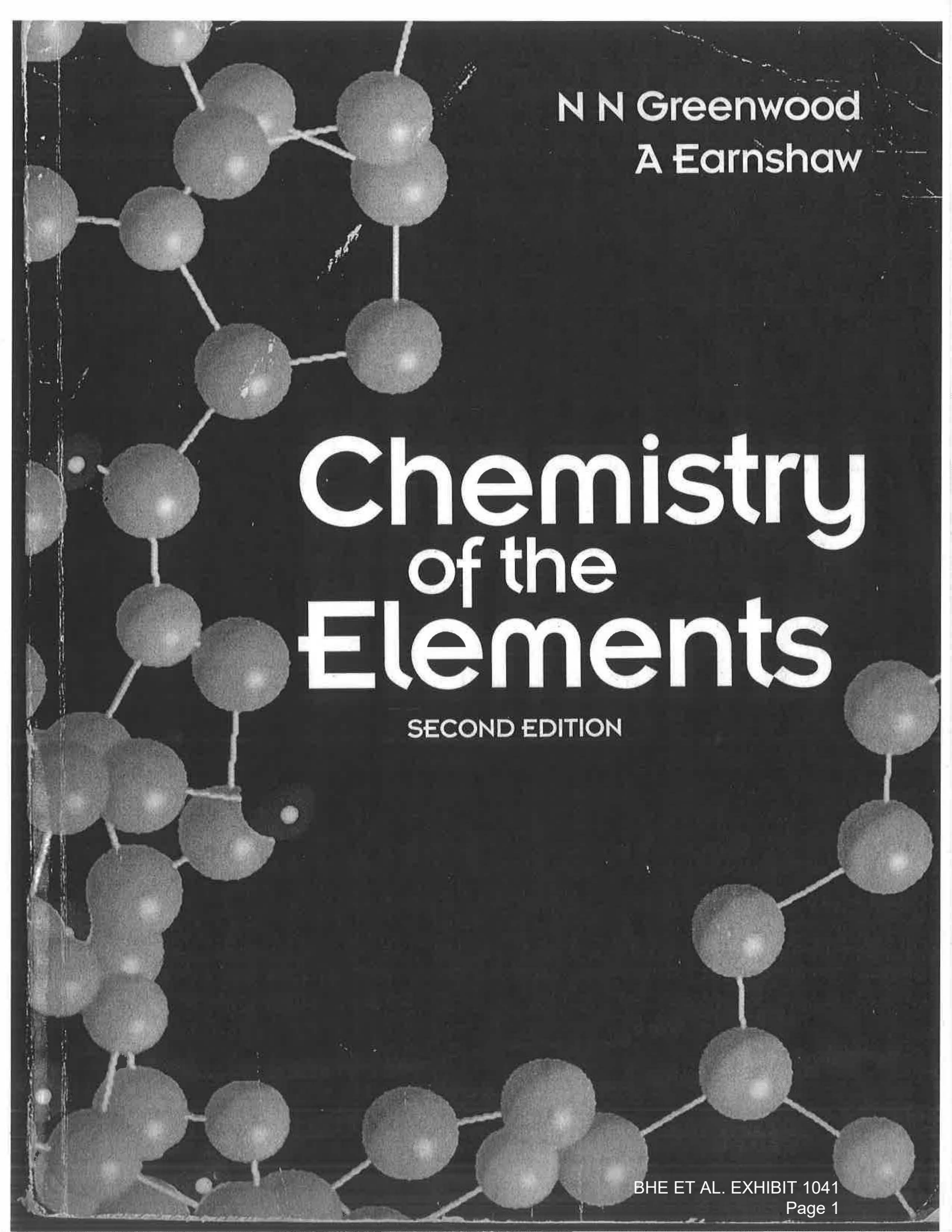




N N Greenwood
A Earnshaw

Chemistry of the Elements

SECOND EDITION

1	H	1s ¹
2	He	1s ²

58	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
4f ¹ 5d ¹ 6s ²	4f ² 6s ²	4f ³ 6s ²	4f ⁴ 6s ²	4f ⁵ 6s ²	4f ⁶ 6s ²	4f ⁷ 6s ²	4f ⁷ 5d ¹ 6s ²	4f ⁹ 6s ²	4f ¹⁰ 6s ²	4f ¹¹ 6s ²	4f ¹² 6s ²	4f ¹³ 6s ²	4f ¹⁴ 6s ²	4f ¹⁴ 5d ¹ 6s ²
59	Pa	Th	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
5f ² 6d ¹ 7s ²	5f ¹ 6d ² 7s ²	5f ³ 6d ¹ 7s ²	5f ³ 6d ² 7s ²	5f ⁴ 6d ¹ 7s ²	5f ⁴ 6d ² 7s ²	5f ⁵ 6d ² 7s ²	5f ⁶ 6d ¹ 7s ²	5f ⁶ 6d ² 7s ²	5f ⁷ 6d ² 7s ²	5f ⁷ 6d ³ 7s ²	5f ⁸ 6d ² 7s ²	5f ⁹ 6d ¹ 7s ²	5f ¹⁰ 6d ¹ 7s ²	5f ¹⁰ 6d ² 7s ²
60	61	62	63	64	65	66	67	68	69	70	71			

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Page 2

Standard Atomic Weights of the Elements 1997

[Scaled to $A_r(^{12}\text{C}) = 12$, where ^{12}C is a neutral atom in its nuclear and electronic ground state]

The atomic weights of many elements are not invariant but depend on the origin and treatment of the material. The standard values of $A_r(\text{E})$ and the uncertainties (in parentheses, following the last significant figure to which they are attributed) apply to elements of natural terrestrial origin. The footnotes to this Table elaborate the types of variation which may occur for individual elements and which may be larger than the listed uncertainties of values of $A_r(\text{E})$. Names have not yet been assigned to elements with atomic numbers 110, 111 and 112 (see p. 1280).

Name	Symbol	Atomic Number	Atomic Weight	Footnotes	Name	Symbol	Atomic Number	Atomic Weight	Footnotes
Actinium*	Ac	89	(227)		Mercury	Hg	80	200.59(2)	
Aluminium	Al	13	26.981538(2)		Molybdenum	Mo	42	95.94(1)	g
Americium*	Am	95	(243)		Neodymium	Nd	60	144.24(3)	g
Antimony	Sb	51	121.760(1)	g	Neon	Ne	10	20.1797(6)	g m
Argon	Ar	18	39.948(1)	g r	Neptunium*	Np	93	(237)	
Arsenic	As	33	74.92160(2)		Nickel	Ni	28	58.6934(2)	
Astatine*	At	85	(210)		Niobium	Nb	41	92.90638(2)	
Barium	Ba	56	137.327(7)		Nitrogen	N	7	14.00674(7)	g r
Berkelium*	Bk	97	(247)		Nobelium*	No	102	(259)	
Beryllium	Be	4	9.012182(3)		Osmium	Os	76	190.23(3)	g
Bismuth	Bi	83	208.98038(2)		Oxygen	O	8	15.9994(3)	g r
Bohrium	Bh	107	(264)		Palladium	Pd	46	106.42(1)	g
Boron	B	5	10.811(7)	g m r	Phosphorus	P	15	30.973762(4)	
Bromine	Br	35	79.904(1)		Platinum	Pt	78	195.078(2)	
Cadmium	Cd	48	112.411(8)	g	Plutonium*	Pu	94	(244)	
Caesium	Cs	55	132.90545(2)		Polonium*	Po	84	(210)	
Calcium	Ca	20	40.078(4)	g	Potassium	K	19	39.0983(1)	
Californium*	Cf	98	(251)		Praseodymium	Pr	59	140.90765(2)	
Carbon	C	6	12.0107(8)	g r	Promethium*	Pm	61	(145)	
Cerium	Ce	58	140.116(1)	g	Protactinium*	Pa	91	231.03588(2)	
Chlorine	Cl	17	35.4527(9)	m	Radium*	Ra	88	(226)	
Chromium	Cr	24	51.9961(6)		Radon*	Rn	86	(222)	
Cobalt	Co	27	58.933200(9)		Rhenium	Re	75	186.207(1)	
Copper	Cu	29	63.546(3)	r	Rhodium	Rh	45	102.90550(2)	
Curium*	Cm	96	(247)		Rubidium	Rb	37	85.4678(3)	g
Dubnium	Db	105	(262)		Ruthenium	Ru	44	101.07(2)	g
Dysprosium	Dy	66	162.50(3)	g	Rutherfordium	Rf	104	(261)	
Einsteinium*	Es	99	(252)		Samarium	Sm	62	150.36(3)	g
Erbium	Er	68	167.26(3)	g	Scandium	Sc	21	44.955910(8)	
Europium	Eu	63	151.964(1)	g	Seaborgium	Sg	106	(266)	
Fermium*	Fm	100	(257)		Selenium	Se	34	78.96(3)	
Fluorine	F	9	18.9984032(5)		Silicon	Si	14	28.0855(3)	r
Francium*	Fr	87	(223)		Silver	Ag	47	107.8682(2)	g
Gadolinium	Gd	64	157.25(3)	g	Sodium	Na	11	22.989770(2)	
Gallium	Ga	31	69.723(1)		Strontium	Sr	38	87.62(1)	g r
Germanium	Ge	32	72.61(2)		Sulfur	S	16	32.066(6)	g r
Gold	Au	79	196.96655(2)		Tantalum	Ta	73	180.9479(1)	
Hafnium	Hf	72	178.49(2)		Technetium*	Tc	43	(98)	
Hassium	Hs	108	(269)		Tellurium	Te	52	127.60(3)	g
Helium	He	2	4.002602(2)	g r	Terbium	Tb	65	158.92534(2)	
Holmium	Ho	67	164.93032(2)		Thallium	Tl	81	204.3833(2)	
Hydrogen	H	1	1.00794(7)	g m r	Thorium*	Th	90	232.0381(1)	g
Indium	In	49	114.818(3)		Thulium	Tm	69	168.93421(2)	
Iodine	I	53	126.90447(3)		Tin	Sn	50	118.710(7)	g
Iridium	Ir	77	192.217(3)		Titanium	Ti	22	47.867(1)	
Iron	Fe	26	55.845(2)		Tungsten	W	74	183.84(1)	
Krypton	Kr	36	83.80(1)	g m	Ununnilium	Uun	110	(269)	
Lanthanum	La	57	138.9055(2)	g	Ununium	Uuu	111	(272)	
Lawrencium*	Lr	103	(262)		Ununbium	Uub	112	(277)	
Lead	Pb	82	207.2(1)	g m	Uranium*	U	92	238.0289(1)	g m
Lithium	Li	3	[6.941(2)] [†]	g m r	Vanadium	V	23	50.9415(1)	
Lutetium	Lu	71	174.967(1)	g	Xenon	Xe	54	131.29(2)	g m
Magnesium	Mg	12	24.3050(6)		Ytterbium	Yb	70	173.04(3)	g
Manganese	Mn	25	54.938049(9)		Yttrium	Y	39	88.90585(2)	
Meitnerium	Mt	109	(268)		Zinc	Zn	30	65.39(2)	
Mendelevium*	Md	101	(258)		Zirconium	Zr	40	91.224(2)	g

*Element has no stable nuclides; the value given in parentheses is the atomic mass number of the isotope of longest known half-life. However, three such elements (Th, Pa and U) do have a characteristic terrestrial isotopic composition, and for these an atomic weight is tabulated.

[†]Commercially available Li materials have atomic weights that range between 6.96 and 6.99; if a more accurate value is required, it must be determined for the specific material.

g Geological specimens are known in which the element has an isotopic composition outside the limits for normal material. The difference between the atomic weight of the element in such specimens and that given in the Table may exceed the stated uncertainty.

m Modified isotopic compositions may be found in commercially available material because it has been subjected to an undisclosed or inadvertent isotopic fractionation. Substantial deviations in atomic weight of the element from that given in the Table can occur.

r Range in isotopic composition of normal terrestrial material prevents a more precise $A_r(\text{E})$ being given; the tabulated $A_r(\text{E})$ value should be applicable to any normal material.

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Preface to the Second Edition

When this book first appeared in 1984 it rapidly established itself as one of the foremost textbooks and references on the subject. It was enthusiastically adopted by both students and teachers and has already been translated into several European and Asian languages. The novel features which it adopted (see Preface to the First Edition) were clearly much appreciated and we have been pressed for some time now to bring out a second edition. Accordingly we have completely revised and updated the text and have incorporated over 2000 new literature references to work which has appeared since the first edition was published. In addition, innumerable modifications and extensions incorporating recent advances have been made throughout the text and, indeed, no single page has been left unaltered. However, by judicious editing we have ensured that all the features which made the first edition so attractive to its readers have been retained.

The main plan of the book has been left unchanged except that the general section on organometallic chemistry has been removed from Chapter 8 (Carbon) and has been incorporated, together with a summary of other aspects of coordination chemistry, in a restyled Chapter 19. However, the chemistry of even the simplest elements has been considerably enriched during the past few years, sometimes by quite dramatic advances. Thus the chemistry of the alkali metals has a complexity that was undreamt of one or two decades ago and lithium, for example, is now known in at least 20 coordination geometries having coordination numbers from 1 to 12. Compounds of alkali metal *anions* and even electrides are known. Likewise, there is expanding interest in the organometallic chemistry of the heavier congeners of magnesium, particularly those with bulky ligands. Boron continues to amaze and confound, and its cluster chemistry continues to expand, as does sulfur–nitrogen chemistry, heteropolyacid chemistry, bioinorganic aspects of the chemistry of many of the elements, lower-valent lanthanide element chemistry, and so on through each of the chapters, up to the synthesis and characterization of the heaviest trans-actinide element, $Z = 112$. It is salutary to reflect that there are now 49 more elements known than the 63 known to Mendeleev when he devised the periodic table of the elements.

A further indication of the rapid advances that have occurred in the chemistry of the elements during the past 15 years can be gauged from the several completely new sections which have been added to review work in what were previously both nonexistent and unsuspected areas. These include (a) coordination compounds of dihapto-dihydrogen, (b) the fullerenes and their many derivatives, (c) the metcars, and (d) high-temperature oxide superconductors.

We hope that this new edition of *Chemistry of the Elements* will continue to stimulate and inform its readers, and that they will experience something of the excitement and fascination which we ourselves feel for this burgeoning subject. We should also like to thank our many correspondents who have kept us informed of their work and the School of Chemistry in the University of Leeds for providing us with facilities.

N. N. Greenwood
A. Earnshaw
August, 1997

1		2																		3	4	5	6	7	8	9	10								
1	H	2	He																	3	Li	4	Be	5	B	6	C	7	N	8	O	9	F	10	Ne
11		12																		13	14	15	16	17	18										
11	Na	12	Mg																	13	Al	14	Si	15	P	16	S	17	Cl	18	Ar				
19		20		21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50		
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		38		39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	
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		56		57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	
55	Cs	56	Ba	57	La	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		
87		88		89	90	91	92	93	94	95	96	97	98	99	100	101	102	103	104	105	106	107	108	109	110	111	112	113	114	115	116	117	118	119	
87	Fr	88	Ra	89	Ac	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	Lr		

2

Chemical Periodicity and the Periodic Table

2.1 Introduction

The concept of chemical periodicity is central to the study of inorganic chemistry. No other generalization rivals the periodic table of the elements in its ability to systematize and rationalize known chemical facts or to predict new ones and suggest fruitful areas for further study. Chemical periodicity and the periodic table now find their natural interpretation in the detailed electronic structure of the atom; indeed, they played a major role at the turn of the century in elucidating the mysterious phenomena of radioactivity and the quantum effects which led ultimately to Bohr's theory of the hydrogen atom. Because of this central position it is perhaps not surprising that innumerable articles and books have been written on the subject since the seminal papers by Mendeleev in 1869, and some 700 forms of the periodic table (classified into 146 different types or subtypes) have been proposed.⁽¹⁻³⁾ A brief historical survey of these developments is summarized in the Panel opposite.

There is no single *best* form of the periodic table since the choice depends on the purpose for which the table is used. Some forms emphasize chemical relations and valence, whereas others stress the electronic configuration of the elements or the dependence of the periods on the shells and subshells of the atomic structure. The most convenient form for our purpose is the so-called "long form" with separate panels for the lanthanide and actinide elements (see inside front cover). There has been a lively debate during the past decade as to the best numbering system to be used for the individual

¹ F. P. VENABLE, *The Development of the Periodic Law*, Chemical Publishing Co., Easton, Pa., 1896. This is the first general review of periodic tables and has an almost complete collection of those published to that time. J. W. VAN SPRONSEN, *The Periodic System of the Chemical Elements*, Elsevier, Amsterdam, 1969, 368 pp. An excellent modern account of the historical developments leading up to Mendeleev's table.

² E. G. MAZURS, *Graphic Representation of the Periodic System during One Hundred Years*, University of Alabama Press, Alabama, 1974. An exhaustive topological classification of over 700 forms of the periodic table.

groups in the table; we will adopt the 1–18 numbering scheme recommended by IUPAC.⁽³⁾ The following sections of this chapter summarize:

- (a) the interpretation of the periodic law in terms of the electronic structure of atoms;
- (b) the use of the periodic table and graphs to systematize trends in physical and chemical properties and to detect possible errors, anomalies, and inconsistencies;
- (c) the use of the periodic table to predict new elements and compounds, and to suggest new areas of research.

³ E. FLUCK, *Pure Appl. Chem.* **60**, 432–6 (1988); G. J. LEIGH (ed.), *Nomenclature of Inorganic Chemistry: IUPAC Recommendations 1990*, Blackwell, Oxford, 1990, 289 pp. The “Red Book”.

2.2 The Electronic Structure of Atoms⁽⁴⁾

The ubiquitous electron was discovered by J. J. Thompson in 1897 some 25 y after the original work on chemical periodicity by D. I. Mendeleev and Lothar Meyer; however, a further 20 y were to pass before G. N. Lewis and then I. Langmuir connected the electron with valency and chemical bonding. Refinements continued via wave mechanics and molecular orbital theory, and the symbiotic relation between experiment and theory still continues

⁴ N. N. GREENWOOD, *Principles of Atomic Orbitals*, revised SI edition, Monograph for Teachers, No. 8, Chemical Society, London, 1980, 48 pp.

Mendeleev's Periodic Table

Precursors and Successors

- 1772 L. B. G. de Morveau made the first table of “chemically simple” substances. A. L. Lavoisier used this in his *Traité Élémentaire de Chimie* published in 1789.
- 1817–29 J. W. Döbereiner discovered many triads of elements and compounds, the combining weight of the central component being the average of its partners (e.g. CaO, SrO, BaO, and NiO, CuO, ZnO).
- 1843 L. Gmelin included a V-shaped arrangement of 16 triads in the 4th edition of his *Handbuch der Chemie*.
- 1857 J. B. Dumas published a rudimentary table of 32 elements in 8 columns indicating their relationships.
- 1862 A. E. B. de Chancourtois first arranged the elements in order of increasing atomic weight; he located similar elements in this way and published a helical form in 1863.
- 1864 L. Meyer published a table of valences for 49 elements.
- 1864 W. Odling drew up an almost correct table with 17 vertical columns and including 57 elements.
- 1865 J. A. R. Newlands propounded his law of octaves after several partial classifications during the preceding 2 y; he also correctly predicted the atomic weight of the undiscovered element germanium.
- 1868–9 L. Meyer drew up an atomic volume curve and a periodic table, but this latter was not published until 1895.
- 1869 D. I. Mendeleev enunciated his periodic law that “the properties of the elements are a periodic function of their atomic weights”. He published several forms of periodic table, one containing 63 elements.
- 1871 D. I. Mendeleev modified and improved his tables and predicted the discovery of 10 elements (now known as Sc, Ga, Ge, Tc, Re, Po, Fr, Ra, Ac and Pa). He fully described with amazing prescience the properties of 4 of these (Sc, Ga, Ge, Po). Note, however, that it was not possible to predict the existence of the noble gases or the number of lanthanide elements.
- 1894–8 Lord Rayleigh, W. Ramsay and M. W. Travers detected and then isolated the noble gases (He), Ne, Ar, Kr, Xe.
- 1913 N. Bohr explained the form of the periodic table on the basis of his theory of atomic structure and showed that there could be only 14 lanthanide elements.
- 1913 H. G. J. Moseley observed regularities in the characteristic X-ray spectra of the elements; he thereby discovered atomic numbers *Z* and provided justification for the ordinal sequence of the elements.
- 1940 E. McMillan and P. Abelson synthesized the first transuranium element ⁹³Np. Others were synthesized by G. T. Seaborg and his colleagues during the next 15 y.
- 1944 G. T. Seaborg proposed the actinide hypothesis and predicted 14 elements (up to *Z* = 103) in this group.

today. It should always be remembered, however, that it is incorrect to "deduce" known chemical phenomena from theoretical models; the proper relationship is that the currently accepted theoretical models interpret the facts and suggest new experiments — they will be modified (or discarded and replaced) when new results demand it. Theories can never be proved by experiment — only refuted, the best that can be said of a theory is that it is consistent with a wide range of information which it interprets logically and that it is a fruitful source of predictions and new experiments.

Our present views on the electronic structure of atoms are based on a variety of experimental results and theoretical models which are fully discussed in many elementary texts. In summary, an atom comprises a central, massive, positively charged nucleus surrounded by a more tenuous envelope of negative electrons. The nucleus is composed of neutrons (${}^1_0\text{n}$) and protons (${}^1_1\text{p}$, i.e. ${}^1_1\text{H}^+$) of approximately equal mass tightly bound by the force field of mesons. The number of protons (Z) is called the atomic number and this, together with the number of neutrons (N), gives the atomic mass number of the nuclide ($A = N + Z$). An element consists of atoms all of which have the same number of protons (Z) and this number determines the position of the element in the periodic table (H. G. J. Moseley, 1913). Isotopes of an element all have the same value of Z but differ in the number of neutrons in their nuclei. The charge on the electron (e^-) is equal in size but opposite in sign to that of the proton and the ratio of their masses is $1/1836.2$.

The arrangement of electrons in an atom is described by means of four quantum numbers which determine the spatial distribution, energy, and other properties, see Appendix 1 (p. 1285). The principal quantum number n defines the general energy level or "shell" to which the electron belongs. Electrons with $n = 1, 2, 3, 4, \dots$, are sometimes referred to as K, L, M, N, $\dots$, electrons. The orbital quantum number l defines both the shape of the electron charge distribution and its orbital angular

momentum. The number of possible values for l for a given electron depends on its principal quantum number n ; it can have n values running from 0 to $n - 1$, and electrons with $l = 0, 1, 2, 3, \dots$, are designated s, p, d, f, $\dots$, electrons. Whereas n is the prime determinant of an electron's energy this also depends to some extent on l (for atoms or ions containing more than one electron). It is found that the sequence of increasing electron energy levels in an atom follows the sequence of values $n + l$; if 2 electrons have the same value of $n + l$ then the one with smaller n is the more tightly bound.

The third quantum number m is called the magnetic quantum number for it is only in an applied magnetic field that it is possible to define a direction within the atom with respect to which the orbital can be directed. In general, the magnetic quantum number can take up $2l + 1$ values (i.e. $0, \pm 1, \dots, \pm l$); thus an s electron (which is spherically symmetrical and has zero orbital angular momentum) can have only one orientation, but a p electron can have three (frequently chosen to be the x , y , and z directions in Cartesian coordinates). Likewise there are five possibilities for d orbitals and seven for f orbitals.

The fourth quantum number m_s is called the spin angular momentum quantum number for historical reasons. In relativistic (four-dimensional) quantum mechanics this quantum number is associated with the property of symmetry of the wave function and it can take on one of two values designated as $+\frac{1}{2}$ and $-\frac{1}{2}$, or simply α and β . All electrons in atoms can be described by means of these four quantum numbers and, as first enumerated by W. Pauli in his *Exclusion Principle* (1926), each electron in an atom must have a unique set of the four quantum numbers.

It can now be seen that there is a direct and simple correspondence between this description of electronic structure and the form of the periodic table. Hydrogen, with 1 proton and 1 electron, is the first element, and, in the ground state (i.e. the state of lowest energy) it has the electronic configuration $1s^1$ with zero orbital angular momentum. Helium, $Z = 2$, has the configuration $1s^2$, and this completes the first period since no

other unique combination of $n = 1$, $l = m = 0$, $m_s = \pm \frac{1}{2}$ exists. The second period begins with lithium ($Z = 3$), the least tightly bound electron having the configuration $2s^1$. The same situation obtains for each of the other periods in the table, the number of the period being the principal quantum number of the least tightly bound electron of the first element in the period. It will also be seen that there is a direct relation between the various blocks of elements in the periodic table and the electronic configuration of the atoms it contains; the s block is 2 elements wide, the p block 6 elements wide, the d block 10, and the f block 14, i.e. $2(2l + 1)$, the factor 2 appearing because of the spins.

In so far as the chemical (and physical) properties of an element derive from its electronic configuration, and especially the configuration of its least tightly bound electrons, it follows that chemical periodicity and the form of the periodic table can be elegantly interpreted in terms of electronic structure.

2.3 Periodic Trends in Properties^(5,6)

General similarities and trends in the *chemical* properties of the elements had been noticed increasingly since the end of the eighteenth century and predated the observation of periodic variations in *physical* properties which were not noted until about 1868. However, it is more convenient to invert this order and to look at trends in atomic and physical properties first.

2.3.1 Trends in atomic and physical properties

Figure 2.1 shows a modern version of Lothar Meyer's atomic volume curve: the alkali metals

⁵ R. RICH, *Periodic Correlations*, W. A. Benjamin, New York, 1965, 159 pp.

⁶ R. T. SANDERSON, *Inorganic Chemistry*, Reinhold Publishing Corp., New York, 1967, 430 pp.

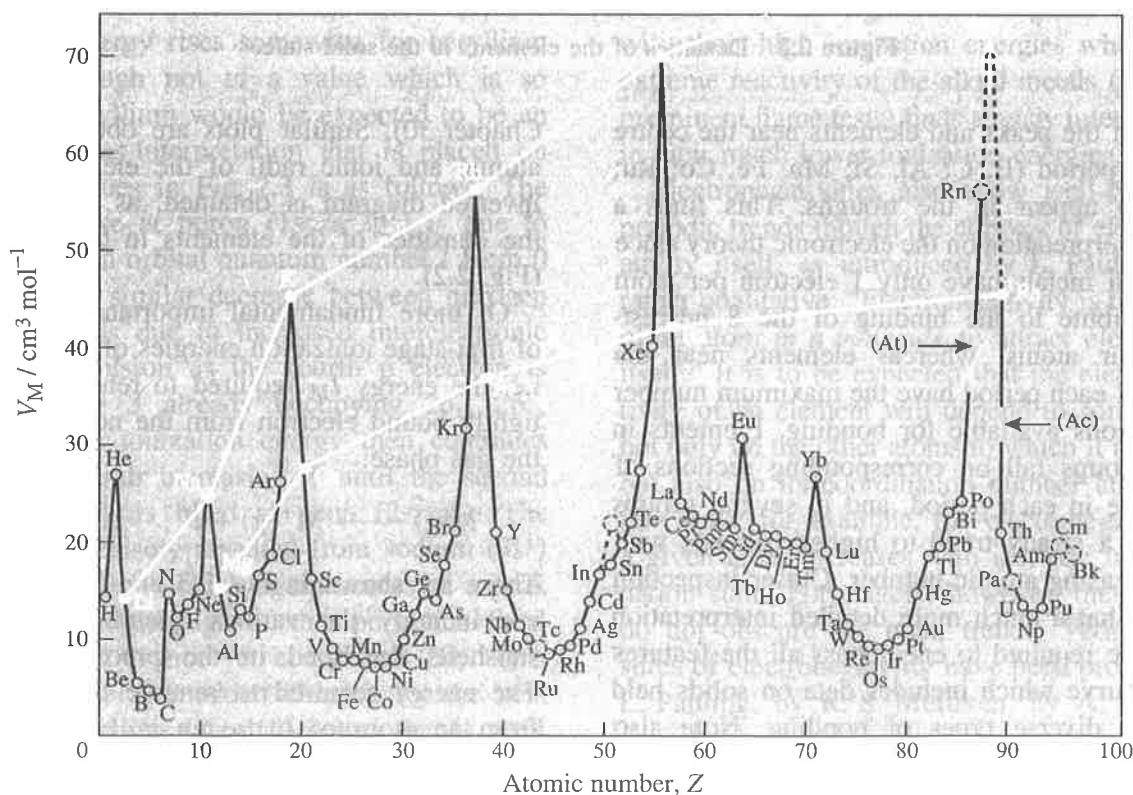


Figure 2.1 Atomic volumes (molar volumes) of the elements in the solid state.

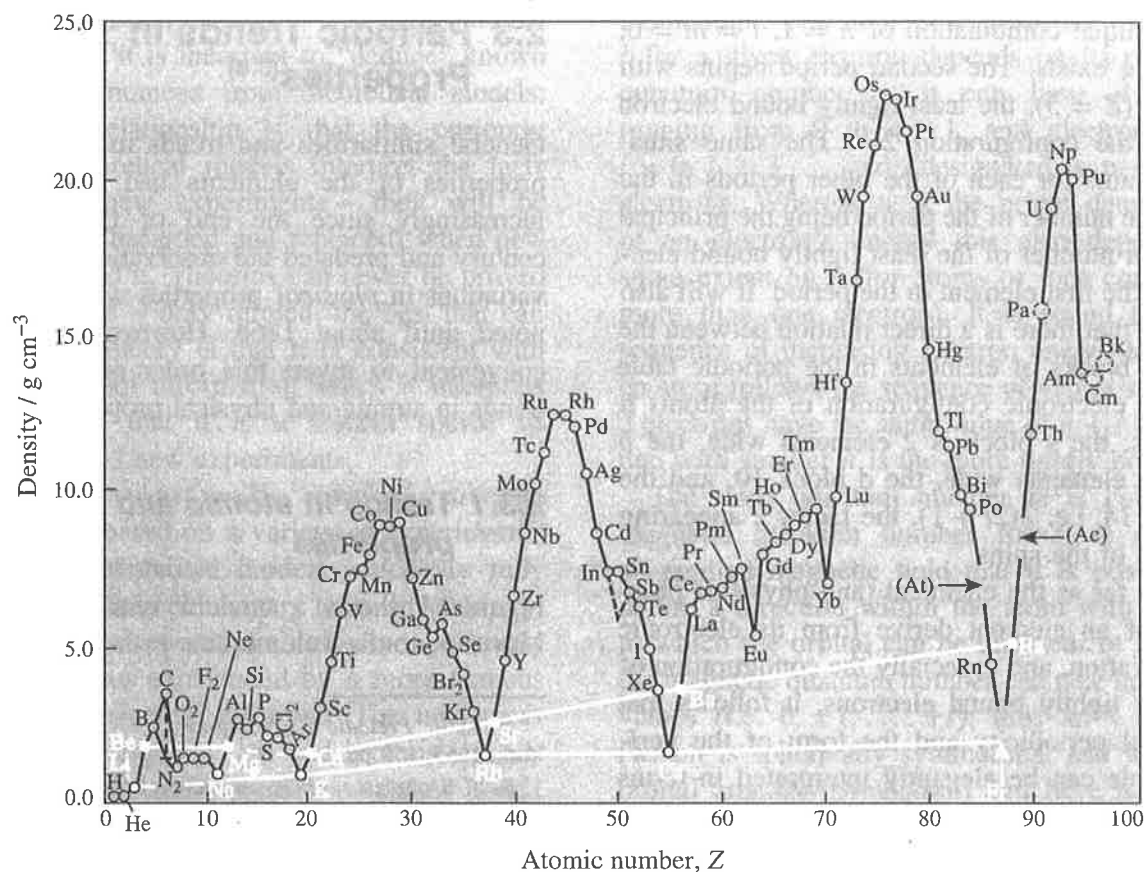
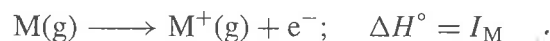


Figure 2.2 Densities of the elements in the solid state.

appear at the peaks and elements near the centre of each period (B, C; Al, Si; Mn, Fe, Co; Ru; and Os) appear in the troughs. This finds a ready interpretation on the electronic theory since the alkali metals have only 1 electron per atom to contribute to the binding of the 8 nearest-neighbour atoms, whereas elements near the centre of each period have the maximum number of electrons available for bonding. Elements in other groups fall on corresponding sections of the curve in each period, and in several groups there is a steady trend to higher volumes with the increasing atomic number. Closer inspection reveals that a much more detailed interpretation would be required to encompass all the features of the curve which includes data on solids held by very diverse types of bonding. Note also that the position of helium is anomalous (why?), and that there are local anomalies at europium and ytterbium in the lanthanide elements (see

Chapter 30). Similar plots are obtained for the atomic and ionic radii of the elements and an inverted diagram is obtained, as expected, for the densities of the elements in the solid state (Fig. 2.2).

Of more fundamental importance is the plot of first-stage ionization energies of the elements, i.e. the energy I_M required to remove the least tightly bound electron from the neutral atom in the gas phase:



These are shown in Fig. 2.3 and illustrate most convincingly the various quantum shells and subshells described in the preceding section. The energy required to remove the 1 electron from an atom of hydrogen is 13.606 eV (i.e. 1312 kJ per mole of H atoms). This rises to 2372 kJ mol⁻¹ for He (1s²) since the positive charge on the helium nucleus is twice that of the

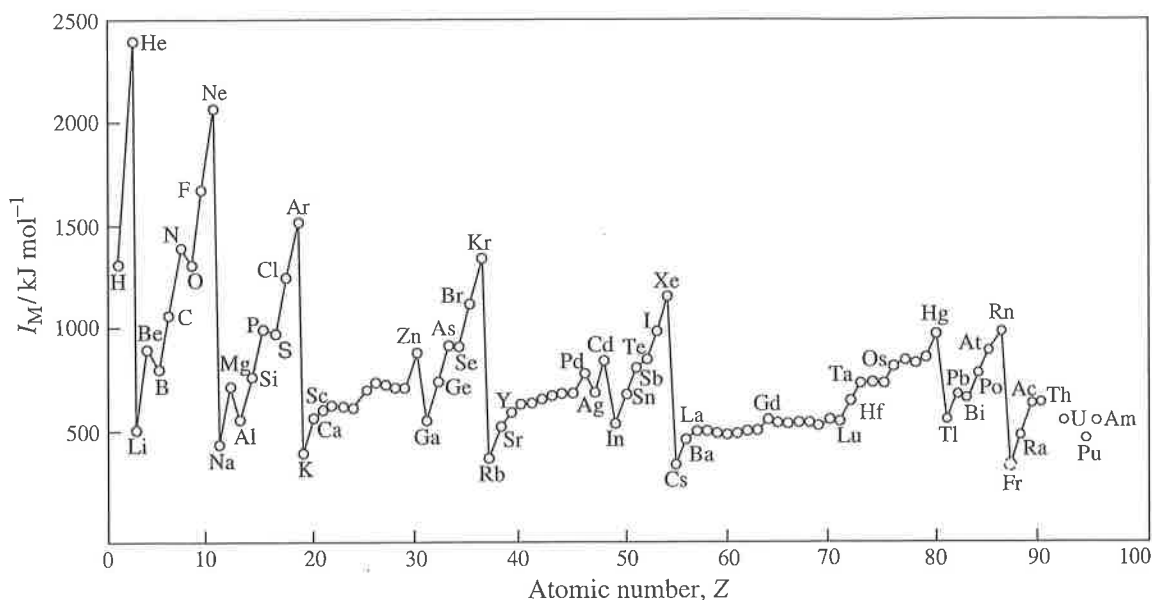


Figure 2.3 First-stage ionization energies of the elements.

proton and the additional charge is not completely shielded by the second electron. There is a large drop in ionization energy between helium and lithium ($1s^22s^1$) because the principal quantum number n increases from 1 to 2, after which the ionization energy rises somewhat for beryllium ($1s^22s^2$), though not to a value which is so high that beryllium would be expected to be an inert gas. The interpretation that is placed on the other values in Fig. 2.3 is as follows. The slight decrease at boron ($1s^22s^22p^1$) is due to the increase in orbital quantum number l from 0 to 1 and the similar decrease between nitrogen and oxygen is due to increased interelectronic coulomb repulsion as the fourth p electron is added to the 3 already occupying $2p_x$, $2p_y$, and $2p_z$. The ionization energy then continues to increase with increasing Z until the second quantum shell is filled at neon ($2s^22p^6$). The process is precisely repeated from sodium ($3s^1$) to argon ($3s^23p^6$) which again occurs at a peak in the curve, although at this point the third quantum shell is not yet completed ($3d$). This is because the next added electron for the next element potassium ($Z = 19$) enters the $4s$ shell ($n + l = 4$) rather than the $3d$ ($n + l = 5$). After calcium ($Z = 20$) the $3d$ shell fills and then the $4p$ ($n + l = 5$, but n higher than for $3d$). The

implications of this and of the subsequent filling of later s , p , d , and f levels will be elaborated in considerable detail in later chapters. Suffice it to note for the moment that the chemical inertness of the lighter noble gases correlates with their high ionization energies whereas the extreme reactivity of the alkali metals (and their prominent flame tests) finds a ready interpretation in their much lower ionization energies.

Electronegativities also show well-developed periodic trends though the concept of electronegativity itself, as introduced by L. Pauling,⁽⁷⁾ is rather qualitative: "Electronegativity is the power of an atom *in a molecule* to attract electrons to itself." It is to be expected that the electronegativity of an element will depend to some extent not only on the other atoms to which it is bonded but also on its coordination number and oxidation state; for example, the electronegativity of a given atom increases with increase in its oxidation state. Fortunately, however, these effects do not obscure the main trends. Various measures of electronegativity have been proposed by L. Pauling, by R. S. Mulliken, by A. L. Allred

⁷ L. PAULING, *J. Am. Chem. Soc.* **54**, 3570 (1932); *The Nature of the Chemical Bond*, 3rd edn., pp. 88–107. Cornell University Press, Ithaca, NY, 1960.

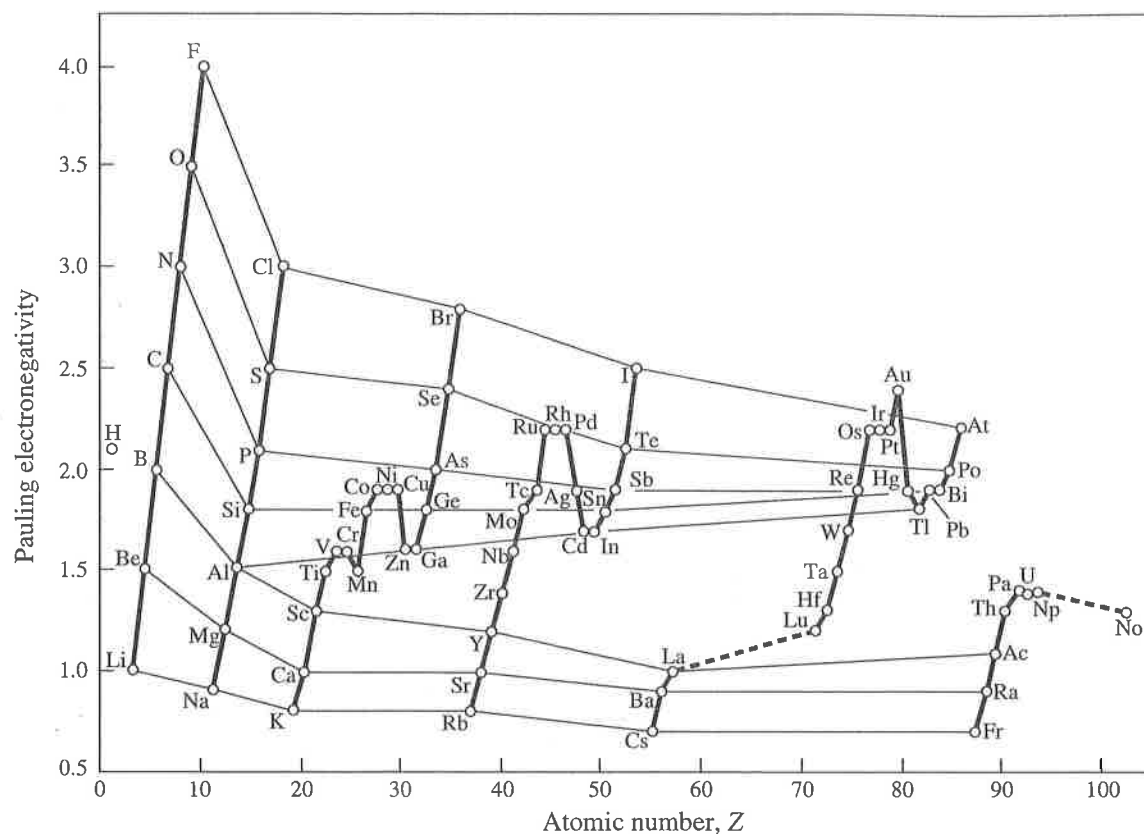


Figure 2.4 Values of electronegativity of the elements.

and E. Rochow, and by R. T. Sanderson, and all give roughly parallel scales. Figure 2.4, which incorporates Pauling's values, illustrates the trends observed; electronegativities tend to increase with increasing atomic number within a given period (e.g. Li to F, or K to Br) and to decrease with increasing atomic number within a given group (e.g. F to At, or O to Po). Numerous reviews are available.⁽⁸⁾

Many other properties have been found to show periodic variations and these can be displayed graphically or by circles of varying size on a periodic table, e.g. melting points of the elements, boiling points, heats of fusion, heats of vaporization, energies of atomization, etc.⁽⁶⁾ Similarly, the properties of simple binary

compounds of the elements can be plotted, e.g. heats of formation, melting points and boiling points of hydrides, fluorides, chlorides, bromides, iodides, oxides, sulfides, etc.⁽⁶⁾ Trends immediately become apparent, and the selection of compounds with specific values for particular properties is facilitated. Such trends also permit interpolation to give estimates of undetermined values of properties for a given compound though such a procedure can be misleading and should only be used as a first rough guide. Extrapolation has also frequently been used, and to good effect, though it too can be hazardous and unreliable particularly when new or unsuspected effects are involved. Perhaps the classic example concerns the dissociation energy of the fluorine molecule which is difficult to measure experimentally: for many years this was taken to be $\sim 265 \text{ kJ mol}^{-1}$ by extrapolation of the values for iodine, bromine, and chlorine (151, 193, and 243 kJ mol^{-1}), whereas the

⁸ K. D. SEN and C. K. JØRGENSEN (eds.), *Structure and Bonding* 66 *Electronegativity*, Springer-Verlag, Berlin, 1987, 198 pp. J. Mullay, *J. Am. Chem. Soc.* 106, 5842-7 (1984). R. T. Sanderson, *Inorg. Chem.* 25, 1856-8 (1986). R. G. Pearson, *Inorg. Chem.* 27, 734-40 (1988).

most recent experimental values are close to 159 kJ mol^{-1} (see Chapter 17). The detection of such anomalous data from periodic plots thus serves to identify either inaccurate experimental observations or inadequate theories (or both).

