

It was of interest to learn whether these relations could be extended in the manner suggested by the deductions of Poma and Albonico<sup>1</sup> regarding the neutral salt effect on the hydrolysis of esters. If their deductions were applicable here equimolecular amounts of metallic salts such as chlorides, for instance, should produce an increasing volatility with the decreasing electro-affinity of the metallic ion of the added salt. Experiments with 0.25 *M* solution of the chlorides of potassium, sodium, barium, strontium, calcium, magnesium, aluminum, manganese, iron and copper were carried out. The volatility was, slightly and progressively, a little increased for each member of this series over the preceding member up to and including aluminum, except in the case of strontium and calcium, for which the order given above should be reversed. The solutions of manganese, iron and copper chlorides showed anomalies and give increases in volatilities lower than aluminum chloride.

Part of the results are given in graphic form in Fig. 4. The results for sodium and barium chlorides are so nearly alike that the results for sodium chloride only were plotted (Curves III and IV).

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

## THE DEGREE OF IONIZATION OF VERY DILUTE ELECTROLYTES.

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The ionic theory in its earlier days would have suffered greater criticism than it received if it had been generally known how great were the discrepancies between the actual behavior of electrolytes and that which was calculated so confidently from the various equations in common use. The failure of the mass law for strong electrolytes was recognized, but in the case of uni-univalent electrolytes, which were most commonly studied, this could be attributed to minor errors in the measurement of conductivity or in Kohlrausch's law of the constancy of ionic mobilities. However, as quantitative data accumulated regarding electromotive force, freezing points, solubilities and the like, it became increasingly evident that the equations generally employed lead to errors which were never trivial and which in some cases became enormous.

The equations in question were based in part upon a safe foundation of thermodynamics, but also in part upon two assumptions of doubtful validity. The first of these assumptions was that the concentration of the ions could be obtained from conductivity ratios. The second was the assumption that the ions and undissociated parts of an electrolyte

<sup>1</sup> *Atti accad. Lincei*, 24, I, 747, 979; II, 43 (1915).

follow the laws of the so-called ideal solutions. The discrepancies to which we have referred show that one at least of these assumptions must be incorrect. It was therefore proposed by Lewis to investigate, for each molecular species yielded by an electrolyte, that which might have been termed the effective thermodynamic concentration, and which he called activity.<sup>1</sup> This is a quantity which, at infinite dilution, may be taken as equal to the concentration, but which deviates from the latter when the solution ceases to behave as an ideal solution. With changing concentration the activity of any dissolved substance is related to the free energy by the equation,

$$dF = RTd\ln a, \quad (1)$$

where  $F$  and  $a$  are respectively the free energy and the activity.

The amount of experimental material for such a calculation was at first very meagre, but by summarizing all available information regarding uni-univalent electrolytes Lewis<sup>2</sup> was able to show that in all cases of moderately dilute solutions the ion activity is lower than the ion concentration as determined by the familiar conductivity method. In other words, the ion activity divided by the total concentration of the electrolyte, which he called the corrected degree of dissociation, is less than  $\lambda/\lambda_0$ . Recent studies of the electromotive force of concentration cells and of the freezing points of salt solutions have added greatly to the material available for such calculations. In this paper we will consider only the latter type of measurements and will describe a simple method of calculating the ion activities from freezing-point data.

In the paper just mentioned an equation was developed which permits in the case of dilute solutions<sup>3</sup> the calculation of the free energy of dilution from freezing-point data. This equation is

$$\int dF = 55.5 \frac{\Delta H}{T} \int \frac{d\theta}{c}, \quad (2)$$

where  $F$  is the partial molal free energy of the solute;  $\Delta H$  the molal heat of fusion of ice;  $T$  the temperature of fusion, 273.1°;  $c$  the number of mols of solute in 1000 g. or in 55.5 mols of water; and  $\theta$  is the lowering of the freezing point. This equation by graphical integration gives the free energy of dilution over any range of dilute solutions for which accurate freezing-point measurements are available. The method is, however, time consuming and does not lend itself to extrapolation to high dilutions where accurate experimental determinations are no longer possible. In order to obviate these difficulties we have sought a satisfactory empirical equation connecting  $c$  and  $\theta$ .

