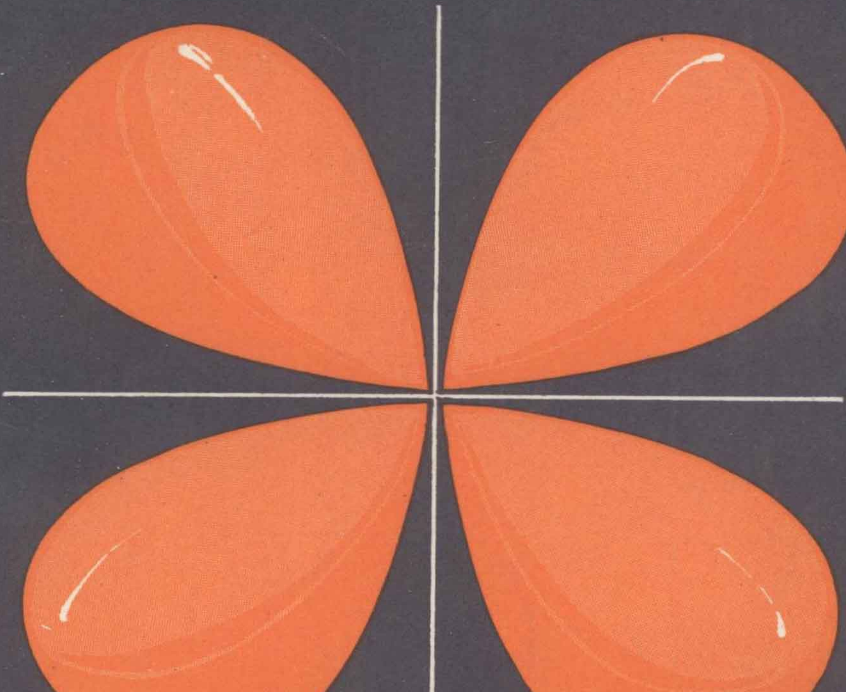
E. Cartmell & G. W. A. Fowles

Valency and Molecular Structure

Fourth edition



Butterworths

Valency and Molecular Structure

Fourth Edition

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VALENCY AND
MOLECULAR STRUCTURE

Preface to the Fourth Edition

Successive editions of undergraduate textbooks tend to get bigger and bigger. So much has happened in chemistry since the first edition of this book appeared twenty years ago that there is every temptation for expansion. We have tried to resist this temptation. This book has been completely rewritten. Some material in earlier editions (e.g. the chapter on Bohr theory) has been removed, while some sections (e.g. structures of crystalline solids) have been expanded. In this connection we are grateful to the Royal Institute of Chemistry for permission to include material written by one of us for an R.I.C. Monograph on Crystal Chemistry.

Details of structures have been revised and extended using the best available values for bond lengths and bond angles. Recent developments are perhaps most noticeably seen in the chapter on complex compounds where the discussion of, for example, compounds of co-ordination number five and seven takes up considerably more space than it did in earlier editions. While these editions included comprehensive references for all the structures discussed, this is no longer possible in a book of this size and we have therefore frequently quoted important review articles from which references to earlier work can be obtained. References to recent work have, however, been included as before.

Undergraduate courses now lay considerable stress on spectroscopic methods and we have included a new chapter to serve as an introduction to the spectroscopy of complex compounds.

E.C.
G.W.A.F.

Contents

1

HISTORICAL INTRODUCTION

1.1 Electricity and Chemical Bonding

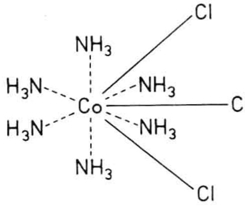
The idea that chemical forces are electrical in nature can be traced back to the beginning of the nineteenth century. In 1800, Nicholson and Carlisle decomposed water into hydrogen and oxygen by passing an electric current through it, and in the next few years many other electrolytic decompositions were reported. Perhaps the outstanding examples were Sir Humphry Davy's isolation of sodium and potassium from caustic soda and caustic potash, respectively, in 1807. Davy, indeed, suggested that the forces governing chemical combination were electrical in nature, the electrification of the combining particles being produced by contact. Electrochemical ideas were also developed by Berzelius in his Dualistic Theory (1812). He assumed that every atom possessed two electric poles of opposite sign, electropositive atoms having the positive pole in excess, electronegative atoms the negative pole in excess. The combination of an element with oxygen might produce a basic oxide (e.g. CuO) with a residual positive polarity, or an acidic oxide (e.g. SO_3) with a residual negative polarity. These oxides could combine because of the attraction of the residual opposite charges: thus

