

CCCXXXVI.—*The Solubilities of Thallous Chloride in Salt Solutions at 0°, 25°, and 50°, and its Heats of Solution.*

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THE determination of heats of solution by means of solubility measurements has been the subject of numerous investigations. The familiar van 't Hoff formula  $d(\log s)/dt = Q/RT^2$ , obtained for ideal solutions, can only be regarded as a rough approximation in the case of electrolytes. Several attempts have been made to obtain the exact relation for such cases: first, by the introduction of the degree of dissociation or the van 't Hoff factor  $i$  in various ways (van 't Hoff, *Z. physikal. Chem.*, 1895, **17**, 147; van Laar, *ibid.*, 1895, **17**, 545; 1900, **35**, 11; Goldschmidt and Maarseveen, *ibid.*, 1898, **25**, 91; Jahn, *ibid.*, 1895, **17**, 550; Rudolphi, *ibid.*, 1895, **17**, 277; Campetti, *Atti R. Accad. Lincei*, 1901, **10**, ii, 99; Noyes and Sammet, *J. Amer. Chem. Soc.*, 1898, **20**, 517; Colson, *Compt. rend.*, 1919, **168**, 681), and more recently by Brönsted on the basis of the exact thermodynamics of solutions, in terms of activities (*Z. physikal. Chem.*, 1922, **100**, 139; compare Lange and Dürr, *ibid.*, 1925, **118**, 129). The expression which is now obtained and applied is a modified form of that of Brönsted.

The condition of equilibrium of a salt with its saturated solution may be written  $F_s = F_s$ , where  $F_s$  is the molar free energy of the solid salt and  $F_s$  its partial molar free energy in the saturated solution. Now the partial free energy in any solution is given by  $F = F_0 + RT \log \alpha$ , where  $\alpha$  is the activity and  $\alpha = \alpha_1 \alpha_2$  for a binary electrolyte,  $\alpha_1$  and  $\alpha_2$  being the corresponding activities

of the two ions. Putting  $\alpha_1 = \gamma_1 c_1$ ,  $\alpha_2 = \gamma_2 c_2$ , where  $\gamma_1$  and  $\gamma_2$ ,  $c_1$  and  $c_2$  are the corresponding activity coefficients and concentrations, respectively, we obtain  $F = F_0 + 2RT \log \gamma c^\pm$ , where  $c^\pm = \sqrt{c_1 c_2}$  and  $\gamma = \sqrt{\gamma_1 \gamma_2}$ . The condition of equilibrium may therefore be expressed:

$$F_s = F_s = F_0 + 2RT \log \gamma_s c_s^\pm$$

where  $c_s^\pm$  is the square root of the solubility product and  $\gamma_s$  the corresponding activity coefficient. Since  $F_s$  and  $F_0$  are constant at a given temperature for a given salt and solvent,  $c_s^\pm \cdot \gamma_s$  has a constant value for all such saturated solutions, and it will be written  $c_s^{0\pm}$ .

We shall now apply the equation  $d(F/T)/dT = -H/T^2$ , where  $H$  is the heat content corresponding to free energy  $F$ , to (1) a very dilute solution of the salt in which the activity coefficient  $\gamma$  is unity, and to (2) the solid salt. In the first case we have

$$F = F_0 + 2RT \log c^\pm$$

and 
$$d(F/T)/dT = d(F_0/T)/dT = -H_0/T^2$$

since  $c^\pm$  is not a function of the temperature.\*

In the second case,

$$d(F_s/T)/dT = H_s/T^2, \text{ whence}$$

$$d\{(F_s - F_0)/T\}/dT = -(H_s - H_0)/T^2 = \Delta H_0/T^2.$$

Since 
$$F_s - F_0 = 2RT \log \gamma_s c_s^\pm = 2RT \log c_s^{0\pm}$$

we find that

$$d(\log \gamma_s c_s^\pm)/dT = d \log c_s^{0\pm}/dT = \Delta H_0/2RT^2 \quad . \quad (1)$$

$\Delta H_0$  being the molar heat of solution in a very dilute solution.

