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ON THE SOLUBILITY OF SALTS IN SALT SOLUTIONS

STUDIES ON SOLUBILITY I

BY

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WITH 10 FIGURES IN THE TEXT



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1. Introduction.

THE fundamental principles for the treatment of the solubility equilibria in salt solutions are pointed out in the well known works of VAN'T HOFF and REICHER¹, W. NERNST² and ARTHUR A. NOYES³. Through these works it was shown that the important conception of the solubility product was able to represent the solubility phenomena in concordance with the VAN'T HOFF theory of the dilute solution and the ARRHENIUS theory of the electrolytic dissociation of salts. Indications, however, are found already 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, is able to account only approximately for the experimental results.

Further investigations by ARRHENIUS⁴ and by STIEGLIETZ⁵ showed the concentration of the unionized portion of the saturating salt to be not even approximately constant as required by the theory of solutions, this concentration decreasing rapidly by increasing concentration of another salt with an ion in common with the saturating salt.

¹ Zeitschrift f. physikalische Chemie 3, 482 (1889).

² Ibidem 4, 372 (1889).

³ Ibidem 6, 241 (1890).

⁴ Zeitschr. f. physik. Chemie 31, 224 (1899).

⁵ Journ. Am. Chem. Soc. 30, 946 (1908).

A considerable amount of work concerning the solubility of salts has been carried out after this, of which notably the important investigations of NOYES and his coworkers¹ deserve special mention. Through this elaborate work experimental results have been brought about to corroborate the view of ARRHENIUS named above, and showing, furthermore, the solubility product in mixed salt solutions to rise considerably with increasing concentration.

To obtain this result the authors apply the method of 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, of the conductance ratio being an accurate measure for 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 doubtful², since the underlying presupposition that the mobility of the ions is constant is shown to be incorrect. Also for other reasons we cannot adopt the conductance method as fitted to account for the constitutions of salt solutions, as it will appear from an inspection of the solubility data. It may be stated f. inst. that even when a fall in the concentration of the

¹ Journ. Am. Chem. Soc. 33, 1643 (1911). 33, 1807 (1911).

² See esp. G. N. LEWIS, Journ. Am. Chem. Soc. 34, 1631, (1912) and P. HERTZ, Ann. d. Physik. [4] 37, 1 (1912).

unionized portion by addition of another salt, may be expected, from the phenomenon well known as the "salting out" effect, this fall 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 kalium nitrate solution, possessing a salting out effect of less than 1 per cent towards non-electrolytes, exhibits an effect more than 30 times as great in the case of undissociated thallic chloride, computed on the base of the conductance method. Furthermore, a satisfactory explanation of the increasing solubility found in many cases in salts on addition of other homoionic salts can hardly be afforded from this point of view. By NOYES and BRAY¹ attention is called to the peculiar behaviour of a moderately soluble uni-bivalent salt on addition of a salt with a common bivalent ion. Neither is this phenomenon easily understood from the standpoint of the ordinary theory. We are justified therefore, in consideration of all of these discrepancies, in concluding that the conductance method affords no serviceable base 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 made in the present paper at a new treatment of the solubility problem makes no pretence of explaining all peculiar characteristics of the various solubility curves. It is intended only to show, that the multiplicity of types of curves found by employment of hetero- as well as homoionic solvents can be accounted for in a simple way and on thermodynamic base by introducing an assumption at any rate approximately true for mixed salt solutions.

¹ Journ. Am. Chem. Soc. 33, 1643 (1908).

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

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 in the case of the validity of the simple gas laws being given by

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

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

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

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

where ξ_c denotes the activity of the solute, a conception introduced by G. N. LEWIS¹ 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 indefinite dilution. For our purpose, however, it may be more suitable to put

¹ Proc. Am. Acad. 43, 259 (1907).