$$\mathrm{C\overset{+}{u}O} + \mathrm{S\overset{-}{O}_3} = \mathrm{CuSO_4}$$

The theory, when subsequently applied to organic chemistry, could not, however, explain the fact that the substitution of negative chlorine for positive hydrogen in many organic molecules produced comparatively little change in chemical properties (cf. CH_3COOH and CCl_3COOH). Moreover, it could not account for Faraday's Laws of Electrolysis.

Electrochemical theories of chemical combination were then neglected for many years; the advances in theoretical organic chemistry associated with the names of Laurent, Gerhardt, Frankland, Williamson and Kekulé did not refer specifically to the electrical nature of combining forces in molecules. The electrical theory was, however, restated by Helmholtz in his Faraday Lecture of 1881, when he said '. . . the very mightiest among the chemical forces are of electric origin. The atoms cling to their electric charges and opposite charges cling to each other'.

Arrhenius, in 1884 and 1887, published a theory of 'electrolytic dissociation' in which he proposed the idea that salts (e.g. sodium chloride) in dilute aqueous solution were dissociated into positive (e.g. sodium) ions and negative (e.g. chloride) ions. This theory of easily dissociated molecules or of 'ionizable' atoms was used by Werner (1891), who discussed the constitution of compounds of the type $CoCl_3,6NH_3$ in terms of 'principal' and 'auxiliary' valencies. The auxiliary valencies were exerted in the co-ordination of a number of atoms, molecules or radicals to the central metal atom, in an 'inner sphere of combination', and the principal valencies represented the attachment of ionizable atoms of groups in an 'outer sphere of combination'. Thus Werner represented $CoCl_3,6NH_3$ as formula (1), where the dotted lines represent the 'auxiliary' bonds and the



(1)

full lines the attachment of the ionizable atoms. Werner's theory was subsequently of great importance in the study of isomerism in inorganic compounds, and in other ways.

J.J. Thomson's (1897) recognition of the negatively charged electron as a constituent of all atoms, and his measurements of the ratio of its charge to its mass, provided a new stimulus to the electrochemical theories. He realized that the chemical properties of elements depended in some way on the arrangement of their electrons, and he suggested that electropositive atoms were those which could achieve a stable electronic state by losing one or two electrons, whereas electronegative atoms achieved stable states by acquiring one or more electrons.

Sir William Ramsay's Presidential Address to the Chemical Society of London in 1908 stressed the role of the electron in valency. Thus he said "... they (the electrons) serve as the 'bonds of union' between atom and atom". He also suggested that in molecules such as NaCl and Cl_2 the electron might form a 'cushion' between the two atoms. Ramsay, and other chemists of the period, believed that the maximum number of electrons involved in compound formation was eight; thus nitrogen, with five available electrons, could acquire three more by combining with three hydrogen atoms to form ammonia, NH_3, whereas NH_4 could only be obtained by removing one electron and forming a positively charged NH_4^+ ion.

Abegg (1904) had postulated that elements had two valencies, a 'normal' and a 'contravalency'. These were of opposite polarity, and the total sum of the two valencies was always eight. J. Newton Friend (1908) distinguished three types of valency – negative, positive and residual – where the negative valency of an atom was defined as being equal to the number of electrons with which it could combine, and the positive valency was related to the loss of electrons from the atom. His use of the term 'residual valency' is of great interest in the light of later developments, for he suggested that when an element exerted its residual valency, it simultaneously parted with, and received, an electron. The hydrogen molecule was represented as $H\rightleftharpoons H$, the arrows indicating the directions in which the electrons were transferred.

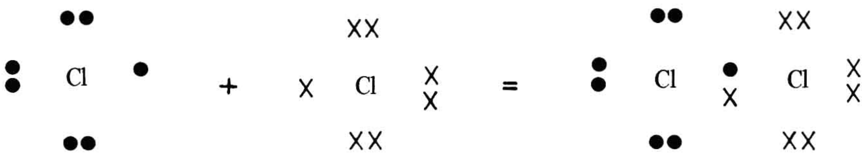
J.J. Thomson made a further important contribution to valency theory in 1914. He emphasized the difference between polar molecules (e.g. NaCl) and non-polar ones (e.g. most organic substances), and observed that the electropositive valency of an element was equal to the number of electrons that could easily be separated from it, while the negative valency was equal to the difference between eight and the positive valency.

