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STUDIES ON SOLUBILITY. I. THE SOLUBILITY OF SALTS IN SALT SOLUTIONS.

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I. Introduction.

The fundamental principles for the treatment of the solubility equilibria in salt solutions have been pointed out in the well known works of van't Hoff and Reicher,[1] W. Nernst[2] and Arthur A. Noyes.[3] By these investigations it has been shown that the important conception of the solubility product is able to represent the solubility phenomena in accordance with the van't Hoff theory of dilute solutions and the Arrhenius theory of the electrolytic dissociation of salts. Indications, however, are found even in these first papers of the fact that the assumption of the constancy of the solubility product, made in the quoted papers and afterwards admitted as a general rule, can account only approximately for the experimental results.

Further investigations by Arrhenius[4] and by Stieglitz[5] showed the concentration of the un-ionized portion of the saturating salt was not even approximately constant as required by the theory of solutions, this concentration decreasing rapidly with increasing concentration of another salt having an ion in common with the saturating salt.

Much work on the solubility of salts has since been carried out, of which notably the important investigations of Noyes and his co-workers[6] deserve special mention. Through this elaborate work experimental results have been obtained corroborating the view of Arrhenius mentioned above, and showing, furthermore, that the solubility product in mixed salt solutions rise considerably with increasing concentration.

To obtain these results the authors apply the method depending on the electric conductance of the solutions, assuming the conductance ratio to be an accurate measure of ionization in pure salt solutions. By introducing the Arrhenius theory of the isohydric solution, and the empirical law which has been found to express the change of the ionization of single salts, an expression is reached which is assumed to govern the equilibria occurring in the mixed saturated solutions.

The results obtained in this way are dependent on the precision of the fundamental assumption, that the conductance ratio is an accurate

[1] *Z. phys. Chem.*, 3, 482 (1889).
[2] *Ibid.*, 4, 372 (1889).
[3] *Ibid.*, 6, 241 (1890).
[4] *Ibid.*, 31, 224 (1899).
[5] THIS JOURNAL, 30, 946 (1908).
[6] *Ibid.*, 33, 1643, 1807 (1911).

measure of the degree of dissociation. There has been much discussion respecting the value of this assumption, and we are justified at least in considering it as highly doubtful,[1] since the underlying presupposition that the mobility of the ions is constant is known to be incorrect. Also for other reasons we cannot adopt the conductance method as fitted to account for the constitutions of salt solutions, as will appear from an inspection of the solubility data. It may be stated, for instance, that even when a decrease in the concentration of the un-ionized portion by addition of another salt is to be expected, from the familiar phenomenon known as the "salting out" effect, this decrease as calculated in the cited papers proves to be of quite a different order of magnitude than in the case of a non-electrolyte. Thus a 0.05 *M* potassium nitrate solution, possessing a salting out effect of less than 1% towards non-electrolytes, exhibits an effect more than 30 times as great in the case of undissociated thallous chloride, computed on the basis of the conductance method. Furthermore, a satisfactory explanation of the increasing solubility found in many cases in salts on the addition of other homoionic salts can hardly be afforded by this point of view. Attention is called by Noyes and Bray[2] to the peculiar behavior of a moderately soluble uni-bivalent salt on addition of a salt with a common bivalent ion. This phenomenon also cannot easily be understood from the standpoint of the ordinary theory. We are justified in consideration of all these discrepancies, in concluding that the conductance method affords no serviceable basis for a theory of solubility. It seems desirable, therefore, to attempt an interpretation of these phenomena from quite a different point of view.

The attempt at a new treatment of the solubility problem contained in the present paper makes no pretence of explaining all the peculiar characteristics of the various solubility curves. It is intended only to show that the multiplicity of types of curves found with hetero- as well as homoionic solvents can be accounted for in a simple way and on a thermodynamic basis by introducing an assumption at any rate approximately true for mixed salt solutions.

Owing to the preliminary nature of this paper an account of the considerable experimental material which has been secured in this laboratory to test the general scope of the new points of view will be postponed for later publication. Only a small number of experiments will be cited in the following sections of this article to elucidate some particularly important conclusions. A more rigorous theoretical treatment of the problem will likewise appear in a subsequent part of this work.

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[1] See G. N. Lewis, This Journal, 34, 1631 (1912); P. Hertz, *Ann. Physik.*, [4] 37, 1 (1912).

[2] This Journal, 33, 1643 (1908).

2. Thermodynamic Functions Applicable to Solutions.

The thermodynamic properties of a dissolved substance can be expressed by means of the chemical potential π, this quantity, assuming the validity of the simple gas laws, being given by

$$\pi = RT \ln c + i_c \qquad (1)$$

for one mol of the solute, where c is the concentration or number of mols of the solute per liter, and i_c is a constant for the same solvent.

If the gas laws do not hold for the solution, this equation may be replaced by

$$\pi = RT \ln \xi_c + i_c \qquad (2)$$

where ξ_c denotes the *activity* of the solute, a conception introduced by G. N. Lewis[1] and conveniently defined by this very equation.

The absolute value of the activity is not determined by (2) and has commonly no significance. It may be established by definition by putting $\xi_c = c$ of the substance in the pure gaseous state at infinite dilution. For our purpose, however, it may be more suitable to put $\xi_c = c$ for the substance at infinite dilution in the solvent used. As a more complete definition of the activity we then have

$$\pi - \pi_\infty = RT \ln \frac{\xi_c}{c_\infty} \qquad (3)$$

where π_∞ and c_∞ indicate the chemical potential and the concentration of the substance at infinite dilution in the solvent concerned.

The ratio of the activity to the concentration:

$$\frac{\xi_c}{c} = f \qquad (4)$$

is called the *activity coefficient*.[2] The value of this is constant when Equation 1 holds good, but otherwise varies with varying concentration. When ξ_c is given by (3) the said constant value will be unity.

While the alteration is ξ_c by changing concentration, as seen from Equations 2 and 3, is a merely experimental quantity, no hypothesis whatever being involved in its theoretical determination, the values of the alterations in c, however, will usually depend upon the method employed for its computation. This uncertainty of course also affects the activity coefficient. Different values must be attributed to f, depending on the method employed for the determination of c.

This uncertainty will be removed by introducing for c the stoichiometrically determined concentration of the dissolved substance instead of the "true" concentration. The activity coefficient thereby becomes a thermodynamic quantity like the activity itself. Defined in this way it may be suitably termed the *stoichiometric activity coefficient*.

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[1] *Proc. Am. Acad.*, **43**, 259 (1907).

[2] Noyes and Bray, THIS JOURNAL, **33**, 1646 (1911).

From the nature of Equation 1 it appears that we need not necessarily employ the c-scale to express the concentration in this equation. By substituting x or the mol fraction for c we obtain

$$\pi = RT \ln x + i_x \qquad (5)$$

analogous to (1) and

$$\pi = RT \ln \xi_x + i_x \qquad (6)$$

analogous to (2). Instead of (3) and (4) we may write

$$\pi - \pi_\infty = RT \ln \frac{\xi_x}{x_\infty} \qquad (7)$$

and

$$\frac{\xi_x}{x} = f. \qquad (8)$$

The activities ξ_c and ξ_x are capable of representing the thermodynamic properties of the solution equally well. On dividing by the corresponding concentrations c and x, the same activity coefficient f will result. As in the case of applying the c-scale we have also here to distinguish between the true and the stoichiometric activity coefficient.

An equation of the same significance for dilute solutions as (1) and (5) is arrived at by expressing the chemical potential of the solvent as a function of the concentration. If by π_0 and π_{00} are indicated the chemical potentials of one mol of the solvent at the concentration x and at infinite dilution, respectively, we have for dilute solutions if the gas laws hold good

$$\pi_0 - \pi_{00} = -RT\, x. \qquad (9)$$

The magnitudes of π and x depend on the molal weights M_0 and M, attributed to the solvent and the solute, respectively. As to M_0 this may, strictly speaking, be chosen arbitrarily but is most conveniently taken as equal to the formula weight of the substance. By fixing M_0 we shall find that the value of M is also determined according to Equation 9. The gas laws being valid for the solution means precisely that M, derived in this way from (9), retains a constant value when the concentration changes.