A method of finding  $c_s^{0\pm}$  has been developed by Lewis and Randall (*J. Amer. Chem. Soc.*, 1921, **43**, 1112). If the values of  $1/c_s^\pm$  for a salt in a series of salt solutions be plotted against the ionic strength  $\frac{1}{2} \sum v^2 c$ , where  $v$  is the valency of an ion of concentration  $c$  and the summation is extended over all the ions present, a series of curves is obtained converging to the value for the pure solvent. When the salt is only slightly soluble, an extrapolation to zero ionic strength can be made with some accuracy, giving the value of  $1/c_s^{0\pm}$ . The activity coefficient of the salt in any of the solutions is then given by  $\gamma = c_s^\pm / c_s^{0\pm}$ .

\* The concentration  $c$  is independent of temperature if it expresses the amount of solute per 1000 g. of solvent. In the practical part of the paper concentrations refer to the amount of solute per litre, a quantity which varies slightly with the temperature. The difference is not important for the present purpose.

When such a series of curves has been obtained at two or more temperatures, equation (1) can be applied.

The partial heat of solution in a given solution differs from that in an infinitely dilute solution by the heat of transfer of the salt from the latter to the former. This quantity can be calculated if the temperature coefficient of the activity coefficient in the given solution is known. For, since the free energy of the transfer is  $\Delta F = 2RT \log \alpha_1/\alpha_0$  and since  $d(\Delta F/T)/dT = -L_1/T^2$ , where  $L_1$  is the partial molar change in heat content in the transfer, and  $\alpha_1 = \gamma_1 c_1^\pm$ ,  $\alpha_0 = c_0^\pm$ , we have

$$d \log \gamma/dT = -L_1/2RT^2 \quad . \quad . \quad . \quad (2)$$

The partial heat of solution of the salt in a given solution is therefore

$$\Delta H = \Delta H_0 + L = 2RT^2 d(\log c_s^\pm)/dT - 2RT^2 d(\log \gamma)/dT \quad . \quad (3)$$

Since  $\log c_s^\pm = \log c_s^\pm + \log \gamma_s$

and  $d \log \gamma_s/dT = \{d \log \gamma/dc\}(dc_s/dT) + d \log \gamma/dT$ ,

(3) reduces to

$$\Delta H = 2RT^2 d(\log c_s^\pm)/dT + 2RT^2 (d \log \gamma/dc)(dc_s/dT)$$

which is identical with Brönsted's equation.

In practice data for applying (1) and (2) separately are more easily obtained.

#### EXPERIMENTAL.

Thallos chloride appeared to be a suitable salt for our purpose; its solubilities have already been extensively investigated at 25° (Noyes, *Z. physikal. Chem.*, 1892, **9**, 606; Noyes and Abbot, *ibid.*, 1895, **16**, 130; Geffeken, *ibid.*, 1904, **49**, 271, 296; Bray and Winninghoff, *J. Amer. Chem. Soc.*, 1911, **33**, 1663) and it seemed desirable on general grounds to extend these measurements to other temperatures. In order to obtain the temperature coefficients entirely from our own data, we repeated some of the earlier determinations; but we took the opportunity to include as solvents some salt solutions not hitherto investigated, particularly lanthanum sulphate, a ter-bivalent electrolyte the solubility influence of which is of some theoretical interest. Solubilities were determined at 0°, 25°, and 50°; the series at 0° and 50° are less comprehensive than that at 25°, first because our analytical method was not suitable for the determination of the low solubilities of thallos chloride in thallos salt solutions at 0°, and, secondly, because we could not obtain concordant values with lanthanum sulphate at 50°, apparently owing to the formation of a compound between the two components.

*Materials.*—Thallos nitrate was prepared from a commercial

specimen of the salt by treatment with hydrogen sulphide in faintly acid solution, followed by treatment with ammonia and crystallising twice from the filtrate. Thallous sulphate was similarly obtained. Thallous chloride was prepared from the mother-liquors of these preparations by precipitation with pure hydrochloric acid and was twice crystallised from boiling water. It was preserved in a moist condition in blackened resistance-glass vessels. A portion recrystallised twice from conductivity water gave identical solubilities.

