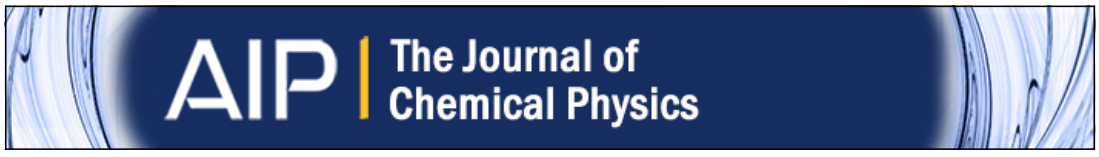

Electrostatic Effects on Ionization Constants

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Electrostatic Effects on Ionization Constants

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(Received May 8, 1939)

The equation of Born for the self-energy of an ion is applied to the heats of ionization of acids and bases, following a treatment by Gurney. In this way the variations in these heats with temperature are quantitatively explained, and approximate ionic radii predicted. Further applications to the ionization of amino acids and the variation of dissociation constants as between different solvents are discussed.

I

IN a recent paper R. W. Gurney[1] has discussed the temperature variation of ionization constants. It is the object of this paper to point out that the theoretical considerations advanced by him may be developed in a more exact and simple way to allow of stricter comparison with experiment. His views may be summarized as follows: If we consider as typical ionization processes:

(1) $C_6H_5NH_3^+ + H_2O \rightleftharpoons C_6H_5NH_2 + H_3O^+$,

(2) $CH_3COOH + H_2O \rightleftharpoons CH_3COO' + H_3O^+$,

(3) $NH_3^+CH_2COOH + H_2O \rightleftharpoons NH_3^+CH_2COO' + H_3O^+$,

(4) $H_2PO_4' + H_2O \rightleftharpoons HPO_4'' + H_3O^+$.

Dissociations of type (1) do not involve the creation of a new electric field, but only the shift of charge from one ion to another ("isoelectric" dissociations). Type (2) requires the formation of the field due to the pair of ions, type (3) of the field due to the Zwitterion, and type (4) of the field due to a pair of ions with further electrical work necessary to separate the positively charged proton from the negative ion.

Now it appears from modern accurate measurements that dissociations of type (1) vary with temperature in the simple way:

$$\log K = A - B/T \qquad (1)$$

(where K is the ionization constant, T the absolute temperature, and A, B constants), which implies that the heat of ionization is constant. This appears from the measurements of Pedersen[2] on anilinium and *o*-chloranilinium, and of Everett and Wynne-Jones[3] on ammonium ions.

Dissociations of the other three types vary with temperature in a different way. Harned and Embree[4] have analyzed the data for several such reactions, and shown that the ionization constants rise with temperature to a maximum, and then decrease. The curves of log K against T are approximately parabolae, and the curves for the different acids and bases are superposable. These conclusions may be written:

$$\log K = \log K_m - p(t-\theta)^2, \qquad (2)$$

where K_m is the maximum value of the dissociation constant, attained at temperature θ, K is the value at temperature t, and p a constant for all acids and bases. That this equation, although a surprisingly good approximation, is not exact and p has not precisely the same value for all systems, is apparent from more detailed investigation.[5]

Gurney has supposed that in ionizations of these three types the work done in creating the field is given by the formula of Born:[6]

$$W = \frac{e^2}{2D}\left(\frac{1}{r_+} + \frac{1}{r_-}\right), \qquad (3)$$

where W is the work done to create the field due to the charges e on the two ions of radii r_+ and r_- in a medium of dielectric constant D. This very simple view has already led to a valuable interpretation of variations in dissociation constants from solvent to solvent,[7] and to an

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[1] R. W. Gurney, J. Chem. Phys. **6**, 499 (1938).

[2] Pedersen, Kgl. Danmske Vidensk. Selsk. Math-fys. Medd **14**, No. 9, **15**, No. 3 (1937).

[3] Everett and Wynne-Jones, Proc. Roy. Soc. (London) **169A**, 190 (1938).

[4] Harned and Embree, J. Am. Chem. Soc. **56**, 1050 (1934).

[5] Walde, J. Phys. Chem. **39**, 478 (1935).

[6] Born, Zeits. f. Physik **1**, 45 (1920).

