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An Attempt to Estimate the Charge Distribution in Sigma-Bond Systems

By

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A classical inductive-effect model has been utilized in an attempt to estimate the charge distribution in relatively complicated σ -bond systems. It is assumed that the formal charge on an atom is given as a vectorial sum of the polarities of the bonds attached to that atom and, further, that each bond induces a constant fraction of its own polarity in all of its neighboring bonds. Significance of the model has been tested for several model compounds which permit the closed-form solutions for the distributions of the internally self-consistent bond polarities. The model has been applied to the calculations of the charge distributions in alkanes, *n*-alkyl halides and hydrated metallic ions; the results are found to be compatible with observations.

1. Introduction

Estimation of the electronic charge distribution in molecules is considered to be one of the central problems prevailing in the entire field of chemistry, inasmuch as the charge distribution often plays an exclusive role in determining physical properties and chemical reactivities of compounds. The problem is, undoubtedly, one to be based on quantum mechanics. For complicated molecules, however, the quantum-mechanical procedure in its sophisticated form is not necessarily manageable, except for high-speed electronic computers; and thus a number of simplified methods of approximation have been proposed. Efforts along this latter line have so far been directed mainly to unsaturated compounds, resulting thus in the appearance of a spate of papers dealing primarily with the conjugative effect associated with the highly mobile character of π -electrons.

For complicated molecules which are made up of σ -bonds alone, quantum-mechanical treatments of charge distribution are still meagre. This scantiness seems to have resulted from the difficulty—or rather the supposed inadequacy—

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of treating σ -electrons within as simple a framework as for π -electrons. Recently, however, several innovating attempts¹⁻⁶⁾ have been made to interpret the behavior of σ -electrons in saturated compounds on the basis of the simple LCAO MO method originally designed for π -electron systems. These theoretical investigations have contributed much to the understanding of the nature of the inductive effect in saturated compounds.

Alternatively, classical theories seem to be equally useful so far as the problem of the σ -charge distribution in molecules is concerned. Among others, the theory of inductive effect developed by Smith, Ree, Magee and Eyring⁷⁾ finds ample use for discussing dipole moments and reactivities of substituted alkanes. The theory is based on a classical picture of mutual interaction between electric polarizations of bonds and effective kernel charges of the atoms forming the bonds.

In this paper, a somewhat intuitive, classical model of inductive effect is proposed, in which the ionic character of a bond in Pauling's sense⁸⁾ is assumed to be influenced by the polarities of its adjacent bonds. Significance of this model will be tested for several model compounds which permit us to obtain analytical solutions for the polarity distributions. Further, rough estimations of the charge distributions will be attempted for several complicated σ -bond systems including molecular ions and coördinated compounds.

2. Calculation Method

The basic principle of the present calculations of the charge distribution in molecules is that the formal charge, Q_i , on an atom i be just the sum of the polarities (or partial ionic characters⁹⁾, $q_{i,j}$, of the bonds attached to the atom under question, *viz.*,

$$Q_i = \sum_j q_{i,j}. \quad (1)$$

Here, $q_{i,j}$ is so defined as to take a positive value if the positive end of a bond dipole is on the atom i and vice versa. From the definition immediately follows the relation:

$$q_{i,j} = -q_{j,i}. \quad (2)$$

Since the polarity of a bond is assumed to be affected by the nature of adjacent bonds, we now have to introduce a relation between polarities of the bonds involved in a molecule. We will assume here that the inductive effect is simply the result of transmission of a fraction of bond ionic characters to adjacent bonds. The fraction transmitted is tentatively assumed to be constant, irrespective of the nature of bonds. Thus,

$$q_{i,j} = q_{i,j}^0 + k \sum_{r \neq j} q_{r,i} + k \sum_{s \neq i} q_{j,s} \quad \text{for all bonds,} \quad (3)$$

where $q_{i,j}^0$ is the standard polarity which the bond $i-j$ would have if it existed without being affected by neighboring bonds; k is the fraction ($0 < k < 1$) of ionicity transmitted from each adjacent bond to the $i-j$ bond; and the summation extends over all the atoms linked to either i or j , the $i-j$ bond not being involved in the summation. The constant k may be referred to as the inductive parameter.

