Exchange Forces and Electrostatic Forces Between Ions in Solution

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Though the treatment of ionic dissociation by thermodynamic methods has been fruitful, the mechanism can be better understood by the use of statistical mechanics. For this purpose one needs to know the potential energy of the ions as a function of temperature. The work D required to dissociate a molecule or molecular ion consists of two parts, one part D_{el} due to electrostatic forces, and the other D_{non} due to nonelectrostatic forces. As the former varies rapidly with temperature, for each species the value of dD/dT is a guide to the value of D_{el}. It is shown that for acid molecules and molecular ions in aqueous solution the relative values of dD/dT for different types are in the order predicted. Further, the characteristic temperature θ at which the dissociation constant passes through a maximum should depend, not on the value of D, but on the relative magnitudes of D_{non} and D_{el}. It is found that the known values of θ fall into line in accordance with this rule. Between two Hg^+ ions, or two Te^- ions, there will be exchange forces of attraction similar to those which give rise to the molecules Na_2 and Br_2; thus in aqueous solution the ions $(Hg_2)^{++}$ and $(Te_2)^{--}$ are stable, although for them D_{el} is negative.

§1

ALTHOUGH the treatment of gaseous molecules by the methods of quantum mechanics has now become habitual, little has been done to use quantum-mechanical forces to describe the stability and the dissociation of molecules in solution. The author has described[1] the mechanism which determines the heat of ionic dissociation, and suggested that the details of dissociation at different temperatures may be understood by recognizing the magnitude of the exchange forces between pairs of simple ions. Similar ideas have been used, particularly by L. P. Hammett,[2] in accounting for the effect of various substituents on the thermodynamic properties of benzene derivatives, etc., in aqueous solution.

A greater insight into the mechanism of such processes than is possible by a thermodynamic treatment, can be obtained by the use of statistical mechanics. For this purpose we require in the first place a knowledge of the mutual potential energy of the ions. Take then a positive and a negative ion first in a vacuum. Leaving aside the Coulomb forces between them, we know that the nonelectrostatic forces will contribute either (*a*) a repulsion only, or (*b*) an attraction as well as a repulsion; that is to say, this contribution, plotted against the separation *r*, will have the form either of curve *a* in Fig. 1 or of curve *b*. To obtain the total potential energy, this contribution must be combined with the electrostatic energy. If the latter is given by curve *c*, on adding the ordinates to those of curve *a*, curve *d* is obtained; and similarly from curve *b* curve *e* is obtained.

Between two positive ions or two negative ions there will be an electrostatic repulsion, repre-

[1] Gurney, *Ions in Solution* (1936), Chapter 13.
[2] Hammett, J. Chem. Phys. **4**, 613 (1936); J. Am. Chem. Soc. **59**, 96 (1937).

sented by curve f in Fig. 1. But in some cases there are in addition strong exchange forces of attraction similar to the familiar forces between neutral atoms. In the diatomic molecules Na_2 and K_2 it is well recognized that the exchange forces of attraction are almost as simple as in the
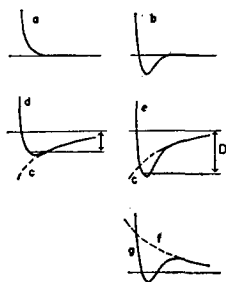
hydrogen molecule H_2, the single valence electron in each atom taking part. Consider now a singly charged calcium ion Ca^+; it has the same electronic configuration as the neutral atom of potassium, namely, with one $4s$ electron outside the core; only the charge on the atomic nucleus is one unit higher. If then we bring together two Ca^+ ions, exchange forces of attraction will be present. But, although two K atoms combine to form K_2, two Ca^+ ions will not in a vacuum combine to form $(Ca)_2{}^{++}$ owing to the electrostatic repulsion between the nuclear charges. If we had some means by which we could cut down the electrostatic repulsion without at the same time cutting down the strength of the exchange forces of attraction, there would be the possibility of obtaining such diatomic ions as $(Ca_2)^{++}$ and $(Hg_2)^{++}$ etc. Now a polar solvent has just the necessary properties. The orientation of the polar solvent molecules causes a large effective reduction in the Coulomb forces. Exchange forces, on the other hand, arise from the rapid circulation of electrons—motion which is so rapid that the heavy solvent molecules can make no response to it. If curve f in Fig. 1 represents the potential energy of a weak electrostatic repulsion, then on combining this with curve b we obtain curve g. In aqueous solution at room temperature the familiar $(Hg_2)^{++}$ ion must possess a potential minimum of this kind sufficiently deep for stability (confirmed by the presence of a Raman spectrum).