<sup>1</sup> Lewis, *Proc. Amer. Acad.*, 43, 259 (1907).

<sup>2</sup> Lewis, *THIS JOURNAL*, 34, 1631 (1912).

<sup>3</sup> The interpretation of freezing-point data in concentrated solutions presents a more complicated problem. See Rodebush, *THIS JOURNAL*, 40, 1204 (1918).

Before discussion the empirical equation we may combine Equations 1 and 2, and find

$$RT \int d \ln a = 55.5 \frac{\Delta H}{T} \int \frac{d\theta}{c}. \quad (3)$$

If the solute is ionized its activity is proportional to the product of the activities of the ions into which the molecule dissociates. Thus in the case of a binary electrolyte if  $a_1$  is the activity of one ion and  $a_2$  of the other, then

$$RT \int d \ln (a_1 a_2) = 55.5 \frac{\Delta H}{T} \int \frac{d\theta}{c}. \quad (4)$$

Now if we write  $x^2 = a_1 a_2$  we may regard  $x$  as the activity of either ion as long as we assume the two to be identical, which in the case of uni-univalent electrolytes is probably justifiable up to a concentration of nearly 0.1 molal. More generally  $x$  is the mean activity of the ions (geometrical mean). Substituting in Equation 4,

$$RT \int d \ln x^2 = 2RT \int d \ln x = 55.5 \frac{\Delta H}{T} \int \frac{d\theta}{c}, \quad (5)$$

or

$$\int d \ln x = \frac{55.5 \Delta H}{2RT^2} \int \frac{d\theta}{c} = \frac{1}{2\lambda} \int \frac{d\theta}{c}, \quad (6)$$

where  $\lambda$ , which we have written in place of  $\frac{RT^2}{55.5 \Delta H}$ , is at once recognized as the theoretical molal lowering, namely  $1.858^\circ$  per mol of solute in 1000 g. of water.<sup>1</sup>

The treatment of a bi-bivalent salt is identical with that just given for uni-univalent salts. In both cases  $x = c$  at infinite dilution, and if we define the thermodynamic, or the corrected, degree of dissociation by the equation  $\gamma = x/c$ , then  $\gamma c$  is the activity of either ion as long as the two activities may be considered as identical. In dealing with an electrolyte of mixed type the matter is a little more complicated. If, in general, a molecule of the electrolyte yields  $n_1$  molecules of the first ion and  $n_2$  of the second, and if we are to define the quantity  $x$  so as to satisfy conditions similar to those above, we must write

$$x = \left[ \left( \frac{a_1}{n_1} \right)^{n_1} \left( \frac{a_2}{n_2} \right)^{n_2} \right]^{1/n}, \quad (7)$$

where  $n = n_1 + n_2$ . Thus for  $\text{La}_2(\text{SO}_4)_3$ ,  $n_1 = 2$ ,  $n_2 = 3$ , and  $n = 5$ . We may still call  $x/c = \gamma$ , the corrected degree of dissociation.

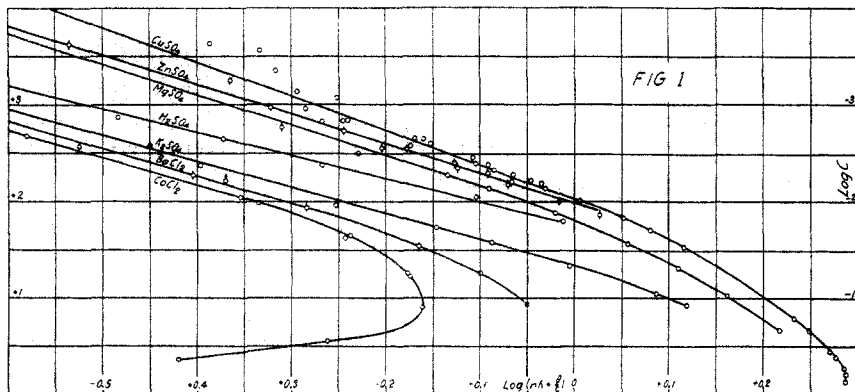
Since the activity of an electrolyte is still proportional to the product of the ion activities raised to the appropriate powers,  $a$  is also proportional to  $x^n$  and we have in general

