

CXVI.—*The Calculation of Activity Coefficients from Solubility Measurements: Thallous Chloride.*

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THE study of activities by the method of solubility measurements with a sparingly soluble salt in the presence of other electrolytes has led to the following generalisations: (1) in very dilute solutions the results furnish a striking verification (Brönsted, *Trans. Faraday Soc.*, 1927, 23, 416) of the Debye-Hückel theoretical equation  $-\log f_{\pm} = A\sqrt{\mu}$ , where  $f_{\pm}$  is the mean ion activity coefficient,  $\mu$  is the ionic strength of the solution, and the constant  $A$  has the value 0.505 for a uni-univalent salt in aqueous solution at 25°; (2) at concentrations greater than 0.01M,  $\log f_{\pm}$  no longer gives a linear relation with  $\sqrt{\mu}$  and depends, moreover, on the nature of the added electrolyte. Thus, Harned (Taylor's "Treatise on Physical Chemistry," 1925, p. 774), speaking of the data on thallous chloride (shown by the series of broken curves in Fig. 2 of this paper), says ". . . the influence of one electrolyte on the activity coefficient of another is a problem of great complexity. Each mixture exhibits individual behavior even in solutions of ionic strength as low as 0.03."

These conclusions are widely accepted, but the figures on which they rest are all based on the assumption that the salts employed are completely dissociated, an assumption which in some instances is invalid. The present paper deals with thallous chloride, the dissociation constant of which is known, and it is shown (1) that in very dilute solutions the value of  $A$  for this salt is much lower than the Debye-Hückel value 0.505, and (2) that when allowance is made for incomplete dissociation, the apparent complexity of the curves disappears, and the activity coefficient is independent of the nature of the other ions present, up to concentrations of 0.1N. Further, this new relationship is shown to be of value for estimating the degree of dissociation of other electrolytes of unknown strength.

*Dissociation Constant of Thallous Chloride.*—The dissociation constant of thallous chloride has been found from conductivity data at 18° to be  $K = 0.31$  (Onsager, *Physikal. Z.*, 1927, **28**, 277) or  $K = 0.30$  (Davies, *Trans. Faraday Soc.*, 1927, **23**, 354). This value has been confirmed by a rather different method (Davies, "Conductivity of Solutions," 1930, p. 141): by evaporating a saturated solution, the Earl of Berkeley (*Phil. Trans.*, 1904, *A*, **203**, 208) found the solubility of the salt to be 0.0132 g.-equiv. per litre (interpolated value at 18°), and by the conductivity method Kohlrausch (*Z. physikal. Chem.*, 1908, **64**, 129) found the value 0.01278 g.-equiv. per litre; the latter figure really represents the ionic concentration of the saturated solution, and the difference between the two values, *viz.*, 0.0004<sub>2</sub>, gives the concentration of undissociated molecules. This agrees very well with the value, 0.00044, calculated from the dissociation constant  $K = 0.30$ .

*Solubility Measurements.*—The solubility of thallous chloride has been measured at 25° in the presence of numerous salts (Noyes, *ibid.*, 1892, **9**, 609; *J. Amer. Chem. Soc.*, 1924, **46**, 1107; Bray and Winninghoff, *ibid.*, 1911, **33**, 1666; Butler and Hiscocks, *J.*, 1926, 2558; Randall and Chang, *J. Amer. Chem. Soc.*, 1928, **50**, 1535). The results in the presence of other univalent chlorides will first be considered, for here the added electrolyte is completely dissociated.

