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The Electrostatic Influence of Substituents on the Dissociation Constants of Organic Acids. I.

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Bjerrum's theory of the influence of substituents on dissociation constants has been extended and amplified. The molecules and ions entering into the ionization equilibria are treated as cavities of low dielectric constant, rather than as structureless regions of the same dielectric constant as the solvent. The theory gives better results than the simple Bjerrum formulation, especially for the short chain dicarboxylic acids, and in the fact that it permits a satisfactory treatment of the influence of dipolar substituents on dissociation constants.

I

THE ratio of the first to the second dissociation constant of a dibasic organic acid is always greater than four, and approaches four as the length of the acid is increased. In 1923 Bjerrum¹ suggested that the ratio of the dissociation constants can be accounted for by the combination of a statistical factor of four and the electrostatic effect of the negative charge of the acid-ion on the dissociation of the second hydrogen, and presented an approximate mathematical discussion. In this paper, following a consideration of the Bjerrum treatment, an extension of the electrostatic theory of dissociation constants will be developed.

A thermodynamic comparison of the dissociation constants K_1 and K_2 of two organic acids HA_1 and HA_2 in the same solvent leads to the following relation

$$RT \log K_1/K_2 = \bar{F}^\circ(HA_1) + \bar{F}^\circ(A_2^-) - \bar{F}^\circ(HA_2) - \bar{F}^\circ(A_1^-), \quad (1)$$

where $\bar{F}^\circ(HA_1)$, $\bar{F}^\circ(A_2^-)$, $\bar{F}^\circ(HA_2)$, and $\bar{F}^\circ(A_1^-)$ are the reference values of the chemical potentials of the respective solute species taken at infinite dilution in the solvent. From a molecular point of view, it is readily seen that $\bar{F}^\circ(HA_1) + \bar{F}^\circ(A_2^-) - \bar{F}^\circ(HA_2) - \bar{F}^\circ(A_1^-)$ is equal to $N\Delta w'$, where N is Avogadro's number and $\Delta w'$ is the average reversible work expended in the transfer of a proton from the carboxylate group of an ion A_2^- to the carboxylate group of an ion A_1^- , situated at an infinite distance from A_2^- in the given solvent. A part of $\Delta w'$ may be regarded as

purely electrostatic in origin, that is, work done in moving the proton in the electric field produced by the average charge distributions of the two ions. We may denote this part by Δw . Another contribution arises from an entropy change associated with differences in molecular symmetry, and equal to $k \log [\sigma(HA_1)\sigma(A_2^-)/\sigma(A_1^-)\sigma(HA_2)]$ where $\sigma(HA_1)$, $\sigma(HA_2)$, $\sigma(A_1^-)$ and $\sigma(A_2^-)$ are the symmetry numbers of the respective particles. The symmetry number gives rise, in the ratio of the dissociation constants of a symmetrical dibasic acid, to the well-known statistical factor of four. Finally, and by no means to be overlooked, is the contribution to $\Delta w'$ associated with the intrinsic structure of the carboxyl group and carboxylate ion. However, if the two acids, HA_1 and HA_2 , are, let us say, of the form R_1CH_2COOH and R_2CH_2COOH , and the possibility of structural resonance is absent, it is reasonable to suppose that the relatively distant substituent groups R_1 and R_2 will have little influence on the structure of the carboxyl group and carboxylate ion, except perhaps for an electrostatic polarization which may be taken into account in Δw , the electrostatic part of $\Delta w'$. Under these circumstances, the structural contributions to the work expended in detaching the proton from HA_2 will be canceled by a contribution of equal magnitude gained by attaching the proton to A_1^- . The net structural contribution to $\Delta w'$ is then zero, and we may write Eq. (1) in the form

$$RT \log K_1/\sigma K_2 = N\Delta w = 2.303RT\Delta pK$$

$$\Delta w = W(HA_1) + W(A_2^-) - W(HA_2) - W(A_1^-) \quad (2)$$

$$\sigma = \sigma(HA_1)\sigma(A_2^-)/\sigma(A_1^-)\sigma(HA_2),$$

¹ Bjerrum, *Zeits. f. physik. Chemie* **106**, 219 (1923); see Greenspan, *Chem. Rev.* **12**, 339 (1933).

