THE
CHEMICAL ELEMENTS
AND THEIR COMPOUNDS

BY

N. V. SIDGWICK

FELLOW OF LINCOLN COLLEGE
HON. STUDENT OF CHRIST CHURCH
FORMERLY PROFESSOR OF CHEMISTRY
IN THE UNIVERSITY OF OXFORD

VOLUME I

OXFORD
AT THE CLARENDON PRESS

THE
CHEMICAL ELEMENTS
AND THEIR COMPOUNDS

PREFACE

THIS book is an attempt to discuss in detail the properties of the elements and their compounds in the light of modern ideas of atomic and molecular structure. The development of these ideas in the last thirty years has made it possible to transform 'Inorganic' Chemistry from a mass of disconnected facts into an ordered system of relations. Inorganic text-books are, however, usually so over-burdened with the details of mineralogy, metallurgy, technical chemistry, and analysis that hardly any space is left for the considerations of the theoretical relations; while the customary exclusion of all but the simplest compounds of carbon deprives us of the help of the best-known and most important of the elements. I have tried to avoid these errors both of excess and of defect, and to give an account of the compounds of all the elements, with special reference to the general relations between them. The basis of classification is, of course, the Periodic Table, the simplest arrangement for exhibiting the relations of the elements.

Among my many obligations I must first express my indebtedness to the great Handbooks of Abegg and of Gmelin (8th edition), as well as to the Abstracts published by the British and the American Chemical Societies: to Professor Linus Pauling's *Chemical Bond* (Cornell University Press, 2nd edition, 1942): and to the *Structural Inorganic Chemistry* of A. F. Wells (Clarendon Press, 1945). The numerous valuable monographs on particular branches of the subject that I have consulted are acknowledged in their places. But I would particularly mention the *Thermochemistry* of F. R. Bichowski and F. D. Rossini (Reinhold, New York, 1936): G. W. Wheland's *Theory of Resonance and its Application to Organic Chemistry* (Wiley, New York, 1944): and the *Chemie der metall-organischen Verbindungen* of E. Krause and A. v. Grosse (Borntraeger, Berlin, 1937).

Among those from whom I have received personal help I must in the first place express my deep gratitude to Professor Linus Pauling, who, in addition to publishing a book of the first importance on molecular structure, has, especially during his residence in Oxford as Eastman Professor, given up much time to answering my questions on a whole series of points large and small, and has read and criticized in detail my introductory section. To my colleagues in Oxford, and especially to Dr. L. E. Sutton of Magdalen College, and to Mr. H. M. Powell, University Reader in Chemical Crystallography, I am very grateful for help and advice on many points. I owe more than I can say to the late Dr. R. V. G. Ewens, formerly Scholar of this College, and Reader in Chemistry at Guy's Hospital Medical School, who up to his untimely death had read nearly the whole of my manuscript, and made numerous corrections and modifications of the greatest value to me. Dr. M. W. Lister of Harwell, now Assistant Professor of Chemistry at Toronto University, has read the whole book in proof and detected many errors. I have been greatly helped by him and by Dr. Charles Coryell of the

Massachusetts Institute of Technology in my account of the uranide elements. In the laborious checking of the numerous references I have had the assistance of Mr. W. T. L. Neal of Exeter College, Mr. B. B. Goalby of New College, Mr. M. F. Hoare of The Queen's College, and Mr. A. Mackay of this College. The indexes were compiled with the help of Mr. C. P. Horgan of Trinity College.

The references I have tried to bring up to the summer of 1948; but the delays· in the publication of original papers and abstracts, and in some subjects the restrictions of military secrecy, make it peculiarly difficult to assign an exact term to this in the immediate post-war years. Many of the statements in this book already need correction and amplification, but that is inevitable in so rapidly advancing a subject.

LINCOLN COLLEGE
    OXFORD
May 1949

ABBREVIATIONS

Journals

Ann. Liebig's *Annalen der Chemie.*

Ann. Rep. Chem. Soc. *Annual Reports of the Chemical Society.*

Atti R. *Atti della Reale Accademia dei Lincei.*

Ber. *Berichte der Deutschen Chemischen Gesellschaft.*

Bull. Soc. *Bulletin de la Société Chimique de France.*

C. or Chem. Centr. *Chemisches Centralblatt.*

C.E.N. *Chemical and Engineering News* (Washington).