2.3.2 Trends in chemical properties

These, though more difficult to describe quantitatively than the trends in atomic and physical properties described in the preceding subsection, also become apparent when the elements are compared in each group and along each period. Such trends will be discussed in detail in later chapters and it is only necessary here to enumerate briefly the various types of behaviour that frequently recur.

The most characteristic chemical property of an element is its valence. There are numerous measures of valency each with its own area of usefulness and applicability. Simple definitions refer to the number of hydrogen atoms that can combine with an element in a binary hydride or to twice the number of oxygen atoms combining with an element in its oxide(s). It was noticed from the beginning that there was a close relation between the position of an element in the periodic table and the stoichiometry of its simple compounds. Hydrides of main group elements have the formula MH_n where n was related to the group number N by the equations $n = N$ ($N \leq 4$), and $n = 18 - N$ for $N > 4$. By contrast, oxygen elicited an increasing valence in the highest normal oxide of each element and this was directly related to the group number, i.e. M_2O , MO , M_2O_3 , ..., M_2O_7 . These periodic regularities find a ready explanation in terms of the electronic configuration of the elements and simple theories of chemical bonding. In more complicated chemical formulae involving more than 2 elements, it is convenient to define the "oxidation state" of an element as the formal charge remaining on the element when all other atoms have been removed as their normal ions. For example, nitrogen has an oxidation state of -3 in ammonium chloride [$\text{NH}_4\text{Cl} - (4\text{H}^+ + \text{Cl}^-) = \text{N}^{3-}$] and manganese

has an oxidation state of $+7$ in potassium permanganate {tetraoxomanganate(1-)} [$\text{KMnO}_4 - (\text{K}^+ + 4\text{O}^{2-}) = \text{Mn}^{7+}$]. For a compound such as Fe_3O_4 iron has an average oxidation state of $+2.67$ [i.e. $(4 \times 2)/3$] which may be thought of as comprising 1Fe^{2+} and 2Fe^{3+} . It should be emphasized that these charges are formal, not actual, and that the concept of oxidation state is not particularly helpful when considering predominantly covalent compounds (such as organic compounds) or highly catenated inorganic compounds such as S_7NH .

The periodicity in the oxidation state or valence shown by the elements was forcefully illustrated by Mendeleev in one of his early forms of the periodic system and this is shown in an extended form in Fig. 2.5 which incorporates more recent information. The predictive and interpolative powers of such a plot are obvious and have been a fruitful source of chemical experimentation for over a century.

Other periodic trends which occur in the chemical properties of the elements and which are discussed in more detail throughout later chapters are:

- (i) The "anomalous" properties of elements in the first short period (from lithium to fluorine) — see Chapters 4, 5, 6, 8, 11, 14 and 17.
- (ii) The "anomalies" in the post-transition element series (from gallium to bromine) related to the d-block contraction — see Chapters 7, 10, 13, 16 and 17.
- (iii) The effects of the lanthanide contraction — see Chapters 21–30.
- (iv) Diagonal relationships between lithium and magnesium, beryllium and aluminium, boron and silicon.
- (v) The so-called inert pair effect (see Chapters 7, 10 and 13) and the variation of oxidation state in the main group elements in steps of 2 (e.g. IF , IF_3 , IF_5 , IF_7).
- (vi) Variability in the oxidation state of transition elements in steps of 1.
- (vii) Trends in the basicity and electropositivity of elements — both vertical trends

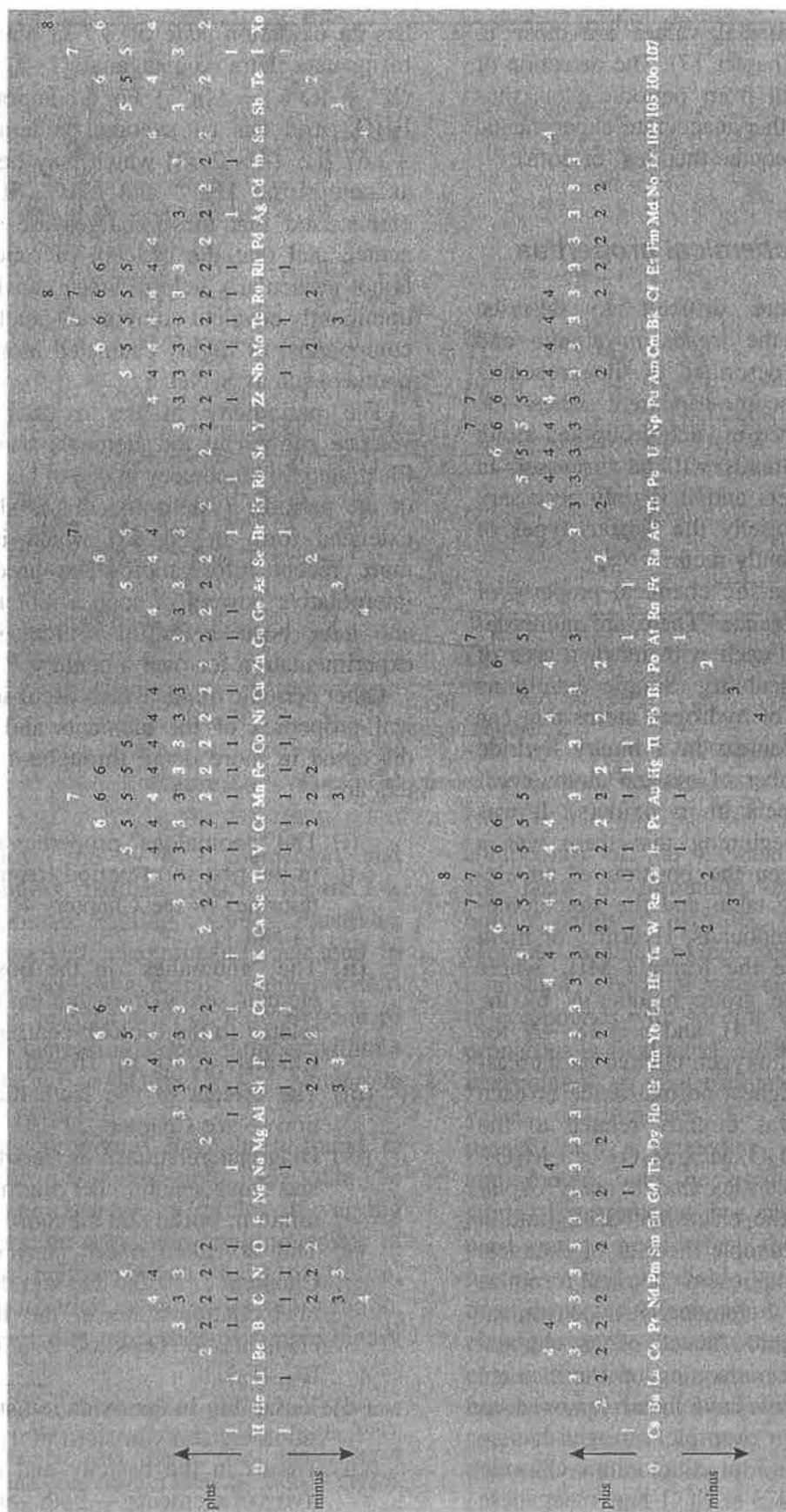


Figure 2.5 Formal oxidation states of the elements displayed in a format originally devised by Mendeleev in 1889. The more common oxidation states (including zero) are shown in white. Nonintegral values, as in B_5H_9 , C_3H_8 , HN_3 , S_8^{2+} , etc., are not included.

- within groups and horizontal trends along periods.
- (viii) Trends in bond type with position of the elements in the table and with oxidation state for a given element.
 - (ix) Trends in stability of compounds and regularities in the methods used to extract the elements from their compounds.
 - (x) Trends in the stability of coordination complexes and the electron-donor power of various series of ligands.

2.4 Prediction of New Elements and Compounds

Newlands (1864) was the first to predict correctly the existence of a "missing element" when he calculated an atomic weight of 73 for an element between silicon and tin, close to the present value of 72.61 for germanium (discovered by C. A. Winkler in 1886). However, his method of detecting potential triads was unreliable and he predicted (non-existent) elements between

rhodium and iridium, and between palladium and platinum. Mendeleev's predictions 1869–71 were much more extensive and reliable, as indicated in the historical panel on p. 21. The depth of his insight and the power of his method remain impressive even today, but in the state of development of the subject in 1869 they were monumental. A comparison of the properties of *eka-silicon* predicted by Mendeleev and those determined experimentally for germanium is shown in Table 2.1. Similarly accurate predictions were made for *eka-aluminium* and gallium and for *eka-boron* and scandium.

Of the remaining 26 undiscovered elements between hydrogen and uranium, 11 were lanthanoids which Mendeleev's system was unable to characterize because of their great chemical similarity and the new numerological feature dictated by the filling of the 4f orbitals. Only cerium, terbium and erbium were established with certainty in 1871, and the others (except promethium, 1945) were separated and identified in the period 1879–1907. The isolation of the (unpredicted) noble gases also occurred at this time (1894–8).

Table 2.1

Mendeleev's predictions (1871) for <i>eka-silicon</i> , M		Observed properties (1995) of germanium (discovered 1886)	
Atomic weight	72	Atomic weight	72.61(2)
Density/g cm ⁻³	5.5	Density/g cm ⁻³	5.323
Molar volume/cm ³ mol ⁻¹	13.1	Molar volume/cm ³ mol ⁻¹	13.64
MP/°C	high	MP/°C	945
Specific heat/J g ⁻¹ K ⁻¹	0.305	Specific heat/J g ⁻¹ K ⁻¹	0.309
Valence	4	Valence	4
Colour	dark grey	Colour	greyish-white
M will be obtained from MO ₂ or K ₂ MF ₆ by reaction with Na		Ge is obtained by reaction of K ₂ GeF ₆ with Na	
M will be slightly attacked by acids such as HCl and will resist alkalis such as NaOH		Ge is not dissolved by HCl or dilute NaOH but reacts with hot conc HNO ₃	
M, on being heated, will form MO ₂ with high mp, and <i>d</i> 4.7 g cm ⁻³		Ge reacts with oxygen to give GeO ₂ , mp 1086°, <i>d</i> 4.228 g cm ⁻³	
M will give a hydrated MO ₂ soluble in acid and easily reprecipitated		"Ge(OH) ₄ " dissolves in conc acid and is reprecipitated on dilution or addition of base	
MS ₂ will be insoluble in water but soluble in ammonium sulfide		GeS ₂ is insoluble in water and dilute acid but readily soluble in ammonium sulfide	
MCl ₄ will be a volatile liquid with bp a little under 100°C and <i>d</i> 1.9 g cm ⁻³		GeCl ₄ is a volatile liquid with bp 83°C and <i>d</i> 1.8443 g cm ⁻³	
M will form MEt ₄ bp 160°C		GeEt ₄ bp 185°C	

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Table 17.1 Early history of the halogens and their compounds

3000 BC	Archaeological evidence for the use of rock-salt
~400 BC	Written records on salt (ascribed to Herodot)
~200 BC	Use of salt as part payment for services (salary)
~21 AD	Strabo described dyeworks for obtaining tyrian purple (dibromindigo) in his <i>Geographica</i>
~100	Use of salt to purify noble metals
~900	Dilute hydrochloric acid prepared by Arabian alchemist Rhazes
~1200	Development of <i>aqua regia</i> (HCl/HNO_3) to dissolve gold — presumably Cl_2 was also formed
1529	Georgius Agricola described use of fluorspar as a flux
~1630	Chlorine recognized as a gas by Belgian physician J. B. van Helmont (see Scheele, 1774)
1648	Concentrated HCl prepared by J.L. Glauber (by heating hydrated ZnCl_2 and sand)
1670	H. Schwanhard (Nürnberg) found that CaF_2 + strong acid gave acid vapours (HF) that etched glass (used decoratively)
1678	J. S. Elsholtz described emission of bluish-white light when fluorspar was heated. Also described by J. G. Wallerius, 1750; the name “fluorescence” was coined in 1852 by G. G. Stokes
1768	First chemical study of fluorite undertaken by A. S. Marggraf
1771	Crude hydrofluoric acid prepared by C. W. Scheele
1772	Gaseous HCl prepared over mercury by J. Priestley
1774	C. W. Scheele prepared and studied gaseous chlorine ($\text{MnO}_2 + \text{HCl}$) but thought it was a compound
1785	Chemical bleaching (eau de Javel: aqueous $\text{KOH} + \text{Cl}_2$) introduced by C.-L. Berthollet
1787	N. Leblanc devised a technical process for obtaining NaOH from NaCl (beginnings of the chemical industry)
1798	Bleaching powder patented by C. Tennant (Cl_2 + slaked lime) following preparation of bleaching liquors from Cl_2 and lime solutions by T. Henry (1788)
1801	W. Cruickshank recommended use of Cl_2 as a disinfectant (widely used in hospitals by 1823; notably effective in the European cholera epidemic, 1831, and in the outbreak of puerperal fever, Vienna, 1845)
1802	Fluoride found in fossil ivory and teeth by D. P. Morichini (soon confirmed by J. J. Berzelius who found it also in bones)
1810	H. Davy announced proof of the elementary nature of chlorine to the Royal Society (15 November) and suggested the name “chlorine” (1811)
1811	B. Courtois isolated iodine by sublimation (H_2SO_4 + seaweed ash)
1811	The term “halogen” introduced by J. S. C. Schweigger to denote the (then) unique property of the element chlorine to combine directly with metals to give salts
1812	A.-M. Ampère wrote to H. Davy (12 August) suggesting the name <i>le fluore</i> (fluorine) for the presumed new element in CaF_2 and HF (by analogy with <i>le chlore</i> , chlorine). Adopted by Davy in 1813
1814	Starch/iodine blue colour-reaction described by J.-J. Colin and H.-F. Gaultier de Claubry; developed by F. Stromeyer in the same year as an analytical test sensitive to 2–3 ppm iodine
1814	First interhalogen compound (ICl) prepared by J.L. Gay Lussac
1819	Potassium iodide introduced as a remedy for goitre by J.-F. Coindet (Switzerland), the efficacy of extracts from kelp having been known in China and Europe since the sixteenth century
1823	M. Faraday showed that “solid chlorine” was chlorine hydrate ($\text{Cl}_2 \cdot \sim 10\text{H}_2\text{O}$ using present-day nomenclature). He also liquefied Cl_2 (5 March) by warming the hydrate in a sealed tube
1825	First iodine containing mineral (AgI) identified by A. M. del Rio (Mexico) and N.-L. Vauquelin (Paris)
1826	Bromine isolated by A.-J. Balard (aged 23 y)
1835	L. J. M. Daguerre’s photographic process (silver plate sensitized by exposure to iodine vapour)
~1840	Introduction of (light sensitive) AgBr into photography
1840	Iodine (as iodate) found in Chilean saltpetre by A. A. Hayes
1841	First mineral bromide (bromyrite, AgBr) discovered in Mexico by P. Berthier — later also found in Chile and France
1851	Diaphragm cell for the electrolytic generation of Cl_2 invented by C. Watt (London) but lack of electric generators delayed exploitation until 1886–90 (Matthes and Weber of Duisberg)
1857	Bromide therapy introduced by Lacock as a sedative and anticonvulsant for treatment of epilepsy
1858	Discovery of Stassfurt salt deposits opened the way for bromine production (for photography and medicine) as a by-product of potash
1863	Alkali Act (UK) prohibited atmospheric pollution and enforced the condensation of by-product HCl from the Leblanc process
1886	H. Moissan isolated F_2 by electrolysis of KHF_2/HF (26 June) after over 70 y of unsuccessful attempts by others (Nobel Prize for Chemistry 1906 — he died 2 months later)
1892–5	H. Y. Castner (US/UK) and C. Kellner (Vienna) independently developed commercial mercury-cathode cell for chlor-alkali production

Table 17.2 Halogens in the twentieth century

~1900	First manufacture of inorganic fluorides for aluminium industry
1902	J. C. Downs (of E. I. du Pont de Nemours, Delaware) patented the first practical molten-salt cell for Cl_2 and Na metal
1908	HCl shown to be present in gastric juices of animals by P. Sommerfeld
1909	P. Friedländer showed that Tyrian Purple from <i>Murex brandaris</i> was 6,6'-dibromoindigo (previously synthesized by F. Sachs in 1904)
1920	Bromine detected in blood and organs of humans and other animals and birds by A. Damiens
1928	T. Midgley, A. L. Henne and R. R. McNary synthesized Freon (CCl_2F_2) as a non-flammable, non-toxic gas for refrigeration
1928	ClF made by O. Ruff <i>et al.</i> ($\text{Cl}_2 + \text{F}_2$ at 250°)
1930	IF_7 made by O. Ruff and R. Keim (IF_5 having been made in 1871 by G. Gore)
1930+	H. T. Dean <i>et al.</i> put the correlation between decreased incidence of dental caries and the presence of fluoride ions in drinking water on a quantitative basis
1931	First bulk shipment of commercial anhydrous HF (USA)
1938	R. J. Plunket discovered Teflon (polytetrafluoroethylene, PTFE)
1940	Astatine made via $^{209}\text{Bi}(\alpha, 2n)$ by D. R. Corson, K. R. Mackenzie and E. Segré
1940–1	Industrial production of $\text{F}_2(\text{g})$ begun (in the UK and the USA for manufacture of UF_6 and in Germany for ClF_3)
1950	Chemical shifts for ^{19}F and nmr signals for ^{35}Cl and ^{37}Cl first observed
1962	ClF_5 (the last halogen fluoride to be made) synthesized by W. Maya
1965	LaF_3 crystals developed by J. W. Ross and M. S. Frant as the first non-glass membrane electrode (for ion-selective determination of F^-)
1965	Perchlorate ion established as a monodentate ligand (to Co) by X-ray crystallography, following earlier spectroscopic and conductimetric indications of coordination (1961)
1968	Perbromates first prepared by E. H. Appelman
1967	First example of $\mu(\eta^1, \eta^1)\text{-ClO}_4^-$ as a bidentate bridging ligand (to Ag^+); chelating $\eta^2\text{-ClO}_4^-$ identified in 1974
1971	HOF first isolated in weighable amounts (p. 856)
1986	First chemical synthesis of F_2 gas (p. 821)

presence of fluorine, but it would be possible, of course, that it might be a perfluoride of hydrogen or even a mixture of hydrofluoric acid and ozone. . . ." For this achievement, which had eluded some of the finest experimental chemists of the nineteenth century [including H. Davy (1813–14), G. Aimé (1833), M. Faraday (1834), C. J. and T. Knox (1836), P. Louyet (1846), E. Frémy (1854), H. Kammerer (1862) and G. Gore (1870)], and for his development of the electric furnace, Moissan was awarded the Nobel Prize for Chemistry in 1906.

Fluorine technology and the applications of fluorine-containing compounds have developed dramatically during the twentieth century.^(2,3) Some highlights are included in Table 17.2 and will be discussed more fully in later sections.

Noteworthy events are the development of inert fluorinated oils, greases and polymers: Freon gases such as CCl_2F_2 (1928) were specifically developed for refrigeration engineering; others were used as propellants in pressurized dispensers and aerosols; and the non-stick plastic polytetrafluoroethylene (PTFE or Teflon) was made in 1938. Inorganic fluorides, especially for the aluminium industry (p. 219) have been increasingly exploited from about 1900, and from 1940 UF_6 has been used in gaseous diffusion plants for the separation of uranium isotopes for nuclear reactor technology. The great oxidizing strength of F_2 and many of its compounds with N and O have attracted the attention of rocket

compounds, pp. 267–466; Organic fluorine compounds, pp. 467–729.

³ R. E. BANKS, D. W. A. SHARP and J. C. TATLOW (eds.), *Fluorine: the First Hundred years*, Elsevier, New York, 1987 399 pp.

² Kirk–Othmer Encyclopedia of Chemical Technology, 4th edn., Vol. 11, 1994: Fluorine pp. 241–67; In-organic fluorine

engineers and there have been growing large-scale industrial applications of anhydrous HF (p. 810).

The aggressive nature of HF fumes and solutions has been known since Schwanhard of Nürnberg used them for the decorative etching of glass. Hydrofluoric acid inflicts excruciatingly painful skin burns (p. 810) and any compound that might hydrolyse to form HF should be treated with great caution.⁽⁴⁾ Maximum allowable concentration for continuous exposure to HF gas is 2–3 ppm (cf. HCN 10 ppm). The free element itself is even more toxic, maximum allowable concentration for a daily 8-h exposure being 0.1 ppm. Low concentrations of fluoride ion in drinking water have been known to provide excellent protection against dental caries since the classical work of H. T. Dean and his colleagues in the early 1930s; as there are no deleterious effects, even over many years, providing the total fluoride ion concentration is kept at or below 1 ppm, fluoridation has been a recommended and adopted procedure in several countries for many years (p. 810). However, at 2–3 ppm a brown mottling of teeth can occur and at 50 ppm harmful toxic effects are noted. Ingestion of 150 mg of NaF can cause nausea, vomiting, diarrhoea and acute abdominal pains though complete recovery is rapid following intravenous or intramuscular injection of calcium ions. The deliberate fluoridation of domestic water supplies has been a controversial, even polemical subject for several decades, though it is important to separate out the biological and toxicological aspects from the moral and philosophical aspects concerning the “right” of individuals to drink untreated water if they wish.^(5–7)

⁴ A. J. FINKEL, Treatment of hydrogen fluoride injuries, *Adv. Fluorine Chem.* 7, 199–203 (1973).

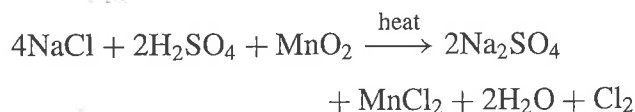
⁵ G. L. WALDBOTT (with A. W. BURGSTAHLER and H. L. MCKINNEY, *Fluoridation: The Great Dilemma*, Coronado Press, Lawrence, Kansas, 1978, 423 pp.

⁶ B. HILEMAN, Fluoridation of Water: A Special Report, *C & E News* August 1, 26–42 (1988). See also B. HILEMAN, *C & E News* February 25, 6–7 (1991).

⁷ B. MARTIN, *Scientific Knowledge in Controversy: The Social Dynamics of the Fluoridation Debate*, State University of New York Press, Albany, N.Y. 1991, 256 pp.

Chlorine

Chlorine was the first of the halogens to be isolated and common salt (NaCl) has been known from earliest times (see Table 17.1). Its efficacy in human diet was well recognized in classical antiquity and there are numerous references to its importance in the Bible. On occasion salt was used as part payment for the services of Roman generals and military tribunes (salary) and, indeed, it is an essential ingredient in mammalian diets (p. 63). The alchemical use of *aqua regia* (HCl/HNO₃) to dissolve gold is also well documented from the thirteenth century onwards. Concentrated hydrochloric acid was prepared by J. L. Glauber in 1648 by heating hydrated ZnCl₂ and sand in a retort and the pure gas, free of water, was collected over mercury by J. Priestley in 1772. This was closely followed by the isolation of gaseous chlorine by C. W. Scheele in 1774: he obtained the gas by oxidizing nascent HCl with MnO₂ in a reaction which would now formally be written as:



However, Scheele believed he had prepared a *compound* (dephlogisticated marine acid air) and the misconception was compounded by C.-L. Berthollet who showed in 1785 that the action of chlorine on water releases oxygen: $[\text{Cl}_2(\text{g}) + \text{H}_2\text{O} \longrightarrow 2\text{HCl}(\text{soln}) + \frac{1}{2}\text{O}_2(\text{g})]$; he concluded that chlorine was a loose compound of HCl and oxygen and called it oxymuriatic acid.[†]

[†] *Muriatic acid* and *marine acid* were synonymous terms for what is now called hydrochloric acid, thus signifying its relation to the sodium chloride contained in brine (Latin *muria*) or sea water (Latin *mare*). Both names were strongly criticized by H. Davy in a scathing paper entitled “Some reflections on the nomenclature of oxymuriatic compounds” in *Phil. Trans. R. Soc.* for 1811: “To call a body which is not known to contain oxygen, and which cannot contain muriatic acid, oxymuriatic acid, is contrary to the principles of that nomenclature in which it is adopted; and an alteration of it seems necessary to assist the progress of the discussion, and to diffuse just ideas on the subject. If the great discoverer of this substance (i.e. Scheele) had signified it by any simple name it would have been proper to have referred to it; but

The two decades from 1790 to 1810 were characterized by two major advances in chemical theory: Lavoisier's demolition of the phlogiston theory of combustion, and Davy's refutation of Lavoisier's contention that oxygen is a necessary constituent of all acids. Only when both these transformations had been achieved could the elementary nature of chlorine and the true composition of hydrochloric acid be appreciated, though some further time was to elapse (Dalton, Avogadro, Cannizaro) before gaseous chlorine was universally recognized to consist of diatomic molecules, Cl_2 , rather than single atoms, Cl . The name, proposed by Davy in 1811, refers to the colour of the gas (Greek $\chi\lambda\omega\rho\acute{o}\varsigma$, *chloros*, yellowish or light green — cf. chlorophyll).

The bleaching power of Cl_2 was discovered by Scheele in his early work (1774) and was put to technical use by Berthollet in 1785. This was a major advance on the previous time-consuming, labour-intensive, weather-dependent method of solar bleaching, and numerous patents followed (see Table 17.1). Indeed, the use of chlorine as a bleach remains one of its principal industrial applications (bleaching powder, elemental chlorine, hypochlorite solutions, chlorine dioxide, chloramines, etc.).⁽⁸⁾ Another all-pervading use of chlorine, as a disinfectant and germicide, also dates from this period (1801), and the chlorination of domestic water supplies is now almost universal in developed countries. Again, as with fluoride, higher concentrations are toxic to humans: the gas is detectable by smell at 3 ppm, causes throat irritation at 15 ppm, coughing at 30 ppm, and rapid death at 1000 ppm. Prolonged exposure to concentrations above 1 ppm should be avoided.

Sodium chloride, by far the most abundant compound of chlorine, occurs in extensive evaporite deposits, saline lakes and brines, and in

the ocean (p. 795). It has played a dominant role in the chemical industry since its inception in the late eighteenth century (p. 71). The now defunct Leblanc process for obtaining NaOH from NaCl signalled the beginnings of large-scale chemical manufacture, and NaCl remains virtually the sole source of chlorine and hydrochloric acid for the vast present-day chlorine-chemicals industry.⁽⁸⁾ This embraces not only the large-scale production and distribution of Cl_2 and HCl , but also the manufacture of chlorinated methanes and ethanes, vinyl chloride, aluminium trichloride catalysts and the chlorides of Mg , Ti , Zr , Hf , etc., for production of the metals. Details of many of these processes are to be found either in other chapters or in later sections of the present chapter. About 15 000 chlorinated compounds are currently used to varying degrees in commerce. Of these, the environmental and health hazards posed by certain polychlorinated hydrocarbons is now well established, though not all such compounds are dangerous: focused selective restrictions rather than a blanket banning of all organochlorine compounds is advocated.⁽⁹⁾ The rôle of chlorofluorocarbons in the depletion of stratospheric ozone above the polar regions has already been mentioned (p. 608).

Bromine

The magnificent purple pigment referred to in the Bible⁽¹⁰⁾ and known to the Romans as Tyrian purple after the Phoenician port of Tyre (Lebanon), was shown by P. Friedländer in 1909 to be 6,6'-dibromoindigo. This precious dye was extracted in the early days from the small purple snail *Murex brandaris*, as many as 12 000 snails being required to prepare 1.5 g of dye. The element itself was isolated by A.-J. Balard in 1826 from the mother liquors remaining after the crystallization of sodium chloride and sulfate from the waters of the Montpellier salt marshes;

'dephlogisticated marine acid' is a term which can hardly be adopted in the present advanced area of the science. After consulting some of the most eminent chemical philosophers in the country, it has been judged most proper to suggest a name founded upon one of its most obvious and characteristic properties — its colour, and to call it *Chlorine*."

⁸ J. S. SCONCE, *Chlorine: Its Manufacture, Properties and Uses*, Reinhold, New York, 1962, 901 pp.

⁹ B. HILEMAN, *C & E News*, April 19, 11–20 (1993). See also B. HILEMAN, J. R. LONG and E. M. KIRSCHNER, *C & E News*, November 21, 12–26 (1994).

¹⁰ Holy Bible, Ezekiel 27:7, 16.

the liquor is rich in MgBr_2 , and the young Balard, then 23 y of age, noticed the deep yellow coloration that developed on addition of chlorine water. Extraction with ether and KOH , followed by treatment of the resulting KBr with $\text{H}_2\text{SO}_4/\text{MnO}_2$, yielded the element as a red liquid. Astonishingly rapid progress was possible in establishing the chemistry of bromine and in recognizing its elemental nature because of its similarity to chlorine and iodine (which had been isolated 15 y earlier). Indeed, J. von Liebig had missed discovering the element several years previously by misidentifying a sample of it as iodine monochloride.⁽¹⁾ Balard had proposed the name *muride*, but this was not accepted by the French Academy, and the element was named bromine (Greek $\beta\rho\omega\mu\omicron\varsigma$, stink) because of its unpleasant, penetrating odour. It is perhaps ironic that the name fluorine had already been pre-empted for the element in CaF_2 and HF (p. 789) since bromine, as the only non-metallic element that is liquid at room temperature, would pre-eminently have deserved the name.

The first mineral found to contain bromine (bromyrite, AgBr) was discovered in Mexico in 1841, and industrial production of bromides followed the discovery of the giant Stassfurt potash deposits in 1858. The major use at that time was in photography and medicine: AgBr had been introduced as the light-sensitive agent in photography about 1840, and the use of KBr as a sedative and anti-convulsant in the treatment of epilepsy was begun in 1857. Other major uses of bromine-containing compounds include their application as flame retardants and as phase-transfer catalysts. The scale of the present-day production of bromine and bromine chemicals will become clear in later sections of this chapter.⁽¹¹⁾

Iodine

The lustrous, purple-black metallic sheen of resublimed crystalline iodine was first observed

by the industrial chemist B. Courtois in 1811, and the name, proposed by J. L. Gay Lussac in 1813, reflects this most characteristic property (Greek $\iota\omega\delta\eta\varsigma$, violet-coloured). Courtois obtained the element by treating the ash of seaweed (which had been calcined to extract saltpetre and potash) with concentrated sulfuric acid. Extracts of the brown kelps and seaweeds *Fucus* and *Laminaria* had long been known to be effective for the treatment of goitre and it was not long before J. F. Coindet and others introduced pure KI as a remedy in 1819.⁽¹²⁾ It is now known that the thyroid gland produces the growth-regulating hormone thyroxine, an iodinated amino acid: $p\text{-(HO)-C}_6\text{H}_2(\text{I})_2\text{-O-C}_6\text{H}_2(\text{I})_2\text{-CH}_2\text{CH(NH}_2\text{)CO}_2\text{H}$.

If the necessary iodine input is insufficient the thyroid gland enlarges in an attempt to garner more iodine: addition of 0.01% NaI to table salt (iodized salt) prevents this condition. Tincture of iodine is a useful antiseptic.

The first iodine-containing mineral (AgI) was discovered in Mexico in 1825 but the discovery of iodate as an impurity in Chilean saltpetre in 1840 proved to be more significant industrially. The Chilean nitrate deposits provided the largest proportion of the world's iodine until overtaken in the late 1960s by Japanese production from natural brines (pp. 796, 799).

In addition to its uses in photography and medicine, iodine and its compounds have been much exploited in volumetric analysis (iodometry and iodimetry, p. 864). Organoiodine compounds have also played a notable part in the development of synthetic organic chemistry, being the first compounds used in A. W. von Hofmann's alkylation of amines (1850), A. W. Williamson's synthesis of ethers (1851), A. Wurtz's coupling reactions (1855) and V. Grignard's reagents (1900).

Astatine

From its position in the periodic table, all isotopes of element 85 would be expected to

¹¹ D. PRICE, B. IDDON and B. J. WAKEFIELD, *Bromine Compounds: Chemistry and Applications*, Elsevier, Amsterdam 1988, 422 pp.

¹² E. BOOTH, *Chem. Ind. (Lond.)* 31 and 52-5 (1979).

be radioactive. Those isotopes that occur in the natural radioactive series all have half-lives of less than 1 min and thus occur in negligible amounts in nature (p. 796). Astatine (Greek $\alpha\sigma\tau\alpha\tau\text{-}\omicron\varsigma$, unstable) was first made and characterized by D. R. Corson, K. R. Mackenzie, and E. Segré in 1940: they synthesized the isotope ^{211}At ($t_{1/2}$ 7.21 h) by bombarding ^{209}Bi with α -particles in a large cyclotron:



In all, some 27 isotopes from ^{194}At to ^{220}At have now been prepared by various routes but all are short-lived. The only ones besides ^{211}At having half-lives longer than 1 h are ^{207}At (1.80 h), ^{208}At (1.63 h), ^{209}At (5.41 h), and ^{210}At (8.1 h): this means that weighable amounts of astatine or its compounds cannot be isolated, and nothing is known of the bulk physical properties of the element. For example, the least-unstable isotope (^{210}At) has a specific activity corresponding to 2 curies per μg , i.e. 7×10^{10} disintegrations per second per μg . The largest preparations of astatine to date have involved about $0.05 \mu\text{g}$ and our knowledge of the chemistry of this element comes from extremely elegant tracer experiments, typically in the concentration range 10^{-11} – 10^{-15} M. The most concentrated aqueous solutions of the element or its compounds ever investigated were only $\sim 10^{-8}$ M.

17.1.2 Abundance and distribution

Because of their reactivity, the halogens do not occur in the free elemental state but they are both widespread and abundant in the form of their ions, X^- . Iodine also occurs as iodate (see below). In addition to large halide mineral deposits, particularly of NaCl and KCl, there are vast quantities of chloride and bromide in ocean waters and brines.

Fluorine is the thirteenth element in order of abundance in crustal rocks of the earth, occurring to the extent of 544 ppm (cf. twelfth Mn, 1060 ppm; fourteenth Ba, 390 ppm; fifteenth Sr, 384 ppm). The three most important minerals are

fluorite CaF_2 , cryolite Na_3AlF_6 and fluorapatite $\text{Ca}_5(\text{PO}_4)_3\text{F}$. Of these, however, only fluorite is extensively processed for recovery of fluorine and its compounds (p. 809). Cryolite is a rare mineral, the only commercial deposit being in Greenland, and most of the Na_3AlF_6 needed for the huge aluminium industry (p. 219) is now synthetic. By far the largest amount of fluorine in the earth's crust is in the form of fluorapatite, but this contains only about 3.5% by weight of fluorine and the mineral is processed almost exclusively for its phosphate content. Despite this, about 7% of the domestic requirement for fluorine compounds in the USA was obtained from fluorosilicic acid recovered as a by-product of the huge phosphate industry (pp. 476, 520). Minor occurrences of fluorine are in the rare minerals topaz $\text{Al}_2\text{SiO}_4(\text{OH},\text{F})_2$, sellaite MgF_2 , villiaumite NaF and bastnaesite $(\text{Ce},\text{La})(\text{CO}_3)\text{F}$ (but see p. 1229). The insolubility of alkaline-earth and other fluorides precludes their occurrence at commercially useful concentrations in ocean water (1.2 ppm) and brines.

Chlorine is the twentieth most abundant element in crustal rocks where it occurs to the extent of 126 ppm (cf. nineteenth V, 136 ppm, and twenty-first Cr, 122 ppm). The vast evaporite deposits of NaCl and other chloride minerals have already been described (pp. 69, 73). Dwarfing these, however, are the inconceivably vast reserves in ocean waters (p. 69) where more than half the total average salinity of 3.4 wt% is due to chloride ions (1.9 wt%). Smaller quantities, though at higher concentrations, occur in certain inland seas and in subterranean brine wells, e.g. the Great Salt Lake, Utah (23% NaCl) and the Dead Sea, Israel (8.0% NaCl, 13.0% MgCl_2 , 3.5% CaCl_2).

Bromine is substantially less abundant in crustal rocks than either fluorine or chlorine; at 2.5 ppm it is forty-sixth in order of abundance being similar to Hf 2.8, Cs 2.6, U 2.3, Eu 2.1 and Sn 2.1 ppm. Like chlorine, the largest natural source of bromine is the oceans, which contain $\sim 6.5 \times 10^{-3}\%$, i.e. 65 ppm or 65 mg/l. The mass ratio Cl:Br is $\sim 300:1$ in the oceans, corresponding to an atomic ratio

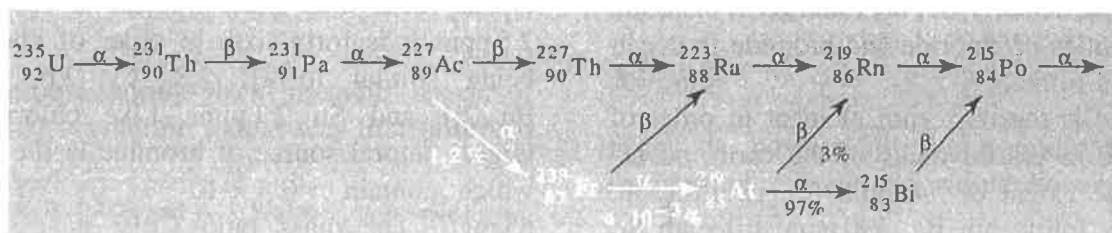
of $\sim 660:1$. Salt lakes and brine wells are also rich sources of bromine, and these are usually proportionately richer in bromine than are the oceans: the atom ratio Cl:Br spans the range ~ 200 – 700 . Typical bromide-ion concentrations in such waters are: Dead Sea 0.4% (4 g/l), Sakscoe Ozoro (Crimea) 0.28% and Searle's Lake (California) 0.085%.

Iodine is considerably less abundant than the lighter halogens both in the earth's crust and in the hydrosphere. It comprises 0.46 ppm of the crustal rocks and is sixtieth in order of abundance (cf. Tl 0.7, Tm 0.5, In 0.24, Sb 0.2). It occurs but rarely as iodide minerals, and commercial deposits are usually as iodates, e.g. lautarite, $\text{Ca}(\text{IO}_3)_2$ and dietzeite, $7\text{Ca}(\text{IO}_3)_2 \cdot 8\text{CaCrO}_4$. Thus the caliche nitrate beds of Chile contain iodine in this form (~ 0.02 – 1 wt% I). These mine workings soon replaced calcined seaweeds as the main source of iodine during the last century, but have recently been themselves overtaken by iodine recovered from brines. Brines associated with oil-well drillings in Louisiana and California were found to contain 30–40 ppm iodine in the 1920s, and independent subterranean brines were located at Midland, Michigan, in the 1960s, and in Oklahoma (1977), which is now the main US source. Natural brine wells in Japan (up to 100 ppm I) were discovered after the Second World War, and exploitation of these now ensures Japan first place among the world's iodine producers. The concentration of iodine in ocean waters is only 0.05 ppm, too low for commercial recovery, though brown seaweeds of the *Laminaria* family (and to a lesser extent *Fucus*) can concentrate this up to 0.45% of their dry weight (see above).

The fugitive radioactive element astatine can hardly be said to exist in nature though the punctillious would rightly point to its temporary participation in the natural radioactive series. Thus ^{219}At ($t_{1/2}$ 54 s) occurs as a rare and inconspicuous branch ($4 \times 10^{-3}\%$) of another minor branch (1.2%) of the ^{235}U ($4n+3$) series (see scheme). Another branch ($5 \times 10^{-4}\%$) at ^{215}Po yields ^{215}At by β emission before itself decaying by α emission ($t_{1/2}$ 1.0×10^{-4} s); likewise ^{218}At ($t_{1/2} \sim 72$ s) is a descendant of the ^{238}U ($4n+2$) series, and traces have been detected of ^{217}At ($t_{1/2}$ 0.0323 s) and ^{216}At ($t_{1/2}$ 3.0×10^{-4} s). Estimates suggest that the outermost kilometre of the earth's crust contains no more than 44 mg of astatine compared with 15 g of francium (p. 69) or the relatively abundant polonium (2500 tonnes) and actinium (7000 tonnes). Astatine can therefore be regarded as the rarest naturally occurring terrestrial element.