where $W(HA_1)$, $W(A_2^-)$, $W(HA_2)$ and $W(A_1^-)$ are the electrostatic free energies of the respective molecules in the given solvent. The Bjerrum theory, in its most general form, is summarized by Eq. (2). Although Bjerrum developed his theory on the basis of a somewhat different argument, his fundamental assumption may be expressed in our terms, namely that the intrinsic structure of the carboxyl group and carboxylate ion is the same in the two acids. Although this assumption can certainly be no more than a close approximation to the facts, that it is essentially correct is supported by the observation that the dissociation constants of two aliphatic acids, R_1CH_2COOH and R_2CH_2COOH generally differ but slightly when R_1 and R_2 are nonpolar radicals.

If we are interested in a comparison of the first and second dissociation constants of a symmetrical dibasic acid, we are concerned with the molecular species H_2A , HA^- , $A^{=}$ and HA^- . Since the symmetry number ratios, $\sigma(H_2A)/\sigma(HA^-)$ and $\sigma(A^{=})/\sigma(HA^-)$ each have the value two, the statistical factor becomes four, and Eq. (2) becomes

$$RT \log K_1/4K_2 = N\Delta w = 2.303RT\Delta pK \quad (3)$$

$$\Delta w = W(H_2A) + W(A^{=}) - 2W(HA^-).$$

Bjerrum's approximation is obtained if Δw is set equal to the electrical work e^2/DR' required to bring the two charges, $-e$, of the acid ions, HA^- from infinity to their distance of separation, R' , in the di-ion $A^{=}$, in a homogeneous medium having the solvent dielectric constant, D . This leads to results of fair accuracy² in the case of elongated straight chain dibasic acids, but with short molecules the values of R' obtained are, in some cases, only a fifth of that expected on the basis of structural considerations.

In the next section we shall describe a more refined calculation of Δw , which, although still somewhat schematic, avoids the treatment of the molecules and ions, in which the charges are imbedded, as structureless regions of dielectric constant D . Instead, we regard the molecules as forming cavities of low dielectric constant, D_i , in the solvent. Of course the introduction of an internal molecular dielectric constant D_i differing from unity is somewhat artificial. Neverthe-

less, its physical significance is clear, for it provides a crude means of allowing for the polarization of a molecule produced by the average charge distributions of polar or ionic substituent groups. A reasonable estimate of D_i for aliphatic compounds is about 2.00, a value in the neighborhood of the dielectric constant of the liquid paraffin hydrocarbons.

For certain purposes it is convenient to write Eq. (3) in the simple Bjerrum form, with the use of an effective dielectric constant, D_E , defined in terms of Δw , where the distance, R , is the separation of the protons in H_2A

$$kT \log K_1/4K_2 = e^2/D_ER$$

$$D_E = e^2/R\Delta w, \quad (4)$$

rather than that of the negative charges in the di-ion $A^{=}$. This mode of expression was introduced by Eucken³ from empirical considerations.

We shall also be concerned with a comparison of the dissociation constants of pairs of monocarboxylic acids similar in structure except for the presence of additional polar groups in one of them. As an example of such a pair, we may mention acetic and chloracetic acids. The statistical factor, σ , is evidently unity in these cases. If we adopt the notation of Eucken, using an effective dielectric constant, D_E , the appropriate form of Eq. (2) is

$$kT \log K_1/K_2 = eM \cos \zeta / D_ER^2 = 2.303kT\Delta pK \quad (5)$$

$$D_E = M \cos \zeta / R^2\Delta w,$$

where M is the dipole moment of the polar group in the acid HA_1 , R is the distance from the proton of the point dipole, and ζ its angle of inclination to the line joining it to the proton. We shall also make use of a more complicated form of Eq. (1) in which the charge distribution is not treated merely as a point dipole. Substitution of D , the dielectric constant of the solvent, for D_E leads, as Eucken showed, to calculated values of R as much as six times smaller than might be expected.