C.R. *Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.*

Gaz. *Gazzetta Chimica Italiana.*

J.A.C.S. *Journal of the American Chemical Society.*

J.C.S. *Journal of the Chemical Society.*

J.S.C.I. *Journal of the Society of Chemical Industry.*

Mon. *Monatshefte für Chemie.*

Trans. Far. Soc. *Transactions of the Faraday Society.*

Books

Abegg. R. Abegg *et al. Handbuch der anorganischen Chemie.* Hirzel, Leipzig, 1905–

Gmelin. *Gmelin's Handbuch der anorganischen Chemie.* Verlag Chemie, Berlin, 8th edition, 1924–

Chem. Bond. L. Pauling, *The Nature of the Chemical Bond.* Cornell Press, 1939, 2nd edition, 1942.

E.T.V. N. V. Sidgwick, *Electronic Theory of Valency.* Clarendon Press, 1927.

Krause and v. Grosse. E. Krause and A. v. Grosse, *Die Chemie der metall-organischen Verbindungen.* Borntraeger, Berlin, 1837.

M.I. C. Willgerodt, *Organische Verbindungen mit mehrwertigem Iod.* Enke, Stuttgart, 1914.

N. Ansch. A. Werner, *Neuere Anschauungen auf dem Gebiete der anorganischen Chemie.* Vieweg, Brunswick (1st edition, 1905 ; 3rd, 1913 ; 5th, revised by P. Pfeiffer, 1923).

NN. I. and W. Noddack, *Das Rhenium.* Voss, Leipzig, 1933.

S.I.C. A. F. Wells, *Structural Inorganic Chemistry.* Clarendon Press, 1945.

Wheland, Resonance. *G. W. Wheland, The Theory of Resonance and its Application to Organic Chemistry.* New York and London, 1944.

---

c = Velocity of light ⎫ see p. xii.
h = Planck's Constant ⎭

ν = Frequency (vibrations per second).

E.A.N. Effective Atomic Number (see p. xvii).

Polar should be used only in the strict sense, meaning 'having a dipole moment'.

Sol^v: grs. anhydrous substance dissolving in 100 grs. solvent.

Square brackets [ ]: (1) in reaction kinetics mean concentrations (usually in moles per litre); (2) in formulae indicate ions.

et al. = and others (authors).

Greek and Latin numerical prefixes (*uni* = mono; *ter* = tri; *sexa* = hexa, &c.) are used indifferently; the supposed objection to 'hybrid' words, of which the first part is derived from Greek and the second from Latin, if it were valid would require us to say quadrifluoride but tetrachloride, would reject 'metastable', and would condemn the Church of England for speaking of the Pananglican Synod. Note that ennea = 9 and dodeca = 12. Symbols like al, hg, mean atom/valency (al = $\frac{1}{3}$ Al : hg = $\frac{1}{2}$ Hg).

In types of formulae A is as a rule put for the central atom and B for the covalently attached atoms. R is used for alkyls or aryls, X for halogens and other monovalent radicals (ionized or not), and Am for NH_3 and similar amines. Other abbreviations are Alk = alkyl; Ar = aryl; Me, Et, Pr, Bu, &c. = methyl, ethyl, propyl, butyl, &c.; Φ = phenyl (C_6H_5); Bz = benzyl ($C_6H_5 \cdot CH_2$); py = pyridine; en or *en* ethylenediamine; Ox = oxalato-group (C_2O_4); Cy = CN. A is sometimes used for the monovalent radical of a diketone or keto-ester (as $C_5H_7O_2$ from $C_5H_8O_2$, acetyl acetone).

SOME USEFUL PHYSICAL CONSTANTS

Lengths: 1 μ = 10^{-4}; 1 $\mu\mu$ = 10^{-7}; 1 A or A.U. = 10^{-8} cm. 1 X unit for X-rays = 1/1000 A (strictly 1/1002 A).

Velocity of light, $c = 2 \cdot 99776 \times 10^{10}$ cm./sec.

Quantum Theory: Energy $E = h\nu$, where ν = frequency (vibrations/second) and h (Planck's constant) = $6 \cdot 620 \times 10^{-27}$ erg-seconds.

Absolute zero = $0°$ K. = $-273 \cdot 16°$ C.

1 calorie = $4 \cdot 183 \times 10^7$ ergs = $4 \cdot 183$ joules.

1 electron-volt (e.v., energy acquired by an electron in moving through a potential drop of 1 volt) is equal to $1 \cdot 591 \times 10^{-12}$ erg, or $23 \cdot 07$ k.cals. per g.-molecule.

1 Faraday = 96,500 coulombs.

Light Quanta

Wave-number = waves per cm. = frequency/c.

Quantum of wave-length 7,000 A (red end of visible) = $40 \cdot 8$ k.cals./g.-mol.: of wave-length 4,000 A (violet end) = $71 \cdot 4$ k.cals./g.-mol.