17.1.3 Production and uses of the elements

The only practicable large-scale method of preparing F_2 gas is Moissan's original procedure based on the electrolysis of KF dissolved in anhydrous HF; (see however p. 821). Moissan used a mole ratio KF:HF of about 1:13, but this has a high vapour pressure of HF and had to be operated at -24° . Electrolyte systems having mole ratios of 1:2 and 1:1 melt at $\sim 72^\circ$ and $\sim 240^\circ\text{C}$ respectively and have much lower vapour pressures of HF; accordingly



these compositions were subsequently favoured. Nowadays, medium-temperature cells ($80\text{--}100^\circ$) are universally employed, being preferred over the high-temperature cells because (a) they have a lower pressure of HF gas above the cell, (b) there are fewer corrosion problems, (c) the anode has a longer life and (d) the composition of the electrolyte can vary within fairly wide limits without impairing the operating conditions or efficiency. The highly corrosive nature of the electrolyte, coupled with the aggressive oxidizing power of F_2 , pose considerable problems of handling, and these are exacerbated by the explosive reaction of F_2 with its co-product H_2 , so that accidental mixing of the gases must be prevented at all costs. Scrupulous absence of grease and other flammable contaminants must also be ensured since they can lead to spectacular fires which puncture the protective fluoride coating of the metal containers and cause the whole system to enflame. Another hazard in early generators was the formation of explosive graphite-fluorine compounds at the anode (p. 289). All these problems have now been overcome and F_2 can be routinely generated with safety both in the laboratory and on a large industrial scale.^(2,13) A typical generator (Fig. 17.1) consists of a mild-steel pot (cathode) containing the electrolyte $\text{KF}\cdot 2\text{HF}$ which is kept at $80\text{--}100^\circ\text{C}$ either by a heating jacket when the cell is quiescent or by a cooling system when the cell is working. The anode consists of a central rod of compacted, ungraphitized carbon, and the product gases are kept separate by a skirt or diaphragm dipping below the electrolyte surface. The temperature is automatically controlled, as is the level of the electrolyte by controlled addition of make-up anhydrous HF. Laboratory generators usually operate at about $10\text{--}50\text{ A}$ whereas industrial production, employing banks of cells, may operate at $4000\text{--}6000\text{ A}$ and $8\text{--}12\text{ V}$. An individual cell in such a bank might typically be $3.0 \times 0.8 \times 0.6\text{ m}$ and hold 1 tonne of electrolyte; it might have 12 anode

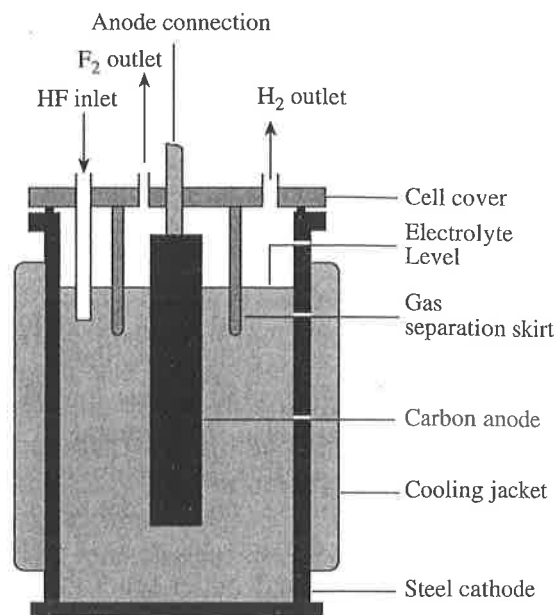


Figure 17.1 Schematic diagram of an electrolytic fluorine-generating cell.

assemblies each holding two anode blocks and produce $3\text{--}4\text{ kg F}_2$ per hour. A large-scale plant can produce *ca.* 9 tonnes of liquefied F_2 per day. The total annual production in the USA and Canada exceeds 5000 tonnes, and similar though somewhat smaller amounts are produced in several European countries (UK, France, Germany, Italy, Russia). Production in Japan approaches 1000 tpa.

Cylinders of F_2 are now commercially available in various sizes from 230-g to 2.7-kg capacity; 1993 price $\sim \$110\text{--}260$ per kg depending on cylinder size. The gas pressure is 2.86 MPa ($\sim 28\text{ atm.}$) at 21°C . Liquid F_2 is shipped in tank trucks of 2.27 tonnes capacity, the container being itself cooled by a jacket of liquid N_2 which boils 8° below F_2 . Alternatively, it can be converted to ClF_3 , bp 11.7°C (p. 828), which is easier to handle and transport than F_2 . In fact, about 70–80% of the elemental F_2 produced is used captively for the manufacture of UF_6 for nuclear power generation (p. 1259). Another important use is in the production of SF_6 for dielectrics (p. 687). The captive use to manufacture the versatile fluorinating agents ClF_3 , BrF_3 and IF_5 is a third important outlet. Fluorination of W and Re to

¹³ H. C. FIELDING and B. E. LEE, in R. THOMPSON (ed.), *The Modern Inorganic Chemicals Industry*, pp. 149–67, Chemical Society Special Publication No. 31, 1977.

their hexafluorides is also industrially important since these volatile compounds are used in chemical vapour deposition of W and Re films on intricately shaped components. Most other fluorinations of inorganic and organic compounds avoid the direct use of F_2 . The former demand for liquid F_2 as a rocket-fuel oxidizer has now ceased.

Chlorine is rarely generated on a laboratory scale since it is so readily available in cylinders of all sizes from 450 g (net) to 70 kg. When required it can also be generated by adding concentrated, air-free hydrochloric acid ($d\ 1.16\text{ g cm}^{-3}$) dropwise on to precipitated hydrated manganese dioxide in a flask fitted with a dropping funnel and outlet tube: the gas formation can be regulated by moderate heating and the Cl_2 thus formed can be purified by passage through water (to remove HCl) and H_2SO_4 (to remove H_2O). The gas, whether generated in this way or obtained from a cylinder, can be further purified if necessary by passage through successive tubes containing CaO and P_2O_5 , followed by condensation in a bath cooled by solid CO_2 and fractionation in a vacuum line.

Industrial production of Cl_2 and chlorine chemicals is on a vast scale and comprises a major section of the heavy chemical industry.^(8,9,14,15) Some aspects have already been discussed on p. 793, and further details are in the Panel.

Bromine is invariably made on an industrial scale by oxidation of bromide ion with Cl_2 . The main sources of Br^- are Arkansas brines (4000–5000 ppm) which account for most of US production, various brines and bitterns in Europe, the Dead Sea (4000–6000 ppm), and ocean waters (65 ppm). Following the oxidation of Br^- the Br_2 is removed from the solution either by passage of steam ("steaming out") or air ("blowing out"), and then condensed and purified. Although apparently simple, these unit operations must deal with highly reactive and corrosive materials, and the industrial processes have been ingeniously developed and refined

¹⁴ R. W. PURCELL, The chlor-alkali industry, in ref. 13, pp. 106–33. A. CAMPBELL, Chlorine and chlorination, *ibid.*, pp. 134–48.

¹⁵ Kirk-Othmer *Encyclopedia of Chemical Technology*, 4th edn., 1, 938–1025 (1991).

Industrial Production and Uses of Chlorine

The large-scale production of Cl_2 is invariably achieved by the electrolytic oxidation of the chloride ion. Natural brines or aqueous solutions of NaCl can be electrolysed in an asbestos diaphragm cell or a mercury cathode cell, though these latter are being phased out for environmental and other reasons (p. 1225). Electrolysis of molten NaCl is also carried out on a large scale: in this case the co-product is Na rather than NaOH. Electrolysis of by-product HCl is also used where this is cheaply available. World consumption of Cl_2 in 1987 exceeded 35 million tonnes. Production is dominated by the USA, but large tonnages are produced in all industrial countries: USA 30%, Western Europe 29%, Eastern Europe 15%, Japan 8.5%, Asia/Pacific 6.8%. Cl_2 was ranked eighth among the large-volume chemicals manufactured in the USA during 1996. Diaphragm cells predominated though there is a growing interest in membrane cells in which the anolyte and catholyte are separated by a porous Nafion membrane (Nafion is a copolymer of tetrafluoroethylene and a perfluorosulfonylethoxy ether and the membrane is reinforced with a Teflon mesh).⁽¹⁵⁾ In addition to cylinders of varying capacity up to 70 kg, chlorine can be transported in drums (865 kg), tank wagons (road: 15 tonnes; rail 27–90 tonnes), or barges (600–1200 tonnes).

The three main categories of use for Cl_2 are:

- Production of organic compounds by chlorination and/or oxychlorination using a fluidized bed of copper chloride catalyst (pre-eminent amongst these are vinyl chloride monomer and propylene oxide which in the USA alone are produced on a scale of 9.0 and 2.0 million tonnes respectively). Production of chlorinated organic compounds accounts for about 63% of the Cl_2 produced.
- Bleaches (for paper, pulp and textiles) sanitation and disinfection of municipal water supplies and swimming pools, sewage treatment and control. These uses account for about 19% of the Cl_2 produced.
- Production of inorganic compounds, notably HCl, Cl_2O , HOCl, $NaClO_3$, chlorinated isocyanurates, $AlCl_3$, $SiCl_4$, $SnCl_4$, PCl_3 , PCl_5 , $POCl_3$, $AsCl_3$, $SbCl_3$, $SbCl_5$, $BiCl_3$, S_2Cl_2 , SCl_2 , $SOCl_2$, ClF_3 , ICl , ICl_3 , $TiCl_3$, $TiCl_4$, $MoCl_5$, $FeCl_3$, $ZnCl_2$, Hg_2Cl_2 , $HgCl_2$, etc. (see index for page references to production and uses). About 18% of Cl_2 production is used to manufacture inorganic chemicals.

to give optimum yields at the lowest possible operating costs.^(16,17)

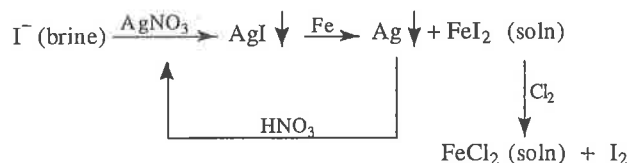
World production of Br₂ in 1990 was about 438 000 tonnes pa, i.e. about one-hundredth of the scale of the chlorine industry. The main producing countries are (tonnes): USA 177 000, Israel 135 000, Russia 60 000, UK 28 000, France 18 000 and Japan 15 000. The production capacity of Israel has recently increased almost threefold because of expanded facilities on the Dead Sea. Historically, bromine was shipped in individual 3-kg (net) bottles to minimize damage due to breakage, but during the 1960s bulk transport in monel metal drums (100-kg capacity) or lead-lined tanks (24 or 48 tonnes) was developed and these are now used for transport by road, rail and ship. The price of Br₂ in tank-car lots was \$975/kg in 1990.

The industrial usage of bromine has been dominated by the single compound ethylene dibromide which has been (with ethylene dichloride) a valuable gasoline (petrol) additive where it acts as a scavenger for lead from the anti-knock additive PbEt_4 . Environmental legislation has dramatically reduced the amount of leaded petrol produced and, accordingly, ethylene dibromide, which accounted for 90% of US bromine production in 1955, declined to 75% a decade later and now represents a mere 16% of the total bromine consumption in the USA (1990). Fortunately this decline has been matched by a steady increase in other applications and the industry worldwide has shown a modest growth. Most of these large-volume applications involve organic compounds, notably MeBr , which is one of the most effective nematocides known (i.e. kills worms) and is also used as a general pesticide (herbicide, fungicide and insecticide). Ethylene dibromide and dibromochloropropane are also used as pesticides. Bromine compounds are extensively used as fire retardants, especially for fibres, carpets, rugs and plastics; they are about 3–4 times as effective (weight for

weight) as chlorocompounds which gives them a substantial cost advantage.

Other uses of bromo-organics include high-density drilling fluids, dyestuffs and pharmaceuticals. Bromine is also used in water sanitation and to synthesize a wide range of inorganic compounds, e.g. AgBr for photography, HBr, alkali metal bromides, bromates, etc. (see later sections). An indication of the overall pattern of use (USA, 1990) is as follows: flame retardants 29%, ethylene dibromide 16%, agrochemicals 16% drilling fluids 11% inorganic bromides 5.5%, water treatment chemicals 5.5%, other 17%.

The commercial recovery of iodine on an industrial scale depends on the particular source of the element.⁽¹⁸⁾ From natural brines, such as those at Midland (Michigan) or in Russia or Japan, chlorine oxidation followed by air blow-out as for bromine (above) is much used, the final purification being by resublimation. Alternatively the brine, after clarification, can be treated with just sufficient AgNO_3 to precipitate the AgI which is then treated with clean scrap iron or steel to form metallic Ag and a solution of FeI_2 ; the Ag is redissolved in HNO_3 for recycling and the solution is treated with Cl_2 to liberate the I_2 :



The newest process to be developed oxidizes the brine with Cl_2 and then treats the solution with an ion-exchange resin: the iodine is adsorbed in the form of polyiodide which can be eluted with alkali followed by NaCl to regenerate the column. About 65% of the iodine consumed in the world comes from brines.

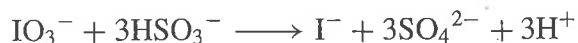
Recovery of iodine from Chilean saltpetre differs entirely from its recovery from brine since it is present as iodate. NaIO_3 is extracted from the caliche and is allowed to accumulate in the mother liquors from the crystallization of NaNO_3

¹⁶ R. B. McDONALD and W. R. MERRIMAN, pp. 168-82 of ref. 13.

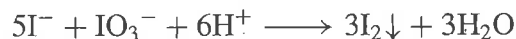
¹⁷ Ref. 2, Vol. 4 (1992), Bromine, pp. 536-60; Bromine compounds, pp. 560-89.

¹⁸ Ref. 2, Vol. 14 (1995), Iodine and Iodine compounds, pp. 709-37.

until its concentration is about 6 g/l. Part is then drawn off and treated with the stoichiometric amount of sodium hydrogen sulfite required to reduce it to iodide:



The resulting acidic mixture is treated with just sufficient fresh mother liquor to liberate all the contained iodine:



The precipitated I_2 is filtered off and the iodine-free filtrate returned to the nitrate-leaching cycle after neutralization of any excess acid with Na_2CO_3 .

World production of I_2 in 1992 approached 15 000 tonnes, the dominant producers being Japan 41%, Chile 40%, USA 10% and the former Soviet Union 9%. Crude iodine is packed in double polythene-lined fibre drums of 10–50-kg capacity. Resublimed iodine is transported in lined fibre drums (11.3 kg) or in bottles containing 0.11, 0.45 or 2.26 kg. The price of I_2 has traditionally fluctuated wildly. Thus, because of acute over-supply in 1990 the price for I_2 peaked at \$22/kg in 1988, falling to \$12/kg in 1990 and \$9.50/kg in 1992. Unlike Cl_2 and Br_2 , iodine has no predominant commercial outlet. About 50% is incorporated into a wide variety of organic compounds and about 15% each is accounted for as resublimed iodine, KI, and other inorganics. The end uses include catalysts for synthetic rubber manufacture, animal- and fowl-feed supplements,

stabilizers, dyestuffs, colourants and pigments for inks, pharmaceuticals, sanitary uses (tincture of iodine, etc.) and photographic chemicals for high-speed negatives. Uses of iodine compounds as smog inhibitors and cloud-seeding agents are small. In analytical chemistry KHgI_3 forms the basis for Nessler's reagent for the detection of NH_3 , and Cu_2HgI_4 was used in Mayer's reagent for alkaloids. Iodides and iodates are standard reagents in quantitative volumetric analysis (p. 864). Ag_2HgI_4 has the highest ionic electrical conductivity of any known solid at room temperature but this has not yet been exploited on a large scale in any solid-state device.

17.1.4 Atomic and physical properties

The halogens are volatile, diatomic elements whose colour increases steadily with increase in atomic number. Fluorine is a pale yellow gas which condenses to a canary yellow liquid, bp -188.1°C (intermediate between N_2 , bp -195.8° , and O_2 , bp -183.0°C). Chlorine is a greenish-yellow gas, bp -34.0° , and bromine a dark-red mobile liquid, bp 59.5° : interestingly the colour of both elements diminishes with decrease in temperature and at -195° Cl_2 is almost colourless and Br_2 pale yellow. Iodine is a lustrous, black, crystalline solid, mp 113.6° , which sublimates readily and boils at 185.2°C .

Atomic properties are summarized in Table 17.3 and some physical properties are in Table 17.4.

Table 17.3 Atomic properties of the halogens

Property	F	Cl	Br	I	At
Atomic number	9	17	35	53	85
Number of stable isotopes	1	2	2	1	0
Atomic weight	18.998 4032(9)	35.4527(9)	79.904(1)	126.90447(3)	(210)
Electronic configuration	$[\text{He}]2s^2 2p^5$	$[\text{Ne}]3s^2 3p^5$	$[\text{Ar}]3d^{10} 4s^2 4p^5$	$[\text{Kr}]4d^{10} 5s^2 5p^5$	$[\text{Xe}]4f^{14} 5d^{10} 6s^2 6p^5$
Ionization energy/ kJ mol^{-1}	1680.6	1255.7	1142.7	1008.7	[926]
Electron affinity/ kJ mol^{-1}	332.6	348.7	324.5	295.3	[270]
$\Delta H_{\text{dissoc}}/\text{kJ mol}(\text{X}_2)^{-1}$	158.8	242.58	192.77	151.10	—
Ionic radius, X^-/pm	133	184	196	220	—
van der Waals radius/pm	135	180	195	215	—
Distance $\text{X}-\text{X}$ in X_2/pm	143	199	228	266	—

Table 17.4 Physical properties of the halogens

Property	F ₂	Cl ₂	Br ₂	I ₂
MP/°C	-219.6	-101.0	-7.25	113.6 ^(a)
BP/°C	-188.1	-34.0	59.5	185.2 ^(a)
<i>d</i> (liquid, T°C)/g cm ⁻³	1.516(-188°)	1.655(-70°)	3.187 (0°)	3.960 ^(b) (120°)
$\Delta H_{\text{fusion}}/\text{kJ mol}(\text{X}_2)^{-1}$	0.51	6.41	10.57	15.52
$\Delta H_{\text{vap}}/\text{kJ mol}(\text{X}_2)^{-1}$	6.54	20.41	29.56	41.95
Temperature (°C) for 1% dissociation at 1 atm	765	975	775	575

^(a)Solid iodine has a vapour pressure of 0.31 mmHg (41 Pa) at 25°C and 90.5 mmHg (12.07 kPa) at the mp (113.6°).

^(b)Solid iodine has a density of 4.940 g cm⁻³ at 20°C.

As befits their odd atomic numbers, the halogens have few naturally occurring isotopes (p. 3). Only one isotope each of F and I occurs in nature and the atomic weights of these elements are therefore known very accurately indeed (p. 17). Chlorine has two naturally occurring isotopes (³⁵Cl 75.77%, ³⁷Cl 24.23%) as also does bromine (⁷⁹Br 50.69%, ⁸¹Br 49.31%). All isotopes of At are radioactive (p. 795). The ionization energies of the halogen atoms show the expected trend to lower values with increase in atomic number. The electronic configuration of each atom (*ns*²*np*⁵) is one p electron less than that of the next succeeding noble gas, and energy is evolved in the reaction $\text{X}(\text{g}) + \text{e}^- \longrightarrow \text{X}^-(\text{g})$. The electron affinity, which traditionally (though misleadingly) is given a positive sign despite the negative enthalpy change in the above reaction, is maximum for Cl, the value for F being intermediate between those for Cl and Br. Even more noticeable is the small enthalpy of dissociation for F₂ which is similar to that of I₂ and less than two-thirds of the value for Cl₂.⁽¹⁹⁾ In this connection it can be noted that N–N single bonds in hydrazines are weaker than the corresponding P–P bonds and that O–O single bonds in peroxides are weaker than the corresponding S–S bonds. This was explained (R. S. Mulliken and others, 1955) by postulating that partial *pd* hybridization imparts some double-bond character

to the formal P–P, S–S and Cl–Cl single bonds thereby making them stronger than their first-row counterparts. However, following C. A. Coulson and others (1962), it seems unnecessary to invoke substantial d-orbital participation and the weakness of the F–F single bond is then ascribed to decreased overlap of bonding orbitals, appreciable internuclear repulsion and the relatively large electron–electron repulsions of the lone-pairs which are much closer together in F₂ than in Cl₂.⁽²⁰⁾ The rapid diminution of bond-dissociation energies in the sequence N₂ ≫ O₂ ≫ F₂ is, of course, due to successive filling of the antibonding orbitals (p. 606), thus reducing the formal bond order from triple in N≡N to double and single in O=O and F–F respectively.

Radioactive isotopes of the halogens have found use in the study of isotope-exchange reactions and the mechanisms of various other reactions.^(21,22) The properties of some of the most used isotopes are in Table 17.5. Many of these isotopes are available commercially. A fuller treatment with detailed references

¹⁹ J. BERKOWITZ and A. C. WAHL, *Adv. Fluorine Chem.* **7**, 147–74 (1973). A. A. WOOLF, *Adv. Inorg. Chem. Radiochem.* **24**, 1–55 (1981). J. J. TURNER, *MTP International Review of Science: Inorganic Chemistry Series 1*, Vol. 3, pp. 253–91, Butterworths, London, 1972.

²⁰ P. POLITZER, Anomalous properties of fluorine, *J. Am. Chem. Soc.* **91**, 6235–7 (1969); Some anomalous properties of oxygen and nitrogen, *Inorg. Chem.* **16**, 3350–1 (1977).

²¹ M. F. A. DOVE and D. B. SOWERBY, in V. GUTMANN (ed.), *Halogen Chemistry*, Vol. 1, pp. 41–132, Academic Press, London, 1967.

²² R. H. HERBER (ed.), *Inorganic Isotopic Syntheses*, W. H. Benjamin, New York, 1962; Radio-chlorine (B. J. MASTERS), pp. 215–26; Iodine-131 (M. KAHN), pp. 227–42. See also G. ANGELINI, M. SEPERANZA, C.-Y. SHIUE and A. P. WOLF, *J. Chem. Soc., Chem. Commun.*, 924–5, (1986) for radio fluorine (¹⁸F).

Table 17.5 Some radioactive isotopes of the halogens

Isotope	Nuclear spin and parity	Half-life	Principal mode of decay (E/MeV)	Principal source
^{18}F	1+	109.77 min	β^+ (0.649)	$^{19}\text{F}(\text{n},2\text{n})$
^{36}Cl	2+	3.01×10^5 y	β^- (0.714)	$^{35}\text{Cl}(\text{n},\gamma)$
^{38}Cl	2-	37.24 min	β^- (4.81, 1.11, 2.77)	$^{37}\text{Cl}(\text{n},\gamma)$
$^{80\text{m}}\text{Br}$	5-	4.42 h	γ (internal trans) (0.086)	$^{79}\text{Br}(\text{n},\gamma)$
^{80}Br	1+	17.68 min	β^- (2.02, 1.35)	$^{80\text{m}}\text{Br}$ (IT)
^{82}Br	5-	35.30 h	β^- (0.44)	$^{81}\text{Br}(\text{n},\gamma)$
^{125}I	$\frac{5}{2}^+$	60.2 d	Electron capture (0.035)	$^{123}\text{Sb}(\alpha,2\text{n})$, $^{124}\text{Te}(\text{d},\text{n})$, or $^{125}\text{Xe}(\beta^-)$
^{128}I	1+	24.99 min	β^- (2.12, 1.66)	$^{127}\text{I}(\text{n},\gamma)$
^{129}I	$\frac{7}{2}^+$	1.57×10^7 y	β^- (0.189)	U fission
^{131}I	$\frac{7}{2}^+$	8.04 d	β^- (0.806)	$^{130}\text{Te}(\text{n},\gamma)$, U or Pu fission

of the use of radioactive isotopes of the halogens, including exchange reactions, tracer studies of other reactions, studies of diffusion phenomena, radiochemical methods of analysis, physiological and biochemical applications, and uses in technology and industry is available.⁽²³⁾ Excited states of ^{127}I and ^{129}I have also been used extensively in Mössbauer spectroscopy.⁽²⁴⁾

The nuclear spin of the stable isotopes of the halogens has been exploited in nmr spectroscopy. The use of ^{19}F in particular, with its 100% abundance, convenient spin of $\frac{1}{2}$ and excellent sensitivity, has resulted in a vast and continually expanding literature since ^{19}F chemical shifts were first observed in 1950.⁽²⁵⁾ The resonances for ^{35}Cl and ^{37}Cl were also first observed in 1950.⁽²⁶⁾ Appropriate nuclear parameters are in Table 17.6. From this it is clear that the ^{19}F resonance can be observed with high receptivity

at a frequency fairly close to that for ^1H . Furthermore, since $I < 1$ there is no nuclear quadrupole moment and hence no quadrupolar broadening of the resonance. The observed range of ^{19}F chemical shifts is more than an order of magnitude greater than for ^1H and spans more than 800 ppm of the resonance frequency.^(27,28) The signal moves to higher frequency with increasing electronegativity and oxidation state of the attached atom thus following the usual trends. Results are regularly reviewed.⁽²⁹⁾ For other halogens, as seen from Table 17.6, the nuclear spin I is greater than $\frac{1}{2}$ which means that the nuclear charge distribution is non-spherical; this results in a nuclear quadrupole moment, and resonance broadening due to quadrupolar relaxation severely restricts the use of the technique except for the halide ions X^- or for tetrahedral species such as ClO_4^- which have zero electric field gradient at the halogen nucleus. The receptivity is also much less

²³ A. J. DOWNS and C. J. ADAMS, in J. C. BAILAR, H. J. EMELÉUS, R. S. NYHOLM and A. F. TROTMAN-DICKENSON, *Comprehensive Inorganic Chemistry*, Vol. 2, pp. 1148-61 (Isotopes), Pergamon Press, Oxford, 1973.

²⁴ N. N. GREENWOOD and T. C. GIBB, *Mössbauer Spectroscopy*, pp. 462-82, Chapman & Hall, London, 1971. R. V. PARISH in G. J. LONG (ed.), *Mössbauer Spectroscopy Applied to Inorganic Chemistry*, Vol. 2, Chap. 9, 391-428 (1987). Plenum Press, New York.

²⁵ W. C. DICKENSON, *Phys. Rev.* **77**, 736-7 (1950). H. S. GUTOWSKY and C. J. HOFFMAN, *Phys. Rev.* **80**, 110-11 (1950).

²⁶ W. G. PROCTOR and F. C. YU, *Phys. Rev.* **77**, 716-7 (1950).

²⁷ J. W. EMSLEY, J. FEENEY and L. H. SUTCLIFFE, *High Resolution Nuclear Magnetic Resonance Spectroscopy*, Vols. 1 and 2, Pergamon Press, Oxford, 1966, Chap. 11, Fluorine-19, pp. 871-968.

²⁸ C. J. JAMESON in J. MASON (ed.) *Multinuclear NMR*, Plenum Press, New York, 1987. Fluorine, pp. 437-46. See also J. H. CLARK, E. M. GOODMAN, D. K. SMITH, S. J. BROWN and J. M. MILLER, *J. Chem. Soc., Chem. Commun.*, 657-8 (1986).

²⁹ *Annual Reports on NMR Spectroscopy*, Vol. 1 (1968)-Vol. 10b (1980) (Fluorine).

Table 17.6 Nuclear magnetic resonance parameters for the halogen isotopes

Isotope	Nuclear spin quantum no. I	NMR frequency rel to $^1\text{H}(\text{SiMe}_4)$ = 100.000	Relative receptivity $D_p^{(a)}$	Nuclear quadrupole moment $Q/(e \cdot 10^{-28} \text{ m}^2)$
^1H	1/2	100.000	1.000	0
^{19}F	1/2	94.094	0.8328	0
^{35}Cl	3/2	9.809	3.55×10^{-3}	-8.2×10^{-2}
^{37}Cl	3/2	8.165	6.44×10^{-4}	-6.5×10^{-2}
$(^{79}\text{Br})^{(b)}$	3/2	25.140	3.97×10^{-2}	0.33
^{81}Br	3/2	27.100	4.87×10^{-2}	0.27
^{127}I	5/2	20.146	9.34×10^{-2}	-0.79

^(a)Receptivity D is proportional to $\gamma^2 NI(I+1)$ where γ is the magnetogyric ratio, N the natural abundance of the isotope, and I the nuclear spin quantum number; D_p is the receptivity relative to that of the proton taken as 1.000.

^(b)Less-favourable isotope.

Table 17.7 Interatomic distances in crystalline halogens (pm)

X	X-X	X...X		Ratio
		Within layer	Between layers	
F	149	324	284	(1.91)
Cl	198	332, 382	374	1.68
Br	227	331, 379	399	1.46
I	272	350, 397	427	1.29

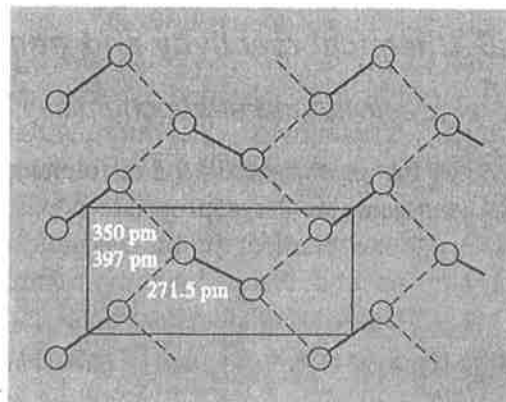
than for ^1H or ^{19}F which accordingly renders observation difficult. Despite these technical problems, much useful information has been obtained, especially in physicochemical and biological investigations.^(30,31) The quadrupole moments of Cl, Br and I have also been exploited successfully in nuclear quadrupole resonance studies of halogen-containing compounds in the solid state.⁽³²⁾

³⁰ B. LINDMAN and S. FORSEN, Chap. 13 in R. K. HARRIS and B. E. MANN (eds.), *NMR and the Periodic Table*, pp. 421-38, Academic Press, London, 1978. B. LINDMAN and S. FORSEN, Physicochemical and biological applications, Vol. 12 of P. DIEHL, E. FLUCK and R. KOSFELD (eds.), *NMR Basic Principles and Progress*, Springer-Verlag, Berlin, 1976, 365 pp.

³¹ J. W. AKITT, in ref. 28, The quadrupolar halides Cl, Br and I, pp. 447-61.

³² T. P. DAS and E. L. HAHN, *Nuclear Quadrupole Resonance Spectroscopy*, Academic Press, New York, 1958, 223 pp; E. A. C. LUCKEN, *Nuclear Quadrupole Coupling Constants*, Academic Press, London, 1969, 360 pp.

The molecular and bulk properties of the halogens, as distinct from their atomic and nuclear properties, were summarized in Table 17.4 and have to some extent already been briefly discussed. The high volatility and relatively low enthalpy of vaporization reflect the diatomic molecular structure of these elements. In the solid state the molecules align to give a layer lattice: F_2 has two modifications (a low-temperature, α -form and a higher-temperature, β -form) neither of which resembles the orthorhombic layer lattice of the isostructural Cl_2 , Br_2 and I_2 . The layer lattice is illustrated below for I_2 the I-I distance of 271.5 pm is appreciably longer than in gaseous I_2 (266.6 pm) and the closest interatomic approach between the molecules is 350 pm within the layer and 427 pm between layers (cf the van der Waals radius of 215 pm). These values are



compared with similar data for the other halogens in Table 17.7 from which two further features of interest emerge: (a) the intralayer intermolecular distances $\text{Cl}\cdots\text{Cl}$ and $\text{Br}\cdots\text{Br}$ are almost identical, and (b) the differences between intra- and inter-layer $\text{X}\cdots\text{X}$ distances decreases with increase in atomic number. (Fluorine is not directly comparable because of its differing structure.)

As expected from their structures, the elements are poor conductors of electricity: solid F_2 and Cl_2 have negligible conductivity and Br_2 has a value of $\sim 5 \times 10^{-13} \text{ ohm}^{-1} \text{ cm}^{-1}$ just below the mp. Iodine single crystals at room temperature have a conductivity of $5 \times 10^{-12} \text{ ohm}^{-1} \text{ cm}^{-1}$ perpendicular to the bc layer plane but this increases to $1.7 \times 10^{-8} \text{ ohm}^{-1} \text{ cm}^{-1}$ within this plane; indeed, the element is a two-dimensional semiconductor with a band gap $E_g \sim 1.3 \text{ eV}$ (125 kJ mol^{-1}). Even more remarkably, when crystals of iodine are compressed they become metallic, and at 350 kbar have a conductivity of $\sim 10^4 \text{ ohm}^{-1} \text{ cm}^{-1}$.⁽³³⁾ The metallic nature of the conductivity is confirmed by its negative temperature coefficient.

The ease of dissociation of the X_2 molecules follows closely the values of the enthalpy of dissociation since the entropy change for the reaction is almost independent of X . Thus F_2 at 1 atm pressure is 1% dissociated into atoms at 765°C but a temperature of 975°C is required to achieve the same degree of dissociation for Cl_2 ; thereafter, the required temperature drops to 775°C for Br_2 and 575°C for I_2 (see also next section for atomic halogens).

17.1.5 Chemical reactivity and trends

General reactivity and stereochemistry

Fluorine is the most reactive of all elements. It forms compounds, under appropriate conditions, with every other element in the periodic table except He, Ar and Ne, frequently combining

directly and with such vigour that the reaction becomes explosive. Some elements such as O_2 and N_2 react less readily with fluorine (pp. 639, 438) and some bulk metals (e.g. Al, Fe, Ni, Cu) acquire a protective fluoride coating, though all metals react exothermically when powdered and/or heated. For example, powdered Fe (0.84 mm size, 20 mesh) is not attacked by liquid F_2 whereas at 0.14 mm size (100 mesh) it ignites and burns violently. Perhaps the most striking example of the reactivity of F_2 is the ease with which it reacts directly with Xe under mild conditions to produce crystalline xenon fluorides (p. 894). This great reactivity of F_2 can be related to its small dissociation energy (p. 80) (which leads to low activation energies of reaction), and to the great strength of the bonds that fluorine forms with other elements. Both factors in turn can be related to the small size of the F atom and ensure that enthalpies of fluorination are much greater than those of other halogenations. Some typical average bond energies (kJ mol^{-1}) illustrating these points are:

X	XX	HX	BX_3	AlX_3	CX_4
F	159	574	645	582	456
Cl	243	428	444	427	327
Br	193	363	368	360	272
I	151	294	272	285	239

The tendency for F_2 to give F^- ions in solution is also much greater than for the other halogens as indicated by the steady decrease in oxidation potential (E°) for the reaction $\text{X}_2(\text{soln}) + 2\text{e}^- \rightleftharpoons 2\text{X}^-(\text{aq})$:

X_2	F_2	Cl_2	Br_2	I_2	At_2
E°/V	2.866	1.395	1.087	0.615	~ 0.3

The corresponding free energy changes can be calculated from the relation $\Delta G = -nE^\circ F$ where $n = 2$ and $F = 96.485 \text{ kJ mol}^{-1}$. Note that $E^\circ(\text{F}_2/2\text{F}^-)$ is greater than the decomposition potential for water (p. 629). Note also the different sequence of values for $E^\circ(\text{X}_2/2\text{X}^-)$ and for the electron affinities of $\text{X}(\text{g})$ (p. 800). A similar "anomaly" was observed (p. 75) for $E^\circ(\text{Li}^+/\text{Li})$ and the ionization energy of $\text{Li}(\text{g})$, and

³³ A. S. BALCHIN and H. G. DRICKAMER, *J. Chem. Phys.* **34**, 1948-9 (1961).

in both cases the reason is the same, namely the enhanced enthalpy of hydration of the smaller ions. Other redox properties of the halogens are compared on pp. 853–6.

It follows from the preceding paragraph that F_2 is an extremely strong oxidizing element that can engender unusually high oxidation states in the elements with which it reacts, e.g. IF_7 , PtF_6 , PuF_6 , BiF_5 , TbF_4 , CmF_4 , $KAg^{III}F_4$ and AgF_2 . Indeed, fluorine (like the other first-row elements Li, Be, B, C, N and O) is atypical of the elements in its group and for the same reasons. For all 7 elements deviations from extrapolated trends can be explained in terms of three factors:

- (1) their atoms are small;
- (2) their electrons are tightly held and not so readily ionized or distorted (polarized) as in later members of the group;
- (3) they have no low-lying d orbitals available for bonding.

Thus the ionization energy I_M is much greater for F than for the other halogens, thereby making formal positive oxidation states virtually impossible to attain. Accordingly, fluorine is exclusively univalent and its compounds are formed either by gain of 1 electron to give F^- ($2s^2 2p^6$) or by sharing 1 electron in a covalent single bond. Note, however, that the presence of lone-pairs permits both the fluoride ion itself and also certain molecular fluorides to act as Lewis bases in which the coordination number of F is greater than 1, e.g. it is 2 for the bridging F atoms in $As_2F_{11}^-$, $Sb_3F_{16}^-$, Nb_4F_{20} , $(HF)_n$ and $(BeF_2)_\infty$. The coordination number of F^- can rise to 3 (planar) in compounds with the rutile structure (e.g. MgF_2 , MnF_2 , FeF_2 , CoF_2 , NiF_2 , ZnF_2 and PdF_2). Likewise, fourfold coordination (tetrahedral) is found in the zinc-blende-type structure of CuF and in the fluorite structure of CaF_2 , SrF_2 , BaF_2 , RaF_2 , CdF_2 , HgF_2 and PbF_2 . A coordination number of 6 occurs in the alkali metal fluorides MF (NaCl type). In many of these compounds F^- resembles O^{2-} stereochemically rather than the other halides, and the radii of the 2 ions are very similar (F^- 133, O^{2-} 140 pm, cf. Cl^- 184, Br^- 196 pm).

The heavier halogens, though markedly less reactive than fluorine, are still amongst the most reactive of the elements. Their reactivity diminishes in the sequence $Cl_2 > Br_2 > I_2$. For example, Cl_2 reacts with CO, NO and SO_2 to give $COCl_2$, $NOCl$ and SO_2Cl_2 , whereas iodine does not react with these compounds. Again, in the direct halogenation of metals, Cl_2 and Br_2 sometimes produce a higher metal oxidation state than does I_2 , e.g. Re yields $ReCl_6$, $ReBr_5$ and ReI_4 respectively. Conversely, the decreasing ionization energies and increasing ease of oxidation of the elements results in the readier formation of iodine cations (p. 842) and compounds in which iodine has a higher stable oxidation state than the other halogens (e.g. IF_7). The general reactivity of the individual halogens with other elements (both metals and non-metals) is treated under the particular element concerned. Reaction between the halogens themselves is discussed on p. 824. In general, reaction of X_2 with compounds containing M–M, M–H or M–C bonds results in the formation of M–X bonds (M = metal or non-metal). Reaction with metal oxides sometimes requires the presence of C and the use of elevated temperatures.

The stereochemistry of the halogens in their various compounds is summarized in Table 17.8 and will be elucidated in more detail in subsequent sections.

Reactivity is enhanced in conditions which promote the generation of halogen atoms, though this does not imply that all reactions proceed via the intermediacy of X atoms. The reversible thermal dissociation of gaseous $I_2 \rightleftharpoons 2I$ was first demonstrated by Victor Meyer in 1880 and has since been observed for the other halogens as well (p. 804). Atomic Cl and Br are more conveniently produced by electric discharge though, curiously, this particularly method is not successful for I. Microwave and radiofrequency discharges have also been used as well as optical dissociation by ultraviolet light. At room temperature and at pressures below 1 mmHg, up to 40% atomization can be achieved, the mean lives of the Cl and Br atoms in glass apparatus being of the order of a few milliseconds. The

Table 17.8 Stereochemistry of the halogens

CN	Geometry	F	Cl	Br	I
0	—	F [•] (g), F ⁻ (soln)	Cl [•] (g), Cl ⁻ (soln)	Br [•] (g), Br ⁻ (soln)	I [•] (g), I ⁻ (soln)
1	—	F ₂ , ClF, BrF ₃ , BF ₃ , RF	Cl ₂ , ICl, BCl ₃ , RCl	Br ₂ , IBr, BBr ₃ , RBr	I ₂ , IX, PI ₃ , RI
2	Linear	NbF ₄ F ₂₀ NbF ₃ (ReO ₃ -type)	ClF ₂ ⁻ YCl ₃ (ReO ₃ -type)	Br ₃ ⁻ , (MeCN) ₂ Br ₂ CrBr ₃ (ReO ₃ -type)	I ₃ ⁻ , ICl ₂ ⁻ , BrICl ⁻ , Me ₃ Nl ₂ BiI ₃ (ReO ₃ -type)
	Bent	(BeF ₂) _α , (HF) _n , Sn ₄ F ₈	ClO ₂ , ClO ₂ ⁻ , Al ₂ Cl ₆ , [Nb ₆ Cl ₁₂] ²⁺ , ClF ₂ ⁺ BeCl ₂ (polym), PdCl ₂ ClO ₃ ⁻ , CdCl ₂ , [Mo ₆ Cl ₈] ⁴⁺ ClF ₃	BrF ₂ ⁺ , Al ₂ Br ₆ BrO ₃ ⁻ , MgBr ₂ BrF ₃	IR ₂ ⁺ , Al ₂ I ₆ , AuI(polymeric) HIO ₃ , IO ₃ ⁻ , CdI ₂ RlCl ₂
3	Trigonal pyramidal T-shaped Planar	MgF ₂ (rutile) CaF ₂ (fluorite) CuF (blende)	SrCl ₂ (fluorite), ClO ₄ ⁻ , FClO ₃ , CuCl	BrO ₄ ⁻ , FBrO ₃ , CuBr BrF ₄ ⁻	IO ₄ ⁻ CuI ICl ₄ ⁻ , I ₂ Cl ₆
4	Tetrahedral Square planar See-saw (C _{2v} , or C _s)		F ₃ ClO, [F ₂ ClO ₂] ⁻ F ₃ ClO ₂	F ₃ BrO, [F ₂ BrO ₂] ⁻ BrF ₅ , [F ₄ BrO] ⁻	[F ₂ IO ₂] ⁻ , IF ₄ ⁺ IF ₅ , [(F ₅ TeO) ₄ IO] ⁻ IO ₅ ³⁻ (?)
5	Square pyramidal Trigonal bipyramidal		ClF ₅ , [F ₄ ClO] ⁻ F ₃ ClO ₂	BrF ₅ , [F ₄ BrO] ⁻	
6	Octahedral	NaF	NaCl	NaBr BrF ₆ ⁻	IO ₆ ⁵⁻ , F ₅ IO, NaI, IF ₆ ⁺ IF ₆ ⁻ (?)
7	Distorted octahedral Pentagonal bipyramidal Hexagonal pyramidal		C ₆ H ₆ .Cl ₂	C ₆ H ₆ .Br ₂	IF ₇
8	Cubic Square antiprismatic		CsCl, TlCl	CsBr, TlBr	CsI, TlI, Zr(IO ₃) ₄

reason for the slow and relatively inefficient reversion to X₂ is the need for a 3-body collision in order to dissipate the energy of combination: X[•] + X[•] + M → X₂ + M^{*}. A fuller account of the production, detection and chemical reactions of atomic Cl, Br and I is on pages 1141–8 and 1165–72 of reference 23.