$\xi_c = c$ for the substance in the employed solvent by indefinite dilution. As a more complete definition of the activity we then have

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

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

The ratio of the activity to the concentration:

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

is called the activity coefficient¹. 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 alterations in ξ_c by changing concentration as seen from equation (2) and (3) is a merely experimental quantity, no hypothesis whatever being involved for its theoretical determination, the values of the alterations in c , however, will usually depend upon the method employed for the computation of this quantity. 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".

¹ NOYES a. BRAY. Journ. Am. Chem. Soc. 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

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

analogous to (1) and

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

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

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

and

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

The activities ξ_c and ξ_x are capable of representing the thermodynamic properties of the solution equally well. In 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 in dependence 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 indefinite dilution respectively, we have for dilute solutions if the gas laws hold good

$$\pi_0 - \pi_{00} = -RTx. \quad (9)$$

The magnitude of π and x depends 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), keeps a constant value when the concentration changes.

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

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

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

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

this ratio called the osmotic coefficient¹ proves to be a thermodynamic quantity also when x is the stoichiometric concentration calculated from 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 formulae

$$(\pi_0 - \pi_{00}) \frac{c}{x} = -RTc \quad (12)$$

and

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

Furthermore we obtain

$$\frac{\eta_c}{c} = \varphi. \quad (14)$$

¹ BJERRUM. Zeitschrift f. Elektrochemie 24, 321 (1918).

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 one of them is preferable to another. It will be found, however, as especially pointed out by BJERRUM¹, that in the case of dilute salt solutions, which we are going 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:

$$xd\pi + d\pi_0 = 0 \quad (15)$$

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

$$x d \ln \xi_x = x d \ln \xi_c = d \eta_x = \frac{x}{c} d \eta_c \quad (16)$$

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

¹ l. c.

$$x_1 d\pi_1 + x_2 d\pi_2 + \dots + d\pi_0 = 0 \quad (17)$$

from which we obtain

$$\text{and} \quad \left. \begin{aligned} \sum x_1 d\ln \xi_{x_1} &= d\eta_x \\ \sum c_1 d\ln \xi_{c_1} &= d\eta_c \end{aligned} \right\} \quad (18)$$

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

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

and

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

where

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

Putting $x_2 = x_3 = \dots = 0$, equation (20) is transformed to the equation given by BJERRUM¹ and valid for binary mixtures.

As we are here going to deal 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 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

$$\pi = \pi' + \pi'' = \text{constant}, \quad (21)$$

or according to (2)

$$\xi' \xi'' = k \quad (22)$$

¹ I. c.

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

$$c' c'' f' f'' = k. \quad (23)$$

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 — to change too 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 by 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 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 base by its means without further assumptions

as to the constitution of the solutions, and especially regardless of 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 FALK¹, who have shown, that the freezing point data for a number of binary salts can be expressed by the equation

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

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

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

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

$$\log^{10} f = -1.37 \alpha \sqrt[3]{c} = -a \sqrt[3]{c}. \quad (26)$$

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

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

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

¹ Journ. Am. Chem. Soc. 32, 1011 (1910).

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 valencies 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 four 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 of the valency. 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 of the employment of a heteroionic solvent.

4. Heteroionic Solvents.

In this case c' and c'' in equation (27) are equal to the solubility or

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

Introducing here

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

we obtain

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

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 1—3 and represented diagrammatically in Fig. 1—5.

In all these diagrams the abscissa represents the molal concentration of the solvent employed, and the ordinate the solubility ratio 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 valency. This influence is seen to be exceedingly marked. Whilst the solubility of an uni-univalent salt is only moderately affected by addition of a 0.1 molal solvent, the effect in the case of a bi-bivalent

Table 1. The solubility ratio s/s_0 for $a = \frac{1}{3}$.
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 2. The solubility ratio s/s_0 for $a = \frac{4}{3}$.
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 3. The solubility ratio s/s_0 for $\alpha = 3$.
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

$s_0 =$ c	0.001	c	0.002	c	0.005
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

$s_0 =$ c	0.01	c	0.02	c	0.05
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

one is very considerable, and in the case of a tri-trivalent one enormous.