Perhaps the most serious approximation in our calculations of Δw which follow is the neglect of possible deviations of the local dielectric constant of the solvent in the neighborhood of a solute molecule from its macroscopic value, D . Such deviations might arise from electrical

² Gane and Ingold, J. Chem. Soc. 2153 (1931).

³ Eucken, Zeits. f. angew. Chemie 45, 203 (1932).

saturation, electrostriction, and other departures of the local density of the solvent from its bulk value. Ingold⁴ has attempted to estimate corrections to the simple Bjerrum formula arising from electrical saturation and electrostriction. However, his calculations are based upon the Clausius-Mosotti equation, which is known to be invalid for polar liquids such as water. Further, even were the general method accurate the effect he calculated would be reduced to a fraction of the indicated magnitude if the solvent were excluded from the volume actually occupied by the molecule. It seems, then, entirely possible that he overestimates the importance of these effects. While the neglect of electrical saturation and electrostriction may lead to some inaccuracy, certainly the present treatment must be undertaken before finer adjustments are considered.

II

In order to calculate the electrostatic free energy of a spherical molecule of radius b , with an arbitrary charge distribution and immersed in a solvent of dielectric constant D , we make use of a formula developed by one of us in another connection.⁵ A slightly different zero of energy is used here, since we have to consider changes of state involving the addition and removal of charges in the molecule.

$$W = \frac{1}{2} \sum_{k,l=1}^{\nu} \frac{e_k e_l}{D_i r_{kl}} + \frac{1}{2} \sum_{n=0}^{\infty} \frac{(D_i - D)(n+1)G_n}{D_i b^{2n+1} [(n+1)D + nD_i]} \quad (6)$$

$$G_n = \sum_{k=1}^{\nu} \sum_{l=1}^{\nu} e_k e_l r_k^n r_l^n P_n(\cos \vartheta_{kl}),$$

where the set of point charges $e_1 \cdots e_i$ characterizes the average distribution of charge in the molecule, r_{kl} is the distance between the charges e_k and e_l , r_k and r_l the distances of e_k and e_l from the center of the sphere, and ϑ_{kl} the angle between r_k and r_l . The functions $P_n(\cos \vartheta_{kl})$ are the ordinary Legendre functions, and D_i is the internal dielectric constant of the molecule. If we

consider the set of molecules HA_1 , HA_2 , A_1^- and A_2^- of equal radii b , in which A_1 contains the charges $e_1 \cdots e_s$ in excess of those contained in A_2^- , a simple calculation shows that

$$\Delta w = - \sum_{k=1}^s \frac{e_k}{D_i R_k} + \frac{1}{2} \left(\frac{1}{D} - \frac{1}{D_i} \right) \sum_{n=0}^{\infty} \frac{(n+1)\Delta G_n}{[(n+1) + nD_i/D] b^{2n+1}} \quad (7)$$

$$\Delta G_n = 2e r^n \sum_{k=1}^s e_k r_k^n P_n(\cos \vartheta_k),$$

where e is the protonic charge, R_k is the distance between e_k and the proton in HA_1 , r and r_k are the lengths of the vectors joining the center of the sphere with the proton and the charge e_k , respectively, and ϑ_k the angle between r and r_k . We note that a similar formulation is possible when the excess of charge of A_1^- over A_2^- is continuously distributed with density ρ . If the ions are those involved in the first and second dissociation of a symmetrical dibasic acid, the charge distribution of the acid-ion HA^- , which corresponds to A_1^- , contains a proton in excess of that of A^- , which corresponds to A_2^- . If we denote by x the ratio $(r/b)^2$, where r is the distance of each proton in H_2A from the center of the spherical cavity of radius b , Eq. (7) becomes