Factors for Absorption and Emission Spectra

Transition	Energy		Wave-length	Wave number, cm.$^{-1}$
	E. volts	Ht/g.-mol.		
Electronic	1–10	23–230 k.cals.	12,350 to 1,235 A	8,100 to 81,000
Oscillational or Vibrational	1/10	2·3 k.cals.	123,500 A = 12·35 μ	810
Rotational	1/1000	23 cals.	1,235 μ = 0·1235 cm.	8·1

Einstein's Equivalence of Mass and Energy

$E = mc^2$. Hence the mass of one hydrogen atom corresponds to 940 million e.v., or of 1 gramme to 2.2×10^{10} k.cals.

Gas constant $R = 1.9885$ cals./degree C.

Avogadro Number N (molecules in 1 g.-molecule) $= 6.025 \times 10^{23}$.

Mean translational energy of N gas molecules at T° is RT, $= ca.$ 600 k.cals. at 25° C.

The fraction N_1/N of the molecules of a gas that have energies of nE or above (where E is the mean energy) is for

$$n = \qquad 5 \qquad\qquad 10 \qquad\qquad 50$$
$$N_1/N = 6.8 \times 10^{-3} \qquad 4.5 \times 10^{-5} \qquad 3.7 \times 10^{-22}$$

There are two scales of atomic weights in use, one physical and the other chemical. On the physical scale the unit is $\frac{1}{16}$th of the mass of the commonest isotope of oxygen ($^{16}O = 16.000$); on the chemical scale it is $\frac{1}{16}$th of the mean atomic mass of the ordinary mixture of oxygen isotopes ($0 = 16.000$). According to Aston (1942) the ratio

$$\frac{\text{Unit of Chemical Atomic Weight}}{\text{Unit of Physical Atomic Weight}} = 1.000275.$$

INTRODUCTION

FUNDAMENTAL PARTICLES[1,2]

THE fundamental particles of which the universe is now believed to be composed are given in the following table, with their dates of discovery, electric charges ($e = 4 \cdot 802 \times 10^{-10}$ E.S.U.),[3] masses (on the physical scale, where $^{16}0 = 16 \cdot 000$), and their average lives.

Particle	Date of discovery	Charge	Mass	Life
Proton	. .	$+e$	$1 \cdot 00758$	Infinite
Neutron	1932	0	$1 \cdot 00894^{a,b}$	Infinite
Electron	1897	$-e$	$0 \cdot 000548^{c}$ (H/1838)	Infinite
Positron	1932	$+e$	$0 \cdot 000548$	ca. 10^{-9} sec.
Meson*	1935	$\{-e, +e$ $(?$ also 0$)$	ca. H/9 and H/6	ca. 10^{-6} sec.
Neutrino	1934	0	? 10^{-18}	. .

$$a = {}^4, \ b = {}^5, \ c = {}^6.$$

Of these the first three alone are of primary importance for chemistry. The proton is, of course, the hydrogen nucleus or positive hydrogen ion (see I. 26).

The neutron[9,10] with a mass number of 1 and an atomic number of zero may be called the first element of the Periodic Table, but as it can hold no electrons it has no chemical properties. Owing to the absence of charge it has an enormous penetrating power; while a proton of velocity 30,000 km./sec. ($c/10$) will travel only one foot in air, a neutron may go several miles in air before it loses all its energy, making only a few collisions on the way. The absence of charge also makes the neutron a very effective projectile for nuclear disruption, since it is not repelled by the nuclear charge as an α-particle would be. If neutrons could be concentrated they would

* There probably[7,8] are at least two kinds of mesons, one with a mass equal to about 200 electrons, and the other about 320. The heavier kind were made artificially in the big Berkeley cyclotron, by passing 380 m.e.v. α-particles through thin plates of beryllium, carbon, or copper.[8]

[1] R. E. Peierls, *Nature*, 1946, **158**, 773.

[2] L. Pauling, *General Chemistry*, S. Francisco, 1947, p. 570.

[3] V. D. Hopper and T. H. Laby, *Proc. Roy. Soc.* 1941, **178**, 243; T. H. Laby, *Nature*, 1942, **150**, 648.   [4] D. J. Hughes, *Phys. Rev*, 1946, ii. **70**, 219.

[5] W. E. Stephens, *Rev. Mod. Phys.* 1947, **19**, 19.

[6] R. T. Birge, *Phys. Rev.* 1941, ii. **60**, 766.

[7] J. Rüling and R. Steinmauer, *Experientia*, 1946, **2**, 108.

[8] See *Chem. and Eng. News*, 22 Mar. 1948 (p. 850).

[9] J. Chadwick, *Nature*, 1932, **129**, 312; *Proc. Roy. Soc.* 1932, **136**, 692; ib. 1933, **142**, 1 (Bakerian Lecture).