[7] Wynne-Jones, Proc. Roy. Soc. (London) **140A**, 440 (1933).

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TABLE I.

$T°C$	D	$1/D$	$-T\frac{\partial \ln D}{\partial T}$	X ($\times 10^3$)
0	88.31	0.01133	1.2886	3.270
5	86.28	.01159	1.3122	3.618
10	84.25	.01187	1.3358	3.986
15	82.30	.01215	1.3594	4.367
20	80.35	.01244	1.3830	4.765
25	78.50	.01274	1.4066	5.180
30	76.73	.01304	1.4303	5.611
35	74.89	.01335	1.4539	6.050
40	73.12	.01368	1.4775	6.532
45	71.44	.01400	1.5011	7.015
50	69.85	.01432	1.5247	7.514
55	68.14	.01467	1.5483	8.044
60	66.62	.01502	1.5719	8.590

approximate theory of solubility in various solvents.[8]

Gurney is thus able to provide a qualitative interpretation of the relationship found by Harned and Embree (Eq. (2)). His subsequent development does not allow of any exact test. These hypotheses will now be developed by the methods of classical thermodynamics, and it will be shown that they are in complete agreement with the experimentally observed variations in heats of ionization with temperature, and permit of comparison of the values of the ionic radii r_+ and r_- with those obtained by other methods.

II

We may put:

$$\Delta F^0 = -RT \ln K$$

(where K refers to infinite dilution so that all species are in their standard states, and ΔF^0 is the free energy difference in this state). Then

$$-RT \ln K = -RT \ln K_x + (\epsilon^2/2D)(1/r_+ + 1/r_-)$$

for an acid or base giving two ions, where this equation serves to define K_x. Hence

$$\ln K = \ln K_x - (\epsilon^2/2DRT)(1/r_+ + 1/r_-),$$

by differentiation

$$\frac{\partial \ln K}{\partial T} = \frac{\partial \ln K_x}{\partial T} + \frac{\epsilon^2}{2R}\left(\frac{1}{r_+}+\frac{1}{r_-}\right)\left(\frac{1}{DRT^2}+\frac{1}{D^2RT}\frac{\partial D}{\partial T}\right)$$

and since

$$\partial \ln K/\partial T = \Delta H/RT^2,$$

if

$$\partial \ln K_x/\partial T \equiv \Delta H_x/RT^2$$

(ΔH = heat of reaction at constant pressure)

$$\left\{\begin{array}{l}\Delta H = \Delta H_x + c \cdot 1/D(1+T\partial \ln D/\partial T) \\ \text{where} \quad c = (\epsilon^2/2)(1/r_+ + 1/r_-)\end{array}\right. \quad (4)$$

A more rigorous derivation should contain a small term for the expansion of the solvent, which is, however, negligible compared with the uncertainties in $\partial \ln D/\partial T$. This equation may then be tested as follows: The experimentally determined values of ΔH for a given acid or base are plotted against $1/D(1+T\partial \ln D/\partial T)$ $(=X)$. If ΔH_x is independent of temperature over the ranges involved, as would be expected by analogy with dissociations of type (1), and the r's are also independent of temperature, the graph should be a straight line and the r's could be calculated from its slope.

The values for $X = 1/D(1+T\partial \ln D/\partial T)$ for water between 0° and 60° were taken from the data of Åkerlöf and Short.[9] These are in good agreement with other recent data given in Landolt-Börnstein's tables. (See Table I.)

The results of comparison of this Eq. (4) with experiment will now be given. For the exact test of the functional form we are confined to the very accurate data of Harned and his collaborators on the ionization constants of carboxylic (all of the aliphatic series) and some inorganic and amino acids. These were obtained

TABLE II. HCOOH = 2518 + 485,300X; H_2O = 16,045 + 490,200X; H_2PO_4' = 3090 + 454,000X.

