_3(g)$$

Alternatively, 'iron(III) hydroxide' can be precipitated by ammonia from iron(III) chloride solution, filtered, washed, dried and strongly heated.

$$Fe^{3+}(aq) + 3OH^-(aq) \rightarrow Fe(OH)_3(s)$$
$$2Fe(OH)_3(s) \rightarrow Fe_2O_3(s) + 3H_2O(g)$$

Iron(III) oxide has been used for a long time as a polishing powder (*jeweller's rouge*) and as a pigment.

Iron(III) oxide is preponderately *basic*. If it has not been too strongly heated, it dissolves fairly readily in the dilute mineral acids, forming the corresponding iron(III) salts, e.g.:

$$Fe_2O_3(s) + 6HCl(aq) \rightarrow 2FeCl_3(aq) + 3H_2O(l)$$

If heated to above 900 K, however, iron(III) oxide does not dissolve at all in dilute nitric acid and only slowly in the other two mineral acids. This oxide also has *very slight acidic* tendencies, forming *ferrates*(III) when heated with concentrated or fused alkali.

$$Fe_2O_3(s) + 2OH^-(aq) \rightleftharpoons 2FeO_2^-(aq) + H_2O(l)$$

In showing *amphoteric* character in this way, it resembles Al_2O_3 and Cr_2O_3. *Ferrates*(VI), e.g. K_2FeO_4, are also known and are analogous to chromates(VI) and manganates(VI).

Iron(III) oxide is reduced to iron when heated strongly with carbon, or in a current of carbon monoxide or hydrogen.

$$Fe_2O_3(s) + 3C(s) \rightarrow 2Fe(l) + 3CO(g)$$
$$Fe_2O_3(s) + 3CO(g) \rightarrow 2Fe(l) + 3CO_2(g)$$
$$Fe_2O_3(s) + 3H_2(g) \rightarrow 2Fe(l) + 3H_2O(g)$$

It is stable to ordinary heating, but is converted to the black oxide of iron at 1600 K.

$$6Fe_2O_3(s) \rightarrow 4Fe_3O_4(s) + O_2(g)$$

Iron(II) diiron(III) oxide (triferric tetroxide), Fe_3O_4

This oxide is black iron oxide. It occurs as the ore, *magnetite*, and is the natural lodestone which, if suspended, will set like a compass needle. In the laboratory, it can be made by burning iron in oxygen or by heating iron at red heat in a current of steam.

$$3Fe(s) + 2O_2(g) \rightarrow Fe_3O_4(s)$$
$$3Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$$

This oxide reacts with warm, moderately concentrated hydrochloric acid to produce iron(II) and iron(III) *chlorides* in solution.

$$Fe_3O_4(s) + 8H^+(\text{conc.aq.}) \rightarrow Fe^{2+}(aq) + 2Fe^3(aq) + 4H_2O(l)$$

It is a *compound oxide* (p. 281); its structure contains iron(II), iron(III), and oxide ions.

'Iron(III) hydroxide' (ferric hydroxide), $Fe(OH)_3$

The hydroxide is precipitated as a gelatinous, reddish-brown solid by the addition of aqueous alkali or ammonia to a solution of an iron(III) salt. The formula of this compound has been represented as $Fe_2O_3.xH_2O$. We will use $Fe(OH)_3$ for convenience.

$$Fe^{3+}(aq) + 3OH^-(aq) \rightarrow \text{`}Fe(OH)_3\text{'}(s)$$

It is unaffected by excess alkali, having no appreciable acidic tendencies. Iron(III) hydroxide is a feeble base, dissolving in the dilute mineral acids to form iron(III) salts, but the solutions are much hydrolysed:

$$\text{`}Fe(OH)_3\text{'}(s) + 3HCl(aq) \rightleftharpoons FeCl_3(aq) + 3H_2O(l)$$

Iron(III) chloride (ferric chloride), $FeCl_3$

Anhydrous iron(III) chloride is prepared as a black sublimate by *heating* iron wire in a current of *dry* chlorine. For experimental details, see p. 367.

$$2Fe(s) + 3Cl_2(g) \rightarrow 2FeCl_3(s)$$

It is very deliquescent and forms a series of hydrates, the common hydrate being the brownish-yellow solid, $FeCl_3.6H_2O$, which forms a yellow solution containing aqua/hydroxo complexes such as $[Fe(H_2O)_5OH]^{2+}$ (see above). The solution is much hydrolysed.

$$FeCl_3(s) + 3H_2O(l) \rightleftharpoons \text{`}Fe(OH)_3\text{'}(s) + 3HCl(aq)$$

Iron(III) chloride (anhydrous) boils at 588 K and, up to 670 K, the density of its vapour relative to hydrogen is about 160, corresponding to a molecule, Fe_2Cl_6. Above 670 K, it decreases, reaching a value of about 80 at 1000 K, which corresponds to a molecule, $FeCl_3$.

$$Fe_2Cl_6(g) \rightleftharpoons 2FeCl_3(g)$$

The comparative volatility of iron(III) chloride, its solubility in ethoxyethane and association to Fe_2Cl_6 indicate mainly *covalent* nature in the anhydrous compound. It is probably similar to aluminium chloride.

The iron(II)–iron(III) interconversion

As already mentioned, iron(II) is quite easily oxidized in acidic aqueous solution; and iron(III) ion in solution is a mild oxidizing agent. The two oxidation states are therefore readily interconvertible.

$$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq) \qquad E^\ominus = +0.77\,V$$

In less acidic solution, iron(II) becomes a stronger reducing agent, but the reaction is complicated by precipitation of hydrolysis products of the iron(III) compounds formed.

(1) *Some examples of the iron* (II) → *iron* (III) *conversion*

(a) *With concentrated nitric acid and heat.* Brown fumes (nitrogen dioxide) are evolved.

$$6Fe^{2+}(aq) + 8H^+(conc.aq.) + 2NO_3{}^-(conc.aq.) \rightarrow$$
$$6Fe^{3+}(aq) + 4H_2O(l) + 2NO(g)$$
$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

(b) *With chlorine water or bromine water.* The halogen colour is discharged.

$$2Fe^{2+}(aq) + Cl_2(aq) \rightarrow 2Fe^{3+}(aq) + 2Cl^-(aq)$$
$$2Fe^{2+}(aq) + Br_2(aq) \rightarrow 2Fe^{3+}(aq) + 2Br^-(aq)$$

(c) *With hydrogen peroxide solution.*

$$2Fe^{2+}(aq) + 2H^+(aq) + H_2O_2(aq) \rightarrow 2Fe^{3+}(aq) + 2H_2O(l)$$

(d) *With acidified potassium manganate*(VII) *solution.* The purple colour of the manganate(VII) is discharged.

$$5Fe^{2+}(aq) + MnO_4{}^-(aq) + 8H^+(aq) \rightarrow 5Fe^{3+}(aq) + Mn^{2+}(aq) + 4H_2O(l)$$

(e) *With acidified potassium dichromate*(VI) *solution.* The golden yellow dichromate(VI) solution turns dark green.

$$6Fe^{2+}(aq) + Cr_2O_7{}^{2-}(aq) + 14H^+(aq) \rightarrow 6Fe^{3+}(aq) + \underset{\text{green}}{2Cr^{3+}(aq)} + 7H_2O(l)$$

Test for iron(III) *salts in solution*

Ammonia. Ammonia solution produces a *reddish-brown, gelatinous precipitate* of 'iron(III) hydroxide'.

$$Fe^{3+}(aq) + 3OH^-(aq) \rightarrow Fe(OH)_3(s)$$

2. *Potassium hexacyanoferate*(II) (*potassium ferrocyanide*) *solution.* This reagent produces a *dark blue precipitate* of 'Prussian blue'.

$$K^+(aq) + [Fe(CN)_6]^{4-}(aq) + Fe^{3+}(aq) \rightarrow \underset{\text{Prussian blue}}{K^+[Fe(Fe(CN)_6)]^-(s)}$$

3. *Potassium thiocyanate solution.* This reagent produces a *blood-red coloration* (not a precipitate). This colour is usually ascribed to the formation of the complex ion $[Fe(H_2O)_5SCN]^{2+}$.

(2) *Some examples of the iron* (III) → *iron* (II) *conversion*

(a) *With zinc and dilute sulphuric or hydrochloric acid.*

$$Zn(s) + 2Fe^{3+}(aq) \rightarrow Zn^{2+}(aq) + 2Fe^{2+}(aq)$$

(b) *With hydrogen sulphide.* Sulphur appears as a yellow precipitate.

$$H_2S(aq) \rightleftharpoons 2H^+(aq) + S^{2-}(aq)$$
$$S^{2-}(aq) + 2Fe^{3+}(aq) \rightarrow 2Fe^{2+}(aq) + S(s)$$

(c) *With sulphur dioxide.* In the cold, the solution may turn red by the formation of an intermediate product. This product is decomposed on heating and the usual pale *green* iron(II) solution is left.

$$SO_2(aq) + H_2O(l) \rightleftharpoons H_2SO_3(aq) \rightleftharpoons 2H^+(aq) + SO_3{}^{2-}(aq)$$
$$SO_3{}^{2-}(aq) + H_2O(l) + 2Fe^{3+}(aq) \rightarrow SO_4{}^{2-}(aq) + 2H^+(aq) + 2Fe^{2+}(aq)$$

Notice that *water* intervenes here as a chemical in the reaction, not merely as a solvent. Sulphite ion is oxidized to sulphate ion.

(d) *With acidified potassium iodide solution.* Iodine is produced, usually as a *brown* solution in excess iodide.

$$2I^-(aq) + 2Fe^{3+}(aq) \rightarrow Fe^{2+}(aq) + I_2(\text{in KIaq.})$$

Tests for iron (II) *salts in solution*

1. *By ammonia.* Ammonia gives *a gelatinous precipitate* of 'iron(II) hydroxide', white if pure but usually *dirty green* by partial oxidation, and

rapidly turning brown where exposed to air.

$$Fe^{2+}(aq) + 2OH^-(aq) \rightarrow Fe(OH)_2(s)$$

2. *By potassium hexacyanoferrate*(III) (*potassium ferricyanide*) *solution.* This reagent gives a *dark blue precipitate* of *Turnbull's blue*, which is chemically the same as Prussian blue. The iron(II) ions appear to reduce some hexacyanoferrate(III) ions to hexacyanoferrate(II) first.

$$Fe^{2+}(aq) + \underset{\text{hexacyanoferrate(III) ion}}{[Fe(CN)_6]^{3-}(aq)} \rightleftharpoons Fe^{3+}(aq) + \underset{\text{hexacyanoferrate(III) ion}}{[Fe(CN)_6]^{4-}(aq)}$$

$$\text{Then } K^+(aq) + Fe^{3+}(aq) + [Fe(CN)_6]^{4-}(aq) \rightarrow \underset{\text{Turnbull's blue}}{K^+[Fe(Fe(CN)_6)]^-(s)}$$

Cyanide complexes of iron

Complexes of the d-block elements have already been considered in a general way (p. 395). It is appropriate to consider the cyanide complexes of iron as specific examples.

Potassium hexacyanoferrate(II), $K_4[Fe(CN)_6]$

Potassium hexacyanoferrate(II) can be produced in the laboratory by adding iron(II) sulphate solution, gradually with shaking, to potassium cyanide solution till a *slight* permanent precipitate is obtained. This represents completion of the reaction:

$$Fe^{2+}(aq) + 6CN^-(aq) \rightarrow [Fe(CN)_6]^{4-}(aq)$$

After filtration, evaporation and cooling, potassium hexacyanoferrate(II) separates out as yellow crystals of the hydrate $K_4[Fe(CN)_6].3H_2O$.

If heated with *dilute* sulphuric acid, it liberates *hydrogen cyanide* (a very dangerous poison).

$$K_4[Fe(CN)_6](s) + 6H^+(aq) \rightarrow 6HCN(g) + Fe^{2+}(aq) + 4K^+(aq)$$

Potassium hexacyanoferrate(II), in solution, will precipitate some heavy metals from solutions of their salts. One of these precipitates is the purplish-brown *copper*(II) *hexacyanoferrate*(II).

$$2Cu^{2+}(aq) + [Fe(CN)_6]^{4-}(aq) \rightarrow Cu_2[Fe(CN)_6](s)$$

This reaction is used as a test for copper(II) ion, Cu^{2+}, and in producing a semi-permeable membrane for osmotic pressure experiments. The structure of the hexacyanoferrate(II) ion is octahedral (see p. 403). The hexacyanoferrates(II) are not particularly poisonous. They ionize to produce a complex ion, and not the simple CN^- ion which is responsible for the very poisonous character of simple cyanides.

Potassium hexacyanoferrate(III), $K_3[Fe(CN)_6]$

Potassium hexacyanoferrate(III) is produced, in solution, by the oxidation of potassium hexacyanoferrate(II) by any one of several oxidizing agents, e.g.

Chlorine $2[Fe(CN)_6]^{4-}(aq) + Cl_2(aq) \rightarrow 2[Fe(CN)_6]^{3-}(aq) + Cl^-(aq)$

Hydrogen peroxide $2[Fe(CN)_6]^{4-}(aq) + 2H^+(aq) + H_2O_2(aq) \rightarrow$
$2[Fe(CN)_6]^{3-}(aq) + 2H_2O(l)$

Potassium manganate(VII) (acidified)

$$MnO_4^-(aq) + 8H^+(aq) + 5[Fe(CN)_6]^{4-}(aq) \rightarrow Mn^{2+}(aq) + 4H_2O(l) + 5[Fe(CN)_6]^{3-}(aq)$$

The salt can be crystallized, after evaporation and cooling, as red crystals, and should be re-crystallized. Both the solid and its solution are affected by light, with some decomposition. The solution should be used fresh and made from hexacyanoferrate(III) washed to remove the surface layers. Hexacyanoferrate(III) is a mild oxidizing agent, accepting electrons in the reaction:

$$[Fe(CN)_6]^{3-}(aq) + e^- \rightarrow [Fe(CN)_6]^{4-}(aq) \qquad E^\ominus = +0.36\,V$$

The structure of the ion is octahedral, like the hexacyanoferrate(II) ion. In hexacyanoferrate(III), 35 electrons are associated with the iron atom, one less than the more stable '36 electron' structures (see p. 399), such as hexacyanoferrate(II). This is why hexacyanoferrate(III) has a tendency to gain electrons and is therefore an oxidizing agent.

Cobalt

Atomic number 27.
Electron arrangement 2.8.15.2 ($1s^22s^22p^63s^23p^63d^74s^2$).
Cobalt has one isotope of mass number 59.
Relative atomic mass 58.94.

Occurrence and extraction

Cobalt usually occurs in association with several other metals such as iron, nickel and silver. *Smaltite* is cobalt arsenide, $CoAs_2$. *Cobalt glance* is CoAsS. It is chiefly obtained from ores in Zaire, Canada, Zimbabwe, and Queensland. Cobalt is found in vitamin B_{12}, a deficiency in which results in Man a form of anaemia.

Because of the association of cobalt with several other metals, the extraction of the element is very complex, and is not considered here.

Cobalt is chiefly used in alloys. Cobalt steel has been used in making permanent magnets (about 10–13 per cent Co is usual). *Stellite* is an alloy containing cobalt, chromium and tungsten (with carbon) and is used in making surgical instruments, and valve seatings in aero-engines. Alloyed with iron and chromium, cobalt produces electrical heating elements and cutlery. Cobalt is also used in 'cobalt blue' pigments.

Properties of cobalt

Cobalt is a bright, bluish-white metal. It has a density of 8.8 g cm^{-3} and melts at 1765 K. It is more magnetic than any other metal except iron and retains its magnetic properties up to about 1370 K. It has the following chemical properties:

1. *With air.* Cobalt is not affected by air at room temperature. It was once used for plating steel, but chromium has now replaced it. If heated in air, cobalt will slowly produce its oxide, Co_3O_4.

2. *With acids.* Cobalt is attacked by hot, dilute sulphuric acid and by hot, concentrated hydrochloric acid, though not rapidly, to form the corresponding *cobalt*(II) salts.

$$Co(s) + 2H^+(aq) \rightarrow Co^{2+}(aq) + H_2(g)$$

It is attacked more rapidly by nitric acid with the usual products—cobalt(II) nitrate and oxides of nitrogen—formed in a complex reaction. Concentrated nitric acid may render the metal *passive* by forming a layer of oxide, Co_3O_4. Alkalis do not attack cobalt.

3. *With carbon monoxide.* Cobalt combines with carbon monoxide to form a *carbonyl*, $Co_2(CO)_8$. The reaction requires a combination of *heat* and *pressure*, and the cobalt should be finely divided. This carbonyl is an orange-coloured powder.

Compounds of cobalt

Oxidation states other than +2 and +3 for cobalt are very rare. Cobalt(III) will oxidize water unless complexed with suitable ligands.

$$[Co(H_2O)_6]^{3+}(aq) + e^- \rightarrow [Co(H_2O)_6]^{2+}(aq) \qquad E^\ominus = +1.82\,V$$

Compounds of cobalt in the +2 oxidation state

Cobalt(II) oxide, CoO

Cobalt(II) oxide is formed if cobalt(II) carbonate or nitrate is heated to about 1300 K in the absence of air.

$$2Co(NO_3)_2(s) \rightarrow 2CoO(s) + 4NO_2(g) + O_2(g)$$
$$CoCO_3(s) \rightarrow CoO(s) + CO_2(g)$$

It is a greenish powder and is *basic*, forming cobalt(II) salts with the dilute mineral acids.

