

the number of molecules of normal salt in the solution, our values are probably a little high. For all practical purposes, however, the difference is not appreciable.

For assistance rendered in the earlier stages of this work, credit should be given to Mr. Gebhard Stegeman.

### Summary

A method of determining solubilities by the use of floating equilibrium is described. This method has been shown to be capable of considerable speed or great accuracy and a reasonable amount of both.

The solubility of lead acetate,  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$ , has been determined between  $0.0^\circ$  and  $50^\circ$ .

Evidence has been produced which supports an explanation for the variation in the values obtained for the solubility of lead acetate.

COLUMBUS, OHIO

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[CONTRIBUTION FROM THE MUSPRATT LABORATORY OF PHYSICAL AND ELECTRO-CHEMISTRY, UNIVERSITY OF LIVERPOOL]

## THE INFLUENCE OF ELECTROLYTES ON THE SOLUBILITY OF NON-ELECTROLYTES

BY ANDREW MCKEOWN

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The mutual relations existing between the solubilities of different substances in the same solution have received much attention in the past, both from the theoretical and from the practical standpoint, and semi-empirical relations have been obtained which represent the experimental facts in particular cases in a more or less satisfactory manner.<sup>1</sup> Investigations have recently been carried out by Dawson<sup>2</sup> on the salting out of phenol from water solution by sodium sulfate, and by Thorne<sup>3</sup> on the solubility of ethyl ether in aqueous solutions of sodium chloride. The data in the latter case are of special interest, since the solubility determinations have been carried out at two different temperatures, *viz.*,  $15^\circ$  and  $25^\circ$ . Thorne finds that his results conform to the equation

$$\frac{1}{c} \cdot \log_{10} \frac{s_0}{s} = k$$

where  $c$  is the concentration of sodium chloride present in solution,  $s$  is the corresponding solubility of ethyl ether,  $s_0$  is the solubility of ether in pure water, and  $k$  is a constant for a given temperature, having the value 0.0555 at  $15^\circ$  and 0.0536 at  $25^\circ$ . As a matter of fact, the solubility of ether in pure water is anomalous, but the equation holds fairly

<sup>1</sup> Compare Rothmund, *Z. Elektrochem.*, **14**, 532 (1908); *Z. physik. Chem.*, **69**, 523 (1909).

<sup>2</sup> Dawson, *J. Soc. Chem. Ind.*, **39**, 151T (1920).

<sup>3</sup> Thorne, *J. Chem. Soc.*, 119, 262 (1921).

accurately for the solubilities of ether,  $s_1$  and  $s_2$ , in salt solutions of concentrations  $c_1$  and  $c_2$ .

From Thorne's data the heats of solution of ether in the various sodium chloride solutions can be calculated by means of the equation

$$\frac{d(\ln s)}{dT} = \frac{\text{heat absorbed}}{R T^2} \quad (1)$$

The use of this expression involves the assumption that solubility  $s$  is closely analogous to a true equilibrium constant. This assumption will be considered later.

If the heat absorbed remains constant over the temperature range  $15^\circ$  to  $25^\circ$ , the above equation may be integrated between these limits giving

$$\ln \frac{s'}{s''} = \frac{Q}{R} \left( \frac{1}{T'} - \frac{1}{T''} \right) \quad (2)$$

where  $Q$  is the heat evolved per mole of ether dissolved. From the equation,  $Q$  may be calculated in the different cases treated by Thorne.

TABLE I  
CALCULATION OF HEAT OF SOLUTION OF ETHER IN SODIUM CHLORIDE SOLUTION

NaCl per 100 g. of soln. g.	Solubility, $s'$ , of ether at $15^\circ$	Solubility, $s''$ , of ether at $25^\circ$	$Q$ Cal.
0	8.43	6.05	5635
1	8.06	5.98	5073
2	7.09	5.28	5010
4	5.49	4.13	4838
5	4.84	3.65	4794
6	4.26	3.22	4754
8	3.30	2.52	4584
10	2.55	1.97	4383
15	1.35	1.11	3327
20	0.71	0.57	3734 (?)
25	0.37	0.31	3007

It will be observed that the heat evolved decreases steadily with increasing salt concentration. It is suggested that this decrease may be related to the decrease in the solubility of the ether in the following manner.