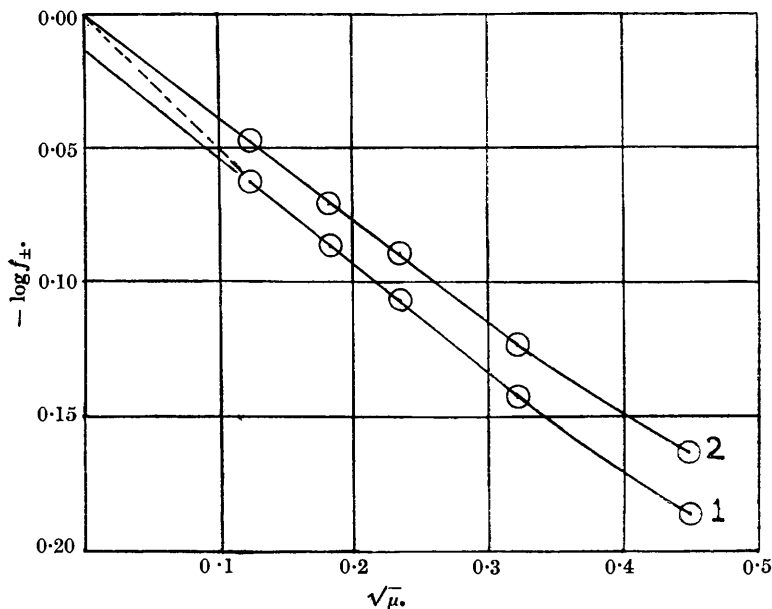
*Solubilities in the Presence of Chlorides of Univalent Metals.*—The degree of dissociation of the pure saturated solution of thallous chloride is first calculated. In the equation  $f_{\pm}^2 c_i^2 / f_u c_u = K$ , where  $c_i$  is the concentration of the ions,  $f_u$  the activity coefficient of the undissociated molecules, and  $c_u$  their concentration, we can put  $K = 0.30$ , and  $f_u$  can be assumed to be equal to unity at low concentrations (compare Randall and Failey, *Chem. Reviews*, 1927, **4**, 291);  $f_{\pm}$  can be calculated from the Debye-Hückel formula by giving  $A$  the value 0.505 as a first approximation, and  $c_i + c_u = 0.01612$ , the solubility of the salt. Solving by successive approximations, we find  $c_i = 0.01552$ ,  $c_u = 0.00060$ ; and for the solubility product,  $S = f_{\pm}^2 \cdot c_i^2 = 18.03 \times 10^{-5}$ .

In a 0.025*N*-potassium chloride solution the solubility of thallous chloride is 0.00872 (Noyes, *loc. cit.*), whence (with  $f_u = 1$ ),  $c_i = 0.00872 - 0.00060 = 0.00812$  and  $f_{\pm}^2 = S / [Cl^-][Tl^+] = 18.03 \times 10^{-5} / 0.03312 \times 0.00812 = 0.6708$ , or  $\log f_{\pm} = 1.9133$ . Fig. 1, Curve 1 shows the values calculated in this way for other concentrations of added chloride plotted against the square root of the ionic strength. The points up to 0.1*N* lie on a straight line, the slope of which should give the value of  $A$ , but the extrapolation of this cannot be reconciled with the limiting value  $\log f_{\pm} = 0$  when  $c = 0$ . This, of course, is because the value  $A = 0.505$  was arbitrarily taken in fixing the

position of the first point of the curve, whereas the experimental points lie on a straight line with the slope 0.40. It will be evident that only one value for the factor  $A$  can be consistent both with the corrected solubility values and with the limiting equation  $-\log f_{\pm} = A\sqrt{\mu}$ . This value lies very close to 0.40, and has been found by trial and error to be  $A = 0.38$ .

It is shown below that this same value holds good when the added salt is other than the chloride of a univalent element. In dilute solutions, therefore, the mean ion activity coefficient of thallos

FIG. 1.



chloride varies with the ionic strength of the solution according to the equation  $-\log f = 0.38\sqrt{\mu}$ . Application of this to the conductivity figures used in calculating  $K$  alters  $K$  from 0.30 to 0.284, and similarly the solubility figures give  $S = 19.18 \times 10^{-5}$ . The data recalculated on this basis are given in Table I and are shown in Fig. 1, Curve 2.

*The Value of the Factor A.*—It is of interest to compare the value  $A = 0.38$  with the results for other uni-univalent electrolytes. The Debye-Hückel theory requires the common value 0.505 and the measurements of Brönsted and La Mer (*J. Amer. Chem. Soc.*, 1924, 46, 555) on complex cobalt salts are in striking agreement with this. On the other hand, some of the most accurate experimental investig-

ations have failed to confirm this value. Nonhebel (*Phil. Mag.*, 1926, 2, 1085), from *E.M.F.* measurements, and Randall and Vanselow (*J. Amer. Chem. Soc.*, 1924, 46, 2418), from freezing-point measurements, both find  $A = 0.39$  for hydrochloric acid; further, the value 0.38 has previously been found for several organic acids (Davies, *Phil. Mag.*, 1927, 4, 244). This value might have been regarded as peculiar to the acids, but it now appears to hold also for thalious chloride. For other univalent electrolytes, the data available, although probably less accurate, have led Noyes (*J. Amer. Chem. Soc.*, 1924, 46, 1098) to suggest for them a common  $A$  value of about 0.41. In view of these results—reached by very diverse methods—there seems to be justification for believing that for the simple inorganic ions and some, at least, of the organic anions, the value of the activity factor  $A$  should, in the absence of experimental evidence, be assumed to be 0.39 and not 0.50. Further data alone can show whether  $A$  in reality varies from ion to ion.

