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XI. *Note on the Variation of the Dissociation Coefficient with Temperature.* By S. ROSLINGTON MILNER, B.Sc., 1851 Exhibition Scholar, University College, Bristol*.

THE general theory of mass-action, when applied to the dissociation of a binary electrolyte, shows that the rate at which dissociation goes on is proportional to the concentration (amount in gramme molecules per unit volume of solution) of the undissociated part of the salt; while, along with this, a reverse process, the *association* of the separated ions to form the original undissociated salt again, proceeds at a rate proportional to the joint product of their concentrations—or, since the ions exist in equal amounts—to the square of the concentration of either. The true velocity of dissociation, which one would measure, is of course the difference between the rates of these two actions, and may be written

$$\frac{dc'}{dt} = kc - k'c'^2;$$

where dc'/dt is the velocity at any stage of the process, at which the concentrations of the undissociated and the dissociated parts of the salt are c and c' respectively. When a salt is dissolved in water and dissociates, c continually diminishes, and c' increases, until

$$kc - k'c'^2 = 0, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

a point being reached at which no further change with time is to be noticed.

Equation (1), therefore, which may be written

$$Kc = c'^2, \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

is the relation which according to mass-action exists, when equilibrium is attained, between the undissociated and the dissociated parts of the solution of a salt, however the *total* concentration of the salt (*i. e.* gr. mols. actually present per litre of solution) may vary. The constancy of the coefficient K or c'^2/c was first arrived at by Ostwald, and experimentally proved by him in the case of a large number of organic acids of slight dissociation†; although in the highly dissociated inorganic acids and salts, formula (2) gives results which are considerably different from the experimental values of the

* Communicated by the Author.

† *Zeit. Phys. Chem.* ii. pp. 36 and 270 (1888).

where p is the osmotic pressure of the undissociated molecules, and R the ordinary gas-constant. Transforming C into c , by means of (2) and (4), we have

$$w = \frac{RT}{2\sqrt{K}} \int_{c_2}^{c_1} \frac{\sqrt{c}(K + 2\sqrt{Kc})}{(c + \sqrt{Kc})^2} dc$$

$$= RT \left\{ 2 \log \frac{\sqrt{c_1} + \sqrt{K}}{\sqrt{c_2} + \sqrt{K}} - \frac{\sqrt{K}(\sqrt{c_1} - \sqrt{c_2})}{(\sqrt{c_1} + \sqrt{K})(\sqrt{c_2} + \sqrt{K})} \right\}, \quad (5)$$

where c_1 and c_2 are the initial and final concentrations of the undissociated part of the electrolyte. If we put $K=0$, this of course coincides with the ordinary formula for the work of expansion of a non-dissociable salt,

$$w = RT \log c_1/c_2.$$

The work done during expansion by the two ions of the electrolyte is

$$w' = 2 \int_{V_1}^{V_2} \frac{p'}{V} dV = 2RT \int_{c_2}^{c_1} \frac{c'}{C^2} dC,$$

p' being the osmotic pressure of either of the ions. Transforming this as before into terms of c' only, we find

$$w' = 2RTK \int_{c_2'}^{c_1'} \frac{c'(K + 2c')}{(c'^2 + Kc')^2} dc',$$

which gives on integration

$$w' = 2RT \left\{ \log \frac{c_1'}{c_2'} \cdot \frac{c_2' + K}{c_1' + K} + \frac{K}{c_2' + K} - \frac{K}{c_1' + K} \right\}, \quad (6)$$

c_1' and c_2' being the concentrations of the ions before and after expansion. In (6) if we put $K=\infty$, or the salt is completely dissociated, the work reduces to

$$w' = 2RT \log c_1'/c_2',$$

the ordinary form for a simple mixture of ions.

