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U.D.C. 543.878

The Concept of Electronegativity. Conclusions and Prospects†

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The principal methods for the determination of the electronegativity (EO) of the elements and radicals are examined—thermochemical, structural, spectroscopic, quantum-chemical, and a method based on ionisation potential. Particular attention is drawn to the necessity of taking into account the characteristic features of the chemical bond—its multiplicity and degree of hybridisation. The problems of the dimensions of the electronegativity of the elements are discussed. A compilation of the recommended electronegativities of atoms, radicals, and ions is given.
The principal applications of the concept of electronegativity are discussed: the determination of the atomic charges in molecules and crystals (good agreement between experimental and theoretical values is demonstrated); an estimate of the multiplicity of chemical bonds in inorganic ions and compounds, which agrees with the determination from the geometrical or spectroscopic characteristics of these substances; the principal physicochemical properties and the behaviour of inorganic substances as a function of the ionic character of their bonds and the difference between the electronegativities of the constituent atoms have been examined (semiconductor and molecular-physical characteristics, acid-base relations, specific features of the trans-effect of atoms in the inner sphere of platinum compounds, the possibility of the synthesis of new inorganic substances). The controversial questions of the nature and limits of applicability of the concept of electronegativity in general chemistry are briefly discussed.

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I. INTRODUCTION

More than one hundred years ago Berzelius[1] put forward the brilliant hypothesis concerning the electrical nature of chemical forces and divided all atoms into electropositive and electronegative. Lewis's theory gave rise to a concrete concept of polarity—regarded as the result of the displacement of the centre of gravity of the electron cloud of the bond towards one of the atoms, which is in fact electronegative in the given molecule.

More intensive experimental studies on polar molecules by various physical methods created the conditions for a new important scientific theory, whose author was Pauling[3]. The latter introduced into chemistry the concept of electronegativity (EO) defined as the capacity of the atom in a molecule (or in general in a compound) to attract valence electrons, and indicated an experimental method for its quantitative determination. This study gave rise to many other attempts to determine empirically the electronegativities of elements with the aid of geometrical, spectroscopic, and energy characteristics of atoms in molecules.

However, towards the beginning of the 1950's it became clear that the electronegativity of the element is not in most cases a constant property of the latter, but depends on the valence and degree of hybridisation of the bonds. Therefore special experimental and quantum-chemical investigations were begun in order to determine the electronegativity of atoms in various valence states and to find the electronegativities of whole groups of atoms (radicals).

The history of the development of the concept of electronegativity (up till 1961) is described in the present author's monograph[4] and the present review therefore considers mainly recent studies, which have made the greatest contributions to the theory and practical application of electronegativity in chemistry. Here too the principal conclusions following from the controversy on the meaning and limits of applicability of the concepts of electronegativity, which took place in recent years in the Soviet Union and to some extent abroad, will be described.

† In publishing this article, the Editorial Board consider it necessary to inform the readers that, although they do not agree with some of the author's views, the publication of the review is useful, since it will enable a wide circle of chemists to become familiar with the present state of the problem.

II. METHODS FOR THE DETERMINATION OF ELECTRONEGATIVITY

Any empirical method for the determination of electronegativity can be used also for the solution of the converse problem, i.e. the calculation of the corresponding physicochemical characteristic of the substance. Therefore particular attention is given here to quantitative methods for the determination and interpretation of electronegativity.

1. The Use of Thermochemical Data

Pauling[3] represented the difference between the energies of the real and purely covalent bonds between atoms A and B in the form of two terms—the electronegativities of the two species involved in the bond:

$$X_A - X_B = 0.208\{E(A-B) - {}^1/_2[E(A-A) + E(B-B)]\}^{1/2}, \quad (1)$$

where X denotes the electronegativity. Bearing in mind that the expression in braces in Eqn. (1) is equal to the heat of reaction Q, Eqn. (1) may be written in the more compact form

$$\Delta X_{AB} = 0.208Q\,. \quad (2)$$

Both these equations assume an arithmetical mean method for the calculation of covalent bond energies. In view of the correlation between bond strength and the product of the atomic wave functions, Pauling suggested that geometric means be used for the calculation of covalent bond energies, i.e. he replaced $\frac{1}{2}[E(A-A) + E(B-B)]$ by $[E(A-A) \times E(B-B)]^{1/2}$. Apart from being theoretically correct, such replacement made it possible to eliminate the disadvantage that in a number of cases (for example in alkali metal hydrides) the energy difference between $E(A-B)$ and half the sum of $E(A-A)$ and $E(B-B)$ were less than zero. By postulating that the electronegativity of hydrogen is 2.1, Pauling was able to calculate the absolute electronegativity of a large number of elements in the Periodic System. The most accurate and most complete data on the "thermochemical" electronegativities are given by Allred[5].

Comparison of Allred's system with Pauling's initial table reveals in a number of cases deviations in the electronegativities exceeding the effect of the experimental error in the determination of the bond energies. They are due to the use in the calculations of a large number of new thermochemical data for various bonds of the same element. If this entails not only a change in the polarity but also in the degree of hybridisation of the bonds, Eqn. (1) automatically reflects all the effects as changes in electronegativity.

At the present time there are unfortunately no general methods for an *a priori* determination of the type and degree of hybridisation, except for the thoroughly investigated case of carbon. Nevertheless the importance of this factor in the calculation of electronegativity is obvious and was recently again demonstrated by Dobrotin[6,7] for rare-earth compounds. Therefore, in relation to the concept of electronegativity, the problem is solved by a purely empirical procedure, by determining the electronegativities of whole groups of atoms (radicals) thereby taking into account the immediate environment of the given atom. This method was first used in 1955 by Pritchard and Skinner[8] and then by Finemann[9,10].

The latter author suggested that the thermochemical electronegativities of radicals be calculated from Pauling's Equation (1), with the atom B replaced by the radical R. It is then necessary to bear in mind that the energy of one of the covalent bonds must also be included in the calculation in the form $E(R-R)$. In some studies this was disregarded and incorrect values were obtained as a result.

The electronegativities of polyvalent atoms or free radicals, for example of the type AB, where A is a di- or tri-valent metal and B a halogen, can be calculated by the thermochemical method. Such calculations were recently performed by the present author[11] with the aid of the formula

$$\Delta X^2_{A^*-B} = \Delta X^2_{A-B} + 0.433[(E_{A^*-B} - E_{A-B}) + {}^1/_2(E_{A-A} - E_{A^*-A^*})]\,, \quad (3)$$

which can be readily derived from Pauling's basic equation for a normal molecule and a free radical. The results of the calculations are presented in Table 1, which includes for comparison the electronegativities of metals in the covalent state used in the calculation. Table 1 shows that the difference between the electronegativities of the metals decreases on formation of free radicals. The physical reason for this consists in the effect of free electrons on bond energies. Thus the presence of a free electron pair lowers the electronegativity of the atom in consequence of the repulsion between this pair and the valence electrons (in Group III elements); an isolated electron has a dual effect —on the one hand it repels the valence electrons and therefore lowers the electronegativity and on the other hand it increases the contribution to bond energy due to electron pairing. Evidently the repulsion effect of the free electron will predominate in small atoms (beryllium) and will gradually decrease with increasing interatomic distances (magnesium etc.); the spin–spin interaction does not depend on bond length and therefore begins to predominate in large atoms (calcium, strontium, and barium).

Table 1. Electronegativities of metals in free radicals.

Atom	X_{A^*}	X_A	Atom	X_{A^*}	X_A
Be	1.3	1.5	B	1.6	2.0
Mg	1.2	1.2	Al	1.3	1.5
Ca	1.2	1.0	Ga	1.2	1.6
Sr	1.2	1.0	In	1.2	1.7
Ba	1.2	0.9			
Zn	1.5	1.6			
Cd	1.5	1.7			

In concluding the description of the results derived by classical thermochemical methods for the determination of electronegativities, data will be presented on the effect of bond multiplicity using the carbon atom as an example. Approximate calculations showed[4] that the electronegativity of carbon decreases in the direction of the multiple bond ($X_{C=} = 2.1$, $X_{C\equiv} = 2.0$), increasing in the opposite direction ($X_{=C-} = 2.9$, $X_{\equiv C-} = 3.6$). Calculation of the average electronegativity of the carbon atom yields $X = 2.5$ for ethylenic carbon and $X = 2.4$ for acetylenic carbon. Thus, on formation of a multiple bond, the capacity of the atom to attract valence electrons changes.

The thermochemical method is the first and fairly accurate procedure for the determination of the electronegativities of the elements and is therefore frequently used as a comparison scale for other methods of calculation of atomic electronegativity. However, it should be recalled that it is not free from disadvantages. Apart from the considerations described above, one other factor

must be pointed out. In Pauling's equation it is postulated that the energy of a polar bond consists of the constant energy of the covalent bond and an additional "ionic" energy, although it is evident that, with increasing ionisation of the atom, the coulombic component of the bond energy will increase and the covalent component will fall. Energetic methods for estimating atomic charges, which will be examined below, have been developed on this basis.

Although the basic equation is formally incorrect, in practice the energy of the covalent bond varies within a small range, as can be readily shown by calculating, for example, the overlap integrals for purely covalent and purely ionic bonds of the same atoms at fixed distances. Furthermore the energy of the covalent bond is significantly lower than the electrostatic energy of the interaction between the same atoms over the same distance and therefore even a large relative error in the covalent components of the energy introduces a small absolute error into the final result.

Recently McDaniel and Yingst[12] proposed a new thermochemical procedure for the calculation of the electronegativities of atoms and radicals. By considering the thermochemical cycle for the dissociation of an acid and its oxidation in aqueous solution, the authors arrived at the following expression after a number of simplifications (and reasonable assumptions):

$$0.059\,\mathrm{pK}\,\Omega - E^0 = (X_A - X_H)^2\,, \qquad (4)$$

where E^0 is the electromotive force of the half-cell in the oxidation of the acid residue A^- and $pK\Omega$ was determined for the acid HA at 25°C. It is significant that it proved possible to calculate by means of this equation the electronegativities not only of elements but also of a number of molecular radicals.

The "thermochemical" electronegativities will be used by the present author subsequently in the compilation of a table of electronegativities.

2. The Use of Geometrical Characteristics

The electronegativity of an atom is evidently determined by the force of attraction of its valence electrons by the effective charge of the nucleus. Therefore it is quite reasonable to employ the geometrical characteristics of atoms and molecules for the calculation of electronegativity.

The concept of electronegativity was first applied in the calculation of interatomic distances by Schomaker and Stevenson[13], who suggested that the bond length be calculated from the formula

$$r_{AB} = r_A + r_B - 0.09\Delta X_{AB}\,, \qquad (5)$$

where r_A and r_B are covalent radii. The Schomaker–Stevenson formula was subsequently justified quantum-chemically and found numerous applications[14–18]; it led to the possibility of the solution of the converse problem—the calculation of electronegativities from atomic radii. The general form of the corresponding equations is

$$X = a\frac{Z^*}{r^n} + b\,, \qquad (6)$$

where $n = 1$ in Gordy's formula[19] and $n = 2$ in Allred and Rochow's equation[20]. The principal result of the application of these expressions is that, for atoms having the inert gas electronic structure, the "geometrical" electronegativities are close to the thermochemical values, but, for atoms containing d- and f-electrons in the outer or penultimate shell, the "geometrical" electronegativities are significantly smaller than the generally accepted values. For example, the thermochemical electronegativities for the copper and zinc subgroups are[5]:

Cu	Ag	Au	Zn	Cd	Hg
1.90	1.93	2.54	1.65	1.69	2.00 .

while the values obtained by Gordy and by Allred and Rochow are respectively:

0.96	0.91	0.92	1.21	1.13	1.12
1.75	1.42	—	1.66	1.46	—

The reason for this difference lies in the inadequacy of Slater's rules, which were used to calculate the effective nuclear charge. The more accurate system of Z^* values put forward recently[21] made it possible to bring the geometrical and thermochemical electronegativities much closer together, the difference between the two series of values remaining virtually the same throughout the Periodic System. For example, the average geometrical electronegativities for metals in copper and zinc subgroups are[22]:

Cu	Ag	Au	Zn	Cd	Hg
1.74	1.66	1.97	1.76	1.68	1.80 .