*Solubilities in the Presence of Other Salts the Degrees of Dissociation of which are known.*—The data, calculated on the same basis as before, are given in Table I, where the concentrations and solubilities (Sol.) are in g.-equivs. per litre.

TABLE I.

$$S = 19.18 \times 10^{-5}.$$

Conc.	Sol.	$\sqrt{\mu}$ .	$-\log f_{\pm}$ .	Conc.	Sol.	$\sqrt{\mu}$ .	$-\log f_{\pm}$ .
Added salt: KCl, NaCl, NH <sub>4</sub> Cl (Noyes).				Added salt: TlNO <sub>3</sub> (Noyes).			
0	0.01612	0.1243	0.0472	0.025	0.00883	0.1793	0.0677
0.025	0.00872	0.1818	0.0707	0.050	0.00626	0.2295	0.0925
0.050	0.00592	0.2350	0.0893	0.100	0.00423	0.3076	0.1216
0.100	0.00397	0.3214	0.1241	Added salt: TlNO <sub>3</sub> (Butler and Hiscocks).			
0.200	0.00269	0.4494	0.1628	0.050	0.00615	0.2291	0.0875
Added electrolyte: HCl (Noyes).				0.100	0.00413	0.3071	0.1147
0.025	0.00869	0.1818	0.0718	Added salt: KNO <sub>3</sub> (Bray and Winninghoff).			
0.050	0.00585	0.2349	0.0884	0.020	0.01716	0.1894	0.0722
0.100	0.00384	0.3212	0.1177	0.050	0.01826	0.2558	0.0936
0.200	0.00254	0.4493	0.1488	0.100	0.01961	0.3366	0.1170
Added salts: Bivalent chlorides (Noyes).				0.300	0.02313	0.5406	0.1649
0.025	0.00901	0.2141	0.0824				
0.050	0.00620	0.2838	0.1039				
0.100	0.00467	0.3918	0.1398				
0.200	0.00283	0.5497	0.1805				

The figures for the bivalent chlorides represent the data of Noyes for magnesium, calcium, barium, zinc, manganous, and cupric chlorides, and it has been assumed that these are completely dissociated.

For thalious nitrate the calculations are complicated by the fact

that the added salt is itself incompletely dissociated, so that the solution contains both undissociated thallos chloride and undissociated thallos nitrate. The concentration of undissociated thallos chloride is the same as that in any other solution saturated with respect to this salt, and the concentration of undissociated thallos nitrate is calculated from its dissociation constant,  $K = 0.56$  (Davies, *loc. cit.*), on the assumption that  $A$  has the value 0.38; an error in this assumption would have only a very small effect on the final results, because the concentration of the undissociated nitrate is itself small. Thus, in 0.025*N*-thallos nitrate the solubility of thallos chloride is 0.00883 g. equiv. per litre (Noyes, *loc. cit.*). Of this quantity, 0.00068 is undissociated molecules, and  $[Cl'] = 0.00815$ . If  $x$  is the concentration of undissociated thallos nitrate,  $[NO'_3] = (0.025 - x)$  and  $[Tl'] = (0.00815 + 0.025 - x)$ ; hence  $f^2 (0.025 - x) (0.03315 - x)/x = 0.56$ , where  $f$ , the mean ion activity coefficient of thallos nitrate is given by  $-\log f = 0.38 \times \sqrt{0.03315 - x}$ , the term under the square-root sign being the ionic strength. By a series of approximations,  $x$  is found to be 0.00101, whence  $[Tl'] = 0.03214$ ,  $f_{\pm}^2 = S/[Cl'][Tl'] = 0.0001918/(0.00815 \times 0.03214)$ , and  $-\log f_{\pm} = 0.0677$ . Similar calculations are applied to the remaining data for thallos nitrate.

When potassium nitrate is the saturating salt, the solution contains three undissociated salts, *viz.*, thallos chloride and nitrate and potassium nitrate ( $K = 1.37$ , Davies, *loc. cit.*). In this case the true concentrations of the ions are calculated by a series of approximations, the method being similar to that just described.

Fig. 2 shows the data for twelve different added salts. The lower series of points, connected by broken lines, is calculated on the assumption that both the thallos chloride and the added salt are completely dissociated; they illustrate the individual differences in behaviour that were formerly believed to exist. The upper series of points, through which a continuous line has been drawn, shows the data as recalculated in this paper. The possible experimental error in the measurements is illustrated by the two bracketed values for the thallos nitrate solution,  $\sqrt{\mu} = 0.308$ ; the lower value was obtained from the figures of Noyes, and the upper from the measurements of Butler and Hiscocks.