If the gas laws are not valid, (9) must be replaced by

$$\pi_0 - \pi_{00} = -RT\, \eta_x \qquad (10)$$

holding for the solution irrespective of its concentration. η_x may be termed the *osmotic concentration* and is, like ξ, a merely thermodynamic quantity. Putting

$$\frac{\eta_x}{x} = \varphi \qquad (11)$$

this ratio called the *osmotic coefficient*[1] proves to be a thermodynamic quantity also when x is the stoichiometric concentration calculated from

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[1] Bjerrum, *Z. Elektrochem.*, 24, 321 (1918).

the above values of M and M_0. Accordingly we have in this case also to distinguish between the true and the stoichiometric coefficient.

Expressing the concentration in the c-scale, (10) and (11) are replaced by the corresponding formulas

$$(\pi_0 - \pi_{00}) \frac{c}{x} = -RT\, c \tag{12}$$

and

$$(\pi_0 - \pi_{00}) \frac{c}{x} = -RT\, \eta_c. \tag{13}$$

Furthermore, we obtain

$$\frac{\eta_c}{c} = \varphi. \tag{14}$$

By the equations above a series of functions, ξ_c, ξ_x, η_c, η_x, f and φ are introduced for the purpose of thermodynamic treatment of solutions. Of course, the introduction of these quantities affords no actual progress in the treatment in comparison with the application of the chemical potential or the affinity. All these quantities are correlated thermodynamically and are thermodynamically of the same worth, and only for the sake of convenience or brevity is one of them perferable to another. It will be found, however, as is especially pointed out by Bjerrum,[1] that in the case of dilute salt solutions, which we are to consider in the following, the activity coefficient and the osmotic coefficient will prove to be of peculiar value for the theoretical treatment.

The correlations between the functions introduced may be deduced by means of the fundamental equation of W. Gibbs:

$$x d\pi + d\pi_0 = 0 \tag{15}$$

which holds for dilute solutions; the same equation that in the form

$$x \frac{dA_1}{dx} + (1 - x) \frac{dA_2}{dx} = 0$$

has proved of value in affinity determinations. Introducing here (2), (6), (10) and (13), we obtain the equation

$$x\, d \ln \xi_x = x\, d \ln \xi_c = d\eta_c = \frac{x}{c} d\eta_c \tag{16}$$

which expresses the relation between the activities and the osmotic concentrations.

If more than one substance is present in dilute solution in the solvent, we have to apply the more general formula

$$x_1 d\pi_1 + x_2 d\pi_2 + \ldots + d\pi_0 = 0 \tag{17}$$

from which we obtain

and

$$\left.\begin{aligned} \Sigma x_1\, d \ln \xi_{x_1} &= d\eta_x \\ \Sigma c_1\, d \ln \xi_{c_1} &= d\eta_c \end{aligned}\right\} \tag{18}$$

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[1] *Loc. cit.*

By insertion of (4), (8), (11) and (14), Equation 18 gives us

$$\Sigma x_1 \frac{d \ln f_1}{dx} = x \frac{d\varphi}{dx} - (1 - \varphi) \tag{19}$$

and

$$\Sigma c_1 \frac{d \ln f_1}{dc} = c \frac{d\varphi}{dc} - (1 - \varphi) \tag{20}$$

where

$$\Sigma x_1 = x \text{ and } \Sigma c_1 = c.$$

Putting $x_2 = x_3 = \ldots = 0$, Equation 20 is tranformed into the equation given by Bjerrum[1] and valid for binary mixtures.

As we are to deal here with solutions containing two or more salts for the purpose of determining the solubility equilibrium, Equations 18–20 may be of special importance.

3. The Theory of the Solubility of Salts in Salt Solutions.

In a saturated solution of a binary salt the chemical potential of the saturating salt must possess a constant value equal to the sum of the chemical potentials of its ions. Denoting by π, π' and π'' the potential of the salt, the cation and the anion, respectively, we have

$$\pi = \pi' + \pi'' = \text{constant} \tag{21}$$

or according to (2)

$$\xi'\xi'' = k \tag{22}$$

which shows the activity product to be constant in a saturated solution. Inserting the activity coefficient by means of (4) we obtain

$$c'c''f'f'' = k. \tag{23}$$

As in this equation c indicates the molal concentration, f must be the stoichiometric activity coefficient. The alteration of f in the case of addition of another salt must cause the product $c'c''$ — the *stoichiometric solubility product*—also to change with the concentration of the added salt, and this change will depend solely upon the alteration in f. The laws according to which the alteration in f takes place must, therefore, also govern the changing solubility product resulting from the addition of extraneous salts.

We shall now, for the further treatment of the problem, introduce the hypothesis referred to in the introduction. We shall assume that the activity coefficient in a mixed salt solution is the same for any ion of the same type. As will appear from the following, this assumption will markedly simplify the problem before us. Then, since we are only dealing with comparatively sparingly soluble salts, the saturated solution will be either so dilute as to annul, at least approximately, the individual character of any salt, or it will consist nearly completely of the solvent

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[1] *Loc. cit.*

alone. It will be possible, therefore, to calculate the activity coefficient by considering only the properties of solutions of single salts.

It is necessary to emphasize, however, the approximative and provisional nature of the above hypothesis. It is introduced here to show only that the general features of the solubility curves may be accounted for on a thermodynamic basis by its means without further assumptions as to the constitution of the solutions, and especially without regard to the degree of dissociation, contingently occurring in the solutions, and hitherto introduced for the treatment of saturated solutions by means of the conductance ratio.

For the calculation of the activity coefficients we can use the results of Noyes and Falk,[1] who have shown that the freezing point data for a number of binary salts can be expressed by the equation

$$2 - i = K\sqrt[3]{c}, \qquad (24)$$

where i is the van't Hoff factor, c the equivalent concentration, and K a constant characteristic of each salt. Introducing $2\alpha = K$, (24) may be written

$$\varphi = 1 - \alpha\sqrt[3]{c} \qquad (25)$$

from which we obtain, by means of (20) and (17),

$$\log_{10} f = -1{,}737\ \alpha\sqrt[3]{c} = -a\sqrt[3]{c}. \qquad (26)$$

If this value be inserted in (23), we have, according to our assumption,

$$\log\,(c'c'') = 2a\sqrt[3]{c_t} + \text{const.} \qquad (27)$$

c_t denoting the total salt concentration in the saturated solution given by $c_t = c + s$.

Properly speaking, on the above assumption this relation (27) will hold good only if the solubility is slight when compared with the concentration of the solvent. Since the values of K, as shown by Noyes and Falk, vary only moderately within the range of salts of the same type, and since the presupposition made by assuming the f-values to be equal is only of approximate nature, no essential restriction in the applicability of (27) will result if the requirement above as to the solubility is dispensed with.

In the case of uni-univalent salts the coefficient a as computed from the data of Noyes and Falk proves to oscillate around a value not far from $^1/_3$. This figure may, therefore, be accepted as an average value and introduced in (27) to express the solubility in this case. If the valences of the ions are higher than unity, a will increase considerably.

From the freezing point data a value for a may be derived which for bi-bivalent salts is approximately 4 times the a value for uni-univalent salts. This is in concordance with theoretical considerations which render it likely that the a values increase proportionately to the square

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[1] THIS JOURNAL, 32, 1011 (1910).

of the valence. In the case of bi-bivalent and tri-trivalent salts the values $a = {}^4/_3$ and $a = 3$, respectively, may be adopted to express the solubility of such salts when introduced in (27).

For the application of this formula we have to distinguish between the cases of the solvent having one ion or none in common with the saturating salt. We may firstly consider the case when a heteroionic solvent is used.