A disadvantage of the geometrical method for the calculation of electronegativities in some cases is the indeterminate valence state of the element in a number of simple compounds from which the interatomic distances were taken. However, in most cases there is no doubt about the valence of the atoms for which the geometrical electronegativity is calculated, and therefore the latter may be used in the compilation of the electronegativities of the elements.

Using the geometrical method, it is possible to determine the electronegativities of carbon atoms involved in multiple bonds. These calculations were performed between 1960 and 1964 [4,22,23] and their results are in good agreement with the data derived by the thermochemical method. When account is taken of the fact that the effective nuclear charge of the carbon atom also depends somewhat on the state of hybridisation and when appropriate ionisation potentials are used to calculate Z^*, then, on the basis of $Z^* = 3.25$ adopted for sp^3-hybridisation, it is easy to show that in the direction of the multiple bond $Z^*_C = 3.09$, $Z^* = 3.39$, for sp^2-hybridisation, and $Z^* = 3.64$ for sp-hybridisation. Hence, using the Allred–Rochow equation and the Gordy–Batsanov formula and also the geometrical characteristics of the multiple bonds taken from the literature[4,22], we arrive at the following electronegativities: 2.5 for sp^3-hybridisation, 2.7 for sp^2-hybridisation, 3.1 for sp-hybridisation, 2.2 for the double bond, and 2.1 for the triple bond.

Thus, if on formation of a multiple bond the electronegativity of the atom decreases in the direction of the bond, the effective charge of the atomic nucleus and its electronegativity become saturated as a result of the enhanced attraction of electrons from the opposite side of the atom. The geometrical method has also been applied in the calculation of the electronegativities of radicals. The first attempt was made by Wilmshurst[24], but, although the results were acceptable in practice, they were nevertheless incorrect from a formal standpoint[4]. A more successful attempt was made by Yan[25], who calculated the electronegativities of radicals with the aid of the equation

$$X = a\frac{n^*}{r^*} + b\,, \qquad (7)$$

where r^* is the effective radius of the central atom of the radical and n^* the number of effective valence electrons

(i.e. actually Z^*) calculated by Sanderson's method (see below).

Somewhat isolated from the trend discussed here is a whole series of studies by Sanderson[26-28], who observed that the average electron density of atoms varies in parallel with their electronegativity. By expressing the electron density of the element as a fraction of the electron density of the corresponding inert gas, Sanderson obtained quantities which he called "stability ratios" (SR) and which are tabulated in the present author's monograph[4] and will not be quoted here. The stability ratios and Pauling's electronegativities are simply related:

$$X^{\frac{1}{2}} = 0.21 \quad \mathrm{SR} + 0.77 \ . \tag{8}$$

We shall return to these studies later.

3. The Use of Spectroscopic Data

The first paper describing the relation between electronegativity and spectroscopic characteristics was published by Gordy[29], who established the following empirical relation:

$$k_{AB} = aN \left(\frac{X_A X_B}{r^2}\right)^{0.75} + b \ , \tag{9}$$

where r is the atomic distance, N the bond multiplicity, a and b are constants, and k is the force constant of the bond. Gordy's "spectroscopic" electronegativities are in good agreement with the thermochemical and geometrical values. However, the use in calculations of electronegativity of dynamic proportionality coefficients reduces the value of Gordy's method, because the determination of bond force constants frequently constitutes a difficult independent problem. Therefore subsequent development of the spectroscopic determination of the electronegativities of atoms and radicals involved the establishment of a direct relation between electronegativities and characteristic vibration frequencies. Without dwelling on the history of the problem, only the general form of functions used will be indicated[30-33]:

$$\nu = a + bX \ . \tag{10}$$

Such a linear relation is at first sight incomprehensible, but if the force constant of a polar bond is put in the simplest form:

$$k \simeq c \frac{Z_1^* Z_2^*}{r^3} \tag{11}$$

and the formula for a harmonic oscillator is then used, it is readily seen that

$$\nu \propto \frac{Z^*}{r^{1.5}} \ . \tag{12}$$

Comparison of Eqns. (6) and (12) shows that the exponent of the atomic radius in Eqn. (12) is the average of the values of n from Gordy's and Allred and Rochow's formulae, i.e. Eqn. (12) is essentially identical with Eqn. (10). Since the latter equation does not involve the mass of the vibrating atoms, in the calculation of electronegativities one usually compares the frequencies of the same A–B bond in molecules of the type ABC_n, where C_n is a variable atom or radical. However, comparison of the data of various workers shows that there is a considerable scatter in their results, which can be explained by the fact that bond frequencies cannot strictly be regarded as isolated, being influenced by the geometry of the molecule in addition to the nature of the chemical bond.

Like the thermochemical and the geometrical procedures, the spectroscopic method shows that the electronegativity of the atom increases in the direction opposite to that of the multiple bond and to a greater extent the larger is the multiplicity of the bond. In the direction of the multiple bond itself, the atomic electronegativity of carbon falls, as follows from the application of Gordy's formula to this case[23]: if it is assumed that $X_C = 2.5$, we have 2.3 and 2.2 respectively for C= and C≡ and similarly for nitrogen we have $X_{N=} = 3.0$ and $X_{N\equiv} = 2.8$.

The calculation of electronegativities from electronic spectroscopic data (optical electronegativities) is very interesting. Here mass does not play a significant role and therefore it is possible in principle to obtain more accurate values. Jörgensen and coworkers[34-36] showed that the wave number of the electronic transition for complexes of the type $MHal_n$ is proportional to the difference between the electronegativities of the central atom and the halogen. On the basis of the generally accepted electronegativities of the halogens, the authors obtained a number of electronegativity values for complex-forming metals.

This development in the calculation of atomic electronegativities is very promising; calculations of this kind can probably detect effects such as the trans-effect and other forms of interatomic interaction in the inner sphere of complex compounds.

Apart from the relation between electronegativities and vibration spectra, definite relations between the electronegativities of atoms and radicals on the one hand and spectroscopic characteristics on the other have been observed also in the radiowave part of the spectrum. This field was pioneered by Dailey and Shoolery[37], who established that the chemical shift (CS) of the nuclear magnetic resonance frequency of the hydrogen atom in alkyl derivatives is linearly related to the electronegativities of the radicals linked to the carbon atom:

$$X = 0.01158\delta + 1.71 \ , \tag{13}$$

where δ is the internal chemical shift in the ethyl group between α- and β-protons. Since these measurements were made in benzene solution and the latter exhibits an anomalous dilution effect, Cavanaugh and Dailey[38] later repeated the measurements in carbon tetrachloride solution and obtained more reliable data, which are described by the equation

$$X = 0.0114\delta + 1.78 \ . \tag{14}$$

The electronegativities of oxygen-containing radicals[39], Group IV elements[40], and Group IIb metals[41] have been calculated from similar equations.

Comparison of "radiowave" electronegativities with the "optical" values shows that in most cases the agreement is satisfactory. However, the electronegativities of certain radicals and in particular of CN, are significantly smaller than the generally accepted values. The reason for this lies in the inadequacy of the method of calculation of electronegativity from an equation of the type of Eqn. (14). Heel and Zeil[42,43] showed that, to a first approximation, the chemical shift measured experimentally consists additively of a term which depends on the chemical bond and terms characterising the geometry of the molecule only:

$$\delta = a + b + c + d, \tag{15}$$

where a is determined by the chemical difference between the protons, b is a diamagnetic correction which depends on the trial form adopted, c depends on the intermolecular interaction, and d characterises the magnetic anisotropy of the atoms and radicals within the molecule. The low value

of the "radiowave" electronegativity is due to the neglect of the factor d by Dailey and Shoolery[37].

To avoid errors, Heel and Zeil suggest that the comparative method be used to establish the relation between the chemical shift and electronegativity. With the available data on the magnetic resonance of two protons in α- and β-positions, it is possible to derive a difference equation in which the factors b and c vanish. Having chosen an appropriate pair of compounds, it is also possible to write yet another difference equation, the combination of which with the previous equation yields a double difference expression, involving only the relation between the factor a and the electronegativity.

A similar idea was developed by Thompson and Davis[44], who suggest that in compounds of the type AB_3, where B is a halogen or an organic radical, the chemical shift depends only on bond polarity and not on the presence of multiple bonds. Therefore the equation for calculations is of the form

$$\delta = a + bX + c\delta_\pi , \qquad (16)$$

where the bond multiplicity δ_π is determined independently. As a result, it is necessary to subtract the term $1.79\delta_\pi$ in order to obtain the polar component of the chemical shift from the measured value of δ.

Very interesting results have been obtained by Muller and Pritchard[45], who established a relation between the quadrupole bond constant in substituted hydrocarbons (CH_3A) as a function of the electronegativity of A and the interatomic distance r_{C-A}:

$$\chi_{C-H} = 22.6X + 40.1r_{C-A} + 5.5 , \qquad (17)$$

The data presented in this section do not exhaust all the results obtained by the application of spectroscopic methods for the determination of the electronegativities of atoms and radicals, but the principal studies carried out in recent years have been examined.

4. The Use of Ionisation Potentials in Quantum-chemical Calculations

Immediately after the development of the thermochemical method for the determination of the electronegativities, Mulliken[46] suggested that atomic ionisation potentials be used to calculate the electronegativity values. According to Mulliken, the arithmetical mean of the ionisation potential and the electron affinity of the atom in the given valence state is a measure of its electronegativity:

$$X \simeq {}^1/_2(I + E) . \qquad (18)$$

In order to convert Mulliken's values into Pauling's electronegativities, it is necessary to divide the former by a constant (for example 3.27, according to Pilcher and Skinner[47]).

Mulliken's method has been justified quantum-chemically both by Mulliken himself[48] and in Moffit's work[49,50]. Having written the wave function for the bond A–B in the form of a superposition of the wave functions for the purely ionic and purely covalent bonds between the same atoms, Moffit varied the coefficients of these terms in a way which ensured that the condition for formation of a non-polar bond is maintained. Assuming further that the energy of the atomic orbital is approximately equal to the ionisation potential of the corresponding electron and that the difference between the energy of the orbital and the coulombic integral is equal to the electron affinity, he arrived at Eqn. (18) as a measure of the electronegativities of atoms A and B.

The most interesting feature of Mulliken's method is the possibility of calculating the electronegativities of atoms in various valence states and for various degrees of hybridisation. In fact both the ionisation potential and the electron affinity depend significantly on the orbital where the relevant electron is located. Hence it is possible to solve also the converse problem—to determine the degree of hybridisation of the atom in a given compound from the known electronegativity (for example, the thermochemical value) and the known electronegativity values for various orbitals.

Skinner and Summer[51] found by Mulliken's method that the electronegativity of copper is 1.36 in the s-state and 3.32 in the d-state. Using the thermochemical electronegativity of copper, they calculated that in the given case copper is present to the extent of 23% in the d-state. Similar calculations have also been made for nickel.

Later Pilcher and Skinner[47] calculated the Mulliken electronegativities for atoms of the Second Period of Mendeleev's Table in various hybridisation states, which are in good agreement with the electronegativities for single and multiple bonds derived by other procedures. Table 2 presents the corresponding data converted into Pauling electronegativities.

Table 2. Effect of hybridisation on atomic electronegativities.

Element	Orbitals				
	p	sp^3	sp^2	sp	s
Be	—	—	—	1.43	—
B	—	—	1.91	—	—
C	—	2.50	2.74	3.20	—
N	2.46	3.51	3.74	4.40	—
O	3.32	4.66	—	—	2.19

A significant advance in the development of an ionisation method for the determination of electronegativities was made by Iczkowski and Margrave[52], who drew attention to the fact that the ionisation energy of the atom can be represented as a function of the charge:

$$I(q) = aq + bq^2 + cq^3 + \ldots , \qquad (19)$$

where a, b, c, ... are coefficients and q is the number of electrons in the valence shell. However, in practice only the first two terms need be retained in Eqn. (19). Differentiation of this equation with respect to q leads to the formula

$$\frac{\partial I}{\partial q} = a + 2bq . \qquad (20)$$

After substituting $q = 1$ and $q = 2$ in Eqn. (20), one obtains (see Iczkowski and Margrave[52] and Klopman[53])

$$\left(\frac{\partial I}{\partial q}\right)_{q=1} = \frac{I_v + E_v}{2} . \qquad (18a)$$

Thus Iczkowski and Margrave's hypothesis that the electronegativity is a derivative of the energy with respect to charge leads to Mulliken's formula.