<sup>1</sup> In the older literature this constant is given as  $1.85^\circ$ . A critical study of the data for the heat of fusion of ice (Lewis, THIS JOURNAL, 30, 681 (1908)) led to the above value, which is now very generally accepted.

$$\int d \ln x = \frac{1}{n\lambda} \int \frac{d\theta}{c} \quad (8)$$

### A General Equation for the Freezing-Point Lowering of Dilute Strong Electrolytes.

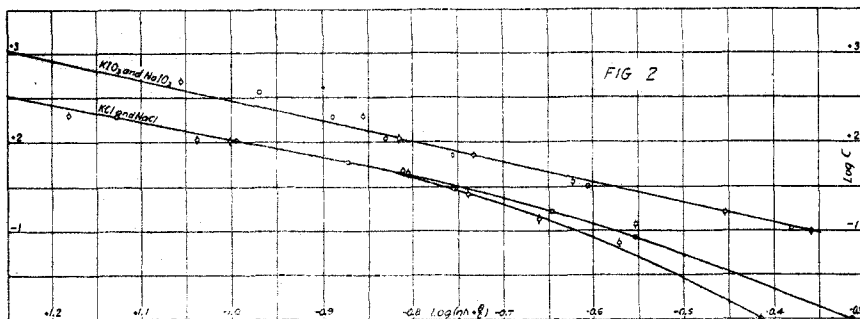
If  $n$  is the number of molecules yielded by the complete ionization<sup>1</sup> of one molecule of the solute the quantity  $(n\lambda - \theta/c)$  approaches zero as  $c$  approaches zero. If we plot the logarithm of this quantity against the logarithm of  $c$  we obtain a most striking result. The curves for all types



of electrolytes approach straight lines as the dilution increases. The more accurate the results, the closer is the agreement with this law, which appears to be one of universal validity. The principle may be expressed in the equation

$$\log(n\lambda - \theta/c) = \alpha \log c + \log \beta, \quad (9)$$

where  $\alpha$  and  $\log \beta$  are constants characteristic of the particular electrolyte. In the plot just referred to  $\alpha$  is the slope of the line, and  $\log \beta$  the inter-

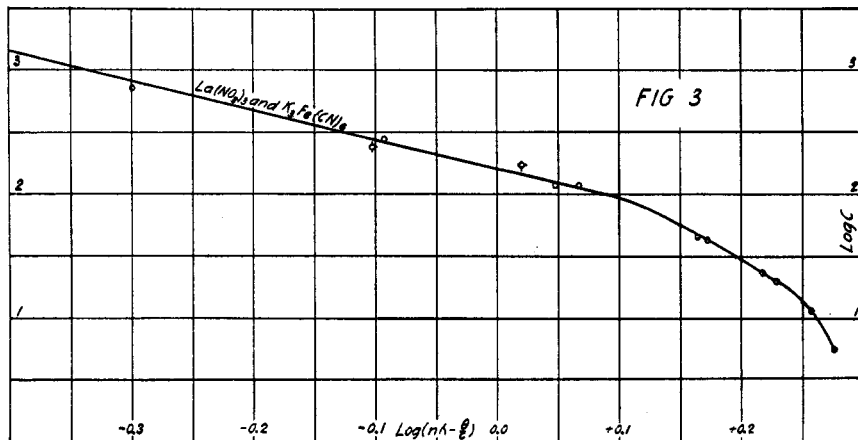


<sup>1</sup> In a thermodynamic calculation such as is to be made here it is of course a matter of choice whether possible intermediate ions are to be considered. For our present purpose it will be more convenient to leave them out of consideration.