[10] See also P. B. Moon, *Ann. Rep. Chem. Soc.* for 1938, **35**, 21.

form a gas half as dense as hydrogen; the idea that liquid neutrons would have an enormous density (with a radius of 2×10^{-13} cm. one c.c. would weigh 25 million tons) is fallacious; the half quantum of zero-point energy (see under helium p. 7) would bring its effective radius nearly up to that of an ordinary atom.

A list of the International Atomic Weights of the elements is given in Table I (p. xxiii).

ATOMIC STRUCTURES

The nucleus of every atom except hydrogen is made up of protons and neutrons; if the mass number is N and the atomic number Z it consists of Z protons and N—Z neutrons; two isotopes have the same Z but different Ns. In a β-ray change we must suppose that a neutron changes into a proton with the emission of an electron. In the neutral atom the nucleus is surrounded by as many electrons as it contains protons; the atomic number is (1) the ordinal number of the element in the periodic system, (2) the number of protons in, and hence the positive charge of, its nucleus, and (3) the number of electrons surrounding the nucleus in the neutral isolated atom.

The electrons are arranged* in groups or shells according to their principal quantum numbers 1, 2, 3, &c. (K, L, M, N, O, P, Q, . . .); the electrons of each group are further divided into subgroups ($s, p, d, f, \ldots$); the maximum number of subgroups is equal to the principal quantum number, and the largest number of electrons that each subgroup can contain is:

Subgroup	s	p	d	f
Max. No.	2	6	10	14

Hence the maximum size of the groups of principal quantum numbers 1, 2, 3, 4, . . . n is 2, 8, 18, 32, . . . $2n^2$.

A list of the structures of the elements is given in Table II, p. xxiv.

THE PERIODIC CLASSIFICATION

The periodic relations of the elements (Newlands, 1864; Mendeleeff, 1869; Lothar Meyer, 1870) can be expressed in two ways, each of which has its advantages. The form adopted by Bohr (Table III), in which each period, beginning and ending with an inert gas, is written in one line, shows most clearly the development of the atomic structures. The elements in brackets are those with an incomplete (between 8 and 18) electronic group in the core (i.e. as well as the outermost valency group); those within double brackets (the lanthanide and uranide elements) have two such groups, the second being between 18 and 32.

The second form of the table, due originally to Mendeleeff (Table IV), is more useful for bringing out the chemical similarities (which are so

---

* For an explanation of the atomic structures see L. Pauling and E. Bright Wilson, Jr., *Introduction to Quantum Mechanics*, McGraw-Hill, New York, 1935.

dependent on the valencies), and is the one adopted in the following chapters. There are nine groups, each except the first and the last with two subgroups. The elements of the Nth group are (with an obvious modification for Group VIII and for the lanthanides and the uranides) those which have either N electrons more than the preceding, or 8—N less than the following inert gas; in the first two (typical and sub-typical) periods one element satisfies both conditions; in the later periods there are two, the elements of the first kind forming subgroup A, and those of the second subgroup B.

MOLECULAR STRUCTURE

The atoms in a molecule are held together through their electrons, and essentially in two ways: (1) by the transfer of electrons from one atom to another, giving rise to an electrostatic (Coulomb) attraction (electro-valency, Kossel, 1916), and (2) by the sharing of pairs of electrons between two atoms, so that in a sense they belong to both (covalency: G. N. Lewis, 1916); the pair may either come one from each atom (normal) or both from one of them (co-ordinate or dative). The conditions which favour the passage of an electrovalency into a covalency are (Fajans, 1923–5) (1) a large charge on the ion, (2) a small size of the cation, (3) a large size of the anion, (4) the possession by the cation of a structure which is not that of an inert gas.

The effective atomic number (E.A.N.) of an atom in a molecule is the number of electrons which it has after these changes, and so is the atomic number plus 1 for each anionic charge, and for every electron from another atom which it shares, and minus 1 for each electron which it loses in becoming a cation. The valency of the atom is the difference between the number of unshared electrons in the isolated atom (the atomic number) and the number in the combined atom (Grimm and Sommerfeld, 1926); its covalency is the number of pairs of shared electrons that it holds. The maximum value of the covalency is limited (save under exceptional circumstances) in accordance with the period of the atom in the table, being 4 for the first short period (Li—F), 6 for the second short and first long periods (Na—Cl, K—Br), and 8 for the heavier elements.

