

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Conductance of Non-Aqueous Solutions. II. The Temperature Coefficient of Conductivity

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In the first paper of this series data were given for the conductivity of sodium triphenylboron and disodium tri- α -naphthylboron at 0° and at 25°.¹ Both of these compounds exhibit a smaller equivalent conductance at the higher temperature. A negative temperature coefficient of conductance has been discussed by Kraus² and many examples given. This is the first time, however, that a negative temperature coefficient has been found for a solution of such high dilution where the simple mass law may be applied to the reaction of dissociation. The purpose of this paper is to discuss the significance of the heat of dissociation as calculated from conductivity measurements.

In general the equivalent conductance of electrolytic solutions increases with rise in temperature. This may be due to two causes, first the increased mobility of the ions, due to a lower viscosity of the solvent at the higher temperature, and second to the fact that the electrolyte, when not completely dissociated, may dissociate more as the temperature is raised. Kraus has explained the negative temperature coefficient as being due to the fact that increased mobility of the ions is more than offset by the decrease in the dielectric constant of the solvent with the result that ionization is less at the higher temperature.

The dielectric constant of a typical ionizing solvent has a negative temperature coefficient. The consequent effect upon the dissociation constant appears at first sight to be of opposite sign, according to whether thermodynamic or molecular-kinetic reasoning is applied. The kinetic picture predicts smaller ionization at higher temperature due to the greater force of attraction which must be overcome. The thermodynamic treatment seems to indicate that ΔH should be positive, since it requires addition of energy to separate charges and therefore the equilibrium constant should increase with rise in temperature.

The solution of this paradox is evident from the following. In the first approximation, the equilibrium constant as given by statistical theory³ assuming purely electrostatic forces is

$$\ln K = -e^2/aDkT$$

It is evident from this equation that two cases of decreasing dielectric constant present themselves. In the first case the dielectric constant may decrease less rapidly than the temperature increases, resulting in an increase in the equilibrium constant with rise in temperature. In the second case the dielectric constant decreases so rapidly that the product DT decreases with rise in temperature. In this case the equilibrium constant will decrease with rise in temperature.

We turn now to the heat of the reaction. The process of separating two ions in solution is not a simple elementary process. Work is required to separate the ions but at the same time the molecules of solvent are subjected to an electrostatic field. It is well known that the polarization of a dielectric whose dielectric constant has a temperature coefficient involves entropy changes. This may be referred to the orientation of the dipole molecules of which the dielectric consists. Providing that there is no other interaction between the electrolyte and the solvent there will be a decrease in the heat content of the system which will be equal to this entropy change multiplied by the temperature. The value of ΔH for the reaction will therefore be equal to the increase in heat content due to the work of separating the ions and the loss of energy associated with the orientation of the dipoles of the solvent. In water solution, this effect causes the heat of dilution of strong electrolytes to have the opposite sign from the free energy, and an analogous effect would be expected to be shown by the heat of ionization in other solvents so long as this is regarded as a purely electrostatic phenomenon. Since the separation of two adjacent ions of opposite sign subjects the surrounding medium to a strong field, and thereby produces a polarization which is an essential part of the mechanism, we must interpret Fuoss' statement about no interaction of the solute with the solvent to mean no interaction other than that just described.⁴

In the general problem of correlating thermodynamic quantities with variation in molecular structure in a series of chemical reactions one

(1) Bent and Dorfman, *THIS JOURNAL*, **57**, 1924 (1935).

(2) Kraus, "The Properties of Electrically Conducting Systems," Chemical Catalog Co., New York, 1922, p. 144.

(3) Fuoss and Kraus, *THIS JOURNAL*, **55**, 1022 (1933).(4) Fuoss, *Chem. Rev.*, **17**, 29 (1935).

chooses the heat of reaction. This is justified by the fact that ΔH for a reaction is usually a less complicated quantity than ΔF . (The change in pV is usually insignificant and therefore justifies the use of the heat of the reaction in place of the change in total energy.) The free energy change for a reaction involves not only the change in internal energy but also the entropy change which in turn depends on the choice of units for expressing concentration. Thus the values for the strength of a bond as determined from an analysis of band spectra are reported as values of ΔH .

In the case of the dissociation of an electrolyte in solution, however, the situation is quite the reverse. ΔF is here a very much simpler quantity than ΔH . This arises from the fact that the contribution to ΔH from the solvent, as a result of orientation of the dipoles of the solvent, is exactly canceled by the entropy change for the process of orientation and hence the free energy change for the reaction is the quantity which is directly related to the work of separating ions.

If the dissociation of an electrolyte is not a purely electrostatic phenomenon then ΔH will become a still more complicated function. Thus in general we might expect to find cases in which the work of separating ions would involve not only electrostatic forces but also an additional amount of work depending on the extent to which the bond holding the ions together in a pair partakes of the non-polar character. A fourth contribution will arise when there is specific interaction of an ion with the solvent such as the formation of a coördinate link between an ion and the solvent. In water solution we have data on only a limited number of types of compounds. Many weak acids in water dissociate less as the temperature is raised. This is in harmony with the fact that the dielectric constant of water is decreasing sufficiently rapidly with rise in temperature to cause the product DT to decrease with rise in tem-

perature. Water itself, however, ionizes more as the temperature is raised. This may be taken to indicate that the bond between H and OH in water has a good deal of the non-polar character and hence that ΔH for dissociation is more positive than one would expect from purely electrostatic considerations. Of course the problem of acids in water solution is complicated by the formation of H_3O^+ ions but this would tend to produce the opposite effect.

The experimental data reported by Bent and Dorfman on sodium triphenylboron and disodium tri- α -naphthylboron may be used to give some idea of the order of magnitude of the quantities involved in ether solution. Since it is impossible to do more than estimate a value of Λ_0 these calculations are only of qualitative importance. The equivalent conductance decreases by about 20% in going from 0 to 25°. If we neglect the effect of the change in viscosity this would mean that ΔH would be about -3 kcal. Taking into account the decreased viscosity of the ether would change this value to -6 kcal. We estimate the dissociation constant to be at least as small as 10^{-9} . This figure is obtained by assuming that Λ_0 is equal to at least 10 ohms $^{-1}$, which is a conservative estimate. Hence ΔF is about $+12$ kcal. This gives for the process of ionization a value of -60 entropy units for ΔS .

Summary

1. The negative temperature coefficient for the conductance of sodium triphenylboron and disodium tri- α -naphthylboron is discussed.
2. The role of the solvent in determining ΔH and ΔS is emphasized.
3. The entropy of ionization of sodium triphenylboron is estimated to be -60 entropy units.

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RECEIVED SEPTEMBER 17, 1935