	HCOOH		H_2O		H_2PO_4'	
T °C	ΔH_{OBS}	ΔH_{CALC}	ΔH_{OBS}	ΔH_{CALC}	ΔH_{OBS}	ΔH_{CALC}
0	+931	931	14,513	14,442	—	—
5	755	762	14,312	14,271	—	—
10	573	584	14,109	14,091	—	—
15	384	389	13,901	13,904	—	—
20	+189	206	13,692	13,709	+903	881
25	−13	+4	13,481	13,506	731	738
30	−221	−205	13,267	13,294	546	543
35	−436	−418	13,051	13,079	347	343
40	−657	−652	12,833	12,843	134	124
45	−884	−886	12,612	12,606	−92	−94
50	−1118	−1129	12,390	12,362	−334	−321
55	−1358	−1386	12,164	12,102	—	—
60	−1602	−1650	11,936	11,834	—	—

[8] Bjerrum and Larsson, Zeits. f. Physik. Chemie **127**, 358 (1927); Brönsted, Delbanco and Volqvartz, *Ibid.* **162A**, 128 (1932).

[9] Åkerlöf and Short, J. Am. Chem. Soc. **58**, 1241 (1936).

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TABLE III.

ACID	$pK_{25}°$	ΔH_x	c	R (A)	REF
Formic	3.754	2,518	$4.85_3 \times 10^5$	0.68	10
Acetic	4.757	1,948	$3.90_8 \times 10^5$	0.85	a
n-Propionic	4.874	2,169	$4.44_3 \times 10^5$	0.75	b
n-Butyric	4.820	1,975	$5.14_0 \times 10^5$	0.65	c
Mono-chloracetic	2.861	1,135	$4.39_0 \times 10^6$	0.76	d
Glycollic	3.831	2,588	$4.65_7 \times 10^5$	0.71	e
Lactic	3.862	2,628	$5.18_0 \times 10^5$	0.64	f
Water	15.741	16,045	$4.90_2 \times 10^5$	0.68	g
H_2PO_4'	7.206	3,090	$4.54_0 \times 10^5$	0.74	h
HBO_2	9.236	5,966	$5.06_5 \times 10^5$	0.66	i
o-Chlorbenzoic	2.943	−1,868	$1.83_6 \times 10^5$	1.84	11, j
o-Nitrobenzoic	2.173	−2,284	$2.15_8 \times 10^5$	1.56	11, j

[a] Harned and Ehlers, J. Am. Chem. Soc. **55**, 652 (1933).
[b] Harned and Ehlers, J. Am. Chem. Soc. **55**, 2383 (1933).
[c] Harned and Sutherland, J. Am. Chem. Soc. **56**, 2039 (1934).
[d] Wright, J. Am. Chem. Soc. **56**, 314 (1934).
[e] Nims, J. Am. Chem. Soc. **58**, 987 (1936).
[f] Nims and Smith, J. Biol. Chem. **113**, 148 (1936).
[g] Harned and Hamer, J. Am. Chem. Soc. **55**, 2198 (1933).
[h] Nims, J. Am. Chem. Soc. **55**, 1946 (1933).
[i] Owen, J. Am. Chem. Soc. **56**, 1695 (1934).
[j] $pK_{25}°$ values from Dippy and Lewis, J. Chem. Soc. (London) 1426, (1937).

by an e.m.f. method involving no liquid junctions. Of these data perhaps the most accurate are those for formic acid, the heats for which were calculated by fitting the log K–T curves to empirical equations involving several parameters.[10]

These values for ΔH were plotted against X, and the best straight line drawn. The values of ΔH_{calc} were then taken from this line. Since $T\partial \ln D/\partial T$ is negative and greater than unity, ΔH decreases with temperature as required by experiment.

The values of ΔH_{calc} and ΔH_{obs} are given in Table II as are also the data for water and $H_2PO_4^-$ (type (4)). The agreement is practically perfect. In Table III are given the values of ΔH_x and c appropriate for all the dissociations of types (2) and (4) measured by this technique. The individual agreement is in all cases about as good as for the examples given. The scatter of the individual points is worst for monochloracetic acid, for which the less accurate quinhydrone electrode was used.

Of the earlier data, those of Schaller[11] are perhaps the only ones sufficiently systematic to test Eq. (4). These were done by the conductivity technique at several temperatures from 0° to 100° for various benzoic and cinnamic acids. Of these most have maxima in or near the range of experiment, and their variations in K are, therefore, small and of the same order as the experimental error. Some, *o*-nitro and *o*-chlor benzoic acids in particular, have maxima at much lower temperatures, and so the changes in the observed range are considerable. The heats were then estimated graphically for these two acids and plotted against X. Good straight lines were obtained, and hence the ΔH_x's and c's given in Table III.