Iczkowski's paper was followed by a series of papers by Hinze and Jaffe[54–56], in which the electronegativities were also determined as $\partial I/\partial q$ and the ionisation energies themselves were calculated for the given valence state quantum-chemically using the experimental or interpolated ionisation potentials for the ground state. A significant feature

of these studies is the fundamental approach to the concept of electronegativity not as a property of an abstract atom but as a property of its concrete electronic orbitals in the given chemical compound. The authors introduce the concept of "orbital electronegativity" (OEO) which characterises the capacity of an atom in a molecule to attract an electron to the given orbital. Hence it is clear that orbital electronegativity is a derivative of the energy of the atom and depends on the number of electrons in the orbital.

It is readily seen that this definition is based on two assumptions: (1) that the number of electrons in the orbital can be arbitrary in the range 0–2, including non-integral values; (2) that the energy is a continuous and differentiable (with respect to q) function. To justify both assumptions, one may refer to the experimentally determined distribution of electrons among the bonds joining atoms in molecules and crystals which leads to fractional charges on the atoms in the case of polar bonds. Another test of these assumptions can be provided by the similarity of the electronegativities calculated in this way to the values determined by independent methods.

Table 3. Group electronegativities according to Hinze and Jaffe.

Group R	R (–R)	R (–F)	R (–H)	Group R	R (–R)	R (–F)	R (–H)
CH_3	2.30	1.93	2.33	NH_2	2.82	2.61	2.96
CH_2Cl	2.47	2.13	2.55	PH_2	2.06	1.76	2.04
$CHCl_2$	2.63	2.32	2.77	OH	3.53	3.45	3.82
CCl_3	2.79	2.50	2.98	SH	2.35	2.11	2.38

The possibility of the determination of group electronegativities by the Hinze–Jaffe method is also very important[55]. These values are calculated on the assumption of a certain degree of hybridisation and polarity of the bond in radicals. Hence it follows immediately that the group electronegativity will depend to a high degree on the atom or radical with which the given group is linked. To characterise this effect, Table 3 lists the group electronegativities for covalent radicals (i.e. for radicals linked to groups of precisely the same kind) and for radicals combined with hydrogen and fluorine. Table 3 shows that the trend in the changes of the electronegativity values for radicals remains constant in all three cases but, if one includes, for example, hydrogen ($X = 2.20$) in this series of radicals, then it is readily seen that its relative position will differ appreciably depending on the atom with which it is combined. We shall return to this problem later.

The use of ionisation potentials for the calculation of electronegativities appears to be a very attractive procedure and this is in fact widely done by various investigators. Of the work of Soviet investigators, one should mention the studies of Nekrasov[57] and Povarennykh[58] and concerning the work of non-Soviet scientists one may refer to Chang's study[59], wherein an extensive calculation was made of the electronegativities of atoms in various states of hybridisation from formulae genetically related to Mulliken's equation. It must, however, be pointed out that ionisation potentials have to be used very cautiously, taking into account the peculiarities of this property. Thus, in an attempt to calculate the ionisation electronegativities of radicals, Pritchard and Skinner[8] used the values of I and E for the ground state and the same conversion factor as for the atomic ionisation potentials in the valence state. According to the data of Hinze and Jaffe, the equation relating the Mulliken electronegativities to Pauling's values is of the form

$$X_P = 0.336(X_M - 0.615) \quad (21)$$

On the other hand, if the ionisation potentials for the ground state are used, the formula is somewhat different:

$$X_P = 0.4(X_M - 0.5) \quad (22)$$

However, even the use of Eqn. (22) does not save the situation. The reason is that the ionisation potential and the electron affinity of a radical are essentially determined for different components, i.e. different atoms. As a simplification, one can of course postulate that the first ionisation potential of the radical corresponds to the removal of an electron from the negatively charged component. Similarly the electron affinity of the radical corresponds to the addition of an electron to the positively charged component. Consequently we are not justified in combining the ionisation potential determined for the radical with its electron affinity. Eqn. (18) can be used only when we can determine for the same atom in the radical both the ionisation potential and the electron affinity.

So far Mulliken's method can be applied to covalent molecules of the type A_2, where the above indeterminacy does not exist. The present author believes that the best way of applying Mulliken's method to molecular problems consists in comparing the sum of ionisation potentials and electron affinities for the molecules and the isolated atoms and then introducing corrections to the standard electronegativity on the basis of this comparison[60,61]. It has been shown[4] that the electronegativity of an isolated A atom is higher by 20% than the value in the molecule A_2. The reason for the increase of electronegativity on going from a covalently linked atom to a free atom consists precisely in the presence of the free valence, which leads to an additional energy gain on formation of the bond due to the electron pairing energy.

Similarly it proved possible to determine also atomic electronegativities for aqueous solutions[62] (Table 4). It is interesting that the electronegativities of metals are sharply reduced as a result of the hydration of the cations in aqueous solutions (Table 4).

Using the ionisation potentials and electron affinities of the carbon atom in various states of hybridisation, it proved possible to show[4] that $X_{C=} = 2.0$, $X_{=C-} = 2.8$, and $X_{\equiv C-} = 3.1$, i.e. to obtain a result similar to that derived by all other methods for the determination of electronegativities.

5. Compilation of Electronegativities

The above data show that the electronegativity of an atom depends on its valence, state and degree of hybridisation of its bonds, and even on the medium in which the given molecule is located. However, this is a characteristic feature of many concepts in structural chemistry. For example, the concept of the atomic radius was initially formulated by Bragg as a constant for a given element. Then the radii were differentiated into ionic and covalent, metallic and van der Waals. Within each Group relations were subsequently established between the radii and the valence of the atom, its coordination number, or bond multiplicity; molecular radii for ions in aqueous solutions have been derived.

Table 4. Electronegativities of the elements in aqueous solutions.

Group / Period	1a	2a	3a	4a	7a	8a			1b	2b	3b	4b	6b	7b
I	H 0.32													
II	Li 0	Be 0.13												F 3.87
III	Na 0.11	Mg 0.17									Al 0.18		S 2.28	Cl 3.15
IV	K 0.06	Ca 0.09	Sc 0.14	Ti 3+ 0.16	Mn 2+ 0.18	Fe 2+ 0.28 3+ 0.35	Co 2+0.28	Ni 2+0.34	Cu 1+ 0.32	Zn 0.38	Ga 0.25			Br 2.71
V	Rb 0.04	Sr 0.08	Y 0.07						Ag 0.55	Cd 0.46	In 0.31	Sn 2+ 0.44		I 2.34
VI	Cs 0.02	Ba 0.06	La 0.06							Hg 0.56	Tl 0.44	Pb 2+ 0.41		
VII		Ra 0.09												

Although this procedure increases our information about the structure of matter, this type of development of a concept reflects the fact that a molecule or a crystal is regarded as approximately a collection of interacting atoms. In a more rigorous approach, where the molecule or a crystal is regarded as a single system, a collection of nuclei and electrons, all the additive concepts of structural chemistry vanish altogether. Therefore a rigorous solution of the many-electron problem is impossible: in practice investigators use the "atoms in the molecule" method and then all that has been said above is valid.

The methods for the determination of electronegativities discussed in Sections 1–4 yield values characterised by different dimensions, which is undesirable for a physical concept. This disturbs some investigators (see, for example, Iczkowski and Margrave[52]) and can lead to misunderstanding of the role and position of the concept of electronegativity in the treatment of the nature of the chemical bond. The point, however, is that the concept of electronegativity is chemical in nature, reflecting one of the aspects of the chemical bond and therefore it cannot be characterised, in principle, by only one physical dimension. Chemical combination of atoms leads to a change in size, energy, and spectroscopic, magnetic, electrical, and other properties of the elements and can be adequately expressed in terms of these properties. However, it is evident that none of the properties enumerated above can exhaustively describe all the specific features of the reaction, the entire chemistry of the phenomenon. One can assert that a wide variety of dimensions of the concept is encountered not only with electronegativities but also with any other chemical concept. This can be demonstrated by examining the possible quantitative characteristics of the dimensions of such concepts as "metal", "hydrogen bond", "acid", "reactivity", etc.

Table 5‡ presents a compilation of the electronegativities of the elements, which can be recommended at the present time on the basis of the results obtained by different methods. Table 6 lists examples of the effect of bond multiplicity on atomic electronegativities.

‡ For hydrogen, antimony, and the actinides, the upper rows correspond to the lower-oxide state, and the lower rows to the higher-oxide state.

The same values can be used for an approximate calculation of the electronegativities of other atoms with multiple bonds, as can be seen in Table 7, where the electronegativities of molecular radicals are compiled. These are the electronegativities of the atoms in the radicals which are combined with the remainder of the molecule, for example, oxygen in NO_3 or nitrogen in NO_2. In compiling Table 7, the data of Ettinger[63] and Huheey[64] were used in addition to those quoted earlier.

In conclusion of this Section, we can consider briefly the problem of the electronegativities of the inert gas atoms. The problem of the calculation of these quantities arose after the publication of work on the fluorides and oxides of the inert gases and therefore the first electronegativities of inert gases were calculated (by Mulliken's method) as late as 1963 by Neiding[65] and Rundle[66]. The data of Sanderson[28] and Fung[67], obtained by means of different methods, are more correct. These values are in fact used in Table 5. Sanderson made the significant remark that the electronegativities of the inert gases must be understood not as the oxidising capacity of the elements but as the capacity of the atoms to resist the removal of their electrons on formation of a polar bond.

III. THE SCOPE OF THE APPLICATION OF THE CONCEPT OF ELECTRONEGATIVITY

As already stated above, any of the methods of calculation can be used to apply electronegativities. In this section we shall examine the use of the concept of electronegativity in the treatment of chemical properties only of substances (mainly inorganic) and various manifestations of the nature of the chemical bond in molecules and crystals. However, before presenting the factual data, several preliminary comments must be made.

The concept of electronegativity is not a theory in the sense that it does not explain experimental findings on the basis of some new hypotheses. It permits only the estimate or measurement of the asymmetry of the electron cloud of the bond, i.e. it makes it possible to say which of the species involved in the bond has a negative and which a positive charge and what is the approximate magnitude of these charges. Having obtained such information, the investigator can set up (on the basis of a familiar theory or

Table 5. Electronegativities of the elements.

1a	2a	3a	4a	5a	6a	7a	8a	1b	2b	3b	4b	5b	6b	7b	8b
														H 2.2	He 2.8
Li 1.0	Be 1.6									B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	Ne 4.4
Na 0.9	Mg 1.2									Al 1.6	Si 1.9	P 2.2	S 2.6	Cl 3.2	Ar 3.5
K 0.8	Ca 1.0	Sc 1.3	Ti II 1.4 IV 1.6	V III 1.5 IV 1.7 V 1.9	Cr II 1.5 III 1.6 VI 2.4	Mn II 1.4 III 1.5 IV 2.1 VII 2.5	Fe II 1.8 III 1.9	Co 1.8	Ni 1.9	Cu I 1.8 II 2.0	Zn 1.6	Ga 1.7	Ge 2.0	As 2.1	Se 2.5	Br 3.0	Kr 3.0
Rb 0.8	Sr 1.0	Y 1.2	Zr II 1.3 IV 1.5	Nb 1.6	Mo IV 1.7 VI 2.3	Tc V 1.9 VII 2.3	Ru III 2.0 IV 2.1	Rh 2.1	Pd 2.1	Ag 1.9	Cd 1.7	In 1.8	Sn II 1.8 IV 2.0	Sb 1.9 2.2	Te 2.3	I 2.6	Xe 2.6
Cs 0.7	Ba 0.9	La 1.1	Hf 1.4	Ta 1.5	W IV 1.6 VI 2.2	Re V 1.9 VII 2.1	Os III 2.0 IV 2.1 VIII 2.4	Ir 2.1	Pt II 2.1 IV 2.2 VI 2.6	Au 2.3	Hg 2.0	Tl 1.4 1.9	Pb II 1.9 IV 2.1	Bi III 2.0 V 2.2	Po 2.2	At 2.3	Rn 2.3
Fr 0.7	Ra 0.9	Ac 1.1															

lanthanides	Ce 1.1	Pr 1.1	Nd 1.2	Sm 1.2	Eu 1.1	Gd 1.2	Tb 1.2	Dy 1.2	Ho 1.2	Er 1.2	Tu 1.2	Yb 1.1	Lu 1.2
actinides	Th 1.2 1.5	Pa 1.3 1.7	U 1.4 1.9	Np 1.4 1.9	Pu → Cf 1.3								

Table 6. Effect of bond multiplicity.