RESONANCE[11]

This crude picture of atomic linkages is considerably modified in practice. Covalent links can sometimes be formed by one or by three electrons, and the links in molecules are often (perhaps usually) of an intermediate or mixed character, owing to the phenomenon of resonance. The equations of wave mechanics show that if a molecule can be represented, on the ordinary structural theory, by two different structures, then under certain

[11] See Pauling, especially *Chemical Bond*, ed. 2, pp. 124–59; G. W. Wheland, *Theory of Resonance and its Application to Organic Chemistry* (New York, 1944), pp. 1–28.

conditions its actual state is not given by either, nor by a mixture of the two in chemical (tautomeric) equilibrium, but is a hybrid between them, and has to some extent the properties of both. The conditions which must be satisfied for this resonance to be possible are three: (1) the positions of the atoms in the two structures must be nearly the same, (2) the energy contents of the two (their relative stabilities) must not differ too greatly, the state of the hybrid being nearer to the more stable form, and (3) the number of unpaired (not of unshared) electrons must be the same in both; this last condition is almost always fulfilled. The resonance produces two important effects: (A) the energy content of the molecule is less, and its stability greater, than in either form, and hence the resonance must always occur when the conditions 1–3 are satisfied; (B) the linked atoms are rather closer together than in either separate form, owing to the greater strength of the link; this result is of great diagnostic importance in giving evidence of resonance.[12]

A typical example is that of carbon dioxide; the possible forms, with their distances and heats of formation from the atoms, are given below, and are compared with the observed values:

	O=C=O	O⇄C→O	O←C⇄O	Observed
Distance	1·22+1·22 2·44	1·37+1·10 2·47	1·10+1·37 2·47	2·30 A
Heat of formation from atoms	173+173 346	81·5+256 337·5	256+81·5 337·5	380 k.cals.

Often, as here, the resonance formulae differ only in the multiplicity of the links. But a very important form of resonance is that between a single covalency and an electrovalency, as in $H—F$ and $H^+ F^-$; this will depend on the relative attractions of the atoms for the shared electrons. Pauling has shown[13] that we can assign electronegativity values to the elements, largely on the basis of their heats of linkage, as follows:

Electronegativities

H	2·1								
Li	1·0	Na	0·9	K	0·8	Rb	0·8	Cs	0·7
Be	1·5	Mg	1·2	Ca	1·0	Sr	1·0	Ba	0·9
B	2·0	Al	1·5	Sc	1·3	Y	1·3	La—Lu ca. 1·3	

V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga   *ca.* 1·6

C	2·5	Si	1·8	Ge	1·7	Sn	1·7	Zr	1·6
N	3·0	P	2·1	As	2·0	Sb	1·8		
O	3·5	S	2·5	Se	2·4	Te	2·1		
F	4·0	Cl	3·0	Br	2·8	I	2·4		

The greater the difference in electronegativity between the two linked atoms the stronger the bond that unites them, and the greater its partial

[12] For lists of the resonance energies and the resonance shortening see Wheland, op. cit., pp. 69, 286.

[13] *Chemical Bond*, eds. 1 and 2, pp. 58–75; *General Chemistry*, 1947, pp. 160, 543.

ionic character. If x_1 and x_2 are the values, the extra energy due to the partial ionic character is about $23(x_1-x_2)^2$ k.cals./mole. With a difference of 1·7 units the link is about 50 per cent. ionic.

It should be noticed that these mixed ionic-covalent links have in some important respects the properties of covalent but not of ionic links. Two of the principal properties by which ionic links are recognized are (1) the independent motions of the ions (conductivity, low molecular weight in solution), and (2) their freedom of position in the molecule, leading to close-packing and the absence of isomers. Neither of these properties is to be found with the ionic-covalent bond; it is a condition of resonance that the atoms must occupy nearly the same places in both forms, so that the ions cannot separate; and as the positions are fixed in the covalent structure but adaptable in the electrovalent, the positions in the hybrid must be those of the covalent form. Thus for many purposes molecules with these mixed links must be regarded as covalent and not ionized.

STEREOCHEMISTRY[14]

The arrangements in space of the covalencies of poly-covalent atoms, while they are subject to small variations seldom exceeding 5° or 10°, tend to conform to one or other of quite a limited number of types. These are very simply related to the size of the valency group of electrons (in Lewis's sense, the shared electrons counting for both atoms) if the imaginary positions of the electronic pairs are taken to be the same whether they are occupied (shared) or not.

I. When the valency group is 4 we have with a covalency of 2 a linear structure (180°) as in Cl—Hg—Cl.

II. When the valency group is 6, if they are all shared we have three covalencies and these are at 120° in a plane with the central atom, as has been shown in boron trifluoride. Where only 4 of the 6 are shared the valency angle is still about 120° (as in stannous chloride).