$$\Delta w = - \frac{e^2}{b} \left\{ \frac{1}{D_i} \frac{1}{(2x(1 - \cos \vartheta))^{1/2}} + \left(\frac{1}{D} - \frac{1}{D_i} \right) \sum_{n=0}^{\infty} \frac{(n+1)x^n P_n(\cos \vartheta)}{n+1 + nD_i/D} \right\} \quad (8)$$

where ϑ is the angle between the lines joining the two protons of H_2A to the center of the molecule. Unless we refer our calculation to the distance between the protons rather than the distance between negative charges in the ions, we neglect the effect of the carboxyl dipole. Although the sum in Eq. (8) may be expressed as a definite integral, an adequate approximation is obtained by expanding in powers of D_i/D , and neglecting all terms in powers of D_i/D higher than the first. Then, making use of the properties of the Legendre functions, the series involved may be summed. When the resulting expression is sub-

⁴ Ingold, J. Chem. Soc. 2179 (1931).

⁵ Kirkwood, J. Chem. Phys. 2, 351 (1934).

stituted in Eq. (3), we obtain

$$\log_{10} K_1/4K_2 = \frac{e^2}{2.303RkT} \left[\frac{f_1}{D} + \frac{f_2}{D_i} \right]$$

$$f_1 = \frac{2(2x(1-\cos\vartheta))^{\frac{1}{2}}}{(1-2x\cos\vartheta+x^2)^{\frac{1}{2}}} - \frac{(2x(1-\cos\vartheta))^{\frac{1}{2}}}{x}$$

$$\times \log_e \frac{(1-2x\cos\vartheta+x^2)^{\frac{1}{2}} + x - \cos\vartheta}{1 - \cos\vartheta}$$

$$f_2 = 1 - \frac{(2x(1-\cos\vartheta))^{\frac{1}{2}}}{(1-2x\cos\vartheta+x^2)^{\frac{1}{2}}}$$

$$R = b(2x(1-\cos\vartheta))^{\frac{1}{2}}, \quad (9)$$

where R is the distance between the protons in H_2A . If we make use of the notation of Eq. (4), in which an effective dielectric constant appears, we have

$$1/D_E = f_1/D + f_2/D_i. \quad (10)$$

In Fig. 1 the values of D_E are shown for all values of \sqrt{x} from zero to one, and for three values of $\cos\vartheta$, namely, -1 , $-1/2$ and 0 , corresponding to the cases in which the protons are on a diameter, placed at an angle, computed from the center, of 120° , and at right angles. D was taken as 78 for water at 25° ; D_i was assigned the value 2.00 . The effective dielectric constant rises, with increase of \sqrt{x} , from D_i when the charges are in the center of the sphere and $\sqrt{x}=0$ to values above the dielectric constant of water when the charges are on the edge of the sphere and $\sqrt{x}=1$. The fact that the effective

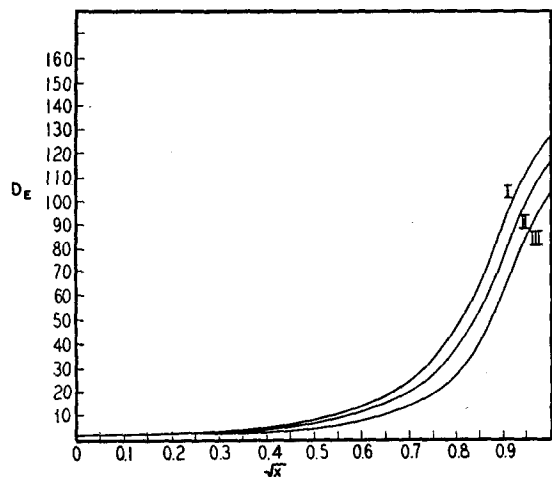


FIG. 1. Plot of D_E for a charged substituent against \sqrt{x} . In curve I $\cos\vartheta = -1$, in curve II $\cos\vartheta = -1/2$ and in curve III $\cos\vartheta = 0$. D_i is 2.00 throughout.