Bond type	X	Bond type	X
C—	2.6	(—C)—	2.6
C⋯	2.3	(⋯C)—	2.7
C=	2.2	(=C)—	2.8
C≡	2.1	(≡C)—	3.2

Table 7. Electronegativities of molecular radicals.

Radical	X	Radical	X	Radical	X
CF_3	3.1	NF_2	3.4	PO_3	3.4
CCl_3	2.8	NC	3.3	BO_3	3.4
CBr_3	2.7	NO_2	3.2	SO_3	3.5
CI_3	2.6	N_3	3.2	CO_3	3.6
CH_3	2.5	NCS	3.1	NO_3	3.8
C_2H_5	2.6	SCN	2.8	PO_4	3.6
C_6H_5	2.8	NH_2	3.0	SO_4	3.7
$CH=CH_2$	2.9	PH_2	2.2	ClO_4	3.9
C≡CH	3.3	OH	3.5		
CHO	2.9	SH	2.6		
COOH	3.0	SeH	2.4		
CN	3.3				

relation) a hypothesis concerning the law governing the variation of the chosen physicochemical property of the substance as a function of the polarity of its bond. Thus, for a successful application of the concept of electronegativity, it is necessary to know how the ionic character of the chemical bond influences a given characteristic and only then introduce quantitative criteria.

The above limitations do not diminish the scope of the concept of electronegativity, since millions of molecules and crystals have structures involving polar bonds and the total number representatives of extreme types of bonds in nature amounts to only several hundred. Therefore the study of polar bonds is of great theoretical and practical importance.

1. Atomic Charges in Molecules and Crystals

Even simple comparison of the electronegativities of two atoms makes it possible to say which of them will behave as an electron donor or acceptor on formation of the bond. However, additional theoretical and experimental data must be used to establish a quantitative relation.

The first functional relation between the ionic bond and the difference between atomic electronegativities was established by Pauling[68] in 1939. Having adopted as the reference points the effective atomic charges in hydrogen halide molecules, calculated from the simple formula

$$i = \frac{\text{dipole moment}}{\text{bond length}} \qquad (23)$$

and the thermochemical electronegativities, he obtained a smooth curve, which fits the following equation:

$$i = 1 - e^{-0.25\Delta X^2}. \qquad (24)$$

After the dipole moment of hydrogen fluoride had been corrected, Pauling modified Eqn. (24):

$$i = 1 - e^{-0.18\Delta X^2}. \qquad (25)$$

Table 8 lists the values calculated by this formula.

The validity of Eqn. (25) has been confirmed theoretically by many investigators (see the present author's monograph[4] for a more detailed description), who obtained by independent methods similar values for the ionic character of hydrogen halide molecules and certain other simple cases. It is significant that even the most accurate atomic charges obtained by Barinskii and Nadzhakov[70] by X-ray spectroscopy are also in fairly good agreement with Pauling's data. The experimental percentages of the ionic character of the bonds§ are listed below (first row) together with the theoretical values (second row) obtained from a comparison of the data in Tables 5 and 8.

CS_2	GeH_4	H_2S	$GeBr_4$	IBr	HCl	$ZnBr_2$
0	5	5	17	10	20	25
0	2	5	20	5	20	32 .

§ Calculated from the atomic charges.

Chronologically the next important study on the use of electronegativities for the calculation of the ionic character of bonds in molecules is that of Sanderson[26-28]. According to Sanderson, the stability ratio (i.e. the electronegativity in his terminology) of any atom in a molecule is equal to the stability ratios of all the remaining atoms, i.e. on formation of the bond the stability ratios of the atoms become equalised. This postulate is almost self-evident, since it is clear that in a stable molecule or bond the electron pair will be located at such a distance from each species involved that the attraction which it exerts is balanced out and this means that the stability ratios are equalised. Sanderson suggests that in practice the geometrical mean stability ratio be calculated as the value for the molecule AB:

$$SR_{AB} = \sqrt{SR_A \times SR_B}\,. \qquad (26)$$

Table 8. Dependence of the ionic character of the bond in molecules on electronegativity.

ΔX	i	ΔX	i	ΔX	i	ΔX	i	ΔX	i	ΔX	i
0.0	0	0.5	7	1.0	20	1.5	35	2.0	51	3.0	80
0.1	1	0.6	9	1.1	23	1.6	38	2.2	58	3.2	84
0.2	2	0.7	11	1.2	26	1.7	41	2.4	64	3.4	88
0.3	3	0.8	14	1.3	29	1.8	44	2.6	70	3.6	91
0.4	5	0.9	17	1.4	32	1.9	47	2.8	75	3.8	93

Having further postulated that the ionic character of the bond in the sodium fluoride molecule amounts to 75%, Sanderson was able to calculate the ionic electronegativities of the sodium and fluorine atoms and then of all the remaining elements in the Periodic System. When the set of covalent and ionic stability ratios is available, it is easy to calculate the ionic character of the bond from the equation

$$i = \frac{SR_{AB} - SR_{A^0}}{SR_{A^+} - SR_{A^0}}\,. \qquad (27)$$

Comparison of the values of the ionic character of the bond obtained by Sanderson's and Pauling's methods shows that the average statistical discrepancy amounts to 10%.

However, extension of Sanderson's method to more complex compounds (including complexes) leads to incorrect results[71]. This is reasonable, since, for example, in potassium sulphate there are two independent (to a first approximation) bond systems, K–O and S–O, and there is no need for the requirements that the stability ratios of the potassium and sulphur atoms should be equalised on formation of this compound.

The present author proposed a modification of Sanderson's method, based on the postulate that the electronegativity of an atom is a characteristic of one valence state[72] (see also Iczkowski and Margrave's definition of electronegativity). Therefore the method of calculating the stability ratio for a compound was modified so that under the root sign the stability ratios of the species involved in the bond were each raised to a power equal to the product of the valence of the atom and the number of such atoms in the given molecule:

$$SR_{A_nB_m} = \sqrt[np+mk]{SR_A^{np} \times SR_B^{mk}}\,, \qquad (28)$$

where p is the valence of atom A, k the valence of atom B, and n and m are the numbers of atoms A and B in the molecule respectively. Since in neutral molecules $np = mk$, Eqn. (28) transforms into

$$SR_{A_nB_m} = \sqrt{SR_A \times SR_B}\,. \qquad (29)$$

Thus on formation of any complex molecule only the stability ratios of linked atoms are equalised and the stability ratio of the molecule must be equal to the geometrical mean of the values for the species involved in the chemical bonds.

The suggested modification of the method makes it possible to avoid the contradictions which arose in the calculation of the stability ratios of molecules containing polyvalent atoms. For example, according to Sanderson the stability ratio of the sodium atom in Na_2O is less than in sodium itself and therefore the ionic character in the first case is lower than in the second, which is incorrect. Sanderson's modified method can also be applied in the calculation of the stability ratios of complex ions, for example the sulphate ion:

$$SR_{SO_4} = \sqrt[7]{SR_S^3 \times SR_O^4}\,. \qquad (30)$$

On comparing the stability ratio of the sulphur atom in the sulphate ion with the values for neutral and positively charged sulphur, it is readily seen that $SR_{SO_4} = 4.48$ corresponds to a charge of +0.15 on the sulphur atom. The stability ratios of a number of oxygen-containing anions, listed in Table 9 together with the charges of their central atoms, were calculated similarly. Comparison of the data in Tables 7 and 9 shows that the sequences of experimental and theoretically calculated electronegativities of radicals are the same.

Table 9. Stability ratios (SR) and charges (Z) of atoms in complex ions.

Ion	SR	Z for central atom	Ion	SR	Z for central atom
BO_3^{3-}	4.05	+0.42	SeO_4^{2-}	4.63	+0.11
CO_3^{2-}	4.49	0.17	TeO_4^{2-}	4.28	0.21
NO_3^-	4.86	0.04	CrO_4^{2-}	4.30	0.20
VO_3^-	4.15	0.22	MoO_4^{2-}	4.19	0.24
ClO_3^-	4.91	0.03	WO_4^{2-}	4.74	0.08
BrO_3^-	4.79	0.06	ClO_4^-	4.91	0.03
IO_3^-	4.44	0.15	BrO_4^-	4.78	0.06
SiO_4^{4-}	3.82	0.82	IO_4^-	4.43	0.15
PO_4^{3-}	4.10	0.32	MnO_4^-	4.28	0.18
AsO_4^{3-}	4.42	0.23	ReO_4^-	4.99	0.01

A procedure for the determination of the ionic character of the bond, similar to Sanderson's method, was developed by Lakatos[73-75], who suggested that, on formation of the molecule AB, the forces which the effective charges of the nuclei of the atoms A and B exert on the valence electrons should be equalised. This hypothesis enabled Lakatos to obtain results differing on average by 7% from the amounts of ionic character calculated by Pauling's method.

Simultaneously with Lakatos, Fereira[76] used the idea of the equalisation of electronegativities on bond formation. He concentrated particularly on the relation between the electronegativity of the atom and its effective charge q.

Having expressed the electronegativity of the real atom by a power series, as suggested by Daudel[77,78]

$$X(q) = X(0) + a\left(\frac{\partial X}{\partial q}\right) + \cdots \quad (31)$$

and having retained only the first and second terms of the expansion, Fereira was able to calculate, on the basis of the postulated equality of $X_A(q)$ and $X_B(q)$ in the A–B bond, the amounts of ionic character in the bonds of hydrogen halides, in good agreement with Pauling's data: 32% for HF, 16% for HCl, 10% for HBr, and 5% for HI.

The equalisation principle has also been used in the method of orbital electronegativities[79-81]. Since in this method the electronegativity of an atom is also represented by a linear function of the charge, the formulae and the results are very similar to those obtained by Fereira.

The data presented show that Sanderson's idea of the equality of the electronegativities of atoms when these form a stable bond has been widely accepted and has given rise to the possibility of calculating the ionic character of the bonds in molecules, the result being in qualitative or even semiquantitative agreement with experiment. It is only fair to mention that Sanderson's postulate originates from the fundamental work of Pauling[68], who established that, when an atom acquires a positive charge, its electronegativity increases (approximately by 0.4 for each +1 unit of charge) and on acquisition of a negative charge it decreases to the same extent. As a result, on formation of a polar bond, the electronegativity of the cationic component of the molecule increases and that of the anionic component falls, i.e. the electronegativities of the two atoms approach one another. The electronegativity increments quoted by Pauling for ± 1 units of charge are, of course, approximate and corrected values will be given below: here it is desired to mention only the fundamental aspect of the problem.

The approach to the determination of the ionic character of bonds in molecules examined above has been criticised by Pearson and Gray[82], who remarked that the equalisation of electronegativities only reduces the mutual electrostatic energy and the change in the overlapping of the wave functions is not taken into account. However, the Coulombic component of the energy of polar bonds is the major component of the total bond energy and therefore the above approximation is in practice quite acceptable. Pritchard[83] took into account the effect of the change in the overlapping of the orbitals for the carbon–nitrogen bond and showed that the electronegativities of the atoms are not then equalised but their values approach one another—after the formation of the bond the difference between the electronegativities of the species in the bond amounts to only 10% of ΔX for these atoms before interaction. This calculation yields a characteristic estimate of the degree of approximation in the "electronegativity equalisation" method.

