

ON THE PROBLEM OF THE IONIC CHARACTER AND THE POLARITY OF THE CHEMICAL BOND

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(Received June 15, 1960)

A general survey of the literature on the ionic character and the degree of polarity of the chemical bonds is given. With this consideration the concept of the effective electric field strength of free atoms and ions and their constituents is introduced. To calculate this was possible by using the ionisation potentials of atoms and ions and by clearing up the exponential dependence of the effective field strength of ions on their charge. In equilibrium, on the basis of the virial-theorem the effective electric field strength of the cationic constituent must be equal to that of the anionic constituent. This equality renders possible to calculate the degree of bond polarity without using experimental degrees of bond polarity or arbitrarily chosen adjusting parameters. In the whole range between ideal ionic and pure covalent bonds there is a fair agreement between degrees of bond polarity calculated by us and experimentally found. The deviation is not greater than $\pm 5\%$. The shortcomings of this method lay in the fact that the properties of the bonded constituents are approximated by the properties of free atoms and ions.

On the basis of our investigations on the periodicity of the physical and chemical properties of the elements [1]—[6] it has been established that the physics and chemistry of elements are ruled by two opposite factors. One of them is the *effective principal quantum number* of the outermost electronic shell of constituent atoms and ions, resp., while the other is the *effective nuclear charge* of the constituents, *i. e.* the screening and shielding numbers (parameters), resp., of electrons subtracted from the positive nuclear charge number. After clearing up this qualitative connection a further aim of our investigations presented itself, namely, to investigate quantitatively the relation between the two main factors and the chemical and physical properties of elements determined by these. Within the scope of this programme the calculation of the degree of polarity and ionic character resp., closely connected with the "electropositive" and "electronegative" character of the atoms was considered to be the most important aim.

The overwhelming majority of the types of the bonds in inorganic compounds is placed between two limiting cases, forming a gradual transition from pure polar (ideal ionic) to pure non-polar (normal covalent) bonds. These are the so called compounds with transition type of bond. *E. g.* in gas-phase molecule Cl_2 , the $\text{Cl}-\text{Cl}$ bond is an ideal non-polar one, in solid KCl it is nearly ideal ionic, while TlCl and AgCl are compounds with transition type of bond. The amount of the ionicity is already a function of the different states of aggregation. Unfortunately, we know only very little about the extent of ionicity of compounds in the solid and liquid phases.

The measure of the ionicity of transition type of bonds in gas phase compounds, that is, where does the type of bond of the given compound take place between two limiting cases, is described with diverse expressions by the different authors [7].

One of them is the concept and the amount of the ionic character (β) [9] of the bond, which can be estimated with the nuclear quadrupole coupling constants [8] and theoretically can be calculated by methods of quantum mechanics (MO—LCAO). According to the LCAO approximation of the molecular orbitals, the wave function of the *binding electron* between atoms *A* and *B* is represented by Eq. $\Psi = a\psi_A + b\psi_B$ where ψ_A and ψ_B are the wave functions of the atomic orbitals of atoms *A* and *B*. If ψ is normalized, then $a^2 + b^2 + 2abS = 1$ where *S* is the so called overlap integral, $S = \int \psi_A \psi_B \cdot d\tau$. Then the measure of the ionic character is:

$$\beta = b^2 - a^2 \quad (1)$$

where $b^2 - a^2$ is the difference of the probability that the electron is found at atoms *A* and *B*. The ionic character is the function of the ratio of the effective nuclear charges and of the difference between the electronegativities of atoms *A* and *B*, respectively, and can be regarded as an absolute measure of the ionicity of the compounds [9].

Another, widely used concept the *polarity*, of the chemical bond had been introduced by K. FÄJANS [10a, 10b]. Later PAULING called this the "ionic character of the bond", what cannot be mistaken for the previous concept defined by quantum mechanics. Taking into consideration the experimentally determined electric dipole moment and the internuclear distance of *AB* binary compound:

$$\text{degree of polarity } (p) = \frac{\mu_{\text{exp.}}}{\mu_{\text{calc.}}} = \frac{\mu_{\text{exp.}}}{e \cdot R_{AB}} \quad (2)$$

$$\text{degree of polarity in p. c. } (p)_{\text{p.c.}} = 100 \frac{\mu_{\text{exp.}}}{e \cdot R_{AB}} \quad (2')$$

where $\mu_{\text{exp.}}$ and $\mu_{\text{calc.}}$ are electric dipole moments experimentally determined and calculated for the assumed idealized binding of rigid ions, *e* is the ionic charge, R_{AB} the interatomic distance accurately determined in an experimental way, $e \cdot R_{AB}$ the calculated bond dipole moment of a hypothetical A^+B^- molecule with an assumed ideal ionic bond. Using the above mentioned concept of the degree of polarity the real charge distribution of molecule *AB* can be written in the following form: $A^{+p}B^{-p}$, where *p* (degree of polarity) gives the partial ionic charge, too. Generally the charge distribution of molecule A_iB_j

can be written by the following formula: $(A^{+\delta^{(A)}})_i(B^{-\delta^{(B)}})_j$, where $\delta^{(A)}$ is the number of partial charges on atom *A*, and $\delta^{(B)}$ that on atom *B*. The relation between δ partial charge number and *p* degree of polarity:

$$\delta = p \cdot \delta_{\text{max}} \quad (2'')$$

where, if $p = 1$ then $\delta_{\text{max}} = \delta$, therefore δ_{max} , in a hypothetical molecule

$(A^{+\delta_{\max}^{(A)}})_i (B^{-\delta_{\max}^{(B)}})_j$, with idealized ionic bond, means the ionic charge, in FAJANS's "quanticule" formula [10c] the overall ionic charge. Thus the charge distribution of molecule $A_i B_j$ can also be written in the following form: $(A^{+p \cdot \delta_{\max}^{(A)}})_i (B^{-p \cdot \delta_{\max}^{(B)}})_j$. * (E. g. in the case of an ideal ionic bond, that is $p=1$ and 100% resp., the formula of molecule SO_2 would be $\text{O}^{2-}\text{S}^{4+}\text{O}^{2-}$, while FAJANS's approximating quanticule formula: $(e)_2\text{S}^{6+}\text{O}_2^{2-}$ therefore $\delta_{\max}^{(S)}=4e$ and $\delta_{\max}^{(O)}=-2e$ mean the ionic charge and in FAJANS's formula the overall ionic charge, resp. The real charge distribution $\text{O}^{p(-2)}\text{S}^{p(+4)}\text{O}^{p(-2)}$, thus if the degree of polarity e. g. $p=0,25$ i. e. of 25% then $\text{O}^{-0,5}\text{S}^{+1}\text{O}^{-0,5}$ or shortly $\text{S}^{+}(\text{O}^{-1/2})_2$ reflects the real charge distribution.) According to the principle of electroneutrality:

$$|+\delta_{\max}^{(A)} \cdot i| = |-\delta_{\max}^{(B)} \cdot j|$$

and

$$|+\delta^{(A)} \cdot i| = |-\delta^{(B)} \cdot j|.$$

On dividing these two equations:

$$+\delta^{(A)}/+\delta_{\max}^{(A)} = -\delta^{(B)}/-\delta_{\max}^{(B)}$$

and taking into consideration Eq. $\delta = p \cdot \delta_{\max}$

$$p^{(A)} = p^{(B)}$$

is given, thus it can be stated that the concept of bond polarity is applicable for the bonds of an arbitrary $A_i B_j$ molecule.

Relation Between the Degree of Polarity of the Bond and the Amount of Its Ionic Character

Regarding that in the literature the expression of the amount of the ionic character of the bond is used for the degree of polarity determined by experimental dipole moments and bond lengths, and that these two different values are used, named as ionic character, to calibrate the same curve of "electronegativity" against the ionic character, after defining the concepts of the degree of polarity and of the ionic character, it seems necessary to examine their relation, too.

* Equation 2'' is obtained by the following conversion of Eq. (2) defining the degree of polarity

$$p = \frac{\delta \cdot e \cdot R_{AB}}{\delta_{\max} \cdot e \cdot R_{AB}} = \frac{\delta}{\delta_{\max}} \quad (2'')$$

where $\delta \cdot e$ is the magnitude of the partial ionic charge on atoms A and B, $\delta_{\max} \cdot e$ is the ionic charge in the case of an assumed ideal ionic bond; e is the elementary charge.



The whole dipole moment contains beside the primary moment determined by the ionic character and the bond length also the deformation caused by the mutual polarization of the constituents, the effect of the hybridization occurring in the bonding atomic orbitals and the overlap of these orbitals [11]—[16]:

$$\mu_{\text{exp}} = e(b^2 - a^2)R_{AB} + \mu_{\text{polarization}} + \mu_{\text{hybridization}} + \mu_{\text{overlap}}. \quad (2a)$$

The first term of the right is the so called *primary dipole moment*:

$$\mu_p = e(b^2 - a^2)R_{AB} = e\beta R_{AB} \quad (2b)$$

which arises from the asymmetrical charge distribution between atoms *A* and *B* of the binding electron or electrons. The latter is the function of the difference between the electronegativities of the two atoms. It can be seen from eqns (1), (2) and (2b) that the ionic character $\beta = u_p/e \cdot R_{AB}$ is the "degree of polarity" corresponding to the primary moment, thus the ionic character can be calculated from experimentally measured dipole moments or the nuclear quadrupole coupling constants, if other terms can be evaluated.