Similar exchange forces between halogen atoms give rise to the molecules F_2, Cl_2, Br_2 and I_2. Now the oxygen atom has one electron less than fluorine, and the atoms of sulphur, selenium and tellurium have one electron less than Cl, Br and I, respectively. The singly charged negative ions O^-, S^-, Se^- and Te^- have the same electronic configurations as the halogen atoms, and between any pair of these ions exchange forces of attraction will be present. In any solvent of high dielectric constant the electrostatic repulsion may be so small that diatomic ions with two negative charges are stable. As long ago as 1923 it was, in fact, discovered[3] that in aqueous solution at room temperature tellurium ions exist in the diatomic form $(Te_2)^{--}$.

§2

In the remainder of this paper we are concerned with the potential energy between ions bearing charges of opposite sign, for which curves d and e in Fig. 1 give the appropriate forms. Let the depth of the minimum of curve e be denoted by D. In curve d the depth of the potential minimum is due entirely to electrostatic forces of attraction; but in curve e these electrostatic forces are superimposed on curve b, which already has a potential minimum due to the nonelectrostatic forces. We may therefore write

$$D = D_{\text{nonelectrostatic}} + D_{\text{electrostatic}}. \tag{1}$$

Species of ions for which the potential energy has the form of curve d in Fig. 1 may form short range ion pairs. It is only for species for which the potential energy has the form of curve e that we can draw a distinction between stable molecules in solution and ion pairs; the depth D of the minimum is the dissociation energy of the molecule in solution. The importance of separating this energy into the two parts $D = D_{\text{non}} + D_{\text{el}}$ lies in the fact that exchange forces between a pair of atoms or ions are characteristic of the species concerned and are independent of temperature; while D_{el} depends on the nature and temperature of the solvent. With rise of temperature the curve c of Fig. 1 becomes steeper, and the depth of the minimum becomes greater,

³ Karsanowsky, Zeits. f. anorg. allgem. Chemie 128, 17 (1923).

the increase in D being equal to the increase in D_{el}. In a solvent of dielectric constant K we shall not expect the increase in D_{el} to be strictly proportional to $1/K$ owing to the familiar electrical saturation of the dielectric in the neighborhood of each ion.

Although the methods of this paper are applicable to the dissociation of all species of molecules and molecular ions, the only types for which recent accurate data are available are acid molecules and ions, where a proton (or deuteron) is transferred from the solute to a solvent molecule; we shall accordingly discuss only these. Some years ago Wynne Jones[4] examined the data on the strength of acids in different solvents, and found that they grouped themselves, as we should expect, into three classes, according as the proton is transferred from (1) a neutral molecule, (2) a negative ion, such as $(H_2PO_4)^-$, or (3) a positive ion such as $(NH_4)^+$.

Since then successful attempts have been made to interpret the effects of polar substituents at room temperature.[5] Hammett[6] has also discussed the change of entropy with temperature, recognizing clearly the separate contributions from the electrostatic and nonelectrostatic forces.