The ionic character of the bond can be calculated also with the aid of overlap integrals (OI). The latter characterise the electron density of the bond and in a series of similar molecules vary quite steadily, namely the overlap integral decreases with increasing ΔX, i.e. bond polarity. However, for a quantitative solution of the problem, it was necessary to normalise the overlap integrals, i.e. to adjust them to a single scale. For this purpose, the present author suggested[21,84,85] that the overlap integral of a real bond A–B be compared with the overlap integral of a purely covalent bond between the same atoms, the latter being defined as a bond whose length is equal to the sum of the covalent radii and whose polarity is zero (the second condition means that the effective charges quoted for the atoms A and B are equal). Then the ratio of the overlap integrals of the real and purely covalent bonds represents the covalent character of the bond A–B. Calculations showed that the results are close to Pauling's data and are described by the same equation:

$$i = 1 - e^{-0.25\Delta X^2}. \quad (32)$$

We now come to the description of methods in which empirical data are used, the reader being referred to the present author's monograph[4] where other theoretical studies on the calculation of the ionic character of ionic bonds in molecules carried out up to 1960 are described. The first method using experimental data for the calculation of the ionic character is that of dipole moments [see Eqn. (23)]. Later it was shown that the dipole moment is a complex function which depends on the ionic character and hybridisation of bonds and also on the effect of isolated electron pairs.

At the present time these other factors cannot be taken into account although certain advances on those lines have been made[86]. Therefore the employment of dipole moment data can be justified only in those cases where all the factors, except the ionic character of the bond, are low or cancel out. This condition obtains in hydrogen halides.

The application of radiospectroscopic data, for example data on quadrupole interaction, which appeared very promising initially, later failed to justify these hopes, since for an unambiguous determination of the ionic character of the bond it is again necessary to know accurately the degree of hybridisation of the bond. In those cases where the latter characteristic is unknown, certain assumptions are made concerning the type and degree of hybridisation[4] and therefore the final data are of no greater value than the initial assumptions. Data on quadrupole interaction can be used directly only for qualitative purposes in comparing similar or genetically related molecules. Fundamentally important results were obtained recently by Mikhailov[87,88] and Gilson[89], who used orbital electronegativities to establish a relation between the ionic character of the bond and the quadrupole coupling constant χ. Since orbital electronegativities are themselves functions of bond hybridisation, it is possible to establish more unambiguous relations between χ and the ionic character of the bond.

A third method whereby experimental data are used to calculate the degree of ionic character of the bond is based on chemical bond energies. The principal idea of this procedure consists in the representation of the bond energy by a set of ionic and covalent terms (supplemented by a polarisation component or account being taken of bond multiplicity). On minimising such a system by the variation of the relative contributions of both terms or by comparing the calculated and experimental values, it is possible to obtain information about the ionic character of chemical bonds. In an elementary form this idea is contained even in Pauling's basic equation [Eqn. (1)] and subsequently only the calculation of the two terms of bond energy was formulated in a concrete form. In the author's monograph[4] the covalent component of bond energy was calculated with the aid of overlap integrals, while Pearson and Gray[82] used the Coulombic and exchange integrals, for complex molecules the latter being calculated with the aid of empirical data on covalent bond energies and ionisation potentials.

In a series of studies by Fereira[90-92] the ionic character of the bond was calculated by the equation

$$E(\mathrm{A}-\mathrm{B}) = E_{\mathrm{cov}} + E_{\mathrm{coul}} + \Delta E_A(q) + \Delta I_B(q), \quad (33)$$

where ΔE and ΔI are the partial electron affinity and partial ionisation potential. These concepts reflect the energies

which must be expended to remove "part of the electron" (in the statistical meaning of this term) or which are evolved on partial addition of the electron to the atom. Subsequently Fereira modified the first two terms of Eqn. (33), namely he established a relation between the covalent energy term and the ionic character of the bond, took account of hybridisation, and varied not only the polarity but also the chemical bond length in order to minimise the energy.

The energy method can be applied, however, only in simple cases—di- or tri-atomic molecules. In more complex molecules it is difficult to take into account the non-valence interatomic interaction and bond hybridisation. This is the reason why it is almost impossible to calculate the ionic character of the bond. Therefore, for fairly complex systems, the only suitable experimental method available at the present time is X-ray spectroscopy. Table 10 compares the results of X-ray spectroscopic studies on the molecules of ferrocene and its analogues[93-95], with the values calculated by the present author[96] using the electronegativity method.

Table 10. Effective atomic charges in π-complexes.

Molecule	X-ray spectrum		EO method	Molecule	X-ray spectrum		EO method
	Refs.93 and 94	Ref.95			Refs.93 and 94	Ref.95	
$Fe(C_5H_5)_2$	0.4	0.73	0.70	$Ni(C_5H_5)_2$	—	0.65	0.55
$Fe(C_5H_5)_2^+$	—	0.68	0.76	$Ni(C_5H_5)_2^+$	1.0	—	0.76
$Co(C_5H_5)_2$	0.4	—	0.70	$Mn(C_6H_5)_2$	1.5	1.6	1.25
$Co(C_5H_5)_2^+$	1.2	0.8	0.94	$Cr(C_6H_6)_2$	1.1	1.5	1.44

It follows from Table 10 that the electronegativity method can be used to describe the distribution of charges in molecules, in good agreement with experiment.

Before concluding the description of the methods of calculating charges in molecules, we must return to the question of taking into account the effect of bond polarities on atomic electronegativities. When a molecule of the type MA_2 formed by the combination of atoms M and A, the latter acquire charges i due to the ionic character of the bond. The appearance of a positive charge i increases the electronegativity while the appearance of a negative charge reduces it. As a result, in order to calculate the ionic character of the second M–A bond it is necessary to compare the electronegativity of the atom A with $X_M + i\dot{p}$, where $\dot{p}$ is a constant coefficient equal to the change in X on appearance of an integral charge. Bearing in mind the equivalence of both M–A bonds in MA_2 molecules, the ionic characters of the first and second M–A bonds must be averaged. This is the general scheme of the calculation of the ionic character of the bonds in complex molecules (for other examples, see the monograph[4]).

The coefficient $\dot{p}$ can be determined using Eqn. (6). For this purpose, a variable value of the atomic radius, varying as a result of ionisation (see the author's monograph[4], p. 176), must be substituted in the formula

$$X = a\frac{Z^*}{r} + 0.54 . \qquad (6)$$

and Z^* must be changed appropriately as a function of i. Calculations for all the electropositive elements of the Periodic System show that $p = 0.4$ for Periods III–VI and $p = 0.8$ for the elements of Period II. For the electronegative elements, $\dot{p} = 0.4$ (chalcogens) and $\dot{p} = 0.8$ (halogens). Thus the value $p = 0.4$ postulated by Pauling has been confirmed in general. However, fundamentally different results are obtained for hydrogen. The formula for the calculation of X_H is of the form

$$X = 0.60\frac{Z^*}{r} + 0.54 . \qquad (6)$$

Assuming that the radius of the hydrogen atom varies according to the same law as for divalent cations (see Ref. 97), it is easy to calculate that the electronegativity increases anomalously with increasing charge:

Charge =	0	+0.1	+0.2	+0.3	+0.4	+0.5 ...
X=	2.1	2.5	3.0	3.6	4.4	5.6 .

Hence it follows that, after the formation of a bond, for example C–H, where the hydrogen atom should acquire a charge of +0.06, the electronegativity of hydrogen increases to 2.4, i.e. significantly approaches the electronegativity of the methyl group. If, as a result of the mutual influence of the atoms in substituted hydrocarbons, the ionic character of the C–H bond increases still further, the relative electronegativities of the carbon and hydrogen atoms may be reversed. This may explain the unusual finding that in many hydrocarbons the methyl group frequently behaves as a more powerful electron donor than hydrogen. This anomalous variation of the electronegativity of the hydrogen atom with increasing positive charge can also constitute the basis for explaining the contradictions which occur in the determination of the direction of the moment in the C–H bond.

Coming now to the determination of the ionic character of bonds in solids, the following fundamental characteristics of the coordination crystals of inorganic compounds must be emphasised: namely the valence of the atoms is as a rule less than the coordination number (CN). If, for simplicity, we consider sodium chloride, it is evident that in the crystalline state, where each sodium atom is surrounded by six chlorine atoms, there can exist only one normal NaCl chemical bond because the Na and Cl atoms are univalent, and the interaction between the sodium ion and the remaining five chloride ions can only be of the Coulombic, ion–dipole type. The ionic character of such an electrostatic bond, i.e. the degree of ion–dipole interaction, can be conveniently calculated by a formula similar to that proposed by Nekrasov[57]:

$$i_{\text{el-stat.}} = \frac{I_B - X_A}{I_B + X_A} . \qquad (34)$$

This formula reflects the relative effects of two forces on the electron cloud of the atom B (in the present case Cl)—its attraction by the atom A (in our case Na), characterised by its electronegativity, and the resistance by the atom B to the withdrawal of electrons, characterised by its ionisation potential.

Since in fact all six Na–Cl bonds within the coordination polyhedron are equivalent, the ionic characters of the electrostatic and the normal chemical bonds must be averaged:

$$i_{\text{cryst}} = \frac{i_{\text{mol}} + (\text{CN} - 1)\, i_{\text{el-stat}}}{\text{CN}} . \qquad (35)$$

In the more general case of compounds consisting of polyvalent atoms we have

$$i_{\text{cryst}} = \frac{i_{\text{mol}} + (\text{CN} - Z)\, i_{\text{el-stat}}}{\text{CN}} , \qquad (36)$$

where Z is the valence. In Eqns. (35) and (36) i_{mol} denotes the ionic character of the bond determined from a comparison of the electronegativities of the atoms, i.e. in the same way as for molecules.

The formulae proposed for the calculation of the ionic character are of course approximate, in particular where account of the polarisation ion–dipole interaction is concerned. Their validity may be assessed by comparing the calculated data with experimental results. For the latter, we used the results obtained by Szigeti's method, by X-ray spectroscopic investigation of crystals, and from thermochemical data for crystalline compounds.

Without dwelling on the theory of Szigeti's method, we shall quote at once the final formula whereby it is possible to calculate the effective charge per bond, i.e. the ionic character of the bond expressed in terms of fractions of an electron:

$$(e^*)^2 = \frac{\pi(\varepsilon - n^2)\cdot \mathrm{M}\,\omega_0^2}{\left(\frac{n^2+2}{3}\right)^2 (Ze)^2 N_a}, \qquad (37)$$

where e^* is the effective charge of the atom (divided by the valence Z) in terms of fractions of the electron, n the refractive index, ϵ the dielectric constant, M the reduced mass of the pair of atoms M–A, M the absolute mass of the atoms, N_a the number of molecules (more precisely the number of formula units per cm^3, and ω_0 the frequency of lattice vibrations. In some cases (for crystals of the type M/A_n) the present author's data differ from the literature values[98–100] because the reduced mass is expressed throughout in the form

$$\mathrm{M} = \frac{M_A\ M_B}{M_A + M_B}, \qquad (38)$$

as is done in spectroscopy (see also Refs. 101 and 102).

Table 11. Comparison of effective charges determined by Szigeti's method (e^*) and by the electronegativity method (i).

Crystal	e^*	i	Crystal	e^*	i	Crystal	e^*	i
LiCl	0.73	0.81	AgCl	0.71	0.66	InAs	0.19	0.19
LiBr	0.68	0.79	AgBr	0.66	0.63	InSb	0.11	0.17
NaBr	0.70	0.80	TlCl	0.80	0.76	Gd_2O_3	0.71	0.70
NaI	0.71	0.77	TlBr	0.82	0.73	Y_2O_3	0.66	0.70
KF	0.96	0.90	BeO	0.63	0.62	Ho_2O_3	0.68	0.70
KCl	0.81	0.84	MgO	0.73	0,75	Er_2O_3	0.66	0.70
KBr	0.78	0.81	CaO	0.75	0.78	Tu_2O_3	0.76	0.70
KI	0.71	0.79	SrO	0.75	0.78	Yb_2O_3	0.74	0.72
RbF	0.93	0.90	ZnO	0.58	0.62	Lu_2O_3	0.73	0.70
RbCl	0.87	0.85	ZnS	0.52	0.46	Y_2O_3	0.73	0.70
RbBr	0.84	0.82	BN	0.38	0 32	CaF_2	0.82	0.86
RbI	0.81	0.79	AlSb	0.16	0.19	SrF_2	0.85	0.86
CsF	0.88	0.91	GaP	0.19	0.23	BaF_2	0.87	0.87
CsCl	0.85	0.86	GaAs	0.14	0.21	EuF_2	0.84	0.84
CsBr	0.78	0.84	GaSb	0.10	0.18	TiO_2	0.56	0.54
CsI	0,74	0.81	InP	0.20	0.21	SiO_2	0.37	0.35

The amounts of ionic character (in fractions of the electron) determined by the electronegativity method were found from Eqn. (36) and from Tables 5 and 8; the values of the ionic character of electrostatic bonds were taken from the present author's monograph[4]. Table 11 shows that the agreement between the theoretical and experimental values of the ionic character of the bond is on average to within 4%.