III. With a complete valency octet (apart from the transitional elements, which require special treatment) the arrangement is tetrahedral; if some pairs are unshared the positions of the rest are only slightly affected (the angles being usually reduced from 109·5° in the direction of 90°) and are for a covalency of 3 (2, 6*) pyramidal, as in NH_3, and for 2 (4, 4) triangular, as in H_2O.

With the transitional elements the size of the valency group is uncertain, as it may include any or all of the electrons above 8 of the previous (penultimate) group. It is found that when this maximum size (n) is not much more than 8, the structure of a 4-covalent atom is tetrahedral, and we may assume that there the valency group is a shared octet, all the

---

* Shared electrons are underlined.

[14] N. V. Sidgwick and H. M. Powell, *Proc. Roy. Soc.* 1940, **176**, 153.

unshared electrons being in the previous group. When, however, n is not much less than 18, the 4-covalent structure is found to be planar; a reason for this is suggested later under V.

IV. When there are 10 valency electrons (the so-called inert pair (see p. 287) if present being counted in), the arrangement is that of a trigonal bipyramid, with two points at the poles of a sphere and the other three symmetrically disposed (at 120°) on the equator (Fig. 1).
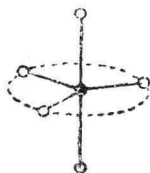
Trigonal Bipyramid   IF₅ Structure
FIG. 1   FIG. 2

With 5-covalent decets (<u>10</u>) this has been established in every case examined, for example, with PF_5, $TaCl_5$, $Fe(CO)_5$, and $Sb(CH_3)_2(hal)_3$.

The 4-covalent decet (2, <u>8</u>) has the structure derived from this with one of the five points empty. This has been established with $K[IO_2F_2]$[15] and with $TeCl_4$[16] (Fig. 2).

The 3-covalent decet occurs in the aryl iodide-chlorides $Ar \cdot ICl_2$, but their structure is unknown. The 2-covalent decet (<u>4</u>, 6) occurs in the trihalide ions, as in $M[ICl_2]$ and $M[I_3]$, which are known to be linear (2 polar points).

V. Duodecet. In its fully shared form AB_6 this gives the octahedron established by Werner. On theoretical grounds[17] the three structures below are all possible: of these II is really a form of I in which the B··B distances
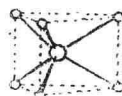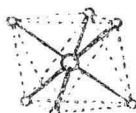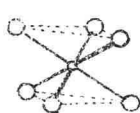
I. Trigonal Antiprism.   II. Octahedron.   III. Trigonal Prism.
FIG. 3

and the valency angles are all equal. Experimentally all AB_6 molecules are found to have the octahedral structure II except a few giant molecules (for instance, MoS_2 III, and nickel arsenide I and III). The reason, no doubt, is that the octahedron gives for a fixed A—B length the greatest distance from one B to another, and so is favoured, owing to the mutual repulsion of the B's, wherever the attraction of neighbouring atoms does not interfere, as it does in the giant molecules.

[15] L. Helmholz and M. T. Rogers, *J.A.C.S.* 1940, 62, 1537.
[16] D. P. Stevenson and V. Schomaker, ib. 1267.
[17] G. E. Kimball, *J. Chem. Phys.* 1940, 8, 188.

The 5-covalent duodecet (2, 10) must occur in IF_5 (Fig. 2), but the structure of this cannot be determined by electron diffraction because of the great difference (53 to 9) between the atomic numbers of iodine and fluorine.

The 4-covalent duodecet is found in the unusual type of $M[ICl_4]$, where the anion has been shown to have a planar square structure, i.e. an octahedron with two trans positions empty. It may be supposed that the same 4, 8 electronic arrangement occurs in the planar 4-covalent derivatives of the later transitional elements, such as $M_2[Ni(CN)_4]$; the nickel here has the atomic composition 2, 8 (16, 8), which presumably should be written 2, 8, 12 (4, 8), giving the same type of duodecet as in $M_2[ICl_4]$.

VI. 14-group. The very few examples of this rare condition that have been measured show two types of structure, one (in $K_3[ZrF_7]$) derived from an octahedron by adding a fluorine atom to the centre of one face,[18] and the other (in $K_2[NbF_7]$ and $K_2[TaF_7]$) from a trigonal prism by adding a fluorine atom at the centre of a prism face,[19] the strain in both cases being eased by distortion.

VII. 16-group: covalency 8. Only one compound of this rare kind has been examined, the very stable octacyanide $K_4[Mo(CN)_8]$; the anion of this salt has been shown[20] to have neither the cubic nor the antiprismatic (twisted cube) form, but that of a dodecahedron.