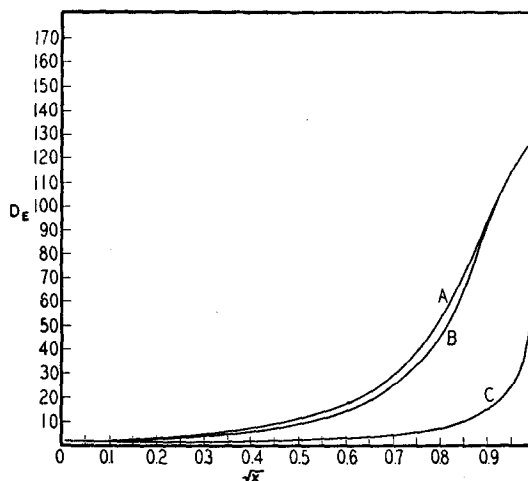


FIG. 2. Curve A, plot of D_E against \sqrt{x} for a charged substituent with $D_i = 2.50$. Curve B, same except $D_i = 2.00$. Curve C, plot of D_E against \sqrt{x} for a dipolar substituent. In all cases $\cos\vartheta = -1$.

dielectric constant is greater, at the edge of the sphere, than the dielectric constant of the medium may at first glance be surprising. This need cause no concern, for D_E is only a dielectric constant by convention, being so defined that our equations take on the simple Bjerrum form. The result is in no way dependent upon the approximation made when Eq. (8) was expanded in powers of D_i/D . In part IV of this paper, the sum in Eq. (8) is expressed as a definite integral, and the exact value of D_E for charges at the edge of a sphere and on a diameter obtained.

In the computation of D_E , no arbitrary parameters enter except the internal molecular dielectric constant, D_i . However, it is assigned a reasonable value, common to all aliphatic molecules, and is not readjusted to meet the demands of individual cases. Further, the value of D_E depends primarily upon the existence of a low internal dielectric constant, and only secondarily upon the exact value assigned to it. In Fig. 2, curve A was computed for charges on a diameter, with $D_i = 2.5$, while curve B was computed for charges on a diameter, with $D_i = 2.0$. The difference, while real, is small.

Besides the effect of substituents bearing a total net charge, we wish to determine the electrostatic free energy difference, Δw , when HA_1 contains a polar group in excess of HA_2 . We may regard the dipole as two equal and opposite

charges, so placed and of such a magnitude that the product of charge by the distance of separation is equal to the dipole moment. Eq. (18) gives the value of Δw in this case. We can also regard the charge distribution as a point dipole. If we restrict our attention to those cases in which the dipole and proton both lie equidistant from the center on a diameter, then

$$\frac{1}{D_E} = \frac{1}{D_i} \left[1 - \frac{4x^{\frac{1}{2}}}{(1+x)^2} \right] + \frac{1}{D} \left[\frac{8x^{\frac{1}{2}}}{(1+x)^2} + \frac{4x^{\frac{1}{2}}}{1+x} - \frac{4}{x^{\frac{1}{2}}} \log(1+x) \right], \quad (11)$$

where all the symbols have their usual significance. In Fig. 2, curve *C* is a plot of D_E , obtained from Eq. (11), against \sqrt{x} .

III

From the known dissociation constants of organic acids and Eqs. (4) and (5) an experimental value of D_E can be obtained for the cases in which HA_1 differs from HA_2 either by a charged or by a dipolar substituent. With charged substituents, D_E varies from 15 to about the dielectric constant of water, with dipolar substituents from about 3 to about 10; in both cases D_E is greater for greater values of r/b . For values of r/b between 0.5 and 0.9 which correspond to actual molecules, Figs. 1 and 2 show that D_E , obtained by our theoretical treatment, varies in a similar manner. We note that the effective dielectric constant is much smaller for a dipolar than for a charged substituent at the same value of r/b .⁶ In this section we wish to present the computations for the application of our equations to a few simple cases.