Cobalt(II) chloride, $CoCl_2$

Cobalt(II) chloride is formed in solution by the action of dilute hydrochloric acid on cobalt(II) oxide or carbonate.

$$CoCO_3(s) + 2HCl(aq) \rightarrow CoCl_2(aq) + H_2O(l) + CO_2(g)$$
$$CoO(s) + 2HCl(aq) \rightarrow CoCl_2(aq) + H_2O(l)$$

It crystallizes as the hydrate, $CoCl_2.6H_2O$, in red crystals, which are readily soluble in water. At about 390 K, the anhydrous chloride, $CoCl_2$, is formed and is *blue* in colour. It gives a *pink* solution in *cold* water, but the solution turns *blue* at about 320 K. The pink colour is ascribed to hydrated ions, such as $[Co(H_2O)_6]^{2+}$. The blue colour is believed to be caused by the presence of complex anions containing cobalt, e.g. $[CoCl_4]^{2-}$.

'Cobalt chloride paper' provides a well-known test for the presence of water. The strips of paper are blue when dry, but turn pink with water.

Cobalt(II) sulphide, CoS

Cobalt(II) sulphide is a black compound, insoluble in water, and precipitated by the action of ammonium sulphide solution on a solution of a cobalt(II) salt; or (better) by passing hydrogen sulphide through a solution of a cobalt(II) salt in the presence of ammonium chloride and ammonia.

$$Co^{2+}(aq) + S^{2-}(aq) \rightarrow CoS(s)$$

This puts cobalt into Group IV of the usual scheme of Qualitative Analysis. This sulphide is not precipitated in the presence of acid and, *immediately* after precipitation, it is amorphous and will dissolve in dilute mineral acids. After standing for a time, it becomes crystalline and insoluble in these acids.

Compounds of cobalt in the +3 oxidation state

As mentioned above, $Co^{3+}(aq)$ is a powerful oxidizing agent and unstable unless complexed by suitable ligands. Indeed, in the presence of ligands such as cyanide ions or ammonia, cobalt(II) is easily oxidized to cobalt(III), often by atmospheric oxygen. Examples of cobalt(III) complexes include $[Co(NH_3)_6]^{3+}$ and $[Co(CN)_6]^{3-}$. Nearly all the complexes of cobalt(III) are octahedral in shape.

Potassium hexanitrocobaltate(III), $K_3[Co(No_2)_6]$

Potassium hexanitrocobaltate(III) (*potassium cobaltinitrite*), $K_3[Co(NO_2)_6]$, is formed by the action of potassium nitrite solution on a solution of a cobalt(II) salt acidified by ethanoic acid.

$$Co^{2+}(aq) + 3K^+(aq) + 7NO_2^-(aq) + 2H^+(aq) \rightarrow K_3[Co(NO_2)_6](aq) + H_2O(l) + NO(g)$$

It precipitates as a yellow crystalline solid. Sodium hexanitrocobaltate(III) is produced in a corresponding way, but is soluble in water. Sodium hexanitrocobaltate(III) solution can be used as a test for the potassium ion, K^+, in solution, by precipitation of the above yellow solid. This test is, however, valid only in the absence of the ions of heavy metals and the alkaline earth metals, and of the ions NH_4^+ and Mg^{2+}, which may accompany K^+ in Group VI of the usual tables of Qualitative Analysis.

Detection of cobalt

Cobalt compounds give a *blue* borax bead (see p. 113). This is a very delicate test.

In the tables of Qualitative Analysis, cobalt is precipitated as its *black sulphide* in Group IV with the sulphides of nickel, manganese and zinc. The last two sulphides are extracted by their ready solubility in dilute hydrochloric acid. The sulphides of nickel and cobalt remain undissolved.

Nickel

Atomic number 28.
Electron arrangement 2.8.16.2 ($1s^2 2s^2 2p^6 3s^2 3p^6 3d^8 4s^2$).
Nickel has isotopes of mass number, in order of abundance, 58, 60, 62, 61, 64.
Relative atomic mass 58.70.

Notice that nickel *follows* cobalt in the Periodic Table, though their atomic relative masses are Co = 58.93, Ni = 58.70. This is because the predominant isotope of cobalt has a mass number of 59 (27 protons + 32 neutrons) while the predominant isotope of nickel is lighter with a mass number of 58 (28 protons + 30 neutrons). The matter is discussed in *Advanced Level Physical Chemistry*, p. 59.

Occurrence and extraction

The Sudbury district of Ontario supplies ores from which more than four-fifths of the world's nickel is obtained. These ores are mainly iron pyrites, FeS_2, and copper pyrites, $CuFeS_2$, containing some *nickel sulphide*, NiS. Some platinum also occurs in the ores. The ore, *garnierite*, occurs in New Caledonia. It is a hydrated silicate containing nickel and magnesium, with some iron.

The ore is treated in a complex series of operations to obtain *matte*, which contains nickel (about 50 per cent), copper and sulphur.

In the Mond process for purifying nickel, this matter is roasted in air to yield nickel and copper oxides. Copper(II) oxide is extracted by warm, dilute sulphuric acid, which leaves nickel(II) oxide unchanged. Copper(II) sulphate is recovered as a by-product.

The nickel(III) oxide is then reduced by heating in water gas.

$$NiO(s) + H_2(g) \rightarrow Ni(s) + H_2O(g)$$

The nickel still contains copper. To refine it, the product is heated to about 320 K in a stream of carbon monoxide. Nickel passes off as its volatile *carbonyl*, $Ni(CO)_4$. The product is passed over nickel shot in a tower at about 470 K. Nickel is deposited by decomposition of the carbonyl and is almost pure.

$$Ni(s) + 4CO(g) \underset{470\text{ K}}{\overset{320\text{ K}}{\rightleftharpoons}} Ni(CO)_4(g)$$

Properties of nickel

Nickel is a silvery metal, both malleable and ductile. It has a high melting point (1726 K) and a density of 8.8 g cm^{-3}. It can be magnetized, though not so intensely as iron, and has the following chemical properties:

1. *With air or oxygen.* Nickel is relatively inert to corrosion and is only slowly tarnished in air at ordinary temperature, but burns to its oxide, NiO, if heated in air or oxygen.
2. *With acids and alkalis.* Nickel is little attacked by dilute hydrochloric

acid or dilute sulphuric acid. It is more rapidly attacked by dilute nitric acid, especially if heated, but concentrated nitric acid makes it *passive*. Nickel is unaffected by alkalis, even when they are fused. Nickel crucibles can be used safely for alkali fusion experiments.

3. *With water*. Nickel does not react with water, but reduces steam at red heat.

$$\mathrm{Ni(s)} + \mathrm{H_2O(g)} \rightarrow \mathrm{NiO(s)} + \mathrm{H_2(g)}$$

4. *With chlorine*. Nickel forms its chloride, $NiCl_2$, if heated in a current of dry chlorine.

Nickel as a hydrogenation catalyst

Finely divided nickel, formed by reduction of its oxide by heating it in hydrogen, has marked catalytic activity in hydrogenations. The most important of these is the reduction of alkenes in the Sabatier process. Typically, the alkene reacts with hydrogen in the presence of the catalyst at about 470 K to form the corresponding saturated compound by a reaction of the type:

$$\mathrm{R.CH{=}CH.R} + \mathrm{H_2} \rightarrow \mathrm{R.CH_2.CH_2.R}$$

The conversion of oils to fats in the margarine industry is a special case of this reaction (p. 32). Other hydrogenations catalysed by heated nickel are:

$$\mathrm{CO(g)} + 3\mathrm{H_2(g)} \rightarrow \mathrm{CH_4(g)} + \mathrm{H_2O(g)}$$
$$2\mathrm{NO(g)} + 5\mathrm{H_2(g)} \rightarrow 2\mathrm{NH_3(g)} + 2\mathrm{H_2O(g)}$$

These are probably cases of adsorption catalysis.

Uses of nickel

(a) As a catalyst for hydrogenations as stated above.

(b) For the manufacture of crucibles, tongs and spatulas for laboratory use.

(c) In the electrical industry as the anode of Edison batteries (NiFe cells).

(d) There are a great many alloys of which nickel is a constituent. Some of them are:

Invar steel (35% Ni) which has a negligible coefficient of expansion and is used in surveying instruments, pendulums, chronometer components, etc.

Monel metal (70% Ni; 30% Cu) used in chemical plant for its resistance to corrosion.

Constantin (40% Ni; 60% Cu) used in electrical resistances.

Nichrome (80% Ni; 20% Cr) used in the heating elements of electric fires for resistance to oxidation.

Nickel silver (10–30% Ni, with Cu and Zn) used as a basis for electroplate.

Coinage alloys, e.g. British 'silver' coins, Cu, 75 per cent; Ni, 25 per cent.

Compounds of nickel

The only stable oxidation state of nickel is + 2; other states (+ 1, + 3, + 4) are rare. (An oxidation state of zero is found in the carbonyl (see below).) This illustrates the decreasing stability of higher oxidation states (i.e. those higher than + 2) across the first transition series. Nickel forms a large number of complexes. Many of the common ones (e.g. $[Ni(H_2O)_6]^{2+}$, $[Ni(NH_3)_6]^{2+}$) are octahedral, but other shapes are possible. $[Ni(CN)_4]^{2-}$ is square planar.

Nickel(II) oxide, NiO

This oxide is produced when e.g. nickel(II) carbonate is heated.

$$NiCO_3(s) \rightarrow NiO(s) + CO_2(g)$$

It is green in colour and is a *basic* oxide, though it is little affected by dilute sulphuric acid. It is reduced by hydrogen when gently heated (about 470 K)

$$NiO(s) + H_2(g) \rightarrow Ni(s) + H_2O(g)$$

The corresponding hydroxide, $Ni(OH)_2$, is a green solid, precipitated from a solution of nickel(II) salt by aqueous alkali or ammonia.

$$Ni^{2+}(aq) + 2OH^-(aq) \rightarrow Ni(OH)_2(s)$$

It is soluble in excess ammonia, forming a blue solution which contains the octahedral complex ion, $[Ni(NH_3)_6]^{2+}$.

Nickel(II) chloride, $NiCl_2$

The anhydrous (yellow) salt can be prepared by heating nickel in dry chlorine. The hydrate ($NiCl_2.6H_2O$) is green and is readily soluble in water, giving rise to the green octahedral aqua complex $[Ni(H_2O)_6]^{2+}$.

Nickel(II) sulphide, NiS

This compound is a black, insoluble solid. It closely resembles cobalt(II) sulphide, CoS, and is produced in a corresponding way (p. 450). When first precipitated, it is soluble in dilute acid, but rapidly changes to a form which is not soluble in dilute acid.

Nickel carbonyl, $Ni(CO)_4$

Nickel carbonyl is made by heating finely divided nickel in a stream of carbon monoxide at about 320 K. It is a very poisonous colourless liquid, boiling at 316 K. When heated to about 450–470 K it decomposes, depositing the metal.

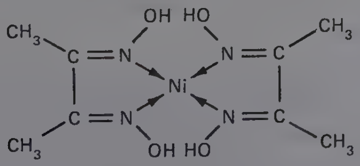
$$Ni(s) + 4CO(g) \underset{450\ K}{\overset{320\ K}{\rightleftharpoons}} Ni(CO)_4(g)$$

These facts are utilized in the Mond purification of nickel (p. 452). The structure of this carbonyl was considered on p. 404.

Detection and estimation of nickel

Nickel salts are green in solution. With ammonia they give a *green* precipitate, $Ni(OH)_2$, which dissolves in excess ammonia to give a *blue* solution containing the complex ion, $[Ni(NH_3)_6]^{2+}$. Nickel forms a *brown* borax bead.

In almost neutral, or alkaline, solution, nickel salts give a scarlet precipitate with *butanedione dioxime* (*dimethylglyoxime*). This is a delicate test for nickel. The precipitate can be washed and dried and used to estimate nickel quantitatively. The butanedione dioxime molecule is a bidentate ligand; the complex is planar and neutral, and the colour is due to extensive delocalization in the ring.



Copper

Atomic number 29.
Electron arrangement 2.8.18.1 ($1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$).
Copper has two isotopes of mass numbers, in order of abundance, 63 and 65.
Relative atomic mass 63.55.

Occurrence

(a) *Native copper* occurs to some extent, e.g. near Lake Superior in Michigan, in the Urals, in Australia and, to a minute extent, in Cornwall. Such deposits have now mostly been exploited.
(b) Copper occurs as copper(I) oxide, Cu_2O, in *cuprite* and copper(II) oxide, CuO, in *tenorite.*
(c) Basic carbonates of copper occur as *malachite*, $CuCO_3.Cu(OH)_2$ and *azurite*, $2CuCO_3.Cu(OH)_2$. Both of these are found in the USA and USSR.
(d) The complex sulphide, $CuFeS_2$, occurs as *chalcopyrite* (copper pyrites) in Zambia, North and South America, Australia, USSR, and some European countries. It is, by far, the most important ore of copper.

Extraction of copper from copper pyrites, $CuFeS_2$

This is a complex and difficult process, partly because the ore is impure, containing much sand and clay, and partly because it contains, atom for atom, as much iron as copper. The following is a summary of the essentials of the process.

1. *Concentration of the ore by flotation* (*selective wetting*). The finely powdered ore is agitated with water, made suitably alkaline by slaked lime and containing a frothing agent. In these conditions, copper-bearing particles collect in the froth. The froth is made to overflow and collected. The concentrate may contain up to 25 per cent of copper.

2. *Roasting.* The ore is then roasted in air. Iron oxidizes more readily than copper and, by suitable adjustment of temperature and air supply, the iron can be mainly converted to iron(II) oxide while copper remains combined with sulphur.

$$2CuFeS_2(s) + 4O_2(g) \rightarrow Cu_2S(s) + 2FeO(s) + 3SO_2(g)$$

The sulphur dioxide can be converted to sulphuric acid.

3. *Smelting.* The product of the roasting is heated in a reverberatory furnace with sand (silica). Iron(II) silicate is formed as a slag, floating on top of a fused *matte*, consisting mainly of copper(I) sulphide, with a little iron(II) sulphide present. The slag is poured off.

$$FeO(l) + SiO_2(l) \rightarrow FeSiO_3(l)$$

4. *Conversion to 'blister copper'.* The fused matte is run into a converter lined with magnesite, $MgCO_3$. Silica (SiO_2) is added and an air-blast is blown. Non-metals present, e.g. sulphur, are eliminated as volatile

oxides; iron is oxidized, combines with the silica and is poured off as a slag of silicate ($FeSiO_3$).

As more air is blown, copper(I) sulphide oxidizes. So much copper(I) oxide is produced that it can react with remaining copper(I) sulphide to produce copper, by the reactions:

$$2Cu_2S(l) + 3O_2(g) \rightarrow 2Cu_2O(l) + 2SO_2(g)$$
$$Cu_2S(l) + 2Cu_2O(l) \rightarrow 6Cu(l) + SO_2(g)$$

The molten copper is poured off. As it cools it emits dissolved sulphur dioxide and acquires a blistered appearance.

5. *Refining of blister copper.* The purest copper is obtained electrolytically. Slabs of the crude metal are made anodes in a solution of copper(II) sulphate (with 5 per cent of sulphuric acid). The cathodes are thin sheets of pure copper. Direct current is passed.

At the anode	*At the cathode*
$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$	$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$
i.e. the copper passes into solution as ions	i.e. copper deposits from the solution

The net effect is to dissolve the anodes, and to thicken the cathodes with pure copper. Any silver or gold present as impurities in the copper do not ionize, but precipitate as 'anode mud' and can be recovered. Impurities such as iron pass into solution as ions. Electrolytic copper is more than 99.95 per cent pure.

Other methods are available for extracting copper from 'lean' ores, including bacterial oxidation of sulphide ores, but they are beyond the scope of this book.

Uses of copper

(a) Apart from silver (which is too expensive for large-scale use), copper has the highest electrical conductivity among common metals. It is widely used in the electrical industries as cables and flex. Copper is also a very good conductor of heat.

(b) Copper is used in many alloys. Some of the important ones are:

(i) *Bronze.* This term was originally applied only to Cu–Sn alloys, but is now used in a wider sense. British coinage-bronze contains Cu, 95 per cent; Sn, 4 per cent; Zn 1 per cent.

(ii) *Brass.* This alloy varies in composition from about 80 per cent copper to 67 per cent copper, with zinc. It is much used in the making of scientific instruments and ornamental objects.

(iii) *Gun metal and bell metal. Gun metal* (mainly copper 88 per cent and tin 10 per cent, with a little zinc and lead) was formerly used in casting cannon and is now used for gears and bearings.

Bell metal (copper 80 per cent, tin 20 per cent) is used in casting bells.

(iv) *So-called silver coinage.* From the reign of Elizabeth I until 1920, the British silver coinage was the *sterling silver* standard—silver 92.5 per cent, copper 7.5 per cent. The copper was present to harden the metal and give better wear. In 1920, the silver coinage was debased to 50 per cent silver, with copper, or copper, nickel and zinc. Since 1947, silver has been completely eliminated from the coinage issued. The alloy used contains copper 75 per cent, nickel 25 per cent.

Properties of copper

Physical properties

Copper is a reddish brown metal. Its melting point is 1356 K when pure. The density of copper is 8.92 g cm^{-3}. It is a very good conductor of both heat and electricity.

Chemical properties

1. *With acids.* Copper is less electropositive than hydrogen, so will not displace hydrogen from water under any conditions, nor from pure dilute sulphuric acid or pure dilute hydrochloric acid.