For the sake of expedience in later sections, we transform equation (3) into

$$q_{i,j} = q_{i,j} + k \sum_{r \neq j} q_{i,r} + k \sum_{s \neq i} q_{s,j} \quad \text{for all bonds,} \quad (4)$$

where the relation (2) has been invoked. Self-consistent bond polarities due to mutual electric induction among the bonds are calculable by solving the set of simultaneous equations (4), if the standard polarity is known for every bond. The solution may be expressed in a compact form:

$$\mathbf{q} = \mathbf{A}^{-1} \mathbf{q}^0. \quad (5)$$

Here \mathbf{q} and \mathbf{q}^0 are the respective column vectors with $q_{i,j}$ and $q_{i,j}^0$ as components, and \mathbf{A}^{-1} is the reciprocal of a square matrix \mathbf{A} , which is set up from the coefficients of q 's in the simultaneous equations (4). The order of \mathbf{A} is equal to the number of the bonds involved.

3. Inductive Effect in Model Compounds

Before performing numerical calculations of the charge distributions in real compounds, we will apply our method to some model compounds of simple arrangements of atoms, keeping both the q^0 terms and k as unknown parameters. This application is particularly useful for demonstrating the significance of our inductive-effect model and the general principle of numerical calculations.

(A) Model Compound I. Linear compounds.

$$A_1 - A_2 - A_3 - \dots - A_N - A_{N+1}$$

The polarity vectors \mathbf{q}^0 and \mathbf{q} and the matrix \mathbf{A} for this case are in the forms:

$$\mathbf{q}^0 = \begin{pmatrix} q_{1,2}^0 \\ -q_{2,3}^0 \\ \vdots \\ (-1)^{i+1} q_{i,i+1}^0 \\ \vdots \\ (-1)^{N+1} q_{N,N+1}^0 \end{pmatrix}, \quad \mathbf{q} = \begin{pmatrix} q_{1,2} \\ -q_{2,3} \\ \vdots \\ (-1)^{i+1} q_{i,i+1} \\ \vdots \\ (-1)^{N+1} q_{N,N+1} \end{pmatrix} \quad \text{and} \quad \mathbf{A} = [k_{ij}] = \begin{pmatrix} 1 & k & & & 0 \\ & k & \ddots & & \\ & & \ddots & \ddots & \\ & & & \ddots & k \\ 0 & & & & k & 1 \end{pmatrix}.$$

by assigning a non-zero value to $q_{1,2}^0$ and a value of zero to all the remaining q^0 's. Equation (6) is then rewritten as

$$(-1)^{i+1}q_{i,i+1} = (A^i/\Delta_N)q_{1,2}^0. \tag{10}$$

By use of equations (7) and (10), we obtain

$$q_{i,i+1} = (\Delta_{N-i}/\Delta_N)k^{i-1}q_{1,2}^0, \tag{11}$$

where Δ_0 has been defined to be identically equal to unity.

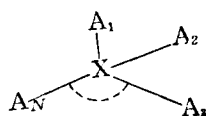
Equation (11) indicates that the polarity of the end bond induces certain extents of electronic displacement in all the other bonds. That is, the inductive effect of substituents propagates along chemical bonds.

It is readily seen from Fig. 1 that for fixed values of N and k the factor (Δ_{N-i}/Δ_N) in equation (11) increases with increasing i . This increase, however, is largely counteracted by the decrease of the factor k^{i-1} , the net effect being a rapid decrease of $q_{i,i+1}$ with increasing i . When k is very small compared with unity, the $q_{i,i+1}$ is essentially equal to $k^{i-1}q_{1,2}^0$. When k is assigned a value of 1/2, the $q_{i,i+1}$ is shown to be such that $q_{i,i+1} = 2[1 - i/(N+1)]q_{1,2}^0$. The charge distribution for these two extreme cases are as follows:

$Q/q_{1,2}^0$	A_1	A_2	A_3	...	A_N	A_{N+1}
for $k \ll 1$	1	$-(1-k)$	$-k(1-k)$...	$-k^{N-2}(1-k)$	$-k^{N-1}$
for $k = 1/2$	$2N/(N+1)$	$-2/(N+1)$	$-2/(N+1)$...	$-2/(N+1)$	$-2/(N+1)$

From these results it is concluded that the inductive effect diminishes along the bonds when the inductive parameter k takes on a positive value smaller than one-half.

(B) Model Compound II. Radial compounds.



