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# EFFECTIVE CHARGES AND ELECTRONEGATIVITY

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## 1. INTRODUCTION

There are concepts which at a certain stage in the evolution of science are useful and progressive, but which in the course of time, with advances in theory and experiment, need revision and critical analysis, because their uncritical employment may become an obstacle to further development. In the present paper our attention will be directed to one such concept, that of electronegativity.

Pauling defines electronegativity as the ability of an atom in a molecule to attract electrons to itself. We are dealing here with the definition of "degree of ionic character" or, to give it a physical formulation, the effective charge on the atom, more exactly the distribution of electron density in the molecule.

Several formulae exist for estimating electronegativity. Pauling was the first to give an empirical formula which defines electronegativity:

$$|X_A - X_B| = 0.208\sqrt{\Delta}, \quad (1)$$

where

$$\Delta = D(A-B) - \tfrac{1}{2}[D(AA) + D(BB)]. \quad (2)$$

Here $X_A - X_B$ is the difference in electronegativity between the atoms A and B, and $D(AB)$, $D(AA)$, and $D(BB)$ are the dissociation energies of the molecules AB, $A_2$, and $B_2$. Pauling's formula is empirical and evidently cannot claim to have any theoretical foundation. For an approximate quantum-chemical description, we can set up a wave function of the molecule as a linear combination of functions representing the covalent state (AB), the ionic state with a positive charge on A and a negative charge on B ($A^+B^-$), and finally the ionic state with a positive charge on B and a negative charge on A ($A^-B^+$):

$$\psi = \alpha\psi(AB) + \beta\psi(A^+B^-) + \gamma\psi(A^-B^+), \quad (3)$$

where $\alpha$, $\beta$, and $\gamma$ are coefficients related to the contribution of the state. An attempt to interpret Pauling's formula leads merely to the postulate that the state $A^+B^-$ increases the bonding energy.

The usefulness of this empirical formula is, of course, determined solely by the extent to which it reproduces the experimental results. But the question first arises as to whether the energy is increased by $A^+B^-$ or by $A^-B^+$. An empirical formula is incapable of answering this question. For a molecule consisting of a "metallic" element A and a "non-metallic" element B, this question seems trivial, but in general it is not so simple. If we consider the CH bond, it follows from data on ionisation potentials and electron affinities that rupture into $C^+$ and $H^-$ requires a smaller consumption of energy (323 kcal) than rupture into $C^-$ and $H^+$ (368 kcal), although it is usually supposed that hydrogen forms the positive end of the CH dipole.

A rational definition of electronegativity was given by Mulliken. If the question is posed as to which requires the

smaller consumption of energy — the production of isolated $A^+$ and $B^-$ ions (in their ground state), or of $A^-$ and $B^+$ ions, from the separated atoms also in the ground state — the answer is plain. The ionisation potential $I$ and the electron affinity $F$ are the governing factors. Thus the sum $I + F$ may be a measure of electronegativity. But this is true only for isolated atoms and ions in their ground states. The situation is incomparably more complicated in the case of molecules, for it is necessary to know not simply the energy of conversion of an atom A into an ion $A^+$ in the ground state, but the energy of conversion into an ion having the same electronic configuration as the atom in the ionic state in the molecule. Thus in the ground state the $Cl^+$ ion has two unpaired electrons ($3p$), and $I = 13.01$ eV, but in the HCl molecule in its "ionic state", which combines with its singlet ground state $^1\Sigma$, $Cl^+$ should also be in a singlet state, so that the ionisation energy of chlorine must include the energy of excitation of the chlorine ion from the $3p$ to an unknown valence state. The quantity observed physically is the bonding energy, and the energy of the valence state is merely a term entering into the calculation of the bonding energy. Mulliken rightly pointed out the inapplicability of the usual values of $I$ and $F$, but in effect provided nothing in exchange, since the energy of the valence state is not observed experimentally. Mulliken approximately equated this to the energy $\frac{1}{2}(^1D + {}^1S)$. The proposed empirical quantities for electronegativity cannot be linked with physically observable quantities, such as bonding energies, ionisation potentials, electron affinities, dipole moments, etc. The literature contains indications of a correlation between electronegativity and dipole moments, for example in the molecules HF, HCl, HBr, and HI. In general, however, atomic dipole moments due to lone electron pairs must be taken into account.

Different scales of electronegativity exist, but we shall not dwell on them, for we are interested in analysing the concept itself. The idea of electronegativity evidently originated from the fact that, thirty years ago, any bond was regarded as resulting roughly from the superposition of a covalent and an ionic bond. This was an attempt to regard any bond as in some way intermediate between two types, covalent (prototype $H_2$) and ionic (prototype, for example, LiF): the concept of electronegativity was assumed by its authors to give some idea of the distribution of electron density, more correctly of the asymmetry of the electron cloud associated with the bond, and an estimate of it by means of an empirical equation.

At the present time such a view of the chemical bond is too simple, and in most cases untenable. We must take into account, together with the possibility of two-centre localised molecular orbitals and ionic bonds, the further possibility of the presence of vacant orbitals, lone electron pairs, donor–acceptor and dative bonds, various types of hybridisation, the possibility of the formation of $\pi$ complexes, delocalised bonds, which entails the necessity to consider the motion of many electrons in a many-centre field, etc. In the light of these possibilities, the concept of electronegativity oversimplifies the picture of a chemical bond except in a small number of comparatively simple cases. Although many papers have appeared on electronegativity, they are mainly trivial and do not add to our knowledge of the chemical bond. It is no wonder that the concept of electronegativity has been subjected to serious criticism by such eminent experts as Coulson, Moffitt, and others.

Analysis of the concept of electronegativity at the present time should not consist in the application of empirical and semiempirical formulae and their illustration by interatomic distances, energies, etc. The urgent need now is the physical investigation of effective charges. Theoretically an approach can be made to this question by quantum-mechanical calculations of the electron density matrix. But this approach does not hold out much immediate promise: it is a matter for the distant future. At the present time, therefore, the main task is to examine experimental methods for determining effective charges.

## 2. NUCLEAR QUADRUPOLE COUPLING

One method for determining effective charge is to measure nuclear quadrupole coupling constants. But unfortunately it is impossible to separate, by means of these data alone, the fraction depending on hybridisation from that depending on effective charge[1]. It is impossible to find two unknowns from one determination. For compounds of mixed type (for example with $sp$ hybridisation), therefore, the ionic character of the bond is not determined unambiguously by measurements of the quadrupole coupling constant. Gordy and Townes find the degree of hybridisation by calculating the ionic character of the bond from specified electronegativities. And, conversely, by substituting the degree of hybridisation obtained from some indirect data, they calculate the effective charge. Thus this method is not sufficiently reliable.

## 3. X-RAY ABSORPTION SPECTRA

Interesting work in this field has been carried out by Barinskii[2,3], Vainshtein[4], and their collaborators. An X-ray quantum expels an electron from the $K$ shell, the atom forming an ion having a charge of +1. The transition of the electron to successive energy levels produces absorption lines in the spectrum. If the atom is involved in a chemical bond and hence has an effective charge $X$ (positive or negative), the resultant charge is $1 + x$ or $1 - x$. The theory of the phenomenon leads to the formulae

$$\varepsilon_n - \varepsilon_\infty = -\frac{e_1^2}{n^2}\,13.6 \text{ eV}, \tag{4}$$

$$\frac{\tau_n}{\tau_\infty} = \frac{4e_1^2}{\pi\Gamma}\frac{n^2-1}{n^5}. \tag{5}$$

where $\epsilon_\infty$ is the energy of transition of an electron to the limit of the continuous spectrum, $\epsilon_n$ the energy of transition of an electron to the $np$ level of the system, $\tau$ the height of the $n$-th absorption line, $\tau_\infty$ the height of the continuous spectrum, $\Gamma$ the width of the absorption lines and of the limit of the continuous spectrum, $e_1$ the effective charge on the $K$-ionised atom, in whose field the electron expelled from the $K$ shell moves, and $n$ the effective principal quantum number of the $n$-th energy level.