To use the methods of statistical mechanics, we need, in addition to the potential energy, a knowledge of the energy levels of the protons. It is well known that in molecules such as HCl the spacing between the vibrational levels is so large that even at temperatures above room temperature practically all the molecules are in their lowest vibrational level. This is due to the small mass of the proton and will be true of the protons with which we shall be concerned here. Suppose first that in a vacuum we have a molecule of an organic acid ROOH and a water molecule side by side; in the ROOH molecule the proton is in a vibrational level inside the electron cloud of one of the oxygen atoms. The water molecule is capable of accommodating an additional proton, to form $(H_3O)^+$; i.e., in the water molecule is a set of vacant vibrational levels for a proton; we are concerned only with

the lowest vibrational level of the set. If the vacant level in the H_2O molecule is higher than the initial occupied level, in order to transfer the proton from one to the other, a certain amount of work will be required. When the proton has been transferred, leaving behind a negative charge on the oxygen atom, an electrostatic field has been created in the surrounding vacuum, having a density of energy equal at every point to $E^2/8\pi$, where E is the intensity of the field; for a molecule in solution similar considerations will apply. The work required to complete the separation of the ions is entirely electrostatic, and D_{el} finally becomes equal to the integral of the energy in the field surrounding the negative ion added to the energy in the field surrounding the $(H_3O)^+$ ion. The latter part is of course the same for all acid molecules. From the usual Born formula,[7] for a molecule which dissociates into a pair of singly charged ions of radius b_+ and b_- we should, in the absence of electrical saturation have

$$D_{el} = \frac{\epsilon^2}{2K}\left(\frac{1}{b_+} + \frac{1}{b_-}\right). \qquad (2)$$

For a pair of small ions in water at room temperature (2) has a value in the neighborhood of 0.1 electron volt. To give the low degrees of dissociation of the familiar weak acids, values of D greater than 0.2 electron volts are required; for most species D_{non} is greater than D_{el}. (If the neutral acid molecule is surrounded by a certain field, because it is polar, the value of D_{el} will more strictly be the difference between the final and initial energies of the field.)

If we consider next processes of the type

$$(NH_4)^+ + H_2O \rightarrow NH_3 + (H_3O)^+$$
$$(C_6H_5NH_3)^+ + H_2O \rightarrow C_6H_5NH_2 + (H_3O)^+ \qquad (3)$$
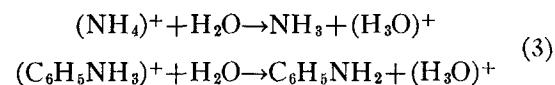
we see that they are different from the dissociation of a neutral molecule, because initially an electrostatic field exists round the positive ion, and the positive charge is merely transferred elsewhere. If the total energy of the field round the $(H_3O)^+$ ion is, for a particular species, the same as the total energy of the field initially surrounding the positive ion, the value of D_{el}

[4] Proc. Roy. Soc. **A140**, 448 (1933).
[5] Schwarzenbach and Egli, Helv. Chim. Acta **17**, 1183 (1934); Schwarzenbach and Epprecht. ibid **19**, 493 (1935).
[6] Hammett, reference 2, p. 101.

[7] Born, Zeits. f. Physik. **1**, 45 (1920); compare Hammett, reference 2, p. 102.

for this process will be zero. It will be convenient to name this an *isoelectric* transference of a proton. For dissociations similar to (3), even when they are not approximately isoelectric, the value of D_{el} will at any rate be much smaller than in those dissociations where we create a positive and a negative charge.

Intermediate between these two types lie dissociations like that of the glycine ion:

$$NH_3^+CH_2COOH + H_2O \rightarrow$$
$$NH_3^+CH_2COO^- + H_3O^+. \quad (4)$$
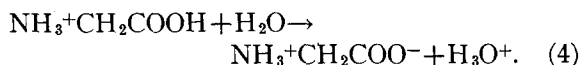
As in (3) we begin with a positive ion, and end with a molecule which as a whole is electrically neutral, but which here bears opposite charges on its two ends; their electrostatic field may possess a considerable energy, though not, of course, as much as a pair of separate ions. The same applies to the other mode of dissociation of glycine:

$$H_2O + NH_2CH_2COO^- \rightarrow$$
$$OH^- + NH_3^+CH_2COO^-. \quad (5)$$
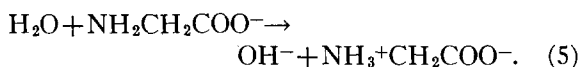
In this case the electrostatic work of transferring the proton should be diminished by the negative charge already on the glycine ion, which will attract the proton. In (4) above the electrostatic work is diminished by the repulsion of the positive charge on the glycine ion; we expect then a smaller D_{el} than that for a neutral ROOH molecule, as already stated. On the other hand, in the dissociation of a negative ion, for example

$$(H_2PO_4)^- + H_2O \rightarrow (HPO_4)^= + H_3O^+ \quad (6)$$

we expect D_{el} to be greater than for a neutral molecule.