The second term is the so called *polarization or induced or atomic core dipole moment* μ_i , including the polarization, induced by the primary moment of the atomic cores (A^+B^-), i. e., of the non-bonding electrons. The polarization moment has a sign always opposite to that of the primary moment. The polarization moment can be evaluated with the classical formula:

$$\mu_i = E_A\alpha_A + E_B\alpha_B \quad (2c)$$

where α_A and α_B are the polarizabilities of ions A^+ and B^- , E_A and E_B are the polarizing electric field strengths. To estimate these latter, e. g. E_A ; it is assumed that it arises from an effective charge on *B* and its extent is $\mu_{\text{exp.}}/R_{AB}^3$. Similarly, the field E_B is calculated from the effective pole on *A*. Thus the value of the polarization moment:

$$\mu_i = \frac{\mu_{\text{exp.}}}{R_{AB}^3} (\alpha_A + \alpha_B). \quad (2d)$$

The third member is the so called *hybridization moment* [17]. It arises from the asymmetry of hybrid atomic orbitals of the valency shell. The correct value of the degree of hybridization is different even referred to the same atom, at present time its reliable evaluation is impossible, as it is proved by the rather different values taken up by several authors. We find quite often strictly opposite views concerning basic problems, e. g. in the case of an atom with positive valency state DAILEY and TOWNES [14] do not take up hybridization, since the energy needed for this is more than two times greater than that of an atom in a covalent bond (e. g. in the case of molecules FCl and FBr), on the other hand according to GORDY [16], in the case of a constituent with positive charge, especially when this positive charge is great, the extent of hybridization may be very considerable (e. g. in the case of molecules FCl, FBr and NF_3). It was possible to make only qualitative conclusions concerning the hybridization and the problem was complicated by

the fact that the effect of hybridization on structural data of the bonds experimentally determined, such as *e. g.* bond lengths, bond angles, bond dipole moments, nuclear quadrupole coupling constants etc. may considerably differ. In general the sign of the hybridization moment related to the primary moment depends on the kind of hybridization.

The fourth term is the so called *overlap moment* [18] (homopolar dipole moment), it arises from the overlap of atomic orbitals with different size. Here the fractional part of the charge distribution of the electron shell is considered, which holds the part of atomic orbital in the overlap range:

$$\mu_S = 4abe \cdot S_{AB} \cdot \bar{z}_S \approx \frac{-2eS_{AB}}{1+S_{AB}} \left(r - \frac{R_{AB}}{2} \right) \quad (2e)$$

where \bar{z}_S is a vectorial distance characterizing the overlap range, r is the covalent radius of the smaller atom. If the negative end of the dipole is formed by a constituent with smaller size, then the overlap moment has an opposite sign to the primary moment and vice versa. According to VENKATESWARLU and JASEJA [16a] the overlap factor is an exponentially decreasing function of the difference in the atomic radii:

$$S^2 = Ae^{-2|r_A - r_B|} \quad (2f)$$

where r_A and r_B are the radii of atoms forming A_2 and B_2 diatomic molecules, the value of the constant is $A = 0.21$.

Unfortunately, the dipole moments and the nuclear quadrupole coupling constants experimentally determined do not make possible an independent evaluation of the different moments [14]. The case is even more complicated by the fact that, according to the recent statements [16], the quadrupole coupling constants are influenced beside the factors above mentioned *i. e.* the primary, hybridization and overlap moments, by the effect of the neighbouring atoms and ions, respectively, and by the distortions of non bonding closed shells of electrons around the nucleus in question. The effect of neighbouring ionic constituents depends on the bond length to the greatest extent [14], [16a], but the quality of the constituents also plays a part. The fact that the curve of the ionic character versus differences in electronegativities turns back at high differences in electronegativity, (*e. g.* $\beta_{LiI} = 0.900$, $\beta_{NaI} = 0.867$; $\beta_{KCl} = 1.000$, $\beta_{CsCl} = 0.968$), is interpreted by the effect of the bond length and of the distortions of the closed shells. The greatest complication in the evaluation of β is that the nuclear quadrupole coupling constant is more sensitive to an electron charge distribution near to the nucleus and not to the electron charge distribution of the overlap range of the valency bond, as the bond dipole moment is [18a].

Mention must be made that the degree of bond multiplicity plays also an important part in forming the value of the dipole moment. Being the problem a complex one, mainly $A-B$ molecules with single bonds used to be investigated.

In the case of molecules with pure ionic bond (*e. g.* potassium chloride) the expression $\mu_{\text{exp}}/e \cdot R_{AB}$ yields the extent of mutual polarization of ions, exerted on each other (beside the primary moment, the polarization moment

is the main factor) while in the case of transition types of bond the polarity can be considered as the sum not only of the ionic character of the bond but of the polarization, hybridization and orbital overlap moments, too.

Most recently the following semiempirical method has been elaborated by FAJANS [18b] to calculate the degree of polarity of alkali halides. The dipole moment (μ_p) formed by rigid, spherical, symmetric ions is diminished, by the superposition of an opposite induced dipole moment (μ_i), induced by another ion in the ion with α polarizability. The equation defining the polarizability of the ion yields a connection between the magnitude of α and that of the induced moment (μ_i) and between the strength of the homogeneous, not too strong electrostatical field (E): $\mu_i = \alpha E$. On applying this equation, FAJANS used the following idealized conditions: one of the ions was considered as a polarizing one and its electric field as homogeneous, its strength was given by expression $E = e/R_{AX}^2$, while the polarizability of the other ion (α and R_D , respectively) in bound state was taken to be the same as in free state. Thus in an idealized case $\mu_i = \alpha E = \alpha e/R_{AX}^2$ hence the degree of polarity $p = \mu_{\text{exp.}}/\mu_{\text{calc.}} = \mu_{\text{exp.}}/\mu_{\text{ionic}} = \mu_{\text{exp.}}/\mu_{\text{primary}} = (\mu_{\text{primary}} - \mu_i)/\mu_{\text{primary}}$, from this:

$$1 - p = \frac{\mu_i}{\mu_{\text{primary}}} = \frac{\alpha \cdot e/R_{AX}^2}{e \cdot R_{AX}} = \frac{\alpha_{A^+} + \alpha_{X^-}}{R_{AX}^3} \quad (2g)$$

Taking into consideration the LORENZ—LORENTZ equation, giving the connection between the mole refraction (R_∞) and the polarizability:

$$1 - p = \frac{\alpha_{A^+} + \alpha_{X^-}}{R_{AX}^3} = 0,3966 \frac{R_\infty(A^+) + R_\infty(X^-)}{R_{AX}^3} \quad (2h)$$

Using the mole refractions of free alkali- and halide-ions in two extreme cases (with lithium iodide and caesium fluoride) extremely great differences were obtained between experimental values and those calculated according to Eq. (2h). At LiI, the small and rigid Li^+ cation penetrates the electron shell of I^- anion, which is the most polarizable halide ion. On the contrary at CsF, F^- being only slightly polarizable, it repulses the electronic shell of the easily polarizable Cs^+ cation. Since in bound state the refraction of the

Table I.
Degree of Polarity* p for Vapor Molecules

HF	0,433	HCl	0,168	HBr	0,116	HI	0,049
LiBr	0,594 (0,590)	LiI	0,544 (0,544)	NaF	— (0,85)	NaCl	0,794 (0,754)
KCl	0,818 (0,787)	KBr	0,768 (0,768)	KI	0,755 (0,744)		
CsF	0,699 (0,699)	CsCl	0,747 (0,753)	CsI	0,709 (0,746)	TlCl	0,364 (0,540)

* The values without parentheses, $p = \mu_{\text{exp.}}/e \cdot R_{AX}$ obtained from observed μ and R_{AX} , those in parentheses calculated using Eq. (2i).

anion is smaller and that of the cation is greater than in free state, it is reasonable that at Lil the calculated $(1-p)$ value was given too high, while in the case of CsF too small. Therefore FAJANS applied in Eq. (2h) instead of theoretical factor 0,3966 empirical 0,3408 (for anions) and 0,4781 (for cations), both being calculated from the experimental degrees of polarity of Lil and CsF, and the following equation was obtained:

$$1-p = 0,3408 \frac{R_{\infty}(X^-)}{R_{AX}^3} + 0,4781 \frac{R_{\infty}(A^+)}{R_{AX}^3} \quad (2i)$$

Data calculated on the basis of Eq. (2i) fairly agree with experimental ones (see Table I.). According to this method of calculation the ideal ionic bond is approximated by sodium fluoride with a calculated value of $p_{NaF} = 0.85$. But there are negative p values for hydrogen halides, since the proton penetrates the electronic shell of halide anions, and this makes the application of the approximation Eq. (2i) rather irreal. In the case of thallium chloride molecule the difference between experimental and calculated values is very significant, what indicates a very high polarizing power and polarizability of the Tl^+ ion with non-noble gas-type configuration. As a close it can be stated that the applicability of this method is very restricted.

Now it is clear that the amount of the ionic character of the chemical bond calculated from the nuclear quadrupole coupling constant, and the numerical value of the degree of bond polarity obtained from the bond dipole moment and bond length may differ from each other even in the case of the same bond, further, being the main factors, the primary and polarization moments always with opposite signs, generally the degree of polarity is smaller than the amount of the ionic character ($I. C. = \beta$):

Table II.

Molecule	<i>I. C.</i>	<i>p</i>	Molecule	<i>I. C.</i>	<i>p</i>
LiBr	0,944	0,594	KI	0,970	0,755
Lil	0,900	0,578	RbCl	0,992	0,785
NaCl	0,990	0,794	CsCl	0,968	0,747
NaI	0,867	0,716	TlCl	0,831	0,364
KCl	1,000	0,818	ClF	0,259	0,113
KBr	0,985	0,768	BrF	0,329	0,153

A Survey of Methods for the Calculation of the Degree of Polarity of Chemical Bonds

1. PAULING's values for electronegativity and different attempts to use these values

PAULING [19] established a pure empirical connection between the difference in the electronegativities of the constituents $|X_A - X_B|$ and the degree of polarity of the bond of AB binary compound in gas-phase. To this end

he made use of FAJANS's values for the degree of polarity (naming it ionic character) and experimental data of HCl, HBr and HI molecules:

$$p = 1 - e^{-\frac{|x_A - x_B|^2}{4}} \quad (3')$$

From this formula 0,6 is given for the value of p_{HF} . Later HANNAY and SMYTH [20] obtained 0,43 experimentally for p_{HF} and they modified Eq. (3'):

$$p = 0,16|x_A - x_B| + 0,035|x_A - x_B|^2. \quad (3)$$

Values of p , belonging to $|x_A - x_B|$, calculated on the basis of Eqs. (3) and (3') are summarized in Table III. For the calculation of the differences in electronegativity $|x_A - x_B|$ the following equation is given:

$$|x_A - x_B|^2 = \frac{A(A-B)}{23,06} \quad (4)$$

from which

$$|x_A - x_B| = \sqrt{1/23,06} \sqrt{A(A-B)} = 0,208 \sqrt{A(A-B)} \quad (4')$$

where

$$A(A-B) = D_{(A-B)} - \frac{1}{2}(D_{(A-A)} + D_{(B-B)}) \quad (5)$$

Table III.