The next most accurate method for the determination for atomic charges in crystalline compounds is X-ray spectroscopy. Here two different approaches have been formulated. In one of them (see the work of Urusov[103] and Nefedov[104]) the shift of X-ray lines on ionisation of atoms is examined and a relation is established by quantum-chemical methods between the magnitude of the shift and the effective charge. The above workers do not specify to what type of charges their values refer, but it is evident from the considerations developed in their papers and the normalisation employed[105] that the charges obtained are of the same type as those which follow from Szigeti's equation and the amounts of ionic character in fractions of the electron are referred to a single valence. The present author believes[4] that such an atomic charge, which is associated with the loss or acquisition of an integral electrostatic charge or a fraction of the latter, can be usefully called the intrinsic atomic charge; the charge is distributed within the limits of the atomic skeleton, i.e. it operates within a sphere described by a radius extending from the nucleus to the outer closed electronic orbitals. Suchet[106] suggests that the intrinsic charges be also called "physical charges".

Apart from the intrinsic atomic charges, it is necessary to introduce the concept of coordination charges which represent the collection of electrons received by the given atom from the atoms in the first coordination sphere and the positive charges acquired by the given atom as a result of losing its valence to the bonds with other atoms[4]. Suchet suggests that such charges be called "chemical charges"[106] (see also Cochran[107]). These verbal formulations are identical with the equations

$$Z^*_{\mathrm{intr}} = iZ;\ Z^*_{\mathrm{coord}} = iZ - (1-i)\mathrm{CN}. \qquad (39)$$

It is evident from these formulae that the intrinsic charge of the atom will be always positive for cations and negative for anions. The effective coordination charge can be of either sign both for cations and anions and in most cases it is small in absolute magnitude (Pauling's electroneutrality rule[108,109]). It is significant that, when the bond has a large proportion of covalent character and the coordination number is likewise large, Z^*_{coord} for metals in compounds can be negative. This problem will be discussed further below.

Table 12. Intrinsic charges of metal atoms in crystals.

Crystal	$Z^*_{\mathrm{X\text{-}ray}}$	Z^*_{EO}	Crystal	$Z^*_{\mathrm{X\text{-}ray}}$	Z^*_{EO}
MgF_2	1.25	1.62	FeF_2	1.91	1.46
$MgSO_4$	1.15	1.56	$FeSO_4\cdot 7H_2O$	1.78	1.84
$MgCO_3$	1.10	1.52	$FeCl_2\cdot 4H_2O$	1.63	1.74
MgO	1.00	1.50	FeC_2O_4	1.65	1.32
			FeS	0.69	1.02
Al_2O_3	1.15	1.89	FeF_3	1.72—2.23	1.95
$AlCl_3$	1.45	0.71	$Fe(NO_3)_3\cdot 9H_2O$	1.70	1.83
AlP	0.60	0.72	$Fe_2(SO_4)_3\cdot 9H_2O$	1.71	1.77
SiO_2	1.30—1.50	1.40	Fe_2O_3	1.58	1.65
P_2O_5	0.75	1.30	$FeCl_3$	0.90	1.47

The values of Z^*_{intr} calculated with the aid of electronegativities and determined from X-ray spectroscopic data are compared in Table 12.[103,104] It follows from the Table that the average difference between the effective charges amounts to 0.12 per bond. Here one must mention in addition the calculations of charges in iron(II) salt hydrates. It is known from structural analysis that in the crystal structure of such salts the iron atom is surrounded by six water molecules arranged octahedrally, i.e. here the situation is the same as in aqueous solutions of iron salts. According to crystal chemists[110,111], the interatomic distances and the nature of the interaction between ions in aqueous solutions and in hydrates are the same. Therefore in calculations of the ionic character of such hydrates the electronegativities of atoms in aqueous solutions should be used (Table 4).

The results of the calculations of the effective charges of atoms in crystals by Eqn. (39) using electronegativities and Barinskii's data[70,93,94], which he obtained by the X-ray spectroscopic method, are compared in Table 13. This group of investigations was undertaken to study the behaviour of the X-ray electron within the first coordination sphere. Calculation of the size of the sphere in which the electron moves leads to a value which is intermediate between the ionic and covalent radii of the metal studied by the X-ray spectroscopic method, which demonstrates the dependence of the behaviour of the electron precisely on the effective charge. This finding was mentioned earlier[4] and was again demonstrated recently in the dependence of the position of the edges of the absorption X-ray K-spectra of manganese on the effective and not on the intrinsic atomic charge in crystalline compounds[112].

Table 13. Comparison of the coordination charges of atoms in crystals.

Metal	Compound	$Z^*_{X\text{-ray}}$	i, %	Z^*_{coord}
Cr	$CrSO_4 \cdot 7H_2O$	1.9	95	1.7
	$Cr(NO_3)_2 \cdot n\,H_2O$	1.2	68	1.1
	K_2CrO_4	0.1	29	0.3
Mn	$Mn(NO_3)_2 \cdot 4H_2O$	1.8	95	1.7
	$K_3Mn(CN)_6$	0.9	62	0.7
Fe	$(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$	1.9	93	1.6
	$K_3Fe(CN)_6$	1.0	54	0.2
Co	$Co(NO_3)_3$	1.2	63	0.8
Os	$K_4Os(CN)_6$	1.5	59	−0.5
	OsO_3	0.8	44	0.6
	K_2OsCl_6	0.8	38	0.3
	K_2OsO_4	0.8	38	1.0
	K_2OsNCl_5	0.7	33	0.6
	$KOsO_3N$	1.0	25	1.2

It is evident from the data presented that, with the exception of osmium hexacyanide, the agreement between the calculated and experimental data may be regarded as good: the average discrepancy amounts to $0.3e$ or 5% of the ionic character. On the other hand, in $K_4Os(CN)_6$ there may be a trans-effect, unless one is dealing simply with an experimental error. In fact in the series of hexacyanides of manganese, iron, and osmium there is a systematic increase of the experimental charge on the central atom together with the increase of its electronegativity. If one remembers that the trans-effect should increase in the same series and that this gives rise to an increase in the ionic character of the central atom–ligand bond, one can understand why the charge of the metal atom increases despite the increase of its electronegativity.

The last method for estimating effective atomic charges in crystalline compounds is based on thermochemical data. By representing the energy of the bonds between atoms in the crystal as a sum of ionic and covalent terms, it is possible to estimate the ionic character of the bond, provided that the interatomic distances are known. The difficulty of this method consists in the fact that the covalent component of bond energy decreases with increasing ionic character according to a law which is, strictly speaking, unknown.

The effective atomic charges obtained by the energy method[113–116] are in good agreement with the values of Z^*_{intr} calculated from Eqn. (39). As an illustration, the "thermochemical" [116] values Z^*_{therm} and the theoretical values calculated for a single valence, i.e. the amount of ionic character of the bonds (i), are compared in Table 14. The average discrepancy amounts to $0.08e$ for each valence.

Thus, when account is taken of the structure of the crystals and ion–dipole interaction, the electronegativity method yields values for the ionic character of the bonds between atoms in crystalline compounds which differ from those determined experimentally by the Szigeti, X-ray spectroscopic, and thermochemical methods by amounts in the range 5–12%. Such precision is quite satisfactory for the majority of physicochemical problems.

Before concluding this Section, dealing with the determination of atomic charges, we shall consider briefly yet another parameter of the chemical bond, namely its multiplicity, which can be also calculated by the electronegativity method.

Table 14. Intrinsic charges of metal atoms determined from thermochemical data.

Crystal	Z_{therm}	i	Crystal	Z_{therm}	i	Crystal	Z_{therm}	i
NaF	0.97	0.89	MgO	0.74	0.75	Na_2S	0.62	0.73
NaCl	0.90	0.82	MgS	0.58	0.63	K_2S	0.65	0.75
NaBr	0.86	0.80	CaO	0.81	0.78	Cu_2S	0.54	0.56
NaI	0.82	0.77	SrO	0.80	0.78	MgF_2	0.89	0.82
KCl	0.98	0.84	ZnO	0.60	0.62	$MgCl_2$	0.70	0.67
KBr	0.96	0.81	ZnS	0.42	0.46	$MgBr_2$	0.70	0.67
KI	0.96	0.81	CdS	0.36	0.44	AlF_3	0.82	0.72
CuCl	0.45	0.64	MnS	0.44	0.50	$AlCl_3$	0.62	0.57
CuBr	0.42	0.60						

There exist two fundamental methods for the experimental determination of bond multiplicity—geometrical and spectroscopic. Both methods are based on a single principle—an increase in bond multiplicity increases its energy and leads to a corresponding decrease of the interatomic distance or an increase of the frequency of bond vibration. The first method was initially proposed by Pauling[68] and then developed by Hanic[16] and the second is due to Siebert[117]. However, in both these methods no account is taken of the effect of the ionic character of the bond on its energy and therefore they yield unambiguous results only for bonds of low polarity. It is of interest to develop an independent method for the determination of the multiplicity of bonds, including significantly polar bonds.

The simplest formulation of the concept of bond multiplicity N is

$$N = \frac{Z}{CN}. \qquad (40)$$

In coordination compounds or crystals $CN > Z$ and the interatomic space contains, apart from the electron cloud of the bond, also electrons withdrawn from the atoms as a result of ion–dipole interaction. Therefore the overall number of electrons per metal atom in coordination crystals is evidently

$$\Sigma = Z + (CN - Z) \cdot (1 - i_{el\text{-}stat}). \qquad (41)$$

Hence we obtain the following formula for the calculation of bond multiplicity in coordination crystals containing univalent anions:

$$N = \frac{\Sigma}{CN}. \qquad (42)$$

In polyvalent anions the overall number of electrons in the interatomic space is

$$\Sigma = Z_{cat.} + (CN \times Z_{an} - Z_{cat.})(1 - i_{el\text{-}stat}), \qquad (43)$$

and bond multiplicity can also be determined from Eqn. (42).

The results of the calculations by Eqns. (41) and (42) are compared in Table 15 with spectroscopic determinations of bond multiplicity in coordination crystals and complex ions.

The application of Eqn. (42) in the calculation of bond multiplicities in coordination crystals of the type AB leads to the following results:

for	$A^{I}B^{VII}N$	varies in the range	0.2—0.5
	$A^{II}B^{VI}$	» » »	0.4—0.7
	$A^{III}B^{V}$	» » »	0.6—0.8 .

It is clear from this equation that an increase in coordination number entails a decrease of N, which implies an increase in bond length. Since on going from a single to a double bond the length usually changes by 0.15–0.24 Å, it can be shown that the changes in N on going from CN = 4 to CN = 6 are consistent with the differences in interatomic distances usually observed in crystal chemistry.

Table 15. Bond multiplicities in hydrides and halides.

Compound	Ref.118	Ref.117	Ion	Ref.118	Ref.117
LiH	0.28	0.38	$(ZnCl_4)^{2-}$	0.61	0 75
NaH	0.27	0.27	$(ZnBr_4)^{2-}$	0.62	0.76
KH	0.26	0.26	$(CbCl_4)^{2-}$	0.62	0.70
CuH	0.42	0.68	$(CdBr_4)^{2-}$	0.62	0.86
BeH_2	0.60	0.69	$(CdI_4)^{2-}$	0.64	0.86
MgH_2	0.41	0.45	$(AlCl_4)^{-}$	0.80	0.99

The results obtained by Eqns. (43) and (42) are compared in Table 16 using oxygen-containing anions as an example. The agreement between the results of different methods can be regarded as satisfactory.

2. Physicochemical Properties and the Behaviour of Inorganic Substances

The knowledge of the ionic character of the bond is important for the understanding and theoretical calculation of many physicochemical properties of chemical compounds.

Table 16. Bond multiplicities in complex ions.