The exact location of the proton in the carboxyl group is still open to question. Available evidence⁷ seems to favor a double potential energy minimum for the proton adjacent to each of the oxygen atoms, at approximately the position of the proton in the normal O—H bond. To avoid undue complications in the calculations, we shall adopt the extended chain model, and conventionally place the proton on the extension

of the bond between the carboxyl carbon atom and its nearest carbon neighbor. Some convention, of which this is the most convenient is necessary solely for the purpose of estimating ϑ , the angle between the lines joining the protons to the center.

The selection of a structural distance between the protons of a dicarboxylic acid for comparison with the value computed from the dissociation constant ratio is further complicated by present ignorance relative to internal rotations in the molecule. We obtain a probable upper limit for the structural distance by using the extended chain model with the proton conventionally located at a distance of 1.45Å from the respective carboxyl carbon atoms on the extensions of the terminal carbon to carbon bonds. The distance of 1.45Å is actually the greatest distance of the projection of the proton on the extension of the terminal carbon-carbon bond, when attached to either oxygen at the covalent distance 0.94Å and with an angle of 90° between the C—O and O—H bonds. For the purpose of comparison we have also calculated the root mean square separation of the protons on the basis of free rotation. In this computation, we have employed the following formula for the mean square distance \bar{R}_n^2 between the terminal atoms in a chain containing n bonds⁸

$$\bar{R}_n^2 = \sum_{k=1}^n l_k^2 + 2 \sum_{k=1}^{n-1} \sum_{s=1}^{k-1} l_k l_s \prod_{m=s}^{k-1} \eta_{m, m-1},$$

where $\eta_{m, m-1}$ is the cosine of the supplement of the angle between the m and $m-1$ bonds, and l_k is the length of the k 'th bond. We are aware of the fact that the free rotation value does not provide an absolute lower bound for the average structural distance. However, it is not unreasonable to suppose that the average structural separation of the protons lies between the extended chain and the free rotation value. In Table I we have presented the data for a few acids which are at least approximately spherical. It is seen that the distance computed from the

⁶ Smallwood [J. Am. Chem. Soc. **54**, 3048 (1932)] has shown by means of a Born cycle that D_E will be unity if certain cancellations in the free energies of solvation, from the hypothetical gaseous state, of the acids and ions occur.

⁷ See Price and Evans, Proc. Roy. Soc. **A162**, 110 (1937).

⁸ A special case of the formula developed by Eyring, Phys. Rev. **39**, 746 (1932). It is worth while pointing out that for the above formula to be valid, free rotation is not actually necessary. The only requirement is that the mean values of $\cos \varphi$ and $\sin \varphi$ vanish for adjacent bonds, φ being the angle specifying the projection of the $i+1$ 'th bond on a plane perpendicular to the i 'th bond. This may occur even if the rotation is highly inhibited.

TABLE I. Separation of protons in dicarboxylic acids.*
Distance in Å.

ACID	MAXIMUM	FREE ROTA- TION	THIS PAPER	BJER- RUM
Oxalic acid	4.44	3.50	3.85	0.91
Dimethyl malonic acid	4.87	4.12	4.15	1.34
Tetramethyl succinic acid	6.66	4.66	4.80	0.96

* The values in column 4 are given to the nearest 0.05Å. Since the computed values of R in Table I refer to a single configuration of the molecule, they are not strictly suitable for comparison with mean distances calculated on the basis of free or inhibited internal rotation. Nevertheless, we have stated the maximum and free rotation distances in order to exhibit a possible range of variation of the interprotonic distance in the acids. With internal rotation, we should properly compute an average value of ΔpK over all internal configurations for comparison with the experimental value. Such a calculation is very tedious and does not seem worth while on the basis of free rotation, since in actual molecules the rotation is doubtless inhibited. We are unable to make the calculation for inhibited rotation, until future information about the hindering torques becomes available.

dissociation constant ratio by means of our equation do actually fall between the suggested limits, while the values computed with the simple Bjerrum formula lie considerably below the free rotation value and are almost certainly too small on any basis. We remark that the Bjerrum formula is by no means as unsatisfactory for the longer chain acids. We have selected for discussion a group of short chain acids the shapes of which roughly approximate spheres, since it is in these cases that the Bjerrum theory needs refinement. In a later paper, we shall develop a formula, on the basis of an ellipsoidal model, which passes asymptotically into the simple Bjerrum formula as the chain length increases. A knowledge of the torques hindering internal rotation would permit a more exact application of our formulas involving a calculation of the average value of ΔpK over all internal configurations of the acids and ions.