4. Heteroionic Solvents.

In this case c' and c'' in Equation 27 are equal to the solubility or

$$\log s = a\sqrt[3]{c_t} + \text{const.} \tag{28}$$

Introducing here

$$\log s_0 = a\sqrt[3]{s_0} + \text{const.} \tag{29}$$

we obtain

$$\log \frac{s}{s_0} = a(\sqrt[3]{c_t} - \sqrt[3]{s_0}). \tag{30}$$

By means of this relation the solubility ratio s/s_0 can be calculated for varying values of s_0, c_t and the coefficient a. The results of this calculation are given in Tables I–III and are represented diagrammatically in Figs. 1 to 5.

In all these diagrams the abscissas represent the molal concentrations of the solvent employed, and the ordinates the solubility ratios s/s_0. The solubility s_0 being assumed to be negligible in the case represented in Fig. 1, this diagram shows only the influence of the a-value, *i. e.*, the influence of the valence. This influence is seen to be exceedingly marked. While the solubility of an uni-univalent salt is only moderately affected by addition of a tenth molal solvent, the effect in the case of a bi-bivalent one is very considerable, and in the case of a tri-trivalent one enormous.

TABLE I.—THE SOLUBILITY RATIO s/s_0 FOR $a = {}^1/_3$.

Heteroionic Solvent.

c.	$s_0 = 0$.	10^{-4}.	10^{-3}.	10^{-2}.	10^{-1}.
0.001	1.080	1.045	1.020	1.006	1.001
0.01	1.180	1.139	1.100	1.045	1.013
0.02	1.232	1.189	1.146	1.078	1.025
0.05	1.327	1.281	1.232	1.148	1.058
0.1	1.428	1.378	1.325	1.228	1.105

TABLE II.—THE SOLUBILITY RATIO s/s_0 FOR $a = {}^3/_4$.

Heteroionic Solvent.

c.	$s_0 = 0$.	10^{-4}.	10^{-3}.	10^{-2}.	10^{-1}.
0.001	1.359	1.193	1.081	1.027	1.009
0.01	1.937	1.687	1.471	1.223	1.084
0.02	2.301	2.001	1.733	1.395	1.170
0.05	3.099	2.693	2.319	1.808	1.405
0.1	4.157	3.611	3.104	2.384	1.784

TABLE III.—THE SOLUBILITY RATIO s/s_0 FOR $a = 3$.
Heteroionic Solvent.

c.	$s_0 = 0$.	10^{-4}.
0.001	1.995	1.496
0.01	4.43	3.27
0.02	6.52	4.80
0.05	12.74	9.40
0.1	24.69	18.27

s_0 =	0.001.		0.002.		0.005.
c.		c.		c.	
0.0008	1.196	...	..	...	...
0.00337	1.633	0.00227	1.365	...	...
0.00778	2.22	0.00629	1.856	0.00320	1.360
0.01673	3.27	0.01454	2.731	0.00999	2.002
0.04361	6.37	0.03933	5.337	0.03045	3.910
0.08762	12.38	0.07932	10.34	0.0621	7.578

s_0 =	0.01.		0.02.		0.05.
c.		c.		c.	
0.0053	1.47	...	..	...	...
0.0107	1.93	0.0038	1.31	...	...
0.0160	2.40	0.0074	1.63	...	...
0.0213	2.87	0.0110	1.95	...	...
0.0267	3.37	0.0142	2.29	0.0015	1.17
0.0310	3.90	0.0172	2.64	0.0025	1.35
0.0358	4.42	0.0198	3.01	0.0030	1.54
0.0443	5.57	0.0243	3.79	0.0031	1.94

The influence of the solubility s_0 is shown in Fig. 2 for uni-univalent salts. The smaller the solubility the more pronounced, obviously, is the

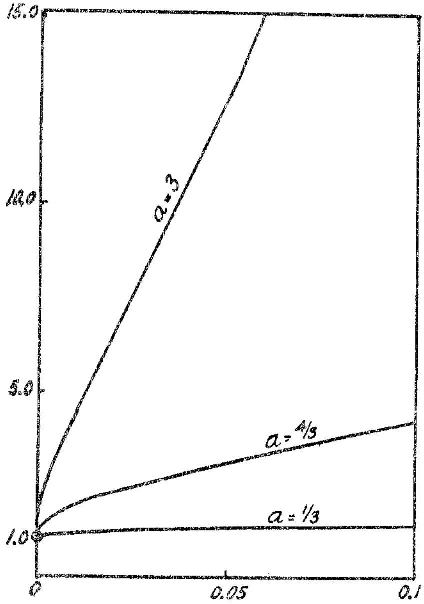


Fig. 1.

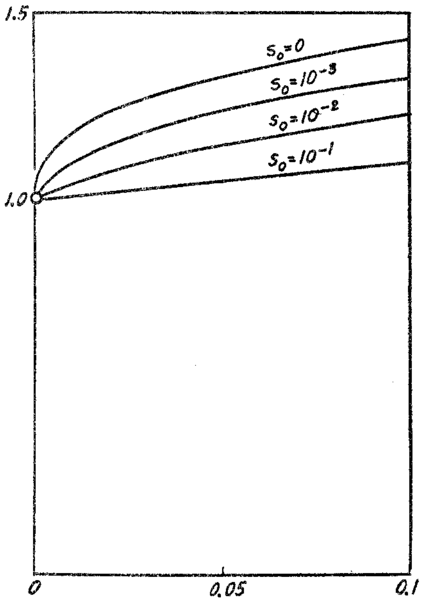


Fig. 2.—Uni-univalent salts.

effect of the added salt. The same is seen to be the case when we consider bi-bivalent salts. With the greater solubilities the curves approach straight lines, while the curvature is very marked in the case of slight solubilities.

For tri-trivalent salts the results are plotted in Figs. 3, 4 and 5. It will be observed that the influence of s_0 on the shape and the slope of the curves is similar to that in the foregoing cases only until the solubility $s_0 = 0.02$ molal. At this concentration the effect exhibits a minimum, and at higher solubilities the curves rise again showing a curvature in the opposite direction of that otherwise found. In this respect the behavior of tri-trivalent salts diverges widely from that of the salts of lower types, as will especially be evident on considering Fig. 5. The significance of the dotted line in this figure and in Fig. 3 will be mentioned later on.

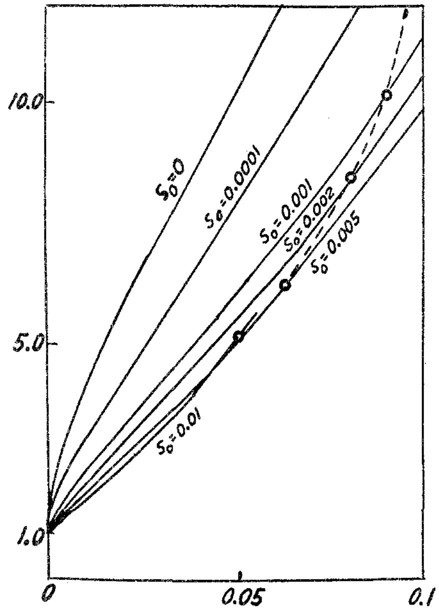


Fig. 3.—Tri-trivalent salts.

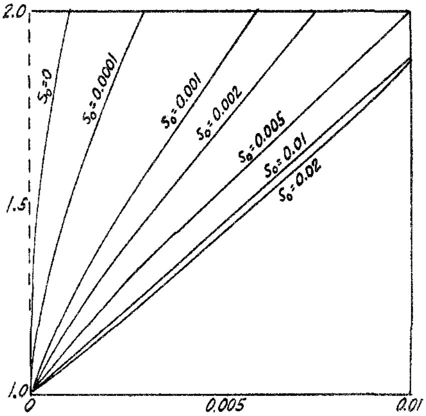


Fig. 4.—Tri-trivalent salts.

In a simpler but somewhat less perspicuous way the calculations according to (30) can be represented by employing the total concentration c_t instead of the concentration c of the solvent as abscissas. For this purpose we first transform Equation 30 into the following

$$\log \frac{s_1}{s_2} = a(\sqrt[3]{c_{t_1}} - \sqrt[3]{c_{t_2}}) \qquad (31)$$

s_1 and s_2 representing the solubilities at the total concentrations c_{t_1} and c_{t_2}, respectively. Putting here $c_{t_2} = 0.1$ we obtain the figures given in Table IV and represented in the graph Fig. 6.