1.2 The Lewis–Langmuir Electron-pair Bond

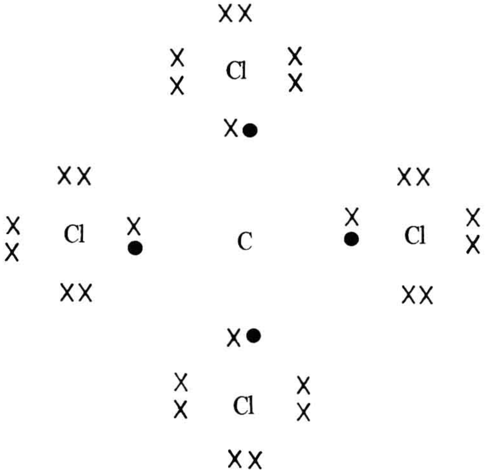
The development of the Rutherford theory of the nuclear atom, and Bohr's work on the hydrogen atom structure, paved the way for a more comprehensive 'electronic theory of valency'. The foundations of this modern theory were laid in two independent publications by W. Kossel and by G.N. Lewis in 1916. Kossel, who was mainly concerned with polar (ionizable) molecules, pointed out that in the periodic system, a noble gas element always separates an alkali metal and a halogen, and that the formation of a negative ion by the halogen atom, and a positive ion by the alkali metal atom, would give each of these atoms the structure of a noble gas. The noble gases were assumed to possess a particularly stable configuration of eight electrons in an outer shell (two electrons in the case of helium). No compounds of these elements were known at that time – indeed until very recently they were usually called the 'inert' gases. Many compounds of xenon and krypton have now been made, but it seems unlikely that stable compounds of helium, neon and argon can be formed and these elements might well still be called inert gases. The stable ions in a compound such as NaCl are, on this view, held together by electrostatic attraction and form what is now called an 'electrovalent' bond or link. The electrovalency of the ion is defined as the number of unit charges on the ion; thus magnesium has a positive electrovalency of two, while chlorine has a negative electrovalency of one. We shall discuss the formation and properties of electrovalent (now usually called ionic) bonds in some detail in Chapter 9.

Lewis discussed atomic structure in terms of a positively charged 'kernel' (i.e. the nucleus plus the 'inner' electrons) and an outer shell that could contain up to eight electrons. He assumed that these outer electrons were arranged at the corners of a cube surrounding the kernel; thus, the single electron in the outer shell of sodium would occupy one corner of the cube, whereas all eight corners would be occupied by the electrons in the outer shell of an inert gas. This octet of electrons represented a particularly stable electronic arrangement, and Lewis suggested that, when atoms were linked by chemical bonds, they achieved this stable octet of electrons in their outer shells. Atoms such as sodium and chlorine could achieve an outer octet by the transfer of an electron from sodium to chlorine, forming Na^+ and Cl^- ions, respectively. This was essentially the mechanism proposed by Kossel, but Lewis proposed a second mechanism to account for the formation of non-polar molecules. Here, there was no transfer of electrons from one atom to another (and thus no ion formation), but the bond resulted from the sharing of a pair of electrons, each atom contributing one electron to the pair.

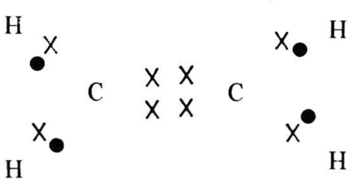
This theory was considerably extended by Langmuir (1919), although he abandoned the idea of the stationary cubical arrangement of the outer electrons; he introduced the term 'covalent bond' to describe the Lewis 'electron-pair' bond or link. We can illustrate the Lewis–Langmuir theory by considering the chlorine molecule, Cl_2. Chlorine, with the electronic configuration (using the modern notation introduced in Chapter 5) $(Ne)3s^2 3p^5$, is one electron short of the inert gas configuration of argon, $(Ne)3s^2 3p^6$, and the formation of the stable diatomic chlorine molecule, Cl_2, results from the sharing of electrons by the two chlorine atoms. If we represent the outer electrons of one chlorine atom by dots, and those of the other by crosses, we can write



where Cl represents the chlorine nucleus and the inner electrons. The atoms linked in this way need not be identical; thus, in carbon tetrachloride, each of the four outer electrons of the carbon pairs with an electron from a chlorine atom to form four covalent bonds. The Lewis–Langmuir theory would represent the structure as