Lanthanum sulphate was prepared from a sample of lanthanum ammonium nitrate, kindly put at our disposal by Professor C. M. Thompson, and known to be free from impurities other than traces of cerous salt. The sulphate was obtained from this by way of the carbonate and crystallised twice. [ $\text{La}_2\text{O}_3 : \text{La}_2(\text{SO}_4)_3$ , found : 0.5755. Calc. : 0.5756.]

The other salts employed were of the purest obtainable "Reagent" quality. They were tested and found to be sufficiently pure.

*Solubility Determinations.*—The solubilities were determined by shaking in a thermostat an excess of thallous chloride with the solution employed as solvent, in special resistance-glass bottles. Sufficient thallous chloride was placed in the bottle and washed with 50 c.c. of the solvent solution. This was rejected and the bottle filled with the same solution and the stopper sealed in with a resin cement and capped. Saturation was approached from both higher and lower temperatures. The solution was withdrawn through a special filter, which could be introduced into the bottle while in the thermostat, and was collected in weighed flasks for analysis.

*Methods of Analysis.*—Except when thallous salts were used as solvents, the thallium content was determined by titration with potassium permanganate. Our observations confirmed those previously recorded (Noyes, *loc. cit.*; Hawley, *J. Amer. Chem. Soc.*, 1907, 29, 300; Berry, *ibid.*, 1922, 44, 394). We found that a satisfactory end-point could only be obtained in the presence of free hydrochloric acid and when the amount of thallium exceeded 0.9 g. per litre; the requisite quantity of the saturated solution was diluted to 200 c.c. and 14–15 c.c. of concentrated hydrochloric acid added. The permanganate solution was run in at a rate of about one drop per second with vigorous mechanical stirring until a perceptible colour persisted for 3 minutes. Strict adherence to these conditions gave readings reproducible to within 0.3%. The permanganate solution was standardised against pure thallous nitrate. Owing to side reactions the thallium factor so obtained differs from the stoichiometrical oxygen factor in the ratio 12.588 : 12.750.

TABLE I.