The equation to be solved for this model compound is such that

$$\begin{pmatrix} q_{X,1}^0 \\ q_{X,2}^0 \\ \vdots \\ q_{X,N}^0 \end{pmatrix} = \begin{pmatrix} 1 & & & \\ & \ddots & & \\ & & k & \\ & & & \ddots \\ & k & & & 1 \end{pmatrix} \begin{pmatrix} q_{X,1} \\ q_{X,2} \\ \vdots \\ q_{X,N} \end{pmatrix}. \tag{12}$$

The elements in the matrix A for this case are expressed by

$$k_{ij} = k + (1-k)\delta_{ij}, \quad (13)$$

where δ_{ij} is Kronecker's delta, which is equal to unity when $i=j$ and is zero otherwise. The solution is

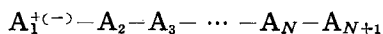
$$\begin{pmatrix} qx_{,1} \\ qx_{,2} \\ \vdots \\ qx_{,N} \end{pmatrix} = \frac{1}{(1-k)[1+(N-1)k]} \begin{pmatrix} 1+(N-2)k & & & -k \\ & \ddots & & \\ -k & & \ddots & \\ & & & 1+(N-2)k \end{pmatrix} \begin{pmatrix} q_{X,1}^0 \\ q_{X,2}^0 \\ \vdots \\ q_{X,N}^0 \end{pmatrix}. \quad (14)$$

We will here consider a special case where all the q^0 's are identically equal to $q_{X,A}^0$. The q 's are then all identical and are given by

$$q_{X,1} = \dots = q_{X,N} = q_{X,A}^0/[1+(N-1)k]. \quad (15)$$

The polarity of each bond and consequently the formal charges on the A atoms will thus decrease with the increase of the value of k . The extent of this decrease in polarity is marked for the systems having many radial bonds.

(C) **Model Compound III.** Linear ions in which the extreme-end atom is a charge center.



For treating this case, we introduce a reasonable, though not necessarily justified, assumption that the charge center A_1^+ (or A_1^-) be linked to an imaginary counter ion A_0^- (or A_0^+) to form a "dummy" bond $A_0^- \cdots A_1^+$ (or $A_0^+ \cdots A_1^-$) such that the ionicity is invariantly unity, *i. e.*, $q_{1,0} \equiv q_{1,0}^0 = +1$ or -1 accordingly as A_1 carries a positive or negative charge. Then, the basic equation to be solved for this case is

$$\begin{pmatrix} -q_{0,1}^0 \\ q_{1,2}^0 \\ -q_{2,3}^0 \\ \vdots \\ (-1)^{N+1} q_{N,N+1}^0 \end{pmatrix} = \begin{pmatrix} 1 & 0 & \dots & \dots & 0 \\ 0 & 1 & k & & \\ 0 & k & \ddots & & \\ \vdots & \vdots & \ddots & \ddots & k \\ 0 & 0 & & k & 1 \end{pmatrix} \begin{pmatrix} -q_{0,1} \\ q_{1,2} \\ -q_{2,3} \\ \vdots \\ (-1)^{N+1} q_{N,N+1} \end{pmatrix}. \quad (16)$$

It can readily be shown that the solution is expressed by exactly the same form as equation (6) except for the appearance of several additional cofactors associated with $i=0$ and $j=0$:

$$\begin{aligned}
 A^{00} &= \Delta_N, \\
 A^{j0} &= 0 \quad \text{for } j = 1, 2, \dots, N,
 \end{aligned}
 \tag{17}$$

and

$$A^{0i} = (-k)^i \Delta_{N-i} \quad \text{for } i = 1, 2, \dots, N.$$

When $q_{i,i+1}^0 = 0$ for $i = 1, 2, \dots, N$, the solution becomes

$$q_{i,i+1} = (\Delta_{N-i}/\Delta_N) k^{i-1} (-kq_{1,0}^0), \quad i = 0, 1, 2, \dots, N, \tag{18}$$

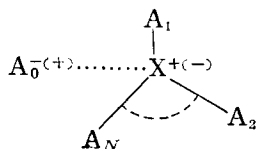
an expression which is identical with that for a neutral linear molecule assumed to have a standard polarity of $-kq_{1,0}^0$ only on its extreme-end bond 1-2. (See equation (11).)

The formal charge on the A_1 is given by

$$Q_1 = q_{1,0} + q_{1,2} = [1 - k(\Delta_{N-1}/\Delta_N)] q_{1,0}^0, \tag{19}$$

the absolute value of which is always smaller than unity.

(D) **Model Compound IV.** Radial ions in which the central atom is a charge center.