Degree of Polarity (p) as a Function of the Differences in Electronegativities, Calculated according to HANNAY and SMITH (3) and PAULING (3'), respectively

$x_A - x_B$	$p(3)\%$	$p(3')\%$	$x_A - x_B$	$p(3)\%$	$p(3')\%$
0,0	0	0	1,8	40,14	55,51
0,1	1,635	0,25	1,9	43,035	59,44
0,2	3,34	1,00	2,0	46,00	63,21
0,3	5,115	2,22	2,1	49,035	66,79
0,4	6,96	3,92	2,2	52,14	70,17
0,5	8,875	6,05	2,3	55,315	73,35
0,6	10,86	8,61	2,4	58,56	76,31
0,7	12,915	11,53	2,5	61,875	79,05
0,8	15,04	14,79	2,6	65,26	81,55
0,9	17,235	18,33	2,7	68,715	83,84
1,0	19,5	22,12	2,8	72,24	85,91
1,1	21,835	25,92	2,9	75,835	87,78
1,2	24,24	30,23	3,0	79,50	89,46
1,3	26,715	33,80	3,1	83,256	90,95
1,4	29,26	38,74	3,2	87,04	92,27
1,5	31,875	43,02	3,3	90,915	93,43
1,6	34,56	47,27	3,4	94,86	94,44
1,7	37,315	51,44	3,5	98,875	95,32
1,8	40,14	55,55	3,6		96,084

or

$$\Delta'(A-B) = D_{(A-B)} - \sqrt{D_{(A-A)} \cdot D_{(B-B)}}. \quad (5')$$

$D_{(A-B)}$, $D_{(A-A)}$, $D_{(B-B)}$ are the bond energies (dissociation energies) of molecules AB , A_2 and B_2 in gas-phase, expressed in kcal/mole, while 23,06 is the conversion factor from kcal to electron volts. According to PAULING's theorem $\Delta(A-B)$ the so called extra ionic resonance energy term is always positive or at most zero, and the cause of this is the "resonance" between the different ionic and covalent structures formed between atoms A and B . Owing to the complicated eqn (2a) a close correlation between $\mu_{\text{exp}}/e \cdot R_{AB}$ and the electronegativity difference cannot be expected, since these latter are in a close connection only with the primary moment, therefore $\mu_{\text{exp}}/e \cdot R_{AB}$ is not a measure for the difference in the electronegativity $|x_A - x_B|$ of atoms A and B . However, the fact that $\mu_{\text{exp}}/e \cdot R_{AB}$ and the corresponding electronegativity differences change near in a parallel way, is an empirical evidence that the contributions of the polarization, hybridization and overlap moments to the primary moment often equalize each other [14], [15], [21].

The heat of formation in the case of gas-phase molecules containing n_N atom of nitrogen and n_O atom of oxygen:

$$Q = 23,06 \Sigma (x_A - x_B)^2 - 55,1 \cdot n_N - 24,2 \cdot n_O. \quad (6)$$

HAISSINSKY [22] by introducing the heat of sublimation (L) made use of the heats of formation for solid state, for the calculation of the electronegativities and extended his investigations to most of the elements of the periodic system. He described the following equation for the heat of formation:

$$Q = 23,0 \Sigma (x_A - x_B)^2 - L - 55,1 \cdot n_N - 24,2 \cdot n_O. \quad (7)$$

Using the recent thermochemical data, the values for electronegativities of the atoms of copper, zinc and the gallium groups were also calculated [23]. Most recently the electronegativities of all the elements of the periodic system were given by GORDY and THOMAS, using recent thermochemical data (see Table IV) [24]. MULLIKEN [25] pointed out that the mean value of the ionization potential (I_A) and of the electron affinity (E_A) of a bounded atom is the measure for PAULING's electronegativity of the atom. Numerically

$$(I_A + E_A)/130 = x_A. \quad (8)$$

Recently SKINNER and PRITCHARD [26] have established a connection between the values of Mulliken's scale for electronegativity $x_M = (I_A + E_A)/2$ and Pauling's values (x_P):

$$x_M = 3 \cdot 15 x_P$$

NYEKRASOV [27] used the quotient of the ionization works and the corresponding ionization degree in order to calculate the polarity of compound AB on a basis that in general the elements having great electron affinity request greater ionization energy and vice versa, elements demanding small ionization work have small electron affinity (excepting rare gases). He has

given the following simple formula for the calculation of the polarity of compound AB :

$$p = g(I_B + I_A)/(I_B - I_A) \quad (9)$$

where g depends on the bond number and shows the bond multiplicity. In a single $A-B$ bond $g=1$. Essentially NYEKRASOV's formula is analogous to MULLIKEN's one and thus the values for p calculated by Eq. (9) well agree with those calculated from PAULING's electronegativity differences.

Most recently LEHMANN and BÄHR [28] have used the atomic core charge number Z^*/n to estimate PAULING's values for electronegativity. On the basis of FINKELNBURG's connection [29] $Z^*/n = \sqrt{\bar{I}/Rhc}$, where Z^* is the effective nuclear charge number, n the principal quantum number, $\bar{I} = \Sigma I/v$, v being the number of ionization degrees. Essentially this formula, too, takes into consideration the ionization works, but expresses them in hydrogen ionization work units and deduces the problem of calculating the degrees of bond po-

Table IV.
PAULING's Values for Electronegativity as Selected by GORDY

Atomic number	Element	Electronegativity	Atomic number	Element	Electronegativity
1	H	2,15	52	Te	2,1
2	He	—	53	I	2,55
3	Li	0,95	54	Xe	—
4	Be	1,5	55	Cs	0,75
5	B	2,0	56	Ba	0,9
6	C	2,5	57	La	1,1
7	N	3,0	58	Ce	1,1
8	O	3,5	59	Pr	1,1
9	F	3,95	60	Nd	~ 1,2
10	Ne	—	61	Pm	~ 1,2
11	Na	0,9	62	Sm	~ 1,2
12	Mg	1,2	63	Eu	~ 1,1
13	Al	1,5	64	Gd	~ 1,2
14	Si	1,8	65	Tb	~ 1,2
15	P	2,1	66	Dy	~ 1,2
16	S	2,5	67	Ho	~ 1,2
17	Cl	3,0	68	Er	~ 1,2
18	Ar	—	69	Tm	~ 1,2
19	K	0,80	70	Yb	~ 1,1
20	Ca	1,0	71	Lu	~ 1,2
21	Sc	1,3	72	Hf	1,4
22	Ti	1,6	73	Ta	1,3 ^{III} 1,7 ^V
23	V	1,4 ^{III} 1,7 ^{IV} 1,9 ^V	74	W	1,6 ^{IV} 2,0 ^{VI}
24	Cr	1,4 ^{II} 1,6 ^{III} 2,2 ^{IV}	75	Re	1,8 ^V 2,2 ^{VII}
25	Mn	1,4 ^{II} 1,5 ^{III} 2,5 ^{VII}	76	Os	2,0

larity to PAULING's method. AHRENS [30] investigated the problem in a similar way on applying the ionization work, considering it as the measure of the anion affinity of the cation. REED [31] studied the connection between the polarizability of the molecule and its ionization work and established simple and reversed proportions.

GORDY [32] emphasized the empirical connection between the bond stretching force constants calculated from spectroscopical data and PAULING's electronegativity values:

$$f = aN \left(\frac{x_A \cdot x_B}{R_{AB}^2} \right)^{3/4} + b \quad (10)$$

where N is the bond order, R_{AB} the bond length, a and b are constants within a certain group of the molecules. WILLIAMS [32a] pointed out that GORDY's result, Eq. (10), according to which the force constant depends on the product of the electronegativities, is only accidental, since the main factors determining the force constant are the number of valency electrons of

Table IV. Continued

Atomic number	Element	Electronegativity	Atomic number	Element	Electronegativity
26	Fe	1,7 ^{II} 1,8 ^{III}	77	Ir	2,1
27	Co	1,7	78	Pt	2,1
28	Ni	1,8	79	Au	2,3
29	Cu	1,8 ^I 2,0 ^{II}	80	Hg	1,8
30	Zn	1,5	81	Tl	1,5 ^I 1,9 ^{III}
31	Ga	1,5	82	Pb	1,6 ^{II} 1,8 ^{IV}
32	Ge	1,8	83	Bi	1,8
33	As	2,0	84	Po	2,0
34	Se	2,4	85	At	2,2
35	Br	2,8	86	Rn	—
36	Kr	—	87	Fr	0,7
37	Rb	0,8	88	Ra	0,9
38	Sr	1,0	89	Ac	1,1
39	Y	1,2	90	Th	1,0 ^{II} 1,4 ^{IV}
40	Zr	1,5	91	Pa	1,3 ^{III} 1,7 ^V
41	Nb	1,7	92	U	1,4 ^{IV} 1,9 ^{VI}
42	Mo	1,6	93	Np	~ 1,1
43	Tc	1,9 ^V 2,3 ^{VII}	94	Pu	~ 1,3
44	Ru	2,0	95	Am	~ 1,2
45	Rh	2,1	96	Cm	~ 1,3
46	Pd	2,0	97	Bk	~ 1,3
47	Ag	1,8	98	Cf	~ 1,3
48	Cd	1,5	99	Es	~ 1,3
49	In	1,5	100	Fm	~ 1,3
50	Sn	1,7 ^{II} 1,8 ^{IV}	101	Md	~ 1,3
51	Sb	1,8	102	No	~ 1,2

both atoms and their covalent radii (see GUGGENHEIMER's Eq. [32b]). Being the electronegativity a simple function of these, GORDY's equation, expressing force constants includes the product of the electronegativities. It is astonishing since most of the physical and chemical properties depend on the differences in electronegativities.