If we assume solubility to be analogous to a true equilibrium constant (as the above use of the van't Hoff isochore relation implies) we may write the solubility  $s$  in moles per liter as equal to: velocity constant of "dissolution"/velocity constant of "precipitation." Let us consider the mechanisms of the dissolution and precipitation processes. The former consists essentially of an ejection of solute molecules from the solid or liquid phase of undissolved solute into the adjoining layer of solution. The expression for the rate of dissolution is, therefore, of the same form as that applying, for example, to the rate of vaporization of molecules from the surface of a liquid, or the rate of thermionic emission of electrons from a

metal surface. The rate of the latter is given by Langmuir<sup>4</sup> from kinetic theory considerations as

$$n = N \sqrt{\frac{kT}{2\pi m}} e^{-w/kT}$$

where  $n$  is the number of electrons escaping from unit surface per second,  $N$  is the number of electrons of mass  $m$  per unit volume of the emitting substance, and  $w$  is the work required to carry an electron through the surface of the metal. We may by analogy write the rate of dissolution, or the number of molecules dissolving per square centimeter per second

$$n_0 = N_0 \sqrt{\frac{RT}{2\pi M}} e^{-E_0/RT} \quad (3)$$

where  $N_0$  is the number of molecules per cc. of undissolved solid or liquid,  $M$  is the molecular weight of the solute, and  $E_0$  is the work required in the dissolution of one mole of solute, that is, the critical increment of dissolution.

In the precipitation process, we have to consider the number of solute molecules in solution which collide on one square centimeter of the surface of the solute phase per second, together with the fraction of these which condense on collision. The first is given by  $kN \sqrt{\frac{RT}{2\pi M}}$ , and the number condensing by

$$n = kN \sqrt{\frac{RT}{2\pi M}} e^{-E/RT} \quad (4)$$

where  $E$  is the critical increment of condensation, and  $k$  is a factor introduced to take account of the specific rate of diffusion of the solute molecules up to the bounding surface. For the moment we will regard  $k$  as a constant at constant temperature, independent of the concentration of the salt solution. When solution has reached its limit, the rates (3) and (4) are equal, so that

$$N = \frac{N_0}{k} \cdot e^{-(E_0-E)/RT} \quad (5)$$

where  $N$  is the number of solute molecules per cc. of solution, and is a measure of the solubility.

Now the heat evolved is the difference of the critical increments of resultants and reactants, that is  $E - E_0 = \text{heat evolved} = Q$ . Hence

$$s = A \cdot e^{Q/RT} \quad (6)$$

where  $A$  is provisionally a constant determined by  $k$  and  $N$ .

If we denote by  $s_1$  the solubility of ether in a 1% solution of sodium chloride at a temperature  $T$ , and by  $s_n$  the solubility in any given salt solution at the same temperature, we have

<sup>4</sup> Langmuir, *J. Am. Electrochem. Soc.*, 29, 12 (1916).

$$\log s_1 = \log A + \frac{Q_1}{RT}$$

$$\log s_n = \log A + \frac{Q_n}{RT}$$

Hence 
$$RT \log \frac{s_1}{s_n} = Q_1 - Q_n \quad (7)$$

In the following table the values of  $RT \log s_1/s_n$  at the temperatures  $15^\circ$  and  $25^\circ$  (Cols. 2 and 3) are compared with the values  $Q_1 - Q_n$  obtained by use of the van't Hoff isochore (compare Table I). In order to reduce the solubility data given by Thorne in grams per 100 g. of solution to grams per 100 cc. of solution, that is, in order to express  $s_1$  and  $s_n$  in volume concentration terms, it is necessary to multiply the ratio of Thorne's values by  $d_1/d_n$ , the ratio of the densities of the solutions.

TABLE II

NaCl conc. limits per 100 g. of soln. G.	$RT \log \frac{s_1}{s_n}$ at $15^\circ$	$RT \log \frac{s_1}{s_n}$ at $25^\circ$	$Q_1 - Q_n$ from Table I
1-2	69.2	69.4	63
1-4	207	206	235
1-5	275	275	279
1-6	346	334	319
1-8	482	481	490
1-10	621	618	690
1-15	964	936.5	1746 (?)
1-20	1310	1309	1339
1-25	1662	1647	2066

The values corresponding to  $s_0$  have been omitted from the above table, since they are at very great variance with one another. Thus 26, 7, 570 are the figures for Cols. 2, 3 and 4, respectively. It is difficult to explain why so great a discrepancy is shown when the solubilities of ether in pure water are employed. Thorne himself has already commented on the abnormality of these data.