A dummy bond is assumed between the charge center and a counter ion. The algebra required for this case is a little involved but straightforward. The solution is

$$\begin{pmatrix} q_{X,0} \\ q_{X,1} \\ \vdots \\ q_{X,N} \end{pmatrix} = \frac{1}{(1-k)[1+(N-1)k]} \begin{pmatrix} (1-k)[1+(N-1)k] & 0 & \dots & 0 \\ -k(1-k) & 1+(N-2)k & & \\ \vdots & \ddots & -k & \\ -k(1-k) & & -k & 1+(N-2)k \end{pmatrix} \begin{pmatrix} q_{X,0}^0 \\ q_{X,1}^0 \\ \vdots \\ q_{X,N}^0 \end{pmatrix}$$

If $q_{X,i}^0 \equiv 0$ for $i = 1, 2, \dots, N$, the solution becomes

$$q_{X,0} = q_{X,0}^0 = \pm 1,$$

and

$$q_{X,i} = -kq_{X,0}^0/[1+(N-1)k] \quad \text{for } i = 1, 2, \dots, N. \tag{20}$$

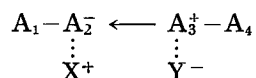
The expression for $q_{X,i}$ is identical with the solution for a neutral radial com-

pound consisting of N bonds of the same standard polarity $-kq_{X,0}^0$. The formal charge on the central atom X is given by

$$Q_X = q_{X,0} + \sum_{i=1}^N q_{X,i} = \left\{ (1-k) / [1 + (N-1)k] \right\} q_{X,0}^0, \quad (21)$$

the absolute magnitude of which is again always smaller than unity as long as the magnitude of k is within the range of 0 to 1.

(E) **Model Compound V.** Coördinated compounds.



Two dummy bonds $A_2^- \cdots X^+$ and $A_3^+ \cdots Y^-$ are assumed here. The basic equation for this case is

$$\begin{pmatrix} q_{X,2}^0 \\ q_{1,2}^0 \\ q_{3,2}^0 \\ q_{3,4}^0 \\ q_{3,Y}^0 \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 \\ k & 1 & k & 0 & 0 \\ k & k & 1 & k & k \\ 0 & 0 & k & 1 & k \\ 0 & 0 & 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} q_{X,2} \\ q_{1,2} \\ q_{3,2} \\ q_{3,4} \\ q_{3,Y} \end{pmatrix}, \quad (22)$$

which splits into

$$q_{X,3} = q_{X,2}^0 \equiv 1, \quad q_{3,Y} = q_{3,Y}^0 \equiv 1$$

and

$$\begin{pmatrix} q_{1,2}^0 - k \\ q_{3,2}^0 - 2k \\ q_{3,4}^0 - k \end{pmatrix} = \begin{pmatrix} 1 & k & 0 \\ k & 1 & k \\ 0 & k & 1 \end{pmatrix} \begin{pmatrix} q_{1,2} \\ q_{3,2} \\ q_{3,4} \end{pmatrix} \quad (23)$$

The last equality in equation (23) corresponds with the basic equation for a linear three-bond system with standard bond ionicities amended according to possible inductive effects of the dummy bonds on the relevant σ -bonds. Such correspondence greatly facilitates the procedure to set up the basic equations for complicated coördination systems.

4. Applications

(A) **Alkanes.**

Numerical calculations of the charge distribution are impracticable unless all the values of q^0 for constituent bonds as well as the magnitude of k are known. For alkanes, however, we need only to know the values of two independent parameters, $q_{H,C}^0$ and k , since $q_{C,C}^0 = 0$. It is thus a fairly easy

task to express the formal charges on atoms as the functions of q_{H^0C} and k . Besides, the calculations are greatly simplified by the possible configurational symmetries of alkanes.

For various H-C and C-C bonds in alkane isomers from CH_4 to C_5H_{12} , the values of $q_{H,C}$ and $q_{C,C}$ were calculated in units of q_{H^0C} by varying the magni-