However, WALSH [33] regards the force constant for the $A-H$ bond to be the measure for the electronegativity of an A atom. Taking into consideration Eq. (10), the bond stretching force constant depends not only on the values for electronegativity, but on the bond distances, too. Therefore WALSH's determination is not unambiguous [24]. Similarly to this SIEBERT [34] also investigated the connection between force constants and the type of binding.

GORDY [35a, b] gives as a measure for the electronegativity of a neutral atom in a stable molecule the potential resulting from effective nuclear charge of the bonded atom, effective on a bonding electron when the electron is at a distance r from the nucleus:

$$x_A = \frac{Z^* e}{r} = \frac{ev - 0,5(v-1)e}{r} = 0,5e(v+1)/r = 0,31 \left(\frac{v+1}{r} \right) + 0,50 \quad (11)$$

where r is the covalent radius, v the number of valency electrons. From the formula it can be seen that, on the basis of PAULING's scheme, the screening number of a valency electron is taken into consideration with 0,5 unit (PAULING had calculated $0,4e$) while the right part of the equation expresses the connection between $(v+1)/r$ and x_A empirically found. Similarly to this LI [35c] obtained the following eqn using the ionic radii (R):

$$x_A = 0,11 Z^*/R + 0,64. \quad (11')$$

Soon after we also have dealt with the calculation of PAULING's electronegativity [35d] (see later) a similar treatment by ALLRED and ROCHOW was elaborated [35e]. ALLRED and ROCHOW used PAULING's definition for the electronegativity according to which the electronegativity of a bonded atom is the measure of the force of attraction of an atom, exerted on the electrons. Thus the expression $e^2 Z^*/r^2$ measures the attractive electrostatic force exerted by the atomic core with eZ^* charge to an electron with e charge, being in r distance from the nucleus. In this expression r is the covalent radius, Z^* the value calculated according to SLATER's rule [35g]. ALLRED and ROCHOW obtained empirically an approximation connection between PAULING's value for electronegativity x_A and Z^*/r^2 :

$$x_A = 0,359 \frac{e^2 Z_{A^0}^*}{r^2} + 0,744. \quad (11a)$$

It is similar to GORDY's empirical Eq. (11). A significant difference, besides the exponent of r is that in Eq. (11) the effective nuclear charge number of the ion with one positive charge is in the numerator, while in formula (11a) the effective nuclear charge of the neutral atom is used. WILMSHURST [35f] applied GORDY's expression for the effective atomic potential (11) to calculate the electronegativities of the radicals.

Recently GORDY and THOMAS [24] have established a simple linear relation between PAULING's electronegativity values and work function of the metals:

$$x_A = a \cdot \varphi + b = 0,44 \cdot \varphi - 0,15$$

where they used the mean value of data on work functions compiled by MICHAELSON [36] (φ in eV). The relation thus established is valid only for metals, for carbon, silicon *etc.*, for semimetals and non-metals it is not. Previous to GORDY and THOMAS's work STEVENSON [37] had established a similar relation on the basis of a consideration that analogously to MULLIKEN's concept the metal work functions can be regarded partly as surface ionization works and partly as the electron affinities of unfilled electron energy levels connected with the Fermi-level of the metals. Thus

$$x_A = \frac{23,06}{130} (I_A + E_A) = 0,1775 (2\varphi) = 0,355$$

where $23,06/130 = 0,1775$ is an empirical scale factor. STEVENSON's values were as general somewhat lower than GORDY and THOMAS's ones.

There were established relations between the ionic character determined by the differences in the electronegativities and the extent of the overlap of atomic orbitals [38]—[42a]. The greater the extent of the ionic character of the bond is, the smaller the overlap.

Some Critical Remarks on PAULING's Methods for the Calculation of Electronegativity of Atom and on Other Similar Attempts

As it can be seen from the previous, the calculation of the degrees of bond polarity by PAULING's electronegativities was only possible when one or more values for the degree of polarity determined by experiments, were applied. The most part of later efforts, instead of a direct calculation of the degrees of polarity, were limited to a possibly accurate calculation of PAULING's values for electronegativity from the physical constants deduced from diverse properties of the atoms and molecules resp., (such as thermochemical data, ionization works, electron affinities, normal covalent radii, force constants, work functions, atomic core charge numbers, *etc.*). All these methods working with fixed values for the electronegativity of an atom have several theoretical difficulties:

1. The electronegativity has the dimensions of force (see later) and so this means the electrostatic attracting force of a bonded atom exerted on the binding electrons described by the expression $a \cdot e/r^2$, where a is a parameter depending on the positive nuclear charge, on the screening and the interaction of electrons, e is the elementary charge and r the distance from the nucleus to the electron in question. But the differences in electronegativities can be calculated by PAULING's Eq. (4)

$$|x_A - x_B| = 0,208 \sqrt{A(A-B)}.$$

Thus $\Delta x = 0,208 [D_{\{(A-B) - 1/2[(A-A) + (B-B)]\}}]^{1/2}$ i.e. the electronegativity is proportional to the square root of the potential energy corresponding to the dissociation energy, i.e. to the expression $\sqrt{a \cdot e/r^2}$ and not to $a \cdot e/r^2$.

2. The value for electronegativity (x_A) is not a characterizing constant of the atom of an element at all, thus *a constant electronegativity of an element cannot have a definite meaning at least in quantitative respect.* [43]—[45].

a) The x_A value for the parameter determining the „ionic character” of the bond changes depending on the valency-state of an atom (A) with the same partner (e.g. the value of x_S considerably differs in SO , SO_2 , S_2O_3 , SO_3 , SO_4 -etc. molecules).

b) In the same valency-state the electronegativity of an element (x_A) also depends on the electronegativity of the partner (x_B), i.e. the partners are in mutual interaction (e.g. the value of the electronegativity of the nitrogen atom in the same valency state $x_{N^{III}}$ is considerably different in compounds NF_3 and NI_3). Namely the closely neighbouring atoms in the bonds mutually influence their field of force, therefore electronegativity is concerned with atoms in molecules rather than with atoms in isolation, that is measurement in a precise way is not easy [7].

An atom may exhibit a *range of electronegativity* depending upon the range of valence state available to it and the partner. There remains the problem of choosing from this range the unique value which the atom achieves in a given molecular environments. In the strictest sense one should speak not of the electronegativity of an atom, but rather of *the electronegativity of atomic orbitals and of bonding molecular orbitals* [7].

P. DAUDEL and R. DAUDEL [45a] pointed out that the extra ionic resonance energy $\Delta(A-B)$, introduced by PAULING, must relate not to the differences in the electronegativity of the neutral atoms but first to the differences in the electronegativities of the so called ionic constituents i.e. bonded atoms with formal charge, being formed on the effect of the differences in electronegativities. Thus in the case of an AB binary molecule instead of PAULING's Eq. (4') they recommended the following:

$$|x_{A^0} - x_{B^0}| = 0,208 \sqrt{\Delta(A-B)} + p(\zeta_{A^+} + \zeta_{B^-}) \quad (4a)$$

where x_{A^0} and x_{B^0} are the electronegativities of neutral atoms, p the degree of polarity of the $A-B$ bond and ζ_{A^+} and ζ_{B^-} are changes in the electronegativities of A and B atoms, if A and B receive a formal unit positive or negative charge. So equation

$$0,208 \sqrt{\Delta(A-B)} = |x_{A^0} - x_{B^0}| - p(\zeta_{A^+} + \zeta_{B^-}) \quad (4a')$$

also indicates that the electronegativity of a bonded atom depends on the atoms bonded with it, i.e. on the partners and the valency-state of the atom. Unfortunately the value of ζ practically can be estimated only roughly.

3. The exchange forces and the resonance, on the basis of which PAULING theoretically deduced the values for electronegativity are without any real basis [46]—[48]. “The concept of the exchange of electrons led to the

incorrect conclusion of the existence of specific exchange forces. In reality there are no exchange forces. In the molecules electric, namely, coulomb forces are acting". [49]. In the conventional explanation of the localized covalent bond formed on the interaction of atoms, the following energy terms are taken into consideration: the kinetic energy of the electrons, the electron — nuclear and nuclear — nuclear potential energies, and the electron-electron potential energy. An adequate discussion of the last of these energy terms requires a consideration of electron correlation on a six-dimensional configuration space. HURLEY [50a, b, c, d] pointed out that the formation and the properties of the localized covalent bond may be understood solely in terms of electrostatical forces of the coulomb type. These forces are completely determined by a single charge distribution function in three-dimensional physical space. This electrostatical treatment of the localized covalent bond, using the term of the optimum orbitals considerably simplifies the question, does not involve any loss of accuracy of the calculation. The electrostatical interpretation of the directed valences of molecular hydrides with a covalent bond established by GRAY and PRITCHARD [50e] indicates, that there is no casual relationship between the mathematical convenience of the orbital approximation and the occurrence of the directed valences. According to FAJANS [50f] and KIMBALL [50g] and Coulson [50h] the nature of the chemical binding forces both in inorganic and organic molecules and complexes, essentially is coulombic, electrostatic.*

As a close it can be stated that the chemical binding forces can be interpreted even without supposing any specific exchange and resonance forces, resp., as essentially coulombic forces.

From the point of view of the interpretation of the origin of PAULING's values of electronegativity it is very important that COTTRELL and SUTTON [51] applied the HEITLER—LONDON—SUGIURA treatment for the two-electron diatomic molecule while HURLEY [52] applied LENNARD—JONES and POPLE's approximate wave-function. It had been pointed out that if the calculated dissociation energy of molecule AB is greater than the mean (arithmetic or geometric) value of the calculated dissociation energies of molecules A_2 and B_2 , this is not caused by an ionic-covalent resonance. Really, mainly the internuclear repulsion energy is reduced in molecule AB , (or generalizing it can be assumed that that between atomic cores decreases) related to the arithmetic or geometric mean of the internuclear repulsion energies in molecules AA and BB . It also had been established that the extra ionic resonance energy $\Delta(A-A)$ may be not only positive but also negative [52], [53].

4. To establish a relationship between the difference in the electronegativities of the constituents and the polarity of the bond of an AB binary compound in gaseous state, it is not practicable to use the data of hydrogen halides [54] since in this molecules according to experimental data, proton deeply penetrates the electronic shell of the anionic constituent. Overlap of such a great extent is never produced in the case of other cations.