Ion	Ref.118	Ref.16	Ref.117	Ion	Ref.118	Ref.16	Ref.117
$(ClO_4)^{-}$	1.84	1.49	1.76*	$(PO_4)^{3-}$	1.45	1.41	1.41
$(SO_4)^{2-}$	1.66	1.53	1.53	$(AsO_4)^{3-}$	1.44	1.28	1.37
$(SeO_4)^{2-}$	1.65	1.45	1.52	$(VO_4)^{3-}$	1.44	1.37	1.49
$(CrO_4)^{2-}$	1.65	1.59	1.53	$(SiO_4)^{4-}$	1.25	1.21	1.19

* For Cl_2O_7.

Examples of the use of the concept of electronegativity for the calculation of interatomic distances and electronic polarisabilities of inorganic substances were given in the author's monograph[4]. In his paper Lakatos[119] quotes interesting examples of the solution of the converse problem. Without dwelling on these questions, which are quite fully described in the papers quoted and also in Ref. 97, we shall examine certain new aspects of the application of the concept of electronegativity in general chemistry.

The problem of the interpretation of the semiconductor properties of certain crystalline compounds was chosen as the first example. At the present time there exists no textbook on the chemistry of semiconductors in which the relation between the electronegativity and the width of the forbidden gap is not considered[120,121]. This is quite natural, since the transition of an electron from the valence band to the conduction band is inevitably associated with the nature of the chemical bonds and the mobility of electrons in the interatomic space, i.e., in other words, with the ionic and metallic character[122,123]. Bearing in mind that the energy of the forbidden gap itself is a consequence of the overall structure of the solid, its band structure, there is no point in seeking a relation between ΔE and ΔX only, which would undoubtedly be incapable of reflecting the entire set of specific features of the chemical compound. It is much more correct to introduce ΔX into an equation which already contains the ΔE values for the components of the compound determined for a purely covalent state (i.e. for the corresponding elements), so as to allow only for the deviation of the bond character in the given compound from the purely covalent state. The Schomaker–Stevenson equation[13] is a classical example of such an application of electronegativity:

$$r_{AB} = r_A + r_B - 0.09\Delta X_{AB} \quad . \qquad (5)$$

In complete agreement with this principle, the present author has proposed the following relation[124] between ΔE and ΔX:

$$\Delta E_{AB} = \Delta E_A + \Delta E_B + a\Delta X_{AB} - b\bar{n}_{AB} \qquad (44)$$

where ΔE_A and ΔE_B are the widths of the forbidden gap for the elements A and B (determined for the corresponding pure elements), $\bar{n}$ the average value of the principal quantum number, and a and b are constants. Tests of this equation using all the values of ΔE_{AB} known in 1964 showed that the average error is 0.2 eV. The equation of course constitutes the simplest method of taking into account the effects of the ionic and metallic character of the bond on the energy of the forbidden gap and requires further improvement, particularly as regards a more correct determination of the role of the metallic character of the bond. However, the principle of the derivation of the equation itself appears to be correct (see also Hooge[125]). Comparison of the electronegativities ΔX of atoms forming crystals having the same structure with their melting points reveals a distinct relation—the greater is the covalent character of the bond the lower is the melting point[126]. Table 17 presents several pairs of compounds with the same structures (coordination numbers) and similar interatomic distances, but which differ appreciably in their electronegativities. Geologists believe[127] that this relation is responsible for the magmatic crystallisation sequence and processes involving the substitution of cations in crystals. The explanation for this relation is that the energy of the Coulombic interactions is much higher than the energy of the covalent component of the bond, and therefore an increase of ΔX entails an increase in the total bond energy (for further details, see Ref. 4). This finding also plays an important role in the determination of the mode of double decomposition reactions which occur with formation of combinations of the most ionic and the most covalent compounds[128] (however, here one should recall that the electronegativity method can be applied directly only to purely molecular cases and account must be taken of the coordination number, etc., when crystals are considered).

The use of the concept of electronegativity to characterise the acid–base properties of chemical compounds has

proved extremely fruitful. On the basis of the Lewis–Brønsted theory, it is readily seen that an increase of the negative charge of the oxygen atom in an oxide will entail an increase in its basic properties. Therefore it is possible to establish a proportionality between ΔX and the acidity of the medium set up by the given combination of atoms. Such an approach is interesting because one need not consider the specific features of the medium and one can characterise objectively the acid–base properties of substances. Examination of the acid–base properties of silicates from the standpoint of the concept of electronegativity is also useful because classical chemical methods are inapplicable to this case[129]. A new finding is that in the usual substitution of the hydroxy-groups in aluminosilicates by fluorine atoms there is an increase in the acid character of the compound.

Table 17. Dependence of the melting point on bond type.

Crystal	Interatomic distance	CN	ΔX	M.p., °C	Crystal	Interatomic distance	CN	ΔX	M.p., °C
AgCl	2.77	6	1.2	455	CaF_2	2.36	8	3.0	1378
NaCl	2.81	6	2.2	800	CdO	2.35	6	1.8	1400
LiI	3 00	6	1.6	450	CaO	2.40	6	2.5	2570
NaBr	2.98	6	2.0	766	Al_2O_3	1.91	6	2.0	2050
$ZnCl_2$	2.60	6	1.5	365	MgO	2.10	6	2.3	2800
$MgCl_2$	2.63	6	1.9	712	SiSi	2.34	4	0	1420
CdF_2	2.34	8	2.3	1100	ZnS	2.35	4	1.0	1850

The electronegativity method makes it possible to understand and to predict the changes in the acid–base properties of organic compounds as a result of changes in their structure or on introduction into the molecular skeleton of definite substituents. The general principle which can be used here is that, in consequence of the higher electronegativity of the carbon combined with the hydroxyl, the oxygen atom of the OH group is forced to saturate the electron affinity on the side of the H atom to a greater extent, as a result of which the latter becomes more polar, i.e. acid. Hence, one may conclude that halogeno-substituted acids will be stronger than the normal acid and that the increase in acid strength will be greater the higher is the electronegativity of the halogen. However, it should be recalled that in comparisons of this kind one must of course select related molecules in which the same number of hydrogen atoms are replaced at the same carbon atom, because otherwise the structural effect may compete with the inductive effect[130]. Thus, the electronegativity method has recently been successful in the interpretation of the ionisation of fluoro-substituted organomercury compounds and the correlations proved to be so precise that it was possible to determine the group electronegativities from the pK data[131].

Since the dissociation of complex ions depends on the relation between the energy of the ligand–central atom bond and the ligand hydration energy, it is clear that the instability constants of complex compounds will be functionally related to the covalent character of the latter and hence to the electronegativities of the atoms. Such relations have been indeed established for numerous examples and have been used successfully in the chemistry of complex compounds (for further details, see Refs. 4 and 132). In general, according to Nyholm[133], the establishment of correlations between bond strengths and the electronegativity of the central atom is extremely promising for the chemistry of complex compounds. In this connection it is of interest to examine Chernyaev's trans-effect rule. The essence of the latter is that, when certain atoms and radicals interact with ligands located in the trans-position with respect to them, they ionise the latter and render them capable of more rapid (and sometimes actually ionic) substitution. A direct relation between the magnitude of the trans-effect and the covalent character of the bond between the given ligand and the central atom is a firmly established fact. It is quite clear that the ionisation of the species in the trans-position leads to a change in energy and in most cases to an increase in the strength of its bond, but the increased effective charge on the ligand results also in a sharp increase of its hydration energy, which facilitates the dissociation of this atom.

On the basis of what has been said above, the parallel variation of the position of the ligands in the trans-effect series and their electronegativities is evident[134] and it is clear why the same ligands, for example thiocyanato- and nitro-groups, can occupy different positions in the trans-effect series depending on the atom via which they are combined with the complex-forming metal.

The most interesting is the case of the combination of the central atom of the complex with a nitro-group and a chlorine atom. The electronegativity of both ligands is 3.2 and, other conditions being equal, their trans-activities should be the same. However, calculation of the effective coordination charge in complexes of di- or tetra-valent platinum by Eqn. (45) shows that in the first case $Z^*_{coord} < 0$ and in the second $Z^*_{coord} > 0$. Since in the N–O bond the positive pole is located at the nitrogen atom and the negative pole at the oxygen atom, it is easy to see that in complexes of divalent platinum with the NO_2 group the N–O bond length will be greater than in similar complexes of tetravalent platinum. These changes in bond length are consistent with the decrease in the multiplicity of the nitrogen–oxygen bond in platinum(II) complexes and its increase in platinum(IV) complexes relative to the normal state of the nitro-group. Since a decrease of the bond multiplicity of a given atom is accompanied by a decrease of its electronegativity on the opposite side, $X_{NO_2}(Pt^{II})$ will be less than X_{Cl} and $X_{NO_2}(Pt^{IV})$ will be greater than X_{Cl}. In accordance with what has been said above, this finding implies that the trans-effect of the nitro-group in platinum(II) compounds will be greater than the trans-effect of chlorine and that the converse relation will obtain in platinum(IV) compounds. It is known[135] that there is indeed a difference between the trans-effects of NO_2 and Cl but the postulated difference between the properties of the nitro-groups in complexes of di- and tetra-valent platinum still requires experimental tests[4,136].

Bearing in mind that in complexes of trivalent cobalt and gold with the nitro-group the central atoms have effective positive coordination charges, as can be readily seen from Tables 5 and 8 and Eqns. (39), the behaviour of the NO_2 group will be the same as in platinum(IV) complexes. On the other hand, in the nitrite complexes of trivalent metals of the platinum group the central atoms have an effective negative coordination charge and therefore the trans-effect of the NO_2 group will be greater than that of chlorine.

If these predictions prove to be valid and considerations based on charges do indeed play an important role in the determination of the trans-effect of the nitro-group, then one may postulate the possibility of a change in the trans-activity of NO_2 even for the same valence of the central atom, for example platinum. Thus in the iodide complexes of tetravalent platinum the nitro-group would exhibit a greater trans-effect than chlorine because here Z^*_{coord} is less than zero, while in fluorine-containing platinum(II) com-

plexes the relations between NO_2 and Cl may become the same as for tetravalent platinum because of the effective positive charge on the central atom of the complex. The variation of the trans-activity of ligands as a function of the composition of the complex can be regarded as a manifestation of the cis-effect in the inner sphere of complex compounds.

Of the entire wide variety of chemical properties and behaviour of simple inorganic compounds, we shall examine in this Section only one example each of the analysis and synthesis of substances, which can be interpreted or predicted from the standpoint of the concept of electronegativity.

The concept of electronegativity was recently successfully applied by Rozen and coworkers[137,138] in the problem of the separation of elements by extraction, or more precisely the problem of selecting optimum organic compounds for use as extractants. These workers showed that the electronegativities of the radicals are an important characteristic of compounds such as substituted tributyl phosphates and the analogous phosphonates. It is significant that the electronegativities found from the extraction of uranyl nitrate also describe satisfactorily the capacity of substances to be extracted by nitric acid, i.e. the relation obtained is of general importance. It has also been shown[138] that the Hammett–Taft equation can be derived from equations involving electronegativities. Therefore the latter can be used successfully also to describe the reactivities of organic compounds.

The findings arrived at with the aid of the electronegativity method proved fruitful also in the synthesis of new compounds. The synthesis of salts with mixed anions of the type MABC ... appears to be very promising, since by varying the anions A, B, and C, it is possible to increase almost without limit the range of chemical compounds of the given metal. Mixed salts are obtained by the combination of homogeneous salts, for example

$$PbF_2 + PbCl_2 = 3PbFCl\,, \qquad (45)$$

or by hydrolytic reactions, for example

$$MoCl_5 + H_2O = MoOCl_3 + 2\,HCl\,, \qquad (46)$$

or by double-decomposition reactions, for example

$$TiBr_4 + Cl_2O = TiOBr_2 + 2\,ClBr\,. \qquad (47)$$

However, it is difficult to expect the formation of substances in new valence states by these reactions. Therefore a very attractive procedure is the preparation of the mixed salts by reactions of the type

$$MA + B = MAB\,, \qquad (48)$$

where B is a halogen or a chalcogen, but there is then a possibility of displacement reactions if the oxidising capacity of the atom B is higher than that of the atom A.

Calculation of the effective coordination charges of variable-valence metals present in crystalline compounds in the lower-valence state showed that in most cases they are negative[4]. This can be understood when the coordination number of the metal is large, and the bonds which it forms with its nearest neighbours are significantly covalent; in other words, when the metal has given up fewer electrons for the formation of the bonds than the number it has received from them. Physically, a negative charge implies that the free electron pairs of the anions interact with the vacant sites of the cations. Finally, we must recall Z^*_{coord} is a concept reflecting the situation in the interatomic space and not within the atomic skeleton and this is in fact an important factor in oxidisation processes.