Table 1 gives some values found for the effective charge $x$. The experimental error is said to be 2–10% of the charge increased by unity, so that with a charge of 1.8 the error does not exceed 0.28 unit. The effective charge obtained characterises the physical distribution of charge between the central ion and the surrounding sheath of water molecules within a distance of the order of 1 Å from the nucleus of the central atom. The results indicate that, both in simple molecules of the type $H_2S$, HCl, and $GeBr_4$, and in complex ions and those of the type $CrO_4^{2-}$, the bond is predominantly covalent and the effective charges are small.

TABLE 1.

| Compound | Atom | Effective charge | Compound | Atom | Effective charge |
|---|---|---|---|---|---|
| Gas $H_2S$ | S | −0.1 | $ZnSO_4 \cdot nH_2O$ | Zn | +2 |
| Gas HCl | Cl | −0.2 | Solid $K_3Fe(CN)_6$ | Fe | +1 |
| Gas $GeBr_4$ | Ge | +0.75 | Solid $K_3Mn(CN)_6$ | Mn | +0.9 |
| Gas $GeBr_4$ | Br | −0.15 | $Mn(C_5H_5)_2$ | Mn | 1.5 |
| Gas $ZnBr_2$ | Zn | +0.5 | $(C_5H_5)Mn(CO)_3$ | Mn | +0.6 |
| Gas $ZnBr_2$ | Br | −0.24 | $KOsO_3N$ | Os | +1.0 |
| Solid $Co(NO_3)_3$ | Co | +1.2 | $K_2OsO_4$ | Os | +0.8 |
| Solid $Cr(NH_3)_5 \cdot nH_2O$ | Cr | 1.2 | $K_2Os(NO)Cl_5$ | Os | +0.7 |
| $Cr^{2+}$ | Cr | 1.9 | $K_2OsCl_6$ | Os | +0.8 |
| $Cr^{3+}$ | Cr | 1.2 | $OsO_2$ | Os | +0.8 |
| Solid $K_2CrO_4$ | Cr | ±0.1 | Gas $Fe(CO)_5$ | Fe | +0.4 |
| Solid $Cr(CO)_6$ | Cr | +0.4 | Liquid $Fe(CO)_5$ | Fe | +0.4 |

TABLE 2.

| Compound | Effective charges in fractions of an elementary charge | |
|---|---|---|
| | on central atom | on one ring |
| $Fe(C_5H_5)_2$ | +0.7 | −0.35 |
| $Fe(C_5H_5)_2^+$ | +0.6 | +0.2 |
| $Co(C_5H_5)_2$ | +0.2 | −0.1 |
| $Co(C_5H_5)_2^+$ | 0.0 | +0.5 |
| $Cr(C_6H_6)_2$ | +1.5 | −0.75 |
| $Cr(C_6H_6)_2^+$ | +1.4 | −0.2 |
| $V(C_5H_5)_2$ | +1 | −0.5 |
| $Cr(C_5H_5)_2$ | +1.7 | −0.85 |

It is curious and paradoxical that "triply charged ions", for example Co in $Co(NO_3)_3$, have a smaller effective charge (1.2) than have "doubly charged ions", *e.g.* $Co^{2+}$ (1.8). It may be that a so-called "triply charged" ion acts to a far greater extent as an acceptor into its vacant orbitals in relation to the surrounding molecules (ligands), and therefore the lone electron pairs of a ligand (for example $H_2O$) are very greatly displaced towards the central atom and considerably diminish its effective charge. The results show that not all the charge in complex ions is located on the central atom, but only part of it (sometimes an insignificant part), and hence that the total charge is to a considerable extent dispersed over all the ligands. In some ions the central atom forms practically entirely covalent bonds ($CrO_4^{2-}$). Therefore references in the literature to multicharged ions are evidently quite unjustified. This unsatisfactory description of the situation is a survival of the past (Kossel, Magnus, van Arkel), when chemists imagined the molecules and crystals as combinations of rigid charged spheres, without considering the magnitude of the effective charge. Modern physical methods enable us to revise these ideas. The data obtained show that the presence of covalent bonds must be taken into account in discussing some complex ions. Electron paramagnetic resonance data and spectroscopic and magnetic properties ($g$ factor, $\Delta$ splitting, $\lambda$) lead to consistent results if each of the two unpaired electrons in the $Ni(H_2O)_6^{2+}$ ion has a probability of 0.69 of being on the nickel atom and a probability of 0.051 of being on a particular water molecule[5]. In other words, the charge is dispersed over all the atoms in the ion.

Considerable interest attaches to the question of the effective charges in the recently synthesised compounds with new types of bonds, namely in the aromatic complexes of metals. Shustorovich and Dyatkina[6] used the molecular orbital method, the most suitable for molecules of sandwich structure, in their calculations. The effective charges are determined in this method as the normalised sums of squares of the coefficients of the atomic orbitals of a given atom in all the occupied molecular orbitals (the non-orthogonality of the orbitals of the central atom and the ligands being neglected). Calculations were made for neutral molecules and for the corresponding ions with the results shown in Table 2.

Experimental data, obtained from the structure of the $K$ edges of the X-ray absorption spectra, are available for ferrocene and the ferricinium ion. Vainshtein *et al.*[4] found a value of +0.7 for both these compounds, in good agreement with theory. The calculations were published before the experimental check was undertaken. Barinskii's calculations[2,3] based on published experimental data led to the following effective charges on the metal atoms: dibenzenechromium +1.1, cobalticene +0.4, +0.5, and the cobalticinium ion +0.5, +0.6. Thus neutral compounds of this type have a positive charge, varying from metal to metal, on the central atom. It is particularly interesting that the charge on the metal atom does not change during ionisation, for example on passing from ferrocene to the ferricinium ion, as is shown by theory and confirmed by experiment. This implies that the electron is removed from the rings on ionisation. Since the rings bear small effective negative charges in the neutral molecule, the ligands readily lose an electron. In the ion the total charge becomes dispersed over the whole molecule, which is more efficient than localisation of the whole charge on the metal. The positive charge increases from +1 with vanadium to +1.7 with chromium and +2 with manganese, the last giving ionic manganocene $Mn(C_5H_5)_2$ with five unpaired electrons. Such a large charge with manganese probably arises from a gain in energy of the $d^5$ shell. The presence of a large effective charge, equal to the nominal charge, is characteristic of those molecules in which there are additional conditions for the internal stabilisation of the ion.