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 effect of the added salt. The

same is the case by consideration of bi-bivalent salts. By the greater solubilities the curves approach straight lines,

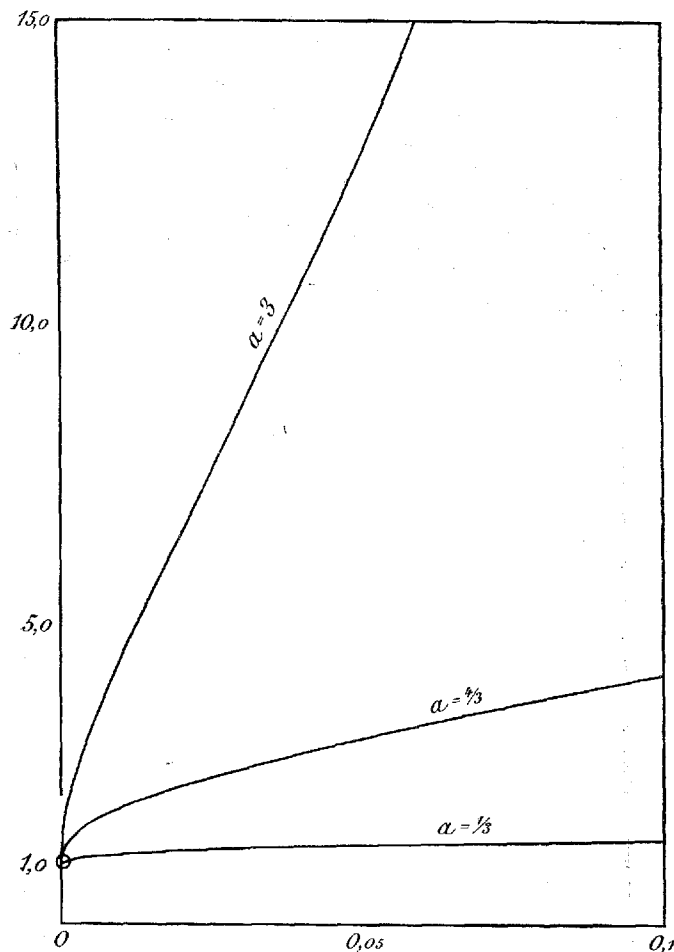


Fig. 12.

while the curvature is very marked in the case of slight solubilities

For tri-trivalents salts the results are plotted in fig. 3—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. By