Solutions and charge-transfer complexes⁽³⁴⁾

The halogens are soluble to varying extents in numerous solvents though their great reactivity

sometimes results in solvolysis or in halogenation of the solvent. Reactions with water are discussed on pp. 855ff. Iodine is only slightly soluble in water (0.340 g/kg at 25°, 4.48 g/kg at 100°). It is more soluble in aqueous iodide solutions due to the formation of polyiodides (p. 835) and these can achieve astonishing concentrations; e.g. the solution in equilibrium with solid iodine and KI₇.H₂O at 25° contains 67.8 wt% of iodine, 25.6% KI and 6.6% H₂O. Iodine is also readily soluble in many organic solvents, typical values of its solubility at 25°C being (gI/kg solvent): Et₂O 337.3, EtOH 271.7, mesitylene 253.1, *p*-xylene 198.3, CS₂ 197.0, toluene 182.5, benzene 164.0, ethyl acetate 157, EtBr 146, EtCN 141,

³⁴ Ref. 23, pp. 1196–220.

$\text{C}_2\text{H}_4\text{Br}_2$ 115.1, Bu^iOH 97, CHBr_3 65.9, CHCl_3 49.7, cyclohexane 27.9, CCl_4 19.2, *n*-hexane 13.2, perfluoroheptane 0.12.

The most notable feature of such solutions is the dramatic dependence of their colour on the nature of the solvent chosen. Thus, solutions in aliphatic hydrocarbons or CCl_4 are bright violet (λ_{max} 520–540 nm), those in aromatic hydrocarbons are pink or reddish brown, and those in stronger donors such as alcohols, ethers or amines are deep brown (λ_{max} 460–480 nm). This variation can be understood in terms of a weak donor–acceptor interaction leading to complex formation between the solvent (donor) and I_2 (acceptor) which alters the optical transition energy. Thus, referring to the conventional molecular orbital energy diagram for I_2 (or other X_2) as shown in Fig. 17.2, the violet colour of I_2 vapour can be seen to arise as a result of the excitation of an electron from the highest occupied MO (the antibonding π_g level) into the lowest unoccupied MO (the antibonding σ_u level). In non-coordinating solvents such as aliphatic hydrocarbons or their fluoro- or chloro-derivatives the transition energy (and hence the colour) remains essentially unmodified.

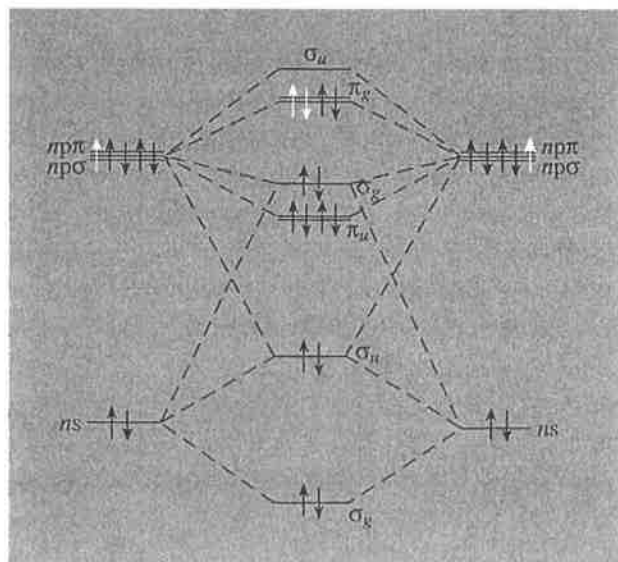
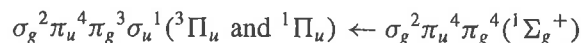


Figure 17.2 Schematic molecular orbital energy diagram for diatomic halogen molecules. (For F_2 the order of the upper σ_g and π_u bonding MOs is inverted.)

However, in electron-donor solvents, L, the vacant antibonding σ_u orbital of I_2 acts as an electron acceptor thus weakening the I–I bond and altering the energy of the electronic transitions:



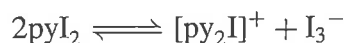
Consistent with this: (a) the solubility of iodine in the donor solvents tends to be greater than in the non-donor solvents (see list of solubilities), (b) brown solutions frequently turn violet on being heated, and brown again on cooling, due to the ready dissociation and reformation of the complex, and (c) addition of a small amount of a donor solvent to a violet solution turns the colour brown. Such donor solvents can be classified as (i) weak π donors (e.g. the aromatic hydrocarbons and alkenes), (ii) stronger σ donors such as nitrogen bases (amines, pyridines, nitriles), oxygen bases (alcohols, ethers, carbonyls), and organic sulfides and selenides.

The most direct evidence for the formation of a complex $\text{L} \rightarrow \text{I}_2$ in solution comes from the appearance of an intense new charge-transfer band in the near ultraviolet spectrum. Such a band occurs in the region 230–330 nm with a molar extinction coefficient ϵ of the order of $5 \times 10^3 - 5 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ and a half-width typically of 4000–8000 cm^{-1} . Detailed physico-chemical studies further establish that the formation constants of such complexes span the range $10^{-1} - 10^4 \text{ l mol}^{-1}$ with enthalpies of formation 5–50 kJ mol^{-1} . Some typical examples are in Table 17.9. The donor strength of the various solvents (ligands) is rather independent of the particular halogen (or interhalogen) solute and follows the approximate sequence benzene < alkenes < polyalkylbenzenes $\approx$ alkyl iodides $\approx$ alcohols $\approx$ ethers $\approx$ ketones < organic sulfides < organic selenides < amines. Conversely, for a given solvent the relative acceptor strength of the halogens increases in the sequence $\text{Cl}_2 < \text{Br}_2 < \text{I}_2 < \text{IBr} < \text{ICl}$, i.e. they are class b or “soft” acceptors (p. 909). Further interactions may also occur in polar solvents leading to ionic dissociation which

Table 17.9 Some iodine complexes in solution

Donor solvent	Formation constant $K(20^\circ\text{C})/\text{mol}^{-1}$	$-\Delta H_f/$ kJ mol^{-1}	Charge-transfer band		
			$\lambda_{\text{max}}/\text{nm}$	ϵ_{max}	$\Delta\nu_{1/2}/\text{cm}^{-1}$
Benzene	0.15	5.9	292	16 000	5100
Ethanol	0.26	18.8	230	12 700	6800
Diethyl ether	0.97	18.0	249	5 700	6900
Diethyl sulfide	210	32.7	302	29 800	5400
Methylamine	530	29.7	245	21 200	6400
Dimethylamine	6 800	41.0	256	26 800	6450
Trimethylamine	12 100	50.6	266	31 300	8100
Pyridine	269	32.6	235	50 000	5200

renders the solutions electrically conducting, e.g.:



Numerous solid complexes have been crystallized from brown solutions of iodine and extensive X-ray structural data are available. Complexes of the type $\text{L} \rightarrow \text{I}-\text{X}$ and $\text{L} \rightarrow \text{I}-\text{X} \leftarrow \text{L}$

($\text{L} = \text{Me}_3\text{N}$, py, etc.; $\text{X} = \text{I}$, Br, Cl, CN) feature a linear configuration as expected from the involvement of the σ_u antibonding orbital of IX (Fig. 17.3a, b, c). When the ligand has two donor atoms (as in dioxan) or the donor atom has more than one lone-pair of electrons (as in acetone) the complexes can associate

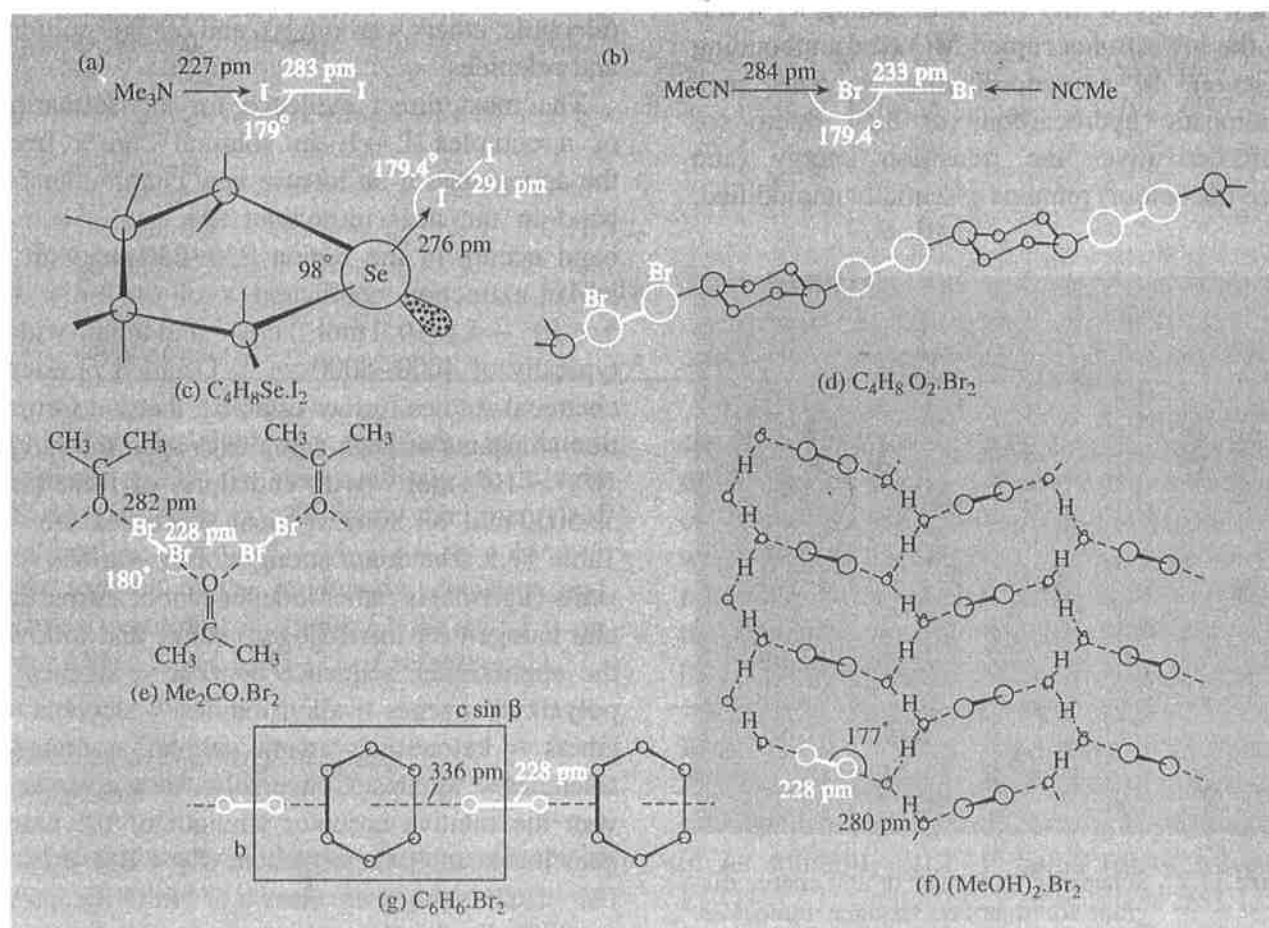


Figure 17.3 Structures of some molecular complexes of the halogens.

into infinite chains (Fig. 17.3d, e), whereas with methanol, the additional possibility of hydrogen bonding permits further association into layers (Fig. 17.3f). The structure of $C_6H_6.Br_2$ is also included in Fig. 17.3(g). In all these examples, the lengthening of the X-X bond from that in the free halogen molecule is notable.

The intense blue colour of starch-iodine was mentioned on p. 790.

17.2 Compounds of Fluorine, Chlorine, Bromine and Iodine

17.2.1 Hydrogen halides, HX

It is common practice to refer to the molecular species HX and also the pure (anhydrous) compounds as hydrogen halides, and to call their aqueous solutions hydrohalic acids. Both the anhydrous compounds and their aqueous solutions will be considered in this section. HCl and hydrochloric acid are major industrial chemicals and there is also a substantial production of HF and hydrofluoric acid. HBr and hydrobromic acid are made on a much smaller scale and there seems to be little industrial demand for HI and hydriodic acid. It will be convenient to discuss first the preparation and industrial uses of the compounds and then to consider their molecular and bulk physical properties. The chemical reactivity of the anhydrous compounds and their acidic aqueous solutions will then be reviewed, and the section concludes with a discussion of the anhydrous compounds as nonaqueous solvents.

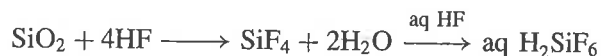
Preparation and uses

Anhydrous HF is almost invariably made by the action of conc H_2SO_4 ($\geq 95\%$) on "acid grade" fluorspar ($\geq 98\%$ CaF_2):



As the reaction is endothermic heat must be supplied to obtain good yields in reasonable

time (e.g. 30–60 min at 200–250°C). Silica is a particularly undesirable impurity in the fluorspar since it consumes up to 6 moles of HF per mole of SiO_2 by reacting to form SiF_4 and then H_2SiF_6 . A typical unit, producing up to 20 000 tonnes of HF pa, consists of an externally heated, horizontal steel kiln about 30 m long rotating at 1 revolution per minute. The product gas emerges at 100–150°C and, after appropriate treatment to remove solid, liquid and gaseous impurities, is condensed to give a 99% pure product which is then redistilled to give a final product of 99.9% purity. The technical requirements to enable the safe manufacture and handling of so corrosive a product are considerable.^(2,13) In principle, HF could also be obtained from the wet-processing of fluorapatite to give phosphoric acid (p. 521) but the presence of SiO_2 preferentially yields SiF_4 and H_2SiF_6 from which HF can only be recovered uneconomically.



Some of the H_2SiF_6 so produced finds commercial outlets (p. 810), but it has been estimated that ~500 000 tonnes of H_2SiF_6 is discarded annually by the US phosphoric acid industry, equivalent to ~1 million tonnes of fluorspar — enough to supply that nation's entire requirements for HF. Production figures and major uses are in the Panel.

Hydrogen chloride is a major industrial chemical and is manufactured on a huge scale. It is also a familiar laboratory reagent both as a gas and as an aqueous acid. The industrial production and uses of HCl are summarized in the Panel on p. 811. One important method for synthesis on a large scale is the burning of H_2 in Cl_2 : no catalyst is needed but economic sources of the two elements are obviously required. Another major source of HCl is as a by-product of the chlorination of hydrocarbons (p. 798). The traditional "salt-cake" process of treating NaCl with conc H_2SO_4 also remains an important industrial source of the acid. On a small laboratory scale, gaseous HCl can be made by treating concentrated aqueous hydrochloric acid

Production and Uses of Hydrogen Fluoride

Anhydrous HF was first produced commercially in the USA in 1931 and in the UK from about 1942. By 1992 some eighteen countries were each producing at least 3000 tonnes pa with North America accounting for some 330 000 tonnes of the estimated annual world production of about 875 000 tonnes. A further 205 000 tonnes was used captively for production of AlF_3 . Price in 1990 was about \$1.50/kg for the anhydrous acid and somewhat less for 70% acid. The primary suppliers ship HF in tank-cars of 20–91-tonne capacity and the product is also repackaged in steel cylinders holding 8.0–900 kg (2.7–635 kg in the UK). Lecture bottles contain 340 g HF. The 70% acid is shipped in tank-cars of 32–80-tonne capacity, tank trucks of 20-tonne capacity, and in polyethylene-lined drums holding 114 or 208 l.

The early need for HF was in the production of chlorofluorocarbons for refrigeration units and pressurizing gases. The large increase in aluminium production in 1935–40 brought an equivalent requirement for HF (for synthetic cryolite, p. 219) and these two uses still account for the bulk of HF produced in North America (comprising the single market of USA, Canada and Mexico), namely 53.0% and 24.3%, respectively. Other outlets are petroleum alkylation catalysts and steel pickling (3.8% each) and the nuclear industry (3.0%). The remaining 12.1% is distributed amongst traditional uses (such as glass etching and the frosting of light bulbs and television tubes, and the manufacture of fluoride salts), and newer applications such as rocket-propellant stabilizers, preparation of microelectronic circuits, laundry soaps and stain removers.

Probably about 50 000 tonnes of HF are used worldwide annually to make inorganic compounds other than UF_4/UF_6 for the nuclear industry. Prominent amongst these products are:

NaF : for water fluoridation, wood preservatives, the formulation of insecticides and fungicides, and use as a fluxing agent. It is also used to remove HF from gaseous F_2 in the manufacture and purification of F_2 .

SnF_2 : in toothpastes to prevent dental caries.

HBF_4 (aq) and metal fluoroborates: electroplating of metals, catalysts, fluxing in metal processing and surface treatment.

H_2SiF_6 and its salts: fluoridation of water, glass and ceramics manufacture, metal-ore treatment.

The highly corrosive nature of HF and aqueous hydrofluoric acid solutions have already been alluded to (pp. 792, 797) and great caution must be exercised in their handling. The salient feature of HF burns is the delayed onset of discomfort and the development of a characteristic white lesion that is excruciatingly painful. The progressive action of HF on skin is due to dehydration, low pH and the specific toxic effect of high concentrations of fluoride ions: these remove Ca^{2+} from tissues as insoluble CaF_2 and thereby delay healing; in addition the immobilization of Ca^{2+} results in a relative excess of K^+ within the tissue, so that nerve stimulation ensues. Treatment of HF burns involves copious sluicing with water for at least 15 min followed either by (a) immersion in (or application of wet packs of) cold MgSO_4 , or (b) subcutaneous injection of a 10% solution of calcium gluconate (which gives rapid relief from pain), or (c) surgical excision of the burn lesion.⁽⁴⁾ Medical attention is essential, even if the initial effects appear slight, because of the slow onset of the more serious symptoms.

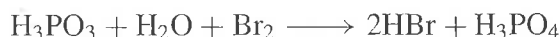
with conc H_2SO_4 . Preparation of DCl is best effected by the action of D_2O on PhCOCl or a similar organic acid chloride; PCl_3 , PCl_5 , SiCl_4 , AlCl_3 , etc., have also been used.

Similar routes are available for the production of HBr and HI . The catalysed combination of H_2 and Br_2 at elevated temperatures (200–400°C in the presence of Pt/asbestos, etc.) is the principal industrial route for HBr , and is also used, though on a relatively small scale, for the energetically less-favoured combination of H_2 and I_2 (Pt catalyst above 300°C). Commercially HI is more often prepared by the reaction of I_2 with H_2S or hydrazine, e.g.:

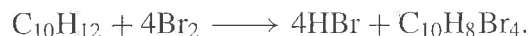


Reduction of the parent halogen with red phosphorus and water provides a convenient

laboratory preparation of both HBr and HI :



The rapid reaction of 1,2,3,4-tetrahydronaphthalene (tetralin) with Br_2 at 20° affords an alternative small-scale preparation though only half the Br_2 is converted, the other half being lost in brominating the tetralin:

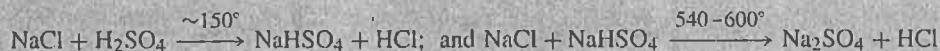


The action of conc H_2SO_4 on metal bromides or iodides (analogous to the “salt-cake” process of HCl) causes considerable oxidation of the product HX but conc H_3PO_4 is satisfactory. Dehydration of the aqueous acids with P_2O_5 is a viable alternative. DBr and DI are obtained by reaction of D_2O on PBr_3 and PI_3 respectively.

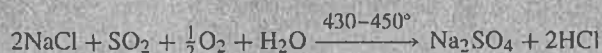
Industrial Production and Uses of Hydrogen Chloride⁽³⁵⁾

World production of HCl is of the order of 10 million tonnes pa, thus making it one of the largest volume chemicals to be manufactured. Four major processes account for the bulk of HCl produced, the choice of method invariably being dictated by the ready availability of the particular starting materials, the need for the co-products, or simply the availability of by-product HCl which can be recovered as part of an integrated process.

1. The classic salt-cake method was introduced with the Leblanc process towards the end of the eighteenth century and is still used to produce HCl where rock-salt mineral is cheaply available (as in the UK Cheshire deposits). The process is endothermic and takes place in two stages:



2. The Hargreaves process (late 19th C) is a variant of the salt-cake process in which NaCl is reacted with a gaseous mixture of SO₂, air and H₂O (i.e. "H₂SO₄") in a self-sustaining exothermic reaction:



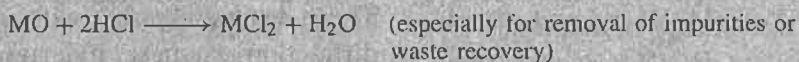
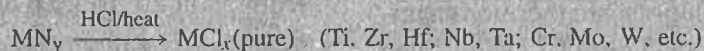
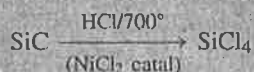
Again the economic operation of the process depends on abundant rock-salt or the need for the by-product Na₂SO₄ for the paper and glass industries.

3. Direct synthesis of HCl by the burning of hydrogen in chlorine is the favoured process when high-purity HCl is required. The reaction is highly exothermic (~92 kJ/mol HCl) and requires specially designed burners and absorption systems.

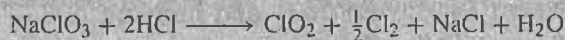
4. By-product HCl from the heavy organic-chemicals industry (p. 798) now accounts for over 90% of the HCl produced in the USA. Where such petrochemical industries are less extensive this source of HCl becomes correspondingly smaller. The crude HCl so produced may be contaminated with unreacted Cl₂, organics, chloro-organics or entrained solids (catalyst supports, etc.), all of which must be removed.

Most of the byproduct HCl is used captively, primarily in oxyhydrochlorination processes for making vinyl chloride and chlorinated solvents or for Mg processing (p. 110). The scale of the industry is enormous; for example, 5.2 million tonnes of HCl per annum in the US alone (1993). HCl gas for industrial use can be transmitted without difficulty over moderate distances in mild-steel piping or in tank cars or trailers. It is also available in cylinders of varying size down to laboratory scale lecture bottles containing 225 g. Aqueous hydrochloric acid consumption (1993) was 1.57 Mt (100% basis). Price for anhydrous HCl is ~\$330/tonne and for 31.4% aqueous acid ~\$73/tonne (1993) depending on plant location and amount required.

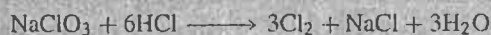
Industrial use of HCl gas for the manufacture of inorganic chemicals includes the preparation of anhydrous NH₄Cl by direct reaction with NH₃ and the synthesis of anhydrous metal chlorides by reaction with appropriate carbides, nitrides, oxides or even the free metals themselves, e.g.:



HCl is also used in the industrial synthesis of ClO₂ (p. 846):



The reaction is catalysed by various salts of Ti, Mn, Pd and Ag which promote the formation of ClO₂ rather than the competing reaction which otherwise occurs:



Panel continues

³⁵ Kirk-Othmer's *Encyclopedia of Chemical Technology*, 4th Edn., Vol. 13, pp. 894-925 (1995).

HCl is also used in the production of Al_2O_3 (p. 242) and TiO_2 (p. 959), the isolation of Mg from sea water (p. 110), and in many extractive metallurgical processes for isolating or refining metals, e.g. Ge, Sn, V, Mn, Ta, W and Ra.

Aqueous HCl is also produced on a vast scale (e.g. 1.57 Mt/yr in the USA, 1993). Most of this is made and consumed captively at the site of production, predominantly for brine acidification prior to electrolysis in Cl_2 /alkali cells. The largest merchant market use is for pickling steel and other metals to remove adhering oxide scale, and for the desulfurization of petroleum. It is also used in pH control (effluent neutralization, etc.), the desliming of hides and chrome tanning, ore beneficiation, the coagulation of latex and the production of aniline from PhNO_2 for dyestuffs intermediates. The manufacture of gelatine requires large quantities of hydrochloric acid to decompose the bones used as raw materials — high purity acid must be used since much of the gelatine is used in foodstuffs for human consumption. Another food-related application is the hydrolysis of starch to glucose under pressure: this process is catalysed by small concentrations of HCl and is extensively used to produce “maple syrup” from maize (corn) starch. At higher concentrations of HCl wood (lignin) can be converted to glucose.

Other uses of HCl are legion and range from the purification of fine silica for the ceramics industry, and the refining of oils, fats and waxes, to the manufacture of chloroprene rubbers, PVC plastics, industrial solvents and organic intermediates, the production of viscose rayon yarn and staple fibre, and the wet processing of textiles (where hydrochloric acid is used as a sour to neutralize residual alkali and remove metallic and other impurities).

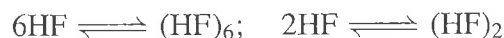
Anhydrous HBr is available in cylinders (6.8-kg and 68-kg capacity) under its own vapour pressure (24 atm at 25°C) and in lecture bottles (450-g capacity). Its main industrial use is in the manufacture of inorganic bromides and the synthesis of alkyl bromides either from alcohols or by direct addition to alkenes. HBr also catalyses numerous organic reactions. Aqueous HBr (48% and 62%) is available as a corrosive pale-yellow liquid in drums or in large tank trailers (15 000 l and 38 000 l).

There seem to be no large-scale uses for HI outside the laboratory, where it is used in various iodination reactions (lecture bottles containing 400 g HI are available). Commercial solutions contain 40–55 wt% of HI (cf. azeotrope at 56.9% HI, p. 815) and these solutions are thermodynamically much more stable than pure HI as indicated by the large negative free energy of solution.

Physical properties of the hydrogen halides

HF is a colourless volatile liquid and an oligomeric H-bonded gas $(\text{HF})_x$, whereas the heavier HX are colourless diatomic gases at room temperature. Some molecular and bulk physical properties are summarized in Table 17.10. The influence of H bonding on the (low) vapour pressure, (long) liquid range and (high) dielectric constant of HF have already been discussed

(pp. 53–5). Note also that the viscosity of liquid HF is lower than that of water (or indeed of the other HX) and this has been taken to imply the absence of a three-dimensional network of H bonds such as occurs in H_2O , H_2SO_4 , H_3PO_4 , etc. However, it should be remembered that the viscosity of HF is quoted for 0°C , i.e. some 80° above its mp and only 20° below its bp; a more relevant comparison might be its value of 0.772 centipoise at -62.5° (i.e. 19° above its mp) compared with a value of 1.00 centipoise for water at 20° . Hydrogen bonding is also responsible for the association of HF molecules in the vapour phase: the vapour density of the gas over liquid HF reaches a maximum value of ~ 86 at -34° . At atmospheric pressure the value drops from 58 at 25° to 20.6 at 80° (the limiting vapour density of monomeric HF is $\frac{20.0063}{2.0159} = 9.924$). These results, together with infrared and electron diffraction studies, indicate that gaseous HF comprises an equilibrium mixture of monomers and cyclic hexamers, though chain dimers may also occur under some conditions of temperature and pressure:



The crystal structure of HF shows it to consist of planar zigzag chain polymers with an F–H...F distance of 249 pm and an angle at F of 120.1° .

The other HX are not associated in the gaseous or liquid phases but the low-temperature forms of crystalline HCl and HBr both feature weakly

Table 17.10 Physical properties of the hydrogen halides

Property	HF	HCl	HBr	HI
MP/°C	-83.5	-114.2	-88.6	-51.0
BP/°C	19.5 ^(a)	-85.1	-67.1	-35.1
Liquid range (1 atm)/°C	103.0	29.1	21.5	15.9
Density(T°C)/g cm ⁻³	1.002(0°) ^(b)	1.187(-114°)	2.603(-84°)	2.85(-47°)
Viscosity(T°C)/centipoise	0.256(0°)	0.51(-95°)	0.83(-67°)	1.35(-35.4°)
Dielectric constant, ϵ	83.6(0°) ^(c)	9.28(-95°)	7.0(-85°)	3.39(-50°)
Electrical conductivity (T°C)/ohm ⁻¹ cm ⁻¹	$\sim 10^{-6}$ (0°)	$\sim 10^{-9}$ (-85°)	$\sim 10^{-9}$ (-85°)	$\sim 10^{-10}$ (-50°)
$\Delta H_f^\circ(298^\circ)/\text{kJ mol}^{-1}$	-271.12	-92.31	-36.40	26.48
$\Delta G_f^\circ(298^\circ)/\text{kJ mol}^{-1}$	-273.22	-95.30	-53.45	1.72
$S^\circ(298^\circ)/\text{J mol}^{-1}\text{K}^{-1}$	173.67	186.80	198.59	206.48
$\Delta H_{\text{dissoc}}(\text{H-X})/\text{kJ mol}^{-1}$	573.98	431.62	362.50	294.58
$r_e(\text{H-X})/\text{pm}$	91.7	127.4	141.4	160.9
Vibrational frequency ω_e/cm^{-1}	4138.33	2990.94(H ³⁵ Cl) 2988.48(H ³⁷ Cl)	2649.65	2309.53
Dipole moment μ/D	1.86	1.11	0.788	0.382

(a) Vapour pressure of HF 363.8 mmHg (48.50 kPa) at 0°.

(b) Density of liquid HF 1.23 g cm⁻³ near melting point. (c) Dielectric constant $\epsilon(\text{HF})$ 175 at -73°C.

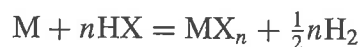
H-bonded zigzag chains similar to those in solid HF. At higher temperatures substantial disorder sets in.

The standard heats of formation ΔH_f° of gaseous HX diminish rapidly with increase in molecular weight and HI is endothermic. The very small (and positive) value for the standard free energy of formation ΔG_f° of HI indicates that (under equilibrium conditions) this species is substantially dissociated at room temperature and pressure. However, dissociation is slow in the absence of a catalyst. The bond dissociation energies of HX show a similar trend from the very large value of 574 kJ mol⁻¹ for HF to little more than half this (295 kJ mol⁻¹) for HI.

Chemical reactivity of the hydrogen halides

Anhydrous HX are versatile and vigorous reagents for the halogenation of metals, non-metals, hydrides, oxides and many other classes of compound, though reactions that are thermodynamically permissible do not always occur in the absence of catalysts, thermal initiation or photolytic encouragement, because

of kinetic factors. For example,⁽³⁶⁾ reaction of HX(g) with elements (M) can thermodynamically proceed according to the equation



providing that ΔG for the reaction [i.e. $\Delta G_f^\circ(\text{MX}_n) - n\Delta G_f^\circ(\text{HX}, \text{g})$] is negative. From the data in Table 17.10 this means that M could be oxidized to the n -valent halide MX_n if:

for the fluoride $\Delta G_f^\circ(\text{MF}_n)$ is $< -274n$ kJ mol⁻¹

for the chloride $\Delta G_f^\circ(\text{MCl}_n)$ is $< -96n$ kJ mol⁻¹

for the bromide $\Delta G_f^\circ(\text{MBr}_n)$ is $< -54n$ kJ mol⁻¹

for the iodide $\Delta G_f^\circ(\text{MI}_n)$ is $< \sim 0$ kJ mol⁻¹

Using tables of free energies of formation it is clear that most metals will react with most HX. Moreover, in many cases, e.g. with the alkali metals, alkaline earth metals, Zn, Al and the lanthanide elements, such reactions are extremely exothermic. It is also clear that Ag should react with HCl, HBr and HI but not with HF, and

³⁶ T. C. WADDINGTON, in V. GUTMANN (ed.), *Main Group Elements: Group VII and Noble Gases*, MTP International Review of Science: Inorganic Chemistry Series 1, Vol. 3, pp. 85-125, Butterworths, London, 1972.

Cu should form CuF_2 with HF but not CuX_2 with the other HX. Iron should give FeCl_3 but in practice the reaction only proceeds to FeCl_2 . TiX_4 can be made, but only at high temperatures. Reactions of Si to form SiX_4 are very favourable for $\text{X} = \text{F}, \text{Cl}, \text{Br}$, but only HF reacts at room temperature. With As, reaction with HF to give AsF_3 is thermodynamically favourable but reactions with the other HX are not. Similar, though more complicated, schemes can be worked out for the reactions of HX with oxides, other halides, hydrides, etc.

HF is miscible with water in all proportions and the phase diagram (Fig. 17.4a) shows the presence of three compounds: $\text{H}_2\text{O} \cdot \text{HF}$ (mp -35.5°), $\text{H}_2\text{O} \cdot 2\text{HF}$ (mp -75.5°) and $\text{H}_2\text{O} \cdot 4\text{HF}$ (mp -100.4° , i.e. 17° below the mp of pure HF). Recent X-ray studies have confirmed earlier conjectures that these compounds are best formulated as H-bonded oxonium salts $[\text{H}_3\text{O}]\text{F}$, $[\text{H}_3\text{O}][\text{HF}_2]$, and $[\text{H}_3\text{O}][\text{H}_3\text{F}_4]$ with three very strong H bonds per oxonium ion and average $\text{O} \cdots \text{F}$ distances of 246.7, 250.2

and 253.6 pm respectively.⁽³⁷⁾ More recently, the low-temperature crystal structure of $\text{Me}_4\text{NF} \cdot 5\text{HF}$ (decomp. -76°C) has revealed the presence of H_5F_6^- , i.e. $[(\text{FH})_2\text{FHF}(\text{HF})_2]^-$, with four terminal $\text{F}-\text{H} \cdots \text{F}$ of 248.4 pm and a very strong central $\text{F}-\text{H} \cdots \text{F}$ of 226.6 pm. $\text{Me}_4\text{NF} \cdot 7\text{HF}$ was also identified (decomp. -110°C).⁽³⁸⁾ Another significant crystal structure, that of tris(ethylenediamine)zinc(II) fluoride dihydrate reveals the strongly H-bonded difluoride cluster $[\text{F}_2(\text{H}_2\text{O})_2]^{2-}$ which adopts a diamond-shaped cyclic structure $\text{F} \cdots \text{HOH} \cdots \text{F} \cdots \text{HOH} \cdots$ with $\text{O}-\text{H} \cdots \text{F}$ distances of 258.6 and 267.9 pm and non-bonded distances across the lozenge of $\text{O} \cdots \text{O}$ 335 pm and $\text{F} \cdots \text{F}$ 406 pm.⁽³⁹⁾ Such H bonds are very relevant to the otherwise surprising observation that, unlike

³⁷ D. MOOTZ, *Angew. Chem. Int. Edn. Engl.* **20**, 791 (1981). See also J. EMSLEY and D. A. JOHNSON, *Polyhedron* **5**, 1109-10 (1986).

³⁸ D. MOOTZ and D. BOENIGK, *Z. anorg. allg. Chem.* **544**, 159-66 (1987).

³⁹ J. EMSLEY, M. ARIF, P. A. BATES and M. B. HURSTHOUSE, *J. Chem. Soc., Chem. Commun.*, 738-9 (1989).

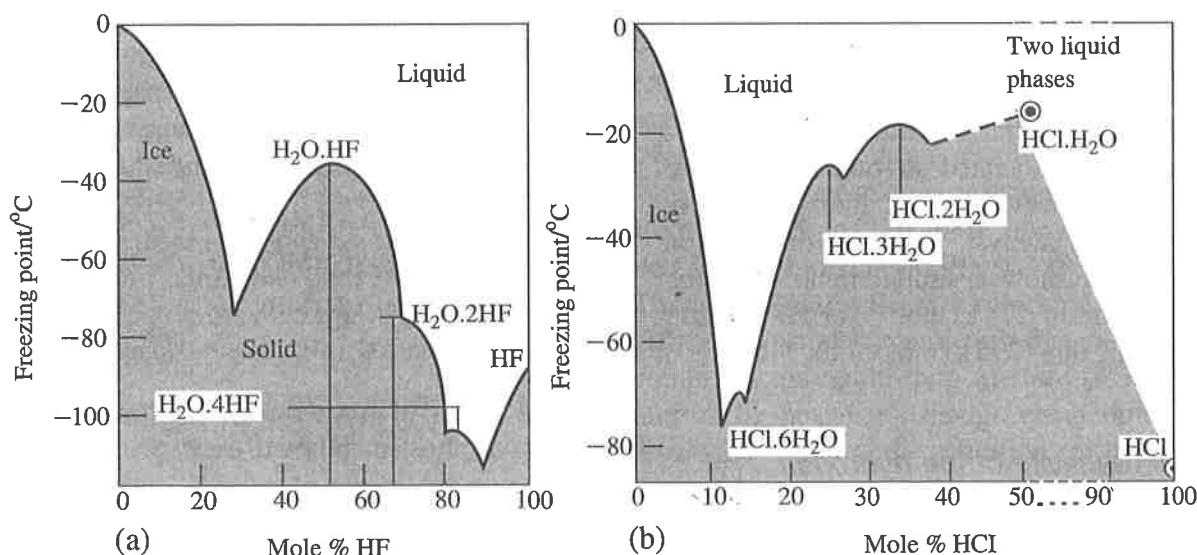
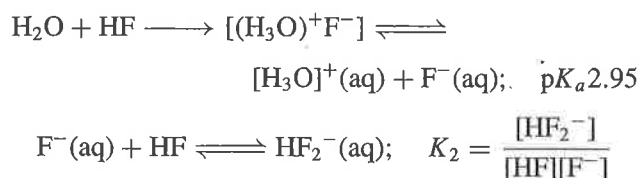


Figure 17.4 The phase diagrams of the systems (a) HF/ H_2O and (b) HCl/ H_2O . Note that for hydrofluoric acid all the solvates contain $\geq 1\text{HF}$ per H_2O , whereas for hydrochloric acid they contain $\leq 1\text{HCl}$ per H_2O . This is because the H bonds $\text{F}-\text{H} \cdots \text{F}$ and $\text{F}-\text{H} \cdots \text{O}$ are *stronger* than $\text{O}-\text{H} \cdots \text{O}$, whereas $\text{Cl}-\text{H} \cdots \text{Cl}$ and $\text{Cl}-\text{H} \cdots \text{O}$ are *weaker* than $\text{O}-\text{H} \cdots \text{O}$. Accordingly the solvates in the former system have the crystal structures $[\text{H}_3\text{O}]^+\text{F}^-$, $[\text{H}_3\text{O}]^+[\text{HF}_2]^-$ and $[\text{H}_3\text{O}]^+[\text{H}_3\text{F}_4]^-$, whereas the latter are $[\text{H}_3\text{O}]^+\text{Cl}^-$, $[\text{H}_5\text{O}_2]^+\text{Cl}^-$ and $[\text{H}_5\text{O}_2]^+\text{Cl}^- \cdot \text{H}_2\text{O}$. The structures of $\text{HCl} \cdot 6\text{H}_2\text{O}$ and the metastable $\text{HCl} \cdot 4\text{H}_2\text{O}$ are not known.

the other aqueous hydrohalic acids which are extremely strong, hydrofluoric acid is a very weak acid in aqueous solution. Indeed, the behaviour of such solutions is remarkable in showing a dissociation constant (as calculated from electrical conductivity measurements) that *diminishes* continuously on dilution. Detailed studies reveal the presence of two predominant equilibria:⁽⁴⁰⁾



The dissociation constant for the first process is only $1.1 \times 10^{-3} \text{ l mol}^{-1}$ at 25°C ; this corresponds to $\text{p}K_a$ 2.95 and indicates a rather small free hydrogen-ion concentration (cf. $\text{ClCH}_2\text{CO}_2\text{H}$, $\text{p}K_a$ 2.85) as a result of the strongly H-bonded, undissociated ion-pair $[(\text{H}_3\text{O})^+\text{F}^-]$. By contrast, $K_2 = 2.6 \times 10^{-1} \text{ l mol}^{-1}$ ($\text{p}K_2$ 0.58), indicating that an appreciable number of the fluoride ions in the solution are coordinated by HF to give HF_2^- rather than by H_2O despite the very much higher concentration of H_2O molecules.