## 4. ATOMIC POLARISATION

It is well known that with several crystals of the NaCl type and others the static, low-frequency dielectric constant $\epsilon_s$ is considerably greater than the square of the refractive index $n^2$. In ionic crystals the difference

$$\Delta\varepsilon = \varepsilon_s - n^2, \tag{6}$$

relating to atomic polarisation is due to the relative displacement of ions of opposite sign, and also to deformation of the electron shells owing to the relative motion of the ions. The characteristic frequencies of displacement of the ions lie in the infra-red range. These shifts contribute a considerable fraction of the static dielectric constant. The ratio of the characteristic frequency of the lengthwise $\omega_e$ to the transverse $\omega_t$ vibrations is $(\epsilon_s/n^2)^{\frac{1}{2}}$. The relation between $\Delta\epsilon$ and the macroscopic charge was found by Born on the assumption that the ions are not deformed and do not overlap. This theory was subsequently improved by Szigeti[7], who derived the following equation for $\Delta\epsilon$:

$$\Delta\varepsilon = \left(\frac{n^2+2}{3}\right)^2 \frac{2\pi e_1^2}{\omega_t^2 a^3 m}, \tag{7}$$

where $e_1$ is the effective charge on the ion, $a$ the interionic

distance ($2.81 \times 10^{-8}$ for NaCl), and $m$ the reduced mass. In the derivation of this equation it is assumed that electrostatic forces act between charges $e_1$ in the lattice, and that the charges of neighbouring ions do not overlap. A ratio $e_1/e < 1$, where $e$ is the elementary charge ($4.8 \times 10^{-10}$), can be interpreted as due to the superposition of covalent forces. Eqn. (7) enables us to determine the effective charge $e_1$, since the remaining quantities in the equation are known from experiment. Szigeti showed also that the compressibility $K$ is linked with $\epsilon_s$ by the relation

$$\frac{1}{K} = \frac{\epsilon_s + 2}{6(n^2+2)} \frac{m\omega_t^2}{a}. \qquad (8)$$

Table 3 gives values of effective charges[8,9] in fractions of an elementary charge for the most reliable cases, in which $K_{calc}/K_{exp}$ is close to unity. The last column indicates differences in electronegativity $\Delta X$ on the Little and Jones scale[10].

Table 3 shows that: (1) the lattices of ordinary binary salts $A^IB^{VII}$ are mainly ionic; (2) even in these salts the effective charges are considerably diminished (by 13–31%) compared with the elementary charge ($4.8 \times 10^{-10}$); (3) there is in general a qualitative correlation between $\Delta X$ and $e_1/e$. The effective charges in crystals of binary salts of the NaCl type are greater than in the gaseous molecules. The presence of considerable effective charges (even though less than unity) explains the dimerisation of the gaseous molecules. It is curious that, although the effective charges in these substances are reduced (to 69%), the lattice energies calculated by Born's method for single charges agree well with experiment. Thus the energy is not really so sensitive to the magnitude of the effective charge.

In connection with the nature of the chemical bond in semiconductor crystals, it is interesting that compounds of the type $A^{III}B^V$ have three valence electrons on each of the A and B atoms, which give ordinary covalent bonds. In addition, the A atom is an acceptor by virtue of its vacant $p$ orbital, and the B atom a donor owing to its lone pair of $s^2$ electrons. This is a case of $sp^3$ hybridisation, and the lattices of these compounds are of the diamond type. The circular infra-red dispersion frequencies have been measured[11], *i.e.* the lattice vibrations for transverse $\omega_t$ and longitudinal vibrations $\omega_e$. The effective charges are related to these vibrations as follows:

$$e_1 = \omega_t \left(\frac{\epsilon_s - \epsilon_\infty}{4\pi}\right)\left(\frac{3}{\epsilon_\infty + 2}\right)(mv)^{1/2}, \dagger \qquad (9)$$

TABLE 3.

| Compound | $\epsilon_s$ | $n^2$ | $\frac{K_{calc}}{K_{exp}}$ | $\frac{e_1}{e}$ | $\Delta X$ |
|---|---|---|---|---|---|
| LiF | 9.27 | 1.92 | 1.0 | 0.87 | 3.13 |
| NaCl | 5.62 | 2.25 | 0.99 | 0.74 | 1.82 |
| NaI | 6.6 | 2.91 | 1.05 | 0.71 | 1.20 |
| KCl | 4.68 | 2.13 | 0.96 | 0.80 | 1.92 |
| KI | 4.94 | 2.69 | 0.99 | 0.69 | 1.30 |

† According to Ref. 11 the first term in brackets should be to the power ½ (Ed. of Translation).

where $v$ is the volume of the unit cell, and $\epsilon_\infty$ the optical, high-frequency, and $\epsilon_s$ the static, low-frequency dielectric constant.

Table 4 gives the relevant data on effective charges $e_1/e$ and widths of the forbidden gap $\Delta E$ in eV.

These data are interesting, since they give an idea of the effective charges arising in the formation of donor–acceptor bonds. Table 4 shows that there is no correspondence between effective charges and the difference in electronegativity. The elements of Group V are generally more electronegative than those of Group III. Since, however, the former are donors, while the latter are acceptors, the result is that the more electronegative atom receives an additional positive charge on interaction, while the more electropositive atom gains a negative charge‡. Further, with nitrogen, phosphorus, and arsenic it is the $2s^2$, $3s^2$, and $4s^2$ electrons respectively which confer donor properties. And although the ionisation potentials characteristic of the removal of the outer $p$ electron fall, the excitation due to the peripheral $s$ electrons and the corresponding ionisation potentials of these $s$ electrons increase, as can be seen from Table 5, compiled from spectroscopic data[12].

Thus the donor properties associated with the $ns^2$ electrons decrease with increase in $n$. This is explained by the $d$ subgroup of electrons strengthening the bonding of the

TABLE 4.

| Compound | $10^{-13}\omega_t$, $sec^{-1}$ | $10^{-13}\omega_e$, $sec^{-1}$ | $\frac{e_1}{e}$ | $\Delta E$, eV |
|---|---|---|---|---|
| AlSb | 5.92 | 6.32 | 0.48 | 1.5 |
| GaAs | 5.04 | 5.35 | 0.43 | 1.1 |
| GaSb | 4.25 | 4.40 | 0.30 | 0.7 |
| InP | 5.74 | 6.38 | 0.60 | 1.25 |
| InAs | 3.95 | 4.38 | 0.56 | 0.33 |
| InSb | 3.28 | 3.46 | 0.34 | 0.18 |

TABLE 5.

| Element | Electronic configuration of atom | Electronic configuration of ion | Energy required to remove an electron, eV | Difference |
|---|---|---|---|---|
| N | $2s^22p^3$ | $\rightarrow N^+2s^22p^2$ | 14.54 | 5.76 |
| N | $2s^22p^3$ | $\rightarrow N^+2s2p^3$ | 20.3 | |
| P | $3s^23p^3$ | $\rightarrow P^+3s^23p^2$ | 11 | 6.5 |
| P | $3s^23p^3$ | $\rightarrow P^+3s3p^3$ | 17.5 | |
| As | $4s^24p^3$ | $\rightarrow As^+4s^24p^2$ | 9.81 | 9.14 |
| As | $4s^24p^3$ | $\rightarrow As^+4s4p^3$ | 18.95 | |

‡ Arsenic as an impurity in silicon is an electron donor, and produces $n$-type conduction. Conversely, aluminium added to silicon is an acceptor, since it captures an electron from the valence band, creating a positive hole in the latter, which produces $p$-type conduction. It is easily seen that these facts do not fit into the framework of the so-called electronegativities (As 2.20, Si 1.74, and Al 1.47).

former electrons in their shell. Correspondingly the ionisation potentials of K, Rb, and Cs are less than those of Cu, Ag, and Au. This effect is reflected in a decrease in the effective charges in the sequence InP, InAs. Quantum-mechanical calculations[13] for the compounds $A^{I}B^{VII}$ (CuCl), $A^{II}B^{VI}$ (ZnS), and $A^{III}B^{V}$ (GaAs) give values of 0.4–0.6 for the effective charges, although zinc, for example, is usually regarded as a doubly charged ion.