For these computations it was necessary to estimate the radii of the spheres. In the absence of specific information, we have fallen back on Traube's rule.⁹ The partial molar volume of dimethyl malonic acid in water, then, is about 99.1 cc, and the diameter of the molecule, considered as a sphere, is 6.77Å. Further, since we have decided, conventionally, to place the protons on the extensions of the terminal carbon to carbon bonds, we may assign the angle $\cos \vartheta = -0.333$ to the lines joining the protons to the center. From Eq. (4) we obtain

$$\sqrt{x}D_E = \frac{e^2}{2.303bkT\Delta pK(2(1 - \cos \vartheta))^{1/2}},$$

$$r/b = \sqrt{x}.$$

⁹ Traube, Saml. chem. chem-tech., Vortr. 4, 255 (1899).

Substituting the value of 2.29 for ΔpK for dimethyl malonic acid found by Gane and Ingold² in this expression, we find $\sqrt{x}D_E$ equal to 19.1. Values of $\sqrt{x}D_E$ computed with the aid of Eq. (10) are given in Table II for varying \sqrt{x} and $\cos \vartheta$. Using this table, the value of \sqrt{x} can be obtained in any particular case by linear interpolation. The computations for the other acids were carried out in a similar fashion, again using the data of Gane and Ingold. The angle between the protons for oxalic and tetramethyl succinic acids was chosen as 180°.

As an example of the effect of a simple dipolar substituent we present the computations for the ratio of the dissociation constant of acetic to chloracetic acids. Since the molecule does not approach a true sphere, we arbitrarily placed the center at the midpoint of the line joining the proton with the midpoint of the carbon-chlorine bond. We employed the value 1.56×10^{-18} e.s.u. for the dipole moment of the C—Cl bond;¹⁰ the values of the dissociation constants of acetic and chloracetic acids were taken from Landholt-Börnstein.¹¹ The data for chloracetic acid are given in Table III. Other calculations have shown that, in chloracetic acid, the acidity is relatively little effected by multipole moments of higher order than the second.

Finally we may mention that, in common with the previous electrostatic theories of dissociation, the temperature coefficients experimentally determined¹² do not agree with those calculated, on the basis of a constant value of R . Although a real variation of the average value of R with

TABLE II. Values of $\sqrt{x}D_E(x)$.

\sqrt{x}	$\cos \vartheta = -1$	$\cos \vartheta = -\frac{1}{2}$	$\cos \vartheta = 0$
0.00	0.00	0.00	0.00
0.10	0.25	0.24	0.23
.20	0.64	0.60	0.55
.30	1.31	1.16	1.02
.40	2.45	2.11	1.76
.50	4.59	3.82	3.02
.60	8.79	7.15	5.42
.70	17.6	14.2	10.6
.80	37.5	30.9	23.3
.90	79.2	68.9	56.4
.95	106.6	96.3	83.2
1.00	127.0	116.3	103.5

¹⁰ Smyth, Am. Chem. Soc. Symposium on Molecular Structure, p. 209 (1937).

¹¹ Landholt-Börnstein, *Physikalische-Chemische Tabellen*, Eq IIIc.

¹² Jones and Soper, J. Chem. Soc. 133 (1936).

TABLE III. Distance between proton and dipole in chloracetic acid in A.

MAXIMUM	FREE ROTATION	MINIMUM	THIS PAPER	BJERRUM
3.39	2.99	1.84	2.90	0.55

temperature is not unlikely, it may be that a more refined theory is necessary before accurate estimates of temperature coefficients can be made. In any case, the temperature coefficients are not large.