Before expressions (5) and (6) can be used, they must be changed into terms of the independent variables C_1 and C_2 , the total concentrations, since c and c' are functions of K . This may be simply done by (2) and (4), substituting from which we obtain

$$\begin{aligned}
 w = RT \left\{ 2 \log \frac{\sqrt{K+4C_1} + \sqrt{K}}{\sqrt{K+4C_2} + \sqrt{K}} \right. \\
 \left. + \frac{2\sqrt{K}}{\sqrt{K+4C_1} + \sqrt{K}} - \frac{2\sqrt{K}}{\sqrt{K+4C_2} + \sqrt{K}} \right\}, \\
 w' = 2RT \left\{ \log \frac{\sqrt{K+4C_1} - \sqrt{K}}{\sqrt{K+4C_2} - \sqrt{K}} \cdot \frac{\sqrt{K+4C_2} + \sqrt{K}}{\sqrt{K+4C_1} + \sqrt{K}} \right. \\
 \left. - \frac{2\sqrt{K}}{\sqrt{K+4C_1} + \sqrt{K}} + \frac{2\sqrt{K}}{\sqrt{K+4C_2} + \sqrt{K}} \right\}.
 \end{aligned}$$

The complete work of expansion W is $w + w'$, or

$$\begin{aligned}
 2RT \left\{ \log \frac{\sqrt{K+4C_1} - \sqrt{K}}{\sqrt{K+4C_2} - \sqrt{K}} - \frac{\sqrt{K}}{\sqrt{K+4C_1} + \sqrt{K}} \right. \\
 \left. + \frac{\sqrt{K}}{\sqrt{K+4C_2} + \sqrt{K}} \right\} \quad \quad (7)
 \end{aligned}$$

This is the external work done by the osmotic pressure while the solution expands isothermally from concentration C_1 to C_2 , the equivalent W of heat being drawn from the surroundings. A further amount of heat H is also absorbed due to the dissociation of the dissolved substance as the dilution proceeds. The amount dissociated during the dilution is

$$\left(\frac{c_2'}{C_2} - \frac{c_1'}{C_1} \right) \text{ gr. mols. ;}$$

so that if Q is the heat absorbed in the dissociation of 1 gr. mol.,

$$H = Q \left(\frac{c_2'}{C_2} - \frac{c_1'}{C_1} \right),$$

or

$$\begin{aligned}
 H = Q \cdot \frac{\sqrt{K}}{2} \left\{ \frac{1}{C_2} (\sqrt{K+4C_2} - \sqrt{K}) \right. \\
 \left. - \frac{1}{C_1} (\sqrt{K+4C_1} - \sqrt{K}) \right\} \quad \quad (8)
 \end{aligned}$$

by (2) and (4).

If this expansion against a semipermeable partition be carried out at temperature T , and then the solution be brought back to its original concentration C_1 by a reverse process at a temperature $T - dT$, the mechanical heat absorbed during this

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cyclic process is

$$W + JH,$$

while the external work performed is

$$\frac{dW}{dT} dT,$$

and by the second law of thermodynamics this last is equal to the fraction dT/T of the heat absorbed. Hence

$$\frac{dW}{dT} dT = \frac{dT}{T} (W + JH). \quad . \quad . \quad . \quad . \quad (9)$$

In equation (7) for W , C_1 and C_2 are constant, so that the only variables are T and K . The differential in T , however, produces $\frac{W}{T} dT$, which goes out with the similar expression on the right-hand side of (9). We therefore have

$$\frac{JH}{T} = \frac{dW}{dK} \cdot \frac{dK}{dT},$$

or, after a little algebraical simplification,

$$\frac{JH}{T} = \frac{2RT}{\sqrt{K}} \cdot \frac{dK}{dT} \left\{ \frac{1}{\sqrt{K+4C_2} + \sqrt{K}} - \frac{1}{\sqrt{K+4C_1} + \sqrt{K}} \right\}.$$

Substituting now the expression (8) for H , we obtain

$$\begin{aligned} & Q \{ (\sqrt{K+4C_2} - \sqrt{K})C_1 - (\sqrt{K+4C_1} - \sqrt{K})C_2 \} \\ &= \frac{4RT^2}{K} \cdot \frac{dK}{dT} \cdot C_1 C_2 \left\{ \frac{1}{\sqrt{K+4C_2} + \sqrt{K}} - \frac{1}{\sqrt{K+4C_1} + \sqrt{K}} \right\}; \end{aligned}$$

or, on simplification,

$$Q = \frac{RT^2}{K} \cdot \frac{dK}{dT},$$

which may be written

$$\frac{d(\log K)}{dT} = \frac{Q}{RT^2},$$

the expression already obtained by van 't Hoff.