The values of  $Q_1 - Q_n$  in Col. 4, obtained from the van't Hoff isochore, agree on the whole (with one exception) with the figures in the two preceding columns. It is easily seen that this result justifies the assumption used above that the factor  $k$  is independent of the concentration of the salt solution. Again, if the values in Cols. 2 and 3 were identical, Col. 4 should correspond strictly to either, since the van't Hoff isochore can be deduced from the statistical equation (7) at two different temperatures thus

$$RT' \log \frac{s_1'}{s_n'} = Q_1 - Q_n$$

$$RT'' \log \frac{s_1''}{s_n''} = Q_1 - Q_n$$

therefore 
$$\log \frac{s_1'}{s_n'} - \log \frac{s_1''}{s_n''} = \frac{Q_1 - Q_n}{R} \left( \frac{1}{T'} - \frac{1}{T''} \right)$$

which is the equation from which the values of  $Q_1 - Q_n$  of Col. 4 are calculated (the ratio of the densities of the two solutions at the two different temperatures being taken as equal). The large divergence to be observed in a few cases (especially for the 1-15% sodium chloride solutions) is considered to be due entirely to multiplication of the error initially present in the solubility data. Indeed, an examination of these data shows that the ether solubilities given by Thorne do not decrease in a perfectly regular manner as the sodium chloride concentration increases. This is especially true for the data referring to 25°. We are, therefore, justified in taking Col. 2, in preference to Col. 3 or 4, as the most accurate measure of the differences of the heats of solution of ether in various sodium chloride solutions.

Finally, the fact that from Equation 7, based on statistical principles, we may deduce an equation of the form

$$\log \frac{s_1'}{s_1''} - \log \frac{s_n'}{s_n''} = \frac{Q_1 - Q_n}{R} \left( \frac{1}{T'} - \frac{1}{T''} \right)$$

which is the difference of two van't Hoff isochores, is evidence in favor of the general correctness of our original mechanism of solubility from which Equation 7 is derived.

The effect of an electrolyte on the solubility of a non-electrolyte may be looked at from a slightly different point of view. Nernst and Jahn have treated in a semi-empirical manner the corrections to be applied to the thermodynamic properties of each constituent of a solution due to the mutual influences of the components, and the latter writer<sup>5</sup> has applied his concepts with considerable success to explain the anomaly of strong electrolytes and the departure of the electromotive force of concentration cells from the values calculated from the simple Nernst formula.

Rothmund, by a similar line of treatment<sup>6</sup> deduces the following relation between the solubilities ( $\eta_4$  and  $\eta'_4$ ) of a non-electrolyte in water and in a salt solution of concentration  $c$

$$RT \log \frac{\eta_4}{\eta'_4} = \alpha_{1,4} c_1 + 2\alpha_{2,4} c_2 \quad (8)$$

where  $c_1$  is the concentration of the undissociated salt, and  $c_2$  is the concentration of either ion;  $\alpha_{1,4}$  and  $\alpha_{2,4}$  are factors representing the respective specific influences of the undissociated molecule and either ion on the properties of the non-electrolyte.

Since it is reasonable to assume that the specific mutual influence of two molecules is small compared with that of an ion and a molecule,  $\alpha_{1,4}$  is put equal to zero, giving

$$RT \log \frac{\eta_4}{\eta'_4} = 2\alpha_{2,4} c_2 \quad (9)$$

<sup>5</sup> Jahn, *Z. physik. Chem.*, **41**, 257 (1902).

<sup>6</sup> Rothmund, *ibid.*, **69**, 523 (1909).

Comparing this with Equation 7, which depends on statistical principles, we see that the difference in the heats of solution of ether in two solutions of sodium chloride is directly proportional to the difference of the ion concentrations in the solutions.