Multiple Links. With the octet the stereochemistry of these is well known; the angles are A $\langle^B_B$ 125·15° and both B=A=B and B—A≡B 180°. The positions of multiple links with larger valency groups are scarcely known theoretically, and not at all practically.

ATOMIC RADII

By X-ray and electron diffraction, from the spectra, and in other ways, the lengths (distances between the nuclei) of a large number of covalent links have been measured, and it has been found that they can be approximately expressed as the sum of two values, one for each of the linked atoms, which are known as the atomic radii (a similar additivity is found to hold for ions, though the values are, of course, different). The observed lengths are, however, subject to small variations, of which the most important are those due to the multiplicities: in general the ratios of the links A—B, A=B, A≡B are roughly 1 : 0·9 : 0·8.[21] Resonance shortens the distances by introducing an element of multiplicity into single links, and in addition by the shortening which resonance itself involves.[22] There are

[18] G. C. Hampson and L. Pauling, *J.A.C.S.* 1938, **60**, 2702.
[19] J. L. Hoard, ib. 1939, **61**, 1252.
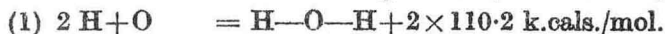[20] J. L. Hoard and H. H. Nordsieck, ib. 1939, **61**, 2853.
[21] J. L. Kavanau, *J. Chem. Phys.* 1944, **12**, 467.
[22] H. A. Skinner, *Trans. Far. Soc.* 1945, **41**, 645.

other modifying influences as well, which are not yet fully understood.[23-5] Where the distances in a molecule have been measured, it is useful to be able to compare them with those derived from some standard series of values of the atomic radii. A list (Table V) is therefore given (p. xxix) of the most probable radii of the atoms in covalent and electrovalent links, and values taken from this are appended (as 'theory') to the measurements quoted in the text. This is merely to facilitate comparison, and the 'theoretical' values must not be supposed to have any special validity.

HEATS OF LINKAGE

The heat of formation H_f of a molecule from its elements in their (specified) standard states—for example, graphite, hydrogen gas, solid iodine—can be ascertained thermochemically. If the heat of volatilization or sublimation of the substance is known, and further the heats of atomization of the component elements from their standard states, the algebraic sum of all these quantities gives H_a, the heat of formation of the gaseous compound from its atoms; this is expressed in k.cals. per g.-molecule. The deduction from this of the heats of formation of individual links is (except with diatomic molecules) to some extent a matter of convention. Thus with water we have the following values (all, of course, for the gas)

(1) $2 H + O \quad = H\!-\!O\!-\!H + 2 \times 110.2$ k.cals./mol.

(2) $\quad H + O\!-\!H = H\!-\!O\!-\!H \quad + 103.5 \quad\quad$,,

(3) $\quad H + O \quad = H\!-\!O \quad\quad + 116.9 \quad\quad$,,

Here we have three different values for the H—O link. The values (2) and (3) depend on the stability of the radical O—H; we are not concerned with this but only with the relation between H_2O molecule and its constituent atoms, i.e. with (1); our object is to get values such that their sum for all the links in a molecule gives its H_a as nearly as possible. Hence the value used for the heat of linkage is got by dividing the H_a of the normal molecule AB_x by x, the number of links that it contains (here H—O = 110.2 k.cals.). With such values the additivity for molecules with several kinds of links is found to hold very nearly, if allowance is made for the resonance energy when this is to be expected; the value of the resonance energy is, in fact, usually obtained by subtracting from the H_a of the substance the sum of the normal ('theoretical') values for the links that it contains. There are other influences which cause small changes in H_a, seldom amounting to 5 k.cals.; these will be discussed as they occur (see, for example, pp. 501-5).

The Tables VI A—D which follow give the most probable values for A (p. xxx) the heats of atomization of the elements from their standard states B (p. xxxi), the heats of formation H_a of single links C (p. xxxii), those of multiple links, and D (p. xxxii), the effects (where known) of change of valency on the heat of formation of the link.

[23] V. Schomaker and D. P. Stevenson, *J.A.C.S.* 1941, **63**, 37.

[24] W. Gordy, *J. Chem. Phys.* 1947, **15**, 81, 305.

[25] L. Pauling, *J.A.C.S.* 1947, **69**, 542 (for metals).