The relationship between the empirical equation of Harned and Embree (Eq. (2)), and the equation for ΔH_x here developed may be most clearly shown by expressing ΔH_T (at a temperature T) in terms of θ, the temperature at which K is a maximum.

Eq. (2) yields at once

$$\Delta H = +2pRT^2(\theta - T). \tag{5}$$

Eq. (4) gives

$$\Delta H_T = \Delta H_x + c1/D_T\left(1 + T\frac{\partial \ln D}{\partial T}\right)_T,$$

whence

$$\Delta H_\theta = 0 = \Delta H_x + c1/D_\theta\left(1 + \theta\frac{\partial \ln D}{\partial T}\right)_\theta,$$

so that

$$\Delta H_T = c\left\{1/D_T\left(1 + T\frac{\partial \ln D}{\partial T}\right)_T - 1/D_\theta\left(1 + \theta\frac{\partial \ln D}{\partial T}\right)_\theta\right\}.$$

To get this into a comparable form, we must know the variation of D with temperature Åkerlöf and Short[9] find their results to be expressible by

$$\ln D = A - BT,$$

whence

$$\Delta H_T = ce^{-A}\{e^{BT}(1 - BT) - e^{B\theta}(1 - B\theta)\}.$$

Expanding the exponentials, and collecting terms, we get

$$\Delta H = ce^{-A}\sum_{n=2}^{\infty}\frac{B^n(\theta^n - T^n)}{n(n-2)!}. \tag{6}$$

By substituting the appropriate values of A, B and taking $\theta = 300°\text{K}$, $T = 320°$, it can easily be shown that this is given to within 1

[10] Harned and Embree, J. Am. Chem. Soc. **56**, 1042 (1934).
[11] Schaller, Zeits. f. physik. Chemie **25**, 497 (1898).

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percent by the first term, so that

$$\Delta H \doteq ce^{-A}B^2(\theta^2 - T^2)/2. \qquad (6^1)$$

We may now consider the predictions of these two equations in the immediate neighborhood of θ (i.e. $T^2 \doteq \theta^2$, $\theta + T \doteq 2\theta$).

Eq. (5) gives

$$\Delta H = 2pR\theta^2\Delta\theta$$

and Eq. (6^1)

$$\Delta H = ce^{-A}B^2\theta\Delta\theta \qquad (7)$$

(where $\Delta\theta = \theta - T$), so that, if Harned and Embree's equation is to be approximately valid, c must increase proportionally to θ. The low values for c for the substituted benzoic acids support this roughly. But it can be seen that p depends on c and θ, and so cannot be simply interpreted in terms of either. Most of the acids in Table III have θ between 270° and 320° Absolute, so that the approximate validity of Eq. (2) can be understood. As, however, p is not exactly the same for all acids,[5] further discussion is hardly profitable.

It is clear then that a formula

$$\log K = A - B/T - C/DT \qquad (8)$$

(where A, B, C are constants for each acid) fits the data well and is, at any rate, a valuable interpolation formula. We may now consider the values of the ionic radii which these graphs would predict. The individual radii r_+ and r_- are not, in general, known. But we may define a mean radius R by $2/R = 1/r_+ + 1/r_-$, and obtain this from the appropriate values of c. (In Table III, c is in calories per mole; taking the proper values for the electronic charge and Avogadro's number, and remembering that W in Eq. (1) is in ergs per molecule, then $2/R = 602c$, where R is in cm.)

By this means the values (in A) of R given in the fourth column of Table III were calculated. These values, though probably too small, are of the right order. It is remarkable that R should vary so little over the series formic -*n*-butyric acids. This would suggest that the charge is localized on one oxygen atom, or, at any rate, on the carboxyl group only.

Other estimates of the radii may be obtained in the following ways:

(1) From crystal lattice data the radius of the O'' ion is about 1.40A. The covalently linked $=O$ has, in the gas phase, a radius 0.60A. The ion $-O'$ should presumably be intermediate in size, i.e. of radius about 1.0A. If the charge were "smeared" over the whole carboxyl group, the radius would be larger.[12] It is possible that the high values of R for the two *o*-substituted benzoic acids are due to some such resonance "ortho-effect."