section of the line with the axis of  $(n\lambda - \Theta/c)$ . By combining the last two terms of (9) and taking the antilogarithms, we may put our equation in the form

$$n\lambda - \Theta/c = \beta c^\alpha. \tag{10}$$

We have collected in the following tables the freezing-point data of a number of experimenters who have succeeded in attaining a high degree of accuracy. The values for potassium chloride are due to L. H. Adams,<sup>1</sup> and those for sodium chloride to Harkins and Roberts,<sup>2</sup> except that the values at molal concentration for these two salts are those obtained by



Rodebush.<sup>3</sup> The values for sulfuric acid, cadmium and zinc sulfates, and most of those for cupric sulfate, are taken from Hausrath.<sup>4</sup> The remaining points for cupric sulfate, taken from Bedford<sup>5</sup> and from Pick-

UNI-UNIVALENT ELECTROLYTES.

TABLE I. KCl.

$\alpha = 0.535; \beta = 1.223.$

c.	$\Theta.$	$\Theta$ calc. — $\Theta$ obs.
0.00506	0.0184	+0.000040
0.00963	0.0348	0.000000
0.01648	0.0590	0.000000
0.03170	0.1122	.....
0.05818	0.2031	.....
0.1168	0.4014	.....
1.000	3.23	.....

TABLE II. NaCl.

$\alpha = 0.535; \beta = 1.223.$

c.	$\Theta.$	$\Theta$ calc. — $\Theta$ obs.
0.005132	0.0187	—0.000004
0.009544	0.0346	—0.000104
0.009604	0.0347	+0.000012
0.02012	0.0716	+0.000126
0.02120	0.0755	—0.000018
0.03516	0.1243	.....
0.06534	0.2286	.....
(0.08360)	(0.2872)	.....
(0.13600)	(0.4689)	.....
1.000	3.33	.....

<sup>1</sup> L. H. Adams, THIS JOURNAL, 37, 494 (1915).

<sup>2</sup> Harkins and Roberts, Ibid., 38, 2676 (1916).

<sup>3</sup> Rodebush, Ibid., 40, 1204 (1918).

<sup>4</sup> Hausrath, Ann. phys., [4] 9, 522 (1902).

<sup>5</sup> Bedford, Proc. Roy. Soc. London, 83A, 454 (1909).

TABLE III.  $KIO_3$ .

$\alpha = 0.442; \beta = 1.1957$

$\epsilon$ .	$\theta$ .	$\theta$ calc. — $\theta$ obs.
0.00274	0.00990	+0.000038
0.00506	0.01815	+0.000071
0.00903	0.03220	-0.000008
0.01358	0.04810	-0.000080
0.03244	0.1125	-0.000517
0.09380	0.3085	+0.000066

TABLE IV.  $NaIO_3$ .

$\alpha = 0.442; \beta = 1.1957.$

$\epsilon$ .	$\theta$ .	$\theta$ calc. — $\theta$ obs.
0.00212	0.00770	+0.000008
0.00499	0.01785	+0.000114
0.00929	0.03310	0.000000
0.01502	0.05300	-0.000009
0.02868	0.0997	-0.000295
0.06329	0.2129	0.000000
0.10100	0.3317	0.000000

## UNI-BIVALENT ELECTROLYTES.

TABLE V.  $K_2SO_4$ .

$\alpha = 0.374; \beta = 3.187.$

$\epsilon$ .	$\theta$ .	$\theta$ calc. — $\theta$ obs.
0.00274	0.0143	+0.000011
0.00404	0.0209	-0.000021
0.00618	0.0318	-0.000294
0.01039	0.0521	-0.000192
0.01756	0.0854	+0.000135
0.02608	0.1241	0.000000
0.04547	0.2085	.....
0.08899	0.3874	.....
0.12050	0.5120	.....

TABLE VI.  $H_2SO_4$ .

$\alpha = 0.417; \beta = 5.404.$

$\epsilon$ .	$\theta$ .	$\theta$ calc. — $\theta$ obs.
0.0001150	0.000564	+0.000063
0.0003315	0.00158	+0.000204
0.0006458	0.00318	+0.000257
0.001339	0.00703	-0.000024
0.002243	0.01155	0.000000
0.004175	0.02102	-0.000041
0.00942	0.04507	+0.000164
0.01646	0.07569	0.000000

TABLE VII.  $BaCl_2$ .