Since, however, we are dealing with thermodynamic properties, it would seem more correct to replace Equation 9 above by

$$RT \log \frac{\eta_1}{\eta_2} = \alpha_{2,4} a_2 + \alpha_{3,4} a_3 \quad (10)$$

the  $a$ 's denoting activities of the ions, and the subscripts 2 and 3 referring to sodium ion and chlorine ion, respectively. It will be noted that the "environmental" effects of the ions are now separated since on the basis of activity, there is no *a priori* reason for assuming them equal. Harned<sup>7</sup> has computed the individual activities of the ions of such salts as potassium, sodium and lithium chlorides, and has shown that the observed activities of these salts in solution agree closely with the values calculated from the separate activity coefficients of the individual ions given by the empirical equation

$$\log F_a = \alpha c - \beta c m$$

where  $\alpha$ ,  $\beta$  and  $m$  are constants for the particular ion considered, and  $F_a$  is the activity coefficient of the ion at the concentration  $c$  of salt (gram-molecules per 1000 g. of solvent).

The following table contains the activities of the sodium and the chlorine ions in the solutions used by Thorne, calculated from the above formula. The revised values of the constants  $\alpha$ ,  $\beta$ ,  $m$  for each ion given by Harned in a more recent communication<sup>8</sup> have been employed.

TABLE III  
CALCULATED ACTIVITIES OF THE SODIUM AND CHLORINE IONS

NaCl per 100 g. of soln. G.	Moles of NaCl per 1000 g. of H <sub>2</sub> O	Na <sup>+</sup>	Activity of Cl <sup>-</sup>
1	0.1728	0.1334	0.1272
2	0.3492	0.2557	0.2381
4	0.7130	0.5040	0.4434
5	0.9006	0.6357	0.5466
6	1.092	0.7755	0.6490
8	1.487	1.086	0.8600
10	1.901	1.447	1.086
15	3.019	2.684	1.736

Subtracting the value of  $\alpha_{2,4} a_2 + \alpha_{3,4} a_3$  for the 1% solution of sodium chloride from the values corresponding to the other solutions, and equating the results to the values of  $(Q_1 - Q_n)$  obtained from Col. 2 of Table II, we obtain the following relations.

<sup>7</sup> Harned, THIS JOURNAL, **42**, 1818 (1920).

<sup>8</sup> Harned, *ibid.*, **44**, 252 (1922).

$$0.1223 \alpha_{2,4} + 0.1109 \alpha_{3,4} = 69.2$$

$$0.3706 \alpha_{2,4} + 0.3162 \alpha_{3,4} = 207$$

$$0.5023 \alpha_{2,4} + 0.4194 \alpha_{3,4} = 275$$

$$0.6421 \alpha_{2,4} + 0.5218 \alpha_{3,4} = 346$$

$$0.9526 \alpha_{2,4} + 0.7328 \alpha_{3,4} = 482$$

$$1.314 \alpha_{2,4} + 0.959 \alpha_{3,4} = 621$$

$$2.551 \alpha_{2,4} + 1.609 \alpha_{3,4} = 964$$

Solving these seven equations in  $\alpha_{2,4}$  and  $\alpha_{3,4}$  by the method of least squares, we obtain as the most probable values  $\alpha_{2,4} = -21.7$ ;  $\alpha_{3,4} = 671$ . Having regard to the admittedly approximate nature of the activity values used, no special significance need be attached to the negative sign of  $\alpha_{2,4}$ , as a small error in any of the data used might easily lead to a positive value of  $\alpha_{2,4}$  of the same order of magnitude as that given above. The result obtained would therefore appear to indicate that *the effect of the cation in the salting out of ether by sodium chloride is negligible compared with the effect of the anion.*

It is believed that the foregoing is the first quantitative treatment of the salting-out effect of an electrolyte from the standpoint of the activities of the individual ions of the salt in solution.

It is proposed to test the conclusions arrived at above by experiments similar to those of Thorne, replacing the sodium chloride by other salts, for solutions of which the individual activity values of the ions are also available.

### Summary

1. The heats of solution of ether in various solutions of sodium chloride have been calculated from Thorne's solubility data at 15° and 25°, making use of a relation between solubility, heat of solution, and temperature of the form of the van't Hoff isochore.

2. Statistical treatment of the phenomena of solution and precipitation leads to an expression for solubility, *viz.*,  $s = Ae^{Q/RT}$ , which is in agreement with the isochore relation mentioned above.

3. The salting-out effect on ether of sodium chloride has been examined insofar as the effect depends on the activities of the ions of the salt. It is shown that the relative specific influences of the cation and anion are  $-21.7$  and  $+671$ , that is the anion is the predominating factor in the process. A mode of further testing this result is indicated.

LIVERPOOL, ENGLAND