DIFFERENCES OF POTENTIAL BETWEEN METALS AND NON-AQUEOUS SOLUTIONS OF THEIR SALTS, II

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According to Nernst, the E. M. F. of a galvanic chain of the type

may be calculated by means of the formula¹

$$\pi = \frac{RT}{n_e e_0} \log \frac{C_1}{C_2},$$

when the minor difference of potential at the junction of the two liquids is not taken into account. In this formula π is the E. M. F. of the combination, R the gas constant, T the absolute temperature, n_e the valence of the metal, e_0 the constant of Faraday's law, and C_1 and C_2 the concentrations of the cations, corresponding to the metal of the electrodes, in the concentrated and dilute solutions respectively. Thus far a fair degree of agreement between observed and calculated values of the E. M. F. has been obtained in the case of a number of chains of this character in which water is used as a solvent.

This formula was developed by Nernst on the basis of the assumption that a metal has a definite electrolytic solution tension toward a solvent, and that the osmotic pressure of the ions — of the same nature as the electrode — in the solution opposes this solution tension. In a previous article² on this subject, it was shown that if such electrolytic solution tension be assumed to exist, it must further be held that it changes greatly with the nature of the solvent, and indeed with the presence of other dissolved substances contained in the solvent.

¹ Compare, for instance, LeBlanc, *Lehrbuch der Elektrochemie*.

² Kahlenberg. *Jour. Phys. Chem.* 3, 379 (1899).

The validity of this formula in cases where non-aqueous solutions are employed in galvanic chains of the type under consideration, has, to my knowledge, not been tested. Such a test seemed desirable because it would determine the applicability of Nernst's theory to the case of non-aqueous solutions.

As is evident from the formula, by using but one solvent in the chain, the troublesome quantity, the solution tension, has been eliminated, it being the same on both sides of the galvanic combination. Now C_1 and C_2 are clearly equal to the concentration of the salt in the respective solutions multiplied by the corresponding degree of dissociation. It is necessary, then, to know the latter in each case. How difficult it is to ascertain the degree of dissociation of salts in non-aqueous solutions was shown in my previous article.¹ Indeed it was pointed out clearly that, according to molecular weight determinations, salts are frequently undissociated and yet are good conductors of electricity, a fact which is not compatible with the theory of electrolytic dissociation.

Assuming the theory of electrolytic dissociation, the degree of dissociation of a salt may be calculated according to the formula $\frac{\mu_v}{\mu_\infty}$, where μ_v is the molecular conductivity of a solution containing 1 g.-mol of the salt in V liters, and μ_∞ the molecular conductivity at infinite dilution.

If, in the above chain, S_1 and S_2 represent the concentrations of the salt in the concentrated and dilute solutions respectively, then the formula for the E. M. F. becomes

$$\pi = \frac{RT}{n_e \epsilon_0} \log \frac{S_1 \frac{\mu_{s1}}{\mu_\infty}}{S_2 \frac{\mu_{s2}}{\mu_\infty}},$$

which reduces to

$$\pi = \frac{RT}{n_e \epsilon_0} \log \frac{S_1 \mu_{s1}}{S_2 \mu_{s2}}.$$

¹ l. c.

From this it appears that in order to test the formula for the E. M. F. of the chain, the concentration of the salt solutions and the electrical conductivities of the latter are the only quantities that need be known. It is fortunate that μ_{∞} thus cancels out, for it is just the quantity that it is generally impossible to ascertain in the case of non-aqueous solutions.¹

The metals employed in making up the galvanic chains measured are silver and cadmium. The solutions used are silver nitrate in pyridine and in acetonitrile and cadmium iodide in acetonitrile. These solutions were chosen because their electrical conductivities have been determined.

The cells measured and the results obtained are as follows :

1. $\overset{+}{\text{Ag}} | n/10 \text{ AgNO}_3 \text{ in pyridine} | n/100 \text{ AgNO}_3 \text{ in pyridine} | \bar{\text{Ag}} \text{ } 0.035 \text{ volt.}$
2. $\overset{+}{\text{Ag}} | n/10 \text{ AgNO}_3 \text{ in pyridine} | n/500 \text{ AgNO}_3 \text{ in pyridine} | \bar{\text{Ag}} \text{ } 0.061 \text{ volt.}$
3. $\overset{+}{\text{Ag}} | n/10 \text{ AgNO}_3 \text{ in pyridine} | n/1000 \text{ AgNO}_3 \text{ in pyridine} | \bar{\text{Ag}} \text{ } 0.076 \text{ volt.}$
4. $\overset{+}{\text{Ag}} | n/8 \text{ AgNO}_3 \text{ in acetonitrile} | n/128 \text{ AgNO}_3 \text{ in acetonitrile} | \bar{\text{Ag}} \text{ } 0.046 \text{ volt.}$
5. $\overset{+}{\text{Cd}} | \text{CdI}_2 \text{ in acetonitrile} | \text{CdI}_2 \text{ in acetonitrile} | \bar{\text{Cd}} \text{ } 0.032 \text{ volt.}$
(1 g.-mol in 48.9 liters) (1 g.-mol in 214.7 liters).