Hot, concentrated sulphuric acid attacks copper readily. The main products are *sulphur dioxide* and *copper*(II) *sulphate*, although the products usually appear black because copper sulphides are also formed.

$$Cu(s) + 2H_2SO_4(l) \rightarrow CuSO_4(aq) + 2H_2O(l) + SO_2(g)$$

Nitric acid attacks copper at almost any concentration, producing *copper*(II) *nitrate* solution and some *oxide of nitrogen*—usually nitrogen oxide and nitrogen dioxide. (See p. 244 for a discussion of these reaction is redox terms.) The two important reactions are:

Cold concentrated nitric acid.

$$Cu(s) + 4HNO_3(\text{conc. aq.}) \rightarrow Cu(NO_3)_2(aq) + 2H_2O(l) + 2NO_2(g)$$

Cold, moderately concentrated nitric acid.

$$3Cu(s) + 8HNO_3(aq) \rightarrow 3Cu(NO_3)_2(aq) + 4H_2O(l) + 2NO(g)$$

2. *With the atmosphere.* In *moist* air, copper slowly acquires a smooth,

green layer, called a *patina*. In inland areas, this layer consists largely of a basic sulphate of copper, $CuSO_4.3Cu(OH)_2$; in areas near the sea it may contain basic chloride, $CuCl_2.3Cu(OH)_2$.

If heated in *dry* air, copper oxidizes superficially, giving a mixture of copper(I) oxide, Cu_2O, and copper(II) oxide, CuO.

3. *With halogens and sulphur.* Copper reacts readily on heating with these elements.

Compounds of copper

Copper(I) compounds are formed by loss of the 4s electron from the ground electronic state of 2.8.18.1. Copper in the +1 state possesses a full 3d sub-shell, and Cu(I) compounds are therefore diamagnetic (see p. 401) and (except for Cu_2O) colourless. Copper(I) is unstable in aqueous solution and disproportionates:

$$2Cu^+(aq) \rightleftharpoons Cu^{2+}(aq) + Cu(s) \qquad E^\ominus = +0.37\ V$$

Copper(II) compounds are based on the 2.8.17 structure for the ion, which therefore possesses one unpaired electron; consequently, copper(II) compounds are paramagnetic and generally coloured (see p. 401).

Compounds of copper in the +1 oxidation state

The copper(I) series shows many gaps. In the presence of water, no copper(I) salt containing oxygen is stable; in particular, copper(I) sulphate, nitrate and carbonate do not exist in aqueous conditions. Any attempt to make them tends to result in the formation of the corresponding copper(II) salt and metallic copper, e.g. the action of copper(I) oxide with dilute sulphuric acid.

$$Cu_2O(s) + H_2SO_4(aq) \rightarrow CuSO_4(aq) + H_2O(l) + Cu(s)$$

This is an example of the disproportionation referred to above.

Copper(I) oxide (cuprous oxide, red copper oxide), Cu_2O

Preparation

Copper(II) sulphate crystals (5 g) are dissolved in hot, distilled water (100 cm^{-3}). Caustic soda (10 g) and sodium potassium tartrate (Rochelle salt), (15 g), are dissolved in water (100 cm^3). The two cold solutions are mixed. The resulting mixture should be dark blue and should contain no precipitate. This solution is known as *Fehling's solution.* Without the Rochelle salt, 'copper(II) hydroxide' would be precipitated. The Rochelle salt holds the copper *in solution* in alkaline conditions (as a complex tartrate) for the following reducing action.

To the dark blue mixture, a glucose solution is added (12 g in 30 cm^3 water). The liquid is stirred and heated slowly. A dark green precipitate is produced which slowly turns scarlet and then reddish-brown. This is copper(I) oxide. After a short period of boiling, the oxide may be filtered off, washed with hot distilled water and allowed to dry.

Glucose acts as a *mild reducing agent.*

$$2Cu^{2+}(aq) + 4OH^-(aq) + C_6H_{12}O_6(aq) \rightarrow Cu_2O(s) + 2H_2O(l) + C_6H_{12}O_7(aq)$$

Glucose is oxidized to gluconic acid (as shown) which forms its sodium salt with the sodium hydroxide present.

This reaction is used as *Fehling's test* for *reducing sugars,* of which glucose is an example.

Uses

(a) Copper(I) oxide is used in the manufacture of red glass. The colour is thought to result from colloidal copper suspended in the glass.
(b) Copper(I) oxide is an ingredient of some anti-rust paints.

Properties of copper(I) oxide

(1) With acids

Copper(I) oxide is *basic* and, with dilute acids, it tends to form salts. But many copper(I) salts disproportionate in aqueous conditions, to give the corresponding copper(II) salt and copper metal (see above). *Concentrated hydrochloric acid.* Copper(I) chloride is probably formed at first, but reacts further to form a complex ion which gives a dark brownish colour to the solution.

$$Cu_2O(s) + 2HCl(conc.\ aq.) \rightarrow 2CuCl(aq) + H_2O(l)$$
$$CuCl(aq) + Cl^-(aq) \rightleftharpoons [CuCl_2]^-(aq)$$

Other complex ions, such as $[CuCl_3]^{2-}$, may also occur.

(2) Reduction of copper (I) oxide

Copper(I) oxide is readily reduced to metallic copper by heating in a stream of dry hydrogen, or with carbon.

$$Cu_2O(s) + H_2(g) \rightarrow 2Cu(s) + H_2O(g)$$
$$Cu_2O(s) + C(s) \rightarrow 2Cu(s) + CO(g)$$

Copper(I) chloride, CuCl

Preparation

1. A few grams of copper(II) chloride (or copper(II) oxide or copper(II) carbonate) are dissolved in excess of *concentrated* hydrochloric acid. Clean copper turnings are added and the mixture is boiled gently in a fume cupboard for about 25–30 minutes. While this is going on, water (about 1200 cm^3) is boiled rapidly for about five minutes (to expel air and so avoid oxidizing the product) and cooled. The other solution is poured into it, with stirring, and produces a *white precipitate* of *copper*(I) *chloride*. After settling, the bulk of the water can be poured away; the precipitate can be filtered off, washed with a solution of sulphur dioxide (to avoid oxidation) and dried in a vacuum desiccator.

During the boiling, copper(II) chloride is reduced by copper:

$$CuCl_2(aq) + Cu(s) \rightarrow 2CuCl(s)$$

but the copper(I) salt is held in solution in the excess of concentrated hydrochloric acid by complex ion formation, as:

$$CuCl(s) + Cl^-(aq) \rightleftharpoons [CuCl_2]^-(aq)$$

Dilution breaks down the complexes and precipitates copper(I) chloride.

2. An alternative preparation is to pass sulphur dioxide through an aqueous solution containing equimolar quantities of copper(II) sulphate and sodium chloride.

$$2Cu^{2+}(aq) + 2Cl^-(aq) + SO_2(g) + 2H_2O(l) \rightleftharpoons 2CuCl(s) + 4H^+(aq) + SO_4{}^{2-}(aq)$$

The copper(I) chloride precipitates and is purified as above.

Properties of copper(I) *chloride*

1. When pure, copper(I) chloride is white, but rapidly *oxidizes* in the presence of air and water to a green, basic copper(II) chloride. This explains the precautions against oxidation in the preparation above.

2. Copper(I) chloride is insoluble in water but dissolves in concentrated

hydrochloric acid by forming complex ions, typically:

$$CuCl(s) + Cl^-(aq) \rightleftharpoons [CuCl_2]^-(aq)$$

It also dissolves in ammonia, again by formation of a complex (cf. silver chloride, p. 479).

$$CuCl(s) + 2NH_3(aq) \rightarrow [Cu(NH_3)_2]^+(aq)$$

In the absence of oxygen, the solution is colourless; if oxygen is present, it is dark blue. The ammonia solution absorbs carbon monoxide and is employed in gas-analysis, and also to remove traces of carbon monoxide in the Bosch process for the manufacture of hydrogen (see p. 31). It also absorbs ethyne, giving a red-brown precipitate of the hydrated copper(I) 'acetylide'. This compound is dangerously explosive when dry.

Copper(I) iodide, CuI

Preparation

A solution of copper(II) sulphate is added to a solution of potassium iodide. Copper(II) iodide (which might be expected) is unstable; the actual products are a *precipitate* of *copper*(I) *iodide* (usually off-white, slightly pinkish in colour) and *iodine*. This remains dissolved if potassium iodide is in excess, forming a *brown* solution.

$$2Cu^{2+}(aq) + 4I^-(aq) \rightarrow 2CuI(s) + I_2\,(\text{in } KI(aq))$$

Careful addition of sodium thiosulphate solution, till the brown colour has just disappeared, will destroy the iodine (see p. 68).

$$2S_2O_3^{2-}(aq) + I_2\,(\text{in } KI(aq)) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$$

These two reactions provide a useful volumetric method for the quantitative determination of copper(II).

Copper(I) cyanide, CuCN

Preparation

Like copper(II) iodide, copper(II) cyanide is unstable, so that the mixing of copper(II) sulphate and potassium cyanide solutions precipitates *copper*(I) *cyanide*, a white solid, with liberation of (poisonous) cyanogen gas.

$$2Cu^{2+}(aq) + 4CN^-(aq) \rightarrow 2CuCN(s) + (CN)_2(g)$$

Copper(I) cyanide is insoluble in water but dissolves in excess of potassium cyanide solution by forming a cyano complex.

$$\text{CuCN(s)} + \text{CN}^-\text{(aq)} \rightleftharpoons [\text{Cu(CN)}_2]^-\text{(aq)}$$
$$\text{or CuCN(s)} + 3\text{CN}^-\text{(aq)} \rightleftharpoons [\text{Cu(CN)}_4]^{3-}\text{(aq)}$$

Formulae of copper(I) salts

It is fairly certain that copper(I) chloride, bromide and iodide are covalent compounds by the X-ray evidence of the inter-atomic distances. The calculated ionic distances are considerably greater. Copper(I) chloride vapour, even at temperatures exceeding 1300 K, has a relative density close to that required by the molecular formula, Cu_2Cl_2 (i.e. about 100), and so appears to be dimerized in the vapour state.

Compounds of copper in the +2 oxidation state

These are usually electrovalent compounds containing the copper(II) ion, Cu^{2+}, derived from the electron configuration 2.8.17.2. In aqueous solution, the characteristic ion is $[Cu(H_2O)_6]^{2+}$. Copper(II) salts are often hydrated and are then green or blue. Their dilute solutions are usually blue. Copper(II) oxide is exceptional among copper(II) compounds; it is black.

Copper(II) oxide (cupric oxide, black copper oxide), CuO

Preparation

Copper(II) oxide can be prepared by the standard methods for metallic oxides described on p. 282.

Properties of copper(II) oxide

1. *Basic character.* Copper(II) oxide is a typical insoluble basic oxide and reacts readily with the hot dilute mineral acids to form the corresponding copper(II) salt and water, e.g.

$$\text{CuO(s)} + \text{H}_2\text{SO}_4\text{(aq)} \rightarrow \text{CuSO}_4\text{(aq)} + \text{H}_2\text{O(l)}$$

2. *Reduction.* Copper(II) oxide is readily reduced to a reddish-brown powder, *copper*, when heated in hydrogen.

$$\text{CuO(s)} + \text{H}_2\text{(g)} \rightarrow \text{Cu(s)} + \text{H}_2\text{O(g)}$$

It is also reduced by heating with carbon or hydrocarbons.

$$4CuO(s) + CH_4(g) \rightarrow 4Cu(s) + CO_2(g) + 2H_2O(g)$$

This behaviour accounts for its use in older method for analysis of organic compounds for their content of hydrogen and carbon. The former is absorbed, as water, by concentrated sulphuric acid and weighed; carbon is absorbed as carbon dioxide by sodalime, and weighed.

'Copper(II) hydroxide', $Cu(OH)_2$

Preparation

'Copper(II) hydroxide' is precipitated as a gelatinous, blue solid by the action of sodium or potassium hydroxide solution on a solution of copper(II) sulphate.

$$Cu^{2+}(aq) + 2OH^-(aq) \rightarrow Cu(OH)_2(s)$$

It is probable that the reaction is better represented as follows:

$$\begin{aligned}[Cu(H_2O)_6]^{2+}(aq) &\rightleftharpoons [Cu(H_2O)_5(OH)]^+(aq) + H^+(aq)\\ &\rightleftharpoons [Cu(H_2O)_4(OH)_2](s) + H^+(aq)\end{aligned}$$

For convenience, the compound will be formulated as $Cu(OH)_2$. If required, the precipitate may be filtered off, washed with *cold*, distilled water and allowed to dry *without heat*.

Properties of 'copper(II) hydroxide'

1. *Action of heat. Basic character.* If heated *in the liquid* (above), copper(II) hydroxide turns to a dark brown precipitate, which has the composition of a hydrate of copper(II) oxide, $4CuO.H_2O$. If heated to red heat, the hydroxide leaves anhydrous copper(II) oxide.

$$Cu(OH)_2(s) \rightarrow CuO(s) + H_2O(g)$$

Copper(II) hydroxide is essentially *basic* and readily forms salts with the dilute mineral acids, e.g.

$$Cu(OH)_2(s) + 2HNO_3(aq) \rightarrow Cu(NO_3)_2(aq) + 2H_2O(l)$$

It is, however, weakly amphoteric, dissolving in excess concentrated alkali to give the blue tetrahydroxocuprate(II) ion.

$$Cu(OH)_2(s) + 2OH^-(aq) \rightarrow [Cu(OH)_4]^{2-}(aq)$$

2. *Behaviour with ammonia.* If a *little* ammonia is added to a solution of

copper(II) sulphate, a pale blue precipitate is obtained, which is usually said to be copper(II) hydroxide, but probably contains some basic copper(II) sulphate. (It is much paler in colour than the precipitate thrown down by the caustic alkalis.)

$$Cu^{2+}(aq) + 2OH^-(aq) \rightarrow Cu(OH)_2(s)$$

If *excess* of ammonia is then added with shaking, the precipitate redissolves to produce a *deep blue solution* containing the *diaquatetraamminecopper*(II) *ion* (formerly known as the cupritetrammine ion).

$$Cu(OH)_2(s) + 4NH_3(aq) + 2H_2O(l) \rightarrow [Cu(NH_3)_4(H_2O)]^{2+}(aq) + 2OH^-(aq)$$

The ion is a distorted octahedron in shape; the four ammonia ligands occupy the four square planar positions around the copper ion, and are closer to it than the water molecules in each of the two polar positions (see p. 401).

The solution containing the deep blue ion is known as *Schweitzer's reagent*. It has been used in the manufacture of artificial fibres. The liquid will dissolve cellulose, and if this solution is projected through very fine holes in a metal disc into dilute acid, the complex ammine ion is destroyed. The cellulose is then precipitated as a continuous thread, which can be washed free of acid, dried and used in the weaving of textiles.

Copper(II) sulphate, $CuSO_4.5H_2O$

Manufacture

Hot, dilute sulphuric acid is sprayed on to scrap copper with a plentiful current of air available. This is done in a tower lined with lead (which resists the action of this acid):

$$2Cu(s) + 4H^+(aq) + 2SO_4^{2-}(aq) + O_2(g) \rightarrow 2CuSO_4(aq) + 2H_2O(l)$$

The solution is circulated until an adequate concentration of copper(II) sulphate has been reached and the salt is then crystallized as $CuSO_4.5H_2O$. In the laboratory, copper(II) sulphate is made by the action of hot, dilute sulphuric acid on copper(II) oxide or (basic) carbonate. The copper(II) oxide is stirred *into hot dilute sulphuric* acid until no more will dissolve. The blue solution is filtered hot, concentrated by evaporation, and allowed to cool and crystallize.

Properties

Copper(II) sulphate is usually encountered, as its pentahydrate, in blue crystals, $CuSO_4.5H_2O$. They are readily soluble in water and efflorescent, forming the trihydrate, $CuSO_4.3H_2O$. The solution is slightly acid due to hydrolysis, in which species such as $[Cu(H_2O)_5(OH)]^+$ are formed.

At 383 K, the pentahydrate is converted to the monohydrate $CuSO_4.H_2O$, which is only slightly coloured bluish. At a higher temperature (about 520 K) the salt becomes white and anhydrous. This behaviour corresponds with the known structure of the hydrated salt, in which four water molecules are in the square planar positions around the copper ion, and the fifth is held by hydrogen bonding.

At about 1000 K, the sulphate is converted to oxide by loss of sulphur trioxide, though this is not a good way of preparing the oxide.

$$CuSO_4(s) \rightarrow CuO(s) + SO_3(g)$$

Anhydrous copper(II) sulphate turns blue in contact with water by hydrating the copper ion. It is used in testing for the presence of water; for example, it will detect small amounts of water in alcohol.

Uses

Copper(II) sulphate has many industrial uses among which are the following:

(a) As an aqueous (acidified) solution in copper plating by electrolysis.
(b) As a mordant in dyeing and calico printing.
(c) For preserving timber.
(d) In solution, mixed with lime (*Bordeaux mixture*), as a fungicide for spraying potatoes, vines, and fruit-trees.

Copper(II) chloride, $CuCl_2$

Preparation

1. Copper(II) chloride can be obtained as a brownish-yellow, anhydrous solid by heating copper at about 520 K in a current of dry chlorine (p. 367).

2. Copper(II) oxide can be dissolved in hot, dilute hydrochloric acid, or basic copper(II) carbonate in the same acid in the cold, and the solutions will yield the green dihydrate, $CuCl_2.2H_2O$, by the usual

process of crystallization.

$$\mathrm{CuO(s) + 2HCl(aq) \rightarrow CuCl_2(aq) + H_2O(l)}$$
$$\mathrm{CuCO_3.Cu(OH)_2(s) + 4HCl(aq) \rightarrow 2CuCl_2(aq) + 3H_2O(l) + CO_2(g)}$$

Properties

At red heat, copper(II) chloride dissociates into copper(I) chloride and chlorine.

$$\mathrm{2CuCl_2(s) \rightleftharpoons 2CuCl(s) + Cl_2(g)}$$

It is soluble in water. Its dilute solutions are blue. More concentrated solutions are yellowish-green and the addition of concentrated hydrochloric acid or potassium chloride solution turns them brown. These colour changes are explained in the following way.