For each value of a only one single curve irrespective of the solubility s_0 is obtained. The results are consequently more completely given by this diagram than by the foregoing. On the other hand, it is more difficult to grasp the significance of s_0 by this method.

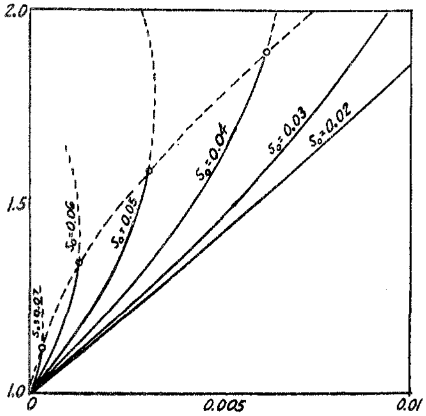


Fig. 5.—Tri-trivalent salts.

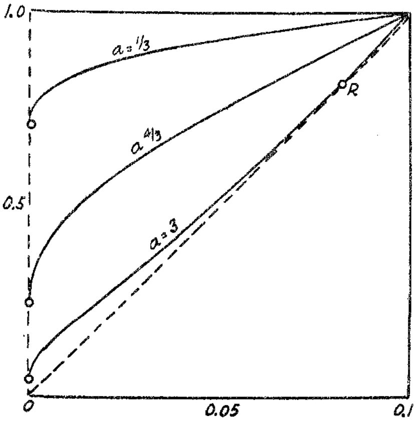


Fig. 6.

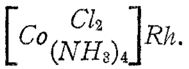
Having now shown the general results furnished by Equations 30 and 31 in the case of heteroionic solvents, we shall turn to their application to some definite examples. In spite of the great amount of experimental work carried out on solubilities partly referred to in the introduction, only a few data are available for the purpose before us. A series of investigations have, therefore, been initiated in this laboratory for supplying this lack, and an ample experimental material has already been procured, chiefly covering salts of the metal-ammonia type.

Table IV.—The Solubility Ratio $s/s_{0.1}$ for Different Values of a Heteroionic Solvent.

$c + s$.	$a = 1/3$.	$a = 4/3$.	$a = 3$.
0.000	0.7003	0.2405	0.0405
0.001	0.7561	0.3269	0.0808
0.002	0.7714	0.3541	0.0967
0.005	0.7984	0.4065	0.1320
0.01	0.8262	0.4660	0.1795
0.02	0.8625	0.5535	0.2642
0.05	0.9291	0.7452	0.5159
0.08	..	..	0.7940
0.1	1.0000	1.0000	1.0000

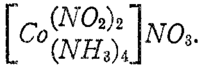
From this series, of which a complete account will be rendered in subsequent articles, a few data may be stated in Tables V to IX. The metal-ammonia salts here in question are the following:

Dichlorotetrammine cobaltic rhodanide or praseo rhodanide



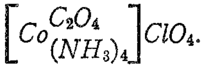
$$\left[Co\,{}^{Cl_2}_{(NH_3)_4}\right]Rh.$$

Trans dinitrotetrammine cobaltic nitrate or croceo nitrate



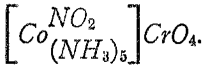
$$\left[Co\begin{matrix}(NO_2)_2\\(NH_3)_4\end{matrix}\right]NO_3.$$

Oxalotetrammine cobaltic perchlorate



$$\left[Co\begin{matrix}C_2O_4\\(NH_3)_4\end{matrix}\right]ClO_4.$$

Nitropentammine cobaltic chromate or xantho chromate



$$\left[Co\begin{matrix}NO_2\\(NH_3)_5\end{matrix}\right]CrO_4.$$

Further, the data of Noyes and Bray[1] on thallous chloride are shown.

Under $(s/s_0)_{\text{calc.}}$ are presented the solubility ratios calculated by means of (30), introducing for a a value such as to make the calculated and the experimental values of s/s_0 agree most closely. It is seen from the tables, first, that agreement can be brought about if we introduce one single a value for any system, second, that these a values for the various systems of uni-univalent salts vary only slightly in the neighborhood of $^1/_3$. In this respect full concordance exists with the requirements of the freezing point formula. In the case of the bi-bivalent xantho chromate the a value 1.80 must be adopted to represent the experimental data. This value also corresponds to the freezing point measurements and is approximately 4 times as great as in the case of uni-univalent salts.

For tri-trivalent salts no experiments have been carried out with tri-trivalent solvents. The results obtained by employing other solvents, however, show the rise in solubility here to be extremely marked, highly exceeding the effect observed in the case of lower valence. This agrees with the corresponding higher values for a, which may be used in this case.

TABLE V.—THE SOLUBILITY OF PRASEO COBALTIC RHODANIDE IN SODIUM CHLORATE SOLUTIONS AT t = 0°, a = 0.30.

c.	s.	(s/s_0) calc.	(s/s_0) found.
0.00	0.00289	1.000	1.000
0.01	0.00306	1.066	1.059
0.03	0.00327	1.132	1.132
0.05	0.00339	1.175	1.173
0.1	0.00360	1.254	1.246

TABLE VI.—THE SOLUBILITY OF CROCEO COBALTIC NITRATE (β-MODIFICATION) IN POTASSIUM FORMATE SOLUTIONS AT t = 0°, a = 0.31.

c.	s.	(s/s_0) calc.	(s/s_0) found.
0.00	0.00494	1.000	1.000
0.02	0.00536	1.092	1.086
0.05	0.005745	1.163	1.164
0.1	0.00621	1.242	1.258

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[1] *Loc. cit.*

TABLE VII.—THE SOLUBILITY OF OXALOTETRAMMINE COBALTIC PERCHLORATE IN SODIUM FORMATE SOLUTIONS AT $t = 0°$, $a = 0.33$.

c.	s.	(s/s_0) calc.	(s/s_0) found.
0.00	0.00508	1.000	1.000
0.05	0.00597	1.174	1.174
0.10	0.00640	1.258	1.260

TABLE VIII.—THE SOLUBILITY OF THALLOUS CHLORIDE IN POTASSIUM NITRATE SOLUTIONS AT $t = 25°$, $a = 0.355$.

c.	s.	(s/s_0) calc.	(s/s_0) found.
0.00	0.01607	1.000	1.000
0.02	0.01716	1.068	1.068
0.05	0.01826	1.136	1.136
0.1	0.01961	1.217	1.220

TABLE IX.—THE SOLUBILITY OF XANTHO COBALTIC CHROMATE IN MAGNESIUM SULFATE SOLUTIONS AT $t = 0°$, $a = 1.80$.

c.	s.	(s/s_0) calc.	(s/s_0) found.
0.00	0.000258	1.00	1.00
0.02	0.000620	2.39	2.40
0.05	0.000908	3.57	3.52
0.1	0.001237	5.3	4.8

As far as these facts go, the established formulas (30) and (31) may thus be looked upon as able to account for the shape of the solubility curves obtained by varying valence of the ions through the use of heteroionic solvents. As will be observed on closer inquiry into the available experiments, the formulas hold generally only approximately in concordance with the individual behavior which the various salts exhibit in solution, as known also from the individuality in the freezing-point curves.

5. Homoionic Solvents.

In the homoionic solvents the solubility phenomena are much more multifarious than when heteroionic solvents are employed. The correctness of the point of view advanced for the treatment of solubility equilibria will, therefore, be subjected to a more severe test by the employment of solvents of this kind.