TABLE I
International Atomic weights 1948

	Symbol	At. No.	At. Wt.		Symbol	At. No.	At. Wt.
Aluminium	Al	13	26·97	Molybdenum	Mo	42	95·95
Antimony	Sb	51	121·76	Neodymium	Nd	60	144·27
Argon	A	18	39·944	Neon	Ne	10	20·183
Arsenic	As	33	74·91	Nickel	Ni	28	58·69
Barium	Ba	56	137·36	Niobium	Nb	41	92·91
Beryllium	Be	4	9·02	Nitrogen	N	7	14·008
Bismuth	Bi	83	209·00	Osmium	Os	76	190·2
Boron	B	5	10·82	Oxygen	O	8	16·0000
Bromine	Br	35	79·916	Palladium	Pd	46	106·7
Cadmium	Cd	48	112·41	Phosphorus	P	15	30·98
Caesium	Cs	55	132·91	Platinum	Pt	78	195·23
Calcium	Ca	20	40·08	Potassium	K	19	39·096
Carbon	C	6	12·010	Praseodymium	Pr	59	140·92
[Cassiopaeum = Lutecium]				Protoactinium	Pa	91	231
Cerium	Ce	58	140·13	Radium	Ra	88	226·05
Chlorine	Cl	17	35·457	Radon	Rn	86	222
Chromium	Cr	24	52·01	Rhenium	Re	75	186·31
Cobalt	Co	27	58·94	Rhodium	Rh	45	102·91
[Columbium = Niobium]				Rubidium	Rb	37	85·48
Copper	Cu	29	63·54	Ruthenium	Ru	44	101·7
Dysprosium	Dy	66	162·46	Samarium	Sm	62	150·43
Erbium	Er	68	167·2	Scandium	Sc	21	45·10
Europium	Eu	63	152·0	Selenium	Se	34	78·96
Fluorine	F	9	19·00	Silicon	Si	14	28·06
Gadolinium	Gd	64	156·9	Silver	Ag	47	107·880
Gallium	Ga	31	69·72	Sodium	Na	11	22·997
Germanium	Ge	32	72·60	Strontium	Sr	38	87·63
Gold	Au	79	197·2	Sulphur	S	16	32·066
Hafnium	Hf	72	178·6	Tantalum	Ta	73	180·88
Helium	He	2	4·003	Tellurium	Te	52	127·61
Holmium	Ho	67	164·94	Terbium	Tb	65	159·2
Hydrogen	H	1	1·0080	Thallium	Tl	81	204·39
Indium	In	49	114·76	Thorium	Th	90	232·12
Iodine	I	53	126·92	Thulium	Tm	69	169·4
Iridium	Ir	77	193·1	Tin	Sn	50	118·70
Iron	Fe	26	55·85	Titanium	Ti	22	47·90
Krypton	Kr	36	83·7	Tungsten	W	74	183·92
Lanthanum	La	57	138·92	Uranium	U	92	238·07
Lead	Pb	82	207·21	Vanadium	V	23	50·95
Lithium	Li	3	6·940	Xenon	Xe	54	131·3
Lutecium	Lu	71	174·99	Ytterbium	Yb	70	173·04
Magnesium	Mg	12	24·32	Yttrium	Y	39	88·92
Manganese	Mn	25	54·93	Zinc	Zn	30	65·38
Mercury	Hg	80	200·61	Zirconium	Zr	40	91·22

TABLE II

Atomic Structures

Group Subgp.	1 s	2 s	 p	3 s	 p	 d	4 s	 p	 d	 f	5 s	 p	 d	 f
1 H	1													
2 He	2													
3 Li	2	1												
4 Be	2	2												
5 B	2	2	1											
6 C	2	2	2											
7 N	2	2	3											
8 O	2	2	4											
9 F	2	2	5											
10 Ne	2	2	6											
11 Na	2	2	6	1										
12 Mg	2	2	6	2										
13 Al	2	2	6	2	1									
14 Si	2	2	6	2	2									
15 P	2	2	6	2	3									
16 S	2	2	6	2	4									
17 Cl	2	2	6	2	5									
18 A	2	2	6	2	6									
19 K	2	2	6	2	6		1							
20 Ca	2	2	6	2	6		2							
21 Sc	2	2	6	2	6	1	2							
22 Ti	2	2	6	2	6	2	2							
23 V	2	2	6	2	6	3	2							
24 Cr	2	2	6	2	6	5	1							
25 Mn	2	2	6	2	6	5	2							
26 Fe	2	2	6	2	6	6	2							
27 Co	2	2	6	2	6	7	2							
28 Ni	2	2	6	2	6	8	2							
29 Cu	2	2	6	2	6	10	1							
30 Zn	2	2	6	2	6	10	2							
31 Ga	2	2	6	2	6	10	2	1						
32 Ge	2	2	6	2	6	10	2	2						
33 As	2	2	6	2	6	10	2	3						
34 Se	2	2	6	2	6	10	2	4						
35 Br	2	2	6	2	6	10	2	5						
36 Kr	2	2	6	2	6	10	2	6						