According to Burstein the effective charge in PbS is 0.8. In coordination lattices a rise in temperature can diminish the role of the covalent bond and increase that of the ionic bond. Accordingly solid InSb has a diamond lattice ($\gamma = 2.8 \times 10^{-8}$) with a covalent $sp^3$ state; fusion at 540° results in a liquid having a short-range order corresponding to an NaCl type of lattice[14] ($\gamma = 3.17 \times 10^{-8}$).

The attempt of some authors to find a correlation between the difference in electronegativity and the width of the forbidden gap in semiconductors is unsuccessful if the whole (not a selection) of the experimental results are taken into account.

It follows from data on the low- and high-frequency dielectric constants of CdTe that the effective charge is close to zero, whereas the width of the forbidden gap $\Delta E$ is 1.5 eV, and $\Delta X = 0.55$. With the same value (0.5) for $\Delta X$, however, $\Delta E$ for PbTe is 0.63. With CuBr $\Delta X = 1$, while $\Delta E = 5$. In CdS, with the same $\Delta X = 1$, $\Delta E = 2.1$; while in PbS, with $\Delta X = 0.9$, $\Delta E = 1.17$. If CdS and ZnO are compared, the values of $\Delta E$ are very similar (2.1 and 2.2 eV), while those of $\Delta X$ differ by a factor of 2 (1 and 2). ZnSe and PbS show similar values of $\Delta X$ (0.8 and 0.9), while those of $\Delta E$ are 2.8 and 1.17. These inconsistencies are not surprising, since electronegativity is not a quantity which can be given a definite physical meaning. The search for a correlation between $\Delta X$ and $\Delta E$ is therefore without justification.

Few data are available on the determination of effective charges in molecular lattices. An important result was obtained by Yakshin *et al.*[15], who studied the refractions at different wavelengths and the dielectric constants of tetrahalides of Group IV elements — $CCl_4$, $SiCl_4$, $TiCl_4$, $GeCl_4$, $SnCl_4$, $SiBr_4$, $GeBr_4$, and $SnBr_4$. They determined the total polarisation $P$ and the electron polarisation $P_{el}$, and hence found the atomic polarisation $P_{at}$. In the case of an oscillator $P_{at}$ is connected with the effective charge $e_1$ by the following relation[16]:

$$P_{at} = \frac{Ne_1^2}{9\pi m_1(\nu_1^2 - \nu^2)}, \qquad (10)$$

where $\nu_1$ is the natural vibrational frequency of the effective mass $m$, and $\nu$ the frequency of the deforming field. If $f_1$ is the corresponding force constant and $\nu_1 = (2\pi)^{-1} \times (f_1/m_1)^{\frac{1}{2}}$, and if $\nu < \nu_1$, then

$$P_{at} = \frac{4\pi}{9}\frac{e_1^2}{f_1}. \qquad (11)$$

For vibrations along a bond of length $l$, $e = d\mu/dl$. In the molecules HCl, HBr, CO, $CO_2$, and $NH_3$, $e_1/e < 0.2$ and $P_{at} \simeq 0.1$ cm³, but in several crystalline substances $P_{at}$ can reach large values. Thus in Magnus' green salt $[Pt(NH_3)_4]\cdot[PtCl_4]$, which contains a Pt–Pt bond of length 3.25 Å, $P_{at} \simeq 55$ cm³ according to Baranova's data[17].

TABLE 6.

| Compound | $P$ | $P_{el}$ | $P_{at}$ | $e_1/e$ | $\Delta X$ |
|---|---|---|---|---|---|
| $CCl_4$ | 28.03 | 25.75 | 2.28 | 0.3 | 0.33 |
| $SiCl_4$ | 32.00 | 27.79 | 4.21 | 0.286 | 1.09 |
| $TiCl_4$ | 40.49 | 35.51 | 4.98 | 0.251 | 1.51 |
| $GeCl_4$ | 36.60 | 30.60 | 6.00 | 0.305 | 0.81 |
| $SnCl_4$ | 46.83 | 33.76 | 13.07 | 0.351 | 1.11 |
| $SiBr_4$ | 45.20 | 39.19 | 6.01 | 0.309 | 1.00 |
| $GeBr_4$ | 49.78 | 42.43 | 7.35 | 0.294 | 0.72 |
| $SnBr_4$ | 54.94 | 45.99 | 8.95 | 0.268 | 1.02 |

For compounds of the type $AX_4$ theory gives[18]

$$P_{at} = \frac{16\pi N}{9}\frac{\mu^2}{f_\delta} + \frac{16\pi N}{9}\frac{e_1^2}{f}, \qquad (12)$$

where $\mu$ is the moment of the bond, $f_\delta$ and $f$ are the respective force constants for bending and stretching, and the effective charge is defined as the differential of the dipole moment with respect to bond length. We finally obtain the equation

$$e_1 = \sqrt{\frac{9}{16\pi N}\left(\frac{P_{at}}{\frac{1/f_\delta}{l^2} + \frac{1}{f}}\right)}. \qquad (13)$$

Table 6 gives values obtained in the above work. The last column gives the electronegativity differences for the corresponding atoms.

It can be seen that the moment of the C–Cl bond in $CCl_4$ is 0.63 D, which is considerably lower than in $CH_3Cl$, for example. Although the above results are based on a rough calculation, the observed variation is interesting and instructive. The effective charges fall on passing from $CCl_4$ to $SiCl_4$ and $TiCl_4$, although $\Delta X$ increases. This of course, contradicts the usual ideas on the ionic nature of the bond and on electronegativity, but nevertheless it is quite in order. In contrast to carbon, which contains no $d$ orbitals of similar energy, silicon possesses close-lying $3d$ orbitals. This means that Si can act as an acceptor by virtue of its $3d$ orbitals, owing to which its effective charge may be diminished. This is still more characteristic of Ti, which has three vacant $d$ orbitals. This phenomenon is associated with an important difference between silicon and carbon compounds. Carbon is the only element in the Periodic System in which the valence state comprises four orbitals each containing one electron, and neither vacant orbitals nor orbitals containing an unshared pair of electrons remain. This is thus the classical example of a quadrivalent element, which explains the unique position of carbon among other elements. With silicon a $3d$ orbital lies close to the $3s$ and $3p$ orbitals, resulting in the new valence possibilities reported recently. It will be shown below that Ti possesses a still greater tendency to accept electrons into its vacant orbitals. As can be seen from Table 6, there is no correspondence between the variation of electronegativity and the effective charges in $GeBr_4$ and $SnBr_4$.