In the presence of excess of chloride ion (from HCl or KCl), copper(II) chloride forms the yellow-brown complex ion, $[\mathrm{CuCl_4}]^{2-}$, as:

$$\mathrm{Cu^{2+}(aq) + 4Cl^-(aq) \rightleftharpoons [CuCl_4]^{2-}(aq)}$$

On dilution, these ions break up, and hydrated copper(II) ions, $[\mathrm{Cu(H_2O)_6}]^{2+}$, are formed. These account for the blue colour. The green colour is transitional between the two extremes.

Copper(II) carbonate

Copper forms no true carbonate but has two *basic* carbonates. Both are found naturally as *malachite*, $\mathrm{CuCO_3.Cu(OH)_2}$, a green solid, and *azurite*, $\mathrm{2CuCO_3.Cu(OH)_2}$, a blue solid.

Addition of sodium carbonate solution to copper(II) sulphate solution precipitates a green solid, which has the same composition as malachite. Sodium carbonate is much hydrolysed in solution, producing a relatively high concentration of $\mathrm{OH^-}$ ion. Then

$$\mathrm{2Cu^{2+}(aq) + CO_3{}^{2-}(aq) + 2OH^-(aq) \rightarrow CuCO_3.Cu(OH)_2(s)}$$

Copper(II) sulphide, CuS

Copper(II) sulphide is an almost black solid precipitated by passage of hydrogen sulphide through a hot, acidified (HCl) solution of copper(II) sulphate.

$$\mathrm{H_2S(aq) \rightleftharpoons 2H^+(aq) + S^{2-}(aq)}$$
$$\mathrm{Cu^{2+}(aq) + S^{2-}(aq) \rightarrow CuS(s)}$$

It can be filtered, washed with hot water and dried, but should be protected from air as far as possible because of a tendency to oxidation when moist.

$$CuS(s) + 2O_2(g) \rightarrow CuSO_4(s)$$

The sulphide is not soluble in a mixture of sodium hydroxide solution and yellow ammonium sulphide, which puts copper into analytical Group 2A of the usual tables of Qualitative Analysis.

Detection and determination of copper

(a) Copper(II) salts are blue in solution and give a very intense dark blue colour in the presence of excess of ammonia solution.

$$Cu^{2+}(aq) + 4NH_3(aq) + 2H_2O(l) \rightarrow [Cu(NH_3)_4(H_2O)_2]^{2+}(aq)$$

(b) Copper(II) salts in solution give a purplish-brown precipitate (or, in traces, a coloration) of copper(II) hexacyanoferrate(II) when potassium hexacyanoferrate(II) solution is added.

$$2Cu^{2+}(aq) + [Fe(CN)_6]^{4-}(aq) \rightarrow Cu_2[Fe(CN)_6](s)$$

(c) Copper salts impart a bluish-green colour to the bunsen flame.

A convenient method of determination of copper(II) ion in solution is to add the solution, in known volume, to *excess* of potassium iodide solution (see p. 462). The iodine liberated is titrated by standard sodium thiosulphate solution.

Zinc

Atomic number 30.
Electron arrangement 2.8.18.2 ($1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2$).
Zinc has *five* isotopes with mass numbers, in order of abundance, 64, 66, 68, 67, 70.
Relative atomic mass 65.38.

Occurrence and extraction

The two important ores from which zinc is extracted are zinc blende, ZnS, and calamine, $ZnCO_3$. Zinc blende is the more important. It is often accompanied by galena, PbS. If so, it is usually concentrated by the physical process of *flotation.*

1. *Flotation.* The details of this are complex and of purely technical

interest. In principle, the powdered ore is agitated with water containing certain chemicals (among them slaked lime, potassium cyanide, and a frothing agent). Galena is removed in the froth. Then, in slightly altered conditions, zinc blende appears in the froth and is removed in a more concentrated state. Separation of the two sulphides is not important if the blast furnace process is used.

2. *Roasting in air.* The concentrated blende, or calamine, are roasted in air. The calamine decomposes.

$$ZnCO_3(s) \rightarrow ZnO(s) + CO_2(g)$$

The blende is oxidized by oxygen of the air.

$$2ZnS(s) + 3O_2(g) \rightarrow 2ZnO(s) + 2SO_2(g)$$

In both cases, zinc oxide is left as a sintered solid. The sulphur dioxide is an important by-product and is usually used in a neighbouring plant for the manufacture of sulphuric acid.

3. *Reduction of zinc oxide.* In the Imperial Smelting Corporation's process the sintered zinc oxide is mixed with coke and limestone and put in a blast furnace. Air is blasted through.

$$C(s) + O_2(g) \rightarrow CO_2(g) \qquad CO_2(g) + C(s) \rightarrow 2CO(g)$$
$$ZnO(s) + CO(g) \rightarrow Zn(g) + CO_2(g)$$
$$ZnO(s) + C(s) \rightarrow Zn(g) + CO(g)$$

Zinc has a boiling point of 1186 K. The top of the furnace is maintained at about 1300 K, so the zinc distils off. Slag, which contains iron with some lead and silver, is run off from the base of the furnace. The zinc vapour is cooled by a spray of molten lead. These are partially miscible in the liquid state, but separate on cooling. The zinc solidifies and floats on the lead, which is recycled. Zinc of 99 per cent purity is obtained.

Zinc may also be obtained by dissolving out the zinc from the ore with dilute sulphuric acid. The solution is then electrolysed. Zinc is deposited on an aluminium cathode. For good deposition of zinc, very pure electrolyte is needed.

Uses of zinc

1. *In 'galvanizing' iron or mild steel.* Iron has the great disadvantage of oxidizing (rusting) readily in damp air. Galvanizing coats the iron with zinc as a protective layer. This can be done in several ways, e.g. the iron (or steel) is cleaned in dilute hydrochloric acid and dipped into molten zinc, excess zinc being removed between rollers; zinc may

be sprayed on to the iron; zinc may be electrolytically deposited on an iron cathode from zinc sulphate solution.

A continuous layer of zinc protects the iron from the action of air and water. The protection continues for a time even if the zinc is pierced (see p. 439).

2. *In alloys.* Zinc is alloyed with copper in the important alloy, *brass*, used decoratively and in the making of many scientific instruments. Brass usually has from 20–33 per cent of zinc.

Die-casting alloys, much used in the automobile industry, contain mostly zinc, with aluminium (4 per cent), copper (about 3 per cent) and a very little manganese.

German silver contains about 25 per cent zinc with copper and nickel.

3. *In 'dry' electric batteries.* Sheet zinc is the cathode and, usually, the container in 'dry' batteries. Its essential function (as a fairly electropositive metal) is to ionize and liberate electrons.

$$Zn(s) \rightarrow Zn^{2+} + 2e^-$$

The electrons pass round the external circuit, doing the useful work of the battery.

4. *In extraction of metals.* Zinc is used in the extraction of silver (p. 475) and gold. Here it acts as an electropositive metal displacing a less electropositive one.

Properties of zinc

Zinc is a grey-white metal, melting point 693 K, boiling point 1180 K. The metal is rather soft. It is brittle at room temperature, but, over a rather narrow temperature range (about 380–420 K), it is both malleable and ductile, becoming brittle again at higher temperature.

Because all the 3d orbitals are full and not involved in bonding, zinc does not behave as a typical transition element except in the formation of complexes. Its oxidation state in compounds is uniformly +2. The compounds are rather more covalent than those of magnesium.

(1) *With air or oxygen*

Zinc is little affected by *dry* air at room temperature. It takes fire at red heat and burns with a bluish flame to form its oxide, ZnO. In *moist* air, zinc acquires a thin, coherent layer of basic carbonate, which protects it from further attack.

(2) *With water*

Zinc has little action with water but decomposes steam at red heat.

$$Zn(s) + H_2O(g) \rightarrow ZnO(s) + H_2(g)$$

(3) *With acids*

(a) *Hydrochloric acid and dilute sulphuric acid.* Provided the zinc contains traces of impurity, hydrochloric acid attacks it readily when concentrated, and more slowly when dilute. It is also attacked, though more slowly, by dilute sulphuric acid; heat is usually necessary for a rapid action. In all these cases, *hydrogen* is evolved and the corresponding *zinc salt* is left in solution.

$$Zn(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g)$$

Very pure zinc acts only very slowly in these cases.

(b) *Nitric acid.* This acid can give very variable products, the nature of which depends on the concentration and temperature of the acid. *Zinc nitrate* is always a product (in solution); others may be *nitrogen dioxide, nitric oxide,* and *ammonium compounds* (in solution), these being *reduction products* of the acid. (See also p. 244.) Hydrogen is never obtained.

(c) *Concentrated sulphuric acid.* This acid has no action with zinc when cold, but, on heating, reacts giving mixed products, which will usually include *sulphur dioxide, hydrogen sulphide* and *sulphur.*

$$Zn(s) + 2H_2SO_4(l) \rightarrow ZnSO_4(aq) + 2H_2O(l) + SO_2(g)$$
$$4Zn(s) + 5H_2SO_4(l) \rightarrow 4ZnSO_4(aq) + 4H_2O(l) + H_2S(g)$$
$$2H_2S(g) + SO_2(g) \rightleftharpoons 2H_2O(l) + 3S(s)$$

(4) *With aqueous alkali*

Powdered zinc reacts with hot, aqueous alkali to liberate *hydrogen* and produce the corresponding metallic '*zincate*' in solution (cf. aluminium, p. 122).

$$Zn(s) + 2OH^-(aq) + 4H_2O(l) \rightarrow [Zn(OH)_4(H_2O)_2]^{2-}(aq) + H_2(g)$$

(5) *With solutions of salts*

Zinc is a fairly strongly electropositive metal. As such, it will precipitate several less electropositive metals from solutions of their salts, e.g.

Copper(II) sulphate $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$
Lead(II) nitrate $Zn(s) + Pb^{2+}(aq) \rightarrow Zn^{2+}(aq) + Pb(s)$

(6) *With non-metals*

Zinc will react, when heated, with chlorine, sulphur and nitrogen, in reactions which produce $ZnCl_2$, ZnS, and Zn_3N_2 (zinc nitride).

Zinc oxide, ZnO

Properties of zinc oxide

1. *Action of heat.* Zinc oxide undergoes no permanent chemical change when heated in air but turns from white to *yellow* in colour; it returns to white on cooling. This behaviour is associated with reversible loss of a little oxygen on heating.

2. *Reduction.* Zinc oxide is reduced by *excess* of carbon at red heat to form the metal.

$$ZnO(s) + C(s) \rightarrow Zn(l) + CO(g)$$

Attempted reduction by carbon monoxide (or less than excess carbon) is unsatisfactory because the reaction

$$ZnO(s) + CO(g) \rightleftharpoons Zn(l) + CO_2(g)$$

is considerably reversible.

Zinc oxide is *not* reduced by heating in a current of hydrogen; zinc reduces steam at red heat.

$$Zn(l) + H_2O(g) \rightarrow ZnO(s) + H_2(g)$$

(3) *Amphoteric nature.* Zinc oxide reacts with both acids and alkalis, as does zinc hydroxide. (See p. 473.)

Uses of zinc oxide

(a) Zinc oxide is used as a white pigment, *zinc white.* It has the advantage over white lead of not blackening in air containing hydrogen sulphide. It is, however, inferior to white lead in covering power.

(b) Zinc oxide is used as a filler for rubber, in the making of glass of low solubility, and in glazing porcelain.

(c) Zinc oxide is a constituent of the antiseptic *zinc ointment.*

Zinc hydroxide, $Zn(OH)_2$

Zinc hydroxide is precipitated, white and gelatinous, by adding aqueous caustic alkali to a solution of zinc sulphate (or other soluble zinc salt). *Excess alkali should be avoided* or the precipitate will redissolve.

$$Zn^{2+}(aq) + 2OH^-(aq) \rightarrow Zn(OH)_2(s)$$

It may be filtered, washed with *warm* distilled water and dried in *warm* conditions (but not at 373 K, at which temperature it decomposes to give the oxide and steam).

Amphoteric nature

Zinc hydroxide is amphoteric in nature. It reacts readily with acids:

$$Zn(OH)_2(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + 2H_2O(l)$$

It also reacts with alkalis to give the 'zincate' ion, a hydroxo-complex.

$$Zn(OH)_2(s) + 2OH^-(aq) + 2H_2O(l) \rightarrow [Zn(OH)_4(H_2O)_2]^{2-}(aq)$$

Zinc hydroxide can be precipitated (partially at least) by the action of dilute ammonia with a zinc salt in solution. The precipitate is soluble in excess ammonia because of the formation of a complex *tetraammine* ion, $[Zn(NH_3)_4]^{2+}$. Zinc hydroxide is *not* precipitated by ammonia when the solution is buffered by the presence of ammonium chloride (as in Group III of the usual Qualitative Analysis tables).

Zinc carbonate, $ZnCO_3$

Zinc carbonate occurs in nature as *calamine*. It can be made in the laboratory, as a white precipitate, by adding sodium hydrogencarbonate solution to a solution of a zinc salt (usually the sulphate).

$$Zn^{2+}(aq) + 2HCO_3^-(aq) \rightarrow ZnCO_3(s) + H_2O(l) + CO_2(g)$$

To purify the precipitate, filter it, wash well with distilled water and dry it.

Notice the use of the hydrogencarbonate as precipitating agent. Sodium carbonate is so much hydrolysed in solution that it always precipitates a *basic* carbonate, e.g.

$$3Zn^{2+}(aq) + CO_3^{2-}(aq) + 4OH^-(aq) + 2H_2O(l) \rightarrow ZnCO_3.2Zn(OH)_2.2H_2O(s)$$

The normal or basic carbonate is decomposed by heat to leave zinc oxide.

$$ZnCO_3(g) \rightarrow ZnO(s) + CO_2(g)$$

The basic carbonate loses steam as well as carbon dioxide.

Calamine acts as a source of zinc and is used in preparing *calamine lotion*, for treatment of irritation of the skin.

Zinc sulphide, ZnS

Zinc sulphide occurs in nature as *zinc blende* and is the chief source of zinc. It precipitates (white) only partially if hydrogen sulphide is passed through a solution of zinc sulphate and not at all if the solution is appreciably acidic. It precipitates readily if hydrogen sulphide is passed through a solution containing a soluble zinc salt which is buffered by ammonium chloride and ammonia.

Zinc sulphide is often phosphorescent if impure, especially if traces of manganese salts are present. Zinc sulphide scintillation screens were essential equipment in Rutherford's early work on radioactive decay.

Zinc chloride, $ZnCl_2$

Anhydrous zinc chloride can be made by heating zinc in either chlorine or hydrogen chloride.

$$Zn(s) + Cl_2(g) \rightarrow ZnCl_2(s); \qquad Zn(s) + 2HCl(g) \rightarrow ZnCl_2(s) + H_2(g)$$

It crystallizes from solution as the monohydrate, $ZnCl_2.H_2O$. It is very deliquescent and has a very high solubility in water (350 g as $ZnCl_2$ in 100 g water at 283 K). In electrolysis of zinc chloride solution, some zinc travels towards the *anode*. This probably arises from the formation of complex anions of the type $ZnCl_4{}^{2-}$. Zinc chloride hydrolyses in aqueous solution, has a low melting point, and is soluble in some non-aqueous solvents. All of this indicates some covalent character.

Detection of zinc

In the course of the usual Qualitative Analysis procedure, zinc is precipitated as its sulphide (*white*, though often discoloured) by hydrogen sulphide in the presence of ammonium chloride and ammonia.

The white → yellow → white colour change on heating zinc oxide and allowing it to cool is characteristic.

This concludes the discussion of the metals in the first transition series. Three more d-block metals, silver, cadmium and mercury will now be briefly discussed.

(2) Other d-block elements

Silver

Atomic number 47.
Electron arrangement 2.8.18.18.1 ($1s^2 2s^2 sp^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^1$).
Silver has two isotopes of mass numbers, in order of abundance, 107 and 109.
Relative atomic mass 107.9.

In old versions of the Periodic Table, copper, silver, and gold were included in Group IB. They are known as the *coinage metals*.

Occurrence

(a) Silver occurs native in Mexico, Nevada, New South Wales, and Bolivia. It is sometimes found, as in South Africa, alloyed with gold.
(b) The principal source of silver is the sulphide, Ag_2S, *argentite* or *silver glance*.
(c) *Horn silver*, AgCl, also occurs in association with lead.

Extraction of silver

The *cyanide process* is mostly used; the principles are as follows. The ore, finely powdered, is treated with a solution of sodium cyanide. The complex dicyanoargentate(I) ion, which takes silver into solution, is formed.

$$Ag^+(aq) + 2CN^-(aq) \rightleftharpoons [Ag(CN)_2]^-(aq)$$

After decanting from insoluble matter, the solution is treated with zinc shavings. Silver is displaced and precipitates. The cyanide complex of zinc is unstable and decomposes to its constituent ions.

$$2[Ag(CN)_2]^-(aq) + Zn(s) \rightarrow Zn^{2+}(aq) + 4CN^-(aq) + 2Ag(s)$$

The silver may be purified by fusion with potassium nitrate or by electrolytic refining.