From Equation 27

$$\log\,(c'c'') = 2a\sqrt[3]{c_t} + \text{const.}$$

we obtain by putting $c' = s$ and $c'' = c_t$ and elimination of the constant

$$\log \frac{sc_t}{{s_0}^2} = 2a(\sqrt[3]{c_t} - \sqrt[3]{s_0}) \tag{32}$$

or

$$\log \frac{s_1 c_{t_1}}{s_2 c_{t_2}} = 2a(\sqrt[3]{c_{t_1}} - \sqrt[3]{c_{t_2}}), \tag{33}$$

where the terms applied have the same meaning as above, and especially the product sc_t indicates the stoichiometric solubility product. By application of these formulas to the various types of salts the corresponding values of a, given on p. 767, must be introduced.

We shall first consider the effect of the addition of a homoionic solvent qualitatively. To that end Equation 32 is differentiated. Thus we obtain

$$\frac{d \ln s}{d \ln c_t} = \frac{a}{0{,}6515} \sqrt[3]{c_t} - 1. \tag{34}$$

If c_t be sufficiently small, the first member of the right-hand expression will vanish, and we can write

$$d \ln s = -d \ln c_t.$$

In this case the solubility product is constant. The solubility must therefore always decrease by increasing concentration of the homoionic solvent if the solubility in pure water be sufficiently small, and the solvent added in sufficiently slight concentration.

From (34) we draw the general inference that the solubility curve must exhibit a minimum when

$$\sqrt[3]{c_t} = \frac{0{,}6515}{a} \tag{35}$$

showing at smaller concentrations a fall and at higher concentrations a rise with a rise in concentration of the solvent. This minimum lies at very different concentrations according to the different values of a. Putting for a the values adopted above for the various types of salts, we obtain the following figures for the minimum concentration.

TABLE X.

Type of salt.	a.	$c_{\text{min.}}$
Uni-univalent....................	$^1/_3$	7.5
Bi-bivalent......................	$^4/_3$	0.12
Tri-trivalent....................	3	0.01

In the case of uni-univalent salts the concentration calculated in this way lies far beyond the domain of the established formulas. For salts of higher types, however, the calculated c_{min} are sufficiently small to render the results reliable. We may, therefore, expect that a minimum in the solubility curve may occur for bi-bivalent and tri-trivalent salts at the total concentration in the neighborhood of 0.1 and 0.01 molal, respectively.

If the solubility in pure water of a bi-bivalent or a tri-trivalent salt exceeds these minimum values 0.1 and 0.01 molal, respectively, the solubility curve must obviously start rising contrarily to the ordinary conception of the influence of a homoionic solvent.

We shall now turn to the numerical calculation of the effect of a homoionic solvent. It is first to be noted that Formula 31 represented in Fig. 6 applies very well also in the case of homoionic solvents when $sc_t/s_0^{\,2}$ is inserted for s^2/s_0^2. In Fig. 6 the curves then represent the square root of the solubility product instead of the solubility itself. A more instructive picture of the correlations in question will, however, be obtained when, as in the foregoing section, the interdependence between the solubility ratio s/s_0 and the concentration of the solvent is represented.

The results of these calculations, according to Equation 32, are given in the following tables, XI, XII, XIII, and the accompanying diagrams:

TABLE XI.—THE SOLUBILITY RATIO s/s_0 FOR $a = {}^1/_3$.
Homoionic Solvent.

c.	s/s_0.	c.	s/s_0.	c.	s/s_0.
0.0001	0.108	0.1	0.119	0.01455	0.545
0.01	0.01296	0.02	0.0651	0.0475	0.253
0.02	0.00706	0.05	0.0302	0.0999	0.146
0.05	0.00328	0.1	0.0175	...	...
0.1	0.00190	..	..	...	...
$s_0 = 10^{-4}$		$s_0 = 10^{-3}$		$s_0 = 10^{-2}$	

TABLE XII.—THE SOLUBILITY RATIO s/s_0 FOR $a = {}^4/_3$.
Homoionic Solvent.

c.	s/s_0.	c.	s/s_0.	c.	s/s_0.
0.001	0.139	0.0098	0.197	0.01295	0.705
0.01	0.0282	0.0199	0.143	0.0445	0.512
0.02	0.0199	0.0499	0.104	0.0954	0.461
0.05	0.0144	0.0999	0.094	...	...
0.1	0.0129	..	...	...	...
$s_0 = 10^{-4}$		$s_0 = 10^{-3}$		$s_0 = 10^{-2}$	

TABLE XIII.—THE SOLUBILITY RATIO s/s_0 FOR $a = 3$.
Homoionic Solvent.

c.	s/s_0.	c.	s/s_0.	c.	s/s_0.
0.00098	0.210	0.00951	0.493	0.0092	1.084
0.01	0.1033	0.0195	0.534	0.0334	1.656
0.02	0.1120	0.0492	0.816	0.0689	3.11
0.05	0.1710	0.0985	1.532	..	...
0.1	0.320	...	...	..	...
$s_0 = 10^{-4}$		$s_0 = 10^{-3}$		$s_0 = 10^{-2}$	

We observe from these that Equation 32 underlying the calculations is able to account for the wide diversities which, according to the available data in this field, are characteristic of solubilities in homoionic solvents. With small a-values, that is, with uni-univalent salts the solubility exhibits a pronounced and steady decrease with increasing concentration of the added salt. With medium values of a, that is, with bi-bivalent salts the solubility is likewise diminished, but the fall is less marked than in the foregoing case, and the curves gradually approach a horizontal line. The curves corresponding to a large value of a, or to tri-trivalent salts, finally show pronounced minima and, at higher concentration, a rapid rise in solubility. In all cases the shape of the curves is markedly influenced by the value of the solubility s_0 in pure water. This value being sufficiently high, we find in the case of a tri-trivalent salt, as mentioned above, that the decreasing portion of the curve will disappear and the curve start rising.

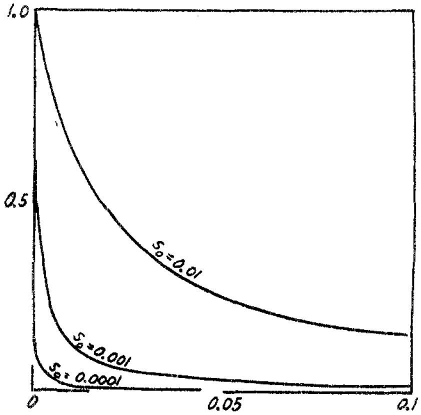


Fig. 7.—Uni-univalent salts.

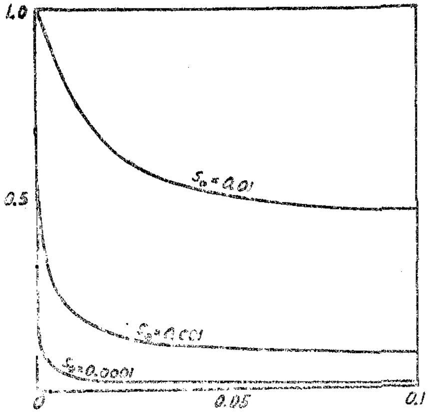
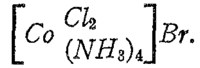


Fig. 8.—Bi-bivalent salts.