## 5. DIPOLE MOMENTS

Dipole moments are often used in estimating effective charges and electronegativities. The effective charges are sometimes determined from the ratio of the moment of

the bond to the product of the elementary charge and the length of the bond. Theoretically, however, this is incorrect. Dipole moments do not give a direct indication of the magnitude of the effective charge for a number of reasons, primarily because the observed moment includes not only the bond moments but also the moments of the atoms themselves, resulting in particular from their lone pairs of electrons. The N–F bond has a moment of 0.18 D (from data on $NF_3$), while that of the N–H bond is 1.5 D, although the electronegativity differences are very similar in the two cases (1.03 and 0.97). The moment of the N–F bond itself is evidently considerably larger, but is opposed by the moment of the nitrogen atom due to its $2s^2$ electrons. In general, a single definite dipole moment cannot be assigned to a bond A–B. The dipole moment depends on the valence state, hybridisation, and the other bonds of a given atom. The C–Cl bond has different moments in $CCl_4$ and in $CH_3Cl$. This is a further demonstration that a definite electronegativity cannot in general be assigned to an atom irrespective of the bond or of the electronic behaviour of the atom in its given state of hybridisation. The ethynyl halides have the following dipole moments:

$CH{\equiv}CF$ $0.75\times10^{-18}$,
$CH{\equiv}CCl$ $0.44\times10^{-18}$,
$CH{\equiv}CBr$ 0.0.

In these compounds the moments are lower than those of C–X in the $sp^3$ state of carbon evidently because the halogens are characterised not only by a positive electron affinity but also by their capacity to act as electron donors, as in $PdCl_2$ and other compounds. Thus fluorine would appear to be a strongly electronegative atom, but we must bear in mind its possible electropositive character, exhibited in the donor properties associated with its three lone pairs of electrons. These donor properties are developed still more clearly in chlorine and bromine. If it were possible to isolate ethynyl iodide, the positive end of its dipole might be expected to lie close to the iodine. The large moment of $CH_3Cl$ arises because in this molecule chlorine cannot act as a donor, whereas in ethynyl chloride it may have a partly double-bond character. We are not completely sure of the direction of the moment in the C–H bond (in the $sp^3$ state). The urge to set up an additive scheme of dipole moments has recently led to an attempt to represent those of C–H bonds as a function of their hybridisation[19]:

CH ($sp^3$) ~ 0.3D,
CH ($sp^2$) ~ 0.68,
CH ($sp$) ~ 1.0,
CH in HCN ~1.13,
CH in CH ≡ CH ~ 1.05 (from infra-red spectra).

In exactly the same way, the following moments have been suggested for C–C bond:

$C^+sp^3 - C^-sp^2$ 0.68,
$C^+sp^2 - C^-sp$ 1.15,
$C^+sp^3 - C^-sp$ 1.48.

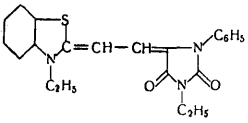
Experiment shows[20], however, that it is impossible by means of these six bond moments to reproduce the dipole moments even of hydrocarbons containing no bonds other than C–C and C–H. Thus for the difference in electronegativity between carbon (2.5) and hydrogen (2.1) the moments can vary from 0.3 to 1.0, and there is no certainty that the more electronegative atom carries the negative charge (in $CH_4$). Table 7 gives values of the moments of compound of the type $XCY_3$ obtained experimentally and calculated from the vector sums.

TABLE 7.

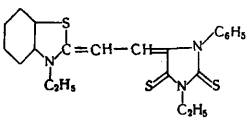
| Compound | Experimental moment | Moment from vector sum |
|---|---|---|
| $CIF_3$ | 0.92 | 0.22 |
| $CBrF_3$ | 0.65 | 0.03 |
| $CClF_3$ | 0.46 | 0.05 |

The deviations from the vector sum evidently depend on the positive double-bond character of the halogens ($I^+ = CF_2F^-$), which increases from chlorine to iodine. This is most clearly shown in the halogenopolynitroalkanes[21]. The moment of nitroform $CH(NO_2)_3$ is 2.71 D. Replacement of the hydrogen by iodine should apparently result in a lower moment, since the halogen usually forms the negative end of the dipole in a C–Hal bond. But the moment of $IC(NO_2)_3$ proves to be 3.79 D, which considerably exceeds that of nitroform. Here the iodine evidently forms the positive end of the dipole owing to its double-bond character and the partly "nitrite" state of the nitro-group. This is confirmed by specific properties of compounds of the type $HalC(NO_2)_3$, such as their ability to hydrolyse with the formation of "hypohalous" acids, to oxidise hydrazine and KI, and to be reduced at a mercury electrode. The ease of these reactions increases from $ClC(NO_2)_3$ through $BrC(NO_2)_3$ to $IC(NO_2)_3$. It follows from these results that in the chlorine derivative the moment of the C–Cl bond is small with the negative charge on the chlorine, in $BrC(NO_2)_3$ the bromine probably already carries a slight positive charge, while in $IC(NO_2)_3$ there is now a considerable positive effective charge on the iodine.

On the usual electronegativity scale oxygen is considerably more electronegative (3.5) than sulphur (2.44). This would appear to be consistent with the fact that sulphur yields sulphonium $-\overset{+}{S}<$ compounds more readily than oxygen gives oxonium derivatives, which (apart from $H_3O^+$) are very unstable. Thus from the ionisation potential and the electron affinity sulphur should be the more electropositive, but if sulphur and oxygen are conjugated with such a powerful donor atom as nitrogen, the sulphur becomes the more electronegative, since its electron affinity is greater than that of oxygen (47 and 35 kcal). This is evident from the dipole moments of the compounds

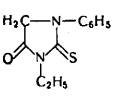


$\mu = 5.54$ D,



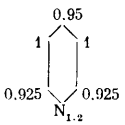
$\mu = 8.83$ D.

These molecules are similar in structure, differing only in the replacement of oxygen by sulphur. Conjugation is achieved in both molecules *via* identical bond systems, and the partly 'onium nitrogen is positive. Conjugation is a decisive factor in these molecules, because



for example, has a considerably lower dipole moment (2.34 D). The two intermediate benzothiazole derivatives in which the five-membered ring contains one oxygen and one sulphur atom have identical moments of 7.35 D. Since the three nitrogen atoms suppress the donor properties of the sulphur atoms, the electron affinity becomes the dominant factor in the latter, leading to a reversal of the electronegativity order.

The question of the significance of electronegativity arises especially in systems having conjugated bonds in which all the electrons must be regarded as in the field of all the nuclei. Five-, six-, and seven-membered rings are known to contain three bonding orbitals for six electrons. That is why the same atom may, depending on the conditions, bear a positive charge in some molecules and a negative charge in others. In the pyridine molecule six electrons move in the field of six nuclei, not counting the lone pair of $2s^2$ electrons on the nitrogen. The electron density is higher on the nitrogen atom, which in fact forms the negative end of the dipole. According to quantum-mechanical calculations the charge distribution is as follows:




The opposite situation occurs in the pyrrole molecule ($\mu$ = 1.8 D). Here the six electrons are in the field of five nuclei, but this sextet now includes the unshared electrons of the nitrogen. Hence the latter move only partly in the field of their own nucleus and partly belong to the four other centres. An approximate quantum-mechanical examination shows that the electron density is fairly uniformly distributed. This creates a deficiency of electrons on the nitrogen, which in this molecule forms the positive end of the dipole. The above examples show the possibility of a reversal of the dipole moment and hence of the electronegativity. This is confirmed by experimental data on the dipole moments of pyrrole derivatives and also on the acid–base properties. Whereas pyridine is a base, pyrrole is a weak acid. The basic dissociation constant of the latter is so low that it has not yet proved possible to determine it. Pyridine and pyrrole are examples of compounds in which nitrogen can produce basic and acidic properties. The biological function of nitrogen as an element giving rise to bases and acids may perhaps be associated with this in some cases.