Uses of silver

1. *For table-ware, artistic objects and the coinage.* The highest quality

silver articles are of 'sterling silver', containing 92.5 per cent silver and 7.5 per cent copper, a standard fixed in Tudor times. This alloy is harder than pure silver.

2. *Electroplating with silver.* Articles such as table ware, vases and cake dishes are shaped in base alloy (such as 'German silver' or cupro-nickel) and made the cathode in a plating bath of *potassium dicyanoargentate*(I) solution. The anode is a plate of pure silver. The complex is in equilibrium with the constituent ions:

$$[Ag(CN)_2]^-(aq) \rightleftharpoons Ag^+(aq) + 2CN^-(aq)$$

The concentration of Ag^+ in the solution always remains small, but there is plenty of reserve in the complex ion. When direct current is passed:

At the cathode	*At the anode*
$Ag^+(aq) + e^- \rightarrow Ag(s)$	$Ag(s) \rightarrow Ag^+(aq) + e^-$
Silver deposits on the article	Silver dissolves, keeping up the concentration of its ions.

If concentration of solution, current density and temperature are correctly adjusted, the layer of silver is coherent and tough, and can be highly polished. Silver is also used in the silvering of mirrors, for plating bearings in engineering and conductors in the radio industry. It is used in quantity to make silver(I) nitrate (p. 479) for the photographic industry, and, with copper, zinc and cadmium, in solders for silver ware.

Properties of silver

Silver is a rather soft, white metal which will take a high polish. It has a high density (10.5 g cm^{-3}). Its melting point is 1234 K. It is very malleable and ductile, and has the highest known thermal and electrical conductivities.

Chemical properties

The oxidation state of silver in its compounds is uniformly $+1$; the only important exception is silver(II) fluoride, AgF_2. Silver is chemically resistant (hence its use in jewellery and objets d'art), but tarnishes with sulphur or sulphides and in air containing hydrogen sulphide.

1. *Action with oxygen.* Silver is not attacked by oxygen in the cold. Just above its melting point, silver will absorb about 20 times its own

volume of oxygen without change of appearance. As it cools, the metal discharges the oxygen almost entirely. This may occur with vigour, causing the *spitting* of silver.

2. *Effect of exposure to air.* Silver is stained black by a layer of silver(I) sulphide, Ag_2S, if the air contains gaseous sulphur compounds (SO_2 or H_2S); otherwise, it remains unchanged.

3. *Action with acids.* Silver is less electropositive than hydrogen and does not replace it from acids. It is attacked by oxidizing acids only. (See *silver*(I) *nitrate* below.)

4. *Action of alkalis.* Silver is not appreciably attacked by alkali or by ammonia in any conditions.

Compounds of silver

The single outer electron of silver may be used for electrovalent combination, leaving the ion Ag^+ with electron structure 2.8.18.18. It may also be used as one electron of a shared pair in covalent combination. Silver can participate in both cationic and anionic complexes. Silver(II) compounds are rare.

Silver(I) oxide, Ag_2O

Silver(I) oxide is precipitated as a hydrated brown solid by the addition of alkali to a solution of silver(I) nitrate. The hydroxide is not obtained.

$$2Ag^+(aq) + 2OH^-(aq) \rightarrow Ag_2O(s) + H_2O(l)$$

The addition of a *little* dilute aqueous ammonia to silver(I) nitrate solution precipitates silver(I) oxide as a brown solid. Addition of *excess* of ammonia then dissolves the precipitate by formation of a cationic complex.

$$Ag^+(aq) + 2NH_3(aq) \rightleftharpoons [Ag(NH_3)_2]^+(aq)$$

If left to stand exposed to air, a solution of silver(I) oxide in excess of ammonia slowly deposits a black powder, probably the azide, AgN_3. It is explosive when dry and is known as *fulminating silver*.

1. *Silver*(I) *oxide as an oxidizing agent in the 'Silver mirror' test.* A solution of silver oxide in excess of aqueous ammonia, known as *ammoniacal silver oxide* (or *nitrate*), is a useful oxidizing agent, especially with organic compounds. If shaken with an aldehyde in a test tube and heated slowly, the solution deposits a silver mirror on the sides of the test tube. The aldehyde is oxidized to a carboxylic acid, which forms its salt,

ammonium ethanoate. The silver mirror should be destroyed with nitric acid to prevent formation of the explosive azide (see above).

2. *Basic properties.* Silver(I) oxide is quite a strong base. It is slightly soluble in water and the solution is alkaline. Consequently, silver does not form basic salts such as are common in copper(II) chemistry. Copper(II) oxide is a much weaker base.

Silver(I) oxide and water (*moist silver oxide*) are used as a mild hydrolysing agent in organic chemistry in cases where aqueous alkalis are too vigorous. Moist silver(I) oxide, heated under reflux with a halogenoalkane, will convert it to the corresponding alcohol.

$$2RI(l) + Ag_2O(s) + H_2O(l) \rightarrow 2ROH(l) + 2AgI(s)$$

3. *Decomposition of silver*(I) *oxide.* Silver will oxidize slowly in air if heated to 370–390 K, but the oxide is decomposed again completely at 570 K.

$$4Ag(s) + O_2(g) \rightleftharpoons 2Ag_2O(s)$$

Halides of silver

Preparation

Silver(I) fluoride, AgF, is very soluble in water, but silver(I) chloride, AgCl, silver(I) bromide, AgBr, and silver(I) iodide, AgI, are all almost insoluble in water and are precipitated by the addition of a solution of a soluble chloride, bromide or iodide to a solution of silver(I) nitrate. If required pure, all should be protected from light, filtered off, washed with hot, distilled water and dried at about 390 K.

The chloride is essentially electrovalent; covalent character increases from chloride to bromide and from bromide to iodide. This change in bonding character is reflected in the differing solubilities of silver(I) halides in ammonia solution. The compounds show a typical halogen gradation in the properties summarized in the table below:

	Solubility product at 298 K ($mol^2\,dm^{-6}$)	*Solubility in dilute ammonia*	*Colour*
AgCl	1.6×10^{-10}	Readily soluble	White
AgBr	4.0×10^{-13}	Sparingly soluble	Pale yellow
AgI	0.94×10^{-16}	Almost insoluble	Stronger yellow

Silver(I) chloride is readily soluble in aqueous solutions of ammonia, potassium cyanide and sodium thiosulphate. In all these cases, complex ions are formed.

$$\mathrm{AgCl(s) + 2NH_3(aq) \rightleftharpoons [Ag(NH_3)_2]^+ + Cl^-(aq)}$$
$$\mathrm{AgCl(s) + 2CN^-(aq) \rightleftharpoons [Ag(CN)_2]^-(aq) + Cl^-(aq)}$$
$$\mathrm{AgCl(s) + 2S_2O_3{}^{2-}(aq) \rightleftharpoons [Ag(S_2O_3)_2]^{3-}(aq) + Cl^-(aq)}$$

Uses of silver halides

Silver(I) chloride is used in making *printing out papers* in photography. Silver(I) bromide is used in making the light-sensitive emulsion for photographic plates and films. For an account of photography, see p. 480.

Silver(I) *fluoride*, AgF

This halide is markedly different from the three considered above by being readily soluble in water (172 g in 100 g water at 293 K). It is made by dissolving silver(I) oxide in hydrofluoric acid and evaporating at very low pressure. Crystals of the hydrate, $AgF.H_2O$, are obtained.

Silver(I) nitrate, $AgNO_3$

Preparation

Silver(I) nitrate is made by dissolving silver with heat in moderately concentrated nitric acid. The main reaction is:

$$\mathrm{3Ag(s) + 4HNO_3(aq) \rightarrow 3AgNO_3(aq) + 2H_2O(l) + NO(g)}$$

Excess silver should be available to reduce the concentration of the remaining nitric acid to a very low value. After filtration, the liquid is greatly reduced in bulk by evaporation. On cooling, it yields colourless, rhombic crystals of silver(I) nitrate, which can be filtered, washed with caution (they are very soluble) and dried.

These crystals are exceptionally soluble in water (122 g at 273 K and 925 g at 373 K per 100 g water).

Action of heat

At about 700 K silver(I) nitrate decomposes producing the *nitrite*.

(In this, it resembles the alkali metal nitrates.)

$$2AgNO_3(s) \rightarrow 2AgNO_2(s) + O_2(g)$$

At about 1000 K, it decomposes, leaving a bright, white mass of *metallic silver*, with evolution of *nitrogen dioxide* and *oxygen.*

$$2AgNO_3(s) \rightarrow 2Ag(s) + 2NO_2(g) + O_2(g)$$

Uses of silver(I) *nitrate*

(a) Silver(I) nitrate is much used in the photographic industry in preparing the emulsions for plates and films.
(b) The solution is widely used in volumetric and qualitative analysis.

Silver compounds in photography

A black and white photographic plate or film consists of an emulsion of silver(I) bromide in gelatine and water, carried on a glass or celluloid backing for strength.

To make the emulsion, silver(I) nitrate solution is added to a mixture of gelatine and potassium bromide in hot water. (A little potassium iodide is usually present, too.) Silver(I) bromide, with a little iodide, is precipitated. The mixture is allowed to stand for a time while still warm. This *ripening* increases the average size of the silver(I) bromide particles and makes the emulsion more sensitive to light. On cooling, it sets and is then shredded and washed with water to remove soluble materials. It is then melted and poured on to the glass or celluloid and dried, leaving a creamy, 'solid' layer of light-sensitive emulsion. All these processes are carried out in a light to which the silver salts are insensitive, i.e. orange light.

The use of the film or plate in photography can be divided into three stages: (1) *exposure to light*; (2) *development* ; (3) *fixation.*

(1) *Exposure*

The emulsion is exposed to light which is controlled, with respect to focusing and intensity, by the lens of a camera, the aperture used, and the time of exposure. The light produces no *visible* effect on the emulsion but the silver halide is reduced to a *latent* image of minute particles of metallic silver at various spots on the emulsion. The concentration of these spots is roughly proportional to the intensity of the light falling on the area.

(2) *Development*

The exposed plate is subjected to the action of a *developer*, which is a mild organic reducing agent. The developer extends the reduction produced by light at the sensitive spots, and gives a black deposit of metallic silver in the gelatine with an intensity roughly proportional to that of the light falling on the areas during exposure. Thus the strongly lighted areas become the blackest after development, and the product is called a *negative*.

(3) *Fixation*

After development, the negative still contains unchanged silver(I) bromide. This is still light sensitive, and must be removed or the negative will 'fog' on exposure to light. To remove it, excess developer is washed off and the negative immersed in a concentrated solution of sodium thiosulphate. The silver bromide is dissolved out by formation of the $[Ag(S_2O_3)_2]^{3-}$ complex ion, leaving a negative containing varying intensities of silver deposits in gelatine and no longer sensitive to light. The negative is then washed thoroughly and dried.

Printing

In *contact printing*, a paper or card coated with a silver bromide emulsion like that on plate or film is used. It is exposed to artificial light behind the corresponding negative for a controlled time. Light is cut off by the blacker parts of the negative and passed by the paler parts, so that the effects of the negative are reversed to produce a black-and-white positive print. It is developed, fixed and washed like a negative.

Detection of silver

(a) Silver is detected in qualitative analysis by precipitation of its chloride from solution by dilute hydrochloric acid or any soluble chloride. The precipitate is readily soluble in ammonia (see p. 479).

$$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$$

(b) A neutral solution of potassium chromate(VI) gives a brick-red precipitate of silver chromate(VI).

Cadmium

Atomic number 48.
Electron arrangement 2.8.18.18.2 ($1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}5s^2$).
Cadmium has isotopes of mass number (in order of abundance) 114, 112, 111, 110, 113, 116, 106, 108.
Relative atomic mass 112.4.

In older forms of the Periodic Table, zinc, cadmium, and mercury were considered as Group IIB.

Occurrence and extraction

Cadmium usually occurs (as CdS) with zinc in zinc blende, ZnS. Cadmium follows the same course of reactions as zinc in the extraction process (p. 468) and appears with zinc in the distillate. Cadmium (boiling point 1038 K) can be separated from zinc (boiling point 1180 K) by further distillation.

Properties and uses of cadmium

Cadmium is a rather soft, white metal, melting point 594 K, boiling point 1038 K, and density 8.64 g cm^{-3}. Like zinc, it is stable in dry air but, in moist air, acquires a coating of oxide and carbonate. Cadmium and its compounds are highly toxic.

Cadmium reacts with all the dilute mineral acids when heated, hydrogen being given off.

$$Cd(s) + 2H^+(aq) \rightarrow Cd^{2+}(aq) + H_2(g)$$

Cadmium differs from zinc in remaining unattacked by aqueous alkalis. Its uses are as follows:

(a) Cadmium is used as a plating for the protection of steel from rusting. It may be deposited by electrolysis or by spraying.
(b) Cadmium is used in alloys, e.g. in low melting point alloys such as *Wood's metal* (50% Bi, 25% Pb, 12.5% each of Cd and Sn; m.p. 340 K). This is used in fire-sensitive situations, such as automatic sprinkler heads and fire-door restraints.
(c) Cadmium, in the form of rods, is a neutron-absorber and is used in controlling energy release in nuclear reactors.
(d) Cadmium, and its sulphate, are used in the Weston standard cell.

Compounds of cadmium

Cadmium compounds, both ionic and covalent, contain the element exclusively in the +2 oxidation state. The oxide and hydroxide are essentially basic, though they are slightly soluble in fused or concentrated alkali, thus showing some amphoteric properties. This tendency is much less than is shown by the corresponding zinc compounds. Cadmium chloride, $CdCl_2$, exists in solution largely as chloro-complexes such as $[CdCl]^+$, $[CdCl_3]^-$. Solid cadmium iodide, CdI_2, has a *layer lattice* structure, intermediate between ionic and covalent. The vapour consists of linear I-Cd-I molecules.

Cadmium sulphide is a bright yellow compound which is precipitated by hydrogen sulphide from an aqueous solution of a cadmium salt *provided that it is not too acidic.* This gives a means of detecting the element.

Mercury

Atomic number 80; electron arrangement
2.8.18.32.18.2 ($1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}4f^{14}5s^25p^65d^{10}6s^2$).
Mercury has isotopes of mass number (in order of abundance) 202, 200, 199, 201, 198, 204, 196.
Relative atomic mass 200.6.

Occurrence and extraction

Mercury has been known for many centuries. Its ease of extraction and unique physical properties made 'quicksilver' a major subject of study by the alchemists. The only important industrial source of mercury is the sulphide, *cinnabar*, HgS.

Extraction

Cinnabar is crushed and the powder is concentrated by flotation. It is then roasted in air (sometimes with the addition of lime or iron to combine with the sulphur).

The main reaction is:

$$HgS(s) + O_2(g) \rightarrow Hg(g) + SO_2(g)$$

Mercury vapour distils off and is condensed.

Purification

Mercury is difficult to purify because it amalgamates so readily with other metals. Repeated distillation under reduced pressure is the most effective method.

Properties of mercury

Mercury is a silvery liquid (*quicksilver*) with a bluish tinge. It is the only liquid metal in room conditions: melting point 234 K. It boils at 630 K and has a high density (13.6 g cm^3 at 293 K.) The volatility of mercury and the very high toxicity of its vapour mean that it is a dangerous but well-recognized hazard. Many mercury compounds, particularly those which are volatile or water-soluble, are extremely toxic.

1. *With air or oxygen.* Mercury is unaffected by air or oxygen at room temperature, but, if heated just below its boiling point, it oxidizes to the *red mercury*(II) *oxide*, HgO. This oxide decomposes again at about 800 K.

2. *With acids.* Mercury is *less* electropositive than hydrogen and does not displace it from any acid. Mercury is attacked by *oxidizing acids* only.

Hot, concentrated sulphuric acid yields *sulphur dioxide* and a sulphate of mercury. This tends to be mercury(I) sulphate, Hg_2SO_4, if mercury is in excess and mercury(II) sulphate, $HgSO_4$, with acid in excess:

$$2Hg(l) + 2H_2SO_4(l) \rightarrow Hg_2SO_4(s) + 2H_2O(l) + SO_2(g)$$
$$Hg(l) + 2H_2SO_4(l) \rightarrow HgSO_4(s) + 2H_2O(l) + SO_2(g)$$

Nitric acid yields similar results. Oxides of nitrogen are liberated in any case; if the acid is *dilute* and only *warm* with mercury in excess, mercury(I) nitrate, $Hg_2(NO_3)_2$, is formed in solution; if the acid is *hot, concentrated and in excess*, mercury(II) nitrate, $Hg(NO_3)_2$, is the dissolved product. Precise equations cannot be written.

Mercury has no reaction with hydrochloric acid or with alkalis.

3. *With chlorine and iodine.* Heated mercury reacts readily with *dry* chlorine to form *mercury*(II) *chloride.*

$$Hg(l) + Cl_2(g) \rightarrow HgCl_2(s)$$

Mercury forms green *mercury*(I) *iodide* if rubbed, in the correct proportions, with iodine (and a little ethanol).

$$2Hg(l) + I_2(s) \rightarrow Hg_2I_2(s)$$

4. *With sulphur.* If rubbed with sulphur in the required proportions (and a little potassium hydroxide solution), mercury forms *mercury*(II) *sulphide*, HgS, which is black at first but slowly turns red and crystalline.

5. *With metals; amalgamation.* Mercury amalgamates with many metals. The following are typical cases. Freshly cut *sodium* amalgamates when pressed under a globule of warm mercury. At first, the process is vigorous and accompanied by a flash of light. The amalgam is a silvery

liquid. Later, the amalgamation is much quieter and the amalgam is a grey solid. *Gold*, *silver*, *cadmium*, *tin*, *lead*, *zinc*, and powdered *copper* amalgamate if rubbed with mercury at ordinary temperature. *Iron*, *cobalt*, and *nickel* do *not* amalgamate directly. The formation of sodium amalgam is a key step in one method for the industrial manufacture of chlorine and sodium hydroxide (see p. 49).