Numerous hydrates also occur in the $\text{HCl}/\text{H}_2\text{O}$ system (Fig. 17.4b), e.g. $\text{HCl} \cdot \text{H}_2\text{O}$ (mp -15.4°), $\text{HCl} \cdot 2\text{H}_2\text{O}$ (mp -17.7°), $\text{HCl} \cdot 3\text{H}_2\text{O}$ (mp -24.9°), $\text{HCl} \cdot 4\text{H}_2\text{O}$ and $\text{HCl} \cdot 6\text{H}_2\text{O}$ (mp -70°). The system differs from $\text{HF}/\text{H}_2\text{O}$ not only in the stoichiometry of the hydrates but also in separating into two liquid phases at HCl concentrations higher than 1:1. The weakness of the $\text{O}-\text{H} \cdots \text{Cl}$ hydrogen bond also ensures that there is very little impediment to complete ionic dissociation, and aqueous solutions of HCl (and also of HBr and HI) are strong acids; approximate values of $\text{p}K_a$ are HCl -7 , HBr -9 , HI -10 . The systems $\text{HBr}/\text{H}_2\text{O}$ and $\text{HI}/\text{H}_2\text{O}$ also show a miscibility gap at high concentrations of HX and also numerous hydrates which feature hydrated oxonium ions:

$\text{HBr} \cdot \text{H}_2\text{O}$: stable under pressure between -3.3° and -15.5° ; $[(\text{H}_3\text{O})^+\text{Br}^-]$
 $\text{HBr} \cdot 2\text{H}_2\text{O}$: mp -11.3° ; presumably $[\text{H}_5\text{O}_2]^+\text{Br}^-$, i.e. $[(\text{H}_2\text{O})_2\text{H}]^+\text{Br}^-$
 $\text{HBr} \cdot 3\text{H}_2\text{O}$: decomp -47.9° ; structure unknown
 $\text{HBr} \cdot 4\text{H}_2\text{O}$: mp -55.8° ; $\{[(\text{H}_2\text{O})_3\text{H}]^+ - [(\text{H}_2\text{O})_4\text{H}]^+(\text{Br}^-)_2 \cdot \text{H}_2\text{O}\}$ (p. 631)
 $\text{HBr} \cdot 6\text{H}_2\text{O}$: decomposes at -88.2°

The compound $\text{HI} \cdot \text{H}_2\text{O}$ does not appear as a stable hydrate in the phase diagram, but the vibrational spectra of frozen solutions of this composition indicate the formulation $[(\text{H}_3\text{O})^+\text{I}^-]$. Higher hydrates appear at $\text{HI} \cdot 2\text{H}_2\text{O}$ (mp $\sim -43^\circ$), $\text{HI} \cdot 3\text{H}_2\text{O}$ (mp $\sim -48^\circ$), and $\text{HI} \cdot 4\text{H}_2\text{O}$ (mp -36.5°C).

Just as the solid/liquid phase equilibria in the systems $\text{HX}/\text{H}_2\text{O}$ show several points of interest, so too do the liquid/gas phase equilibria. When dilute aqueous solutions of HX are heated to boiling the concentration of HX in the vapour is less than that in the liquid phase, so that the liquid becomes progressively more concentrated and the bp progressively rises until a point is reached at which the liquid has the same composition as the gas phase so that it boils without change in composition and at constant temperature. This mixture is called an azeotrope (Greek α , without; $\xi\epsilon\iota\eta$, *zein*, to boil; $\tau\rho\omicron\pi\eta$, *trope*, change). The phenomenon is illustrated for HF and HCl in Fig. 17.5. Conversely, when more concentrated aqueous solutions are boiled, the concentration of HX in the vapour is greater than that in the liquid phase which thereby becomes progressively diluted by distillation until the azeotropic mixture is again reached, whereupon distillation continues without change of composition and at constant temperature. The bps and azeotropic compositions at atmospheric pressure are listed below, together with the densities of the azeotropic acids at 25°C :

Azeotrope	HF	HCl	HBr	HI
BP (1 atm)/ $^\circ\text{C}$	112	108.58	124.3	126.7
$g(\text{HX})/100 \text{ g soln}$	38	20.22	47.63	56.7
Density(25°)/ g cm^{-3}	1.138	1.096	1.482	1.708

⁴⁰ L. G. SILLÉN and A. E. MARTELL, *Stability Constants of Metal-Ion Complexes*, Special Publication No. 17, pp. 256-7, The Chemical Society, London, 1964; *Supplement No. 1* (Special Publication No. 17), pp. 152-3 (1971). See also P. McTIGUE, T. A. O'DONNELL and B. VERITT, *Aust. J. Chem.* **38**, 1797-807 (1985).

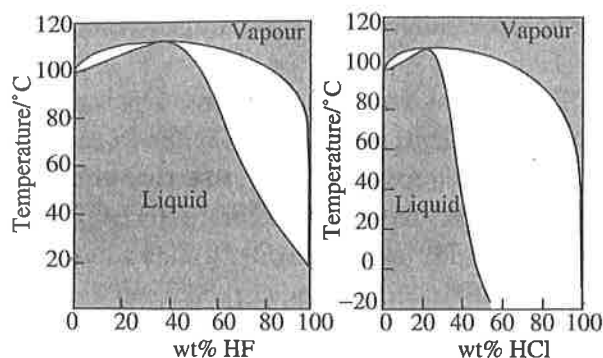


Figure 17.5 Liquid/gas phase equilibria for the systems HF/H₂O and HCl/H₂O showing the formation of maximum boiling azeotropes as described in the text.

Of course, the bp and composition of the azeotrope both vary with pressure, as illustrated below for the case of hydrochloric acid (1 mmHg = 0.1333 kPa):

<i>P</i> /mmHg	50	250	500	700
BP/°C	48.72	81.21	97.58	106.42
g(HX)/100 g soln	23.42	21.88	20.92	20.36
Density(25°)/g cm ⁻³	1.112	1.104	1.099	1.097

<i>P</i> /mmHg	760	800	1000	1200
BP/°C	108.58	110.01	116.19	122.98
g(HX)/100 g soln	20.222	20.16	19.73	19.36
Density(25°)/g cm ⁻³	1.0959	1.095 ₅	1.093	1.091 ₅

The occurrence of such azeotropes clearly restricts the degree to which aqueous solutions of HX can be concentrated by evaporation. However, they do afford a ready means of obtaining solutions of precisely known concentration: in the case of hydrochloric acid, its azeotrope is particularly stable over long periods of time and has found much use in analytical chemistry.

The hydrogen halides as nonaqueous solvents

The great synthetic value of liquid NH₃ as a nonaqueous solvent (p. 424) has encouraged the extensive study of the other neighbour of H₂O in the periodic table, namely, HF.^(36,41–44) Early studies were hampered by the aggressive nature of anhydrous HF towards glass and quartz,

but the pure acid can now be safely handled without contamination using fluorinated plastics such as polytetrafluoroethylene. The self-ionic dissociation of the solvent, as evidenced by the residual electrical conductivity of highly purified HF, can be represented as $\text{HF} \rightleftharpoons \text{H}^+ + \text{F}^-$; however, since both ions will be solvated it is more usual to represent the equilibrium as



The fluoride ion has an anomalously high conductance, λ_∞ , as shown by the following values obtained at 0°:

Ion	Na ⁺	K ⁺	H ₂ F ⁺	BF ₄ ⁻	SbF ₆ ⁻	HF ₂ ⁻
$\lambda_\infty/\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$	117	117	79	183	196	273

As the specific conductivity of pure HF is $\sim 10^{-6}\text{ ohm}^{-1}\text{cm}^2$ at 0°, these values imply concentrations of $\text{H}_2\text{F}^+ = \text{HF}_2^- \simeq 2.9 \times 10^{-6}\text{ mol l}^{-1}$ and an ionic product for the liquid of $\sim 8 \times 10^{-12}\text{ mol}^2\text{ l}^{-1}$ (cf. values of $\sim 10^{-33}$ for NH₃ and $\sim 10^{-14}$ for H₂O).

The high dielectric constant, low viscosity and long liquid range of HF make it an excellent solvent for a wide variety of compounds. Whilst most inorganic fluorides give fluoride ions when dissolved (see next paragraph), a few solutes dissolve without ionization, e.g. XeF₂, SO₂, HSO₃F, SF₆ and MF₆ (M = Mo, W, U, Re and Os). It is also probable that VF₅ and ReF₇ dissolve without ionizing. Perhaps more surprisingly liquid HF is now extensively used in biochemical research: carbohydrates, amino acids and proteins dissolve readily, frequently with only minor chemical consequences. In particular, complex organic compounds that are potentially

⁴¹ H. H. HYMAN and J. J. KATZ, Chap. 2 in T. C. WADDINGTON (ed.), *Nonaqueous Solvent Systems*, pp. 47–81, Academic Press, London, 1965.

⁴² M. KILPATRICK and J. G. JONES, Chap. 2 in J. J. LAGOWSKI (ed.), *The Chemistry of Nonaqueous Solvents*, pp. 43–99, Vol. 2, Academic Press, New York, 1967.

⁴³ T. A. O'DONNELL, Chap. 25 in *Comprehensive Inorganic Chemistry*, Vol. 2, pp. 1009–106, Pergamon Press, Oxford, 1973.

⁴⁴ R. J. GILLESPIE and J. LIANG, *J. Am. Chem. Soc.* **110**, 6053–7 (1988).

capable of eliminating the elements of water (e.g. cellulose, sugar esters, etc.) often dissolve without dehydration. Likewise globular proteins and many fibrous proteins that are insoluble in water, such as silk fibroin. These solutions are remarkably stable: e.g. the hormones insulin and ACTH were recovered after 2 h in HF at 0° with their biological activity substantially intact.

Many of the ionic fluorides of M^I , M^{II} and M^{III} dissolve to give highly conducting solutions due to ready dissociation. Some typical values of the solubility of fluorides in HF are in Table 17.11: the data show the expected trend towards greater solubility with increase in ionic radius within the alkali metals and alkaline earth metals, and the expected decrease in solubility with increase in ionic charge so that $MF > MF_2 > MF_3$. This is dramatically illustrated by AgF which is 155 times more soluble than AgF₂ and TlF which is over 7000 times more soluble than TlF₃.

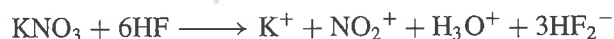
With inorganic solutes other than fluorides, solvolysis usually occurs. Thus chlorides, bromides and iodides give the corresponding fluorides with evolution of HX, and fluorides are also formed from oxides, hydroxides, carbonates and sulfites. Indeed, this is an excellent synthetic route for the preparation of anhydrous metal fluorides and has been used with good effect for TiF₄, ZrF₄, UF₄, SnF₄, VOF₃, VF₃, NbF₅, TaF₅, SbF₅, MoO₂F₂, etc. (Note, however, that AgCl, PdCl₂, PtCl₄, Au₂Cl₆ and ICl are apparently exceptions.⁴²) Less-extensive solvolysis occurs with sulfates, phosphates and certain other oxoanions. For example, a careful cryoscopic study of

solutions of K₂SO₄ in HF (at ~ -84°C) gave a value of $\nu = 5$ for the number of solute species in solution, but this increased to about 6 when determined by vapour-pressure depressions at 0°. These observations can be rationalized if unionized H₂SO₄ is formed at the lower temperature and if solvolysis of this species to unionized HSO₃F sets in at the higher temperatures:



Consistent with this, the ¹⁹F nmr spectra of solutions at 0° showed the presence of HSO₃F, and separate cryoscopic experiments with pure H₂SO₄ as the sole solute gave a value of ν close to unity.

Solvolysis of phosphoric acids in the system HF/P₂O₅/H₂O gave successively H₂PO₃F, HPO₂F₂ and H₃O⁺PF₆⁻, as shown by ¹⁹F and ³¹P nmr spectroscopy. Raman studies show that KNO₃ solvolyses according to the reaction



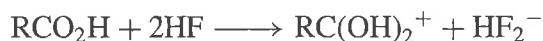
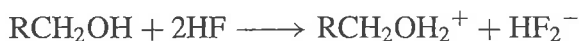
Permanganates and chromates are solvolysed by HF to oxide fluorides such as MnO₃F and CrO₂F₂.

Acid-base reactions in anhydrous HF are well documented. Within the Brønsted formalism, few if any acids would be expected to be sufficiently strong proton donors to be able to protonate the very strong proton-donor HF (p. 51), and this is borne out by observation. Conversely, HF can protonate many Brønsted bases, notably water,

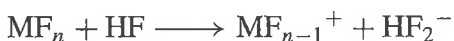
Table 17.11 Solubility of some metal fluorides in anhydrous HF (in g/100 g HF and at 12°C unless otherwise stated)

LiF 10.3	NaF(11°) 30.1	NH ₄ F(17°) 32.6	KF(8°) 36.5	RbF(20°) 110	CsF(10°) 199	AgF 83.2	TlF 580
Hg ₂ F ₂ 0.87	BeF ₂ (11°) 0.015	MgF ₂ 0.025	CaF ₂ 0.817	SrF ₂ 14.83	BaF ₂ 5.60	AgF₂ 0.54	CaF ₂ 0.010
HgF ₂ 0.54	CdF ₂ (14°) 0.201	ZnF ₂ (14°) 0.024	CrF ₂ (14°) 0.036	FeF ₂ 0.006	NiF ₂ 0.037	PbF ₂ 2.62	
AlF ₃ 0.002	CeF ₃ 0.043	TlF₃ 0.081	MnF ₃ 0.164	FeF ₃ 0.008	CoF ₃ 0.257	SbF ₃ 0.536	BrF ₃ 0.010

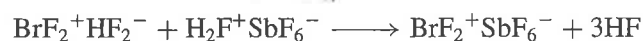
alcohols, carboxylic acids and other organic compounds having one or more lone-pairs on O, N, etc.:



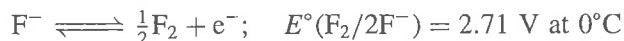
Alternatively, within the Lewis formalism, acids are fluoride-ion acceptors. The prime examples are AsF_5 and SbF_5 (which give MF_6^-) and to a lesser extent BF_3 which yields BF_4^- . A greater diversity is found amongst Lewis bases (fluoride-ion donors), typical examples being XeF_6 , SF_4 , ClF_3 and BrF_3 :



Such solutions can frequently be "neutralized" by titration with an appropriate Lewis acid, e.g.:



Oxidation-reduction reactions in HF form a particularly important group of reactions with considerable industrial application. The standard electrode potentials $E^\circ(\text{M}^{n+}/\text{M})$ in HF follow the same sequence as for H_2O though individual values in the two series may differ by up to ± 0.2 V. Early examples showed that CrF_2 and UF_4 reduced HF to H_2 whereas VCl_2 gave VF_3 , 2HCl and H_2 . Of more significance is the very high potential needed for the anodic oxidation of F^- in HF:



This enables a wide variety of inorganic and organic fluorinations to be effected by the electrochemical insertion of fluorine. For example, the production of NFH_2 , NF_2H and NF_3 by electrolysis of NH_4F in liquid HF represents the only convenient route to these compounds. Again, $\text{CF}_3\text{CO}_2\text{H}$ is most readily obtained by electrolysis of $\text{CH}_3\text{CO}_2\text{H}$ in HF. Other examples of anodic oxidations in HF are as follows:

Reactant	Products	Reactant	Products
NH_4F	NF_3 , NF_2H , NFH_2	NMe_3	$(\text{CF}_3)_3\text{N}$
H_2O	OF_2	$(\text{MeCO})_2\text{O}$	CF_3COF
$\text{SbCl}_2, \text{SF}_4$	SF_6	$\text{SMe}_2, \text{CS}_2$	CF_3SF_5 , $(\text{CF}_3)_2\text{SF}_4$
NaClO_4	ClO_3F	MeCN	CF_3CN , $\text{C}_2\text{F}_5\text{NF}_2$

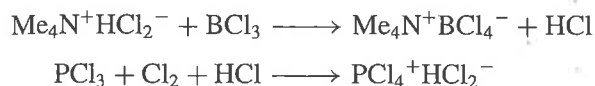
The other hydrogen halides are less tractable as solvents, as might be expected from their physical properties (p. 813), especially their low bps, short liquid ranges, low dielectric constants and negligible self-dissociation into ions. Nevertheless, they have received some attention, both for comparison with HF and as preparative media with their own special advantages.^(36,45,46) In particular, because of their low bp and consequent ease of removal, the liquid HX solvent systems have provided convenient routes to BX_4^- , BF_3Cl^- , $\text{B}_2\text{Cl}_6^{2-}$, NO_2Cl , Al_2Cl_7^- , R_2SCl^+ , RSCl_2^+ , PCl_3Br^+ , $\text{Ni}_2\text{Cl}_4(\text{CO})_3$ (from nickel tetracarbonyl and Cl_2) and $\text{Ni}(\text{NO})_2\text{Cl}_2$ (from nickel tetracarbonyl and NOCl). Solubilities in liquid HX are generally much smaller than in HF and tend to be restricted to molecular compounds (e.g. NOCl , PhOH , etc.) or salts with small lattice energies, e.g. the tetraalkylammonium halides. Concentrations rarely attain 0.5 mol l^{-1} (i.e. $0.05 \text{ mol/100 g HF}$). Ready protonation of compounds containing lone-pairs or π bonds is observed, e.g. amines, phosphines, ethers, sulfides, aromatic olefins, and compounds containing $-\text{C}\equiv\text{N}$, $-\text{N}=\text{N}-$, $>\text{C}=\text{O}$, $>\text{P}=\text{O}$ etc. Of particular interest is the protonation of phosphine in the presence of BX_3 to give $\text{PH}_4^+\text{BCl}_4^-$, $\text{PH}_4^+\text{BF}_3\text{Cl}^-$, and $\text{PH}_4^+\text{BBr}_4^-$. $\text{Fe}(\text{CO})_5$ affords $[\text{Fe}(\text{CO})_5\text{H}]^+$ and $[\text{Fe}(\eta^5-\text{C}_5\text{H}_5)(\text{CO})_2]_2$ yields $[\text{Fe}(\eta^5-\text{C}_5\text{H}_5)(\text{CO})_2]_2\text{H}^+$. Solvolysis is also well established:



⁴⁵ M. E. PEACH and T. C. WADDINGTON, Chap. 3 in T. C. WADDINGTON (ed.), *Nonaqueous Solvent Systems*, pp. 83–115, Academic Press, London, 1965.

⁴⁶ F. KLANBERG, Chap. 1 in J. J. LAGOWSKI (ed.), *The Chemistry of Nonaqueous Solvents*, Vol. 2, pp. 1–41, Academic Press, New York, 1967.

Likewise ligand replacement reactions and oxidations, e.g.:



The preparation and structural characterization of the ions HX_2^- has been an important feature of such work.⁽³⁶⁾ As expected, these H-bonded ions are much less stable than HF_2^- though crystalline salts of all three anions and of the mixed anions HXY^- (except HBrI^-) have been isolated by use of large counter cations, typically Cs^+ and NR_4^+ ($\text{R} = \text{Me}, \text{Et}, \text{Bu}^n$) — see pp. 1313–21, of ref. 23 for further details. Neutron and X-ray diffraction studies suggest that $[\text{Cl}-\text{H}\cdots\text{Cl}]^-$ can be either centrosymmetric or non-centrosymmetric depending on the crystalline environment. An example of the latter mode involves interatomic distances of 145 and 178 pm respectively and a bond angle of $\sim 168^\circ$ ($\text{Cl}\cdots\text{Cl}$ 321.2 pm).⁽⁴⁷⁾

17.2.2 Halides of the elements

The binary halides of the elements span a wide range of stoichiometries, structure types and properties which defy any but the most grossly oversimplified attempt at a unified classification. Indeed, interest in the halides as a class of compound derives in no small measure from this very diversity and from the fact that, being so numerous, there are many examples of well-developed and well-graded trends between the limiting cases. Thus the fluorides alone include OF_2 , one of the most volatile molecular compounds known (bp -145°), and CaF_2 , which is one of the least-volatile “ionic” compounds (bp 2513°C). Between these extremes of discrete molecules on the one hand, and 3D lattices on the other, is a continuous sequence of oligomers, polymers and extended layer lattices which may be either predominantly covalent [e.g. ClF , $(\text{MoF}_5)_4$, $(\text{CF}_2)_\infty$, $(\text{CF})_\infty$,

p. 289] or substantially ionic [e.g. $\text{Na}^+\text{F}^-(\text{g})$, $(\text{SnF}_2)_4$, $(\text{BeF}_2)_\infty$ (quartz type), SnF_4 , NaF (cryst)], or intermediate in bond type with secondary interactions also complicating the picture. The problems of classifying binary compounds according to presumed bond types or limiting structural characteristics have already been alluded to for the hydrides (p. 64), borides (p. 145), oxides, sulfides, etc. Such diversity and gradations are further compounded by the existence of four different halogens (F, Cl, Br, I) and by the possibility of numerous oxidation states of the element being considered, e.g. CrF_2 , Cr_2F_5 , CrF_3 , CrF_4 , CrF_5 and CrF_6 , or S_2F_2 , SF_2 , SF_4 , S_2F_{10} and SF_6 .

A detailed discussion of individual halides is given under the chemistry of each particular element. This section deals with more general aspects of the halides as a class of compound and will consider, in turn, general preparative routes, structure and bonding. For reasons outlined on p. 805, fluorides tend to differ from the other halides either in their method of synthesis, their structure or their bond-type. For example, the fluoride ion is the smallest and least polarizable of all anions and fluorides frequently adopt 3D “ionic” structures typical of oxides. By contrast, chlorides, bromides and iodides are larger and more polarizable and frequently adopt mutually similar layer-lattices or chain structures (cf. sulfides). Numerous examples of this dichotomy can be found in other chapters and in several general references.^(48–52) Because of this it is convenient to discuss fluorides as a group first, and then the other halides.

⁴⁸ V. GUTMANN (ed.), *Halogen Chemistry*, Academic Press, London, 1967; Vol. 1. 473 pp.; Vol. 2, 481 pp.; Vol. 3, 471 pp.

⁴⁹ R. COLTON and J. H. CANTERFORD, *Halides of the First Row Transition Elements*, Wiley, London, 1969, 579 pp.; *Halides of the Second and Third Row Transition Elements*, Wiley, London, 1968, 409 pp.

⁵⁰ Ref. 43, pp. 1062–1106; ref. 23, pp. 1232–80.

⁵¹ A. F. WELLS, *Structural Inorganic Chemistry*, 5th edn. pp. 407–44, Oxford University Press, Oxford, 1984.

⁵² B. MÜLLER, *Angew. Chem. Int. Edn. Engl.* **26**, 1081–97 (1987).

⁴⁷ W. KUCHEN, D. MOOTZ, H. SOMBERG, H. WUNDERLICH and H.-G. WUSSOW, *Angew. Chem. Int. Edn. Engl.* **17**, 869–70 (1978).

Fluorides

Binary fluorides are known with stoichiometries that span the range from C_4F to IF_7 (or even, possibly, XeF_8). Methods of synthesis turn on the properties of the desired products.^(50,53-57)

If hydrolysis poses no problem, fluorides can be prepared by halide metathesis in aqueous solution or by the reactions of aqueous hydrofluoric acid with an appropriate oxide, hydroxide, carbonate, or the metal itself. The following non-hydrated fluorides precipitate as easily filterable solids: LiF , NaF , NH_4F ; MgF_2 , CaF_2 , SrF_2 , BaF_2 ; SnF_2 , PbF_2 ; SbF_3 . Gaseous SiF_4 and GeF_4 can also be prepared from aqueous HF . Furthermore, the following fluorides separate as hydrates that can readily be dehydrated thermally, though an atmosphere of HF is required to suppress hydrolysis except in the case of the univalent metal fluorides:

$KF \cdot 2H_2O$	$CuF_2 \cdot 4H_2O$	$AlF_3 \cdot H_2O$
$RbF \cdot 3H_2O$	$ZnF_2 \cdot 4H_2O$	$GaF_3 \cdot 3H_2O$
$CsF \cdot 1\frac{1}{2}H_2O$	$CdF_2 \cdot 4H_2O$	$InF_3 \cdot 3H_2O$
$TiF_2 \cdot 2HF \cdot \frac{1}{2}H_2O$	$HgF_2 \cdot 2H_2O$	$LnF_3 \cdot xH_2O$
$AgF \cdot 4H_2O$	$MF_2 \cdot 6H_2O$	($Ln = \text{lanthanide metal}$)
	($M = Fe, Co, Ni$)	

By contrast $BeF_2 \cdot xH_2O$, $TiF_4 \cdot 2H_2O$ and $ThF_4 \cdot 4H_2O$ cannot be dehydrated without hydrolysis.

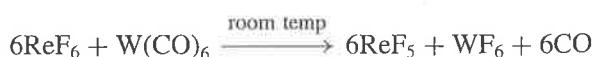
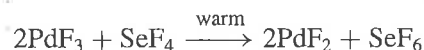
When hydrolysis is a problem then the action anhydrous HF on the metal (or chloride) may prove successful (e.g. the difluorides of Zn , Cd , Ge , Sn , Mn , Fe , Co , Ni ; the trifluorides of Ga , In , Ti and the lanthanides; the tetrafluorides of

Ti , Zr , Hf , Th , U ; and the pentafluorides of Nb and Ta). However, many higher fluorides require the use of a more aggressive fluorinating agent or even F_2 itself. Typical of the fluorides prepared by oxidative fluorination with F_2 are:

difluorides:	Ag, Xe
trifluorides:	Cl, Br, Mn, Co
tetrafluorides:	$Sn, Pb, Kr, Xe, Mo, Mn, Ce, Am, Cm$
pentafluorides:	$As, Sb, Bi, Br, I, V, Nb, Ta, Mo$
hexafluorides:	$S, Se, Te, Xe, Mo, W, Tc, Ru, Os, Rh, Ir, Pt, U, Np, Pu$
heptafluorides:	I, Re
octafluorides:	$Xe(?)$

Wherever possible the use of elementary F_2 is avoided because of its cost and the difficulty of handling it; instead one of a graded series of halogen fluorides can often be used, the fluorinating power steadily diminishing in the sequence: $ClF_3 > BrF_5 > IF_7 > ClF > BrF_3 > IF_5$. Other "hard" oxidizing fluorinating agents are AgF_2 , CoF_3 , MnF_3 , PbF_4 , CeF_4 , BiF_5 and UF_6 . When selective fluorination of certain groups in organic compounds is required, then "moderate" fluorinating agents are employed, e.g. HgF_2 , SbF_5 , $SbF_3/SbCl_5$, AsF_3 , CaF_2 or KSO_2F . Such nucleophilic reagents may replace other halogens in halohydrocarbons by F but rarely substitute F for H . An electrophilic variant is ClO_3F . Most recently XeF_2 , which is available commercially, has been used to effect fluorinations via radical cations: it can oxidatively fluorinate CC double bonds and can replace either aliphatic or aromatic H atoms with F . Even gentler are the "soft" fluorinating agents which do not cause fragmentation of functional groups, do not saturate double bonds, and do not oxidize metals to their highest oxidation states; typical of such mild fluorinating agents are the monofluorides of H , Li , Na , K , Rb , Cs , Ag and Tl and compounds such as SF_4 , SeF_4 , COF_2 , SiF_4 and Na_2SiF_6 .

The fluorination reactions considered so far can be categorized as metathesis, oxidation or substitution. Occasionally reductive fluorination is the preferred route to a lower fluoride. Examples are:



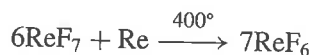
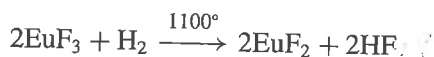
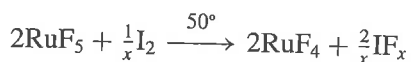
⁵³ E. L. MUETTERTIES and C. W. TULLOCK, Chap. 7 in W. L. JOLLY (ed.), *Preparative Inorganic Reactions*, Vol. 2, pp. 237-99 (1965). R. J. LAGOW and L. J. MARGRAVE, *Prog. Inorg. Chem.* **26**, 161-210 (1979). M. R. C. GERSTENBERGER and A. HAAS, *Angew. Chem. Int. Edn. Engl.* **20**, 647-67 (1981).

⁵⁴ J. PORTIER, *Angew. Chem. Int. Edn. Engl.* **15**, 475-86 (1976).

⁵⁵ R. D. PEACOCK, *Adv. Fluorine Chem.* **7**, 113-45 (1973).

⁵⁶ B. ZEMVA, K. LUTAR, A. JESIH, W. J. CASTEEL and N. BARTLETT, *J. Chem. Soc., Chem. Commun.*, 346-7 (1989).

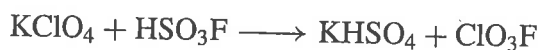
⁵⁷ G. A. OLAH, G. K. S. PRAKASH and R. D. CHAMBERS (eds.), *Synthetic Fluorine Chemistry*, Wiley, Chichester, 1992, 416 pp.



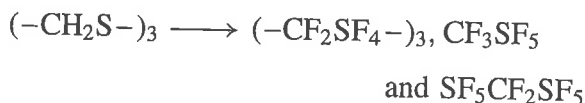
Further examples of this last type of reductive fluorination in which the element itself is used to reduce its higher fluoride are:

Product	ClF	CrF ₂	GeF ₂	
Reactants	Cl ₂ /ClF ₃	Cr/CrF ₃	Ge/GeF ₄	
T/°C	350	1000	300	
Product	MoF ₃	UF ₃	IrF ₄	TeF ₄
Reactants	Mo/MoF ₅	U/UF ₄	Ir/IrF ₆	Te/TeF ₆
T/°C	400	1050	170	180

The final route to fluorine compounds is electrofluorination (anodic fluorination) usually in anhydrous or aqueous HF. The preparation of NF_xH_{3-x} (x = 1, 2, 3) has already been described (p. 818). Likewise a reliable route to OF₂ is the electrolysis of 80% HF in the presence of dissolved MF (p. 638). Perchloryl fluoride has been made by electrolysis of NaClO₄ in HF but a simpler route (p. 879) is the direct reaction of a perchlorate with fluorosulfuric acid:



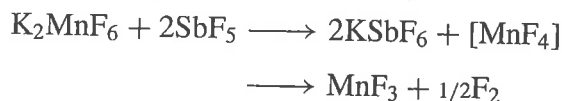
Electrolysis of organic sulfides in HF affords a variety of fluorocarbon derivatives:



where R_f is a perfluoroalkyl group.

The application of the foregoing routes has led to the preparation and characterization of fluorides of virtually every element in the periodic table except the three lightest noble gases, He, Ne and Ar. The structures, bonding, reactivity, and industrial applications of these compounds will be found in the treatment of the individual elements and it is an instructive exercise to gather this information together in the form of comparative tables. (2,50,53-62)

One important postscript can be added — the achievement by K. O. Christe in 1986 of synthesizing fluorine itself by chemical means alone, a goal that had eluded chemists for at least 173 years.⁽⁶³⁾ In this context, the term *chemical synthesis* excludes techniques such as electrolysis, photolysis, discharge, etc., or the use of F₂ in the synthesis of any of the starting materials. It is well known that high oxidation states can often be stabilized by complex-ion formation. Christe's ingenious strategy was to treat just such a complex fluoride with a strong fluoride-ion acceptor, thus liberating the unstable metal fluoride which then spontaneously decomposed to a lower oxidation state with the liberation of F₂. He chose to use K₂MnF₆ and SbF₅, both of which can be readily prepared from HF solutions without the use of F₂ itself:



The reaction was carried out in a passivated Teflon-stainless steel reactor at 150°C for 1 hour, and the yield was >40%. Fluorine pressures of more than 1 atm were generated in this way.

Chlorides, bromides and iodides

A similar set of preparative routes is available as were outlined above for the fluorides, though the range of applicability of each method and the products obtained sometimes vary from halogen to halogen. When hydrolysis is not a problem

⁵⁸ A. J. EDWARDS, *Adv. Inorg. Chem. Radiochem.* **27**, 83-112 (1983).

⁵⁹ P. HAGENMÜLLER (ed.), *Inorganic Solid Fluorides*, Academic Press, N.Y., 1985, 628 pp.

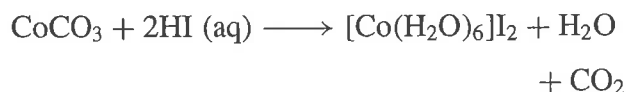
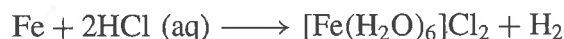
⁶⁰ J. F. LIEBMAN, A. GREENBERG and W. R. DOLBIER (eds.), *Fluorine-containing Molecules: Structure, Reactivity, Synthesis and Applications*, VCH Publishers, N.Y. 1988, 350 pp.

⁶¹ A. E. COMYNS (ed.), *Fluoride Glasses*, Wiley, Chichester, 1989, 219 pp.

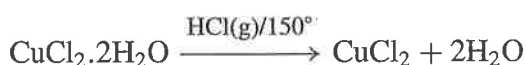
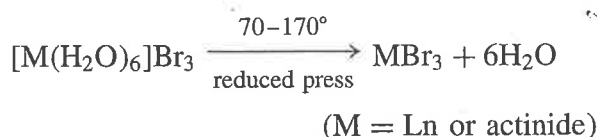
⁶² J. S. THRASHER and S. H. STRAUSS (eds.) *Inorganic Fluorine Chemistry Towards the 21st Century*, ACS Symposium Series **555**, 1994, 437 pp.

⁶³ K. O. CHRISTE, *Inorg. Chem.* **25**, 3721-2 (1986). See also *C & E News*, March 2, pp. 4-5 (1987) for discussion of the implications.

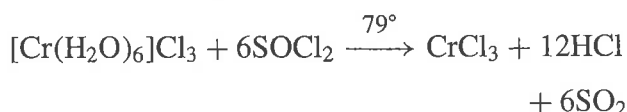
or when hydrated halides are sought, then wet methods are available, e.g. dissolution of a metal or its oxide, hydroxide or carbonate in aqueous hydrohalic acid followed by evaporative crystallization:



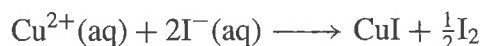
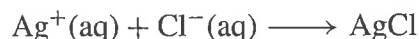
Dehydration can sometimes be effected by controlled removal of water using a judicious combination of gentle warming and either reduced pressure or the presence of anhydrous HX:



Hydrated chlorides that are susceptible to hydrolysis above room temperature can often be dehydrated by treating them with SOCl_2 under reflux:



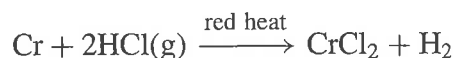
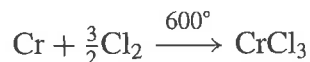
Alternative wet routes to hydrolytically stable halides are metathetical precipitation and reductive precipitation reactions, e.g.:



More complex is the hydrolytic disproportionation of the molecular halogens themselves in aqueous alkali which is a commercial route to several alkali-metal halides:

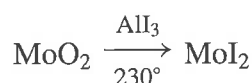
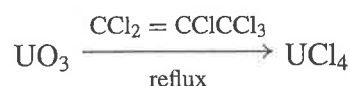
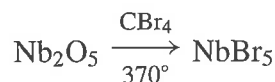
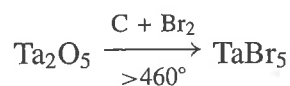
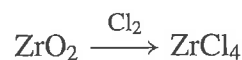


When the desired halide is hydrolytically unstable then dry methods must be used, often at elevated temperatures. Pre-eminent amongst these methods is the oxidative halogenation of metals (or non-metals) with X_2 or HX; when more than one oxidation state is available X_2 sometimes gives the higher and HX the lower, e.g.:

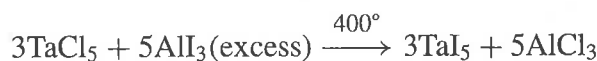
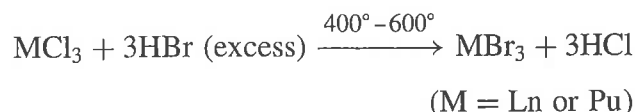
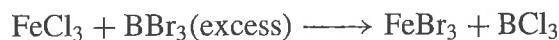


Similarly, Cl_2 sometimes yields a higher and Br_2 a lower oxidation state, e.g. MoCl_5 and MoBr_3 .

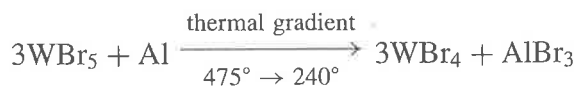
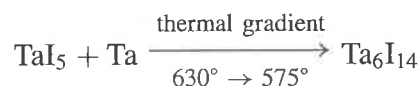
Other routes include the high-temperature halogenation of metal oxides, sometimes in the presence of carbon, to assist removal of oxygen; the source of halogen can be X_2 , a volatile metal halide CX_4 or another organic halide. A few examples of the many reactions that have been used industrially or for laboratory scale preparations are:



The last two of these reactions also feature a reduction in oxidation state. A closely related route is halogen exchange usually in the presence of an excess of the "halogenating reagent", e.g.:



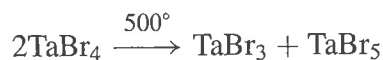
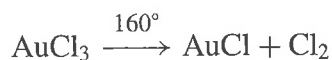
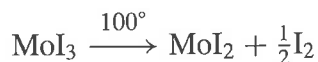
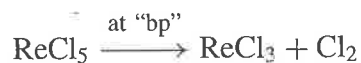
Reductive halogenation can be achieved by reducing a higher halide with the parent metal, another metal or hydrogen:





(M = Sm, Eu, Yb, etc., X = Cl, Br, I)

Alternatively, thermal decomposition or disproportionation can yield the lower halide:



Many significant trends are apparent in the structures of the halides and in their physical and chemical properties. The nature of the element concerned, its position in the periodic table, the particular oxidation state, and, of course, the particular halogen involved, all play a role. The majority of pre-transition metals (Groups 1, 2) together with Group 3, the lanthanides and the actinides in the +2 and +3 oxidation states form halides that are predominantly ionic in character, whereas the non-metals and metals in higher oxidation states ($\geq +3$) tend to form covalent molecular halides. The "ionic-covalent transition" in the halides of Group 15 (P, As, Sb, Bi) and 16 (S, Se, Te, Po) has already been discussed at length (pp. 495, 558, 772) as has the tendency of the refractory transition metals to form cluster halides (pp. 991, 1021, etc.). The problems associated with the ionic bond model and its range of validity were considered in Chapter 4 (p. 79). Presumed bond types tend to show gradual rather than abrupt changes within series in which the central element, the oxidation state or the halogen are systematically varied. For example, in a sequence of chlorides of isoelectronic metals such as KCl, CaCl_2 , ScCl_3 and TiCl_4 the first member is predominantly ionic with a 3D lattice of octahedrally coordinated potassium ions; CaCl_2 has a framework structure (distorted rutile) in which Ca is surrounded by a distorted octahedron of 6Cl; ScCl_3 has a layer structure and TiCl_4 is a covalent molecular liquid.

The sudden discontinuity in physical properties at TiCl_4 is more a function of stoichiometry and coordination number than a sign of any discontinuous or catastrophic change in bond type. Numerous other examples can be found amongst the transition metal halides and the halides of the post-transition elements. In general, the greater the difference in electronegativity between the element and the halogen the greater will be the tendency to charge separation and the more satisfactory will be the ionic bond model. With increasing formal charge on the central atom or with decreasing electronegativity difference the more satisfactory will be the various covalent bond models. The complexities of the situation can be illustrated by reference to the bp (and mp) of the halides: for the more ionic halides these generally follow the sequence $\text{MF}_n > \text{MCl}_n > \text{MBr}_n > \text{MI}_n$, being dominated by coulombic interactions which are greatest for the small F^- and least for the large I^- , whereas for molecular halides the sequence is usually the reverse, viz. $\text{MI}_n > \text{MBr}_n > \text{MCl}_n > \text{MF}_n$ being dictated rather by polarizability and London dispersion forces which are greatest for I and least for F. As expected, intermediate halides are less regular as the first sequence yields to the reverse, and no general pattern can be discerned. Physical techniques such as $^{35,37}\text{Cl}$ nmr spectroscopy and nuclear quadrupole resonance spectroscopy are being increasingly used to probe such trends.⁽⁶⁴⁾

Similar observations hold for solubility. Predominantly ionic halides tend to dissolve in polar, coordinating solvents of high dielectric constant, the precise solubility being dictated by the balance between lattice energies and solvation energies of the ions, on the one hand, and on entropy changes involved in dissolution of the crystal lattice, solvation of the ions and modification of the solvent structure, on the other: $[\Delta G(\text{cryst} \rightarrow \text{saturated soln}) = 0 = \Delta H - T\Delta S]$. For a given cation (e.g. K^+ , Ca^{2+}) solubility in water typically follows the sequence

⁶⁴ T. L. WEEDING and W. S. VEEMAN, *J. Chem. Soc., Chem. Commun.*, 946-8 (1989).

$MF_n < MCl_n < MBr_n < MI_n$. By contrast for less-ionic halides with significant non-coulombic lattice forces (e.g. Ag) solubility in water follows the reverse sequence $MI_n < MBr_n < MCl_n < MF_n$. For molecular halides solubility is determined principally by weak intermolecular van der Waals' and dipolar forces, and dissolution is commonly favoured by less-polar solvents such as benzene, CCl_4 or CS_2 .

Trends in chemical reactivity are also apparent, e.g. ease of hydrolysis tends to increase from the non-hydrolysing predominantly ionic halides, through the intermediate halides to the readily hydrolysable molecular halides. Reactivity depends both on the relative energies of $M-X$ and $M-O$ bonds and also, frequently, on kinetic factors which may hinder or even prevent the occurrence of thermodynamically favourable reactions. Further trends become apparent within the various groups of halides and are discussed at appropriate points throughout the text.

17.2.3 Interhalogen compounds⁽⁶⁵⁻⁶⁷⁾

The halogens combine exothermically with each other to form interhalogen compounds of four stoichiometries: XY , XY_3 , XY_5 and XY_7 where X is the heavier halogen. A few ternary compounds are also known, e.g. $IFCl_2$ and IF_2Cl . For the hexatomic series, only the fluorides are known (ClF_5 , BrF_5 , IF_5), and IF_7 is the sole example of the octatomic series. All the interhalogen compounds are diamagnetic and contain an even number of halogen atoms. Similarly, the closely related polyhalide anions XY_{2n}^- and polyhalonium cations XY_{2n}^+ ($n = 1, 2, 3$) each have an odd

number of halogen atoms: these ions will be considered in subsequent sections (pp. 835, 839).