* See e. g. Ephraim f. in his book Inorganic Chemistry (Oliver and Boyd, Edinburgh and London, 1954, 6th Edition) applies FAJANS's polarisation and quanticule theory, respectively.

From practical points of view there are two complications in connection with the electronegativities:

1. Parameters determining the "ionicity" of the chemical bond (x_A, x_B) can be calculated from different empirical data. The inaccuracies and the insufficient number of such data (electron affinities, work functions of metal, heats of dissociation, *etc.*) and the different participation of the electronegativities in the values of diverse physical constants, largely limit the general validity of the relations.

2. A great part of the different definitions for electronegativity is not simple (*e. g.* PAULING's) [33] or if it is simple as *e. g.* MULLIKEN's definition, then there are complications in its application in simple form. (The author himself admits that because of the dependence of ionization potentials and electron affinities on the valency state, values often related not to the normal state are to be used. [25].)

2. Critical Review of SANDERSON's Method

SANDERSON's values for the electronegativity, the so called stability ratios [55a—f] considerably differ from PAULING's ones both from point of view of the method and the numerical value. As the measure for the electronegativity of an active atom SANDERSON considers the ratio of the average electron density of an atom (ED) and the average electron density of a real or hypothetical isoelectronic inert atom. This is the so called stability-ratio (SR) for the given element:

$$SR = \frac{(ED)}{(ED)_i} = \frac{Z}{4/3 r^3 \pi (ED)_i} = \frac{Z}{4,19 r^3 (ED)_i}, \quad (12)$$

where Z is the number of electrons of the active atom in question (non inert-gas), r the nonpolar covalent atomic radius or the ionic radius, (ED) the average electronic density of the atoms *i. e.* the average number of electrons per \AA^3 ; $(ED)_i$ the average electron density of an isoelectronic inert atom real, or hypothetical, determined by linear interpolation between the average real values of two inert-gas atoms placed nearest before and after the atom in question in the periodic system.

During the formation of a chemical bond *i. e.* when the atoms of the active elements combine into molecules, *the attractions of the atoms or atomic cores of the molecules on the valency electrons equalize thus a stabile bond is formed*, their electronegativities (SR) become equal.

SANDERSON had postulated that the SR_m of the molecule is a geometrical mean of the SR s of all the atoms of the molecule before the combina-

tion. Thus in the case of a binary compound $A_i B_j$ $SR_m = \sqrt[i+j]{SR_A^i \cdot SR_B^j}$. This postulate was proved so that calculating the the atomic radii within the molecule from its SR_m by formula

$$r = \sqrt[3]{\frac{Z}{4,19 \cdot (ED)_i \cdot SR_m}}$$

the bond lengths as sums of two radii calculated in this way fairly agree with experimental data in case of near 700 investigated bonds, but also certain corrections were necessary, taking into consideration geometrical points of view at some bonds [55a], [55c].

SANDERSON assumed that *the change in the electronegativity, i. e. in the SR, is linear to that in the charge*, thus $\delta^{(A)}$ partial charge on atom A of the molecule and ions, resp.,:

$$\frac{SR_A - SR_{A^{v+}}}{v} : (SR_m - SR_A) = 1 : \delta^{(A)} \quad (13)$$

from this

$$\delta^{(A)} = \frac{SR_m - SR_A}{(SR_A - SR_{A^{v+}})/v} \quad (13a)$$

where $SR_{A^{v+}} = \frac{Z_{A^{v+}}}{4,19 \cdot r_{A^{v+}}^3 (ED)_i}$ [55e]. Regarding that the value of $\delta^{(A)}$ refers

to the partial charge of the constituent atoms of the molecules in gas-phase in order to calculate $SR_{A^{v+}}$ and $SR_{B^{v-}}$ of the electronegativities of the ions, the crystal ionic radii cannot be used. The only experimental values for ionic radii in gas-phase are obtained in case of atoms of alkali metal group, univalent atoms of alkali earth metal and aluminium groups and of halide and hydride ions [56]—[58]. However, it is possible to calculate theoretical values in the case of all the isolated ions with BOHR's formula [59].

Thus for sodium and fluoride ions the following values can be given:

Radius	Experimental Data	Calculated from Polarizability	Theoretically calculated
r_{F^-}	1,04 Å	1,02 Å	1,03 Å
r_{Na^+}	0,89 Å	0,57 Å	0,50 Å

Thus $(SR)_{NaF} = \sqrt{SR_{Na} \cdot SR_F} = \sqrt{0,70 \cdot 5,75} = 2,01$.

Using these data:

$$SR_{F^-} = \frac{10}{4,19(1,04)^3 \cdot 1,06} = 2,00$$

$$SR_{Na^+} = \frac{10}{4,19(0,89)^3 \cdot 1,06} = 3,19$$

$$\delta^{(F)} = \frac{2,01 - 5,75}{5,75 - 2,00} = -0,997$$

$$\delta^{(Na)} = \frac{2,01 - 0,70}{3,19 - 0,70} = 0,526$$

Therefore the so obtained charge distribution $Na^{+0,53}F^{-1,00}$ contradicts to the principle of electroneutrality and does not correspond to the real charge dis-

tribution of sodium fluoride molecule. In our opinion the cause of this discrepancy is that SANDERSON's postulate for the geometrical mean value referring to SR_m does not correspond to the conditions existing in the real charge distribution of the molecule. Thus a considerable difference arises *e. g.* between the bond lengths of sodium fluoride, calculated according to SANDERSON and RITTNER's [56] values:

$$r_{\text{Na}^+} = r_{\text{F}^-} = \frac{10}{4,19 \cdot 1,06 \cdot 2,01} = 1,039 \text{ \AA}$$

thus $d_{\text{NaF}} = 1,039 + 1,039 = 2,078 \text{ \AA}$, while d_{NaF} from RITTNER's radii: $1,93 \text{ \AA}$. In table VI. we give some correct values for bond length of alkali halides determined experimentally, and also those calculated according to SANDERSON. At the methods I and II the corresponding values for inert gas radius and $(ED)_i$ are the following (Table V):

Table V.

Atom	I. method		II. method		Other method	
	Univalent radii	$(ED)_i$	Crystal* ionic radii	$(ED)_i$	Radii after ROWLINSON	$(ED)_i$
He	0,93	0,61	0,93	0,59	1,28	0,23
Ne	1,12	1,70	1,31	1,06	1,39	0,89
Ar	1,54	1,18	1,74	0,82	1,71	0,86
Kr	1,70	1,78	1,89	1,27	1,80	1,45
Xe	1,90	1,87	2,09	1,41	2,0	1,61
Rn	2,2	1,93	2,14*	2,09*	—	—

The above data show that there is a very significant difference between experimental data and those calculated according to SANDERSON, especially at values for $(ED)_i$ recently used in the II group (excepting lithium halides).

In other cases it is true that the principle of electroneutrality is not valid for values of partial charge calculated by using geometrical mean value postulate referring to SR_m and by using the values of experimentally found and theoretically calculated ionic radii in gas-phase. This complication was eliminated by SANDERSON so that he arbitrarily chose a bond, that of the isolated sodium fluoride molecule, and chose it in 90% of "ionic character". (It is to be noted that for isolated sodium fluoride molecule there are no experimental data from which the "ionic character" of the sodium fluoride bond could be estimated.) After this, using equation

$$\delta^{(\text{F})} \text{ referring to } \delta^{(\text{F})} = \frac{2,01 - 5,75}{5,75 - SR_{\text{F}^-}} = 0,90 \text{ and another}$$

$$\delta^{(\text{Na})} = \frac{2,01 - 0,70}{SR_{\text{Na}^+} - 0,70} = 0,90$$

* see ref. [60]

the value for SR_{Na^+} and SR_{F^-} can be obtained. Using these values in a successive approximation it becomes possible to calculate the SR of the most different free cations and anions [55b]. *Using the arbitrarily chosen adjustable parameter the method lost its advantage to the previous ones.* However, on comparing it with PAULING—HAUSSINSKY's method, it has the merit of a more general applicability *e.g.* it simply can be used to calculate the ionic character of bonds in transition metal compounds, different complexes and organic molecules.

Table VI.

Formula	Experimental value	References	BOND DISTANCE	
			SANDERSON'S	
			I. Method	II. Method
LiF	$1,51 \pm 0,08$	[60]	1,92	1,69
LiBr	2,1704	[58]	2,48	2,35
LiJ	2,3919	[58]	2,77	2,54
KCl	2,6666	[58]	2,82	2,93
KBr	2,8207	[58]	2,98	3,11
RbCl	2,7867	[61]	2,94	3,09
CsF	2,3453	[58]	2,64	2,86
CsCl	2,9062	[58]	3,05	3,31
CsJ	3,3150	[58]	3,46	3,76
TlCl	2,541	[62]		2,47

Recently SANDERSON has taken the "ionicity" of the sodium fluoride bond to be of 75% and so the previous values for the partial charge, calculated with 90%, must be multiplied with 0,833. This change was done in order to obtain for uniatomic anions (fluoride, chloride, etc.) the theoretically expected lower ED value than those obtained for $(ED)_i$ of isoelectronic inert gas atoms with a greater nuclear charge and thus a more compact electronic shell.