Uses of mercury

(a) The major use of mercury is as the cathode in the electrolytic manufacture of chlorine and sodium hydroxide (see p. 49).
(b) Mercury is used in *thermometers*, where it has the advantages of a high boiling point, good conduction of heat, even expansion and good visibility. Various other scientific instruments and pieces of apparatus make use of the high density and good conductivity of mercury.
(c) Mercury is also used to manufacture the sulphide, HgS, as *vermilion*, and 'mercury fulminate', $Hg(CNO)_2$, which is used in detonators as it explodes on percussion.
(d) The electrical industry uses mercury in arc rectifiers and switches.
(e) Amalgams are used as dental fillings, especially with gold, silver, and tin. They are plastic for a time and then set very hard. They are said to be insoluble under physiological conditions. Sodium amalgam (with water or dilute acid) is used as a reducing agent.
(f) Mercury(II) sulphate acts as a catalyst in the manufacture of ethanal (acetaldehyde) from ethyne.

Compounds of mercury

Although it possesses a full d sub-shell, mercury can form compounds based on two oxidation states, (+1 and +2). The ion Hg^+ does not exist. Mercury(I) compounds contain the ion Hg_2^{2+}. This possesses a metal–metal bond with a covalent nature, which is very rare. X-ray studies have confirmed the structure as $^+Hg{-}Hg^+$. The $Hg_2^{2+}(aq)$ ion tends to disproportionate to $Hg^{2+}(aq)$ and mercury.

$$Hg_2^{2+}(aq) \rightleftharpoons Hg(l) + Hg^{2+}(aq)$$

The presence of metallic mercury will help to stabilize a solution of a mercury(I) salt. If a mixture of mercury and mercury(II) chloride is heated with no water present, mercury(I) chloride sublimes out.

$$Hg(l) + HgCl_2(s) \rightarrow Hg_2Cl_2(g)$$

Mercury(I) compounds

A solution containing mercury(I) ions can be obtained by treating an *excess* of mercury with *dilute* nitric acid. (Excess of *hot, concentrated* acid gives mercury(II) nitrate.)

$$6Hg(l) + 8H^+(aq) + 2NO_3^-(aq) \rightarrow 3Hg_2^{2+}(aq) + 2NO(g) + 4H_2O(l)$$

Mercury(I) chloride and mercury(I) sulphate can be precipitated by adding the appropriate dilute acid to the mercury(I) nitrate solution.

The existence of true mercury(I) oxide, Hg_2O, is doubtful. Few complexes exist which contain mercury in the + 1 oxidation state.

Mercury(II) compounds

Mercury(II) oxide, HgO

This compound is formed when an alkali is added to a solution containing Hg^{2+} ions. It is also formed, reversibly, by gentle heating of mercury in air or oxygen (see p. 484). It exists in yellow and red forms. The yellow form turns to red on warming. Mercury(II) oxide is basic in its properties.

Mercury(II) chloride, $HgCl_2$

This is a white, extremely poisonous solid. It can be obtained by: (a) dissolving mercury(II) oxide in hydrochloric acid; (b) heating mercury in dry chlorine; (c) sublimation from a hot mixture of mercury(II) sulphate and sodium chloride.

The low conductivity of the solution indicates the existence of $HgCl_2$ molecules rather than free ions. The solid dissolves in ethoxyethane (ether), which suggests a covalent nature. X-ray studies of the solid and electron diffraction studies of the vapour indicate a linear Cl-Hg-Cl molecule.

Mercury(II) chloride is reduced by tin(II) chloride solution, initially to a *white precipitate* of mercury(I) chloride, and then to metallic mercury, which appears as a black deposit.

Addition of excess chloride ion to a solution of mercury(II) chloride gives the complexes $[HgCl_3]^-$ and $[HgCl_4]^{2-}$.

Mercury(II) iodide

Mercury(II) iodide is obtained as a precipitate by careful addition of potassium iodide to mercury(II) chloride, both in solution.

$$HgCl_2(aq) + 2KI(aq) \rightarrow HgI_2(s) + 2KCl(aq)$$

The precipitate is at first *yellow*, but rapidly turns red.

Further addition of potassium iodide solution redissolves the scarlet precipitate, with formation of a complex *tetraiodomercury*(II) ion.

$$HgI_2(s) + 2I^-(aq) \rightleftharpoons [HgI_4]^{2-}(aq)$$

When this solution is made alkaline by the addition of potassium hydroxide, the resulting solution is known as *Nessler's reagent.* It is a very sensitive test for the ammonium ion, NH_4^+, in solution. With the Nessler reagent in excess, this ion yields a yellow or *brown precipitate.* If the concentration of the ion, NH_4^+, is very small, the effect may be only a brown coloration, not a precipitate. This test is very important in water analysis.

Detection of mercury

(a) Fusion of any compound of mercury with sodium carbonate gives a grey deposit of mercury.
(b) Addition of dilute hydrochloric acid to a solution of a mercury(I) compound gives a white precipitate which is blackened when treated with ammonia solution.
(c) Solutions containing mercury(II) give a yellow precipitate of mercury(II) oxide when treated with a solution of sodium or potassium hydroxide.

Questions

1 What is the essential oxidizing behaviour of potassium dichromate(VI) in electronic terms? Illustrate this behaviour by detailed reference to *three* cases involving inorganic materials and *one* involving an organic material.

2. Explain the following: (a) the acidification of potassium chromate(VI) solution turns it from yellow to orange; addition of caustic alkali solution in slight excess reverses the change; (b) distillation of a mixture of potassium dichromate(VI), common salt and concentrated sulphuric acid liberates brown fumes; if they are led into water, a yellow solution is formed; (c) heating of ammonium dichromate(VI) leaves a bulky green powder with evolution of gaseous material, (d) if potassium dichromate(VI) solution is shaken with sulphur dioxide, a dark green, clear liquid is left; if the gas used is hydrogen sulphide, the green liquid contains a precipitate.

3. Starting, in both cases, from copper(II) oxide, how would you prepare in the laboratory reasonably pure samples of (a) copper(I) oxide, (b) copper(I) chloride? How, and in what conditions, does copper(I) oxide react with (i) hydrogen, (ii) sulphuric acid, and copper(II) sulphate react with (iii) ammonia, (iv) potassium iodide? How would you detect a very small proportion of Cu^{2+} ion in water?

4. Describe in essential outline the extraction of zinc from its sulphide ore. How, and in what conditions, does zinc react with (a) mineral acids, (b) caustic alkalis? Give an account of the use of zinc in galvanizing and in *two* other ways. Account, in ionic terms, for the amphoteric character of zinc hydroxide.

5. Starting in all cases from zinc foil, how would you prepare reasonably pure samples of: (a) zinc oxide, (b) anhydrous zinc chloride, (c) normal zinc carbonate, (d) zinc sulphide? Describe and explain what occurs if (b) is dissolved in water and potassium hydroxide solution is added, slowly with shaking, till the alkali is in excess.

6. Outline the production of cast iron in the blast furnace. State briefly the important characteristics of this form of iron and relate them to its uses. Give a concise account of the conversion of iron to steel. What is meant by the *tempering* of steel and what is its purpose?

7. Relate the electronic configuration of the iron atom to the existence of iron(II) and iron(III) compounds. Describe *three* different reactions by which iron(II) sulphate (in dilute sulphuric acid) can be oxidized and *three* by which iron(III) chloride in aqueous solution can be reduced. Give *one* chemical test in each case by which the conversions can be confirmed.

8. Write an essay on the rusting of iron and its prevention.

9. What are the chief characteristics of a *transition element*? Illustrate them by reference to the chemistry of *either* manganese *or* iron.

10. Give an account of the occurrence and extraction of iron, paying particular attention to the physicochemical principles involved.

Describe how iron is converted to steel and discuss the essential differences between these two substances.

Comment briefly on the fact that, although iron is only some two-thirds as common as aluminium in the earth's crust, weight for weight it costs only about one quarter as much. (L.)

11. The elements scandium to zinc are generally listed in a separate 'block' of the Periodic Table.

(a) Review the major characteristics common to this block of elements which are not generally shown by elements in other blocks of the Periodic Table. Explain how the chemical properties of these elements or their compounds can be understood in terms of electronic structure.

(b) Illustrate these characteristics by reference to *one* member of the series scandium to zinc, and discuss critically the extent to which this member exhibits all the characteristics outlined in your answer to (a). (L.)

12. (a) Ammonium vanadate(V) solution may be regarded as containing the element vanadium in the ion VO_2^+ with an oxidation number of $+5$. Use the data given below to predict which of the following reagents will reduce the vanadium compound, and to what lower oxidation state of the metal: sulphur dioxide, zinc dust, iron(II) ions, copper dust, and bromine.

	$E^\ominus$(V)		$E^\ominus$(V)
$VO_2^+ + 2H^+ + e^- \rightleftharpoons VO^{2+} + H_2O$	$+1.0$	$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$	$+1.52$
$VO^{2+} + 2H^+ + e^- \rightleftharpoons V^{3+} + H_2O$	$+0.34$	$SO_4^{2-} + 4H^+ + 2e^- \rightleftharpoons SO_2 + 2H_2O$	$+0.17$
$V^{3+} + e^- \rightleftharpoons V^{2+}$	-0.27	$Zn^{2+} + 2e^- \rightleftharpoons Zn$	$+0.76$
		$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	$+0.77$
		$\frac{1}{2}Br_2 + e^- \rightleftharpoons Br^-$	$+1.07$
		$Cu^{2+} + 2e^- \rightleftharpoons Cu$	$+0.34$

(b) Explain why it is feature of transition elements that they show different oxidation states.

(c) A solution of ammonium vanadate(V) (NH_4VO_3), concentration 5.85 g dm^{-3}, was prepared in dilute sulphuric acid. Two 25 cm^3 samples of this solution were boiled for five minutes (i) with sodium sulphite, and (ii) with zinc. Each solution was then reoxidized quantitatively with a solution of potassium manganate(VII) and required 12.5 cm^3 and 37.5 cm^3 respectively.

Compare the changes in oxidation number of the vanadium during this experiment with your predictions from the data.

What is the molar concentration of the potassium manganate(VII) solution?

$(H = 1.0, N = 14, O = 16, K = 39, V = 51, Mn = 55)$ (L.)

13. Outline the chemistry of the manufacture of (a) pig iron, (b) *either* manganese *or* chromium.

How, starting from iron filings, would you prepare specimens of (i) iron(III) oxide, (ii) anhydrous iron(II) chloride? (C.)

14. Give (a) the structure, (b) a method of formation of each of the following complex ions.
(i) $[Fe(CN)_6]^{4-}$; (ii) $[Fe(CN)_6]^{3-}$; (iii) $[Cu(NH_3)_4]^{2+}$; (iv) $[Cu(NH_3)_2]^+$; (v) $[Cu(CN)_4]^{3-}$. (A.E.B.)

15. Explain concisely each of the following.

(a) On heating, copper(II) sulphate pentahydrate readily loses four molecules of water, but the fifth is only removed with difficulty.

(b) When aqueous potassium cyanide is added to a solution of copper(II) sulphate, a white precipitate, soluble in an excess of reagent, is formed, and a gas is evolved. No precipitate is formed when hydrogen sulphide is passed into the resulting solution.

(c) Both copper(I) chloride and copper(II) chloride dissolve readily in concentrated hydrochloric acid.

(d) When ethyne (acetylene) is passed into a solution of copper(I) chloride in aqueous ammonia, a red-brown precipitate is formed. (A.E.B.)

16. List the commonly occurring oxidation states in aqueous solution of each of the first row transition elements from Ti to Cu. Indicate any changes in stability of these states across the row.

Give *two* examples (using two different transition elements) to illustrate how a change of ligand can influence the oxidation-reduction behaviour of particular oxidation states.

Compare and contrast the chemistry of copper(II) (aq) and cobalt(II) (aq) by discussing the reactions of aqueous solutions of their sulphates with
(i) concentrated hydrochloric acid,
(ii) concentrated aqueous ammonia in the presence of air. (J.M.B.)

17. This question concerns the elements zinc, iron and copper.

(a) Give *one* method of extraction of *one* of the elements from a *named* ore.

(b) Describe the formation of *one* cationic complex of *either* copper *or* iron, and give its structure.

(c) Explain each of the following.

(i) Excluding the free state, copper and iron exist in several oxidation states whereas zinc exists in only one.

(ii) The standard electrode potential of zinc is more negative than that of copper.
(iii) Copper and iron form coloured ions but zinc does not. (A.E.B.)

18. (a) What type of reaction is represented by the following equilibrium?

$$[M(H_2O)_6]^{n+} + mH_2O \rightleftharpoons [M(OH)_m(H_2O)_{6-m}]^{(n-m)+} + mH_3O^+$$

Discuss, with examples, how the position of the equilibrium will be influenced by the charge and size of the ion M^{n+} and show how you could promote the forward reaction.

(b) Discuss ligand substitution reactions of hydrated transition metal ions by showing, with *one* example in each case, how to bring about the following:
(i) ligand substitution with *no* change in coordination number;
(ii) ligand substitution with a change in coordination number;
(iii) ligand substitution which favours a change in oxidation state of the transition metal. (J.M.B.)

19. In their compounds, the early members of the first transition series are usually in the highest possible oxidation states, whereas this is not true of the later members of the series.

Discuss this statement including in your answer referrence to the following:
(a) The common oxidation states of titanium and vanadium.
(b) The common oxidation states of cobalt and nickel, including examples of actual compounds. Suggest why cobalt has two stable oxidation states.
(c) The reasons for the differences between (a) and (b).
(d) The effect of change of ligand on oxidation-reduction behaviour. (J.M.B.)

20. (a) Give explanations for the following:
(i) concentrated aqueous copper(II) chloride solution is bright green in colour; on dilution with water it changes to a light-blue solution;
(ii) a solution of copper(I) chloride in hydrochloric acid absorbs carbon monoxide;
(iii) copper(I) chloride is soluble in several organic solvents.

(b) From the following information determine the correct formula of a double salt $Cu(NH_4)_xCl_y.zH_2O$ (x, y, and z are whole numbers):
(i) its molar mass is 277.5 g;
(ii) the chloride in 1.388 g of the salt is precipitated as silver chloride; after washing and drying the mass of the precipitate is 2.870 g;
(iii) when 1.388 g of the salt is boiled with excess aqueous sodium hydroxide the ammonia liberated neutralizes 10.0 cm^3 of hydrochloric acid of concentration 1.00 mol dm^{-3}. (A.E.B.)

21. Explain why:
(a) iron can exist in the oxidation states 2, 3, 4, 5 and 6;
(b) compounds of iron are generally coloured;
(c) the atomic radius of iron is about the same as that of manganese.

Give the structures of *one* anionic complex and *one* cationic complex of iron stating, with reasons, the oxidation state of the metal.

How do you account for each of the following?
(d) When aqueous solutions of iron(II) sulphate and sodium hydrogen carbonate are mixed a precipitate is formed and a gas is evolved.
(e) A gas is evolved when a mixture of iron(II) sulphate and concentrated sulphuric acid is heated.

(f) A dark brown substance is formed when nitrogen oxide (NO) is bubbled into aqueous iron(II) sulphate. (A.E.B.)

22. Iron is a transition element with atomic number 26.

(a) Using s, p, d notation, write the detailed electronic structures of (i) an iron atom, (ii) the iron(II) ion, (iii) the iron(III) ion.

Explain why iron is referred to as a *transition* element.

(b) State *three* general characteristics of a *transition* element, illustrating them by examples from the chemistry of iron.

(c) Why has a solution of an iron(III) salt in water a pH less than 7?

(d) Describe the uses of

(i) an iron compound in qualitative analysis,

(ii) an iron compound in titrimetric analysis. (A.E.B.)

General questions

1. Outline how aluminium is obtained on an industrial scale. Describe a method of preparing anhydrous aluminium chloride. Comment on the variation of the relative vapour density of this compound with temperature. What happens when aluminium chloride is added to (a) water, (b) sodium hydroxide solution, (c) a solution of chloromethane in benzene? (W.)

2. Give an account of the chemistry of magnesium and its compounds, paying particular attention to what you would expect from its position in the Periodic Table. How would you prove the presence of magnesium and aluminium in a sample of an alloy containing the two metals? What are the particular uses of such alloys? (L.)

3. Describe, with the essential experimental details, how you would prepare the following in a reasonably pure dry condition: (a) copper(I) chloride, starting from metallic copper, (b) iron(III) sulphate (hydrate), starting from metallic iron, (c) normal magnesium carbonate, starting from magnesium oxide. (J.M.B.)

4. Compare the chemistry of chlorine with that of iodine by reference to the following reactions: (a) concentrated sulphuric acid is added to solid sodium halide, (b) a solution of sodium hydroxide is treated with the halogen, (c) the solution obtained in (b) is acidified with sulphuric acid, (d) the action of heat on solid sodium chlorate(V) and sodium iodate(V) respectively, (e) silver nitrate is added to a solution of sodium halide followed by the addition of ammonia solution. State the conditions giving the reactions you describe. (W.)

5. (a) Describe in outline (i) the preparation of hydrogen from water gas, (ii) the manufacture of steel from pig iron. (b) What happens when iron is placed in (i) dilute nitric acid, (ii) concentrated nitric acid? What explanation can you offer in explaining the results? (c) Give *two* tests whereby iron(III) and iron(II) may be distinguished in qualitative analysis. (J.M.B.)