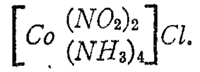
A few of the results which have been furnished by the examination of metal-ammonia salts dissolved in homoionic solvents may be stated here for a closer illustration of the applicability of the theory. The salts in question are the following:

Dichlorotetrammine cobaltic bromide or praseo bromide,



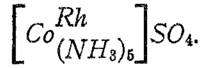
$$\left[Co\begin{matrix}Cl_2\\(NH_3)_4\end{matrix}\right]Br.$$

Trans-dinitrotetrammine cobaltic chloride or croceo chloride,



$$\left[Co\begin{matrix}(NO_2)_2\\(NH_3)_4\end{matrix}\right]Cl.$$

Iso-rhodanopentammine cobaltic sulfate,



$$\left[Co\begin{matrix}Rh\\(NH_3)_5\end{matrix}\right]SO_4.$$

Table XIV.—The Solubility of Praseo Bromide in Potassium Bromide Solutions at $t = 0°$, $a = 0.355$.

c.	s_{found}.	s_{calc}.
0.00	0.00635	....
0.02	0.00212	0.00212
0.05	0.00107	0.00107
0.1	0.000635	0.000634

TABLE XV.—THE SOLUBILITY OF CROCEO CHLORIDE IN POTASSIUM CHLORIDE SOLUTIONS AT $t = 0°$, $a = 0.38$.

c.	s_{found}.	s_{calc}.
0.00	0.02216	....
0.02	0.01515	0.01516
0.05	0.01005	0.00991
0.1	0.00640	0.00647

TABLE XVI.—THE SOLUBILITY OF ISO-RHODANOPENTAMMINE COBALTIC SULFATE IN MAGNESIUM SULFATE SOLUTIONS AT $t = 0°$, $a = 1.73$.

c.	s_{found}.	s_{calc}.
0.00	0.01177	....
0.02	0.01005	0.0096
0.05	0.00980	0.0099
0.1	0.01034	0.0116

TABLE XVII.—THE SOLUBILITY OF THALLOUS CHLORIDE IN POTASSIUM CHLORIDE SOLUTIONS AT $t = 25°$, $a = 0.40$.

c.	s_{found}.	s_{calc}.
0.00	0.01607	....
0.025	0.00869	0.00873
0.05	0.00590	0.00587
0.1	0.00396	0.00391

The data for these salts and the data of Bray and Winninghoff[1] for thallous chloride are given in Tables XIV to XVII.

The agreement between the calculated values and those found experimentally in all cases proves satisfactory. The values of a to be chosen for producing this agreement are quite concordant with the a values found using heteroionic solvents and by the freezing-point measurements. We observe especially that the a values for the bi-bivalent salt must again be chosen nearly 4 times as great as for uni-univalent ones. The appearance of a minimum in the curve for the bi-bivalent salt is likewise in accordance with the theory as mentioned above.

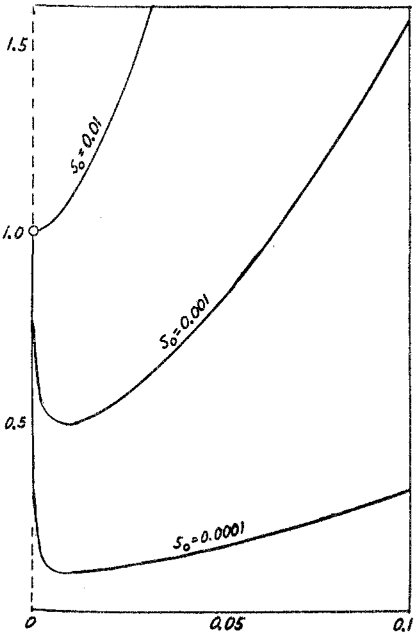


Fig. 9.—Tri-trivalent salts.

6. The Liquid-Liquid Equilibrium.

Some interesting phenomena whose occurrence may be suspected from the established formulas, such as (30), in the case of polyvalent ions, may

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[1] THIS JOURNAL, 33, 1663 (1911).

be mentioned now. As seen from the diagram, Fig. 6, the curvature of the curves for small values of a has the same sign through the whole range of concentrations. As a becomes greater the course of the curves becomes more rectilinear at the higher concentrations and, finally, when a sufficiently large value of a is reached, an inflexion point appears in the curve. Beyond this point the curvature is inverted, and at a certain point (R) the tangent of the curve may pass through the origin.

This case is more clearly represented in Fig. 10 for the addition of a homoionic salt. The solubility s is plotted against the total concentration c_t. The point R corresponds to the point R mentioned in Fig. 6. We have here

$$\frac{ds}{dc_t} = \frac{s}{c_t}$$

or

$$d \ln s = d \ln c_t = d \ln c. \qquad (36)$$

Introducing here $s = \xi_1/f$ and $c = \xi_2/f$, ξ_1 and ξ_2 denoting, respectively, the activities of the saturating salt s_1 and the salt s_2 serving as solvent, we obtain

$$d \ln \xi_1 = d \ln \xi_2 \qquad (37)$$

or, since ξ_1 = constant on account of the solution being saturated with s_1

$$d\xi_2 = 0. \qquad (38)$$

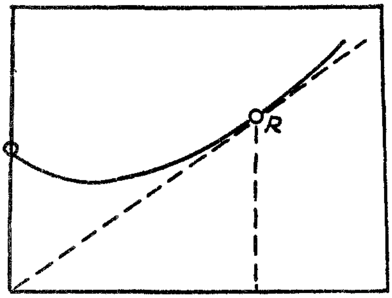

Fig. 10.

At concentrations corresponding to the point of contact R the activity of s_2 will thus remain constant with rising concentration. While in all stable solutions addition of any substance must cause the potential or activity of this substance to rise we have here arrived at a critical point for the stability of the solution. According to the theory of miscibility of liquids a separation in two liquid layers must take place before this critical concentration is attained. The situation of this point is determined by (36). Combining this with (28) we obtain

$$\sqrt[3]{c_R} = \frac{1.303}{a} \qquad (39)$$

where c_R indicates the mentioned critical concentration.

According to Equation 18 the point R is also characterized by

$$d\eta = 0,$$

which indicates that the osmotic concentration here shows a maximum. Since this will be the case also in pure salt solutions, the phenomenon of separation here in question must occur in pure salt solutions too.

The same result is easily found by applying Formula 26,

$$\log f = -a\sqrt[3]{c}.$$

Putting here $f = \xi/c$ we have

$$\log \xi = \log c - a\sqrt[3]{c},$$

or, since $d \log \xi = 0$ by $c = c_R$

$$\sqrt[3]{c_R} = \frac{1.303}{a}$$

corresponding to (39).

As a result of these computations we see that the activity of a dissolved salt, increasing with increasing concentration in dilute solution, at higher concentrations will reach a maximum and thereafter decrease. These computations of course have a physical meaning only if the critical point R is reached by solutions which are sufficiently dilute for the applicability of the formulas involved. Introducing in (39) the values of a used above to represent the behavior of the various types of salts, we can calculate the following values of c_R.

Table XVIII.

Type of salt.	a.	c_R.
Uni-univalent..................	$^1/_3$	0.59
Bi-bivalent.....................	$^4/_3$	0.93
Tri-trivalent....................	3	0.082

Only in the case of tri-trivalent salts, as seen from the figures, does the calculation of c_R afford a trustworthy result, as only in this case is the calculated magnitude of c_R small enough to render the applied formulas at all valid. Even the concentration 0.08 computed for such salts may be regarded as a rough estimation, on account of the deviation from the formulas used increasing rapidly with increasing valence of the ions. We are justified, however, in expecting the separation phenomenon in the case of polyvalent ions at least at fairly small concentrations.

Similarly, the separating layer may be expected to contain a small amount of the solvent. It may naturally be regarded as a salt in liquid state saturated with water under the prevailing conditions. If the melting point of the salt be very low, the liquid-liquid system in certain cases may be a stable one. Usually, however, the equilibrium can exist only because of the insufficient velocity of crystallization, the tendency of the concentrated layer to separate the solid phase being thereby obscured.

According to this view the solubility of salts of higher types may remain far below the solubility of the liquid layer[1] or *a fortiori* far below the critical concentration c_R. In fact, the solubility determinations with such salts, carried out in connection with the above-mentioned investigation on metal ammonia salts, clearly confirms this conclusion, as in all cases solubilities not surpassing 0.001 molal were found.

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[1] See J. N. Brønsted, *Z. physik. Chem.*, 56, 683 (1906).

Regarding the separation of a liquid layer from a salt solution, this phenomenon has been realized in a number of cases by admixture of solutions of polyvalent ions of different sign. The separation was in all cases studied by mixing two samples of the solutions concerned under the microscope. Usually the separation occurs instantaneously forming clouds of minute particles gradually uniting to larger liquid drops. The change of the liquid salt into the solid phase usually takes place rapidly. Notably, however, in the case of the trivalent triethylene-diamine cobalt ion the liquid system may be fairly stable, and the procedure of the growth of the drops and their ultimate crystallization furnish a clear illustration of the nature of the phenomenon.