(2) The data on activity coefficients of acetic acid in salt solutions[13] are well represented by the Debye-Huckel equation with the mean distance of closest approach 3.5A, i.e. a radius of 1.75A. This is not strictly comparable with the radii here defined and is probably larger, particularly if collision between ions is frequently prevented by intervening water molecules.

(3) Carboxylate ion mobilities are, in general, about 35 in the conventional units at 25°. This would, assuming Stokes' law, imply a radius of 2.6A, which should represent the maximum cross section of the ion, not the radius of the charge bearing group. This value is, therefore, again not strictly comparable with the values in Table III. It follows that, although the ionic radii there given seem rather small, no independent estimate of their value is obtainable.

The possibility of using Born's equation implies the neglect of the effects due to covalent forces between the ions and solvent molecules, and to dipole saturation. The first of these would affect only the ΔH_x in formula (4), unless the specific heat differences involved were large. The simple behavior observed for "isoelectric" dissociations makes this improbable. It is, however, clear that such effects enter directly, and not, as here, simply through specific heat effects, into expressions for heats of transfer and integral heats of dilution for ions. These heats could hardly be expected, therefore, to be given by the simple Born equation.

The dipole effects have been considered by Webb.[14] His treatment predicts that Born's equation could not be valid for any ion of radius less than about 10A, and that the self-energy should be larger by a factor depending on the

[12] Radii from Sidgwick, *The Covalent Link in Chemistry* (Cornell University Press, 1933), p. 85.
[13] Harned and Robinson, J. Am. Chem. Soc. **50**, 3157 (1928).
[14] Webb, J. Am. Chem. Soc. **48**, 2589 (1926).

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size of the ion, which would be about 10 for 1A radius. These conclusions depend, however, on the assumption that the solvent dipoles are free to rotate without doing any work except against the electric field. It has since been shown by Debye[15] that this assumption yields a value for the change of dielectric constant with field strength for water about 3500 times as large as that observed. For ether the agreement is almost quantitative. Debye accounts for this abnormal behavior of water by assuming a barrier of about $10kT$ which must be surmounted on rotation, and this value is supported by the abnormal orientation polarization. It has also been pointed out that the same assumption of restricted rotation will account well for the thermodynamic peculiarities of typical "associated" solvents.[16]

It is clear, therefore, that Webb's treatment would exaggerate enormously the effects in "associated" solvents while for normal solvents his conclusions should, presumably, be valid. Hence, Born's equation should be more nearly exact the smaller the "free angle ratio" of the solvent. Unfortunately no data on the variation of heats of dissociation with temperature exist for systems in any pure solvents other than water, so that this conclusion cannot be tested. The results obtained for acetic acid in water-dioxane and water-methanol mixtures[17] can simply be explained by assuming preferential concentration of water around the ions.

This view, that saturation effects may be neglected, has received further support from the recent work of Kirkwood and Westheimer[18] on the ratio of the two dissociation constants of a dicarboxylic acid. They have shown that, if a correction be applied to Bjerrum's simple treatment to take into account the field strength inside the cavity in the solvent caused by the molecule, the lengths of hydrocarbon chains predicted are in excellent agreement with those to be expected from free rotation, even if the chain length is small. This again suggests that the electric saturation and similar effects are not very large.

III

We may now attempt to extend these conclusions to the data for the two ionizations of aminoacids. The two processes are (for glycine):

$$(K_a)\ NH_3{}^+CH_2COOH + H_2O \rightleftharpoons NH_3{}^+CH_2COO' + H_3O^+$$

$$(K_b)\ NH_3{}^+CH_2COO' + H_2O \rightleftharpoons OH_3{}^+ + NH_2CH_2COO'.$$

Calculation on the lines of the preceding treatment would require the estimation of the electrostatic field energy due to the dipole Zwitterion. For the work done in establishing the dipole μ in the center of a sphere of radius a, Martin[19] has derived the formula:

$$W = \mu^2/3a^3(1/D). \qquad (9)$$

This formula neglects the field in the dipole sphere itself, which has been taken into account in later treatments,[20] and assumes also that the dipole is located at a point, and so is only approximate. These more correct formulae involve the "internal dielectric constant" of the sphere, about which little is known, various values from 1 to 3 having been suggested for it. Since it has been shown[21] that the formula of Martin is in as good agreement with the experi-

TABLE IV. *Heats of first dissociation of amino acids.*

	Glycine*		*dl*-leucine†	
$T°$	ΔH_{OBS}	ΔH_{CALC}	ΔH_{OBS}	ΔH_{CALC}
1	—	—	1510	1524
10	1562	1596	—	—
12.5	—	—	1210	1188
15	1439	1453	—	—
20	1305	1304	—	—
25	1159	1149	800	784
30	1000	987	—	—
35	829	827	—	—
37.5	—	—	320	337
40	646	642	—	—
45	449	460	—	—
50	—	—	−250	−154

* glycine, reference 22.
† *dl*-leucine, reference 24.