6. State what you would observe and write equations for the reactions which occur when (a) sodium chloride, (b) potassium iodide, is heated with concentrated sulphuric acid. Compare briefly the properties of sodium chloride with those of tetrachloromethane, and show how the differences may be accounted for by considering the electronic structures of these two compounds. (J.M.B.)

7. Make a classification of the oxides, defining and giving *one* example of each class. A gaseous oxide, A_xO_y, on being sparked with oxygen forms a higher oxide according to the following equation:

$$1 \text{ volume } A_xO_y + 2 \text{ volumes } O_2 = 3 \text{ volumes of a higher oxide.}$$

From this equation deduce the simplest formula for A_xO_y and the higher oxide. Give your reasoning in full. (J.M.B.)

8. Give an account of the preparation and collection of a sample of carbon monoxide. How and under what conditions does carbon monoxide react with (a) nickel, (b) copper(I) chloride, (c) sodium hydroxide, (d) hydrogen? (Lond. Inter.)

9. Give an account of the physical and chemical properties which distinguish a metal from a nonmetal, relating them to the electronic structures.

Name and discuss (a) one element classed as a metal which has some non-metallic properties, and (b) one non-metal with some metallic properties. (L.)

10. What general principles are involved in the extraction of metals from purified ores? Illustrate your answer by reference to the extraction of iron, zinc, titanium, sodium and aluminium. (Details of chemical plant are *not* required.)

1.77 g of a mixture of iron and zinc were dissolved in excess dilute sulphuric acid. When reaction was complete, the resulting solution was titrated with 0.02 M potassium manganate(VII) 40.0 cm^3 were decolorised. Calculate the percentage of iron in the mixture. (J.M.B)

11. When potassium chromate(VI), sodium chloride and concentrated sulphuric acid are gently heated together, a red liquid *R* is produced which contains only chromium, chlorine and oxygen. When the red liquid *R* is added to aqueous sodium hydroxide, a yellow solution *S* is obtained.

(i) The slow addition of silver nitrate solution to a neutralized sample of solution *S* produced, first, a white precipitate and then a red one.

(ii) Acidification of the yellow solution *S* with dilute sulphuric acid gave an orange solution *T* which contained chromium in oxidation state + 6. *T* liberated iodine from aqueous potassium iodide, leaving a green solution containing chromium in oxidation state + 3.

(iii) Quantitatively, 0.155 g of liquid *R* gave a solution *S* which needed 2.0 mmol of silver nitrate to produce the first trace of red colour; also 0.155 g of *R* gave enough *T* to liberate 1.5 mmol of iodine(I_2) from aqueous potassium iodide.

Deduced the formula of *R* and explain the reactions which have occurred. What is the structural formula of *R* and to what class of compound does it belong? (L.)

$$(Cr = 52, Cl = 35.5, O = 16)$$

12. For *either* aluminium *or* iron write an account of the chemistry of the metal including in your account reference to the following points: (a) the occurrence of the metal and the principles underlying its extraction from the naturally occurring compounds; (b) the physical and chemical properties of the metal and their relation to its use in everyday life; (c) the problem of its corrosion, and the methods used to prevent corrosion, paying attention to the principles underlying those methods. (L.)

13. The chemistry of the elements and their compounds is often studied by consideration of a period or group of the Periodic Table.

Indicate the structural differences seen in the elements of (a) the second short period (sodium to argon), and (b) Group IV (carbon to lead).

Compare the trends in the properties of the chlorides of the elements in each case. (L.)

14. Suggest an explanation for each of the following observations.

(a) A water molecule and a neon atom contain the same number of electrons; yet water boils at 100°C whereas neon boils at -246°C.

(b) In aqueous solution, iron(III) forms a dark-red compound with thiocyanate ions; in the presence of potassium fluoride, no such coloration is observed.

(c) In its complex compounds, cobalt(III) has a co-ordination number of 6; however, the formula of the complex ion formed by cobalt(III) with 1, 2-diaminoethane is

$$[Co(H_2N{-}CH_2{-}CH_2{-}NH_2)_3]^{3+}, \text{not } [Co(H_2N{-}CH_2{-}CH_2{-}NH_2)_6]^{3+}.$$

(d) When concentrated hydrobromic acid is added to a concentrated solution of sodium chloride, a white precipitate is formed. (L.)

15. (a) Discuss the bonding in (i) calcium oxide, (ii) tetrachloromethane, (iii) ice, (iv) the molecule Al_2Cl_6.

(b) What are the spatial arrangements of the atoms in (i) boron trichloride, (ii) ammonia, (iii) the gaseous compound SF_6? (O.)

16. Discuss and explain the following statements:

(a) An aqueous solution of copper(II) sulphate has a pH less than 7.

(b) The fluoride of molecular formula N_2F_2 exists in two forms.

(c) Beryllium chloride in the fused state is a very poor conductor of electricity.

(d) A mixture of hydrogen and chlorine explodes in bright sunlight. (O.)

17. Nitrogen, sulphur, and chlorine all combine directly with hydrogen under suitable conditions to form gaseous hydrides.

(a) Write balanced equations and give the conditions for the formation of these hydrides. (Indicate any tendency to reversibility in the reaction.)

Each hydride dissolves to some extent in water.

(b) Arrange the hydrides in order of *increasing* strength as acids, i.e. the *weakest* acid *first.*

(c) Give the formulae of the ions present in each aqueous solution.

(d) With chlorine, sulphur forms a pale yellow liquid of formula S_2Cl_2 and boiling point 411 K.

Draw a structural formula to indicate the number of bonds between each pair of atoms in the molecule.

Comment on whether you expect the molecule to be linear. Predict the nature of the chemical bonds in the molecule. (C.)

18. Identify the substances A, B, C and D and explain the observations, giving equations where appropriate.

A is a green crystalline solid which decomposes on heating to give a red powder, a volatile liquid and two gases, one of which decolorises aqueous potassium permanganate and the other of which gives a white precipitate with aqueous barium chloride.

B is a colourless flammable gas which reduces copper(II) oxide and, when passed through a warm nickel tube, forms a volatile liquid. At high temperatures and pressures B reacts with aqueous sodium hydroxide to form a salt.

C is a white powder which when heated to a high temperature with carbon gives off a flammable gas and leaves a solid residue. Addition of cold water to the residue liberates another flammable gas and leaves a white solid.

D is a coloured crystalline solid which decomposes on heating to give a volatile liquid, two gases (one of them brown) and a green residue. The residue is insoluble in water but dissolves in both aqueous sodium hydroxide and sulphuric acid. (A.E.B.)

19. Identify the substances A, B, C, D, E, F, G, and H and explain your reasoning.

(a) A is a pink deliquescent crystalline solid which, on heating, forms a black residue B. The action of heat on a mixture of B, potassium hydroxide and potassium chlorate, followed by addition of water, gave a green solution of C. Passage of chlorine through this solution gave a purple compound D.

(b) E is a yellow solid which on heating with potassium chloride and concentrated sulphuric acid, gave a red liquid F, which was readily hydroly-ed by water to give a solution of G. Acidification of E followed by addition of hydrogen peroxide gave a blue coloration, whilst the action of heat on a mixture of E and ammonium chloride, gave a residue H. (A.E.B.)

20. Give concise explanations for each of the following:

(a) A brown coloration forms when aqueous solutions of sodium hydrogen sulphite and potassium iodate(V) are mixed.

(b) Iodine is much more soluble in aqueous potassium iodide than in water.

(c) An aqueous solution of chromium(III) chloride is violet but becomes green on addition of potassium chloride solution.

(d) The solid formed on heating calcium (or magnesium) oxide with carbon gives a colourless gas when treated with water.

(e) Hydrogen chloride is evolved when calcium (or magnesium) chloride crystals are heated.

(f) Although copper(I) chloride is insoluble in both water and dilute hydrochloric acid, it dissolves readily in concentrated hydrochloric acid. (A.E.B.)

21. Identify as fully as possible each of the following compounds, and explain the reactions involved.

(a) A is a white solid which dissolves readily in water. Powdered sulphur dissolves in the boiling solution, and on cooling colourless crystals are deposited. These crystals, like those of A (i) evolve a pungent gas on treatment with dilute hydrochloric acid and (ii) decolourise an aqueous solution of iodine.

(b) B is a coloured crystalline solid which is easily soluble in water. Addition of aqueous potassium cyanide gives a precipitate which dissolves in an excess of reagent whereas addition of aqueous potassium iodide gives a white-grey precipitate with the liberation of iodine. On gentle heating B releases 80% of its water of crystallization.

(c) C is a colourless gas which reduces hot copper(II) oxide with the liberation of an inert gas, and reacts with hot sodium forming a solid and liberating a flammable gas. C reacts in stages with chlorine to give, finally, a highly explosive liquid. (A.E.B.)

22. You are given six aqueous solutions labelled A to F, each containing *one* of the following solutes (no two solutions are the same): NaOH; K_2CO_3; $BaCl_2$; $Cr_2(SO_4)_3$; $NiCl_2$; $(NH_4)_2SO_4$.

Using these solutions together with a known solution of dilute hydrochloric acid and red and blue litmus paper, devise a *logical* series of tests which allows you to identify the solute in each case. (No other reagent may be used and test-tubes and a bunsen burner are the only permitted apparatus.)

Suggest also *one* confirmatory test for the cation in each solution, for which any suitable reagents and apparatus may be used. (J.M.B.)

23. (a) Survey, giving examples, *three* general methods available for the extraction of metals from their purified ores. Give reasons for the choice of method in the examples you quote.

(b) Explain the following facts.

(i) When tin reacts with concentrated nitric acid, hydrated tin(IV) oxide is obtained.

(ii) Cobalt dissolves in concentrated hydrochloric acid to give a blue solution but it dissolves in dilute sulphuric acid to give a pink solution.

(iii) Lead dissolves in dilute nitric acid but the solution gives a white precipitate when dilute hydrochloric acid is added. (J.M.B.)

24. Describe the structure of the water molecule and of liquid water.

Explain briefly what happens when a soluble anhydrous salt of a transition metal is added to water. Survey the reactions in aqueous solution of ions of the first row transition elements with (a) ammonia and (b) chloride ions. (J.M.B.)

25. Give examples of the use of lithium aluminium hydride and sodium borohydride as reducing agents in inorganic and organic chemistry. Describe briefly the bonding in the hydrides of sodium, silicon and chlorine. Comment on the trend in the type of bond across the second period (Li–Ne).

Describe the reactions of the chlorides of magnesium and of silicon with water at room temperature. How far are the reactions of these chlorides typical of the reactions of chlorides of metals and non-metals in general? (J.M.B.)

26 For *each* of the following processes used in the isolation of elements from their compounds, describe *one* suitable example and state why the process described is the preferred method: (a) electrolysis; (b) reduction with carbon; (c) reduction with a metal. (A.E.B.)

27. (a) In general a metal is produced by reduction of one of its compounds which *either* occurs naturally *or* can be produced from a naturally-occurring compound.

Illustrate the above statement by giving an *outline* of the reduction process used for the production of *one* metal from *each* of the following groups of metals:

(i) uranium, chromium, titanium;

(ii) zinc, iron, copper.

(b) Explain why aluminium cannot be produced by electrolysis of the molten chloride or by reduction of its oxide with carbon.

(c) Given the following enthalpy changes of formation:

$$\begin{array}{ll} MgO & -\ 602\ \text{kJ mol}^{-1}; \\ Al_2O_3 & -1700\ \text{kJ mol}^{-1}; \end{array}$$

calculate the enthalpy change for the reaction:

$$Al_2O_3 + 3Mg \rightarrow 2Al + 3MgO$$

Does your answer indicate whether magnesium will reduce aluminium oxide? Give an explanation. (A.E.B.)

28. Each of the following statements contains at least one inaccuracy. In each case

(i) explain the inaccuracies,
(ii) define the terms in italics,
(iii) write a corrected statement.

(a) The *oxidizing agent* potassium manganate(VII) (potassium permanganate) is used as a *primary standard* in volumetric analysis.

(b) The addition of sodium carbonate solution to an aqueous solution of the *transition metal* ion, Al^{3+}, gives a white precipitate of aluminium carbonate.

(c) The addition of aqueous ammonia to copper(II) sulphate solution gives a precipitate which dissolves in an excess of reagent, showing that copper(II) hydroxide is *amphoteric*.

(d) The *d-block element* iron forms two chlorides, $FeCl_2$ and $FeCl_3$, which may be prepared in their anhydrous states by dissolving iron in dilute and concentrated hydrochloric acid respectively, evaporating the solutions and strongly heating the residues. (A.E.B.)

29. Identify each of the following compounds as fully as possible and explain the reactions involved.

(a) A is a colourless gas which on heating decomposes explosively and shows a volume increase of 50%. When A is bubbled through a suspension of lead(II) sulphide in water a white solid is formed and the reaction of A with aqueous potassium iodide gives a brown coloration.

(b) B, a pale blue viscous liquid, is miscible with water in all proportions and decomposes explosively on heating. In acid solution B will oxidize iron(II) ions to iron(III) ions while in alkaline solution the reduction of iron(III) to iron(II) occurs.

(c) C is a colourless liquid which is only very weakly ionized and is only slightly decomposed even at temperatures as high as 2000 °C. It readily oxidizes sodium and forms a cationic complex with copper(II) ions.

(d) D is a colourless flammable gas which combines with many metals, including sodium, and with many non-metals, including sulphur. It readily reduces copper(II) oxide to the metal. When compounds containing it are electrolysed D may be evolved either at the anode or at the cathode. (A.E.B.)

Scholarship level questions

1. ‘Oxidation and reduction are electron transfer reactions.’ Discuss this statement. Name *two* compounds which can function as both oxidizing and reducing agents. Give an illustrative reaction in each case. (W.)

2. Give an account of variable oxidation number as exhibited by the elements of the first two periods of the periodic system and discuss the explanation of the phenomena given by the modern electronic theory. What properties do you associate with (a) electrovalent linkage, (b) covalent linkage? Comment on the types of chemical bond present in (c) HCl, (d) KCl, (e) NH_4Cl, (f) CO, (g) HNO_3. (L.)

3. How would you remove the chemically active constituents of air in order to show that part of it is inert? What part did the discovery of the noble gases play in the development of modern chemical ideas? (O.C.)

4. Discuss the reactions of (a) carbon, (b) magnesium, (c) iron, with air and water respectively. (W.)

5. Describe and explain what takes place when an electric current passes between platinum electrodes immersed in: (a) an aqueous solution of copper(II) sulphate, (b) a hot aqueous solution of potassium chloride, (c) fused sodium ethanoate, (d) a concentrated aqueous solution of potassium hydrogensulphate at 373 K, (e) a solution of silver cyanide in potassium cyanide solution. (J.M.B.)

6. Comment on features of outstanding interest in respect of the preparation, properties and stability of *three* of the following: (a) the allotropes of sulphur, (b) the halides of mercury, (c) the oxy-acids of phosphorus, (d) the hydrides of nitrogen, phosphorus and arsenic. (J.M.B.)

7. Discuss the application of the electronic theory of valency to account for the properties of the following: methane, sodium chloride, ammonia, phosphorus pentachloride. It is often found difficult to assign to a molecule or an ion a single electronic formula which adequately represents its properties. Cite such an example and comment very briefly on the present interpretation of its structure. (W.)

8. Give a solution of tetraoxophosphoric(V) acid (orthophosphoric acid), how would you prepare crystalline samples of its three sodium salts? Explain the principles involved in the preparations. (O.C.)

9. Give a brief account of the present theory of atomic structure and show how it accounts for (a) the periodic system of the elements, (b) the existence of isotopes, (c) the principal types of valence bonds occurring in chemical compounds. (J.M.B.)

10. In elementary work, chemical bonding can be regarded as resulting either from the transfer of electrons ('electrovalency') or from the sharing of pairs of electrons ('covalency'). Write a systematic account of cases where this simple picture is inadequate or inappropriate. (L.)

11. A pale green chloride of chromium, *X*, was investigated with the following results:

(a) When 1.00 g was heated in air to constant mass, water and hydrogen chloride were evolved and a residue of 0.286 g of chromium(III) oxide, Cr_2O_3, remained.

(b) When 1.00 g of *X* was dissolved in water, acidified with dilute nitric acid and treated with silver nitrate solution, 1.077 g of silver chloride (AgCl) was immediately precipitated. On boiling the solution until no further change occurred, a further 0.538 g of silver chloride was precipitated.

(c) On drying in a desiccator over concentrated sulphuric acid, 1.00 g of *X* lost 0.068 g of water.

Elucidate as far as possible from this information the formula of the compound and comment on its stereochemistry.

What isomers of *X* would you expect to exist? State which one of these isomers would be soluble in ether and why.

$(H = 1, O = 16, Cl = 35.5, Cr = 52, Ag = 108)$ (L.)

12. The electron pair repulsion theory enables chemists to make predictions about the shapes of simple molecules by considering the electrostatic interactions between bond pairs and between bond pairs and lone pairs of electrons.

(a) Summarize the essential rules underlying the application of the electron pair repulsion theory and apply them to the following molecules:

$$BCl_3, CH_4, NH_3, H_2O \text{ and } SF_6.$$

(b) BCl_3 and NH_3 form an addition compound of formula $BCl_3.NH_3$. What type of bonding exists between the two constituent molecules? Apply the electron pair repulsion theory to suggest a likely structure of the addition molecule. (L.)

13. Water is not only one of the most abundant materials in nature, but also one of the most widely used substances in chemistry.

(a) Discuss the role played in chemistry by water.

(b) Relate the chemical uses of water to its properties as a liquid or in the molecular state as appropriate. (L.)