In the next section we shall examine the rate of variation of D with temperature for these four types of dissociation. We shall expect no correlation between this rate and the value of the total D. For a large or small value of D_{el} may be accompanied by a large or small D_{non}; and it is only D_{el} that changes. Over the range of temperature from 0°C to 60°C for which measurements are available, the dielectric constant of water falls from 88.31 to 66.62;[8] the value of $1/K$ rises from 0.01133 to 0.01502, that is, by 33 percent. If then the electrostatic energy were strictly proportional to $1/K$, the value of D_{el}

would also increase by 33 percent. Though this will not be so, we must expect that dD/dT will be large when D_{el} is large, and small when D_{el} is small.

<center>§3</center>

In expressing the dissociative equilibrium at temperature T, to ensure that the partition functions of the various particles are measured from the same zero of energy, the factor $e^{-D/kT}$ must be inserted. The relation between the activities of the positive and negative ions, a_+ and a_-, and the activity of the neutral molecule a, is then

$$a_+ a_-/a = \mathbf{K} = Ce^{-D/kT}, \quad (7)$$

where the statistical factor C depends on the solvent only, and is the same for all solutes. (In the second dissociation of an acid an additional statistical factor $\frac{1}{4}$ enters.) For substances in aqueous solution at room temperature it is well known that for some species the dissociation constant $\mathbf{K}$ increases with rise of temperature, and for others falls. The description given here accounts for the characteristic behavior of each type. For (7) takes the form

$$-\ln \mathbf{K}/C = D_{non}/kT + D_{el}/kT. \quad (8)$$

For a dissociation which is approximately isoelectric the last term will be absent, and (8) is found to take the form

$$-\log \mathbf{K} = A/T + B, \quad (9)$$

where A and B are constants.[9] For neutral molecules, on the other hand, this will not be so. For five species of neutral molecule Harned and his co-workers find that the value of $\mathbf{K}$ passes through a maximum value at a certain temperature θ characteristic of each substance, and the variation of log $\mathbf{K}$ can in each case be represented approximately by a parabola

$$\log \mathbf{K}_{max} - \log \mathbf{K} = p(T - \theta)^2 \quad (10)$$

with the same value of p for all.[10] It will appear that this approximate regularity of behavior is due to the change in the dielectric constant of the water in which all the substances are dissolved.

[8] Akerlof, J. Am. Chem. Soc. **58**, 1842 (1936).

[9] Pedersen, Dansk. Vidensk. Selsk. 14 (1937); also measurements for the $(NH_4)^+$ ion over the range from 5° to 45°C will be published shortly by Wynne Jones.

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

Consider any two substances in aqueous solution at temperature T. Let their dissociation constants be $\mathbf{K}$ and $\mathbf{K}_r$, respectively; and at temperature T' let the values be $\mathbf{K}'$ and $\mathbf{K}_r'$. Then from (7) we shall have the equations

$$D' - D = kT \ln \mathbf{K} - kT' \ln \mathbf{K}'$$
$$\qquad - kT \ln C + kT' \ln C',$$
$$D_r' - D_r = kT \ln \mathbf{K}_r - kT' \ln \mathbf{K}_r' \qquad (11)$$
$$\qquad - kT \ln C + kT' \ln C'.$$

On subtracting the second from the first, we obtain

$$(D' - D) - (D_r' - D_r)$$
$$\qquad = kT \ln (\mathbf{K}/\mathbf{K}_r) - kT' \ln (\mathbf{K}'/\mathbf{K}_r'). \qquad (12)$$