[15] Debye, Physik. Zeits. **36**, 193 (1935). Cf. also Malsch, *Ibid.* **30**, 837 (1929); Gundermann, Ann. d. Physik **6**, 545 (1930).
[16] Kincaid and Eyring, J. Chem. Phys. **6**, 620 (1938).
[17] Harned and Embree, J. Am. Chem. Soc. **57**, 1669 (1935); Harned and Kazanjian, J. Am. Chem. Soc. **58**, 1812 (1936).
[18] Kirkwood and Westheimer, J. Chem. Phys. **8**, 506, 513 (1938).
[19] Martin, Phil. Mag. **8**, 547 (1929).
[20] R. P. Bell, J. Chem. Soc. (London), p. 1371 (1931); Trans. Faraday Soc. **27**, 297 (1931); Kirkwood, J. Chem. Phys. **2**, 351 (1934).
[21] W. H. Banks, Trans. Faraday Soc. **33**, 215 (1937).

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TABLE V. *Values of ΔH_x, c for first dissociations of amino acids.*

	ΔH_0	c	REF.
Glycine	3091	3.75×10^5	22
dl-alanine	2365	3.27	23
dl-alanine	2866	4.02	24
dl-amino *n*-butyric	2700	4.66	24
dl-amino *n*-valeric	2800	4.40	24
dl nor-leucine, *dl* aminoiso-butyric	2850	4.53	24
dl valine	2500	4.72	24
dl leucine	2770	4.66	24
dl isoleucine	2770	4.90	24

mental data on free energies of transference of acetic acid, monochloracetic acid, and ammonia between various solvents as are these more complex formulae, with the internal dielectric constant taken as unity, it has been adopted for the provisional calculations which follow.

For the first process (K_a), it is evident that this formula leads to Eq. (4) valid for dissociation into a pair of ions, but with $c=\mu^2/3a^3$ instead of $(e^2/2)(1/r_+ + 1/r_-)$. The data for the ΔH's can, therefore, be plotted precisely as before. We have available data for glycine,[22] for alanine[23] and for alanine and seven other α-amino acids.[24] The test of the Eq. (4) with experiment for glycine and *dl*-leucine is shown in Table IV, and in Table V are given the values of ΔH_x and c appropriate for all these aminoacids. The considerable discrepancy between the two sets of values for alanine indicates that these data are perhaps not sufficiently accurate in themselves for a crucial test of the functional form of ΔH with respect to T. The following further points may be noticed:

(1) If we take $\mu=15\times10^{-18}$ e.s.u. for glycine, then we arrive at $a=1.45\times10^{-8}$ cm for glycine instead of the proper value 3×10^{-8}.[25] This is perhaps as good agreement as could be expected in view of the theoretical uncertainties mentioned.

(2) The dipole moment of the α-aminoacids will probably remain constant when the chain is sufficiently long. It follows that the radius a must remain about the same, since the c's in Table V are all approximately equal, for aminoacids with chains longer than that of alanine. This points to localization of the dipole at the end of the molecule. Banks[21] has pointed out that this conclusion is necessitated by the data on the transference energies of some aminoacids between water and *n*-butyl alcohol, and of several α-bromoacids between various solvents. The agreement of these two methods of approach supports the view that the theory here developed is essentially correct—even if too crude for exact numerical prediction of the size of the dipole sphere. It would be of great interest to measure the temperature coefficients of ionization of β, $\gamma\cdots$ aminoacids.

(3) In the ionization of a carboxylic acid the two dipoles RCOOH and H_2O disappear. The corresponding electrostatic term in the free energy, and hence in the heat of ionization, can then be estimated from the known values of the μ's. Taking the a's as 1A, this involves only a 2 percent correction to the c's, and as this correction varies inversely as the cube of the a's, and as they are certainly considerably larger than 1A, it is negligible for the ionization of these acids.