14. It is customary to classify the chemical elements in the Periodic Table according to their electronic configuration into s-block elements, p-block elements and d-block elements (another group of elements, called f-block elements, need not concern you here).

(a) Give a concise summary of the major characteristics which you associate with the elements of each block. (Your answer should be illustrated by examples of general validity: information concerning specific elements only should not be given.)

(b) In the light of your knowledge of the chemistry of the elements, examine the extent to which the behaviour and properties of elements, and their compounds, in different 'blocks' of the Periodic Table overlap. (L.)

15. A compound *X* contained copper(II), ammonium, and chloride ions, in addition to water. An aqueous solution *Y* was prepared which contained 27.75 g of compound *X* per litre. Analysis of this solution gave the following results:

(1) 25.0 cm^3 of *Y*, on treatment with excess aqueous sodium hydroxide, gave enough ammonia to react with 50.0 cm^3 of 0.1 M HCl.

(2) 25.0 cm^3 of *Y* precipitated 1.435 g of silver chloride from an acidified silver nitrate solution.

(3) 25.0 cm^3 of *Y*, on treatment with excess potassium iodide solution, gave sufficient iodine to react with 25.0 cm^3 of 0.1 M of sodium thiosulphate solution.

$$Cu^{2+} + 2I^- \rightarrow CuI(s) + \tfrac{1}{2}I_2$$
$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$$

(a) Find the formula of *X*.

(b) Comment on the following observation.
On heating in an ignition tube, the blue crystals of *X* gave off water vapour, formed a white sublimate, and left a very dark residue which melted at the temperature of the Bunsen flame. (L.)

16. 'The shapes of simple molecules can readily be deduced from the distribution of bonding electrons.' Give an outline of the principles and rules underlying the electron-pair repulsion theory and apply these to the following species: (a) the ammonia molecule; (b) the hydrogen sulphide molecule; (c) the carbonate ion; (d) the ethene (ethylene) molecule; (e) the sulphur hexafluoride molecule. (L.)

17. The first member of a group in the periodic table has properties which are not typical of the other members of the group.

Discuss and illustrate this statement with respect to one metal and two non-metallic elements. (O.)

18. (a) Illustrate and explain the different types of isomerism which occur in inorganic chemistry.

(b) Comment on the structure and properties of two of the following: sulphur hexafluoride, potassium hexacyanoferrate(III), phosphorus pentachloride. (O.)

19. Astatine (chemical symbol At), the element with atomic number 85, is placed in Group VII of the Periodic Table. From your knowledge of the corresponding properties of the other members of this group, predict, giving reasons, as many of the chemical and physical properties of astatine as you are able. (C.)

20. Interpret the following observations, writing balanced chemical equations where possible and indicating the composition of any complex ions that may be formed.

(i) Copper(II) hydroxide dissolves in aqueous sulphuric acid to give a pale blue solution but gives a yellow solution when dissolved in concentrated hydrochloric acid.

(ii) An aqueous solution of copper(II) sulphate reacts with an excess of potassium iodide to give a white precipitate and a red-brown coloured solution. The red-brown coloured solution can be decolorized with sodium thiosulphate.

(iii) When an aqueous solution of ammonia is gradually added to a pale blue aqueous solution of copper(II) sulphate, a pale blue precipitate, A, forms which redissolves in an excess of aqueous ammonia to give a deep blue solution, B. Reduction of B with hydrazine sulphate gives a colourless solution, C. When C is acidified with dilute sulphuric acid, a pale blue solution (as in A) and a dark brown precipitate, D, are formed. D does not dissolve in dilute non-oxidizing acids.

(iv) Copper metal does not react with warm dilute hydrochloric acid but does so when thiocarbamide (thiourea, $(NH_2)_2CS$) is added. The reaction produces hydrogen gas and a colourless solution. (C.)

21. Discuss the bonding that exists at room temperature and pressure in the listed elements, making use (with the aid of a graph, or otherwise) of the data given. Explain, as far as you are able, the observed variations in m.p. and b.p.

Element	At. No.	m.p./K	b.p./K
Lithium	3	450	1590
Fluorine	9	50	85
Sodium	11	370	1165
Chlorine	17	170	240
Potassium	19	340	1050
Bromine	35	270	330
Rubidium	37	310	960
Iodine	53	390	460

(C.)

22. Write an essay on the consequences of the presence of lone electron pairs in molecules and ions. (C.)

23. (a) Compare concisely the aqueous solution chemistry of *either* copper(II) and chromium(II), or manganese(II) and zinc(II).

(b) Suggest a brief explanation of why, in aqueous solution, iron(III) and manganese(III) are oxidizing agents but chromium(II) is a reducing agent. [$E^\ominus(Mn^{3+}/Mn^{2+}) = +1.51$ V].

(c) Give what explanations you can of the similarities and the differences in the chemistry of copper(I) and zinc(II). (C.)

24. Give what explanation you can of *four* of the following.

(a) Sodium hydride is a solid which reacts with water to form hydrogen. Hydrogen chloride is a gas which gives an acidic solution in water.

(b) Aluminium hydride decomposes completely to its elements at 373 K, whereas ammonia is stable at the same temperature.

(c) Magnesium oxide is a solid which melts at 3070 K in air. Sulphur monoxide, SO, is an unstable compound which is very readily oxidized to sulphur dioxide by oxygen at 100 K.

(d) Phosphorus forms a pentachloride, PCl_5, but the arsenic analogue, $AsCl_5$, is unknown.

(e) The chlorate(VII) ion, ClO_4^-, is a weaker oxidizing agent than the bromate(VII) ion, BrO_4^-. (C.)

25. Comment on the effect of the ligands attached to the metal atom on the relative stability of the different oxidation states of cobalt in 1 M acid as shown by the observations that

(i) the ion $[Co(NH_3)_6]^{3+}$ is stable in aqueous solution,
(ii) the ion $[Co(H_2O)_6]^{3+}$ oxidizes water to oxygen,
(iii) the ion $[CoCl_4]^{2-}$ is stable in aqueous acid solution,
(iv) the ion $[Co(CN)_6]^{4-}$ reduces water to hydrogen.

Give any examples you can of the influence of ligands on the relative stability of the oxidation states of iron *and either* chromium *or* manganese. (C.)

26. Discuss and explain the following:

(a) mercury(II) oxide is insoluble in water, but it dissolves in an aqueous solution of potassium iodide to give an alkaline solution;

(b) silver(I) chloride dissolves in aqueous ammonia solution, but not in sodium hydroxide solution;

(c) pure anhydrous magnesium chloride cannot be prepared by the action of heat on magnesium chloride hexahydrate;

(d) it is preferable to refer to a solution of ammonia in water as "aqueous ammonia" rather than as "ammonium hydroxide";

(e) a dilute solution of sodium chloride in water is neutral, but one of sodium fluoride is slightly alkaline. (A.E.B.)

27. (a) 1.73 g of a compound, A, which contains carbon, manganese, nitrogen, and oxygen only, was dissolved in distilled water and the volume made up to 250 cm^3.

25 cm^3 of the solution was treated to convert the manganese in the dissolved compound A to manganate(VII) (permanganate). The resulting solution contained sufficient manganate(VII) to react with 50 cm^3 of a solution of iron(II) ammonium sulphate of concentration 0.1 mol dm^{-3}.

Calculate the percentage of manganese in A.

(b) 25 cm^3 of the solution of A, as used in (a), was treated to convert the nitrogen in the dissolved compound, A, to ammonia. The ammonia was dissolved in water and the solution titrated with a solution of hydrochloric acid of concentration 0.1 mol dm^{-3}; 30 cm^3 of the hydrochloric acid solution were required.

Calculate the percentage of nitrogen in A.

(c) On heating 1.73 g of the compound, A, in air, all the carbon in it was converted to carbon dioxide. The volume of carbon dioxide was 224 cm^3 at s.t.p.

Calculate the percentage of carbon in A.

(d) From your calculated percentages of manganese, nitrogen and carbon, and given that its relative molecular mass is 173, determine the molecular formula of A. (A.E.B.)

Answers to numerical questions

Chapter 3 (p. 39)
5. 18

Chapter 4 (p. 78)
4. $Na_2CO_3.H_2O$

Chapter 8 (p. 271)
12. 2.09 g dm^{-3} of NO_2^-

Chapter 11 (p. 487)
12. (c) 0.02 mol dm^{-3}
20. (b) $x = 2, y = 4, z = 2$

General questions (p. 492)
7. A_3O_2, AO_2
10. 12.6%
11. CrO_2CI_2
27. (c) $\triangle H = -106$ kJ mol^{-1}

Scholarship questions (p. 497)
11. $[Cr(H_2O)_5Cl]\ Cl_2.H_2O$
15. $Cu(NH_4)_2Cl_4.2H_2O$
27. Mn 31.8%, N 24.3%, C 6.9%; $MnCN_3O_4$

TABLE OF RELATIVE ATOMIC MASSES TO FOUR SIGNIFICANT FIGURES

(Scaled to the relative atomic mass $^{12}C = 12$ *exactly)*

Values quoted in the table, unless marked* or †, are reliable to at least ±1 in the fourth significant figure. A number in parentheses denotes the atomic mass number of the isotopes of longest known half-life.

At. No.	*Name*	*Symbol*	*Relative Atomic Mass*	*At. No.*	*Name*	*Symbol*	*Relative Atomic Mass*
1	Hydrogen	H	1.008	53	Iodine	I	126.9
2	Helium	He	4.003	54	Xenon	Xe	131.3
3	Lithium	Li	6.941*†	55	Caesium	Cs	132.9
4	Beryllium	Be	9.012	56	Barium	Ba	137.3
5	Boron	B	10·81†	57	Lanthanum	La	138.9
6	Carbon	C	12.01	58	Cerium	Ce	140.1
7	Nitrogen	N	14.01	59	Praseodymium	Pr	140.9
8	Oxygen	O	16.00	60	Neodymium	Nd	144.2
9	Fluorine	F	19.00	61	Promethium	Pm	(145)
10	Neon	Ne	20.18	62	Samarium	Sm	150.4
11	Sodium	Na	22.99	63	Europium	Eu	152.0
12	Magnesium	Mg	24.31	64	Gadolinium	Gd	157.3
13	Aluminium	Al	26.98	65	Terbium	Tb	158.9
14	Silicon	Si	28.09	66	Dysprosium	Dy	162.5
15	Phosphorus	P	30.97	67	Holmium	Ho	164.9
16	Sulphur	S	32.06†	68	Erbium	Er	167.3
17	Chlorine	Cl	35.45	69	Thulium	Tm	168.9
18	Argon	Ar	39.95	70	Ytterbium	Yb	173.0
19	Potassium	K	39.10	71	Lutetium	Lu	175.0
20	Calcium	Ca	40.08†	72	Hafnium	Hf	178.5
21	Scandium	Sc	44.96	73	Tantalum	Ta	180.9
22	Titanium	Ti	47.90*	74	Wolfram (Tungsten)	W	183.9
23	Vanadium	V	50.94	75	Rhenium	Re	186.2
24	Chromium	Cr	52.00	76	Osmium	Os	190.2
25	Manganese	Mn	54.94	77	Iridium	Ir	192.2
26	Iron	Fe	55.85	78	Platinum	Pt	195.1
27	Cobalt	Co	58.93	79	Gold	Au	197.0
28	Nickel	Ni	58.70	80	Mercury	Hg	200.6
29	Copper	Cu	63.55	81	Thallium	Tl	204.4
30	Zinc	Zn	65.38	82	Lead	Pb	207.2†
31	Gallium	Ga	69.72	83	Bismuth	Bi	209.0
32	Germanium	Ge	72.59*	84	Polonium	Po	(209)
33	Arsenic	As	74.92	85	Astatine	At	(210)
34	Selenium	Se	78.96*	86	Radon	Rn	(222)
35	Bromine	Br	79.90	87	Francium	Fr	(223)
36	Krypton	Kr	83.80	88	Radium	Ra	(226)
37	Rubidium	Rb	85.47	89	Actinium	Ac	(227)
38	Strontium	Sr	87.62†	90	Thorium	Th	232.0
39	Yttrium	Y	88.91	91	Protactinium	Pa	(231)
40	Zirconium	Zr	91.22	92	Uranium	U	238.0†
41	Niobium	Nb	92.91	93	Neptunium	Np	(237)
42	Molybdenum	Mo	95.94*	94	Plutonium	Pu	(244)
43	Technetium	Tc	(97)	95	Americium	Am	(243)
44	Ruthenium	Ru	101.1	96	Curium	Cm	(247)
45	Rhodium	Rh	102.9	97	Berkelium	Bk	(247)
46	Palladium	Pd	106.4	98	Californium	Cf	(251)
47	Silver	Ag	107.9	99	Einsteinium	Es	(254)
48	Cadmium	Cd	112.4	100	Fermium	Fm	(257)
49	Indium	In	114.8	101	Mendelevium	Md	(258)
50	Tin	Sn	118.7	102	Nobelium	No	(259)
51	Antimony	Sb	121.8	103	Lawrencium	Lr	(260)
52	Tellurium	Te	127.6				

* Values so marked are reliable to ±3 in the fourth significant figure.

† Values so marked may differ from the atomic weights of the relevant elements in some naturally occurring samples because of a variation in the relative abundance of the isotopes.

Index

ELECTRONIC ARRANGEMENTS IN ELEMENTS (1)

	1*s*	2*s*	2*p*	3*s*	3*p*	3*d*	4*s*	4*p*	4*d*	4*f*	5*s*	5*p*	5*d*	6*s*	6*p*	6*d*	7*s*
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	8		1													
12 Mg	2	8		2													
13 Al	2	8		2	1												
14 Si	2	8		2	2												
15 P	2	8		2	3												
16 S	2	8		2	4												
17 Cl	2	8		2	5												
18 Ar	2	8		2	6												
19 K	2	8		8			1										
20 Ca	2	8		8			2										
21 Sc	2	8		8		1	2										
22 Ti	2	8		8		2	2										
23 V	2	8		8		3	2										
24 Cr	2	8		8		5	1										
25 Mn	2	8		8		5	2										
26 Fe	2	8		8		6	2										
27 Co	2	8		8		7	2										
28 Ni	2	8		8		8	2										
29 Cu	2	8		8		10	1										
30 Zn	2	8		8		10	2										
31 Ga	2	8		18			2										
32 Ge	2	8		18			2	2									
33 As	2	8		18			2	3									
34 Se	2	8		18			2	4									
35 Br	2	8		18			2	5									
36 Kr	2	8		18			2	6									
37 Rb	2	8		18			8				1						
38 Sr	2	8		18			8				2						
39 Y	2	8		18			8		1		2						
40 Zr	2	8		18			8		2		2						
41 Nb	2	8		18			8		4		1						
42 Mo	2	8		18			8		5		1						
43 Tc	2	8		18			8		6		1						
44 Ru	2	8		18			8		7		1						
45 Rh	2	8		18			8		8		1						
46 Pd	2	8		18			8		10								

ELECTRONIC ARRANGEMENTS IN ELEMENTS (2)

	1*s*	2*s* 2*p*	3*s* 3*p* 3*d*	4*s* 4*p*	4*d*	4*f*	5*s*	5*p*	5*d*	6*s*	6*p*	6*d*	7*s*
47 Ag	2	8	18	8	10		1						
48 Cd	2	8	18	8	10		2						
49 In	2	8	18	18			2	1					
50 Sn	2	8	18	18			2	2					
51 Sb	2	8	18	18			2	3					
52 Te	2	8	18	18			2	4					
53 I	2	8	18	18			2	5					
54 Xe	2	8	18	18			2	6					
55 Cs	2	8	18	18			8			1			
56 Ba	2	8	18	18			8			2			
57 La	2	8	18	18			8		1	2			
58 Ce	2	8	18	18		1	8		1	2			
59 Pr	2	8	18	18		2	8		1	2			
60 Nd	2	8	18	18		3	8		1	2			
61 Pm	2	8	18	18		4	8		1	2			
62 Sm	2	8	18	18		5	8		1	2			
63 Eu	2	8	18	18		6	8		1	2			
64 Gd	2	8	18	18		7	8		1	2			
65 Tb	2	8	18	18		8	8		1	2			
66 Dy	2	8	18	18		9	8		1	2			
67 Ho	2	8	18	18		10	8		1	2			
68 Er	2	8	18	18		11	8		1	2			
69 Tm	2	8	18	18		12	8		1	2			
70 Yb	2	8	18	18		13	8		1	2			
71 Lu	2	8	18	18		14	8		1	2			
72 Hf	2	8	18	32			8		2	2			
73 Ta	2	8	18	32			8		3	2			
74 W	2	8	18	32			8		4	2			
75 Re	2	8	18	32			8		5	2			
76 Os	2	8	18	32			8		6	2			
77 Ir	2	8	18	32			8		7	2			
78 Pt	2	8	18	32			8		8	2			
79 Au	2	8	18	32			8		10	1			
80 Hg	2	8	18	32			8		10	2			
81 Tl	2	8	18	32			18			2	1		
82 Pb	2	8	18	32			18			2	2		
83 Bi	2	8	18	32			18			2	3		
84 Po	2	8	18	32			18			2	4		
85 At	2	8	18	32			18			2	5		
86 Rn	2	8	18	32			18			2	6		
87 Fr	2	8	18	32			18			8			1
88 Ra	2	8	18	32			18			8			2
89 Ac	2	8	18	32			18			8		(1)	(2)
90 Th	2	8	18	32			18			8		(2)	(2)
91 Pa	2	8	18	32			18			8		(3)	(2)
92 U	2	8	18	32			18			8		(4)	(2)

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