$\alpha = 0.364; \beta = 2.660.$

$\epsilon$ .	$\theta$ .	$\theta$ calc. — $\theta$ obs.
0.00273	0.0144	-0.000030
0.00534	0.0276	-0.000000
0.01142	0.0577	0.000000
0.02982	0.1458	.....
0.05611	0.2682	.....
0.11358	0.5330	.....

TABLE VIII.  $CoCl_2$ .

$\alpha = 0.362; \beta = 2.456.$

$\epsilon$ .	$\theta$ .	$\theta$ calc. — $\theta$ obs.
0.00173	0.00930	-0.000082
0.00209	0.01110	0.000000
0.00892	0.04575	0.000000
0.01008	0.05149	+0.000019
0.02251	0.1126	.....
0.02375	0.1188	.....
0.05475	0.2688	.....
0.05973	0.2933	.....
0.1256	0.6134	.....
0.2772	1.3932	.....
0.4217	2.1899	.....

## BI-BIVALENT ELECTROLYTES.

TABLE IX.  $MgSO_4$ .

$\alpha = 0.293; \beta = 3.404.$

$\epsilon$ .	$\theta$ .	$\theta$ calc. — $\theta$ obs.
0.00320	0.01000	-0.000131
0.00535	0.01595	0.000000
0.00746	0.02165	+0.000029
0.01310	0.03615	-0.000000
0.02668	0.06730	.....
0.04878	0.1182	.....
0.09566	0.2163	.....
0.2210	0.4566	.....

TABLE X.  $CdSO_4$ .

$\alpha = 0.325; \beta = 4.421.$

$\epsilon$ .	$\theta$ .	$\theta$ calc. — $\theta$ obs.
0.000239	0.00084	-0.000032
0.000704	0.00236	-0.000038
0.001511	0.00482	-0.000014
0.002685	0.00819	+0.000053
0.006560	0.01858	-0.000015
0.01151	0.03094	.....
0.01950	0.04957	.....
0.03120	0.07556	.....



ering,<sup>1</sup> are not of the highest accuracy, but are given to show the trend of the curve in the more concentrated solutions. The same is true of Bedford's values for potassium ferricyanide. The data for all the remaining salts are taken from Hall and Harkins.<sup>2</sup>

These various values have been plotted in Figs. 1, 2 and 3,<sup>3</sup> and the values of  $\alpha$  and of  $\beta$  obtained from the plots are given in the individual tables. The remarkable agreement with the straight line formula is shown not only by the curves but also in the tables, where the difference between the observed values of  $\Theta$  and those calculated from our formula are given for the more dilute solutions.<sup>4</sup>

### Calculation of the Thermodynamic or Corrected Degree of Dissociation.

By rearrangement of Equation 10 we may write

$$\Theta = \lambda nc - \beta c^{\alpha+1}. \quad (11)$$

Differentiating,

$$d\Theta = n\lambda dc - \beta(\alpha + 1)c^{\alpha}dc \quad (12)$$

and dividing both sides by  $n\lambda c$ ,

$$\frac{d\Theta}{n\lambda c} = d\ln c - \frac{\beta(\alpha + 1)c^{\alpha-1}}{n\lambda} dc. \quad (13)$$

This form of our empirical equation we may now combine with the thermodynamic Equation 8, giving

$$\int d\ln x = \int d\ln c - \frac{\beta(\alpha + 1)}{n\lambda} \int c^{\alpha-1} dc. \quad (14)$$

Integrating between  $c_0$  and  $c$ ,

$$\ln x - \ln x_0 = \ln c - \ln c_0 - \frac{\beta(\alpha + 1)}{n\lambda\alpha} (c^{\alpha} - c_0^{\alpha}). \quad (15)$$

Now if we take one of our limits at infinite dilution, namely,  $c_0 = 0$ , then  $x_0 = c_0$ , and

$$\ln x = \ln c - \frac{\beta(\alpha + 1)c^{\alpha}}{n\lambda\alpha} \quad (16)$$

and writing  $\gamma = x/c$ ,

$$\ln \gamma = - \frac{\beta(\alpha + 1)c^{\alpha}}{n\lambda\alpha}, \quad (17)$$

or with common logarithms,

$$\log \gamma = - \frac{\beta(\alpha + 1)c^{\alpha}}{2.303 n\lambda\alpha} \quad (18)$$

<sup>1</sup> Pickering, *Ber.*, 25, 1314 (1892).