The more accurate treatment of Kirkwood and Westheimer[18] gives the electrostatic energy of a dipole as $f_1/D+f_2/D_2$, where f_1/D is the term corresponding to the effect of the solvent (of dielectric constant D) and f_2/D_2 the term for the electrostatic effect of the cavity (internal dielectric constant D_2) in the solvent due to the molecule. For explicit expressions for f_1, f_2 see their papers.

The first of these terms we have replaced by Martin's approximation. The second, and larger (since f_1, f_2 are of the same order, and $D_2 \ll D$), will be independent of temperature if D_2 is. Hence, the dipole effects will be very much larger than here estimated, but will affect the ΔH_x's of our formula (4) almost exclusively. Examination of the ΔH_x, c values in Table III for acetic and monochloracetic acids shows the c's to vary by only 10 percent, although the ΔH_x's vary by a factor of two. Since the difference between the pK's of these acids is well accounted for by Kirkwood and Westheimer's detailed electrostatic theory, our conclusion, that the

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[23] Nims and Smith, J. Biol. Chem. **101**, 401 (1933).
[24] Smith, Taylor and Smith, J. Biol. Chem. **122**, 109 (1937).
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dipole effects on the c's in Eq. (4) are small for carboxylic acids, is justified even on their more detailed picture.

(4) We may now consider the heats ΔH_b of the second stage of ionization of aminoacids. Here the Zwitterion disappears, and a pair of ions is formed. Examination of the c's in Tables III and V shows that the electrostatic work done in these processes will be almost equal. Hence, the ΔH for the second process will vary but slightly with temperature. This conclusion is supported by the data of Smith, Taylor and Smith,[24] which show the deviations from constancy to be small for all six aminoacids measured. Thus they give for alanine at 1°, 12.5°, 25°, 37.5°, 50° the pK_b values 10.586, 10.225, 9.866, 9.548, 9.256; a constant ΔH of $-10{,}920$ cal. would predict 10.579, 10.228, 9.877, 9.554, 9.256. This very small variation in ΔH, which these results establish (the constant heat predictions are probably within the experimental error), is just what the theory here developed would predict.

IV

Since $\ln K = \ln K_x - c/DRT$ at any one temperature T, K_x can be calculated from a knowledge of c and D, and has the significance of a dissociation constant at infinite dielectric constant. The K_x's so predicted have not the significance of dissociation constants where no electrostatic work is done on separating the ions for the following reasons. We may regard the ionic sphere (carboxyl or oxygen) as surrounded to an extent q by the solvent of dielectric constant D, and to an extent s by the rest of its own molecule. The dielectric constant Z of this will presumably be roughly that of a paraffin, and so independent of temperature. Hence, the simple Born expression must be replaced by

$$\frac{e^2}{2}\left(\frac{1}{r_+}+\frac{1}{r_-}\right)\left(\frac{q}{D}+\frac{s}{Z}\right).$$

This will then, if Z is independent of temperature give agreement with Eq. (4), but with $1/R$ replaced by q/R. A simple geometric interpretation of q/s as the ratio of solid angles subtended at the center of the ion by the solvent and the rest of the molecule, should give $q=0.7$–0.8. This would make the ionic radii in Table III too large by about 20 percent. As however $Z \ll D$, $1/Z \gg 1/D$, and the true dissociation constants for zero electrostatic work will be mainly determined by the unknown s/Z term.

TABLE VI.

	log $K_{H_2O,\ 25°}$	log $K'_{25°,\ H_2O}$	log K_x	log K_x'	log K_∞'	log K_y'
Acetic	−4.757	0	−1.11	0	0	0
Formic	−3.754	+1.00	+0.79	1.90	0.75	0.88
Glycollic	−3.831	+0.93	+0.52	1.63	0.70	0.83
Mono-chloracetic	−2.861	+1.90	+1.25	2.36	1.83	1.83
o-chlorbenzoic	−2.943	+1.82	−0.12	0.99	2.05	2.09
o-nitrobenzoic	−2.973	+2.58	−1.23	−0.12	2.75	2.81

All K_∞' values from Minnick and Kilpatrick (reference 26), except formic and o-nitrobenzoic from Wynne-Jones (reference 7).