If now the dissociation to which $\mathbf{K}_r$ refers is nearly isoelectric, while the other is not, the value of $(D_r' - D_r)$ will be small compared with $(D' - D)$. The variation of $\mathbf{K}_r$ will be given by an expression of the form (9) above. If, taking the observed values of $\mathbf{K}$ for several other species of molecules, we substitute them in (12), we can obtain values of the change in D for each of them relative to a single reference substance (or relative to each other). This has been done for different types in Table I.[11] Similarly the relative values of dD/dT at 25°C have been obtained from the expression

$$(d/dT)(D - D_r) = (d/dT)(kT \ln (\mathbf{K}_r/\mathbf{K}) \qquad (13)$$

using the empirical power series given in the original papers. Apart from the figures in the last column, the values have been calculated taking $\log \mathbf{K}_r = A/T + B$, with B equal to 0.614, the value found recently by Pedersen[9] for the

TABLE I.

	TEMP.	$(D'-D)$ $-(D_r'-D_r)$ ELECTRON VOLTS	$(d/dT)(D-D_r)$ AT 25°C ϵ-VOLTS PER 1°C	
$(H_2PO_4)^-$	20°–50°C	0.0414 in 30°	13.1×10⁻⁴	15.4×10⁻⁴
Acetic acid	0°–60°	0.0662 in 60°	10.8	13.1
Glycine $\mathbf{K}_B$	10°–45°	0.0205 in 35°	5.5	7.8
Glycine $\mathbf{K}_A$	10°–40°	0.0126 in 30°	4.2	6.5
Anilinium		(0.00)	(0.0)	2.3

[11] I have not included values for the $(HSO_4)^-$ ion, derived from the measurements of Hamer (J. Am. Chem. Soc. **56**, 860 (1934)), because in Chicago I learned from Professor T. F. Young that a calorimetric measurement of the heat of dissociation had yielded a value twice as great as that given by Hamer; a still higher value has recently been published by Pitzer (J. Am. Chem. Soc. **59**, 2365 (1937)).

TABLE II.

	TEMP.	D IN ELECTRON VOLTS	dD/dT AT 25°C
$(H_2PO_4)^-$	50°C	0.534	15.3×10⁻⁴
	0°	0.486	
Acetic acid	60°	0.433	13.0
	0°	0.353	
Glycine $\mathbf{K}_B$	45°	0.369	7.7
	10°	0.341	
Chloracetic acid	40°	0.289	10.5
	0°	0.247	
Glycine $\mathbf{K}_A$	40°	0.252	6.4
	10°	0.233	
H_3PO_4	50°	0.257	10.2
	0.3°	0.206	
Water *	60°	1.090	15.1
	0°	0.998	
HCl estimate †	25°	−0.31	—

* Harned and Hamer, J. Am. Chem. Soc. **55**, 2194 (1933).
† Ebert, Naturwiss. **13**, 393 (1925); Wynne Jones, J. Chem. Soc. 1064 (1930).

anilinium ion. In the last column of the table are given for comparison values calculated taking B equal to 1.772, the value found by Pedersen for the o-chlor-anilinium ion.[12]

It will be seen that for the different types the values lie in the order predicted above. The most rapid variation with temperature is found for the negative ion $H_2PO_4^-$. Next comes the neutral molecule of acetic acid; and the values for the other similar acids fall here. Then the glycine values lie between acetic acid and the anilinium ion, as they should.

§4

As these results derived from (7) are satisfactory, we may discuss (7) further. When dissociation of a molecule or ion has taken place, the result is that the proton is now vibrating in the interior of a water molecule instead of in the interior of the original molecule or ion. In a solution we need to know the ratio of the number of available levels for the proton in the solvent molecules to the number of levels in the solute; this ratio determines the statistical equilibrium. As we are concerned only with the lowest vibrational level in each case, there is one level for the proton in each water molecule. The activities a_+ and a_- are usually expressed in moles per liter; since one liter of water contains 55.5 mole of water, the value to be assigned to the factor C in (7) according to the above simple scheme is 55.5 for the first dissociation of any acid. For the second dissociation of a dibasic

[12] Pedersen, Dansk. Vidensk. Selsk. 15 (1937).

acid, the value will be one-quarter of this, that is 13.9. As it seems worth while at least to explore the simplest assumptions, values of D calculated in this way from experimental values of $\mathbf{K}$ are given in Table II. If 55.5 is held to represent merely an upper limit to the number of available levels in the water molecules, each value of D in the table must be regarded as an upper limit.