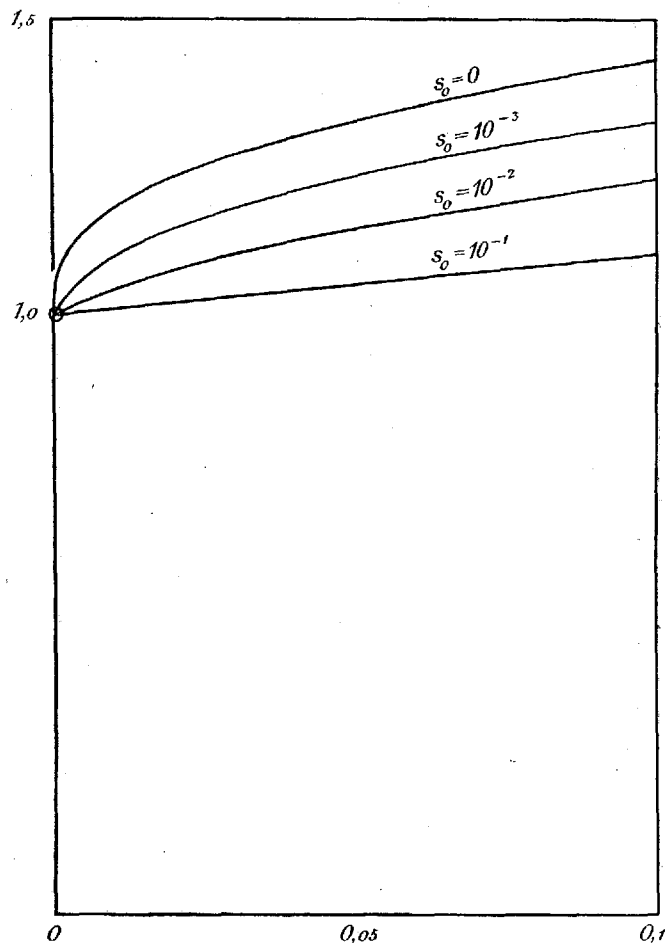


Fig. 2. Uni-univalent salts.

this concentration the effect exhibits a minimum, and by higher solubilities the curves rise again showing a curvature in the opposite direction of that otherwise found. In this respect the behaviour 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.

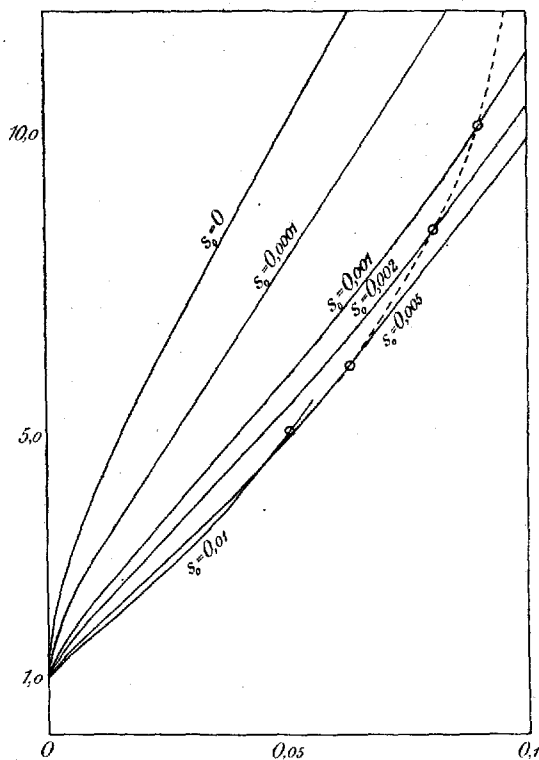


Fig. 3. Tri-trivalent salts.

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

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

s_1 and s_2 representing the solubilities at the total concentrations c_{t1} and c_{t2} respectively. Putting here $c_{t2} = 0.1$ we obtain the figures given in Table 4 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 conse-

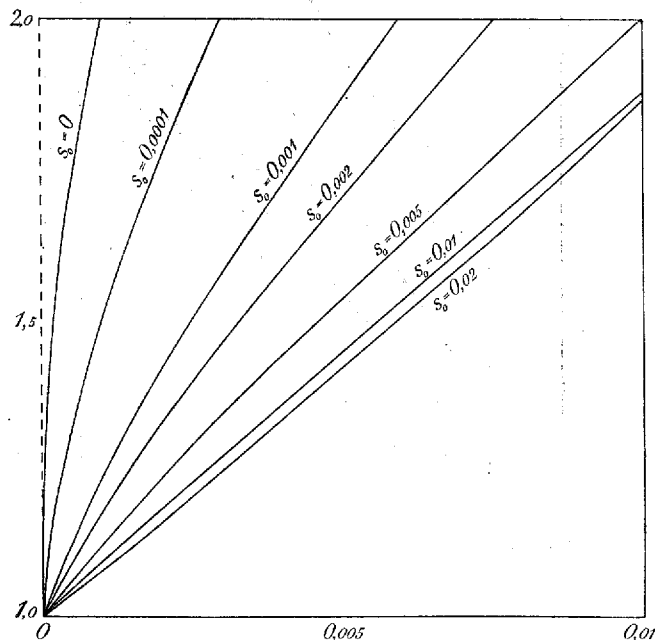


Fig. 4. Tri-trivalent salts.

quently 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.