This simple picture would make this correction independent of solvent. The values of K_x should, therefore, be directly comparable with the K_∞ values of the theory of Wynne-Jones.[7] He has shown that $\log K_{A,D} - \log K_{B,D}$ should be linear in $1/D$ where $K_{A,D}$, $K_{B,D}$ are the dissociation constants of the acids A, B in a solvent of dielectric constant D. Extrapolation to $1/D=0$ gives K_∞. This equation follows from the equation of Born if the ionic radii of the anions are independent of solvent, and if "exchange" forces can be neglected. By considering, as he does, only the differences in the log K's one avoids the difficulties due to chemical solvation of the proton, and to uncertainty as to the concentration scale on which free energy differences should be expressed to be comparable in different solvents, and the exchange effects are reduced to the differences as between various acids. This equation has been recently investigated by Minnick and Kilpatrick,[26] who show it to be valid for similar solvents such as water, the alcohols and dioxane-water mixtures if $D>25$ or so, but to fail for solvents of different chemical type or lower D, in agreement with the conclusions of Section II.[27]

In Table VI are given the values of log K_∞' (referred to acetic acid as a standard; taking Minnick and Kilpatrick's value of log K_∞ benzoic $-\log K_\infty$ acetic as $+0.65$), log K_x predicted from the data in Table III, and log K_x' these adjusted to log K_x acetic as zero. It can be seen that the agreement is bad, and a more exact treatment of the whole problem is needed. (In the

[26] Minnick and Kilpatrick, J. Phys. Chem. **43**, 259 (1939).

[27] Cf. also the data of Verhoek, J. Am. Chem. Soc. **58**, 2577 (1936) on acid strengths in formamide.

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second column are given the log K's for water at 25° adjusted to this standard for comparison). In view of this discrepancy which might be expected from the discussion in Section II, it is surprising that a single value Y can be found for the dielectric constant for which the differences between the log K's predicted from the equation $\log K_Y = \log K_X - c/YRT$, are equal to the differences between the log K_∞'s. These values (with $Y=87.7$) are given in the last column of Table VI.

This correlation implies that the shift in the ratio of two dissociation constants in water on going at 25° ($1/D=0.01274$) to an imaginary solvent of $1/D=0.0114$, the slope of the $\log K - 1/D$ graphs being obtained from the temperature coefficients in water, is the same for all the dissociation constants listed, as the shift on going from water at 25° to an imaginary solvent with $1/D=0$, if the slopes are taken from the differences in log K' for different hydroxylic solvents. In terms of the Born equation, this means that the ionic radii to be obtained from the solvent shifts, are greater by a factor of about 9 than those from the temperature coefficients in water, and that this factor is the same for all acids. In this connection, it is suggestive that the values for ionic radii obtained from the ratio of the differences in log K for uncharged and singly positively charged acids in water and m-cresol, would have to be given the high value 5A, if this ratio were interpreted by Born's equation.[28] Further data are needed to be sure that this correlation is not numerical coincidence.

The views advanced by Gurney provide therefore a valuable approximation to the problem of electrostatic influences on ionic dissociation, and predict values of the ionic radii of the correct order of magnitude. Exact test of these values is not at present possible. The equations deduced for the variation in heats of ionization with temperature are supported by the experimental data to within their probable error. The radii so obtained do not, however, account for changes in dissociation constant from solvent to solvent.

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The Effect of Temperature on the Structure of Mercury

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X-ray diffraction patterns of mercury at eight temperatures ranging from −36°C to 250°C have been obtained using Mo $K\alpha$ radiation. The x-ray beam was diffracted from an open mercury surface using the small angle of incidence of 4° 11′, thus permitting observation of a previously unreported peak at a diffraction angle of about 10°. Fourier analyses of the intensity curves gave distribution functions showing the expected shifting and broadening of the maxima with increasing temperature. A small subsidiary peak, which changes position with temperature more rapidly than the others, occurs between the first and second main concentrations of atoms.

INTRODUCTION

THE atomic distribution functions for liquid sodium[1] and potassium[2] have been investigated over a considerable portion of their liquid ranges, but no attempt has been made to investigate mercury above room temperature. Coster and Prins[3, 4] and Debye and Menke[5, 6]

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