The most important conclusion to be drawn is that up to a concentration of about 0.1*N*, the mean ion activity coefficient of thallos chloride depends only upon the ionic strength of the solution and not upon the nature of the other ions present. That the corrections here applied for incomplete dissociation should have so uniformly removed the specific deviations seems, apart from its intrinsic interest, to provide strong support for the dissociation constants derived from

conductivity measurements. It is also noteworthy that the linear relationship between  $\log f$  and  $\sqrt{u}$  is found to hold for thallous

negligibly small, and that step (2) may be disregarded as a first approximation. The dissociation constant of the first stage,  $K_1$ , can now be calculated from the solubility measurements in the following way. In 0.02*N*-thallous sulphate solution the solubility of thallous chloride is 0.01034 (Bray and Winninghoff, *loc. cit.*). If  $x$  is the concentration of  $\text{TlSO}_4'$ , the concentrations of the other species present are as follows:  $[\text{TlCl}] = 0.00068$ ;  $[\text{Cl}'] = 0.01034 - 0.00068 = 0.00966$ ;  $[\text{SO}_4''] = 0.01 - x$ ;  $[\text{Tl}'] = 0.00966 + 0.02 - x$ . The ionic strength of the solution is  $0.03966 - 2x$ , and we have  $f_{\pm}^2[\text{Tl}'][\text{Cl}'] = S$ , in which  $-\log f_{\pm} = 0.38\sqrt{\mu}$ . By successive approximations  $x$  can be found, and the left-hand side of the equation

$$\frac{[\text{Tl}'][\text{SO}_4'']}{[\text{TlSO}_4']} = \frac{K_1 \cdot f_{\text{TlSO}_4'}}{f_{\text{Tl}'} \cdot f_{\text{SO}_4''}} = K'_1$$

is thereby determined. The figures are shown in Table II, where the concentration of added salt and the solubility are in g.-equiv./l., and col. 4 gives  $K'_1$ , the "apparent dissociation constant" of the thallosulphate ion. Col. 5 shows the value of  $K_1$ , the true dissoci-

TABLE II.

Added salt : Thallous sulphate.

Conc.	Solubility.	$\sqrt{\mu}$ .	$K'_1$ .	$K_1$ .
0	0.01612	0.1243	—	—
0.020	0.01034	0.1868	0.0876	0.0371
0.050	0.00626	0.2588	0.125	0.0380
0.100	0.00423	0.3463	0.169	0.0343

ation constant of this ion, calculated from  $K'_1$  on the assumptions that, at any ionic strength,  $f_{\text{TlSO}_4'} = f_{\text{Tl}'}$ , and  $f_{\text{SO}_4''}$  is given by the Debye-Hückel equation  $-\log f_{\text{SO}_4''} = 2.0\sqrt{\mu}$ : the values are as constant as could be expected in view of the probable errors of calculation and measurement; the mean value of  $K_1$  also agrees well with a second determination by a different method, which will be described in another paper. These figures are of interest as being the first obtained, on the basis of the interionic attraction theory, for the dissociation of a uni-bivalent salt, and they further emphasise the errors involved in a general application of the "complete dissociation of salts" hypothesis. Thus, the value  $K_1 = 0.036$  implies that in a 0.05*M*-solution of thallous sulphate about one-third of the total sulphate radical exists as  $\text{TlSO}_4'$ .

For thallous chlorate a single measurement is available; Noyes (*loc. cit.*) found the solubility of thallous chloride in 0.025*N*-thallous chlorate to be 0.00895 g.-equiv. per litre. Applying the same methods of calculation as before, we find the thallous chlorate to

be 6.4% undissociated, and give  $K = 0.34$  as a provisional value for the dissociation constant of this salt.

*Summary.*

In determining activity coefficients by measuring the solubility of one salt in the presence of others, allowance must be made for the incomplete dissociation of the salts concerned. The necessary corrections are applied to the data for thalious chloride with the following results.

(1) The logarithm of the activity coefficient gives a straight line when plotted against the square root of the ionic strength up to a value of the latter considerably greater than 0.1.

(2) The slope of the curve is not 0.505, as the Debye-Hückel theory requires, but 0.38, a value previously found for several monobasic acids.

(3) The irregularities previously attributed to specific influences of the added ions disappear below a concentration of 0.1*N*, being due to neglect of incomplete dissociation of the salts.

(4) The dissociation constant of the  $\text{TlSO}_4'$  ion is found to be 0.036, and that of thalious chlorate to be 0.34.