It will be noticed that the values of dD/dT are almost identical with the corresponding values in the last column of Table I. The reason for this is that Pedersen's empirical expression for the o-chlor-anilinium ion, used above, may be written $\mathbf{K} = 59.2e^{-D/kT}$. Or, in other words, use of the value $C = 55.5$ is equivalent to expressing results relative to a reference $\mathbf{K}_r$ given by $\log \mathbf{K}_r = A/T + \log 55.5$.

Included in the table are values for the self-dissociation of water: $2H_2O \rightarrow H_3O^+ + OH^-$, which has the equilibrium

$$a_+ a_- / a^2 = e^{-D/kT}, \qquad (14)$$

where a^2 has been taken equal to $55.5^2 = 3080$. The very small dissociation of water must be due to the presence of a large D_{non}; there is no reason why D_{el} should be very different, since the dissociation produces a $(H_3O)^+$ ion and a negative ion, as from any neutral molecule. As we are taking the magnitude of dD/dT as a guide to the value of D_{el}, we expect the value of dD/dT for water to be similar to that for acetic acid, or a little larger, since the OH^- ion has a small radius and the energy of its electrostatic field may be somewhat larger than for a $(ROO)^-$ ion. It is satisfactory to see from Table II that this is so.

We have hitherto spoken of the dissociation energy D as if it were necessarily positive. There is, however, no difficulty in imagining a neutral acid molecule in which the energy level of the proton is higher than the vacant level in the solvent molecule. For such a substance in dilute solution nearly all the protons will have been transferred to solvent molecules, the small number remaining behind, to form acid molecules, being in accordance with the Boltzmann law. The electrostatic part of D is necessarily positive; but, when D_{non} has a large negative value, the total dissociation energy D may be negative.
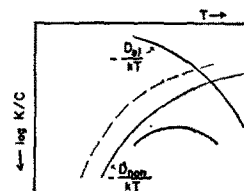

FIG. 2.

For a particular species of acid molecule the value of D may clearly be positive in one solvent and negative in another. For illustration a rough value of D for HCl in water has been included in Table II, based on estimates of $\mathbf{K}$.

§5

The variation of D_{el} with temperature is intimately connected with the characteristic temperature θ at which $\mathbf{K}$ becomes a maximum. As Table III shows, there is no correlation at all between the degree of dissociation of a substance and the value of θ assigned to it. The ideas outlined in this paper may therefore be subjected to a severe test by enquiring whether they account for these seemingly haphazard values.

When with rising temperature the value of $\mathbf{K}$ reaches a maximum, and begins to fall off, this is because the potential minimum of curve e in Fig. 1 is becoming rapidly deeper. Eq. (8) may be put into the form

$$-\log \mathbf{K}/C = A/T + f(T), \qquad (15)$$

where $A = D_{non}/k$, and $f(T) = D_{el}/kT$. In Fig. 2 the principal intersecting curves are intended to represent $-A/T$ and $-f(T)$, respectively, for a particular species of molecule, e.g., acetic acid. Adding the ordinates of these two curves, one obtains the lower curve with a maximum, which is Harned and Embree's parabola. The diagram shows clearly how the characteristic temperature θ, at which the maximum occurs, depends upon the relative magnitudes of the electrostatic

TABLE III.