In connection with this, mention must be made of the fact that it is possible to calculate the value of δ instead of geometrical mean value postulate with SANDERSON's method using the following less arbitrary method. Supposing that the change of SR is linear to the change in the partial charge and taking into consideration that if the compact, more negative atom takes a partial charge from a more positive atom, the originally more compact shell of the negative atom becomes loose while the less compact shell of the positive atom becomes more compact, supposing that this process lasts until the SR_A of the cationic constituent equals to the SR_B of the anionic constituent, thus in case of AB molecule

$$SR_m = \delta \cdot SR_{B^-} + (1 - \delta) SR_B = \delta \cdot SR_{A^+} + (1 - \delta) SR_A$$

(autoequivalent equation) from which the value of

$$\delta = \frac{SR_A - SR_B}{(SR_{B^-} - SR_B) + (SR_A + SR_{A^+})}$$

Table VII.
SANDERSON'S Values for Electronegativity (SR = stability ratio)

A	$\log SR_A$	SR_A	$(SR_A - SR_{Av^+})/v$	A	$\log SR_A$	SR_A	$(SR_A - SR_{Av^+})/v$
H	0,5502	3,55	3,919	As	0,5922	3,91	4,112
Li	-0,1308	0,74	1,789	Se	0,6284	4,25	4,289
Be	0,2810	1,91	2,923	Br	0,6561	4,53	4,426
B	0,4533	2,84	3,545	Rb	-0,2757	0,53	1,514
C	0,5786	3,79	4,050	Sr	0,0414	1,10	2,267
N	0,6523	4,49	4,408	Y	0,2430	1,75	2,752
O	0,7168	5,21	4,749	Zr	0,3541	2,26	3,126
F	0,7597	5,75	4,988	Ag	0,3617	2,30	3,155
Na	-0,1549	0,70	1,741	Cd	0,4133	2,59	3,347
Mg	0,1931	1,56	2,661	In	0,4564	2,86	3,517
Al	0,2878	1,94	2,968	Sn	0,4914	3,10	3,663
Si	0,4183	2,62	3,418	Sb	0,5276	3,37	3,819
P	0,5238	3,34	3,802	Te	0,5587	3,62	3,958
S	0,6138	4,11	4,216	I	0,5843	3,84	4,077
Cl	0,6929	4,93	4,618	Cs	-0,3098	0,49	1,456
K	-0,2518	0,56	1,556	Ba	0,0086	1,02	2,189
Ca	0,0864	1,22	2,376	La	0,2923	1,96	2,912
Sc	0,2742	1,88	2,852	Au	0,4518	2,83	3,500
Ti	0,3560	2,27	3,272	Hg	0,4669	2,93	3,584
Cu	0,3856	2,43	3,243	Tl	0,4800	3,02	3,646
Zn	0,4533	2,84	3,529	Pb	0,4857	3,06	3,679
Ga	0,5092	3,23	3,772	Bi	0,4969	3,14	3,727
Ge	0,5551	3,59	3,942				

calculated from this eqn is between the values calculated with a reference standard of 90% and 75% ionic character for NaF (see Table VIII).

The *ED* values of the elements give the mean value of the compactness of the electron shell around the atomic nucleus. It can be expected that in case of atoms with compact electronic shell the expression $ED = Z/4 \cdot 19 \cdot r^3$ well approximates this, *i. e.* in case of atoms with loose electronic shell the approximation is very poor. Really, especially in the case of alkali metal and alkaline earth metal atoms one does not obtain even the order qualitatively expected, therefore SANDERSON, taking into account the ionization works, modified the *ED* and *SR* values of these elements. However, there is only a slight difference between the revised values for lithium and sodium related to those between the values of potassium and sodium. Thus the "ionic character" of lithium compounds differs only with 1% from those of sodium compounds while the difference between the "ionic character" of sodium and potassium compounds is with 5% greater. Really, lithium compounds, due to the small size and great polarizing force of lithiumion, have considerably smaller "ionic character" and polarity, respectively, than other alkali metal compounds.

Table VIII.

Compound	$p_{\text{NaF}} = 90\%$	Autoequ. with Experim. Radii	$p_{\text{NaF}} = 75\%$
NaF	0,90	0,817	0,75
NaCl	0,798	0,69	0,665
NaBr	0,74	0,667	0,62
NaI	0,648	0,60	0,54
KF	0,95	0,817	0,793
KCl	0,85	0,695	0,71
CsF	0,9795	0,83	0,816
BrCl	0,053	0,048	0,0442

The values for degrees of bond polarity calculated according to SANDERSON's method considerably differ from the experimental ones, in general they are smaller, especially those obtained by most recently used $p_{\text{NaF}} = 0,75$ standard calibration value (see later Table IX).

It can be proved that SANDERSON' *SR* values are directly proportional to the attractive forces exerted by the atom on the valence electrons:

$$SR = \frac{Z}{4,19 \cdot r^2 \cdot r(ED)_i}$$

is converted, on substituting BOHR's formula for atomic radius, into

$$r = \frac{a_H \cdot n^2}{Z - S} = \frac{a_H \cdot n^2}{Z^*}$$

where $a_H = 0,5292 \text{ \AA}$ is BOHR's radius of the hydrogen atom n the principal

quantum number of the orbit for electrons detached during ionization of the atom in question, S the screening number of electrons remained after ionization. Thus, $Z-S=Z^*$ expresses the so-called effective nuclear charge number of the remained atomic core

$$SR = \frac{ZZ^*}{4,19 \cdot r^2 a_H n^2 (ED)_i}$$

Introducing the notation

$$\frac{Z}{4,19 \cdot a_H n^2 (ED)_i} = C,$$

where C is constant in the case of isoelectronic ions, or approximately constant by elements of the same period. Thus

$$SR = C \cdot \frac{Z^*}{r^2}.$$

This term expresses the magnitude of attractive forces exerted by one atom of the molecule on the electrons.

The exact form of the correlation between the difference of PAULING's electronegativity and bond energy as evolved by P. DAUDEL and R. DAUDEL yields for the degree of ionic character and polarity, respectively, the following formula:

$$p = \frac{|x_A^0 - x_B^0| - 0,208 \sqrt{A(A-B)}}{\zeta_{A^+} + \zeta_{B^-}}$$

which greatly resembles to SANDERSON's equation

$$\delta^{(A)} = p \cdot \delta_{\max}^{(A)} = \frac{SR_m - SR_A}{(SR_A - SR_{A+v})/v}$$

$$\delta^{(B)} = p \cdot \delta_{\max}^{(B)} = \frac{SR_m - SR_B}{(SR_B - SR_{B-v'})/v'}$$

in them we find in both cases the difference between the electronegativities of the neutral atom and the ionic constituent with partial charge of the molecule in the numerator, or an amount directly proportional to it, whilst the denominator measures the changes in electronegativity in A and B when they acquire unit positive and unit negative formal charge, respectively. This close similarity indicates that the terms in P. DAUDEL's and R. DAUDEL's equation also correspond to SANDERSON's definition of electronegativity.

PRITCHARD and SKINNER [7] pointed out that calculating the $(ED)_i$ values for the inert gas atoms, there are some complications when choosing the normal covalent radii of the inert gas atoms, since they form no compound. Such radii can be interpolated only from univalent crystal radii of isoelectronic ions or from crystal ionic radii. In Table V it can be seen that SANDERSON's and ROWLINSON's [63] recent values considerably differ from each other. But PRITCHARD and SKINNER's opinion, according to which the origin of alter-

nations in electronegativity (SR) found in the major groups of the periodic system can be found in the values for normal covalent radius and (ED); of inert gas atoms chosen by SANDERSON, is faulty. Really this alternation can be found already in the normal covalent atomic radii of the elements of the major groups, while its interpretation is yielded by *transition metal contraction* and the *double (transition metal + lanthanide) contraction* [64a].

Both SANDERSON's and ROCHOW's values for electronegativity well show the alternation within one column of the major group of the periodic system. Therefore it is rather odd and without sense to bring this into correlation with PAULING's values for electronegativity, which do not show this alternation, *i. e.* plotted against each other on the same curve (see *e. g.* [35e], [64b]). Thus it is reasonable that sometimes there is a difference of about 0,5 electronegativity units between correlated and original values.

Another practical complication of SANDERSON's method had already been pointed out by DOERFFEL, according to him the inaccuracy of the radius is more emphasized, since it takes place at its third power [64c]. At last the linear relation between the stability ratio and the partial charge cannot be proved.

3. RITTNER's Method

On the basis of the classical electrostatic model, by introducing certain simplifications, RITTNER has elaborated a semiempirical method for the calculation of the bond energy and the degree of polarity and dipole moments, resp., of alkali halides solely [56]. This method has been applied by KLEMPERER and MARGRAVE [56a] for the calculation of the dipole moments and binding energies of alkali hydrides. This application was criticized by ALTSHULLER [56b] on the basis that the penetration of alkali metal anions into hydride anions is of considerably greater extent than that into halide anion, therefore the simplified model applied to alkali halides is not suitable for alkali hydrides. According to KLEMPERER and MARGRAVE there was a great difference between calculated and experimental values already in the case of alkaline-earth-metal oxides. Generally RITTNER's method was to be applied only for alkali halides of high degrees of polarity, and even here the agreement between the most recent experimental values for the degree of polarity and those calculated with this method is very poor.

New Ways for Calculating the Degree of Polarity

On the basis of the above critical review of these semiempirical methods it is clear that the task of further investigations is not to seek new values for the electronegativity, reflecting more exactly the chemical character of the elements, or to deduct and calculate more useful values for PAULING's electronegativities from other physical constants of atoms and molecules. The aim is to elaborate such a *new method*, in which we can start from data experimentally obtained independently of the bond length and of the bond dipole moment to be evaluated, theoretically calculated with methods of the quantum

mechanics, and it is desired that these data precisely can be measured and we have many of them. The further task is to elaborate a method of calculation which takes into consideration actual forces, based on a reasonable structure, without using any other experimentally determined degree of polarity or any other adjustable parameters arbitrarily chosen. Naturally the polarity of the ionic character of a given molecule must be yielded precisely by this method of calculation considering each case as a special one.

The present paper starts from FAJANS's approach to the chemical binding forces, supported experimentally and quantum mechanically. FAJANS's approach is the so called "quanticule and polarization theory" of the chemical bond. [10c], [50f]. According to FAJANS's quanticule theory, the nature of chemical binding forces is coulombic, *i. e.* the interactions in molecules, crystals, melts and solutions can be traced back to the electrostatic interactions between nuclei and electrons. In first approximation, these may be investigated as electrostatic interactions of quanticules: namely, of atomic nuclei or atomic cores, further of binding electron groups and of antibinding electron groups (molecular or atomic quanticules). The qualitative results of these interactions on the bond polarity are summarized in FAJANS's polarization rules, according to which the degree of polarity is the smaller, the stronger the field of the deforming ion (the atomic core quanticule) and the larger the polarizability of the deformed ion (anionic quanticule) are. Both depend on the charge, size and electron configuration of the ion in question.