Related to the interhalogens chemically, are compounds formed between a halogen atom and a pseudohalogen group such as CN , SCN , N_3 . Examples are the linear molecules $ClCN$, $BrCN$, ICN and the corresponding compounds $XSCN$ and XN_3 . Some of these compounds have already been discussed (p. 319) and need not be considered further. A microwave study⁽⁶⁸⁾ shows that chlorine thiocyanate is $CISCN$ (angle $Cl-S-C$ 99.8°) rather than $CINCS$, in contrast to the cyanate which is $CINCO$. The corresponding fluoro compound, $FNCO$, can be synthesized by several low-temperature routes but is not stable at room temperature and rapidly dimerizes to $F_2NC(O)NCO$.⁽⁶⁹⁾ The chemistry of iodine azide has been reviewed⁽⁷⁰⁾ — it is obtained as volatile, golden yellow, shock-sensitive needles by reaction of I_2 with AgN_3 in non-oxygen-containing solvents such as CH_2Cl_2 , CCl_4 or benzene: the structure in the gas phase (as with FN_3 , ClN_3 and BrN_3 also) comprises a linear N_3 group joined at an obtuse angle to the pendant X atom, thereby giving a molecule of C_s symmetry.

Diatomic interhalogens, XY

All six possible diatomic compounds between F , Cl , Br and I are known. Indeed, ICl was first made (independently) by J. L. Gay Lussac and H. Davy in 1813–4 soon after the isolation of the parent halogens themselves, and its existence led J. von Liebig to miss the discovery of the new element bromine, which has similar properties (p. 794). The compounds vary considerably in thermal stability: ClF is extremely robust; ICl and IBr are moderately stable and can be obtained in very pure crystalline form at room temperature; $BrCl$ readily dissociates reversibly into its

⁶⁵ Ref. 23, pp. 1476–1563, see also D. M. MARTIN, R. ROUSSON and J. M. WEULERSSE, in J. J. LAGOWSKI (ed.), *The Chemistry of Nonaqueous Solvents*, Chap. 3, pp. 157–95, Academic Press, New York, 1978.

⁶⁶ A. I. POPOV, Chap. 2, in V. GUTMANN (ed.), *MTP International Review of Science: Inorganic Chemistry Series* 1, Vol. 3, pp. 53–84, Butterworths, London, 1972.

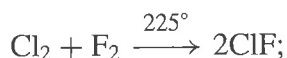
⁶⁷ K. O. CHRISTE, *IUPAC Additional Publication 24th Int. Congr. Pure Appl. Chem.*, Hamburg, 1973, Vol. 4. *Compounds of Non-Metals*, pp. 115–41, Butterworths, London, 1974.

⁶⁸ R. J. RICHARDS, R. W. DAVIS and M. C. L. GERRY, *J. Chem. Soc., Chem. Commun.*, 915–6 (1980).

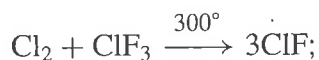
⁶⁹ K. GHOLIVAND and H. WILLNER, *Z. anorg. allg. Chem.* **550**, 27–34 (1987).

⁷⁰ K. DEHNICKE, *Angew. Chem. Int. Edn. Engl.* **18**, 507–14 (1979).

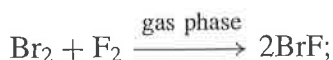
elements; BrF and IF disproportionate rapidly and irreversibly to a higher fluoride and Br₂ (or I₂). Thus, although all six compounds can be formed by direct, controlled reaction of the appropriate elements, not all can be obtained in pure form by this route. Typical preparative routes (with comments) are as follows:



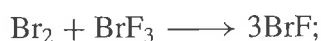
must be purified from ClF₃ and reactants



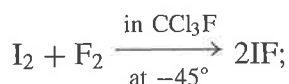
must be purified from excess ClF₃



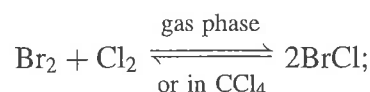
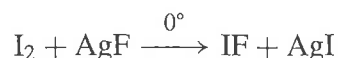
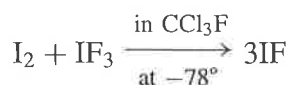
disproportionates to Br₂ + BrF₃ (and BrF₅)
at room temp



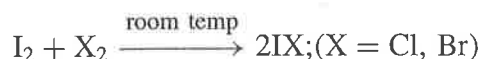
BrF favoured at high temp



disproportionates rapidly to I₂ + IF₅
at room temp



compound cannot be isolated free from
Br₂ and Cl₂



purify by fractional crystallization of
the molten compound

In general the compounds have properties intermediate between those of the parent halogens, though a combination of aggressive chemical reactivity and/or thermal instability militates against the determination of physical properties such as mp, bp, etc., in some instances. However, even for such highly dissociated species as BrCl, precise molecular (as distinct from bulk) properties can be determined by spectroscopic techniques. Table 17.12 summarizes some of the more important physical properties of the

Table 17.12 Physical properties of interhalogen compounds XY

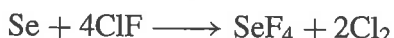
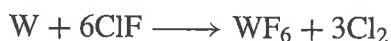
Property	ClF	BrF	IF	BrCl	ICl	IBr
Form at room temperature	Colourless gas	Pale brown (Br ₂)	Unstable	Red brown gas	Ruby red crystals	Black crystals
MP/°C	-155.6	ca. -33 Disprop ^(a)	— Disprop ^(a)	ca. -66 Dissoc ^(a)	27.2(α) 13.9(β)	41 Some dissoc ~116 ^(b)
BP/°C	-100.1	ca. 20	—	ca. 5	97-100 ^(b)	~116 ^(b)
ΔH _f ^o (298 K)/kJ mol ⁻¹	-56.5	-58.6	-95.4	+14.6	-35.3(α)	-10.5 (cryst)
ΔG _f ^o (298 K)/kJ mol ⁻¹	-57.7	-73.6	-117.6	-1.0	-13.95(α)	+3.7(gas)
Dissociation energy/ kJ mol ⁻¹	252.5	248.6	~277	215.1	207.7	175.4
d(liq. T°C)/g cm ⁻³	1.62(-100°)	—	—	—	3.095(30°)	3.762(42°)
r(X-Y)/pm	162.81	175.6	190.9	213.8	232.07	248.5
Dipole moment/D	0.881	1.29	—	0.57	0.65	1.21
κ(liq. T°C)/ ohm ⁻¹ cm ⁻¹	1.9 × 10 ⁻⁷ (-128°)	—	—	—	5.50 × 10 ⁻³	3.4 × 10 ⁻⁴

^(a)Substantial disproportionation or dissociation prevents meaningful determination of mp and bp; the figures merely indicate the approximate temperature range over which the (impure) compound is liquid at atmospheric pressure.

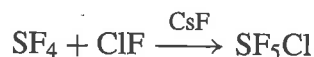
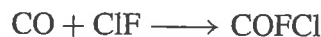
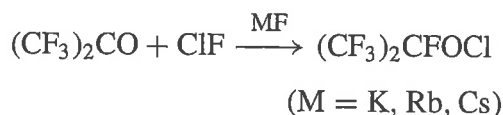
^(b)Fused ICl and IBr both dissociate into the free halogens to some extent: ICl 0.4% at 25° (supercooled) and 1.1% at 100°C; IBr 8.8% at 25° (supercooled) and 13.4% at 100°C.

diatomic interhalogens. The most volatile compound, ClF, is a colourless gas which condenses to a very pale yellow liquid below -100° . The least volatile is IBr; it forms black crystals in which the IBr molecules pack in a herring-bone pattern similar to that in I_2 (p. 803) and in which the internuclear distance $r(\text{I}-\text{Br})$ is 252 pm, i.e. slightly longer than in the gas phase (248.5 pm). ICl is unusual in forming two crystalline modifications: the stable (α) form crystallizes as large, transparent ruby-red needles from the melt and features zigzag chains of molecules (Fig. 17.6) with two different ICl units and appreciable interchain intermolecular bonding. The packing is somewhat different in the yellow, metastable (β) form (Fig. 17.6) which can be obtained as brownish-red crystals from strongly supercooled melts.

The chemical reactions of XY can be conveniently classified as (a) halogenation reactions, (b) donor-acceptor interactions and (c) use as solvent systems. Reactions frequently parallel those of the parent halogens but with subtle and revealing differences. ClF is an effective fluorinating agent (p. 820) and will react with many metals and non-metals either at room temperature or above, converting them to fluorides and liberating chlorine, e.g.:



It can also act as a chlorofluorinating agent by addition across a multiple bond and/or by oxidation, e.g.:



Reaction with OH groups or NH groups results in the exothermic elimination of HF and the (often violent) chlorination of the substrate, e.g.:



Lewis acid (fluoride-ion acceptor) behaviour is exemplified by reactions with NOF and MF to give $[\text{NO}]^+[\text{ClF}_2]^-$ and $\text{M}^+[\text{ClF}_2]^-$ respectively (M = alkali metal or NH_4). Lewis base (fluoride ion donor) activity includes reactions with BF_3 and AsF_5 :

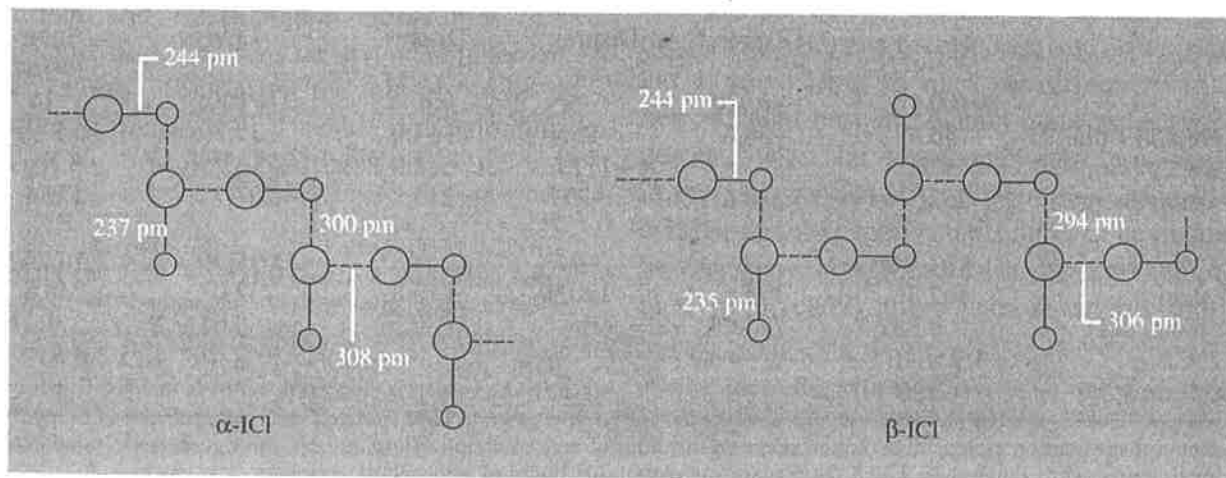
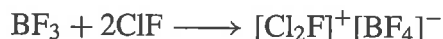


Figure 17.6 Structures of α - and β -forms of crystalline ICl.

be isolated by extraction rather than by precipitation, and solvolysis is a further complicating factor.

Tetra-atomic interhalogens, XY_3

The compounds to be considered are ClF_3 , BrF_3 , IF_3 and ICl_3 (I_2Cl_6). All can be prepared by direct reaction of the elements, but conditions must be chosen so as to avoid formation of mixtures of interhalogens of different stoichiometries. ClF_3 is best formed by direct fluorination of Cl_2 or ClF in the gas phase at 200–300° in Cu, Ni or Monel metal apparatus. BrF_3 is formed similarly at or near room temperature and can be purified by distillation to give a pale straw-coloured liquid. With IF_3 , which is only stable below –30° the problem is to avoid the more facile formation of IF_5 ; this can be achieved either by the action of F_2 on I_2 suspended in CCl_3F at –45° or more elegantly by the low-temperature fluorination of I_2 with XeF_2 :



I_2Cl_6 is readily made as a bright-yellow solid by reaction of I_2 with an excess of liquid chlorine at –80° followed by the low-temperature evaporation of the Cl_2 ; care must be taken with this latter operation, however, because of the very ready dissociation of I_2Cl_6 into ICl and Cl_2 .

Physical properties are summarized in Table 17.13. Little is known of the unstable

IF_3 but ClF_3 and BrF_3 are well-characterized volatile molecular liquids. Both have an unusual T-shaped structure of C_{2v} symmetry, consistent with the presence of 10 electrons in the valency shell of the central atom (Fig. 17.7a,b). A notable feature of both structures is the slight deviation from colinearity of the apical F–X–F bonds, the angle being 175.0° for ClF_3 and 172.4° for BrF_3 ; this reflects the greater electrostatic repulsion of the nonbonding pair of electrons in the equatorial plane of the molecule. For each molecule the X–F_{apical} distance is some 5–6% greater than the X–F_{equatorial} distance but the mean X–F distance is very similar to that in the corresponding monofluoride. The structure of crystalline ICl_3 is quite different, being built up of planar I_2Cl_6 molecules separated by normal van der Waals' distances between the Cl atoms (Fig. 17.7c). The terminal I–Cl distances are similar to those in ICl but the bridging I–Cl distances are appreciably longer.

ClF_3 is one of the most reactive chemical compounds known⁽⁷³⁾ and reacts violently with many substances generally thought of as inert. Thus it spontaneously ignites asbestos, wood, and other building materials and was used in incendiary bomb attacks on UK cities during the Second World War. It reacts explosively with water and with most organic substances, though

⁷³ L. STEIN, in V. GUTMANN (ed.), *Halogen Chemistry*, Vol. 1, pp. 133–224, Academic Press, London, 1967.

Table 17.13 Physical properties of interhalogen compounds XY_3

Property	ClF_3	BrF_3	IF_3	I_2Cl_6
Form at room temperature	Colourless gas/liquid	Straw-coloured liquid	Yellow solid (decomp above –28°)	Bright yellow solid
MP/°C	–76.3	8.8	—	101 (16 atm)
BP/°C	11.8	125.8	—	—
$\Delta H_f^\circ(298\text{ K})/\text{kJ mol}^{-1}$	–164 (g)	–301 (l)	ca. –485 (g) calc	–89.3 (s)
$\Delta G_f^\circ(298\text{ K})/\text{kJ mol}^{-1}$	–124 (g)	–241 (l)	ca. –460 (g) calc	–21.5 (s)
Mean X–Y bond energy of $XY_3/\text{kJ mol}^{-1}$	174	202	ca. 275 (calc)	—
Density($T^\circ\text{C}$)/ g cm^{-3}	1.885 (0°)	2.803 (25°)	—	3.111 (15°)
Dipole moment/D	0.557	1.19	—	—
Dielectric constant $\epsilon(T^\circ)$	4.75 (0°)	—	—	—
$\kappa(\text{liq}, T^\circ\text{C})/\text{ohm}^{-1}\text{cm}^{-1}$	$6.5 \times 10^{-9}(0^\circ)$	$8.0 \times 10^{-3}(25^\circ)$	—	$8.6 \times 10^{-3}(102^\circ)$

be isolated by extraction rather than by precipitation, and solvolysis is a further complicating factor.

Tetra-atomic interhalogens, XY_3

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$\Delta G_f^\circ(298\text{ K})/\text{kJ mol}^{-1}$	–124 (g)	–241 (l)	ca. –460 (g) calc	–21.5 (s)
Mean X–Y bond energy of $XY_3/\text{kJ mol}^{-1}$	174	202	ca. 275 (calc)	—
Density($T^\circ\text{C}$)/g cm ^{–3}	1.885 (0°)	2.803 (25°)	—	3.111 (15°)
Dipole moment/D	0.557	1.19	—	—
Dielectric constant $\epsilon(T^\circ)$	4.75 (0°)	—	—	—
$\kappa(\text{liq}, T^\circ\text{C})/\text{ohm}^{-1}\text{cm}^{-1}$	$6.5 \times 10^{-9}(0^\circ)$	$8.0 \times 10^{-3}(25^\circ)$	—	$8.6 \times 10^{-3}(102^\circ)$

1														3		4							
H														B		C							
He														N		O							
5														F		Ne							
7														11		12							
Li														Al		Si							
9														P		S							
Na														Cl		Ar							
														17		18							
19		20		21		22		23		24		25		26		27		28		29		30	
K		Ca		Sc		Ti		V		Cr		Mn		Fe		Co		Ni		Cu		Zn	
35		36		37		38		39		40		41		42		43		44		45		46	
Rb		Sr		Y		Zr		Nb		Mo		Tc		Ru		Rh		Pd		Ag		Cd	
51		52		53		54		55		56		57		58		59		60		61		62	
Cs		Ba		La		Hf		Ta		W		Re		Os		Ir		Pt		Au		Hg	
67		68		69		70		71		72		73		74		75		76		77		78	
Fr		Ra		Ac		Rf		Db		Sg		Bh		Hs		Mt		Uun		Uuu		Uub	
89		90		91		92		93		94		95		96		97		98		99		100	
Th		Pa		U		Np		Pu		Am		Cm		Bk		Cf		Es		Fm		Md	
103		104		105		106		107		108		109		110		111		112		113		114	
Lr																							

29

Zinc, Cadmium and Mercury

29.1 Introduction

The reduction of ZnO by charcoal requires a temperature of 1000°C or more and, because the metal is a vapour at that temperature and is liable to reoxidation, its collection requires some form of condenser and the exclusion of air. This was apparently first achieved in India in the thirteenth century. The art then passed to China where zinc coins were used in the Ming Dynasty (1368–1644). The preparation of alloyed zinc by smelting mixed ores does not require the isolation of zinc itself and is much more easily achieved. The small amounts of zinc present in samples of early Egyptian copper no doubt simply reflect the composition of local ores, but Palestinian brass dated 1400–1000 BC and containing about 23% Zn must have been produced by the deliberate mixing of copper and zinc ores. Brass was similarly produced by the Romans in Cyprus and later in the Cologne region of Germany.

Zinc was not intentionally made in medieval Europe, though small amounts were obtained by accidental condensation in the production of lead, silver and brass; it was imported from China by

the East India Company after about 1605. The English zinc industry started in the Bristol area in the early eighteenth century and production quickly followed in Silesia and Belgium. The origin of the name is obscure but may plausibly be thought to be derived from *Zinke* (German for spike, or tooth) because of the appearance of the metal.

Mercury is more easily isolated from its ore, cinnabar, and was used in the Mediterranean world for extracting metals by amalgamation as early as 500 BC, possibly even earlier. Cinnabar, HgS, was widely used in the ancient world as a pigment (vermillion). For over a thousand years, up to AD 1500, alchemists regarded the metal as a key to the transmutation of base metals to gold and employed amalgams both for gilding and for producing imitation gold and silver. Because of its mobility, mercury is named after the messenger of the gods in Roman mythology, and the symbol, Hg, is derived from *hydrargyrum* (Latin, liquid silver).

Cadmium made its appearance much later. In 1817 F. Stromeyer of Göttingen noticed that a sample of “cadmia” (now known as “calamine”), used in a nearby smelting works, was yellow

instead of white. The colour was not due to iron, which was shown to be absent, but arose instead from a new element which was named after the (zinc) ore in which it had been found (Greek *καδμεία*, cadmean earth, the ancient name of calamine).

29.2 The Elements

29.2.1 Terrestrial abundance and distribution

Zinc (76 ppm of the earth's crust) is about as abundant as rubidium (78 ppm) and slightly more abundant than copper (68 ppm). Cadmium (0.16 ppm) is similar to antimony (0.2 ppm); it is twice as abundant as mercury (0.08 ppm), which is itself as abundant as silver (0.08 ppm) and close to selenium (0.05 ppm). These elements are "chalcophiles" (p. 648) and so, in the reducing atmosphere prevailing when the earth's crust solidified, they separated out in the sulfide phase, and their most important ores are therefore sulfides. Subsequently, as rocks were weathered, zinc was leached out to be precipitated as carbonate, silicate or phosphate.

The major ores of zinc are ZnS (which is known as zinc blende in Europe and as sphalerite in the USA) and ZnCO₃ (calamine in Europe, smithsonite in the USA[†]). Large deposits are situated in Canada, the USA and Australia. Less important ores are hemimorphite, Zn₄Si₂O₇(OH)₂·H₂O and franklinite, (Zn,Fe)O·Fe₂O₃. Cadmium is found as greenockite, CdS, but its only commercially important source is the 0.2–0.4% found in most zinc ores. Cinnabar, HgS, is the only important ore and source of mercury and is found along lines of previous volcanic activity. The most famous and extensive deposits are at Almaden in Spain; these contain up to 6–7% Hg and have been worked since Roman times. Other deposits, usually containing <1% Hg, are situated in the former Soviet Union, Algeria, Mexico, Yugoslavia and Italy.

[†] After James Smithson, founder of the Smithsonian Institution, Washington. The name calamine is applied in the USA to a basic carbonate.

29.2.2 Preparation and uses of the elements⁽¹⁾

The isolation of zinc, over 90% of which is from sulfide ores, depends on conventional physical concentration of the ore by sedimentation or flotation techniques. This is followed by roasting to produce the oxides; the SO₂ which is generated is used to produce sulfuric acid. The ZnO is then either treated electrolytically or smelted with coke. In the former case the zinc is leached from the crude ZnO with dil H₂SO₄, at which point cadmium is precipitated by the addition of zinc dust. The ZnSO₄ solution is then electrolysed and the metal deposited — in a state of 99.95% purity — on to aluminium cathodes.

A variety of smelting processes have been employed to effect the reduction of ZnO by coke:



These formerly involved the use of banks of externally heated, horizontal retorts, operated on a batch basis. They were replaced by continuously operated vertical retorts, in some cases electrically heated. Unfortunately none of these processes has the thermal efficiency of a blast furnace process (p. 1072) in which the combustion of the fuel for heating takes place in the same chamber as the reduction of the oxide. The inescapable problem posed by zinc is that the reduction of ZnO by carbon is not spontaneous below the boiling point of Zn (a problem not encountered in the smelting of Fe, Cu or Pb, for instance), and the subsequent cooling to condense the vapour is liable, in the presence of the combustion products, to result in the reoxidation of the metal:



The problem can be overcome by spraying the zinc vapour with lead as it leaves the top of the furnace. This chills and dissolves the zinc

¹ Kirk-Othmer *Encyclopedia of Chemical Technology*, Interscience, New York. For Zn, see Vol. 24, 3rd edn., 1984, pp. 807–51. For Cd, see Vol. 4, 4th edn., 1992, pp. 748–60. For Hg, see Vol. 16, 4th edn., 1995, pp. 212–28.

so rapidly that reoxidation is minimal. The zinc then separates as a liquid of nearly 99% purity and is further refined by vacuum distillation to give a purity of 99.99%. Any cadmium present is recovered in the course of this distillation. The use of a blast furnace has the further advantage that the composition of the charge is not critical, and mixed Zn/Pb ores can be used (ZnS and PbS are commonly found together) to achieve the simultaneous production of both metals, the lead being tapped from the bottom of the furnace.

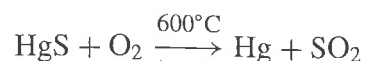
World production of zinc (1995) is about 7 million tonnes pa: of this, about 1 million tonnes pa is produced by each of Canada and Australia and 800 000 tonnes pa by China. Cadmium is produced in much smaller quantities (~20 000 tonnes pa) and these are dependent on the supply of zinc.

Zinc finds a wide range of uses. The most important, accounting for 40% of output, is as an anti-corrosion coating. The application of the coating takes various forms: immersion in molten zinc (hot-dip galvanizing), electrolytic deposition, spraying with liquid metal, heating with powdered zinc ("Sherardizing"), and applying paint containing zinc powder. In addition to brasses (Cu plus 20–50% Zn), a rapidly increasing number of special alloys, predominantly of zinc, are used for diecasting and, indeed, the vast majority of *pressure* diecastings are now made in these alloys. Zinc sheeting is used in roof cladding and the manufacture of dry batteries (see Panel, p. 1204) is a further use, though this has declined considerably in recent years.

The major uses of cadmium are in batteries (67%) and coatings (7%). In the form of its compounds it is used in pigments (CdS —15%) and stabilizers, in PVC for instance, to prevent degradation by heat or ultraviolet radiation (10%).

The isolation of mercury is comparatively straightforward. The most primitive method consisted simply of heating cinnabar in a fire of brushwood. The latter acted as fuel and condenser, and metallic mercury collected in the ashes. Modern techniques are of course less crude than this but the basic principle is much the same. After being crushed and concentrated by

flotation, the ore is roasted in a current of air and the vapour condensed:



Alternatively, in the case of especially rich ores, roasting with scrap iron or quicklime is used:



Blowing air through the hot, crude, liquid metal oxidizes traces of metals such as Fe, Cu, Zn and Pb which form an easily removable scum. Further purification is by distillation under reduced pressure. About 4000 tonnes[†] of mercury are used annually but only half is from primary, mine production the other half being secondary production and sales from stockpiles. The main primary producer is now Spain, but several other countries, including the former Soviet Union, China and Algeria, have capacity for production.

The use of mercury for extracting precious metals by amalgamation has a long history and was extensively used by Spain in the sixteenth century when her fleet carried mercury from Almaden to Mexico and returned with silver. However, environmental concerns have resulted in falling demand and excess production capacity. It is still used in the extraction of gold and in the Castner–Kellner process for manufacturing chlorine and NaOH (p. 72), and a further major use is in the manufacture of batteries. It is also used in street lamps and AC rectifiers, while its small-scale use in thermometers, barometers and gauges of different kinds, are familiar in many laboratories.

29.2.3 Properties of the elements

A selection of some important properties of the elements is given in Table 29.1. Because the elements each have several naturally occurring isotopes their atomic weights cannot be quoted with great precision.

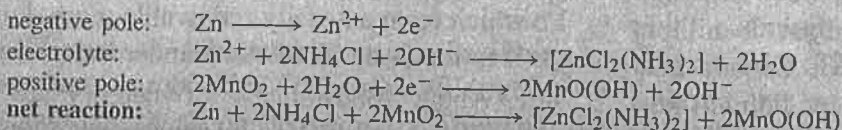
[†] Mercury is sold in iron flasks holding 76 lb of mercury and this is the unit in which output is normally measured.

Dry Batteries

A portable source of electricity, if not a necessity, is certainly a great convenience in modern life and is dependent on compact, sealed, dry batteries. The main types are listed below and they incorporate the metals Zn, Ni, Hg and Cd as well as MnO_2

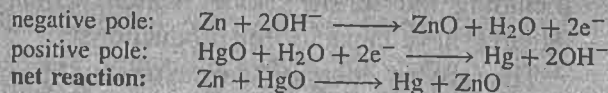
(a) Carbon-zinc cell

The first dry battery was that patented in 1866 by the young French engineer, G. Leclanché. The positive pole consisted of carbon surrounded by MnO_2 (p. 1048) contained in a porous pot, and the negative pole was simply a rod of zinc. These were situated inside a glass jar containing the electrolyte, ammonium chloride solution thickened with sand or sawdust. This is still the basis of the most common type of modern dry cell in which a carbon rod is the positive pole, surrounded by a paste of MnO_2 , carbon black, and NH_4Cl , inside a zinc can which is both container and negative pole. The reactions are:



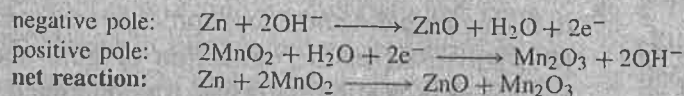
(b) Mercury cell

The negative pole of pressed amalgamated zinc powder and the positive pole of mercury(II) oxide and graphite are separated by an absorbent impregnated with the electrolyte, conc KOH:



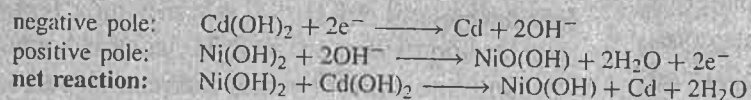
(c) Alkaline manganese cell

This is similar in principle to (a) but is constructed in a manner akin to (b). The negative pole of powdered zinc, formed into a paste with the electrolyte KOH, and the positive pole of compressed graphite and MnO_2 are separated by an absorbent impregnated with the electrolyte:

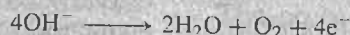


(d) Nickel-cadmium cell

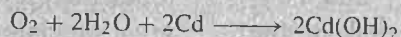
Unlike the cells above, which are all primary cells, this is a secondary (i.e. rechargeable) cell, and the two poles are composed in the uncharged condition of nickel and cadmium hydroxides respectively. These are each supported on microporous nickel, made by a sintering process, and separated by an absorbent impregnated with electrolyte. The charging reactions are:



During discharge these reactions are reversed. A crucial feature of the construction of this cell is that oxygen produced at the positive pole during charging by the side-reaction:



can migrate readily to the negative pole to be recombined in the reaction:



But for this rapid migration and recombination, the cell could not be sealed.

Table 29.1 Some properties of the elements zinc, cadmium and mercury

Property	Zn	Cd	Hg
Atomic number	30	48	80
Number of naturally occurring isotopes	5	8 ^(a)	7
Atomic weight	65.39(2)	112.411(8)	200.59(2)
Electronic configuration	[Ar]3d ¹⁰ 4s ²	[Kr]4d ¹⁰ 5s ²	[Xe]4f ¹⁴ 5d ¹⁰ 6s ²
Electronegativity	1.6	1.7	1.9
Metal radius (12 coordinate)/pm	134	151	151
Effective ionic radius/pm			
II	74	95	102
I	—	—	119
Ionization energies/kJ mol ⁻¹			
1st	906.1	876.5	1007
2nd	1733	1631	1809
3rd	3831	3644	3300
$E^\circ(\text{M}^{2+}/\text{M})/\text{V}$	-0.7619	-0.4030	+0.8545
MP/°C	419.5	320.8	-38.9
BP/°C	907	765	357
$\Delta H_{\text{fus}}/\text{kJ mol}^{-1}$	7.28(±0.01)	6.4(±0.2)	2.30(±0.02)
$\Delta H_{\text{vap}}/\text{kJ mol}^{-1}$	114.2(±1.7)	100.0(±2.1)	59.1(±0.4)
$\Delta H_{(\text{monatomic gas})}/\text{kJ mol}^{-1}$	129.3(±2.9)	111.9(±2.1)	61.3
Density (25°C)/g cm ⁻³	7.14	8.65	13.534(1)
Electrical resistivity (20°C)/μohm cm	5.8	7.5	95.8

(a) The half-life of $9.3 \pm 1.9 \times 10^{15}$ y for ^{113}Cd is the longest known for any β -emitter; note that this is 2 million times the age of the earth (4.6×10^9 y).

Their most noticeable features compared with other metals are their low melting and boiling points, mercury being unique as a metal which is a liquid at room temperature. Zinc and cadmium are silvery solids with a bluish lustre when freshly formed. Mercury is also unusual in being the only element, apart from the noble gases, whose vapour is almost entirely monatomic, while its appreciable vapour pressure (1.9×10^{-3} mmHg, i.e. 0.25 Pa, at 25°C), coupled with its toxicity, makes it necessary to handle it with care. The electrical resistivity of liquid mercury is exceptionally high for a metal, and this facilitates its use as an electrical standard (the international ohm is defined as the resistance of 14.4521 g of Hg in a column 106.300 cm long and 1 mm² cross-sectional area at 0°C and a pressure of 760 mmHg).

The structures of the solids, although based on the typically metallic hexagonal close-packing, are significantly distorted. In the case of Zn and Cd the distortion is such that, instead of having 12 equidistant neighbours, each atom has 6 nearest neighbours in the close-packed plane with the 3 neighbours in each of the adjacent planes

being about 10% more distant. In the case of (rhombohedral) Hg the distortion, again uniquely, is the reverse, with the coplanar atoms being the more widely separated (by some 16%). The consequence is that these elements are much less dense and have a lower tensile strength than their predecessors in Group 11. These facts have been ascribed to the stability of the d electrons which are now tightly bound to the nucleus: the metallic bonding therefore involves only the outer s electrons, and is correspondingly weakened.

29.2.4 Chemical reactivity and trends

Zinc and cadmium tarnish quickly in moist air and combine with oxygen, sulfur, phosphorus and the halogens on being heated. Mercury also reacts with these elements, except phosphorus and its reaction with oxygen was of considerable practical importance in the early work of J. Priestley and A. L. Lavoisier on oxygen (p. 601). The reaction only becomes appreciable at temperatures of about 350°C, but above about 400°C HgO decomposes back into the elements.

None of the three metals reacts with hydrogen, carbon or nitrogen.

Non-oxidizing acids dissolve both Zn and Cd with the evolution of hydrogen. With oxidizing acids the reactions are more complicated, nitric acid for instance producing a variety of oxides of nitrogen dependent on the concentration and temperature. Mercury is unreactive to non-oxidizing acids but dissolves in conc HNO_3 and in hot conc H_2SO_4 forming the Hg^{II} salts along with oxides of nitrogen and sulfur. Dilute HNO_3 slowly produces $\text{Hg}_2(\text{NO}_3)_2$. Zinc is the only element in the group which dissolves in aqueous alkali to form ions such as aquated $[\text{Zn}(\text{OH})_4]^{2-}$ (zincates).

All three elements form alloys with a variety of other metals. Those of zinc include the brasses (p. 1178) and, as mentioned above, are of considerable commercial importance. Those of mercury are known as amalgams and some, such as sodium and zinc amalgams, are valuable reducing agents: in a number of cases, high heats of formation and stoichiometric compositions suggest chemical combination. Na_5Hg_8 and Na_3Hg for instance have been isolated and structurally characterized. They consist of "widespread" close-packed mercury ($\text{Hg}-\text{Hg} > 500 \text{ pm}$) with respectively, all vacancies filled and all octahedral vacancies plus 5/6 tetrahedral vacancies filled with sodium atoms.⁽²⁾ From caesium amalgams CsHg has been obtained and shown⁽³⁾ to contain isolated square planar Hg_4 clusters ($\text{Hg}-\text{Hg} \sim 300 \text{ pm}$ whereas intercluster separation = 419 pm). Amalgams are most readily formed by heavy metals, whereas the lighter metals of the first transition series (with the exception of manganese and copper) are insoluble in mercury. Hence iron flasks can be used for its storage.

Chemically, it is clear that Zn and Cd are rather similar and that Hg is somewhat distinct. The lighter pair are more electropositive, as indicated both by their electronegativity coefficients and electrode potentials (Table 29.1), while Hg has a

positive electrode potential and is comparatively inert. With the exception of the metallic radii, all the evidence indicates that the effects of the lanthanide contraction have died out by the time this group is reached. Compounds are characterized by the d^{10} configuration and, with the exception of derivatives of the Hg_2^{2+} ion, which formally involve Hg^{I} , they almost exclusively involve M^{II} (but see page 1213). The ease with which the s^2 electrons are removed compared with the more firmly held d electrons is shown by the ionization energies. The sum of the first and second is in each case smaller than for the preceding element in Group 11, whereas the third is appreciably higher. Even so the first two ionization energies are high for mercury (as they are for gold) — perhaps reflecting the poor nuclear shielding afforded by the filled 4f shell — and this, coupled with the small hydration energy associated with the large Hg^{II} cation, accounts for the positive value of its electrode potential.

In view of the stability of the filled d shell, these elements show few of the characteristic properties of transition metals (p. 905) despite their position in the d block of the periodic table. Thus zinc shows similarities with the main-group metal magnesium, many of their compounds being isomorphous, and it displays the class-a characteristic of complexing readily with O-donor ligands. On the other hand, zinc has a much greater tendency than magnesium to form covalent compounds, and it resembles the transition elements in forming stable complexes not only with O-donor ligands but with N- and S-donor ligands and with halides and CN^- (see p. 1216) as well. As mentioned above, cadmium is rather similar to zinc and may be regarded as on the class-a/b borderline. However, mercury is undoubtedly class b: it has a much greater tendency to covalency and a preference for N-, P- and S-donor ligands, with which Hg^{II} forms complexes whose stability is rarely exceeded by those of any other divalent cation. Compounds of the M^{II} ions of this group are characteristically diamagnetic and those of Zn^{II} , like those of Mg^{II} , are colourless. By contrast, many compounds of

² H. J. DEISEROTH and D. TOELSTEDE, *Z. anorg. allg. Chem.* **615**, 43–8 (1992).

³ H. J. DEISEROTH, A. STRUNK and W. BAUHOFFER, *Z. anorg. allg. Chem.* **575**, 31–8 (1989).

Table 29.2 Stereochemistries of compounds of Zn^{II} , Cd^{II} and Hg^{II}

Coordination number	Stereochemistry	Zn	Cd	Hg
2	Linear	ZnEt_2	CdEt_2	$[\text{Hg}(\text{NH}_3)_2]^{2+}$
3	Planar	$[\text{ZnMe}(\text{NPh}_3)]_2$		$[\text{HgI}_3]^-$
	T-shaped			$[\text{Hg}(\text{SC}_6\text{H}_2\text{Bu}_3)_2(\text{py})]$
4	Tetrahedral	$[\text{Zn}(\text{H}_2\text{O})_4]^{2+}$, $[\text{Zn}(\text{NH}_3)_4]^{2+}$	$[\text{CdCl}_4]^{2-}$	$[\text{Hg}(\text{SCN})_4]^{2-}$
	Planar	$[\text{Zn}(\text{glycyl})_2]$		
5	Trigonal bipyramidal	$[\text{Zn}(\text{terpy})\text{Cl}_2]$	$[\text{CdCl}_5]^{3-}$	$[\text{Hg}(\text{terpy})\text{Cl}_2]$
	Square pyramidal	$[\text{Zn}(\text{S}_2\text{CNEt}_2)_2]_2$	$[\text{Cd}(\text{S}_2\text{CNEt}_2)_2]_2$	$[\text{Hg}\{\text{N}(\text{C}_2\text{H}_4\text{NMe}_2)_3\}\text{I}]^+$
6	Octahedral	$[\text{Zn}(\text{en})_3]^{2+}$	$[\text{Cd}(\text{NH}_3)_6]^{2+}$	$[\text{Hg}(\text{C}_5\text{H}_5\text{NO})_6]^{2+}$
7	Pentagonal bipyramidal	$[\text{Zn}(\text{H}_2\text{dapp})(\text{H}_2\text{O})_2]^{2+(a)}$	$[\text{Cd}(\text{quin})_2(\text{NO}_3)_2\text{H}_2\text{O}]^{(b)}$	
8	Distorted dodecahedral	$[\text{Zn}(\text{NO}_3)_4]^{2-(c)}$		
	Distorted square antiprismatic			$[\text{Hg}(\text{NO}_2)_4]^{2-}$

(a) $\text{H}_2\text{dapp} = 2,6\text{-diacetylpyridinebis}(2'\text{-pyridylhydrazon})$.

(b) The 2 nitrate ions are not equivalent (both are bidentate but one is coordinated symmetrically, the other asymmetrically) and the structure of the complex is by no means regular (p. 1217).

(c) The distortion arises because the bidentate nitrate ions are coordinated asymmetrically to such an extent that the stereochemistry may alternatively be regarded as approaching tetrahedral (p. 1217).

Hg^{II} , and to a lesser extent those of Cd^{II} , are highly coloured due to the greater ease of charge transfer from ligands to the more polarizing cations. The increasing polarizing power and covalency of their compounds in the sequence, $\text{Mg}^{\text{II}} < \text{Zn}^{\text{II}} < \text{Cd}^{\text{II}} < \text{Hg}^{\text{II}}$, is a reflection of the decreasing nuclear shielding and consequent increasing power of distortion in the sequence: filled p shell < filled d shell < filled f shell.

A further manifestation of these trends is the increasing stability of σ -bonded alkyls and aryls in passing down the group (p. 1221). Those of Zn and Cd are rather reactive and unstable to both air and water, whereas those of Hg are stable to both. (The Hg–C bond is not in fact strong but the competing Hg–O bond is weaker.) However, the M^{II} ions do not form π complexes with CO, NO or olefins (alkenes), no doubt because of the stability of their d^{10} configurations and their consequent inability to provide electrons for “back bonding”. Likewise their cyanides presumably owe their stability primarily to σ rather than π bonding. The filled d shell also prevents π acceptance and complexes with cyclopentadienide ions (which are good π donors) are σ - rather than π -bonded.

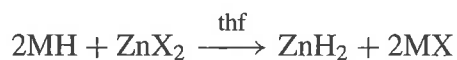
The range of stereochemistries found in compounds of the M^{II} ions is illustrated in Table 29.2. Since the d^{10} configuration affords no crystal field stabilization, the stereochemistry of a particular compound depends on the size and polarizing power of the M^{II} cation and the steric requirements of the ligands. Thus both Zn^{II} and Cd^{II} favour 4-coordinate tetrahedral complexes though Cd^{II} , being the larger, forms 6-coordinate octahedral complexes more readily than does Zn^{II} . However, the still larger Hg^{II} also commonly adopts a tetrahedral stereochemistry, and octahedral 6-coordination is less prevalent than for either of its congeners.[†] When it does occur it is usually highly distorted with 2 short and 4 long bonds, a distortion which in its extreme form produces the 2-coordinate, linear stereochemistry which is characteristic of

[†] An example of trigonal prismatic coordination has been reported for Hg in the green, zero-valent mixed-metal cluster $[\text{Hg}\{\text{Pt}(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{NC})\}_6]$; Y. YAMAMOTO, H. YAMAZAKI, and T. SAKURAI, *J. Am. Chem. Soc.* **104**, 2329–30 (1982). In $[\text{Hg}(\text{mac})_2](\text{HgBr}_4)$, (mac = 1-thia-4,7-diazacyclononane) the coordination in the cation is intermediate between octahedral and trigonal prismatic; U. HEINZEL and R. MATTES, *Polyhedron* **11**, 597–600 (1992).