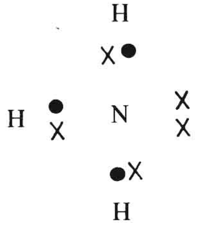


Double and triple bonds are considered to involve the sharing of four and six electrons, respectively, so that the structures of ethene (ethylene) and ethyne (acetylene) would be written

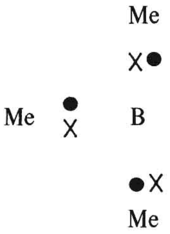


and

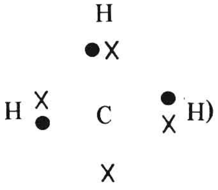
In these molecules (Cl_2, CCl_4, C_2H_4 and C_2H_2) the electron pair for each single bond is provided by the two combining atoms, each contributing one electron. Perkins (1921) postulated a related type of link in which both electrons for the electron-pair bond come from only one of the two combining atoms. An example is provided in the combination of ammonia with boron trimethyl, $B(CH_3)_3$. Ammonia may be written



each hydrogen atom pairing its electron with a nitrogen electron to form three electron-pair bonds; the two unused outer electrons on the nitrogen atom form a so-called 'lone pair'. In boron trimethyl, however, there are



(where Me represents the methyl radical



only six electrons around the boron atom, since the boron atom itself only has three outer electrons, which it uses to form three electron-pair bonds with the carbon atoms of the three methyl groups, as shown above. A compound $H_3N \rightarrow BMe_3$ can now be formed. The nitrogen atom is the 'donor' and the boron atom the 'acceptor' in this operation; the arrow indicates the relationship donor → acceptor. It should be emphasized that 'donation' is a special case of electron 'sharing', and no complete transfer of electrons takes place; nevertheless, the nitrogen atom has, in effect, 'lost' one electron (it now only shares two electrons both of which it had entirely to itself), and the boron atom has, so to say, 'gained' an electron. The formation of this type of bond thus involves a charge displacement, producing what is called an electric 'dipole' in the molecule. (We refer again to this term in Chapter 11.) Nitrogen acquires a 'formal' positive charge, and boron a 'formal' negative charge in $H_3N \rightarrow BMe_3$. Apart from this charge displacement the bond, once formed, does not differ in any way from the normal covalent bond of the Lewis–Langmuir theory.

The Lewis–Langmuir electron-pair or covalent bond is now often referred to as the homopolar bond, whereas the complete transfer of electrons, resulting in ion formation (e.g. Na^+, Mg^{2+}, Cl^-) gives rise to the electrovalent, or ionic, or heteropolar, bond by the attraction of opposite charges. Bonds formed by the Perkins mechanism were originally called 'co-ordinate' links, but the terms 'donor' or 'dative' bond have also been used. The production of formal charges on the atoms linked in this way is emphasized by the term 'semi-polar' bond, which implies that the bond has something of the character of the polar (i.e. ionic) link; another term introduced by Palmer (1944) – the co-ionic bond – also indicates that the bond has characteristics of both the covalent and the ionic bond. In bond diagrams, the covalent bond may be represented either by the colon, as in Cl:Cl, or, more usually, by the dash, Cl–Cl. Co-ordinate links may be represented, as we saw in the $H_3N{\rightarrow}BMe_3$ example, by a single arrow showing the direction of the electronic charge displacement. An alternative method is to write $H_3\overset{+}{N}{-}\overset{-}{B}Me_3$, where + and - are used to indicate the formal charges. The different names given above are often a source of confusion to beginners, so they are collected together for clarity as follows:

Polar = Heteropolar = Ionic = Electrovalent
Non-polar = Homopolar = Covalent
Semi-polar = Co-ordinate = Dative = Co-ionic = Donor–Acceptor

1.3 Quantum Theory of Chemical Bonding

The modern theory of the covalent bond with which this book is mainly concerned started with the recognition at the beginning of the century that the classical laws of physics did not apply to radiation. The quantum theory of radiation was developed by M. Planck (1900) to account for the way in which radiation from a 'black body' varied with wavelength (see p.9). His concept of corpuscles or 'quanta' of radiant energy was applied by A. Einstein (1905) to explain the photoelectric effect (p.11), and by N. Bohr (1913) to explain the spectrum of atomic hydrogen (p.13).