The apparatus used and the method employed in making the determinations have been previously described.² The measurements are accurate to one millivolt. In each case, after measuring the E. M. F. of the above chains, the electrodes were washed with distilled water, then thoroughly wiped with clean filter-paper and interchanged, after which the E. M. F. was again determined. The results thus obtained always agreed to within 0.001 volt. The silver electrodes were cut from one and the same piece of pure sheet silver. The cadmium electrodes were in the form of sticks and were made from one and the same stick of Schuchardt's C. P. cadmium.

In the formula

¹ Compare the discussion in my previous article, 1. c.

² Kahlenberg. 1. c.

$$\pi = \frac{RT}{n_e \epsilon_0} \log \frac{S_1 \mu_{s1}}{S_2 \mu_{s2}}$$

$\frac{RT}{n_e \epsilon_0} = 0.058$, when $T = 290$, and $n_e = 1$, as in the case of silver. when $n_e = 2$, as in the case of cadmium, $\frac{RT}{n_e \epsilon_0} = 0.029$.

The molecular conductivities of the solutions used in the above chains are as follows:

AgNO_3 in pyridine¹ (at 25° C.)

V.	μ
10	24.7
100	31.57
500	41.8
1000	47.5 (extrapolated)

AgNO_3 in acetonitrile² (at 25° C.)

V.	μ
8	54.5
128	118.3

CdI_2 in acetonitrile² (at 25° C.)

V.	μ
48.9	33.7
214.7	37.7

The calculated E. M. F. of the above chains are therefore as follows:

¹ According to Lincoln. Trans. Wis. Acad. Sciences, Arts and Letters, 12, 395 (1899). Also Jour. Phys. Chem. 3, 457 (1899).

² According to Dutoit and Friderich. Bull. Soc. Chim. Paris, (3) 19, 321 (1898).

	Found
1. $0.058 \log \frac{0.1 \times 24.7}{0.01 \times 31.57} = 0.052$ volt	0.035 volt
2. $0.058 \log \frac{0.1 \times 24.7}{0.002 \times 41.8} = 0.085$ "	0.061 "
3. $0.058 \log \frac{0.1 \times 24.7}{0.001 \times 47.5} = 0.099$ "	0.076 "
4. $0.058 \log \frac{0.125 \times 54.5}{0.0078 \times 118.3} = 0.050$ "	0.046 "
5. $0.029 \log \frac{0.02045 \times 33.7}{0.0046576 \times 37.7} = 0.017$ "	0.032 "

The found voltages have been placed in the last column to facilitate comparison.

The utter disagreement between calculated and found values is at once apparent. Only in chain (4) do we have a tolerable agreement. It is to be noted that in this chain the solutions used are silver nitrate in acetonitrile and that the conductivity of these solutions is relatively high, approximating that of solutions of silver nitrate in water. The application of Nernst's formula to a chain like (4), in which water is used as a solvent, has also yielded satisfactory results.

To be sure, in calculating the E. M. F. according to the formula here used, the difference of potential at the junction of the two solutions has been neglected. Unfortunately, it is not possible to take this into consideration in the calculation,—as might be done by using Nernst's complete formula¹—for the reason that data concerning the rate of migration of the ions in non-aqueous solutions have not been ascertained up to the present time. Still the change that the above calculated values would sustain by such a correction would no doubt be slight, as the E. M. F. at the contact of the solutions in question is very likely relatively small. Just what this E. M. F. at the contact of the solutions is, could, of course, be ascertained experimentally ;

¹ Compare LeBlanc, l. c.

but this would involve making up rather long galvanic combinations, the potential of which would be difficult to measure with a sufficient degree of accuracy, in most cases, at least, on account of the high resistance that non-aqueous solutions generally have.

The results here given show that Nernst's formula does not, in general, enable one to calculate the E. M. F. of concentration chains in which non-aqueous solutions are used. The single exception above noted, in which a tolerably satisfactory agreement between calculated and found values is obtained, is possibly a mere coincidence due to the fact that the conductivity of the non-aqueous solution approximates that of the aqueous solution in this case.

In the face of these facts and those presented in my previous article, it would be well to subject this formula to a more rigid test, even in the case of aqueous solutions. The electrical conductivity of non-aqueous solutions is being investigated further in this laboratory. As the results of these labors are obtained, they will be employed in testing further the formula here under consideration.

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