In ordinary binary gaseous molecules of the NaCl type the dipole moment is large and quite close to the product of the charge and the bond length. But even in this case the picture is not really so clear as it appears to be in the primitive view of electronegativity. The dipole moment of CsCl [22] is 7.88 ± 0.17 instead of 11.23 (4.8 × 2.34) D. It is interesting that the bond length is less in CsF (2.34 Å) than in CsH (2.49 Å). It is possible that the CsF molecule has partial double-bond character, which is impossible in caesium hydride.

## 6. VACANT ORBITALS AND LONE ELECTRON PAIRS

It follows then that the view of a bond as the superposition of one covalent (electron pair in the field of two nuclei) and one ionic state is too rough a simplification. All the valence possibilities must be taken into account in bonds: (1) formation of molecular orbitals by unpaired electrons: (2) utilisation of the vacant orbitals of some atoms and of lone pairs of others; (3) the presence of many-centre orbitals (all the electrons in the field of all the nuclei); (4) the specific character of the given hybridisation; and (5) the participation of *d* orbitals and dative bonds. In conformity with this, the same atom in a given bond can act simultaneously both as a donor and as an acceptor, *i.e.* as both an electropositive and an electronegative atom.

It is useful to compare from this point of view elements of the Second and Third Periods. With the former, having a principal quantum number of 2, *d* orbitals are impossible, or more precisely a transition to 3*d* orbitals is possible only with a very great excitation energy which is not available in chemical compounds. With elements of the Third Period, however, 3*d* orbitals, which do not greatly differ in energy from 3*p* orbitals, are available. Published data show that the electron affinity is greater with elements of the Third than with similar elements of the Second Period [23] (see Table 8). The most reliable of the data in Table 8 are those for C, Si, O, F, Cl, and S.

A consideration of even beryllium on the basis of a superposition of an ordinary covalent bond ($2s2p$) and an ionic bond is clearly inadequate. A very characteristic feature of the chemical behaviour of beryllium is the presence of two vacant *p*-orbitals. Hence the dimerisation of $BeCl_2$, the polymerisation of $Be(CH_3)_2$, etc. In other words, Be is characterised by acceptor properties. Both beryllium and other elements in Group II exhibit acceptor properties with respect to oxygen. The attempt to represent ZnO as a lattice composed of $Zn^{2+}$ and $O^{2-}$, and ZnS as consisting of $Zn^{2+}$ and $S^{2-}$, is evidently mistaken [24]. Oxygen has an affinity for one electron of 35 kcal and yields a stable $O^-$ ion. The energy of the oxygen–electron system is represented by the usual type of potential curve with a minimum. But the affinity for a second electron with formation of $O^{2-}$ is characterised by a curve showing merely repulsion at all distances. An endothermic heat of this reaction can be found in the literature (~200 kcal). This is a fictitious quantity, resulting from calculations based on the assumption that in lattices of the MO type the M is a doubly charged positive ion, and the oxygen a doubly charged negative ion. In effect that value of the energy of formation of $O^{2-}$ is calculated which would be necessary for the energy of the hypothetical ionic lattice to agree with the heat of formation of the MO crystal. In other words, an *ad hoc* hypothesis is put forward, an arbitrary calculation is made, then the hypothesis is forgotten, the lattice begins to be regarded as ionic, oxygen with two negative charges begins to be regarded as real, and the affinity of oxygen for two

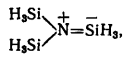
TABLE 8.

| Element | Electron affinity, eV | Element | Electron affinity, eV |
|---|---|---|---|
| Li | 0.5 | Na | 0.7 |
| B | 0.3 | Al | 0.4 |
| C | 1.13 | Si | 1.9 |
| N | 0.2 | P | 0.8 |
| O | 1.48 | S | 2.07 |
| F | 3.62 | Cl | 3.82 |

electrons and the "size of the $O^{2-}$ ion" begin to make their way from book to book as a real affinity and a real ionic dimension. The quantities obtained in this calculation have a considerable scatter. The effective charges (~0.4 for ZnO and 0.96 for ZnS) show that multicharged elementary ions evidently do not exist. The situation is different in complex or polyatomic ions, since the total charge is then dispersed over many atoms (for example $PtCl_4^{2-}$).

Elements of Group III are characterised by acceptor properties due to the presence of a vacant *p* orbital. Hence the dimerisation of $AlCl_3$, in which, in spite of the great electronegativity of chlorine compared with aluminium, the bridge chlorine donates its lone pairs of 3*p* electrons to the vacant 3*p* orbital of aluminium. Compounds of these elements are characterised by three-centre orbitals with an electron deficit, of the type of $Al_2(CH_3)_6$ for example[25,26]. This also explains the specific character of the boron hydrides, in which the coordination number of boron reaches six.

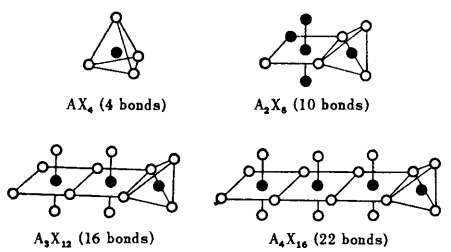
Group IV shows the striking difference in properties between $CO_2$ and $SiO_2$. Whereas $CO_2$ gives a molecular lattice and has a triple point at -56.6°, $SiO_2$ melts at 1600°–1700°. What is the reason for such a difference between two neighbouring elements in the Group? The important point is that silicon contains a low-lying 3*d* orbital, so that this element can act as an acceptor by virtue of its *d* orbitals, which is impossible for carbon, since with a principal quantum number of 2 the *d* orbitals do not exist, while excitation to 3*s* orbitals requires a very large amount of energy in the case of carbon. In several organosilicon molecules the silicon forms the negative end of the dipole, especially in the case of conjugated systems, when the positive charge may be delocalised, for example in aromatic compounds of silicon[27]. Whereas the C–O–C angle in ethers is 105°, close to the tetrahedral value, the Si–O–Si angle is about 150°, for example in $H_3Si–O–SiH_3$. This is characteristic also of silicates, in which the Si–O–Si angle (for example in $SiO_2$) is 142° or above§. The $N(CH_3)_3$ molecule is pyramidal, as is to be expected with nitrogen, which forms three bonds with its 2*p*-electrons; the $N(SiH_3)_3$ molecule is planar, for in it we must now reckon with conjugation of the type



corresponding to $sp^2$ hybridisation of the nitrogen. Hence $N(SiH_3)_3$ is a far weaker base than $N(CH_3)_3$. This ability to act as an acceptor is still more inherent in titanium, which has five vacant *d* and *p* orbitals (in the $d^2sp$ state). This is the reason for the tendency shown by compounds of the type $Si(OR)_4$ and $Ti(OR)_4$ to dimerisation and polymerisation.

§ The fact that the Si — O — Si angle in silicates is considerably greater than the tetrahedral angle (~140°) cannot be explained by the repulsion of $Si^{4+}$ ions, primarily because ions of silicon with four positive charges do not exist in lattices, and also because the tetrahedral angle is preserved in other cases of pure $sp^3$ hybridisation. Consequently the explanation must not be sought in the hypothesis that the silicon–oxygen chains are readily distorted and supposedly adjust themselves to the cations of a crystal lattice, but in the increased multiplicity of the Si–O bond due to the vacant 3*d* orbitals of the silicon and the donor properties of the oxygen. This is also the reason for the increase in the angle in organosilicon molecules containing Si–O–Si links.