*Solubilities of Thallous Chloride in Salt Solutions at 0°, 25°, and 50°.*

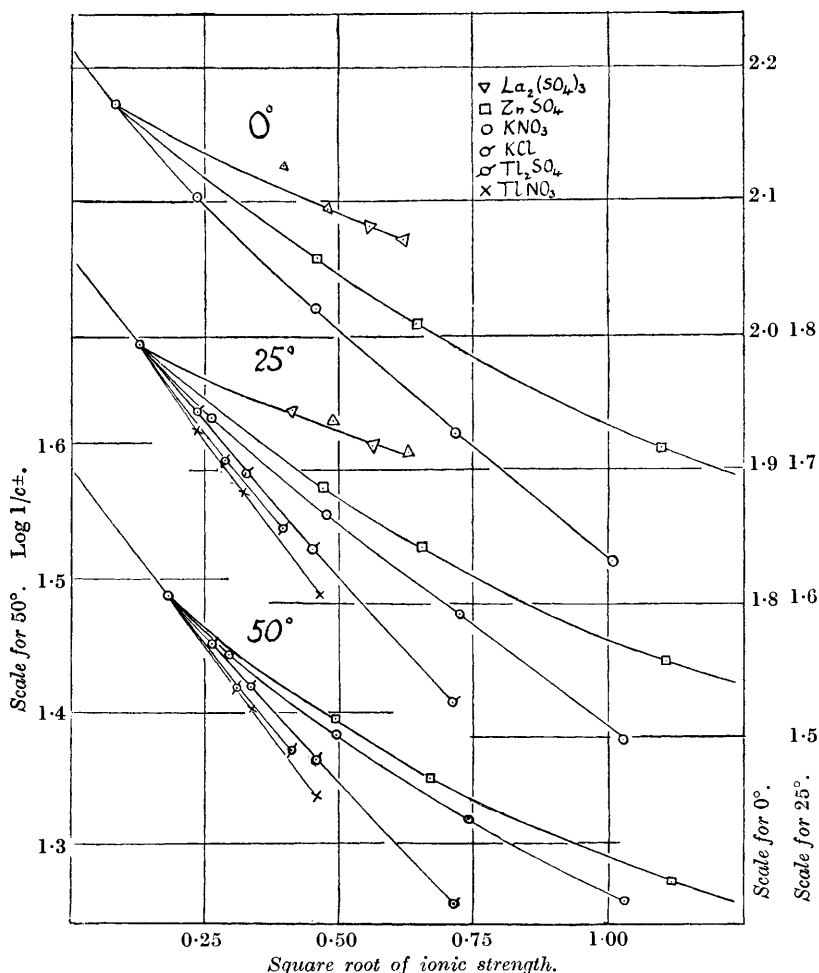
Solvent.	Conc. (mol./ litre).	Solubility. (mol./ litre).	$a_4^*$ .	$1/c_3^{\pm}$ .	$\mu^{1/2}$ .	$\gamma^*$ .
0°						
Water.	—	0.00670	1.0014	149.26	0.08185	0.912
KNO <sub>3</sub> .	0.05	0.00787	1.0039	127.07	0.2405	0.776
	0.2	0.00955	1.0155	104.71	0.4578	0.640
	0.5	0.01184	1.0349	84.46	0.7154	0.516
	1.0	0.01472	1.0661	67.93	1.0073	0.415
ZnSO <sub>4</sub> .	0.05	0.00875	1.0105	114.29	0.4569	0.698
	0.1	0.00979	1.0188	102.14	0.6402	0.624
	0.3	0.01214	1.0674	82.37	1.101	0.503
	0.5994	0.01423	1.1015	70.27	1.553	0.430
La <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> .	0.01	0.00746	1.0063	134.05	0.3968	(0.783)
	0.015	0.00805	1.0088	124.23	0.4827	0.759
	0.02	0.00828	1.0110	120.77	0.5552	0.736
	0.025	0.00845	1.0135	118.34	0.6193	0.722
25°						
Water.	—	0.01607	1.0004	62.23	0.1268	0.863
KCl.	0.05	0.00586	1.0003	55.27	0.2364	0.766
	0.1	0.00387	1.0033	49.88	0.3223	0.692
	0.2	0.00258	1.0063	43.74	0.4501	0.606
	0.5	0.00176	1.0203	33.65	0.7084	0.467
TiNO <sub>3</sub> .	0.05	0.00615	1.0079	53.82	0.2370	0.746
	0.1	0.00413	1.0202	48.22	0.3227	0.668
	0.2	0.00300	1.0399	40.52	0.4506	0.562
Ti <sub>2</sub> SO <sub>4</sub> .	0.025	0.00680	1.0098	50.88	0.2861	0.706
	0.05	0.00463	1.0186	45.43	0.3933	0.629
KNO <sub>3</sub> .	0.05	0.01826	1.0038	54.76	0.2613	0.759
	0.2	0.02151	1.0138	46.49	0.4706	0.645
	0.5	0.02556	1.0327	39.12	0.7250	0.542
	1.0	0.03030	1.0619	33.00	1.0257	0.458
ZnSO <sub>4</sub> .	0.05	0.01801	1.0097	48.57	0.4697	0.673
	0.1	0.01836	1.0184	43.88	0.6502	0.608
	0.3	0.01913	1.0515	36.10	1.1080	0.500
	0.5994	0.01937	1.0993	31.22	1.5588	0.432
La <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> .	0.01	0.01801	1.0055	55.52	0.4099	(0.766)
	0.015	0.01836	1.0079	54.46	0.4933	(0.747)
	0.02	0.01913	1.0098	52.27	0.5649	(0.731)
	0.025	0.01937	1.0122	51.63	0.6280	0.716
50°						
Water.	—	0.03265	0.9950	30.63	0.1807	0.803
KCl.	0.05	0.01835	0.9943	28.24	0.2614	0.741
	0.1	0.01281	0.9957	26.31	0.3358	0.688
	0.2	0.00893	0.9996	23.15	0.4571	0.607
	0.5	0.00606	1.0121	18.06	0.7714	0.474
TiNO <sub>3</sub> .	0.1	0.01381	1.0131	25.22	0.3374	0.662
	0.2	0.01010	1.0321	21.71	0.4584	0.569
Ti <sub>2</sub> SO <sub>4</sub> .	0.025	0.02061	1.0012	26.21	0.3092	0.688
	0.05	0.01567	1.0140	23.52	0.4070	0.617
KNO <sub>3</sub> .	0.05	0.03598	0.9989	27.79	0.2932	0.729
	0.2	0.04136	1.0088	24.18	0.4913	0.634
	0.5	0.04794	1.0273	20.86	0.7402	0.547
	1.0	0.05524	1.0571	18.10	1.0273	0.475
ZnSO <sub>4</sub> .	0.05	0.04027	1.0046	24.83	0.4902	0.651
	0.1	0.04457	1.0249	22.44	0.6668	0.589
	0.3	0.05349	1.0459	18.70	1.1196	0.490
	0.5994	0.06163	1.0952	16.23	1.5682	0.426