If we now return to Eqn. (48), we readily see that, when there is a negative charge on the atom M, the effect of the oxidant B should lead not to displacement of A but to an increase of the valence of M, i.e. the formation of a salt with mixed anions. Experiments confirmed this conclusion: with salts of copper, mercury, thallium, tin, chromium, manganese, and platinum, the present author succeeded in obtaining oxidised salts with mixed anions[139-149].

A few words must also be said about the change in the nature of the bond on heating and about the effects of such changes on chemical properties. It is clear from general considerations that the chemical bond can change as the molecule or crystal is heated. On heating, a solid melts and is then converted into a gas. Evidently, these processes are accompanied by a decrease of the ionic character of chemical bonds. One can also arrive at the conclusion that, within the same state of aggregation, heating increases the covalent character of the bond. In fact on heating the material expands due to the increased amplitude of atomic vibrations. The increase in volume may be interpreted in terms of the statistical decrease of the coordination number, which should entail a decrease of the ionic character of the bond. Physically, this has the following meaning: as the vibration amplitude increases, there is an increased frequency of instances when the oppositely charged ions approach one another to a distance so short that one can speak of the formation for a very brief instant of a molecule or molecular complex; the increase in the proportion of the molecular state in the crystal as the latter is heated is in fact consistent with the increased contribution of the covalent component to the chemical bonds of the substance.

The above considerations have found experimental justification. Thus Jones et al.[99] showed by Szigeti's method that, as alkali halide crystals are heated, their effective charges fall, i.e. there is an increase in the covalent component of the bond. Quantitatively this increase amounts on average to $0.02e$ per 100 deg.

Such increase in covalent character may give rise to significant changes in the distribution of the effective charges in the crystal. For example, when MnO is heated to 350°C, the ionic character of the bond decreases by $0.07e$ or from $0.71e$ (see Ref. 4, p. 173) to $0.64e$. Hence the effective coordination charge of the manganese atom in the MnO crystal changes from ± 0.26 to -0.16, i.e. there is a reversal of the sign of the charge. It is interesting that it is precisely at this temperature that the heating curve for MnO in air shows an exothermic maximum corresponding to the oxidation of manganous oxide to Mn_2O_3. This example illustrates the possibility of regarding oxidisation reactions which occur on heating from the standpoint of the system of the effective atomic charges in the substance and the effect of heating on the dynamics of this system. Knowing the ionic character of the bond in the initial state of the substance, it is possible to estimate the temperature ranges in which oxidation processes can begin.

The most pronounced changes in bond polarity are to be expected in coordination or dative bonds formed in the inner sphere of complex compounds, because the latter are formed by virtue of additional atomic orbitals and their energy frequently makes them less stable than the usual chemical bonds. This is why one may expect very considerable changes in chemical behaviour in complex compounds when the latter are heated even slightly.

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The above factual and theoretical data show that the concept of electronegativity can be successfully applied in the determination of atomic charges in molecules and crystals; at any rate, at the present time there is no other method for the determination of the ionic character of the bond as universal and simple as the electronegativity method. However, this method shows what the charge should be only if the latter is determined only by the normal valence bonds between atoms; when hydrogen bonds, trans-effects of atoms, or any other additional interaction is present, the atomic charges determined by the electronegativity method may differ from the actual values, but the difference itself can serve as a characteristic of the given type of interaction.

The formulae for and the magnitudes of the electronegativities of atoms permit the calculation of the fundamental properties of matter–bond energies and lengths, ionisation potentials, optical characteristics, and the distribution of electron density. This is why electronegativity will retain for a long time its importance in structural chemistry within the framework of the additive approach to the problems of molecular structure. Therefore, the present author believes that even the discovery of new properties and effects of the chemical bond will not entail the rejection of this concept.

The above view does not of course imply that the concept of electronegativity is free from disadvantages and that it is able to reflect all the features of the atomic and electronic structure of matter known at the present time. In this connection it is useful to consider briefly the controversy concerning the role and limits of applicability of the concept of electronegativity which occurred recently.

The concept of electronegativity, like other methods of theoretical chemistry, has its critics as well as supporters. The former can be divided into two groups—some workers criticise particular schemes for the calculation or application of electronegativity and propose new more successful ones (from their point of view); others see fundamental defects in the concept of electronegativity and suggest that it be completely excluded from the arsenal of theoretical chemistry. The first group is the most numerous and includes many investigators who have been fruitfully developing the concept of electronegativity, but their electronegativity values will not be considered here, particularly since later studies, which incorporate all the constructive postulates put forward in recent years, are quoted in the present review.

The first negative criticism of the concept of electronegativity was made in the paper by Fajans[140], who reviewed Pauling's book. Fajans noted that, by ascribing to each element of the Periodic System a constant electronegativity value, one cannot arrive even at a qualitatively correct understanding of chemical phenomena and the physical properties of substances. For example, in chloroacetylene the chlorine atom has a positive charge, in chloroethylene a zero charge, and in chloroethane a negative charge, while $X_{Cl} > X_C$. We now know that the electronegativity of the carbon atoms varies with the degree of hybridisation of its bonds and can assume values ranging from 2.0 to 3.3 (see Table 6). Comparison of these electronegativities of carbon with the constant electronegativity of chlorine shows that the sign of the charge on the chlorine atom should indeed change on going from chloroacetylene to chloroethane.

The second serious criticism of Pauling's concept was made by Hückel[151], who tested the principle of additivity in calculations of electronegativity and compared the amounts of ionic character calculated from the dipole moments of halogeno-hydrocarbons and interhalogen compounds. In the same paper Hückel formulated for the first time the question of the dimensions of electronegativity and expressed his perplexity concerning the physical significance of the dimension "(energy)$^{1/2}$". Without dwelling on the factual inaccuracies which were pointed out in the present author's review of Hückel's work[152], we may mention that his comparison of the dipole moments of various molecules with the aim of determining the ionic character of the bonds is without foundation, since, on changing the composition, the contributions of the various components of the dipole moment can also change. The large relative errors observed by Hückel in additive calculations involving electronegativity are purely an arithmetical effect, which arises when a constant absolute error (0.1 electronegativity unit) is compared with the small difference $\Delta X = 0.3–0.9$, and has almost no influence on the accuracy of the calculation of chemical bond energies.

The dimensions of the concept of electronegativity were discussed above, and, concerning Pauling's values of X, one can only add that Pauling himself calculated the ionic character of the bonds by Eqns. (24) or (25), which involve ΔX^2. The present author has already pointed out[152] that there is a definite analogy between ΔX and the wave function, bearing in mind that in the latter case it is precisely $|\psi|^2$ that is physically significant.

In the critical article of Lakatos[86] the arguments of Fajans and Hückel are quoted and it is emphasised that electronegativity is not a constant, since it must have a certain range of values depending on the valence state, the ionic character of the bond, hybridisation, etc. Lakatos also points out that the amounts of ionic character of bonds are determined from various atomic properties and therefore it is frequently difficult to make them consistent.

Iczkowski and Margrave[52] again draw attention to the differences in the dimensions of electronegativities determined by different methods and believe that the most correct representation of electronegativity is in the form of a potential. Together with Hückel, these authors believe that the main reason for the successful application of electronegativity in chemistry is that this quantity reflects the periodic variation of properties in Mendeleev's system.

In 1962 Syrkin[153] published a critical paper on the concept of electronegativity. Noting that in the early stage of development this concept constituted an advance, he now concluded that at the present time it can no longer be used for a satisfactory interpretation of experimental facts and even less so for their prediction. This paper is unfortunately not free from factual inaccuracies and Syrkin does not employ the most accurate system of electronegativities, as pointed out in the present author's review[154], but fundamentally his formulation of the problem is valid. The facts which have accumulated at the present time no longer fit within the Procrustean bed of constant electronegativities and require successive corrections for ionic character, multiplicity, and other characteristics of the chemical bond which are frequently unknown *a priori*. The question arises whether the numerous corrections and additions are justified by the results which can be gained with the aid of electronegativity. Syrkin gives a negative answer. The data presented above suggest that the answer is yes.

Finally in recent years Spiridonov and Tatevskii[155] published a series of papers in which they repeated the concrete objections of Hückel and Iczkowski but, in contrast to the other authors, they suggest a fundamental contradiction between the concept of electronegativity and quantum mechanics and therefore they reject the concept itself. They called for the application in chemistry of the rigorous methods of quantum mechanics. However, the trouble is

that such methods do not exist at the present time and it is not clear whether the many-electron problem can be solved rigorously, in principle, in a general form. For this reason, no one, including Spiridonov and Tatevskii, uses rigorous quantum-mechanical methods in their practical work. In reply to the criticism of these workers[156,157], a detailed analysis of their comments was made and it was shown on concrete examples that their wish for more rigorous solutions is at the present time unrealistic. The views of Spiridonov and Tatevskii are indirectly disproved by the use and development of the method of electronegativity by outstanding specialists in the field of quantum chemistry such as Pauling, Mulliken, Hinze and Jaffe, and finally Coulson[158].

Considering the criticism of the concept of electronegativity as a whole, we arrive at the paradoxical conclusion that here everyone is right—both the adherents and the opponents of the concept. The question is evidently what are the limits of applicability of this method. The present author has already stated earlier and believes it superfluous to repeat that, with the aid of electronegativity, one can determine directly the sign and magnitude of the charge only for atoms in molecules and crystals. In all remaining cases it is necessary to determine whether or not the given property depends on the polarity of the chemical bond and only if the answer is in the affirmative can one proceed to consider the concrete application of electronegativity values in familiar or newly derived equations.

The greatest defect of the concept of electronegativity is that the simplicity of the mathematical formulation led to the disappearance of the potential barrier which must be overcome by the investigator in order to master a given field and therefore the concepts and values of electronegativity are sometimes employed by incompetent persons. Incorrect application of the method merely brings it into disrepute.

Returning to the problems of the chemical bond, one would wish to mention in conclusion, a general characteristic of the modern state of this field of science. As our knowledge about the electronic structure of matter deepens, the theory of the chemical bond simultaneously develops, many simple physical characteristics and concepts become complex, and acquire a characteristic "structure". This was the case earlier with the dipole moment. A similar change is now taking place in the "chemical shift". Simple facts such as the shortening of the bond or the increase of the dissociation energy are in fact the result of at least two simultaneous trends, changes in the polarity and hybridisation of bonds, and this is why it is impossible to derive from such values unambiguous information about the nature of the chemical bond.

Precisely for this reason our concepts such as atomic radii, refractions, and electronegativities become complex and require that account be taken of the specific features of the environment of the given element. This is quite reasonable and one may hope that, as science progresses, the theoretical armoury of structural chemistry based on the principle of additivity will constitute an organic component of a more general and rigorous theory.

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Methods of Preparation and Chemical Properties of Aliphatic Halogenonitro-compounds

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The review deals with the literature on the nitrohalogenation of unsaturated compounds by addition to the latter of nitryl and nitrosyl halides and by the reaction of the unsaturated compounds with mixtures of nitrogen tetroxide and halogens. The condensation of nitro-alkanes with halogeno-carbonyl compounds, the nitration of halogeno-derivatives of aliphatic hydrocarbons, and the halogenation of nitro-compounds have also been described. Work on the reaction of polyhalogeno-alkanes with metal nitrites and the replacement of a carboxy-group by a halogen and a nitro-group have been reviewed. Dehydrohalogenation, dehalogenation, and also reactions involving the substitution of the halogen atoms have been examined in the analysis of the chemical properties of halogenonitro-compounds. The review also deals with work on the reactions of halogenonitro-compounds with participation of the nitro-group. A brief report is given on the applications of halogenonitro-compounds.

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I. INTRODUCTION

Among aliphatic nitro-compounds considerable interest attaches to halogenonitro-compounds in which there are two or three reaction centres: the halogen atom, the nitro-group, and, for substances with a primary or a secondary nitro-group, two or one "mobile" hydrogen atom. The presence of several reaction centres permits a wide range of reactions with these compounds.

Despite their undoubted interest, the chemistry of halogenonitro-compounds has not been reviewed so far. The present review presents a compilation of data on the syn