<sup>2</sup> Hall and Harkins, *THIS JOURNAL*, 38, 2658 (1916).

<sup>3</sup> In the figures the plain circles are used to denote KCl, KIO<sub>3</sub>, CuSO<sub>4</sub>, MgSO<sub>4</sub>, H<sub>2</sub>SO<sub>4</sub>, K<sub>2</sub>SO<sub>4</sub>, CoCl<sub>2</sub> and La(NO<sub>3</sub>)<sub>3</sub>. The circles with lines drawn through them are used to denote NaCl, NaIO<sub>3</sub>, ZnSO<sub>4</sub>, BaCl<sub>2</sub> and K<sub>3</sub>Fe(CN<sub>6</sub>).

<sup>4</sup> At concentration below 0.001 *M* no great weight can be given to any individual measurement, for below this concentration a large percentage error is inevitable even in the most careful work; thus, at 0.001 *M* an error of 0.0001° is an error of 1% to 3%, depending upon the type of electrolyte.





This equation offers an extremely simple and, we believe, an entirely accurate method of calculating the corrected degree of dissociation of any electrolyte when the constants  $\alpha$  and  $\beta$  are obtained from freezing-point measurements. It is of course applicable only in the range of concentration where the linear formula holds. It would be an easy matter to proceed to higher concentrations either by adding a new term with a new constant to our empirical formula, or by plotting the difference between the actual results and those of the linear formula and thus by graphical methods obtain corrections to the results obtained by Equation 18. However, since the deviations from the linear formula appear at about the concentration where the heat of dilution begins to be measurable, and since these heats of dilution, which are necessary for a calculation of the degree of dissociation at other temperatures, are now being subjected to a thorough investigation in this laboratory, we will here content ourselves with the application of Equation 18 to the dilute solutions where the linear formula holds.

The values for the corrected degree of dissociation, which are obtained from Equation 18 by the use of the values of  $\alpha$  and  $\beta$  given in the preceding tables, are valid for any ordinary temperatures. The values of the percentage ionization,  $100\gamma$ , are given in Table XV.

The extraordinary divergence between the degree of ionization obtained by thermodynamic methods and the degree of ionization as it is ordinarily obtained from conductivity data is very pronounced even in these extremely dilute solutions. The greatest divergence occurs in the case of cupric sulfate, where it has already been observed by Lewis and Lacey.<sup>1</sup> In order to show how great this difference is we give in Table XVI our values of  $\gamma$  at 0.01 molal by the side of the values of  $\lambda/\lambda_0$  given by Noyes and Falk.<sup>2</sup> Even at 0.001  $M$   $\lambda/\lambda_0$  for cupric sulfate is 86.2, while our value is only 52.6.

TABLE XVI.

 $c = 0.01 M.$ 

	KCl.	NaCl.	KIO <sub>3</sub> .	NaIO <sub>3</sub> .	K <sub>2</sub> SO <sub>4</sub> .	BaCl <sub>2</sub> .	CdSO <sub>4</sub> .	CuSO <sub>4</sub> .	La(NO <sub>3</sub> ) <sub>3</sub> .
$\gamma$ .....	0.925	0.925	0.872	0.872	0.687	0.716	0.338	0.290	0.571
$\lambda/\lambda_0$ ....	0.941	0.936	0.928	0.917	0.872	0.883	0.614	0.629	0.802

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<sup>1</sup> Lewis and Lacey, *THIS JOURNAL*, 36, 804 (1914).<sup>2</sup> Noyes and Falk, *Ibid.*, 34, 474 (1912).