It remains to be said that the phenomenon of the appearance of a salt in liquid state by precipitation is known from other fields of research. The interest of the phenomenon, and its importance for our conception of salt solution, however, makes a closer theoretical and experimental investigation desirable. We shall there have the opportunity of considering the experimental results from this laboratory and from other quarters more closely.

In Figs. 3 and 5 the critical points on the curves are indicated by circles. The dotted line drawn through these points forms the limit of stable solutions. All parts of the curves beyond this limit are dotted in the figures in order to show the unstable or hypothetical character.

Using homoionic solvents a limiting curve of similar significance can be drawn. In all cases the critical points can be determined as points of contact of the tangent passing through the origin.

7. Theoretical Considerations.

Through the results obtained in the foregoing sections we are justified in concluding that the solubility phenomena of salts in solutions of other salts with or without an ion in common may be accounted for on a thermodynamic basis by the simple assumption of the equality of the activity coefficients for salts or ions of the same type in a mixed salt solution.

In particular cases this assumption may prove to hold very exactly, for instance, in mixed solutions of potassium chloride and potassium bromide of slight concentration. Solutions of such a kind will behave in a markedly simple manner at constant total concentration, and may suitably be termed ideal salt solutions. Apart from such solutions, the assumption of the equality of the activity coefficients, as already emphasized in the foregoing, pretends to be only an approximation. It is important to note, however, that the activity coefficients of mixed salts cannot vary independently but, as mentioned in Section 2, are subject to thermodynamic correlations. In a subsequent paper we shall deal with these correlations more thoroughly.

Like our chief assumption concerning the activity coefficient, the cube root expression employed for log f is also an approximation. It is clear, therefore, that all the formulas derived in the preceding sections represent only the general shape of the solubility curves, but are not able to explain the peculiar behavior of a particular system. In order to ascertain whether the hypothesis advanced may, properly modified, be able to form the base of a more precise theory of solubility, it must preferably be looked upon in the light of the theory of the complete electrolytic dissociation supported by Bjerrum[1] and Milner.[2]

In a recent paper[3] I have shown that this theory may be applied advantageously in the case of mixed salt solutions to explain the decrease in activity exhibited by a dissolved salt on addition of another salt. From this point of view the increased solubility of salts in heteroionic solvents follows simply from the diminution of the activity coefficient of the ions, no assumption as to the formation of undissociated molecules being involved. In the case of a homoionic addition the solubility product for the same reasons must rise, producing either a rise or a fall in the solubility itself, according to the type of the added salt and the prevailing conditions of the system as a whole.

According to the definite character of the activity in any given solution, the stoichiometric activity coefficient defined in Section 2 and reckoned with throughout this paper, must obviously be equal to the activity coefficient arrived at by the suggestion of complete dissociation, since in this case the actual concentration of the ion is equal to its stoichiometric concentration.

If the calculations carried through by Milner, to determine the influence of the electric charges of the ions, held good for real salts, the activity should be the same in all cases for the same type of salt, and the above approximate hypothesis would then be a rigid law. The deviations manifested by salt solutions, when examined with regard to freezing point or solubility, proves, however, that the ions possess a markedly separate or individual behavior which is appreciable even at fairly small concentrations. From the usual point of view this individuality should be ascribed to diversities in the degree of dissociation. On the basis of the theory of complete dissociation it becomes necessary to attribute to any separate ion a secondary power beside the primary Milner effect which can exert a specific action on ions of the same or of another type. The necessity of introducing such a secondary effect becomes quite natural when we bear in mind that the computations of Milner rest on the presupposition of ideal conditions in the solutions, the ions being considered as charged

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[1] *Proc. 7th Intern. Cong. Appl. Chem.* (London), 1909. Sec. X, *Z. Elektrochem.*, 24, 321 (1918).

[2] *Phil. Mag.*, [6] 23, 553 (1912); 25, 742 (1913).

[3] *Meddelanden från K. Vetenskabsakademiens Nobelinstitut*, 5, No. 25 (1919).

mass-points, and no regard being paid to the possible hydration of the ions. When the ions are considered as particles of finite sizes, and provided with electrical charges at finite distances from one another, and moreover often combined with a large number of water molecules, they must behave otherwise than the ideal ions which Milner deals with. It is easily understood, therefore, why the theory of Milner is not able to give an exact picture of the behavior of salt solutions.

Considering now the laws of the strong electrolytes as being governed merely by these primary and secondary forces, the interpretation of several solubility phenomena which, according to the ordinary view of such solutions, require particular assumptions for their explanation will appear especially simple. To explain the increasing solubility, which is exhibited by sparingly soluble salts on addition of a homoionic solvent in fairly considerable concentration, we thus commonly suspect the formation of "complex" ions to take place in the solution. Of course in many cases this conclusion may be correct. The solubility of silver cyanide in potassium cyanide, for instance, is undoubtedly due to the formation of a complex silver cyanide ion The rise in solubility produced in this way is no exceptional phenomenon, however, but generally met with, as mentioned above, when the coefficient a has reached a certain value. From the theory advanced the explanation is given by the double action of the added salt in raising the activity on account of the increasing concentration of the ion concerned, and in causing it to fall on account of the rising electric forces operating between the ions the last mentioned effect exceeding the first in the case of increased solubility. In a solution of hexammine cobaltic sulfate, for instance, we have no reason for believing the ions tend to form complexes. Nevertheless, the solubility of this salt increases rapidly with increasing concentration of a sodium sulfate solution serving as solvent. In this, as in similar cases, the explanation follows as a simple consequence of the electric action which must be associated with the ions according to our theory.

In this connection we may mention a phenomenon to which attention is called by Noyes and Bray.[1] It is stated by these observers that, though in all cases of moderately soluble uni-bivalent salts the solubility is reduced in at least rough conformity with the requirements of the solubility product principle when a salt is added having a univalent ion in common, the decrease of the solubility caused by the addition of an equivalent quantity of a salt with a common bivalent ion does not exceed a few per cent., and the addition of a larger quantity causes the solubility to increase slightly. In other words, the effect on the solubility in the last-mentioned case is on the whole very slight. Harkins[2] emphasizes

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[1] *Loc. cit.*

[2] THIS JOURNAL, 33, 1807 (1911).

this phenomenon as having no resemblance to what would be expected from an application of the solubility product principle.

From our point of view, however, a distinction between the two cases does not exist. Consider a uni-bivalent salt, for instance, lead chloride. Let s_1 and s_2 be the solubility in equivalents in a solution of potassium chloride of the concentration c_1 and in a solution of lead nitrate of the equivalent concentration c_2. Then we have

$$\frac{s_1}{2}(s_1 + c_1)^2 f_1 f_1'^2 = \frac{s_2 + c_2}{2} s_2^2 f_2 f_2'^2$$

where f_1, f_1' and f_2, f_2' indicate the activity coefficients of the lead ion and the chlorine ion in the first and second solution, respectively. Assume the total equivalent concentration to be equal ($= c_t$) in the two cases, and the activity coefficients of the two ions to depend only on the total concentration. The above equation then simplifies to

$$s_1 c_t = s_2^2. \tag{40}$$

This equation shows that a rapid fall in solubility by increasing concentration of an added salt having a univalent ion in common with the saturating salt is easily compatible with the solubility being unaltered by addition of a salt with a common bivalent ion. As in dilute solutions the gas laws approach validity, s_1 will decrease more rapidly in this region, than corresponding to $s_2 = s_1 c_t = k$, and s_2 consequently will not be constant but decrease slightly. At increasing concentrations the fall in s_1 may gradually diminish, corresponding to s_2 passing through a minimum, and thereafter increasing. The effect observed is thus not an abnormal one, but rather in full concordance with what would be expected from the standpoint adopted.