The link between radiation, described in classical terms by a wave theory, and energy quanta was formalized by L. de Broglie (1924); he related wavelength (λ), characteristic of a wave theory, with momentum p (= $m \times v$), characteristic of a particle theory. The de Broglie relationship

$$\lambda = h/p = h/mv$$

received experimental verification with the discovery of electron diffraction in 1927. We shall see that the fundamental constant of nature h, the Planck constant, is involved in the the theory of all these very different phenomena – black-body radiation, the photoelectric effect, the spectrum of atomic hydrogen and the de Broglie relationship.

The implications of a wave theory of electrons were worked out independently by W. Heisenberg (1925), E. Schrödinger (1926) and P. Dirac (1928). They developed quantum mechanical theories of electron behaviour in atoms and their methods were then applied to electrons in molecules by H. Heitler and F. London who, for the first time, calculated, approximately, the strength of the electron-pair bond in the hydrogen molecule. Their method – the so-called valence-bond method – was developed by L. Pauling and by J.C. Slater, while at the same time (1927) Ø. Burrau, R.S. Mulliken and J.E. Lennard-Jones were developing the complementary 'molecular-orbital' method of treating valency problems.

The discovery of the diffraction of X-rays by crystals (M. von Laue, W. Friedrich and P. Knipping, 1912) and the subsequent development of crystal structure determination by W.H. and W.L. Bragg led to a very satisfactory theory of bonding in electrovalent (ionic) compounds in terms of electrostatic interactions between charged ions.

In fact the 'chemical bond' is rarely purely covalent or purely ionic. The detailed quantum-mechanical theory of the covalent bond has to take account of partial 'ionic character' of the bond, just as the more simple electrostatic treatment of the ionic bond breaks down when the bond has 'covalent character'. The quantum theory of electrons in molecules provides a method of calculating the charge distribution in any system, the energies of the electrons and the bond lengths, angles and dissociation energies. The calculations involved are of a formidable complexity even for a simple diatomic molecule such as H_2, and it is only in recent years, with the development of very large computers, that detailed calculations on larger molecules have become possible.

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2

THE EXPERIMENTAL FOUNDATION OF THE QUANTUM THEORY

2.1 Energy Units

The international system of units (S.I.) expresses fundamental physical quantities such as mass, time, thermodynamic temperature and amount of substance in terms of the units metre (m), kilogram (kg), second (s), kelvin (K) and mole (mol), respectively.

Energy is expressed in joules (J). Many chemists have been brought up in the C.G.S. system and have been accustomed to expressing energy in calories or kilocalories, which are not S.I. units. Many existing reference books also list energies in calories. The appropriate conversion factor is

$$1 \text{ 'thermochemical' calorie} = 4.184 \text{ J}$$

The energies of electrons in atoms can very conveniently be expressed in electron-volts (eV), where 1 eV is the energy acquired by an electron when it is accelerated by a potential difference of one volt:

$$1 \text{ eV} = 1.6021 \times 10^{-19} \text{ J}$$

In radiation theory, wavelength λ and frequency ν are related by

$$\nu = c/\lambda$$

where c is the velocity of electromagnetic radiation in a vacuum ($c = 2.9979 \times 10^8$ m s^{-1}). The frequency unit, ν, is called the hertz (Hz). The wave number, $\bar{\nu}$, is often used in spectroscopy.

$\bar{\nu} = 1/\lambda$ and the wavenumber unit is thus the reciprocal metre, m^{-1}; in practice, chemists normally find it more convenient to use the reciprocal centimetre, cm^{-1}. A wave number $\bar{\nu}$ is related to a frequency ν by

$$c \text{ (m s}^{-1}) \times \bar{\nu} \text{ (m}^{-1}) = \nu \text{ (Hz)}$$

We can now use the Planck expression for the quantum of energy (see p.11), $E = h\nu = hc\bar{\nu}$, to associate energy and wavenumber units. Substitution of $h = 6.6256 \times 10^{-34}$ J s and $c = 2.9979 \times 10^8$ m s^{-1} in this expression gives

$$E \text{ (J)} = 19.863 \times 10^{-26} \, \bar{\nu} \text{ (m}^{-1})$$

These values relate to single atoms. Chemists usually refer to energy changes per mole of substance, where 1 mole is the amount of substance