IV

In this section we shall present some of the mathematical details omitted earlier in the paper. Eq. (7) may be written in the following form.

$$\Delta w = e \sum_{k=1}^s e_k H_k$$

$$H_k = \frac{1}{D_i R_k} + \frac{1}{b} \left(\frac{1}{D} - \frac{1}{D_i} \right) S(x_k, \cos \vartheta_k) \quad (12)$$

$$S(x, \alpha) = \sum_{n=0}^{\infty} \frac{(n+1)x^n P_n(\alpha)}{1+n(1+\omega)},$$

where x_k is equal to rr_k/b^2 and ω is the ratio, D_i/D . From the properties of the Legendre functions, we may write

$$S_0(t, \alpha) = \sum_{n=0}^{\infty} t^n P_n(\alpha) = \frac{1}{(1-2\alpha t+t^2)^{1/2}}. \quad (13)$$

It is readily verified that $S(x, \alpha)$ may be expressed in the form

$$S(x, \alpha) = \frac{\partial}{\partial x} \left[x^{\omega/(1+\omega)} \int_0^{x^{1/(1+\omega)}} S_0(t^{1+\omega}, \alpha) dt \right]. \quad (14)$$

Simplification of Eq. (14) leads to

$$S(x, \alpha) = \frac{1}{1+\omega} \left\{ S_0(x, \alpha) + \frac{\omega}{1+\omega} S_1(x, \alpha) \right\}$$

$$S_1(x, \alpha) = x^{-1/(1+\omega)} \int_0^x t^{-\omega/(1+\omega)} \times [1-2\alpha t+t^2]^{-1/2} dt. \quad (15)$$

Expansion in powers of ω with the neglect of terms in ω^2 gives

$$S(x, \alpha) = S_0(x, \alpha) + \omega [S_1^0(x, \alpha) - S_0(x, \alpha)]$$

$$S_1^0(x, \alpha) = -\frac{1}{x} \log \left[\frac{(1-2x+x^2)^{1/2} + x - \alpha}{1-\alpha} \right]. \quad (16)$$

Evaluation of $S_1(x, \alpha)$ by graphical quadrature shows that the expansion (16) is adequate in all cases of interest although D_E calculated from (10) is 2 percent high at $x=1$. Substitution in Eq. (12) gives

$$H_k = \frac{1}{Db} \left\{ 2[1-2x_k \cos \vartheta_k + x_k^2]^{-1/2} - \frac{1}{x_k} \log \left[\frac{(1-2x_k \cos \vartheta_k + x_k^2)^{1/2} + x_k - \cos \vartheta_k}{1 - \cos \vartheta_k} \right] \right\}$$

$$+ \frac{1}{D_i} \left\{ \frac{1}{R_k} - \frac{1}{b} [1-2x_k \cos \vartheta_k + x_k^2]^{-1/2} \right\}. \quad (17)$$

Eq. (9) for the symmetrical dibasic acid follows at once from Eqs. (12) and (17), only one term occurring in the sum of Eq. (12). For a dipolar distribution consisting of two point charges $+e$, and $-e$, Eq. (12) takes the form

$$\Delta w = e^2 [H_+ - H_-], \quad (18)$$

where H_+ and H_- are to be computed from Eq. (17) for the respective charges. We note that H_k may be regarded as a function $H(\mathbf{r}_k, \mathbf{r})$ where \mathbf{r}_k and \mathbf{r} are the vectors extending from the center of HA_2 to the charge k and the carboxyl proton, respectively. Thus for a point dipole, we may write

$$\Delta w = e \mathbf{M} \cdot \nabla_1 H(\mathbf{r}_1, \mathbf{r}), \quad (19)$$

where \mathbf{M} is the vector moment and ∇_1 the gradient operator associated with the position \mathbf{r}_1 of the dipole. The general expression is rather complicated and will not be given. However, for a molecule in which the proton and dipole are located on a diameter, Eqs. (17) and (19) yield Eq. (11) of Section II.