\* Figures in brackets are smoothed values obtained from the curves. In other cases the smoothed curve coincides with the experimental points.

In the thallium salt solutions the amount of chloride was determined by precipitation and weighing as silver chloride.

The solubilities are collected in Table I, together with the calculated values of  $1/c_{\pm}^{\pm}$  and the ionic strengths ( $\mu$ ) of the

FIG. 1.



solutions. Usually four determinations were made in each case and the maximum deviation from the mean was rarely more than 0.00002. The solubilities agree moderately well with the determinations of Bray and Winninghoff (*loc. cit.*), but the divergencies are greater than those of our own determinations among themselves;

they are less than 0.00010, except in the case of *N*-potassium nitrate, where the discrepancy is 0.00042. Considering the difficult nature of the end-point on which the values depend this is perhaps to be expected. In Fig. 1 the values of  $1/c_s^\pm$  are plotted against the square roots of the ionic strengths, giving a group of curves converging to the value for water for each temperature. It will be seen from the form of the curves that accurate extrapolation to zero ionic strength for the value of  $1/c_s^0$  is not possible, and to obtain this limiting value the theoretical equation of Debye and Hückel was utilised (*Physikal. Z.*, 1923, **24**, 185; 1924, **25**, 97). For a binary electrolyte and for small concentrations this equation reduces to

$$\log_{10} \gamma = -7.77 \times 10^{15} \sqrt{2\mu} / \{ \sqrt{1000} \times 1.982(\epsilon T)^{3/2} \}$$

where  $\epsilon$  is the dielectric constant.

Using the following values for the dielectric constant of water (Noyes, *J. Amer. Chem. Soc.*, 1924, **46**, 1098; Baxter, *ibid.*, 1926, **48**, 615. Value at 50° obtained by interpolation from those given by these authors at 0°, 25°, and 75°):  $\epsilon = 87.8$  at 0°, 78.8 at 25°, and 70.7 at 50°, we obtain

$$\log_{10} \gamma = -0.489\sqrt{\mu} \text{ at } 0^\circ; -0.505\sqrt{\mu} \text{ at } 25^\circ; -0.526\sqrt{\mu} \text{ at } 50^\circ,$$

from which the values of  $\gamma$  in the saturated solutions in water can be calculated and thence the values of  $1/c_s^{0\pm}$ . It may be remarked that somewhat large deviations from the Debye equation occur within the concentration range over which it is applied here, but no data exist for applying the modified equation for higher concentrations, and the extrapolation on the basis of the simple equation fits the curves at least as well as any other extrapolation which could be made.

The following values of  $1/c_s^{0\pm}$  were thus obtained: \*

At 0°, 163.6; at 25°, 72.1; and at 50°, 38.1.

Substitution of these in equation (1) gives the following values for  $\Delta H_0$ :

$$0-25^\circ, \Delta H_0 = 10,560 \text{ cal.}; 25-50^\circ, \Delta H_0 = 9,740 \text{ cal.}$$