Starting from FAJANS's quanticule and polarization theory, as a first step it is necessary to take into consideration quantitatively the polarizing power of the cation. Several attempts of this kind can be found in literature. In 1926 GOLDSCHMIDT [65] introduced ve/r^2 and ve/R_{AB}^2 resp., as the measure for the field strength of the cation [66a, b], where v is the valency and charge, respectively, of the ion, e the elementary charge and r the cationic radius, R_{AB} the distance between the anion and the cation. Yet CARTLEDGE [67] in 1928 used the expression ve/r to take quantitatively into consideration the polarizing power of the cation. A common inadequacy both of the magnitude of the field strength and the ionic potential is that owing to the use of macroscopic ionic charge, v , does not reflect the difference between the polarizing power of ions with the same charge and size but with different electronic configuration [68, 69], as it had been pointed out already by FAJANS [10a]. The measure for the attraction force of the cations with the same size and charge but with different electronic configuration, exerted on a given anion, or simplifying the question, on an outer electron, is the ionization work needed for the detachment of this electron. That is why a more general applicability of the ionic potential and the electric field strength expressions was attempted by several authors, when they introduced the ionization work (I). AHRENS [70a, 70b] introduced the expression of the "electric intensity" and the "field strength" ($F = I/r$), resp., measuring anion affinity of a cation, with the same charge and the same size in volt per Å. GOLDSCHMIDT in his recent book [71] takes as the measure for the polarizing force the value of the ionization work needed for the detachment of the last electron during the forming of the cation in question, referred to unit ionic charge:

shortly the potential per unit charge (I/v). Regarding, that the shielding and screening effects (Se) of electrons with different configuration (having different principal, azimuthal, magnetic and spin quantum numbers) exerted on the nucleus with $+Ze$ charge, are very different, and this difference has some effect on the ionization work needed for the detachment of the outermost electron, the endeavour to use the so called effective nuclear charge $Z^* \cdot e = e(Z - S)$ proposed by some authors [28, 35a, b, 72] can be regarded quite obvious. So GORDY has applied the term Z^*e/r , while LEHMANN and BÄHR Z^*/n , as a measure for PAULING's electronegativity of the atoms. The values of Z^* used by GORDY and LEHMANN considerably differ from each other, since GORDY used PAULING's scheme for the estimation of the screening number (the screening number 0,5 *per* one valency electron). LEHMANN and BÄHR used FINKELNBURG's [73] screening number and Z^* values, resp., on the basis of $Z^*/n = \sqrt{I/Rhc}$. GORDY's Z^*e/r values were calculated again by PRITCHARD and SKINNER [74], using SLATER's rule [75]. Most recently AHRENS has introduced $S_{eff} = 5v^{1,27}/I\sqrt{r}$ under the name "shielding efficiency of the cations" [76].

The method essentially already described by us [35d] has been applied by FERREIRA [77] for PAULING's and P. DAUDEL and R. DAUDEL's equation respectively, where he used KOHLRAUSCH's [59] screening constants for the calculation of the degrees of polarity. With his method he succeeded only to calculate the degree of polarity of hydrogen halides, in the case of other bonds he could not make calculations for them due to complications in choosing the screening constants for the different hybridization states:

ALLRED and ROCHOW calculate in the expression $P^* = \frac{Z_A^* e^2}{r^2}$, the effective nuclear charge number of the constituent atom on the basis of the SLATER-rule, while r is the covalent atomic radius experimentally obtained.

Mention must be made that GOLDSCHMIDT doubted [78] the real physical meaning of the ionic potential, and according to CRAIG [79] in complex compounds the "relative capacity of attraction" for a metal ion, exerted on the ligands can be measured better with the expression of the field strength than with that of the ionic potential.

After all, considering all these attempts we thought that the most suitable is to introduce the concept of the "effective electric field strength" (F^*) where the absolute value of the effective electric field strength is $F^* = Z^* \cdot e/r^2$ and $Z^* \cdot e/R_{AB}^2$. (In the expression r , depending on the problem to be investigated may be a value theoretically calculated, the true radius of the free atoms or ions, or a radius obtained from the interionic or interatomic distances in crystal lattices, or ionic radius deduced from the bond length of molecules in gas-state while R_{AB} is the bond length of compounds in gas or solid state, *i. e.* the anion-cation distance and in the case of elements the shortest bond length.)

The polarizability of the anions can be calculated from mole refractions precisely determined experimentally (R_∞) by the LORENZ—LORENTZ equation:

$$\alpha = \frac{3}{4\pi N} \frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{s} = \frac{3}{4\pi N} R_\infty$$

where n is the refractive index for $\lambda = \infty$, M the molecular weight, s the density, and N AVOGADRO'S number. Theoretically, on the basis of the BORN—

HEISENBERG relationship $\alpha = \frac{C}{Z^{*3}}$ where C is an amount proportional to the sixth power of the effective principal quantum number, thus α is proportional to r^3 . According to RICE [80] the polarizability $\alpha = 0,76 \nu r^3$ where ν is the valence of the anion, *i. e.* the negative charge number. Most recently the concept of the anionic potential ν/r has been introduced by SZÁDECZKY [81] analogously to the cationic potential (ν the valence of the negative ion, or its charge number). Considering that strongly polarizable anions have small positive effective electric field strength (actually it may be negative) and *vice versa*, so we can introduce the expression $F^* = Z^*e/r^2$ of the effective electric field strength for anions, too as measure of its polarizability.

In a common quantitative treatment of the polarizing force and polarizability, taking into consideration all the previous attempts (see *e. g.* reference [81]) a difficulty arises that the polarizing force is inversely proportional to the size of the constituent ion or atom, while the polarizability is directly proportional to it. SZÁDECZKY'S method is a common treatment, where the potential of the compound combines from the anionic and cationic potentials, and the atomic potentials, resp. In accordance with the experimental results, a larger cationic potential shows always greater polarizing force. But regarding the question from the side of the polarizability of the anions, the following contradiction arises: in the case of an ions with the same charge but with difference size, the decrease of the anionic potential means an increasing polarisability (*e. g.* F^- , Cl^- , Br^- and I^- anionic row), while at anions with near the same size but having different charge, the polarizability decreases together with the decrease of the anionic potential (*e. g.* OH^- and O^{2-}). To avoid this the problem of the polarizability was deduced to the problem of the polarizing force, whenever both was quantitatively taken into consideration with the effective electric field strength. This attempt involves no contradiction, since in the comparison we must take into consideration that FAJANS'S approximating formulae represent limiting cases with ideal ionic bond, and FAJANS'S polarization rules refer to the same, what informs us to what an extent does the real charge distribution of the molecule in question differ from the ideal ionic bond state. With FAJANS'S own words: "In my theory Li^+H^- and $S^{6+}(O^{2-})_4$ express correctly the quantization, while the continuous polarization which automatically follows from these formulations and from the polarization properties of the ions, leads to the charge distribution $Li^{p+}H^{p-}$ etc. [82]". However, the effective electric field strength value of the anionic and cationic constituents considerably differs from that of the corresponding free, ideal, rigid ions, *i. e.* from the polarizing force and the polarizability, too. To understand this the following must be considered. According to SANDERSON'S definition, the electronegativity of an atom is represented by the force, with which the atom in the molecule affects the electron. A molecule being formed, if in the beginning the attraction force of the constituents differed, it must be equalized by a charge shift (see *e. g.* SANDERSON'S concept), *i. e.* the more electronegative atom expands thereby lessening its attraction for the valence

electrons, and the less electronegative atom contracts, thereby increasing its attraction for the valence electrons, shortly on the other side the cation deforms the electronic shell of the anion until the *effective electric field strength of the cationic constituent becomes equal to that of the anionic component*. The extent of the charge shift, calculated on the basis of the equality of the effective electric field strength, gives us information about the degree of polarity of the bond. According to our investigations the effective electric field strength of the constituent, in equilibrium, is always in the positive range during the formation of the most diverse molecules and never becomes negative (a negative value, as a rule, would correspond to a limit case, to the effective electric field strength of the free anion). At last the polarizability of the anion was substituted by the polarizing force of the anionic constituent. Now, we must emphasize that there is an important difference between our concept of the "effective electric field strength" and the concept of the "field strength" widely used by FAJANS and others. *E. g.* the electrostatic field strength of the fluoride ion, effective in macroscopical dimension (in $d \gg r$ distance), is a negative value $-e/r^2$ and $-e/d^2$, at the same time the electrostatic field strength of the fluoride ion formed just around itself, *i. e.* the absolute value of an electrostatic attraction force exerted on a unit negative charge placed at a distance of the radius of the isolated fluoride ion (0,954 Å) from the fluoride-nucleus, the so called "effective electric field strength" the absolute value of which is $F_F^* = +0,3426 \cdot e/\text{\AA}^2$ positive value, since the ten electrons of the fluoride ion do not perfectly screen the nuclear charge with the magnitude of $Z = +9e$. The nuclear charge screened by ten electrons of fluoride ion with neon configuration $8,6882 \cdot e$ and so the effective nuclear charge of the fluoride ion $(9 - 8,6882)e = 0,3118 \cdot e$, therefore the effective electric field strength: $e \cdot Z^*/r^2 = e \cdot 0,3118 / (0,954)^2 \text{\AA}^2 = 0,3426 e/\text{\AA}^2$. In our investigations the charge shift in question within a molecule was to be calculated by taking into consideration quantitatively these power ratios with microscopical character. In order to calculate the effective nuclear charge number, the screening number, the effective principal quantum number and the radius of the atomic or ionic constituents of the bond, the method of approximation using the properties of free, isolated atoms and ions was applied [35d]. Here GLOCKLER—LISITZIN's equation for ionization works of free, isoelectric ions:

$$I = aZ^2 + bZ + c$$

was taken into consideration together with KOHLRAUSCH's equation for the ionization works:

$$I = Rhc \frac{(Z - S)^2 e^2}{(n^*)^2} - \gamma.$$

From these equations the following results were deducted:

$$S = -b/2a$$

$$(n^*)^2 = Rhc/a = 13,595/a$$

$$\gamma = \frac{b^2}{4a} - c.$$

These two main factors determine the average distance of the electron and maximum electron charge-density, respectively, from the nucleus, *i. e.* the radius of the atomic or ionic constituent in question:

$$r = a_H(n^*)^2/Z^* = 0,529172(n^*)^2/Z^* \quad (\text{in } \text{\AA}).$$

When carrying out calculations for elements of the fields S and P by using the most reliable data for the ionization potentials we have the values of the effective nuclear charge number, screening number, effective principal quantum number, contraction work (γ) and radius of all the atoms and ions with whole number positive or negative charges. Afterwards the amount of the microscopic effective electric field strength of these free ions and atoms was calculated ($F^* = Z^*e/r^3$). This can be regarded as an absolute measure of the electronegativity of free, isolated ions and atoms and fully consistent with SANDERSON's original definition of electronegativity for the free ions and atoms. Further investigations proved that the effective electric field strength of free ions and atoms is an exponential function of their charge. When a molecule forms, a charge shift will occur as compared to the charge distribution of the free ions. As a consequence of this charge shift, the value of the effective charge on ions and together with this their dimensions change and accordingly the effective electric field strength around the ions changes, too. The extent of this charge shift is determined at the equilibrium state by the classical *virial-theorem*, according to which the effective electric field strength of the cationic constituent must be equal to that of the anionic constituent:

$$\frac{Z_A^{*+p\delta_{\max}^{(A)}}}{r_{A^{*+p\delta_{\max}^{(A)}}}^2} = \frac{Z_B^{*-p\delta_{\max}^{(B)}}}{r_{B^{*-p\delta_{\max}^{(B)}}}^2}$$

where p is the degree of polarity of the bond in question, δ_{\max} is the maximal charge on the constituents A and B , when supposing an ideal ionic bond. The extent of the charge shift obtained this way determined the degree of the bond polarity or using PAULING's term, the degree of the ionic character of the bond:

$$p = \frac{\log F_B^* - \log F_A^*}{(\log F_{A^+}^* - \log F_A^*) \cdot \delta_{\max}^{(A)} + (\log F_B^* - \log F_{B^-}^*) \cdot \delta_{\max}^{(B)}}$$

where F_A^* and F_B^* are the effective electric field strengths of free, isolated A and B atoms, while $F_{A^+}^*$ and $F_{B^-}^*$ are those of the isolated, free A^+ and B^- ions. On comparing the results obtained by using this equation and those obtained by the methods so far common in literature with the experimental values, ours are in a considerably better agreement (Table IX). Greater differences occur only in the case of molecules where FAJANS's approximation formula differs from the more simple formula applied by us. The cause of this can be found in the shortcomings of the method of calculation, namely by this method the properties of bonded constituents were approximated with the properties of free atoms and ions. In case of great number of bonds the numerical values of the degrees of bond polarity calculated in the S , P , D -fields

Table IX.

Molecular formula	FAJANS's approximation formula	Degree of bond polarity (p)			
		Experimental	PAULING (HANNAY and SMYTH)	SAMDERSON ($p_{\text{NAF}} = 0,75$)	Present paper
ClF	Cl^+F^-	0,113	0,195	0,085	0,157
BrF	Br^+F^-	0,153	0,24	0,130	0,168
BrCl	Br^+Cl^-	0,056	0,03	0,044	0,016
ICl	I^+Cl^-	0,100	0,007	0,125	0,149
IBr	I^+Br^-	0,110	0,03	0,081	0,133
ClF_3	$(e)_4 \text{Cl}^{7+} (\text{F}^-)_3$	0,090	—	0,044	0,121
BrF_3	$(e)_4 \text{Br}^{7+} (\text{F}^-)_3$	0,127	—	0,067	0,129
BrF_5	$(e)_2 \text{Br}^{7+} (\text{F}^-)_5$	0,125	—	0,045	0,105
IF_5	$(e)_2 \text{I}^{7+} (\text{F}^-)_5$	0,178	—	0,075	0,173
SO_2	$(e)_2 \text{S}^{6+} (\text{O}^{2-})_2$	0,116	0,195	0,042	0,119
NO_2	$(e) \text{N}^{5+} (\text{O}^{2-})_2$	0,042	0,09	0,027	0,047
PCl_3	$(e)_2 \text{P}^{5+} (\text{Cl}^-)_3$	0,073	0,17	0,099	0,176
$\text{P} = \text{O}$	$\text{P}^{5+} \dots \text{O}^{2-}$	0,105	0,29	0,066	0,133
AsF_3	$(e)_2 \text{As}^{5+} (\text{F}^-)_3$	0,259	0,46	0,106	0,212
AsCl_3	$(e)_2 \text{As}^{5+} (\text{Cl}^-)_3$	0,139	0,195	0,060	0,128
AsBr_3	$(e)_2 \text{As}^{5+} (\text{Br}^-)_3$	0,110	0,15	0,037	0,118
SbCl_3	$(e)_2 \text{Sb}^{5+} (\text{Cl}^-)_3$	0,197	0,24	0,097	0,202
SbBr_3	$(e)_2 \text{Sb}^{5+} (\text{Br}^-)_3$	0,155	0,195	0,073	0,193
CO	$\text{C}^{4+} (e)_{10} \text{O}^{6+}$	0,011	0,20	0,080	0,155
CO_2	$\text{O}^{2-} \text{C}^{4+} \text{O}^{2-}$	0,105	0,195	0,056	0,107
CS_2	$\text{S}^{2-} \text{C}^{4+} \text{S}^{2-}$	0,030	0,00	0,013	0,024
SiF_4	$\text{Si}^{4+} (\text{F}^-)_4$	0,307	0,52	0,168	0,272
SnCl_2	$(e)_2 \text{Sn}^{4+} (\text{Cl}^-)_2$	0,267	0,28	0,153	0,267
BF_3	$\text{B}^{3+} (\text{F}^-)_3$	0,273	0,47	0,186	0,244
TiCl	$(e)_2 \text{Ti}^{3+} \text{Cl}^-$	0,364	0,32	0,158	0,306
LiCl	$\text{Li}^+ \text{Cl}^-$	0,608	0,46	0,650	0,601
LiBr	$\text{Li}^+ \text{Br}^-$	0,594	0,40	0,610	0,594
LiI	$\text{Li}^+ \text{I}^-$	0,544	0,35	0,528	0,556
KF	$\text{K}^+ \text{F}^-$	0,703	0,87	0,793	0,716
KCl	$\text{K}^+ \text{Cl}^-$	0,818	0,52	0,708	0,818
KBr	$\text{K}^+ \text{Br}^-$	0,768	0,46	0,664	0,809
KI	$\text{K}^+ \text{I}^-$	0,755	0,40	0,582	0,768
CsF	$\text{Cs}^+ \text{F}^-$	0,699	0,91	0,816	0,685
CsCl	$\text{Cs}^+ \text{Cl}^-$	0,747	0,55	0,731	0,747
CsBr	$\text{Cs}^+ \text{Br}^-$	0,711	0,49	0,687	0,740

of the periodic table were published in a set of publications appearing in *Acta Chim. Hung.* [83] and [35d].

The effective electric field strength of the anionic and cationic constituents was measured with the expression $F^* = Z^* \cdot e/r^2$, and this or the other $Z^* \cdot e/R_{AB}^2$ expression is generally used when investigating a force or physical chemical constants being in close connection with the effective forces. In energetical calculations or in a quantitative treatment of constants connected with these we shall use the expression of the "effective ionic potential" $Z^* \cdot e/r$, and $Z^* \cdot e/R_{AB}$. Both expressions truly reflect the dependence of the field strength and potential, resp., of the questioned atoms or ions not only on its size and charge but on its electron configuration, too. The reality and the usefulness of the concept of the "effective electric field strength" is proved by that it had been used with success during the quantitative investigations of the physical properties of elements and metals, together with the derivative of the effective electric field strength. We succeeded in developing a connection between force constants calculated from the values for melting points, compressibility and specific heat at low temperature of metals, and the effective electric field strength of metal ions placed in the lattice point, namely it was given as a linear function of the derivative of the force constant of the effective field strength in distance.

Summarizing these results, the effective ionic potential, effective electric field strength and the derivative of the effective electric field strength opened new ways for the quantitative treatment of the physical-chemical constants of the elements and their compounds, based on a simple and real structure.

* * *

The author wishes to express his gratitude to Professor Z. G. SZABÓ, for the valuable discussions and his help thorough the whole work and also to Dr. M. T. BECK for the careful reading over of the manuscript of the present paper. Thanks are due to R. ZÁNTÓ, the librarian of the Institut for the translation of this communication.

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О ПРОБЛЕМЕ ПОЛЯРНОСТИ И ИОННОГО ХАРАКТЕРА ХИМИЧЕСКОЙ СВЯЗИ

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Автор, изучая проблему полярности и ионного характера попытался рассчитать степень полярности связи определенную Фаянсом. Определение степени полярности было возможно только при помощи дифференций в электроотрицательности Паулинга, применяя другие, экспериментально заранее определенные степени полярности. Последние стремления в большей части были ограничены к возможно точнейшему вычислению величин электроотрицательности Паулинга из всевозможных «постоянных» атомов и молекул. Величины электроотрицательности, так называемые «связи стабильности», вычислены Сандерсоном с такой же целью, значительно отличаются от этих же Паулинга, но здесь также нужно было употреблять одну величину калибровки: ($P_{NaF} = 0,75$).

В настоящей работе для количественного подхода к рулям поляризации Фаянса автором была введена концепция «эффективной силы поля» (F^*), абсолютное значение которой $F^* = Z^* \cdot e/r^2$ где Z^* — число эффективных зарядов ядра данной изолированной формации (иона или атома), r — се радиус. В равновесии, эффективная сила поля катионного компонента равна той же анионного компонента, это дает возможность рассчитать размер смещения заряда или степень полярности связи с 5 процентов точностью.

$Z^* \cdot e/r^2$ — так называемое выражение эффективного ионного потенциала и эффективная сила поля является производным по дистанции предыдущего в энергетических расчетах, так как производное по дистанции эффективной силы поля открыло новые возможности при количественном подходе постоянных натяжений связей полученных из разных физических постоянных элементов и металлов.