The significance of the valence of the ions is accounted for by assigning according to the type of the salts, different values to the coefficient a in the formulas employed. The relationship between valence and activity coefficient is suggested by Bjerrum[1] and explained through the attracting forces operating between the ions, these forces varying proportionately to the product of the electric charges. No formal derivation of this dependency, however, is given and at the present moment it is not quite decided whether the molal or the equivalent concentration would apply most suitably in the formulas. At any rate, the rapid rise in the electric forces by increasing valence manifests itself very distinctly in the solubility measurements.

As shown in the foregoing, there will be a fall in the activity with increasing concentration if the coefficient a be sufficiently great; that is to say, in the case of tri-trivalent salts. This is easily understood when we consider the solution constituted by ions of high charges. As the concen-

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[1] *Z. Elektrochem.*, 24, 321 (1918).

tration increases, the attracting forces between the ions will tend to diminish the activity contrarily to the effect otherwise prevailing in dilute systems, and at a certain point, therefore, the activity will pass through a maximum. This corresponds to the separation of another liquid layer in equilibrium with the solution, as mentioned above. This phenomenon is quite similar to the break in continuity produced by the compression of a gas beyond the saturation point, the cohesive forces between the molecules here replacing the electric forces operating between the ions. As the incomplete miscibility of liquids according to the theory of Hildebrand[1] is sensibly dependent upon the difference in internal pressure of the liquids concerned, we must suggest the supercooled liquid salts of high valence to be in possession of extremely high internal pressure, as is exactly to be expected from the conception of the salts being, in the solid and the liquid state, also more or less completely dissociated. At any rate the assumption of a decreasing dissociation of the salts with increasing concentration may not be able to account for the separation phenomenon appearing in very dilute solutions in a similarly simple way.

Finally, we may consider briefly some other fields in which the theory supposedly may be advantageously applied. It is clear that the effect which is here assumed to increase the solubility of a salt by addition of other salts, must exist also in the case of unsaturated solutions and may be able to alter the equilibrium occurring in homogeneous solutions as a whole.

Consider first the electrolytic dissociation of the solvent itself. In accordance with the above view an addition of salt to pure water must diminish the activity coefficient of the hydrogen and the hydroxyl ion. As on the other hand, the potential of the water suffers no perceptible alteration on small additions of salt, a rise in the dissociation of the water must ensue. The "dissociation constant" is thus actually no constant, but increases with the concentration of the solute, say a uni-univalent salt, in the same way as the solubility product of a correspondingly soluble salt. If by *k* we denote the dissociation product in pure water, the value of the product of the two ions at varying concentration of an added uni-univalent salt, calculated by means of (27) may be expressed approximately by the following figures:

TABLE XIX.—THE DISSOCIATION PRODUCT OF WATER IN SALT SOLUTIONS OF THE CONCENTRATION *c*.

c.	$c_{H^+} \cdot c_{OH^-}$
0.	k.
0.001	1.17
0.01	1.39
0.02	1.51
0.05	1.77
0.1	2.05

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[1] THIS JOURNAL, **38**, 1452 (1916).

The alteration in the dissociation product is thus very considerable. In a tenth molal solution it is about twice the value in pure water. That such a change has not been observed hitherto is due to the fact that usually only the activity of the ions, and not their true concentrations, are available for the experiment. If the activity coefficient be altered to the same degree for the two ions, the effect must then be obscured.[1]

As in the case of water, we shall find an effect of the same kind with other weak electrolytes. We may establish quite generally the fact that any equilibrium in aqueous solution involving incompletely dissociated electrolytes may be influenced correspondingly by addition of salts. By consideration of such cases, however, the phenomenon known as the "sailing out" effect must be not disregarded. This effect will cause the activity of a non-electrolyte, or of the undissociated portion of a weak electrolyte, to increase with increasing salt concentration. The solubililty of a slightly soluble weak acid, for instance, will for these reasons exhibit a maximum at a certain salt concentration at which the Milner effect is compensated by the "salting out" effect. Experiments of Hoffmann and Langbeck[2] with weak acids have given results which confirm this view.

For the treatment of the solubility phenomena of the strong electrolytes the results obtained with non-electrolytes or weak electrolytes, however, are of wide consequence. For it may be surmised that the "salting out" effect is not restricted to uncharged molecules alone but is present in the case of widely dissociating salts also. It is very probable that the "secondary effect" mentioned in the previous sections as being peculiar to the individual salts, respecting their solvent power, may be found to be in close connection with the salting out effect. As an illustration may be noted that potassium hydroxide, showing the most pronounced salting out effect upon non-electrolytes, also reduces the solubility of salts much more markedly than other solvents examined in this respect.[3] This fact has caused A. E. Hill[4] to surmise without paying attention to the exceptional character of the substance used that the solubility generally diminishes on addition of heteroionic solvents.

Having now in the present paper advanced the general points of view

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[1] If the H^+ and the OH^- ions are hydrated to a different extent, increasing concentration of an added substance must alter the dissociation equilibrium of water in favor of the anhydride of the most hydrated ion. This fact being appreciable in strong solutions makes it possible to explain a divergence of such solutions from the neutral state, as indicated by electrometric measurements. Possibly the results of Palmaer and Melander (*Z. Elektrochem.*, 21, 418 (1915)) are to be interpreted in this way.

[2] Hoffmann and Langbeck, *Z. physik. Chem.*, 51, 385 (1905).

[3] J. N. Brønsted, Meddelanden fr. K. Vetenskapsakademiens Nobelinstitut, 5, No. 25 (1919).

[4] A. E. Hill, This Journal, 32, 1186 (1910).

from which the solubility equilibrium in salt solutions supposedly ought to be considered, we may in subsequent articles turn to a more detailed treatment of the whole problem in connection with the publication of the remaining part of the experimental results.

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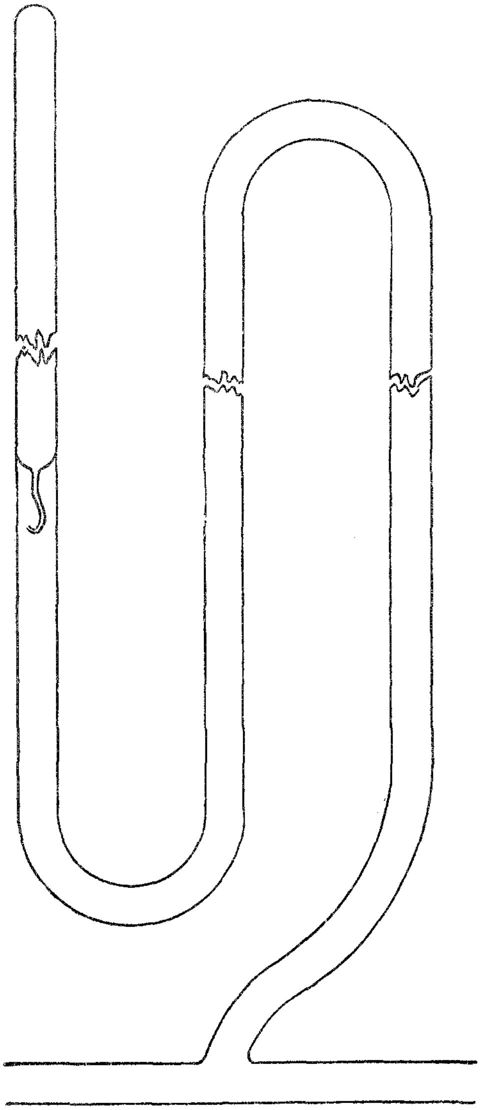
NOTE.



Manometer for Vacuum Distillation.—The form of manometer commonly employed in vacuum distillations suffers from two principal disadvantages, the first consisting in the danger of air or moisture being carried into the vacuous space by the repeated movements of the mercury with change of pressure; the second, which is the more serious, consisting in the liability of the sealed end of the manometer tube to be broken by the impact of the mercury on suddenly readmitting atmospheric pressure into the apparatus.

Both of these defects may be eliminated by the use of a hook-shaped trap such as is commonly employed on accurate barometers. This trap effectually prevents the passage of air into the vacuous space, and if the capillary of which the hook consists be sufficiently fine as to retard the movement of the mercury, the danger of breaking the tube is effectually prevented.

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