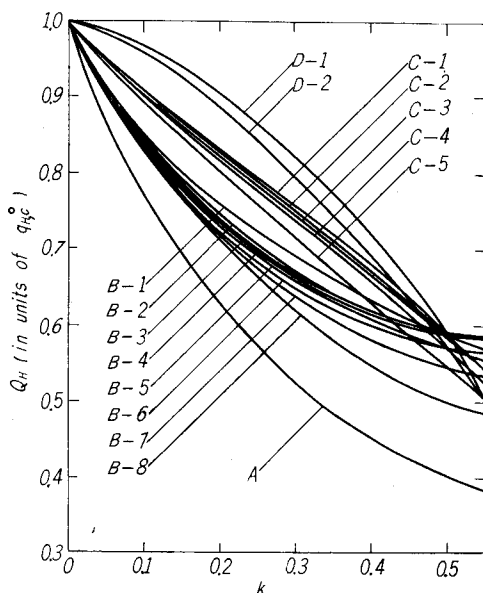
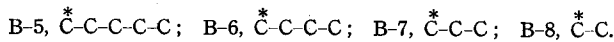
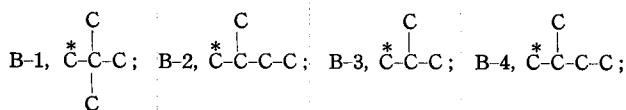


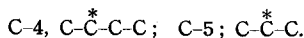
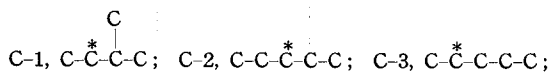
Fig. 2. Calculated formal charges of alkane hydrogens.

A: CH_4 (methane)

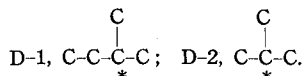
B: CH_3 (primary)



C: CH_2 (secondary)



D: CH (tertiary)



*C is the carbon atom bearing the hydrogen atom for which the formal charge is calculated.

tude of k in the range of 0 to 0.5. Variation of $q_{H,C}$ with k is demonstrated in Fig. 2.

It is seen in Fig. 2 that, in the region where $0 < k < 0.2$, the values of the polarity, $q_{H,C}$, for H-C bonds and consequently those of the formal charge, Q_H , on hydrogen atoms are distinctly grouped according to the nature of the carbon atoms to which the hydrogen atoms are linked. If a positive value is assigned to $q_{H^0,C}$, the values of Q_H come out to be positive in sign for all alkanes and increase in the order of methane, primary, secondary and tertiary carbons as long as the k is in the range between 0 and 0.35. These results are in good agreement with the observation for the proton nuclear magnetic resonance in alkanes, the chemical shift parameter, δ , as the measure of electron density on hydrogen atoms being 4.8, 4.1, 3.7 and 3.5 (in ppm referred to water) for hydrogens in methane, CH_3 , CH_2 and CH groups, respectively.⁹⁾ Thus it seems very likely that our $q_{H^0,C}$ is a positive quantity and that k is some constant in the region of 0.1 to 0.2.

(B) *n*-Alkyl Halides.

For the sake of simplicity, we shall assume *n*-alkyl halides to be planar zigzag chains and leave the C-H bonds out of consideration. The formulation of the inductive effect developed for Model Compound I is then applicable to the approximate structures of the halides.

Table 1. Dipole moments of *n*-alkyl halides.

<i>n</i> -Alkyl halide	Dipole moments (Debye)			
	Obsd. ^{a)}	Calcd.		
		$k=0.1$	$k=0.2$	$k=0.35$
F-C ($q_{C^0,F}=0.267$)	1.81	(1.81)	(1.81)	(1.81)
F-C-C	1.92	1.90	2.06	2.44
Cl-C ($q_{C^0,Cl}=0.220$)	1.86	(1.86)	(1.86)	(1.86)
Cl-C-C	2.03	1.94	2.08	2.41
Cl-C-C-C	2.10	1.96	2.15	2.77
Cl-C-C-C-C	2.11	1.96	2.17	2.89
Br-C ($q_{C^0,Br}=0.194$)	1.78	(1.78)	(1.78)	(1.78)
Br-C-C	2.02	1.85	1.97	2.29
Br-C-C-C	2.15	1.87	2.05	2.60
Br-C-C-C-C	2.15	1.87	2.07	2.76
I-C ($q_{C^0,I}=0.163$)	1.64	(1.64)	(1.64)	(1.64)
I-C-C	1.87	1.70	1.81	2.08
I-C-C-C	2.01	1.72	1.87	2.35
I-C-C-C-C	2.08	1.72	1.89	2.44

a) Taken from refs. 3 and 7.

The standard polarities, $q_C^0 X$, for carbon-halogen bonds were determined by fitting the dipole moments calculated for diatomic systems C-X to the values observed for the corresponding methyl halides. By use of these $q_C^0 X$ values and equation (11), the magnitudes of $q_{C.C}$'s and $q_{C.X}$'s of higher linear homologues were calculated for different values of k . Dipole moments of the linear halides were then calculated by vectorial addition of bond dipoles corresponding to the $q_{C.C}$'s and $q_{C.X}$'s obtained above. The results are summarized in Table 1. Agreement of the calculated moments with the observed is most satisfactory in the case where $k=0.2$.