Having now shown the general results furnished by the 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.

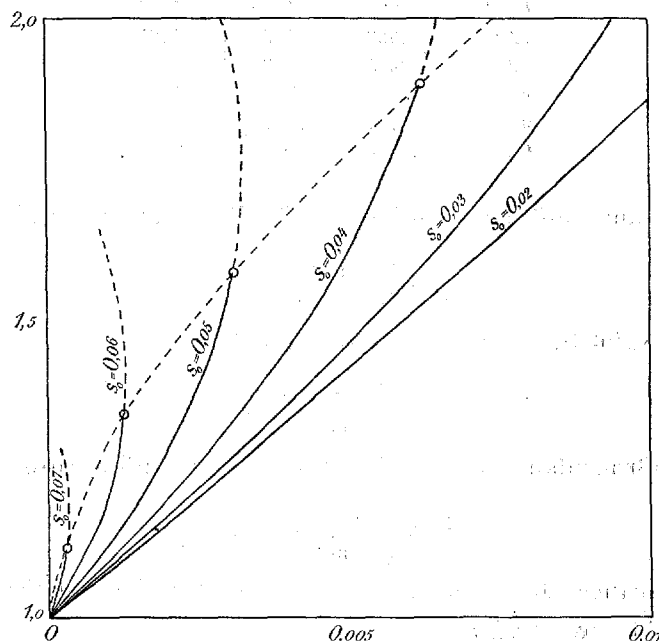


Fig. 5. Tri-trivalent salts.

From this series, of which a complete account will be rendered in subsequent articles, a few data may be stated in Tab. 5—9. The metal ammonia salts here in question are the following:

Dichlorotetrammine cobalt rhodanide or praseo rhodanide

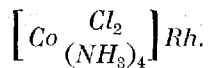
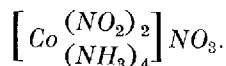


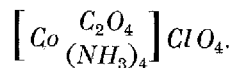
Table 4. The solubility ratio $s/s_{0.1}$ for different values of a Heteroionic solvent.

$c + s$	$a = \frac{1}{3}$	$a = \frac{2}{3}$	$a = 3$
0.000	0.7003	0.2405	0.0405
0.001	7561	3269	808
0.002	7714	3541	967
0.005	7984	4065	1320
0.01	8262	4660	1795
0.02	8625	5535	2642
0.05	9291	7452	5159
0.08	7940
0.1	1.0000	1.0000	1.0000

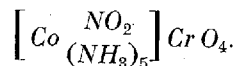
Trans dinitrotetrammine cobalt nitrate or croceo nitrate



Oxalotetrammine cobalt perchlorate



Nitropentammine cobalt chromate or xantho chromate



Further the data of NOYES and BRAY¹ on thallic chloride are shown.

Under $\left(\frac{s}{s_0} \right)_{\text{theor.}}$ 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, firstly, that agreement can be brought about if we introduce one single a value for any system, secondly, that these a values for the various systems of uni-univalent salts vary only

¹ l. c.

slightly in the neighbourhood of $\frac{1}{3}$. In this respect full concordance exists with the requirements of the freezing-point formula. In the case of the bi-bivalent Xanthochromate the \bar{a} value 1.80 must be adopted to represent the experimental data. This value also corresponds to the