		$-\log \mathbf{K}$ at 25°	θ	dD/dT at 25°
(1)*	H_3PO_4	2.123	$-18.0°C$	8.0×10^{-4}
(2)	Glycine $\mathbf{K}_A$	2.350	$+53.9$	4.2
(3)	Chloracetic acid	2.861	-5.4	8.6
(4)	Formic acid	3.752	$+24.7$	8.7
(5)	Glycine $\mathbf{K}_B$	4.219	93.0	5.5
(6)	Acetic acid	4.757	22.6	10.8
(7)†	n-Butyric acid	4.817	8.0	11.7
(8)	$(H_2PO_4)^-$	7.206	43.1	13.1

* Nims, J. Am. Chem. Soc. 56, 1110 (1934).
† Harned and Sutherland, J. Am. Chem. Soc. 56, 2040 (1934).

and nonelectrostatic parts of the dissociation energy. In comparing two different species of molecules, if we have nearly the same electrostatic forces but weaker exchange forces, a curve for D_{non}/kT like the broken line in Fig. 2 will be used for the latter. It is obvious that, on adding the ordinates, the maximum of the lower curve will be shifted upward and to the left; i.e. the substance will be more highly dissociated and the maximum will occur at a lower temperature. The behavior of phosphoric and chloracetic acids, relative to acetic acid, affords an illustration of this. Their values of K are respectively about 500 times and 100 times as large as for acetic acid, while θ lies below the freezing point; the values $-18°$ and $-5.4°$ have been assigned to them, respectively. If the high degree of dissociation were due mainly to weak electrostatic forces, θ would be *higher* than for acetic acid, as is clear from Fig. 2. But, as the dissociation creates a positive and a negative ion, we expect a normal D_{el}, and indeed the value of dD/dT shown in Table II indicates a value of D_{el} differing little from the other acids. The low value of D is therefore due to a small D_{non}, and the low value of θ is anticipated. On the other hand, for both dissociations of glycine we believe the electrostatic forces to be small. Their exceptionally high values of θ, namely $53°$ and $93°C$ are therefore satisfactory.

In the further dissociation of the $(H_2PO_4)^-$ ion we have strong electrostatic forces, and these

FIG. 3.

by themselves would make the value of θ lower. The observed value of θ is, however, $43.1°$, as compared with $22.6°$ for acetic acid. This is not in disagreement with the theory but affords additional evidence in its favor; for the value of K is some 300 times *smaller* than for acetic acid, showing the presence of a much larger D_{non}, which in Fig. 2 shifts the maximum of the curve downwards and to the right. This behavior may be contrasted with that of the bisulphate ion $(HSO_4)^-$; here, in spite of the large D_{el}, the value of K is nearly 1000 times *greater* than that of acetic acid; we should expect an exceptionally low value of θ; and, indeed, Harned assigned the value $-27.6°$ to it, a temperature lower than for any other substance investigated.

The value of θ for any substance thus depends upon the relative magnitudes of the two parts of the dissociation energy D_{non} and D_{el}. But it would perhaps be more convincing to express this in terms of experimental quantities, without mentioning D_{non} and D_{el}. Now for different species we have been taking the value of $(d/dT)(kT \ln (K_r/K))$ as a relative measure of D_{el}; and for different species the value of $\log K$ is a relative measure of the total D. Suppose then that for each dissociation we define a quantity x by

$$x = (-\log K)/(dD/dT), \qquad (16)$$

both terms being taken at room temperature, then x is a measure of the ratio of D to D_{el}, and θ should be a smooth function of x (though it shows no correlation with either the numerator or the denominator taken separately). The success of this maneuver, shown in Fig. 3, is satisfactory. In the figure the numbering of the points corresponds to the numbering of the substances in Table III, where they are arranged in the order of $\log K$. This treatment should have equal success for substances in nonaqueous solution, when sufficient data are available.

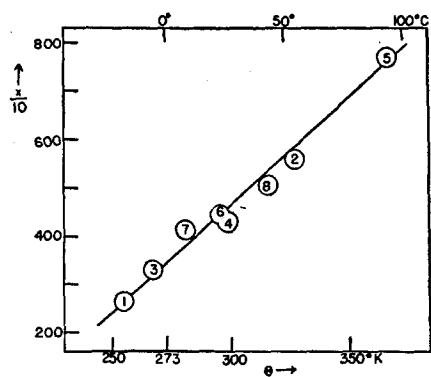The simplified discussion given in these last two paragraphs is merely a step towards a more elaborate statistical treatment.