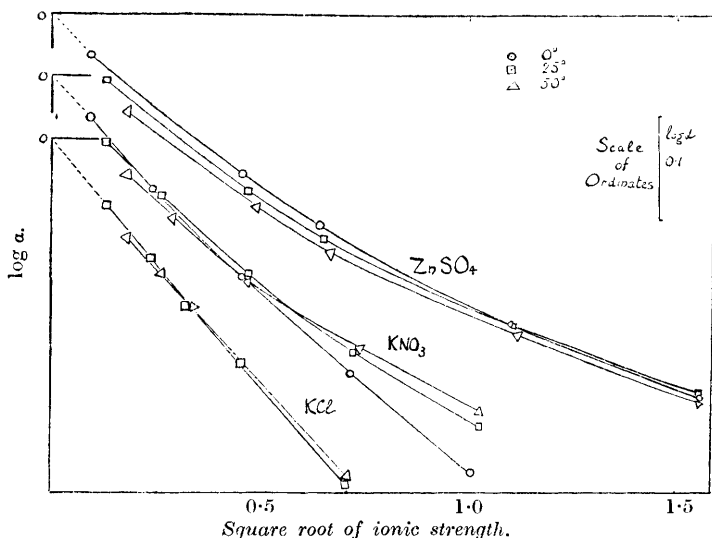
#### *The Temperature Coefficients of the Activity Coefficients.*

In order to find the partial heat content of thallos chloride in a given solution by equation (2) it is necessary to ascertain the tem-

\* The value of  $1/c_s^{0\pm}$  obtained by Lewis and Randall (*J. Amer. Chem. Soc.*, 1921, **43**, 1139) by direct extrapolation of the plot of  $1/c_s^\pm$  against  $\mu^{1/2}$  was 70.3 at 25°. Theoretically, at small dilutions  $\log 1/c_s^\pm$  is proportional to  $\mu^{1/2}$ , but plotting these quantities brings out differences in the slopes of the curves which are suppressed by the other method. Hence we did not feel justified in attempting a direct extrapolation.

perature coefficient of the activity coefficient in that solution. The solubility method gives directly the activity coefficients in a series of saturated solutions which differ in the content of thallos chloride at different temperatures. It was thought that the true temperature coefficient for a solution would be given by taking values *at the same ionic strength* on the solubility curves. An examination of these showed, however, that the deviations from the ionic-strength rule were so great even at small dilutions that the temperature coefficient for constant ionic strength on the solubility curves could not be identified with that of a given solution. We were therefore unable to apply equation (2).

FIG. 2.



The effect of temperature on the activity coefficient-ionic strength curves of some typical series is shown in Fig. 2, which gives a general idea of the magnitude of the effect.

#### Conclusions.

The data obtainable from solubility measurements are thus not by any means ideal for the thermodynamical calculation of heats of solution. Equation (1) can only be applied to solubility measurements through an extrapolation to zero-concentration. In the present instance, we were obliged to make use of a theoretical extrapolation which is probably not exact. The use of equation (1) demands a knowledge of (a) the solubilities, and (b) the activity coefficients in the saturated solutions of a salt, at different tem-



peratures. The latter quantities are better obtained by direct determinations of the activities over a range extending from very low concentrations up to the saturated solution. Data for the application of equation (2) would also be better obtained from direct determinations of activity coefficients in the same solution at two or more temperatures.

*Summary.*

1. A relation is obtained between the heats of solution and the temperature coefficient of solubility which, though equivalent to one deduced by Brönsted, can be more easily applied to experimental data.

2. The solubilities of thallos chloride in a number of salt solutions at 0°, 25°, and 50° have been determined. The activity coefficients in these solutions are obtained by means of an extrapolation based on the equation of Debye and Hückel. The activity coefficients in solutions of the ter-bivalent electrolyte, lanthanum sulphate, deviate somewhat widely from the requirements of the ionic-strength rule.

3. Values of  $1/c_0^{\pm}$  (*i.e.*, the reciprocal of the theoretical solubility in a solution of zero ionic strength) at the above temperatures have led to values for  $\Delta H_0$ , the heat of solution of thallos chloride in an infinitely dilute solution.

4. The temperature coefficient of the activity coefficient of a salt cannot be obtained with certainty from solubility measurements.

We wish to express our indebtedness to Mr. Roy Evans, B.Sc., and to Mr. S. O. Rees, B.Sc., for carrying out solubility determinations in lanthanum sulphate solutions and in thallos salt solutions, respectively, and to Professor J. E. Coates, D.Sc., for facilities provided for this work.