(C) Hydrated Metallic Ions.

By combining the techniques used for Model Compounds III to V, the charge distribution of a number of hydrated metallic ions were calculated. The standard polarity of each atomic pair involved was obtained by invoking Pauling's relation between partial ionic character and electronegativity difference for diatomic molecules⁸⁾, *viz.*,

Table 2. Hydrated metallic ions as Brönsted acid.

Hydrated metallic ions ^{a)}	Q_O	Q_H	$pK_A^{b)}$
$[\text{Fe}(\text{H}_2\text{O})_6]^{+3}$	-0.3749	0.3981	2.2
$[\text{Tl}(\text{H}_2\text{O})_6]^{+3}$	-0.3824	0.3941	1.1
$[\text{In}(\text{H}_2\text{O})_6]^{+3}$	-0.3918	0.3890	4.4
$[\text{Cr}(\text{H}_2\text{O})_6]^{+3}$	-0.3974	0.3860	3.9
$[\text{Al}(\text{H}_2\text{O})_6]^{+3}$	-0.4049	0.3820	4.9
$[\text{Sc}(\text{H}_2\text{O})_6]^{+3}$	-0.4180	0.3749	4.9
$[\text{Hg}(\text{H}_2\text{O})_6]^{+2}$	-0.4405	0.3628	3.7
$[\text{Cu}(\text{H}_2\text{O})_6]^{+2}$	-0.4405	0.3628	8.0
$[\text{Pb}(\text{H}_2\text{O})_6]^{+2}$	-0.4481	0.3588	7.8
$[\text{Fe}(\text{H}_2\text{O})_6]^{+2}$	-0.4481	0.3588	8.2
$[\text{Ni}(\text{H}_2\text{O})_6]^{+2}$	-0.4481	0.3588	10.6
$[\text{Cd}(\text{H}_2\text{O})_6]^{+2}$	-0.4574	0.3537	9.0
$[\text{Zn}(\text{H}_2\text{O})_6]^{+2}$	-0.4630	0.3507	9.7
$[\text{Mg}(\text{H}_2\text{O})_6]^{+2}$	-0.4893	0.3366	11.4
$[\text{Ca}(\text{H}_2\text{O})_6]^{+2}$	-0.5005	0.3305	12.6
$[\text{Ba}(\text{H}_2\text{O})_6]^{+2}$	-0.5061	0.3275	13.2
$[\text{Co}(\text{NH}_3)_2(\text{H}_2\text{O})_4]^{+3}$	-0.4171	0.3755	3.4
$[\text{Co}(\text{NH}_3)_3(\text{H}_2\text{O})_3]^{+3}$	-0.4349	0.3660	4.7
$[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{+3}$	-0.4520	0.3567	5.2
$[\text{CO}(\text{NH}_3)_5(\text{H}_2\text{O})]^{+3}$	-0.4690	0.3486	5.7

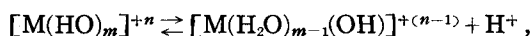
a) The coordination number of six was assumed for all the metallic ions.

b) Taken from ref. 10.

$$q_{X^{\circ}Y} = -[(x_X - x_Y)/|x_X - x_Y|] \left\{ 1 - \exp[-(x_X - x_Y)^2/4] \right\}, \quad (24)$$

where x_X and x_Y are Pauling's electronegativity scales for atoms X and Y , respectively, and the factor outside the braces has been introduced to take account of the direction of the bond dipole. Although there is no justification for applicability of equation (24) to bonds in complicated molecules, the relation will provide some meaningful results so long as a series of similar compounds are treated. The inductive effects in the hydrated ions were amplified here by assigning the inductive parameter, k , a value of 0.35.

In Table 2 the calculated formal charges of oxygen atoms and hydrogen atoms in hydrated metallic ions are compared with the pK_A values¹⁰⁾ observed for their acid dissociation equilibria:



Both calculated charges are seen to be reasonably correlated with the strength of hydrated metallic ions as Brønsted acids.

The observed correlation between Q_H and pK_A is perhaps meaningful, since in this particular series of acid dissociations the primary reactions leading to the establishment of equilibrium are the heterolytic dissociation of a single sort of chemical bond, *i. e.*, an OH bond.

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