Hg^{II} . This is also found in organozinc and organocadmium compounds but only with Hg^{II} is it one of the predominant stereochemistries. Explanations of this fact have been given in terms of the promotional energies involved in various hybridization schemes, but it may be regarded pictorially as a consequence of the greater deformability of the d^{10} configuration of the large Hg^{II} ion. Thus, if 2 ligands are considered to approach the cation from opposite ends of the z -axis, the resulting deformation increases the electron density in the xy -plane and so discourages the close approach of other ligands. Coordination numbers greater than 6 are rare and generally involve bidentate, O -donor ligands with a small "bite", such as NO_3^- and NO_2^- .

29.3 Compounds of Zinc, Cadmium and Mercury⁽⁴⁻⁶⁾

Zinc hydride can be isolated from the reaction of LiH with ZnBr_2 or NaH with ZnI_2 :



The alkali metal halide remains in solution and ZnH_2 is precipitated as a white solid of moderate stability at or below room temperature.⁽⁷⁾ CdH_2 and HgH_2 are much less stable and decompose rapidly even below 0° . The complex metal hydrides LiZnH_3 , Li_2ZnH_4 and Li_3ZnH_5 have each been prepared as off-white powders by the reaction of LiAlH_4 with the appropriate organometallic complex $\text{Li}_n\text{ZnR}_{n+2}$.

The carbides of these metals (which are actually acetylides, MC_2 , p. 297) and also the

nitrides are unstable materials, those of mercury explosively so.

29.3.1 Oxides and chalcogenides

The principal compounds in this category are the monochalcogenides, which are formed by all three metals. It is a notable indication of the stability of tetrahedral coordination for the elements of Group 12 that, of the 12 compounds of this type, only CdO , HgO and HgS adopt a structure other than wurtzite or zinc blende (both of which involve tetrahedral coordination of the cation — see below). CdO adopts the 6-coordinate rock-salt structure; HgO features zigzag chains of almost linear $\text{O}-\text{Hg}-\text{O}$ units; and HgS exists in both a zinc-blende form and in a rock-salt form.

The normal oxide, formed by each of the elements of this group, is MO , and peroxides MO_2 are known for Zn and Cd . Reported lower oxides, M_2O , are apparently mixtures of the metal and MO .

ZnO is by far the most important manufactured compound of zinc⁽⁸⁾ and, being an inevitable byproduct of primitive production of brass, has been known longer than the metal itself. It is manufactured by burning in air the zinc vapour obtained on smelting the ore or, for a purer and whiter product, the vapour obtained from previously refined zinc. It is normally a white, finely divided material with the wurtzite structure. On heating, the colour changes to yellow due to the evaporation of oxygen from the lattice to give a nonstoichiometric phase Zn_{1+x}O ($x \leq 70$ ppm); the supernumerary Zn atoms produce lattice defects which trap electrons which can subsequently be excited by absorption of visible light.⁽⁹⁾ Indeed, by "doping" ZnO with an excess of 0.02–0.03% Zn metal, a whole range of colours — yellow, green, brown, red — can be obtained. The reddish hues of the naturally

⁴ M. FARNSWORTH, *Cadmium Chemicals*, International Lead Zinc Research Org. Inc., New York, 1980, 158 pp.

⁵ C. A. McAULIFFE (ed.), *The Chemistry of Mercury*, Macmillan, London, 1977, 288 pp.

⁶ B. J. AYLETT, Group IIB, Chap. 30, pp. 187–328, in *Comprehensive Inorganic Chemistry*, Vol. 3, Pergamon Press, Oxford, 1973.

⁷ J. J. WATKINS and E. C. ASHBY, *Inorg. Chem.* **13**, 2350–4 (1974).

⁸ See pp. 530–2 of W. BÜCHNER, R. SCHLIEBS, G. WINTER and K. H. BÜCHEL, *Industrial Inorganic Chemistry*, VCH, Weinheim 1989.

⁹ N. N. GREENWOOD, *Ionic Crystals, Lattice Defects and Nonstoichiometry*, Chaps. 6 and 7, pp. 111–81, Butterworths, London, 1968.

occurring form, zincite, arise, however, from the presence of Mn or Fe.

The major industrial use of ZnO is in the production of rubber where it shortens the time of vulcanization. As a pigment in the production of paints it has the advantage over the traditional "white lead" (basic lead carbonate) that it is non-toxic and is not discoloured by sulfur compounds, but it has the disadvantage compared to TiO₂ of a lower refractive index and so a reduced "hiding power" (p. 959). It improves the chemical durability of glass and so is used in the production of special glasses, enamels and glazes. Another important use is in antacid cosmetic pastes and pharmaceuticals. In the chemical industry it is the usual starting material for other zinc chemicals of which the soaps (i.e. salts of fatty acids, such as Zn stearate, palmitate, etc.) are the most important, being used as paint driers, stabilizers in plastics, and as fungicides. An important small scale use is in the production of "zinc ferrites". These are spinels of the type $\text{Zn}_x\text{M}_{1-x}^{\text{II}}\text{Fe}_2^{\text{III}}\text{O}_4$ involving a second divalent cation (usually Mn^{II} or Ni^{II}). When $x = 0$ the structure is that of an inverse spinel (i.e. half the Fe^{III} ions occupy octahedral sites — see p. 1081). Where $x = 1$, the structure is that of a normal spinel (i.e. all the Fe^{III} ions occupy octahedral sites), since Zn^{II} displaces Fe^{III} from the tetrahedral sites. Reducing the proportion of Fe^{III} ions in tetrahedral sites lowers the Curie temperature. The magnetic properties of the ferrite can therefore be controlled by adjustment of the zinc content.

ZnO is amphoteric (p. 640), dissolving in acids to form salts and in alkalis to form zincates, such as $[\text{Zn}(\text{OH})_3]^-$ and $[\text{Zn}(\text{OH})_4]^{2-}$. The gelatinous, white precipitate obtained by adding alkali to aqueous solutions of Zn^{II} salts is Zn(OH)₂ which, like ZnO, is amphoteric.

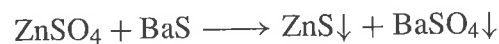
CdO is produced from the elements and, depending on its thermal history, may be greenish-yellow, brown, red or nearly black. This is partly due to particle size but more importantly, as with ZnO, is a result of lattice defects — this time in an NaCl lattice. It is more basic than ZnO, dissolving readily in acids but hardly at all in alkalis. White Cd(OH)₂ is precipitated from

aqueous solutions of Cd^{II} salts by the addition of alkali and treatment with very concentrated alkali yields hydroxocadmates such as Na₂[Cd(OH)₄]. Cadmium oxide and hydroxide find important applications in decorative glasses and enamels and in Ni–Cd storage cells. CdO also catalyses a number of hydrogenation and dehydrogenation reactions.

Treatment of the hydroxides of Zn and Cd with aqueous H₂O₂ produces hydrated peroxides of rather variable composition. That of Zn has anti-septic properties and is widely used in cosmetics.

HgO exists in a red and a yellow variety. The former is obtained by pyrolysis of Hg(NO₃)₂ or by heating the metal in O₂ at about 350°C; the latter by cold methods such as precipitation from aqueous solutions of Hg^{II} by addition of alkali (Hg(OH)₂ is not known). The difference in colour is entirely due to particle size, both forms having the same structure which consists of zigzag chains of virtually linear O–Hg–O units with Hg–O 205 pm and angle Hg–O–Hg 107°. The shortest Hg...O distance between chains is 282 pm.

Zinc blende, ZnS, is the most widespread ore of zinc and the main source of the metal, but ZnS is also known in a second naturally occurring though much rarer form, wurtzite, which is the more stable at high temperatures. The names of these minerals are now also used as the names of their crystal structures which are important structure types found in many other AB compounds. In both structures each Zn is tetrahedrally coordinated by 4 S and each S is tetrahedrally coordinated by 4 Zn; the structures differ significantly only in the type of close-packing involved, being cubic in zinc-blende and hexagonal in wurtzite (Fig. 29.1). Pure ZnS is white and, like ZnO, finds use as a pigment for which purpose it is often obtained (as "lithopone") along with BaSO₄ from aqueous solution of ZnSO₄ and BaS:



Freshly precipitated ZnS dissolves readily in mineral acids with evolution of H₂S, but roasting renders it far less reactive and it is then an acceptable pigment in paints for children's toys since it is harmless if ingested. ZnS also has

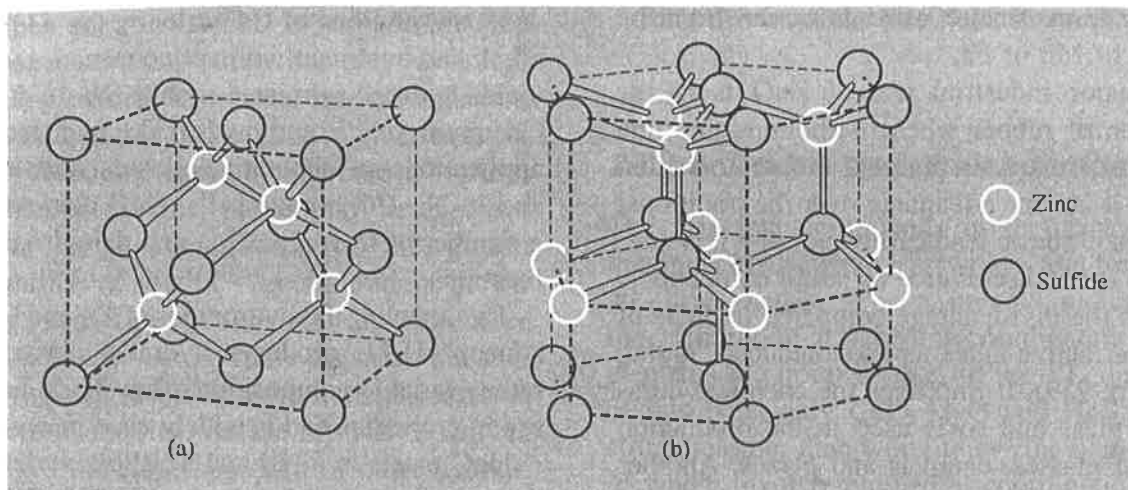


Figure 29.1 Crystal structures of ZnS. (a) Zinc blende, consisting of two, interpenetrating, ccp lattices of Zn and S atoms displaced with respect to each other so that the atoms of each achieve 4-coordination ($\text{Zn-S} = 235 \text{ pm}$) by occupying tetrahedral sites of the other lattice. The face-centred cube, characteristic of the ccp lattice, can be seen — in this case composed of S atoms, but an extended diagram would reveal the same arrangement of Zn atoms. Note that if all the atoms of this structure were C, the structure would be that of diamond (p. 275). (b) Wurtzite. As with zinc blende, tetrahedral coordination of both Zn and S is achieved ($\text{Zn-S} = 236 \text{ pm}$) but this time the interpenetrating lattices are hexagonal, rather than cubic, close-packed.

interesting optical properties. It turns grey on exposure to ultraviolet light, probably due to dissociation to the elements, but the process can be inhibited by trace additives such as cobalt salts. Cathode rays, X-rays and radioactivity also produce fluorescence or luminescence in a variety of colours which can be extended by the addition of traces of various metals or the replacement of Zn by Cd and S by Se. It is widely used in the manufacture of cathode-ray tubes and radar screens.

Yellow ZnSe and brown ZnTe are structurally akin to the sulfide and the former especially is used mainly in conjunction with ZnS as a phosphor.

Chalcogenides of Cd are similar to those of Zn and display the same duality in their structures. The sulfide and selenide are more stable in the hexagonal form whereas the telluride is more stable in the cubic form. CdS is the most important compound of cadmium and, by addition of CdSe, ZnS, HgS, etc., it yields thermally stable pigments of brilliant colours from pale yellow to deep red, while colloidal dispersions are used to colour transparent glasses.

CdS and CdSe are also useful phosphors. CdTe is a semiconductor used as a detector for X-rays and γ -rays,⁽¹⁰⁾ and mercury cadmium telluride⁽¹¹⁾ has found widespread (particularly military) use as an ir detector for thermal imaging.

HgS is polymorphic. The red α -form is the mineral cinnabar, or vermilion, which has a distorted rock-salt structure and can be prepared from the elements. β -HgS is the rare, black, mineral metacinnabar which has the zinc-blende structure and is converted by heat to the stable α -form. In the laboratory the most familiar form is the highly insoluble[†] black precipitate obtained by the action of H_2S on aqueous solutions of Hg^{II} . HgS is an unreactive substance, being attacked only by conc HBr, HI or aqua regia. HgSe and

¹⁰ M. HAGE-ALI and P. SIFFERT, pp. 219–334 of *Semiconductors and Semimetals*, Vol. 43, Academic Press, San Diego, 1995.

¹¹ *ibid.* Vol. 18, 1981, 388 pp. devoted to mercury cadmium telluride.

[†] The solubility product, $[\text{Hg}^{2+}][\text{S}^{2-}] = 10^{-52} \text{ mol}^2 \text{ dm}^{-6}$ but the actual solubility is greater than that calculated from this extremely low figure, since the mercury in solution is present not only as Hg^{2+} but also as complex species. In acid solution $[\text{Hg}(\text{SH})_2]$ is probably formed and in alkaline

Table 29.3 Halides of zinc, cadmium and mercury (mp, bp, in parentheses)

Fluorides	Chlorides	Bromides	Iodides
ZnF ₂ white (872°, 1500°)	ZnCl ₂ white (275°, 756°)	ZnBr ₂ white (394°, 702°)	ZnI ₂ white (446°, d > 700°)
CdF ₂ white (1049°, 1748°)	CdCl ₂ white (568°, 980°)	CdBr ₂ pale yellow (566°, 863°)	CdI ₂ white (388°, 787°)
HgF ₂ white (d > 645°)	HgCl ₂ white (280°, 303°)	HgBr ₂ white (238°, 318°)	HgI ₂ α red, β yellow (257°, 351°)
Hg ₂ F ₂ yellow (d > 570°)	Hg ₂ Cl ₂ white (subl 383°)	Hg ₂ Br ₂ White (subl 345°)	Hg ₂ I ₂ yellow (subl 140°)

HgTe are easily obtained from the elements and have the zinc-blende structure.

29.3.2 Halides

The known halides are listed in Table 29.3. All 12 dihalides are known and in addition there are 4 halides of Hg₂²⁺ which are conveniently considered separately. It is immediately obvious that the difluorides are distinct from the other dihalides, their mps and bps being much higher, suggesting a predominantly ionic character, as also indicated by their typically ionic three-dimensional structures (ZnF₂, 6:3 rutile; CdF₂ and HgF₂, 8:4 fluorite). ZnF₂ and CdF₂, like the alkaline earth fluorides, have high lattice energies and are only sparingly soluble in water, while HgF₂ is hydrolysed to HgO and HF. The anhydrous difluorides can be prepared by the action of HF (in the case of Zn) or F₂ (Cd and Hg) on the metal.

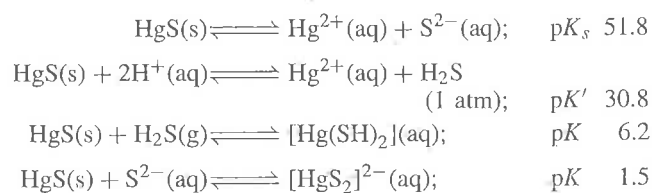
The other halides of Zn^{II} and Cd^{II} are in general hygroscopic and very soluble in water (~400 g per 100 cm³ for ZnX₂ and ~100 g per 100 cm³ for CdX₂). This is at least partly because of the formation of complex ions in solution, and the anhydrous forms are best prepared by

the dry methods of treating the heated metals with HCl, Br₂ or I₂ as appropriate. Aqueous preparative methods yield hydrates of which several are known. Significant covalent character is revealed by their comparatively low mps, their solubilities in ethanol, acetone and other organic solvents, and by their layer-lattice (2D) crystal structures. In all cases these may be regarded as close-packed lattices of halides ions in which the Zn^{II} ions occupy tetrahedral, and the Cd^{II} ions octahedral, sites. The structures of CdCl₂ (CdBr₂ is similar) and CdI₂ are of importance (Fig. 29.2) since they are typical of MX₂ compounds in which marked polarization effects are expected (see chap. 3, pp. 37–61 of ref. 9). Electron diffraction studies show that ZnX₂ (X = Cl, Br, I) have linear X–Zn–X structures in the gas phase.⁽¹²⁾

Concentrated, aqueous solutions of ZnCl₂ dissolve starch, cellulose (and therefore cannot be filtered through paper!), and silk. Commercially ZnCl₂ is one of the important compounds of zinc. It has applications in textile processing and, because when fused it readily dissolves other oxides, it is used in a number of metallurgical fluxes as well as in the manufacture of magnesia cements in dental fillings. Cadmium halides are used in the preparation of electroplating baths and in the production of pigments.

Covalency is still more pronounced in HgX₂ (X = Cl, Br, I) than in the corresponding

solution, [HgS₂]²⁻: the relevant equilibria are:



¹² M. HARGITTAI, J. TREMMEL and I. HARGITTAI, *Inorg. Chem.* **25**, 3163–6 (1986).

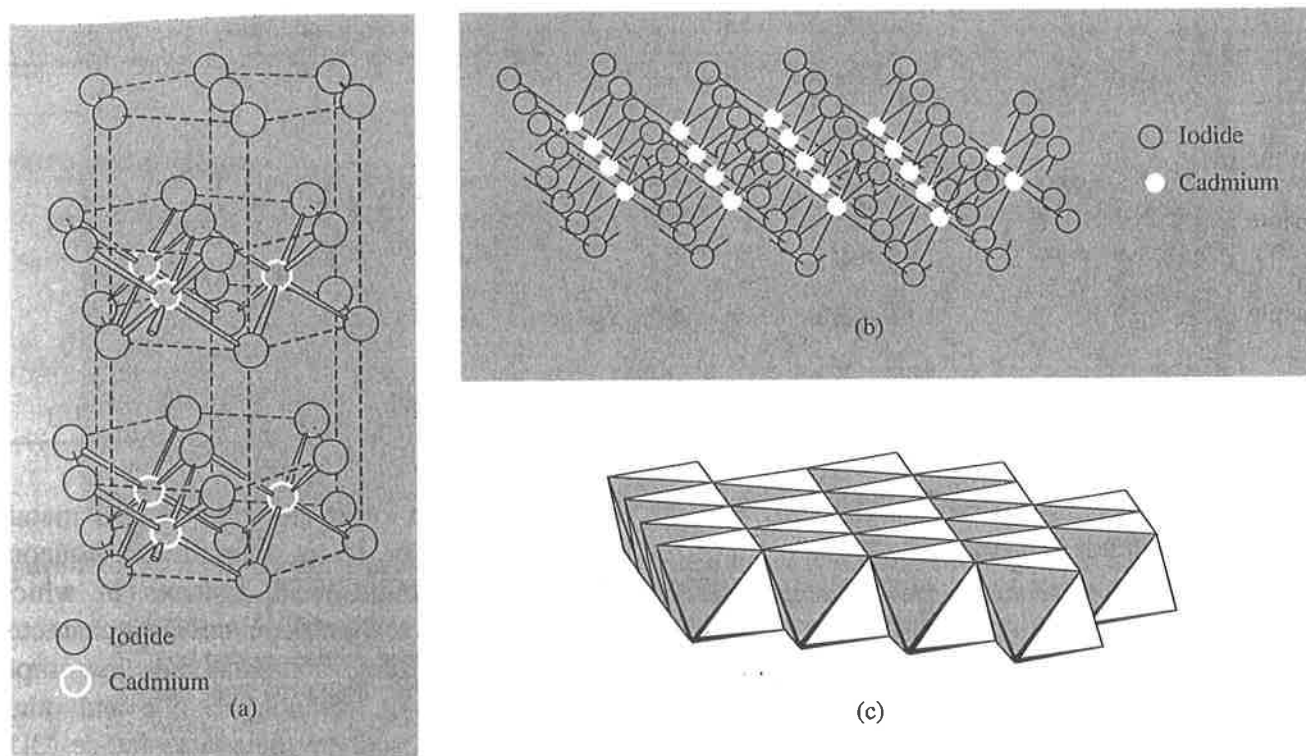


Figure 29.2 The layer structure of crystalline CdI_2 : (a) Shows the hexagonal close-packing of I atoms with Cd atoms in alternate layers of octahedral sites sandwiched between layers of I atoms. In CdCl_2 the individual composite layers are identical with those in CdI_2 , but they are arranged so that the Cl atoms are ccp. (b) Shows a portion of an individual composite layer of CdI_6 (or CdCl_6) octahedra. (c) Shows the same portion of a composite layer as in (b) and viewed from the same angle, but with CdI_2 (or CdCl_2) units represented by solid, edge-sharing octahedra.

halides of Zn and Cd. These compounds are readily prepared from the elements and are low-melting volatile solids, soluble in many organic solvents. Their solubilities in water, where they exist almost entirely as HgX_2 molecules, decrease with increasing molecular weight, HgI_2 being only slightly soluble, and they may be precipitated anhydrous from aqueous solutions by metathetical reactions. Their crystalline structures reveal an interesting gradation. HgCl_2 is composed of linear Cl-Hg-Cl molecules ($\text{Hg-Cl} = 225 \text{ pm}$ and the next shortest $\text{Hg} \cdots \text{Cl}$ distance is 334 pm); HgBr_2 and HgI_2 have layer structures. However, in the bromide although the Hg^{II} may be regarded as 6-coordinated, two Hg-Br distances are much shorter than the other four (248 pm compared to 323 pm). In the red variety of the iodide the Hg^{II} is unambiguously tetrahedrally 4-coordinated ($\text{Hg-I} = 278 \text{ pm}$). At temperatures above 126°C HgI_2 exists as a

less-dense, yellow form similar to HgBr_2 . In the gaseous phase all 3 of these Hg^{II} halides exist as discrete linear HgX_2 molecules. Comparison of the Hg-X distances in these molecules ($\text{Hg-Cl} = 228 \text{ pm}$, $\text{Hg-Br} = 240 \text{ pm}$; $\text{Hg-I} = 257 \text{ pm}$) with those given above, indicate an increasing departure from molecularity in passing from the solid chloride to the solid iodide.

HgCl_2 is the "corrosive sublimate" of antiquity, formerly obtained by sublimation from HgSO_4 and NaCl and used as an antiseptic. It is, however, a violent poison and was widely used as such in the Middle Ages.⁽⁵⁾

The halides are the most familiar compounds of mercury(I) and all contain the Hg_2^{2+} ion (see below). Hg_2F_2 is obtained by treating Hg_2CO_3 (itself precipitated by NaHCO_3 from aqueous $\text{Hg}_2(\text{NO}_3)_2$ which in turn is obtained by the action of dil HNO_3 on an excess of metallic mercury) with aqueous HF . It dissolves in water

but is at once hydrolysed to the "black oxide" which is actually a mixture of Hg and HgO. On heating, it disproportionates to the metal and HgF₂. The other halides are virtually insoluble in water and so, being free from the possibility of hydrolysis, may be precipitated from aqueous solutions of Hg₂(NO₃)₂ by addition of X⁻. Alternatively, they may be prepared by treatment of HgX₂ with the metal. Hg₂Cl₂ and Hg₂Br₂ are easily volatilized and their vapour densities correspond to "monomeric HgX". However, the diamagnetism of the vapour (Hg^I in HgX would be paramagnetic) and the ultraviolet absorption at the wavelength (253.7 nm) characteristic of Hg vapour, make it clear that decomposition to Hg + HgX₂ is the real reason for the halved vapour density. Hg₂I₂ decomposes similarly but even more readily, and the presence of finely divided metal is thought to be the cause of the greenish tints commonly found in samples of this otherwise yellow solid.

Calomel,[†] Hg₂Cl₂, has been widely used medicinally but possible contamination by the more soluble and poisonous HgCl₂ renders this a hazardous nostrum:

29.3.3 Mercury(I)

Raman spectra, indicative of [M-M]²⁺ ions, are produced by the yellow glass obtained from the melt of Zn in ZnCl₂ and also by the colourless, very moisture sensitive crystals of Cd₂Al₂Cl₈ obtained from melts of Cd in CdCl₂ and AlCl₃. X-ray studies show that the latter contains "ethane-like" [Cd₂Cl₆]⁴⁻ groups with Cd-Cd reported as 257.6 pm⁽¹³⁾ and 256.1 pm⁽¹⁴⁾ (cf 302 pm in the metal itself). The ¹¹³Cd nmr

spectrum⁽¹⁵⁾ of [Cd{HB(3,5-Me₂pz)₃}]₂ (pz = polycyclic pyrazolyl ligand) yields a ¹¹¹Cd-¹¹³Cd coupling constant of 20 646 Hz, indicating a Cd-Cd bond; the first to be observed in a molecular complex of Cd. However, only for mercury is the formal oxidation state I of importance.

Mercury(I) compounds in general may be prepared, like the halides just discussed, by the reduction of the corresponding Hg^{II} salt, often by the metal itself, or by precipitation from aqueous solutions of the nitrate. The nitrate is known as the dihydrate, Hg₂(NO₃)₂·2H₂O, and is stable in water if this is acidified, otherwise basic salts such as Hg(OH)(NO₃) are precipitated. The perchlorate is the only other appreciably soluble salt, the rest being either insoluble or, like the sulfate, chlorate and salts of organic acids, only sparingly soluble. In all cases the dinuclear Hg₂²⁺ ion is present rather than mononuclear Hg⁺. The evidence for this is overwhelming and includes the following:

- (1) In crystalline mercury(I) compounds, instead of the sequence of alternate M⁺ and X⁻ expected for MX compounds, Hg-Hg pairs are found in which the separation, though not constant, lies in the range 250-270 pm⁽⁵⁾ which is shorter than the Hg-Hg separation of 300 pm found in the metal itself.
- (2) The Raman spectrum of aqueous mercury(I) nitrate has, in addition to lines characteristic of the NO₃⁻ ion, a strong absorption at 171.7 cm⁻¹ which is not found in the spectra of other metal nitrates and is not active in the infrared; it is therefore diagnostic of the Hg-Hg stretching vibration since homonuclear diatomic vibrations are Raman active not infrared active.[†] Similar data have subsequently been produced for a number of other compounds in the solid state and in solution.

[†] Calomel, derived from the Greek words καλός (beautiful) and μέλας (black), seems an odd name for a white solid. It might arise from the colour of the material obtained when Hg₂Cl₂ is treated with ammonia; this is a product of variable composition (see below) which owes its colour to the presence of metallic mercury. Other more fanciful derivations are listed in the *Oxford English Dictionary* 2, 41 (1970).

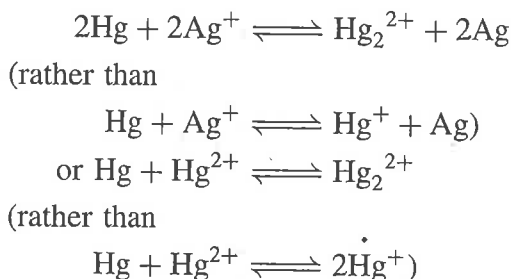
¹³ R. FAGGIANI, R. J. GILLESPIE and J. E. VEKRIS, *J. Chem. Soc., Chem. Commun.*, 517-8 (1986).

¹⁴ T. STAFFEL and G. MEYER, *Z. anorg. allg. Chem.* 548, 45-54 (1987).

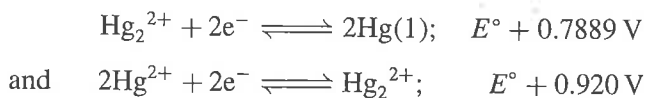
¹⁵ D. L. REGER, S. S. MASON and A. L. RHEINGOLD, *J. Am. Chem. Soc.* 115, 10406-7 (1993).

[†] Indeed, this is perhaps the earliest example of a new structural species to be established by Raman spectroscopy. (L. A. WOODWARD, *Phil. Mag.* 18, 823-7 (1934).)

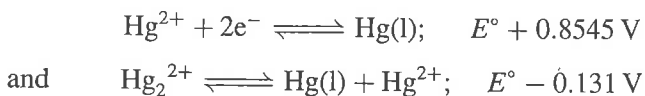
- (3) Mercury(I) compounds are diamagnetic, whereas the monatomic Hg^+ ion would have a $d^{10}s^1$ configuration and so be paramagnetic.
- (4) The measured emfs of concentration cells of mercury(I) salts are only explicable on the assumption that a 2-electron transfer is involved. This would not be the case if Hg^+ were involved: $[E = (2.303RT/nF) \log a_1/a_2]$ where $n = 2$ for Hg_2^{2+} and $n = 1$ for Hg^+ .
- (5) It is found that "equilibrium constants" are in fact only constant if the concentration $[\text{Hg}_2^{2+}]$ is employed rather than $[\text{Hg}^+]^2$, i.e. the equilibria must be of the type:



In order to understand the formation and stability of mercury(I) compounds it is helpful to consider the relevant reduction potentials:



From this it follows that



Now, $E^\circ = (RT/nF) \ln K$,

i.e. $E^\circ = (0.0591/n) \log_{10} K$

Hence, $\log_{10} K = -(0.131/0.0591) = -2.217$,

i.e. $K = [\text{Hg}^{2+}]/[\text{Hg}_2^{2+}] = 0.0061$

Thus, at equilibrium, aqueous solutions of mercury(I) salts will contain around 0.6% of mercury(II) and the rather finely balanced equilibrium is easily displaced. The presence of any reagent which reduces the activity (in effect the concentration) of Hg_2^{2+} more than that of Hg_2^{2+} , either by forming a less-soluble

salt or a more-stable complex of Hg^{2+} will displace the equilibrium to the right and cause the disproportionation of the Hg_2^{2+} . There are many such reagents, including S^{2-} , OH^- , CN^- , NH_3 and acetylacetone. This is why the most stable Hg_2^{2+} salts are the insoluble ones and why there are few stable complexes. Those which are known all involve either *O*- or *N*-donor ligands,[†] the linear $\text{O}-\text{Hg}-\text{Hg}-\text{O}$ group being a common feature of the former.

Polycations of mercury

The $\text{Hg}-\text{Hg}$ bond in Hg_2^{2+} may be ascribed to overlap of the 6s orbitals with little involvement of 6p orbitals or of the filled d^{10} shell of each atom. If this is regarded as the coordination of Hg to an Hg^{2+} cation, the coordination of a second Hg ligand is also feasible. Accordingly, $\text{Hg}_3(\text{AlCl}_4)_2$ can be obtained from a molten mixture of HgCl_2 , Hg and AlCl_3 and contains the discrete, virtually linear cation



in which the formal oxidation state of Hg is $+\frac{2}{3}$.

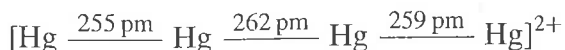
Still more interesting is the oxidation of Hg by AsF_5 in liquid SO_2 :^(16,17) in this process the AsF_5 serves both as an oxidant (being reduced to AsF_3) and also as a fluoride-ion acceptor to give AsF_6^- . In a matter of minutes the colour of the solution becomes bright yellow then deepens to red as the Hg simultaneously turns to a shiny golden-yellow solid; the solid then begins to dissolve to give an orange and, finally, a colourless solution. By controlling the quantity of oxidant, AsF_5 , and removing the solution at the appropriate stages, it is possible to crystallize a series of extremely moisture-sensitive materials:

[†] For this reason, although Hg_2^{2+} must be regarded as a class-b cation (e.g. the aqueous solubilities of its halides decrease in the order F^- to I^-), it is evidently less so than Hg^{2+} which has a notable preference for *S* donors.

¹⁶ I. D. BROWN, W. R. DATARS and R. J. GILLESPIE, pp. 1-41 in *Extended Linear Chain Compounds*, Plenum Press, New York, Vol. III (1982).

¹⁷ R. J. GILLESPIE, P. GRANGER, K. R. MORGAN and G. J. SCHROBILGEN, *Inorg. Chem.* 23, 887-91 (1984).

- (a) deep red-black $\text{Hg}_4(\text{AsF}_6)_2$, the cation of which is the almost linear



with Hg in the formal average oxidation state $+\frac{1}{2}$;

- (b) orange $\text{Hg}_3(\text{AsF}_6)_2$, containing the trimeric cation mentioned above; and
 (c) colourless $\text{Hg}_2(\text{AsF}_6)_2$, containing the dimeric Hg^{I} cation.

By working at lower temperatures (-20°C) to reduce the reaction rate, or by using specially designed apparatus which limits the access of AsF_5 to the Hg, it has been possible to isolate large single crystals of the intermediate golden-yellow solid having dimensions up to $35 \times 35 \times 2 \text{ mm}^3$. X-ray analysis, supported by neutron diffraction, shows that it consists of a tetragonal lattice ($a = b \neq c$) of octahedral AsF_6^- anions with two non-intersecting and mutually perpendicular chains of Hg atoms running through it in the a and b directions. Chemical analysis suggests the composition $\text{Hg}_3(\text{AsF}_6)$ and a formal oxidation state of $\text{Hg} = +\frac{1}{3}$. However, the measured Hg–Hg separation of 264 pm along the chains is not commensurate with the parallel dimensions of the lattice unit cell, $a = b = 754 \text{ pm}$ (cf. $3 \times 264 \text{ pm} = 792 \text{ pm}$) and implies instead the nonstoichiometric composition $\text{Hg}_{2.82}(\text{AsF}_6)$ or more generally $\text{Hg}_{3-\delta}(\text{AsF}_6)$ since the composition apparently varies with temperature. Partially filled conduction bands formed by overlap of Hg orbitals produce a conductivity in the a – b plane which approaches that of liquid mercury and the material becomes superconducting at 4 K.

Use of SbF_5 instead of AsF_5 produces a series of entirely analogous compounds including $\text{Hg}_{3-\delta}(\text{SbF}_6)$ but because the unit cell of the $(\text{SbF}_6)^-$ lattice is somewhat larger than that of $(\text{AsF}_6)^-$, it is formulated as $\text{Hg}_{2.90}(\text{SbF}_6)$. Oxidations of Hg by $\text{Hg}(\text{MF}_6)_2$ ($\text{M} = \text{Nb}, \text{Ta}$) in SO_2 also yield $\text{Hg}_{3-\delta}(\text{MF}_6)$ but, unlike the As and Sb compounds, these convert in a few hours into silver platelets of Hg_3MF_6 which consist of

two sheets of F atoms separated by hexagonal sheets (rather than linear chains) of Hg atoms.⁽¹⁸⁾

29.3.4 Zinc(II) and cadmium(II)⁽¹⁹⁾

The almost invariable oxidation state of these elements is +2 and, in addition to the oxides, chalcogenides and halides already discussed, salts of most anions are known. Oxo-salts are often isomorphous with those of Mg^{II} but with lower thermal stabilities. The carbonates, nitrates, and sulfates all decompose to the oxides on heating. Several, such as the nitrates, perchlorates and sulfates, are very soluble in water and form more than one hydrate. $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$ is probably the predominant aquo species in solutions of Zn^{II} salts. Aqueous solutions are appreciably hydrolysed to species such as $[\text{M}(\text{OH})(\text{H}_2\text{O})_x]^+$ and $[\text{M}_2(\text{OH})(\text{H}_2\text{O})_x]^{3+}$ and a number of basic (i.e. hydroxo) salts such as $\text{ZnCO}_3 \cdot 2\text{Zn}(\text{OH})_2 \cdot \text{H}_2\text{O}$ and $\text{CdCl}_2 \cdot 4\text{Cd}(\text{OH})_2$ can be precipitated. Distillation of zinc acetate under reduced pressure yields a crystalline basic acetate, $[\text{Zn}_4\text{O}(\text{OCOMe})_6]$. The molecular structure of this consists of an oxygen atom surrounded by a tetrahedron of Zn atoms bridged across each edge by acetates. It is isomorphous with the basic acetate of beryllium (p. 121) but, in contrast, the Zn^{II} compound hydrolyses rapidly in water, no doubt because of the ability of Zn^{II} to increase its coordination number above 4.

The coordination chemistry of Zn^{II} and Cd^{II} , although much less extensive than for preceding transition metals, is still appreciable. Neither element forms stable fluoro complexes but, with the other halides, they form the complex anions $[\text{MX}_3]^-$ and $[\text{MX}_4]^{2-}$, those of Cd^{II} being moderately stable in aqueous solution.⁽⁴⁾ By using the large cation $[\text{Co}(\text{NH}_3)_6]^{3+}$ it is also possible to isolate the trigonal bipyramidal $[\text{CdCl}_5]^{2-}$.

¹⁸ I. D. BROWN, R. J. GILLESPIE, K. R. MORGAN, Z. TUN and P. K. UMMAT, *Inorg. Chem.* **23**, 4506–8 (1984).

¹⁹ R. H. PRINCE, Zinc and Cadmium Chap. 56.1, pp. 925–1045, in *Comprehensive Coordination Chemistry*, Vol. 5, Pergamon Press, Oxford, 1987.

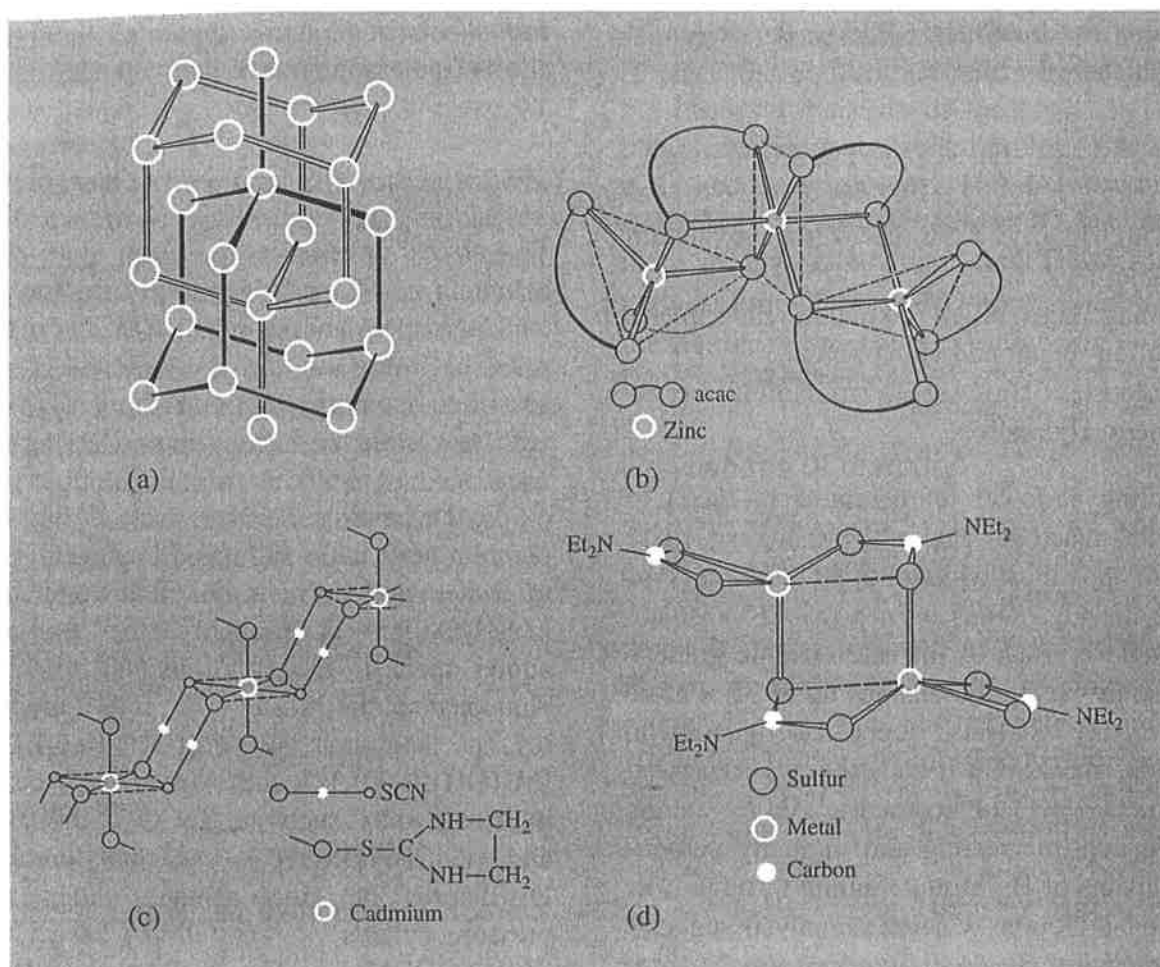


Figure 29.3 Some polymeric complexes: (a) Interpenetrating “adamantine” frameworks in $M(CN)_2$, $M = Zn, Cd$. (Only M shown; straight lines are CN forming linear $MCNM$ “rods”.) (b) $[Zn(acac)_2]_3$, (c) $[Cd\{S=C(NHCH_2)_2\}_2(SCN)_2]$, and (d) $[M(S_2CNEt_2)_2]_2$, $M = Zn, Cd, Hg$. (Note that M is 5-coordinate but with one $M-S$ distance appreciably greater than the other four.)

$[MX_3]^-$ and $[MX_4]^{2-}$ are formed in CH_3CN solutions also.⁽²⁰⁾ Tetrahedral complexes are the most common type and are formed with a variety of O -donor ligands (more readily with Zn^{II} than Cd^{II}), more stable ones with N -donor ligands such as NH_3 and amines. Some of the apparently 3-coordinate complexes have a higher coordination number because of aquation or association but, no doubt because the ligand is bulky, 2-coordinated Zn occurs in $[Zn\{N(CMe_3)(SiMe_3)\}]$, the first homoleptic zinc amide to be structurally characterized.⁽²¹⁾

The ability of CN^- to co-ordinate through either C or N has interesting stereochemical consequences. Crystalline $M(CN)_2$ consist of linear $M-C-N-M$ “rods” and tetrahedrally coordinated M^{II} , arranged so as to form interpenetrating “adamantine” frameworks (Fig. 29.3a). Each “rod” projects through a cyclohexane-like “window” of the other framework with the M atoms at each end occupying cavities of the other framework.⁽²²⁾ When aqueous solutions of $CdCl_2 + K[Cd(CN)_4]$ are left in contact with liquids such as $CCl_4, CMeCl_3, \dots, CMe_4$, crystals of the clathrates $Cd(CN)_2 \cdot G$ form at the interface

²⁰ D. P. GRADDON and C. S. KHOO, *Polyhedron* **7**, 2129–33 (1988).