Owing to their vacant orbitals, silicon and titanium are able to raise their coordination number from four to six (transition from a tetrahedron to an octahedron) if their immediate neighbour can donate lone pairs of electrons. On polymerisation the tetrahedra in a compound $A(OR)_4$ are converted into octahedra with a common edge. One tetrahedron remains at the end of the chain, two of its corners at the same time forming an edge of an octahedron. The total number of bonds in *n* isolated molecules is $4n$, whereas on polymerisation $6n-2$ bonds are formed. Thus the number of bonds increases by $2n-2$. Thus two tetrahedral molecules yield an octahedron–tetrahedron, three yield two linked octahedra and a tetrahedron, etc. (see diagram). The physical meaning of such polymerisation [for example in colloidal $Si(OR)_4$] is that the central atom by means of its vacant orbitals forms six instead of four bonds, while the oxygen atoms link two central atoms and one radical by means of their lone pairs. The mean energy of a Ti–Cl bond in the $TiCl_4$ molecule is 102.6 kcal, or 107.2 kcal allowing for the valence state, whereas according to Pauling it should be 85 kcal.[28] This increase in energy, which is not allowed for by Pauling's formula, is explained by the appearance of additional bonds due to the vacant orbitals and lone pairs. Thus although the electronegativity of titanium is nominally lower than that of carbon (1.32 and 2.5), titanium nevertheless attracts electrons more strongly to itself. The reason is that the nominal electronegativity takes no account of the acceptor properties of the element, and therefore cannot characterise it, except in very rare cases. As an example, Table 9 gives several cases of marked discrepancies between experimental bonding energies and those calculated from electronegativities.




In exactly the same way phosphorus in Group V is less electronegative than nitrogen (2.06 and 3.07), but nitrogen yields only $NCl_3$, while phosphorus gives $PCl_3$, $PCl_5$, and the octahedral ion $PCl_6^-$: *i.e.* it forms bonds by means of

TABLE 9.

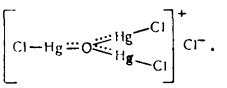
| Bond | Energy of bond from electronegativity, kcal | Expt. energy of bond, kcal |
|---|---|---|
| NCl | 76 | 115 |
| MnBr | 103 | 58 |
| MnI | 79 | 28 |
| FeCl | 82 | 69 |
| CuF | 148 | 69 |
| HgF | 273 | 140 |
| MnF | 224 | 81 |

3*d* orbitals. In the $Sb(CH_3)_3$ molecule antimony can exhibit donor properties, but in $Sb(CF_3)_3$ these properties are strongly repressed owing to the state

$$\bar{F}F_2C=\overset{+}{S}b\begin{matrix}CF_3\\CF_3\end{matrix}.$$

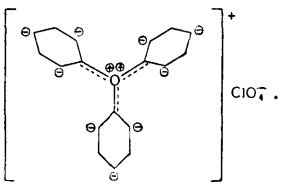
In Group VI of the Periodic System oxygen is regarded as the most electronegative element. Nevertheless, it forms compounds in which it donates its two lone pairs of $2s^2$ and $2p^2$ electrons. It is true that oxonium compounds, in which only one lone pair of electrons is donated, are usually unstable. The only exception is the stable oxonium ion $H_3O^+$. Products of the addition of acids of the type of HCl to ethers are not oxonium but molecular compounds, owing their existence to a hydrogen bond[29]. The bonding energy then varies from 4 kcal with ordinary ethers [for example $(CH_3)_2O$] to 11 kcal with tetrahydrofuran. Even in the case of three-membered rings, which, as might be expected, are able to exist as positive ions, for example diphenylcyclopropenone, interaction with HCl is confined to the formation of a hydrogen bond[30]. Meerwein compounds of the type $R_3OCl$ are very unstable and are readily hydrolysed. But the situation is quite different when oxygen forms two donor bonds apart from those due to the two unpaired electrons. Utilisation of all its $2s^22p^4$ electrons in bond formation is possible if the neighbouring atoms (1) possess electron affinity, (2) have vacant orbitals, *i.e.* are capable of acting as acceptors, and (3) have charges which can be delocalised, *i.e.* which can stabilise the molecule. Three types of oxonium compounds are then possible[31]. In the *first case* the oxygen forms bonds with four neighbours ($sp^3$ hybridisation) tetrahedrally, by means of two unpaired electrons and two lone pairs. In the *second case* the oxygen in the $sp^2$ state has three neighbours in a plane (angle 120°) and forms three $\sigma$ bonds and one $\pi$ bond. A cation then results, the odd electron passing to an atom or a group of atoms possessing electron affinity (for example $Cl^-$, $ClO_4^-$). Delocalisation of the charge contributes to the stability of the resulting ion. In the *third case* the oxygen is combined with two atoms in the *sp* state (angle 180°) and forms two $\sigma$ and two $\pi$ bonds. The first case is represented in the lattices of BeO, PtO, PdO, etc. In BeO the oxygen has tetrahedral coordination with very stable bonds (m.p. 2530°) in which all bonding possibilities are utilised, namely the $2s^2$ electrons of the beryllium, the $2s^2$ and $2p^4$ electrons of the oxygen, and the two vacant orbitals of the beryllium. The same is characteristic of ZnO also. In PtO the oxygen forms an irregular tetrahedron ($sp^3$), and the platinum a planar rectangle ($dsp^2$). A tetrahedral configuration is determined not by the "radius" of $O^{2-}$ but by the appropriate hybrid state of the oxygen.

The second case occurs, for example, in the $Hg_3OCl_4$ lattice (incorrectly written $HgO.2HgCl_2$). The structure of this substance[32,33] is



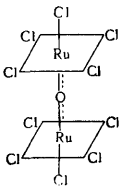
In this compound oxygen forms three coplanar bonds at angles of 120°. Mercury forms two *sp* bonds at an angle of 175°–180° with partial double-bond character delocalised among three atoms, and one chloride ions is outside the complex. Another example of compounds of this type is apparently provided by the triphenyloxonium compounds $[(C_6H_5)_3O]^+ClO_4^-$ prepared by Nesmeyanov and Tolstaya[34].

In contrast to the Meerwein trialkyloxonium compounds, they are extremely stable. Their structure can be represented as follows:



If our hypothesis about this structure is correct, the oxygen forms three bonds in a plane, not making a pyramid as in oxonium compounds (*i.e.* $sp^2$ hybridisation, not $p^3$). One negative charge is delocalised over the nine *ortho-* and *para*-positions of the phenyl rings, which should tend to stabilise these substances. Such stabilisation is impossible in Meerwein's trialkyloxonium compounds. Triphenyloxonium compounds should exhibit *ortho–para* orientation. All the $2s^22p^4$ electrons of the oxygen are utilised in the bonds.

The *sp* oxonium state with a coordination number of two and an angle of 180° is achieved in several cases, for example in the binuclear ruthenium complex $[Ru_2Cl_{10}O]^{4-}$. In this compound[35] the two ruthenium atoms are linked by an oxygen bridge:



The ion is diamagnetic, which can be understood when it is remembered that oxygen forms donor bonds with the ruthenium atom and that all the $d^5sp^3$ orbitals are occupied. In compounds of titanium with an oxygen bridge, the same state is achieved with two $\sigma$ and two $\pi$ bonds formed by oxygen at an angle of 180°.