²¹ W. S. REES JR., D. M. GREEN and W. HESSE, *Polyhedron*, **11**, 1697–9 (1992).

²² B. F. HOSKINS and R. ROBSON, *J. Am. Chem. Soc.* **112**, 1546–54 (1990).

of the immiscible liquids.⁽²³⁾ In these, the guest molecules G, occupy the cavities of a single adamantane framework. $(\text{NMe}_4)[\text{Cu}^{\text{I}}\text{Zn}(\text{CN})_4]$ consists of a similar framework but this time half the cavities are occupied by NMe_4^+ cations. Another type of framework is found in $\text{Cd}(\text{CN})_2 \cdot \frac{2}{3}\text{H}_2\text{O} \cdot \text{Bu}'\text{OH}$ which crystallizes from 50% aqueous $\text{Bu}'\text{OH}$ solutions of $\text{Cd}(\text{CN})_2$. It contains CdCNCD "rods" but this time they are bent, $\frac{2}{3}$ of the Cd atoms are tetrahedrally co-ordinated by 4CN^- , the other $\frac{1}{3}$ being octahedrally co-ordinated by 4CN^- and $2\text{H}_2\text{O}$. The result is a honeycomb framework with linear channels of hexagonal cross-section containing disordered $\text{Bu}'\text{OH}$ molecules.⁽²⁴⁾ Linear channels are also found in $\text{Cd}(\text{CN})_2 \cdot \text{G}$ ($\text{G} = \text{dmf}, \text{dmsO}$)⁽²⁵⁾ but the large cation in $(\text{PPh}_4)_3[(\text{CN})_3\text{CdCNCD}(\text{CN})_3]$ apparently prevents the formation of a 3D framework and instead stabilizes the discrete anion.⁽²⁶⁾

Complexes of higher coordination number are often in equilibrium with the tetrahedral form and may be isolated by increasing the ligand concentration or by adding large counter ions, e.g. $[\text{M}(\text{NH}_3)_6]^{2+}$, $[\text{M}(\text{en})_3]^{2+}$ or $[\text{M}(\text{bipy})_3]^{2+}$. With acetylacetone, zinc achieves both 5- and 6-coordination by trimerizing to $[\text{Zn}(\text{acac})_2]_3$ (Fig. 29.3b). Five-coordination is also found in adducts such as the distorted trigonal bipyramidal $[\text{Zn}(\text{acac})_2(\text{H}_2\text{O})]$ and $[\text{Zn}(\text{glycinate})_2(\text{H}_2\text{O})]$ while the hydrazinium sulfate $(\text{N}_2\text{H}_5)_2\text{Zn}(\text{SO}_4)_2$ contains 6-coordinated zinc. This is isomorphous with the Cr^{II} compound (p. 1031) and in the crystalline form consists of chains of Zn^{II} bridged by SO_4^{2-} ions, with each Zn^{II} additionally coordinated to two *trans*- N_2H_5^+ ions. The zinc porphyrin complex, $[\text{Zn}(\text{porph})(\text{thf})]$, (porph = *meso*-tetraphenyltetrabenzoporphyrin)

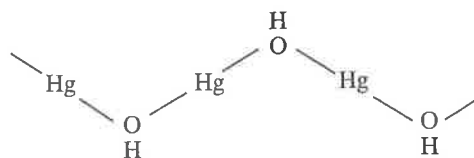
is approximately square pyramidal with thf at its apex. Being somewhat flexible the porphyrin is distorted into a saddle shape, 2 N being displaced above its mean plane and 2 N below it.⁽²⁷⁾

Complexes with SCN^- throw light on the relative affinities of the two metals for *N*- and *S*-donors. In $[\text{Zn}(\text{NCS})_4]^{2-}$ the ligand is *N*-bonded whereas in $[\text{Cd}(\text{SCN})_4]^{2-}$ it is *S*-bonded. SCN^- can also act as a bridging group, as in $[\text{Cd}\{\text{S}=\text{C}(\text{NHCH}_2)_2\}_2(\text{SCN})_2]$ when linear chains of octahedrally coordinated Cd^{II} are formed (Fig. 29.3c). A number of zinc-sulfur compounds are used as accelerators in the vulcanization of rubber. Among these are the dithiocarbamates, of which $[\text{Zn}(\text{S}_2\text{CNET}_2)_2]_2$, and the isostructural Cd^{II} and Hg^{II} compounds achieve 5-coordination by dimerizing (Fig. 29.3d).

Coordination numbers higher than 6 are rare and in some cases are known to involve chelating NO_3^- ions which not only have a small "bite" but, may also be coordinated asymmetrically so that the coordination number is not well defined.

29.3.5 Mercury(II)⁽²⁸⁾

The oxide (p. 1209), chalcogenides (p. 1210) and halides (p. 1211) have already been described. Of them, the only ionic compound is HgF_2 but other compounds in which there is appreciable charge separation are the hydrated salts of strong oxoacids, e.g. the nitrate, perchlorate, and sulfate. In aqueous solution such salts are extensively hydrolysed (HgO is only very weakly basic) and they require acidification to prevent the formation of polynuclear hydroxo-bridged species or the precipitation of basic salts such as $\text{Hg}(\text{OH})(\text{NO}_3)$ which contains infinite zigzag chains:



²³ T. KITAZAWA, S. NISHIKIORI, A. YAMAGISHI, R. KURODA and T. IWAMOTO, *J. Chem. Soc., Chem. Commun.*, 413-5 (1992); T. KITAZAWA, T. KIKOYAMA, M. TAKEDA and T. IWAMOTO, *J. Chem. Soc., Dalton Trans.*, 3715-20 (1995).

²⁴ B. F. ABRAHAMS, B. F. HOSKINS and R. ROBSON, *J. Chem. Soc., Chem. Commun.*, 60-1 (1990).

²⁵ J. KIM, D. WHANG, Y.-S. KOH and K. KIM, *J. Chem. Soc., Chem. Commun.*, 637-8 (1994).

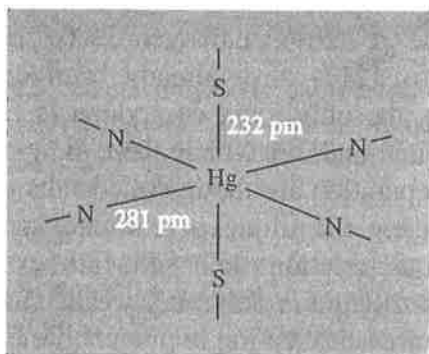
²⁶ T. KITAZAWA and M. TAKEDA, *J. Chem. Soc., Chem. Commun.*, 309-10 (1993).

²⁷ R.-J. CHENG, Y.-R. CHEN, S. L. WANG and C. Y. CHENG, *Polyhedron*, 12, 1353-60 (1993).

²⁸ K. BRODERSEN and H.-U. HUMMEL, Mercury, Chap. 56.2, pp. 1047-1130, in *Comprehensive Coordination Chemistry*, Vol. 5, Pergamon Press, Oxford, 1987.

Their ionic character is symptomatic of the marked reluctance of Hg^{II} to form covalent bonds to oxygen. In the presence of excess NO_3^- ions the aqueous nitrate forms the complex anion $[\text{Hg}(\text{NO}_3)_4]^{2-}$ in which 8 oxygen atoms from the bidentate nitrate groups are equidistant from the mercury at 240 pm, which is almost precisely the sum of the ionic radii (140 + 102 pm). Also, the unusual regular octahedral coordination is found in complexes with *O*-donor ligands: $[\text{Hg}(\text{C}_5\text{H}_5\text{NO})_6]^{2+}$ ($\text{Hg}-\text{O} = 235$ pm), $[\text{Hg}(\text{H}_2\text{O})_6]^{2+}$ ($\text{Hg}-\text{O} = 234$ pm), and $[\text{Hg}(\text{Me}_2\text{SO})_6]^{2+}$ ($\text{Hg}-\text{O} = 234$ pm). In contrast, the more covalently bonding β -diketonates do not form complexes.

The most usual type of coordination in compounds of Hg^{II} with other donor atoms is a distorted octahedron with 2 bonds much shorter than the other 4. In the extreme, this results in linear 2-coordination in which case the bonds are largely covalent. $\text{Hg}(\text{CN})_2$ is actually composed of discrete linear molecules (*C*-bonded CN^-), whereas crystalline[†] $\text{Hg}(\text{SCN})_2$ is built up of distorted octahedral units, all SCN groups being bridging:



With both these pseudo halides, an excess produces complex anions $[\text{HgX}_3]^-$ and the tetrahedral $[\text{HgX}_4]^{2-}$.

Similar halogeno complexes are produced in solution, and several salts of $[\text{HgX}_3]^-$ have been isolated and characterized; they display a variety of stereochemistries. In $[\text{HgCl}_3]^-$ the environment of the Hg^{II} is either distorted octahedral (with small cations such as NH_4^+

or Na^+) or distorted trigonal bipyramidal (with larger cations such as $[\text{NEt}_4]^+$, $[\text{SMe}_3]^+$ or $[\text{NH}_2\{(\text{CH}_2)_2\text{NH}_3\}_2]^{3+}$ ⁽²⁹⁾), whereas in salts of $[\text{HgBr}_3]^-$ and $[\text{HgI}_3]^-$ the coordination is more commonly distorted tetrahedral. In $[\text{NBu}_4^+][\text{HgI}_3^-]$ the anion is planar but, with one $\text{I}-\text{Hg}-\text{I}$ angle 115° , its symmetry is C_{2v} rather than D_{3h} . In aqueous solution spectroscopic evidence suggests that $[\text{HgCl}_3]^-$ is planar with $2\text{H}_2\text{O}$ completing a trigonal bipyramidal coordination sphere; $[\text{HgI}_3]^-$ is pyramidal with H_2O completing a tetrahedral coordination sphere, while $[\text{HgBr}_3]^-$ shows features of both structures.⁽³⁰⁾

In the presence of excess halide, $[\text{HgX}_4]^{2-}$ complex ions are produced and in comparison with those of Zn^{II} and Cd^{II} it can be seen that their stabilities increase with the sizes of the anion and the cation so that $[\text{HgI}_3]^{2-}$ is the most stable of all. Thus, the normally very insoluble HgI_2 will dissolve in aqueous solutions of I^- which can then be made strongly alkaline without precipitation occurring. Such solutions are known as Nessler's reagent, which is used as a sensitive test for ammonia since this produces a yellow or brown coloration due to the formation of $\text{Hg}_2\text{NI} \cdot \text{H}_2\text{O}$, the iodo salt of Millon's base (see p. 1220). Adducts of the halides HgX_2 , with *N*-, *S*-, and *P*-donor ligands are known, those with *N*-donors being especially numerous. Their stereochemistries are largely of the expected tetrahedral, or grossly distorted octahedral, types.

$\text{Hg}^{\text{II}}-\text{N}$ compounds^(5,28)

Mercury has a characteristic ability to form not only conventional ammine and amine complexes but also, by the displacement of hydrogen, direct covalent bonds to nitrogen, e.g.:



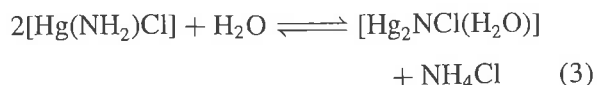
²⁹ The compound $[\text{NH}_2\{(\text{CH}_2)_2\text{NH}_3\}_2]_2\text{HgCl}_8$ contains the trigonal bipyramidal anion $[\text{HgCl}_5]^{3-}$; see L. P. BATTAGLIA, A. B. CORRADI, L. ANTOLINI, T. MANFREDINI, L. MENABUE, G. C. PELLACANI and G. PONTICELLI, *J. Chem. Soc., Dalton Trans.*, 2529-33 (1986).

³⁰ T. R. GRIFFITHS and R. A. ANDERSON, *J. Chem. Soc., Faraday*, **86**, 1425-35 (1990).

[†] Pellets of the dry powder, when ignited in air, form snake-like tubes of spongy ash of unknown composition — the so-called "Pharaoh's serpents".

Thus in the presence of an excess of NH_4^+ , which suppresses this forward reaction, and counteranions such as NO_3^- and ClO_4^- , which have little tendency to coordinate, complexes such as $[\text{Hg}(\text{NH}_3)_4]^{2+}$, $[\text{Hg}(\text{L-L})_2]^{2+}$ and even $[\text{Hg}(\text{L-L})_3]^{2+}$ ($\text{L-L} = \text{en}$, bipy, phen) can be prepared. But, in the absence of such precautions, amino, or imino-compounds are likely to be formed, often together. Because of this variety of simultaneous reactions and their dependence on the precise conditions, many reactions between Hg^{II} and amines, although first performed by alchemists in the Middle Ages, remained obscure until the application of X-ray crystallography and, still more recently, spectroscopic techniques such as nmr, infrared and Raman.

The action of aqueous ammonia on HgCl_2 , for instance, may be described by the three reactions:



In general, all these products are obtained in proportions which depend on the concentrations of NH_3 and NH_4^+ and on the temperature, but more or less pure products can be prepared by suitably adjusting the conditions.

The diammine $[\text{Hg}(\text{NH}_3)_2\text{Cl}_2]$, descriptively known as “fusible white precipitate”, can be isolated by maintaining a high concentration of NH_4^+ , since reactions (2) and (3) are thereby inhibited, or better still by using non-polar solvents. It is made up of a cubic lattice of Cl^- ions with linear $\text{H}_3\text{N}-\text{Hg}-\text{NH}_3$ groups inserted so as to give the common, distorted octahedral coordination about Hg^{II} ($\text{Hg}-\text{N} = 203 \text{ pm}$, $\text{Hg}-\text{Cl} = 287 \text{ pm}$) (Fig. 29.4a).

By using a low concentration of NH_3 and with no NH_4^+ initially present, the amide $[\text{Hg}(\text{NH}_2)\text{Cl}]$, “infusible white precipitate” is

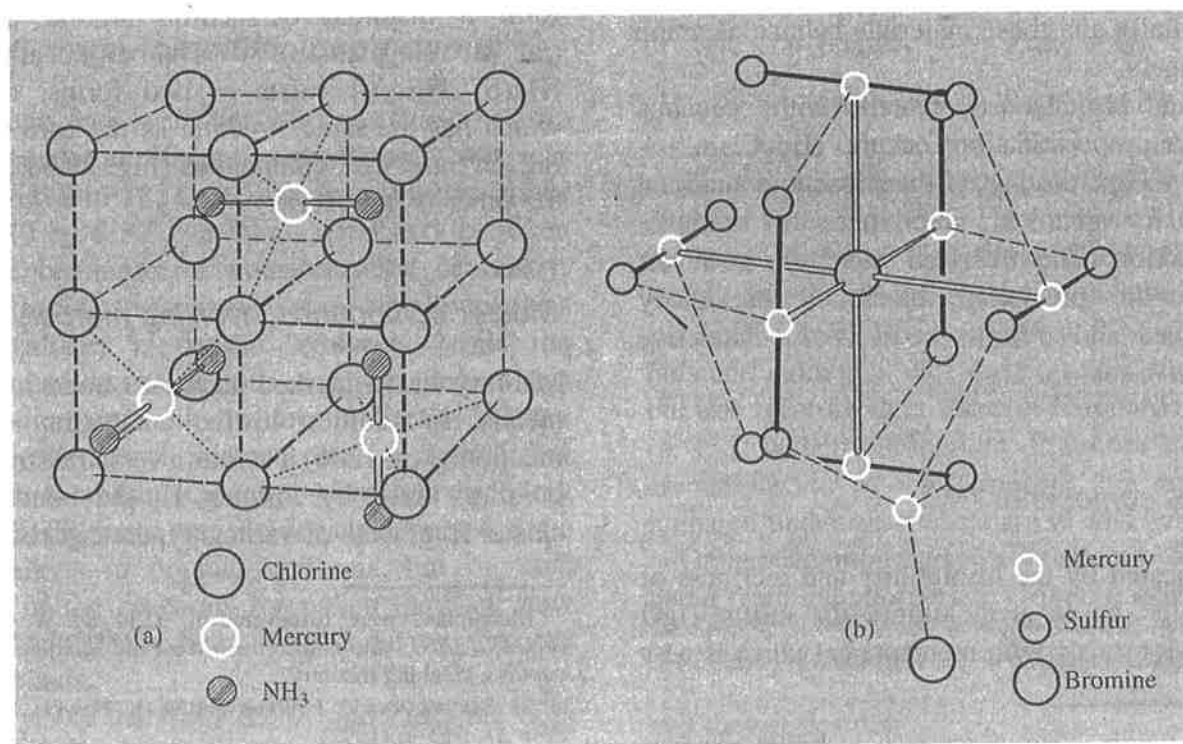
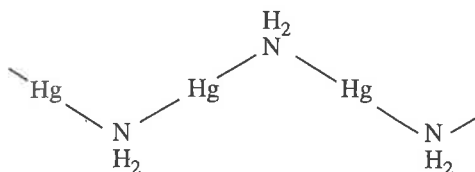


Figure 29.4 (a) Crystal structure of $\text{Hg}(\text{NH}_3)_2\text{Cl}_2$ showing linear $\text{NH}_3-\text{Hg}-\text{NH}_3$ groups inside a lattice of chloride ions. (b) Central $\text{Hg}_7\text{S}_{12}\text{Br}_2$ core of $[\text{Hg}_7(\text{SC}_6\text{H}_{11})_{12}\text{Br}_2]$ showing, in an idealized manner, the octahedron of Hg atoms around a central Br . The tetrahedral coordination of the seventh Hg is completed with the second Br .



obtained. This consists of parallel chains of $\{\text{Hg}(\text{NH}_2)\}_\infty$ as above, separated by Cl^- ions.

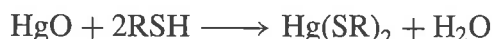
$[\text{Hg}_2\text{NCl}(\text{H}_2\text{O})]$ is the chloride of Millon's base, $[\text{Hg}_2\text{N}(\text{OH})\cdot(\text{H}_2\text{O})_2]$, and can be obtained either by heating the diammine, or amide with water or, better still, by the action of hydrochloric acid on Millon's base which is best prepared by the method, used in 1845 by its discoverer, of warming yellow HgO with aqueous NH_3 . Replacement of the OH^- yields a series of salts, $[\text{Hg}_2\text{NX}(\text{H}_2\text{O})]$, the structures of which (and that of the base itself) consist, with only minor variations, of a network of $\{\text{Hg}_2\text{N}\}^+$ units linked so that each N is tetrahedrally linked to 4 Hg and each Hg is linearly linked to 2 N ($\text{Hg}-\text{N} = 204\text{--}209\text{ pm}$ depending on X).⁽³¹⁾ The X^- ions and water molecules are accommodated interstitially and these materials behave as anion exchangers.

When Hg_2Cl_2 is treated with aqueous NH_3 disproportionation occurs ($\text{Hg}_2\text{Cl}_2 \longrightarrow \text{HgCl}_2 + \text{Hg}$); the HgCl_2 then reacts as outlined above to give a precipitate of variable composition. The liberated mercury, however, renders the precipitate black, as previously mentioned, and so forms the basis of a distinctive qualitative test for Hg_2^{2+} .

$\text{Hg}^{\text{II}}-\text{S}$ compounds⁽³²⁾

As indicated by the insolubility and inertness of HgS , Hg^{II} has a great affinity for sulfur. HgO reacts vigorously with mercaptans (which is why

RSH were given the name mercaptans[†]), displacing the H as with amines:



These mercaptides are low-melting solids, soluble in CHCl_3 and C_6H_6 . Though their structures depend on R and some, such as $\text{Hg}(\text{SR})_2$, ($\text{R} = \text{Bu}^t$, Ph) are polymers containing tetrahedral HgS_4 units, most contain linear (or nearly linear) $\text{S}-\text{Hg}-\text{S}$. Even in $[\text{Hg}(\text{SC}_6\text{H}_2\text{Bu}_3)_2(\text{py})]$ where the Hg is 3-coordinate and T-shaped the $\text{S}-\text{Hg}-\text{S}$ is still nearly linear (172°).⁽³³⁾ Most of the thioether (SR_2) complexes which have been prepared are adducts of the Hg^{II} halides and include both monomeric and polymeric (i.e. X-bridged) species as is the case with mixed thiolate-halide complexes. In $[\text{Hg}_7(\text{SC}_6\text{H}_{11})_{12}\text{Br}_2]$, which is obtained as colourless crystals when methanolic solutions of HgBr_2 and sodium cyclohexanethiolate are mixed, six Hg atoms are 4-coordinate but contain almost linear $\text{S}-\text{Hg}-\text{S}$ (av. angle = 159.3°) and the seventh Hg is tetrahedrally coordinated. The six Hg atoms form a distorted octahedron around a central Br (Fig. 29.4b).⁽³⁴⁾ The dithiocarbamate $[\text{Hg}(\text{S}_2\text{CNET}_2)_2]$ exists in two forms, one of which has the same structure as the corresponding Zn^{II} and Cd^{II} compounds (Fig. 29.3d), while the other is polymeric.

Cluster compounds involving mercury^(35,36)

Mercury has a marked ability to bond to other metals. In addition to the amalgams already mentioned (p. 1206) it acts as a versatile structural building block by forming $\text{Hg}-\text{M}$ bonds with cluster fragments of various types: e.g. reduction

[†] Mercaptans were discovered in 1834 by W. C. Zeise (pp. 930, 1167) who named them from the Latin *mercurium captans*, catching mercury.

³³ M. BOCHMANN, K. J. WEBB and A. K. POWELL, *Polyhedron* **11**, 513–6 (1992).

³⁴ T. ALSINA, W. CLEGG, K. A. FRASER and J. SOLA, *J. Chem. Soc., Chem. Commun.*, 1010–1 (1992).

³⁵ L. H. GADE, *Angew. Chem. Int. Edn. Engl.* **32**, 23–40 (1993).

³⁶ R. B. KING, *Polyhedron*, **7**, 1813–7 (1988).

³¹ A. F. WELLS, *Structural Inorganic Chemistry*, 5th edn., Oxford University Press, Oxford, 1984: the structural chemistry of mercury is reviewed on pp. 1156–69.

³² J. G. WRIGHT, M. J. NATAN, F. M. MACDONNELL, D. M. RALSTON and T. V. O'HALLORAN, *Prog. Inorg. Chem.* **38**, 323–412 (1990).

Table 29.4 Comparison of some typical organometallic compounds MR_2

R	Zn		Cd		Hg	
	MP/°C	BP/°C	MP/°C	BP/°C	MP/°C	BP/°C
Me	-29.2	46	-4.5	105.5	—	92.5
Et	-28	117	-21	64 (19 mmHg)	—	159
Ph	107	d 280	173	—	121.8 (subl)	204 (10 mmHg)

of $[\text{RhCl}(\text{PMe}_3)_3]$ with Na amalgams gives $\text{Hg}_6[\text{Rh}(\text{PMe}_3)_3]_4$ which consists of an Hg_6 octahedron, four faces of which are capped by $\text{Rh}(\text{PMe}_3)_3$ groups. Again, Hg^{II} halides react with carbonylate anions yielding products such as $[\text{Os}_3(\text{CO})_{11}\text{Hg}]_3$ comprising a most unusual "raft" structure in which three Os_3 triangles surround a central Hg_3 triangle in a planar array. From $[\text{Os}_{10}\text{C}(\text{CO})_{24}]^{2-}$ it is possible to obtain $[\text{Os}_{20}\text{Hg}(\text{C})_2(\text{CO})_{48}]^{2-}$ the central portion of which is an HgOs_2 triangle. Whereas the "raft" cluster has no redox chemistry, the $\{\text{Os}_{20}\text{Hg}\}$ cluster like the Os_{10} cluster (p. 1108) from which it is formed, gives rise to five different redox states.

29.3.6 Organometallic compounds⁽³⁷⁾

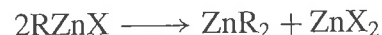
Although they were not the first organometallic compounds to be prepared (Zeise's salt was discovered in 1827) the discovery of zinc alkyls in 1849 by Sir Edward Frankland may be taken as the beginning of organometallic chemistry. Frankland's studies led to their employment as intermediates in organic synthesis, while the measurements of vapour densities led to his suggestion, crucial to the development of valency theory, that each element has a limited but definite combining capacity. After their discovery in 1900 Grignard reagents largely superseded the zinc alkyls in organic synthesis, but by then many of the reactions for which they are now used had already been worked out on the zinc compounds.

Alkyls of the types RZnX and ZnR_2 are both known and may be prepared by essentially the

original method of heating Zn with boiling RX in an inert atmosphere (CO_2 or N_2):



and then raising the temperature to distil the dialkyl:



These reactions work best with $\text{X} = \text{I}$ but the less-expensive RBr can be used in conjunction with a Zn-Cu alloy instead of pure Zn. Diaryls are best obtained from appropriate organoboranes or organomercury compounds:

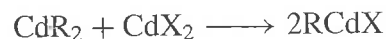


ZnR_2 are covalent, non-polar liquids or low-boiling solids (Table 29.4). They are invariably monomeric in solution with linear $\text{C}-\text{Zn}-\text{C}$ coordination at the Zn atom. They are very susceptible to attack by air and those of low molecular weight are spontaneously flammable, producing a smoke of ZnO . Their reactions with water, alcohols and ammonia, etc., are generally similar to, but less vigorous than, those of Grignard reagents (p. 132) with the important difference that they are unaffected by CO_2 ; indeed, they are often prepared under an atmosphere of this gas.

Organocadmium compounds are normally prepared from the appropriate Grignard reagents:



and then if desired:



They are thermally less stable than their Zn counterparts but generally less reactive (not normally

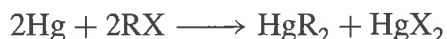
³⁷ J. L. WARDELL, *Organometallic Compounds of Zinc, Cadmium and Mercury*, Chapman & Hall, London, 1985, 220 pp.

catching fire in air), and so their most important use (but see also ref. 38) is to prepare ketones from acid chlorides:

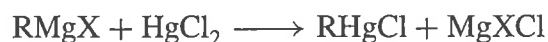


The use of Grignard reagents is impracticable here since they react further with the ketone.

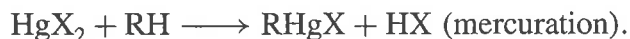
An enormous number of organomercury compounds are known. They are predominantly of the same stoichiometries as those of Zn and Cd, viz. $RHgX$ and HgR_2 , and may be prepared by the action of sodium amalgam on RX :



More usually they are made by the reaction of Grignard reagents on $HgCl_2$ in thf:



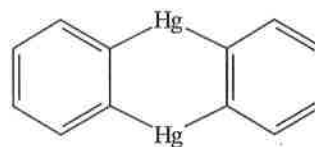
or simply by the action of HgX_2 on a hydrocarbon:



$RHgX$ are crystalline solids, and HgR_2 are extremely toxic liquids or low-melting solids (Table 29.4). They are essentially covalent materials except when $X^- = F^-$, NO_3^- or SO_4^{2-} , in which cases the former are water-soluble and apparently ionic, $[RHg]^+X^-$. There are several reasons for the attention which these compounds have received. The search for pharmacologically valuable drugs has provided a continuing stimulus, and the existence of convenient preparative methods, coupled with their remarkable stability to air and water, has led to their extensive use in mechanistic studies. This stability sets them apart from the organic derivatives of Zn, Cd and Group 2 metals but arises from the extreme weakness of the $Hg-O$ bond rather than an inherently strong $Hg-C$ bond. In fact the latter is weak, being commonly only $\sim 60 \text{ kJ mol}^{-1}$ and organomercury compounds are

thermally and photochemically unstable, in some cases requiring to be stored at low temperatures in the dark. Indeed, because of the weakness of the bond, Hg can be replaced by many metals which give stronger $M-C$ bonds and the preparation of organo derivatives of other metals (e.g. of Zn and Cd as referred to above) is the most important application of these compounds.

It appears that all $RHgX$ and HgR_2 compounds are made up of linear $R-Hg-X$ or $R-Hg-R$ units, which could arise from sp hybridization of the metal.[†] In some cases polymerization is necessary to achieve this linearity. Thus, for instance, *o*-phenylene-mercury, which could conceivably be formulated as



is in fact a cyclic trimer (Fig. 29.5a).⁽³⁹⁾ Organomercury compounds generally have little tendency to coordinate to further ligands. Exceptions include irregularly 3-coordinated $[HgMe(bipy)]NO_3$ ⁽⁴⁰⁾ and $[HgR(Hdz)]$,⁽⁴¹⁾ T-shaped $[Hg(2\text{-pyridylphenyl})Cl]$ ⁽⁴²⁾ (Fig. 29.5b, c, d) and the tetrahedral $[HgMe(np_3)]^+$ (np_3 is the "tripod" phosphine $N\{CH_2CH_2PPh_2\}_3$).⁽⁴³⁾

Among the versatile and synthetically useful reactions are those typified by the absorption of alkenes (olefins) by methanolic solutions of salts, particularly, the acetate of Hg^{II} . The products are not π complexes, but σ -bonded addition

[†] Other possibilities which have been suggested include ds hybridization and minimization of interaction between metal d and non bonding ligand p orbitals — see pp. 351–2 of ref. 32.

³⁹ D. S. BROWN, A. G. MASSEY and D. A. WICKENS, *Acta Cryst.* **B34**, 1695–7 (1978).

⁴⁰ A. J. CANTY and B. M. GATEHOUSE, *J. Chem. Soc., Dalton Trans.*, 2018–20 (1976).

⁴¹ A. T. HUTTON and H. M. N. H. IRVING, *J. Chem. Soc., Chem. Commun.*, 1113–4 (1979).

⁴² E. C. CON'TABLE, T. A. LEESE and D. A. TOCHER, *J. Chem. Soc., Chem. Commun.*, 570–1 (1989).

⁴³ C. A. GHILARDI, P. INNOCENTI, S. MIDOLLINI, A. ORLANDINI and A. VACCA, *J. Chem. Soc., Chem. Commun.*, 1691–3 (1992).

³⁸ P. R. JONES and P. J. DESIO, *Chem. Revs.* **78**, 491–516 (1978).

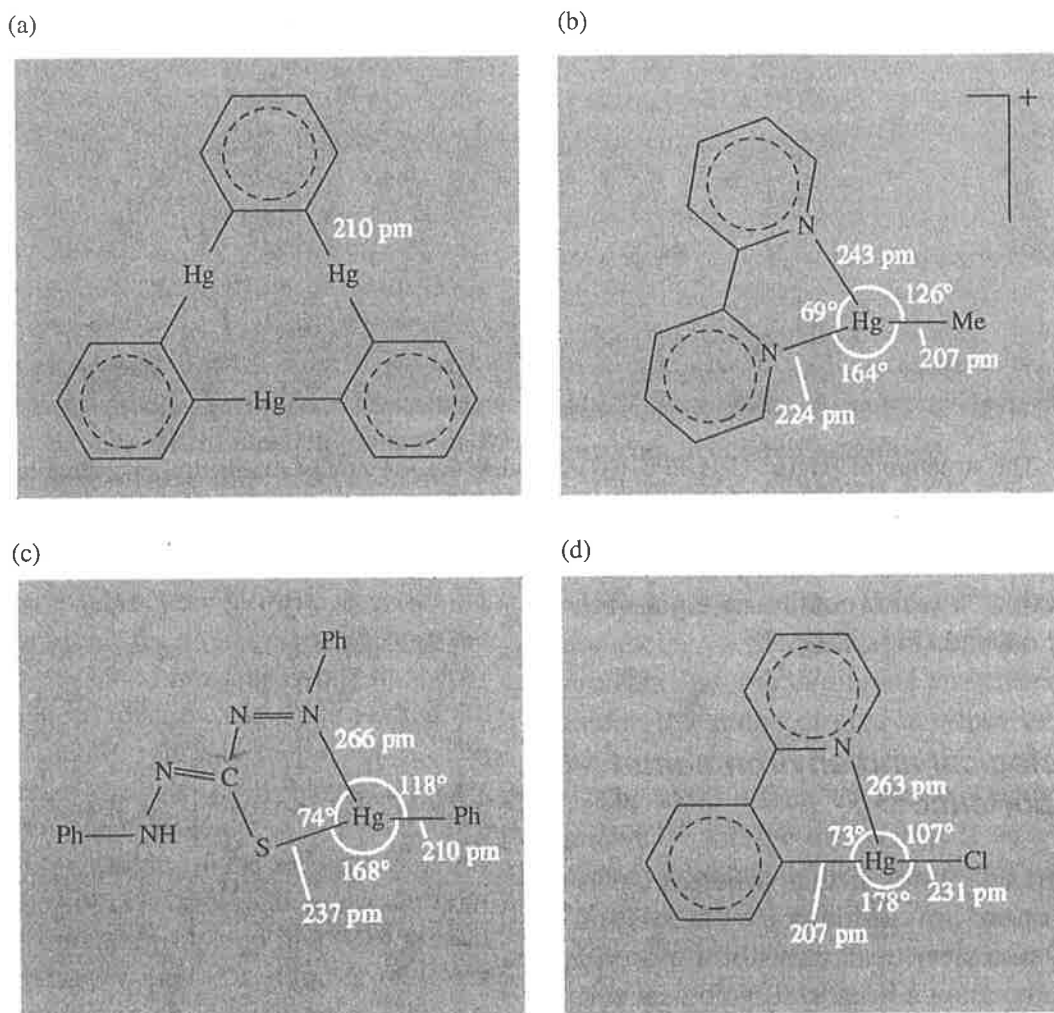
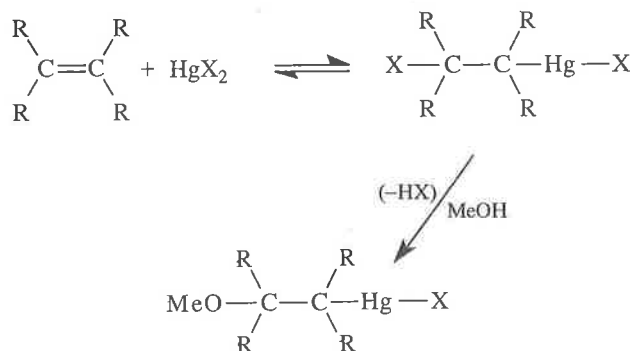
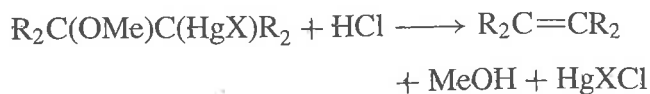


Figure 29.5 (a) *o*-Phenylenemercury trimer, (b) the planar cation in $[\text{HgMe}(\text{bipy})]\text{NO}_3$, (c) phenylmercury(II)di-thizonate, and (d) the approximately T-shaped $[\text{Hg}(\text{2-pyridylphenyl})\text{Cl}]$.

compounds, e.g.:



Regeneration of the alkene occurs on acidification, e.g. with HCl:

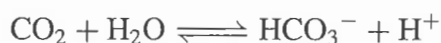


Methanolic solutions of Hg^{II} also absorb CO and the products, of the type $\text{XHgC}(=\text{O})\text{OMe}$ are again σ -bonded.

A similar reluctance to form π bonds is seen in the cyclopentadienyls of mercury such as $[\text{Hg}(\eta^1\text{-C}_5\text{H}_5)_2]$ and $[\text{Hg}(\eta^1\text{-C}_5\text{H}_5)\text{X}]$. As they are photosensitive and single crystals are very difficult to obtain, structural information has been derived mainly from infrared and nmr data. These show that the rings are monohapto and the compounds fluxional, i.e. the point of attachment of the Hg to the ring changes rapidly on the nmr time scale so that the 5 carbons are indistinguishable — the phenomenon of “ring whizzing”. In the case of $[\text{Hg}(\eta^1\text{-C}_5\text{H}_4\text{PPh}_3)\text{I}_2]_2$ it has been possible to determine the structure by

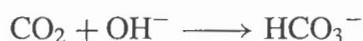
such as attack by the carboxyl group of a second glutamate residue in the enzyme have also been considered. In any event it is evident that the conformation of the enzyme provides a hydrophobic pocket, close to the Zn, which accommodates the non-polar side-chain of the protein being hydrolysed, and that this protein is, throughout, held in the correct position by H bonding to appropriate groups in the enzyme.

Carbonic anhydrase was the first Zn metalloenzyme to be discovered (1940) and in its several forms is widely distributed in plants and animals. It catalyses the equilibrium reaction:



In mammalian erythrocytes (red blood-cells) the forward (hydration) reaction occurs during the uptake of CO_2 by blood in tissue, while the backward (dehydration) reaction takes place when the CO_2 is subsequently released in the lungs. The enzyme increases the rates of these reactions by a factor of about one million.

The molecular weight of the enzyme is about 30 000 and the roughly spherical molecule contains just one zinc atom situated in a deep protein pocket, which also contains a number of water molecules arranged in an ice-like order. This Zn is coordinated tetrahedrally to 3 imidazole nitrogen atoms of histidine residues and to a water molecule. Once again the precise details of the enzyme's action are not settled, but it seems probable that the coordinated H_2O ionizes to give $\text{Zn}-\text{OH}^-$ and the nucleophilic OH^- then interacts with the C of CO_2 (which may be held in the correct position by H bonds to its two oxygen atoms) to yield HCO_3^- . This is equivalent to replacing the slow hydration of CO_2 with H_2O , by the fast reaction:



The latter would normally require a high pH and the contribution of the enzyme is therefore presumed to be the provision of a suitable environment, within the protein pocket, which allows the dissociation of the coordinated H_2O to occur in a medium of pH 7 which would otherwise be much too low.

A more recently established function of zinc is in proteins responsible for recognizing base-sequences in DNA and so regulating the transfer of genetic information during the replication of DNA. These so-called "zinc-finger" proteins contain 9 or 10 Zn^{2+} ions each of which, by coordinating to 4 amino acids, stabilizes a protruding fold (finger) in the protein. The protein wraps around the double strand of DNA, each of the fingers binding to the DNA, their spacing matching the base sequence in the DNA and thus ensuring accurate recognition.⁽⁵⁰⁾

Cadmium is extremely toxic and accumulates in humans mainly in the kidneys and liver; prolonged intake, even of very small amounts, leads to dysfunction of the kidneys. It acts by binding to the $-\text{SH}$ group of cysteine residues in proteins and so inhibits SH enzymes. It can also inhibit the action of zinc enzymes by displacing the zinc.

The toxic effects of mercury have long been known,⁽⁵⁾ and the use of HgCl_2 as a poison has already been mentioned. The use of mercury salts in the production of felt[†] for hats and the dust generated in ill-ventilated workshops by the subsequent drying process, led to the nervous disorder known as "hatter's shakes" and possibly also to the expression "mad as a hatter".

The metal itself, having an appreciable vapour pressure, is also toxic, and produces headaches, tremors, inflammation of the bladder and loss of memory. The best documented case is that of Alfred Stock (p. 151) whose constant use of mercury in the vacuum lines employed in his studies of boron and silicon hydrides, caused him to suffer for many years. The cause was eventually recognized and it is largely due to Stock's publication in 1926 of details of his experiences that the need for care and adequate ventilation is now fully appreciated.

⁵⁰ N. P. PAVLETICH and C. O. PABO, *Science* 261, 1701-7 (1993).

[†] It was apparently helpful to add Hg^{II} to the dil HNO_3 used to roughen the surface of the animal hair employed in the making of felt which is a non-woven fabric of randomly oriented hairs.

Still more dangerous than metallic mercury or inorganic mercury compounds are organomercury compounds of which the methyl mercury ion HgMe^+ is probably the most ubiquitous.⁽⁵¹⁾ This and other organomercurials are more readily absorbed in the gastrointestinal tract than Hg^{II} salts because of their greater permeability of biomembranes. They concentrate in the blood and have a more immediate and permanent effect on the brain and central nervous system, no doubt acting by binding to the $-\text{SH}$ groups in proteins. Naturally occurring anaerobic bacteria in the sediments of sea or lake floors are able to methylate inorganic mercury (Co-Me groups in vitamin B_{12} are able to transfer the Me to Hg^{II}) which is then concentrated in plankton and so enters the fish food chain.

The Minamata disaster in Japan, when 52 people died in 1952, occurred because fish, which formed the staple diet of the small fishing community, contained abnormally high concentrations of mercury in the form of MeHgSMe . This was found to originate from a local chemical works where Hg^{II} salts were used (inefficiently) to catalyse the production of

acetylene from acetaldehyde, and the effluent then discharged into the shallow sea. Evidence of a similar bacterial production of organomercury is available from Sweden where methylation of Hg^{II} in the effluent from paper mills has been shown to occur. The use of organomercurials as fungicidal seed dressings has also resulted in fatalities in many parts of the world when the seed was subsequently eaten.

It is now apparent that bacteria have developed resistance to heavy metals and the detoxifying process is initiated and controlled by *metallo-regulatory* proteins which are able selectively to recognize metal ions. MerR is a small DNA-binding protein which displays a remarkable sensitivity to Hg^{2+} . The metal apparently binds to S atoms of cysteine and this has been a major incentive to recent work on Hg-S chemistry.⁽³²⁾

Public concern about mercury poisoning has led to more stringent regulations for the use of mercury cells in the chlor-alkali industry (pp. 71–3, 798). The health record of this industry has, in fact, been excellent, but the added costs of conforming to still higher standards have led manufacturers to move from mercury cells to diaphragm cells, and this change has been made a legal requirement in Japan.

⁵¹ S. KRISHNAMURTHY, *J. Chem. Ed.* **69**, 347–50 (1992).