Apart from the above cases of oxonium compounds, in which the oxygen donates two lone pairs, quadrivalent oxygen is theoretically possible as a result of excitation of one paired 2*p* electron to the 3*s* state, when $1s^22s^22p^33s$ oxygen with four unpaired electrons would be obtained. But such excitation requires 207 kcal, so that it is extremely improbable.

We shall not dwell here on cases in which the coordination number of oxygen is six, for example in lattices of the NaCl type (MgO, CaO, NiO, etc.), for this question will be considered in another paper, on covalent bonds in solids. It may be pointed out only that again there are no grounds for assuming the existence of an ion of atomic oxygen carrying two negative charges. The effective charge on oxygen in such lattices is close to unity, and the oxygen forms delocalised $\sigma$ bonds.

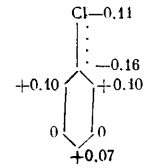
The possibility of the formation of multiple bonds by oxygen has been shown by Dyatkina *et al.*[36] to be the reason for the existence of inorganic "yls", such as uranyl, neptunyl, plutonyl, osmyl, vanadyl, zirconyl, etc. compounds. The U:O link in uranyl $UO_2$ is not a double bond but is of greater multiplicity, since the oxygen acts as a donor and the uranium as an acceptor by virtue of its large number of

vacant orbitals. The stability of the uranyl compounds and the variable multiplicity follow from the experimental results, and are explained on the hypothesis of partial transfer of the lone electron pairs of the oxygen to the vacant orbitals of the metal. As a result of its stability, the $UO_2$ group passes unchanged from one compound to another in a series of reactions. The strengthening of the bond and the increase in multiplicity are accompanied by a decrease in its length, which is 1.710 Å in the $UO_2$ group. The formation of "yls"is characteristic of metals having vacant orbitals, and able to form acceptor bonds in addition to the usual covalent bonds with oxygen.

On passing from oxygen to sulphur, we must allow for the possibility of bond formation by means of *d* orbitals. Sulphur can therefore be both more electropositive and more electronegative than oxygen. Sulphur is readily converted into the sulphonium state $R_3S^+$, with a low activation energy[37], by the interaction of $R_2S$ and RCl molecules. But whereas oxonium oxygen, combined with three atoms in the $p^3$ state, can carry only a positive charge, sulphur can be linked to three atoms and be either positive or negative (if its partner donates a lone pair of electrons to form a bond with the 3*d* orbital of the sulphur). This yields not sulphonium but sulphane $>\bar{S}-$ compounds[38]. This constitutes an important difference between sulphur in sulphane compounds and oxygen in oxonium compounds.

The elements of Group VII have a considerable electron affinity, forming an inert gas shell $s^2p^6$. They are regarded as typically electronegative. But even with fluorine donor properties can be developed to a slight extent (in acetyl fluoride for example)¶. With the other halogens (Cl, Br, I) donor properties determine the structure of many compounds. These include all bridge compounds, in which chlorine forms two equivalent bonds ($PdCl_2$, etc.) by means of the unpaired *p* electron and one lone pair of *p* electrons. Thus the "electronegative chlorine" (electronegativity 2.83) is the donor, while the palladium (1.35) is the acceptor. This again shows that the concept of electronegativity, applicable to compounds of the NaCl type, is quite inapplicable to halides of the transition metals. With Br and I the tendency to form donor bonds is considerably more marked than with chlorine. But even the electronegativity of chlorine itself should not be oversimplified, *i.e.* understood solely as a tendency to form a negative ion having an $s^2p^6$ shell. Chlorine can act as an acceptor by virtue of its vacant *d* orbitals if the other partner exhibits donor properties. The chlorine can then form two bonds (*p* and *d*), one a covalent bond involving the unpaired *p* electron and the other an acceptor bond in a *d* orbital with an effective negative charge. In other words, in conjugated systems chlorine can be bicovalent and negatively charged. A quantum-chemical investigation of this point has recently been made in the cases of vinyl chloride and chlorobenzene[39]. Partial double-bond character and a reduction in energy result from $d_\pi-p_\pi$ hybridisation of the orbitals of the chlorine atom.

This compels us to reexamine the problem of dipole moments, energy of conjugation, intensity of ultra-violet spectra, quadrupole coupling constants, etc. With chlorobenzene, therefore, in addition to what has been considered in previous work, we must also take into account the following charge distribution:




This helps us to explain the variation in the relative rates of mononitration of benzene derivatives ($C_6H_6$ 1, $C_6H_5CH_5$ 24.5, $C_6H_5F$ 0.15, $C_6H_5Cl$ 0.033, and $C_6H_5Br$ 0.03). We must in general be cautious in associating the tendency to attract an electron with electronegativity. We come up against this in the so-called hyperconjugation effect. According to this idea, compounds of the type $H_3C-C\equiv X$ show some double bonding between the two carbon atoms (in the $sp^3$ and *sp* states). This double-bond character is supposed to be due to a positive charge on the hydrogen atoms of the methyl group caused by the electronegativity of the atom or group X. Thus in the case of acetonitrile it is supposed that the double bonding is due to the state $\dot{H}CH_2=C=\bar{N}$. If this is so, it might be expected that the more electronegative is X, the more the electron is drawn away, the greater the hyperconjugation, and the shorter the C–C distance (owing to admixture of the $\pi$ state). Experiments show, however, that the C–C distance is the same in all derivatives of methylacetylene, independently of their electronegativity. It is identical at 1.46 Å in methylacetylene, dimethylacetylene, prop-1-ynyl iodide and bromide, trifluoromethylacetylene, acetonitrile, malononitrile, trichloroacetonitrile, and trifluoroacetonitrile. Thus the interatomic distance depends on the hybridisation and is insensitive to hyperconjugation, if the latter exists at all in the ground state of the molecule[40]. This question is not yet sufficiently clear. Whether the absence of a relation between double-bond character and electronegativity is a real or an imaginary problem is difficult to say, since as an individual characteristic of an element electronegativity has no clear or fully valid physical meaning. In most cases it is an empirical criterion, being neither a qualitative nor a quantitative characteristic of a chemical bond, as the present paper has tried to show.

¶ Barinskii and Malyukov[41] investigated the X-ray absorption spectrum of sulphur hexafluoride, and found the sulphur to have a negative charge of about -1, so that the fluorine atoms carry appreciable positive charges of about +0.16. This interesting experimental result can be explained only on the assumption that partly unoccupied 3*d* orbitals remain when sulphur forms six bonds, and these are acceptors for the lone electron pairs of the fluorine. These workers found zero charges on sulphur and chlorine in $SOCl_2$ and $SO_2Cl_2$, and hence also on the oxygen.

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# THE CHEMISTRY OF DIBORANE

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## INTRODUCTION

The chemistry of diborane and of the higher hydrides of boron was discussed in Stock's monograph [1] published in 1933, and subsequently reviews [2-11] and monographs [12-14] have appeared dealing with certain stages in the development and individual aspects of the chemistry of the boron hydrides. During recent years the chemistry of diborane has been developing very rapidly, and therefore a brief account of the progress made in this field is opportune.

The great theoretical achievement is the formulation of general quantum-chemical principles underlying the so-called "three-centre bonds" which have provided an explanation of the peculiarities of structure of the boron hydrides. The application of physical methods had led to the establishment of the geometrical structure of many interesting functional derivatives of diborane.

Considerable success was achieved in working out methods for obtaining diborane, alkyl- and aryl-diboranes, amine complexes of diborane and its chlorine derivatives, which formed the basis for a more thorough study of the chemical properties both of diborane itself and of its compounds.