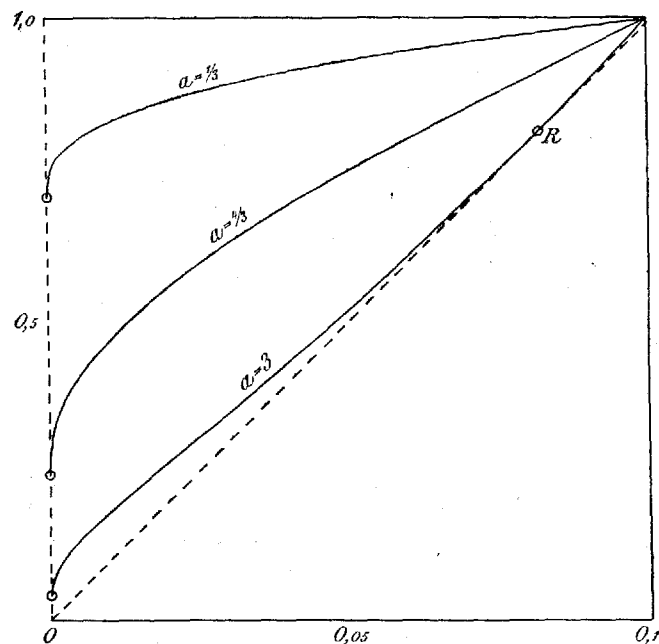


Fig. 6.

freezing-point measurements and is approximately 4 times as great as in the case of uni-univalent salts.

For tri-tri-valent salts no experiments have been carried out with tri-tri-valent 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 valency. This agrees with the corresponding higher values for a , which may be used in this case.

Table 5. The solubility of praseo cobalt rhodanide in sodium chlorate solutions at $t = 0^\circ$. $a = 0.30$.

c	s	(s/s_0) theor.	(s/s_0) exp.
0.00	0.00289	1.000	1.000
0.01	306	1.066	1.059
0.03	327	1.132	1.132
0.05	339	1.175	1.173
0.1	360	1.254	1.246

Table 6. The solubility of croceo cobalt nitrate (β -modification) in kalium formiate solutions at $t = 0^\circ$. $a = 0.31$.

c	s	(s/s_0) theor.	(s/s_0) exp.
0.00	0.00494	1.000	1.000
0.02	536	1.092	1.086
0.05	5745	1.163	1.164
0.1	621	1.242	1.258

Table 7. The solubility of oxalotetrammine cobalt perchlorate in sodium formiate solutions at $t = 0^\circ$. $a = 0.33$.

c	s	(s/s_0) theor.	(s/s_0) exp.
0.00	0.00508	1.000	1.000
0.05	597	1.174	1.174
0.10	640	1.258	1.260

Table 8. The solubility of thallic chloride in kalium nitrate solutions at $t = 25^\circ$. $a = 0.355$.

c	s	(s/s_0) theor.	(s/s_0) exp.
0.00	0.01607	1.000	1.000
0.02	1716	1.068	1.068
0.05	1826	1.136	1.136
0.1	1961	1.217	1.220

Table 9. The solubility of xantho cobalt chromate in magnesium sulphate solutions at $t = 0^\circ$.
 $a = 1.80$.

c	s	(s/s_0) theor.	(s/s_0) exp.
0.00	0.000258	1.00	1.00
0.02	620	2.39	2.40
0.05	908	3.57	3.52
0.1	1237	5.3	4.8

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

5. Homoionic Solvents.

In the case of homoionic solvents the solubility phenomena are much more multitudinous 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

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

or

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

where the terms applied have the same meaning as above, and especially the product $s c_t$ indicates the stoichiometric solubility product. By application of these formulae to the various types of salts the corresponding values of a , given p. 14, must be introduced.

We shall first consider the effect of the addition of an homoionic solvent qualitatively. To that end equation (32) is differentiated. Hence we obtain

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

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

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

showing by smaller concentrations a fall and by higher concentrations a rise by 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 10.

type of salt	a	$c_{min.}$
uni-uni-valent ...	$\frac{1}{2}$	7.5
bi-bi-valent	$\frac{4}{5}$	0.12
tri-tri-valent	3	0.01

In the case of uni-univalent salts the concentration calculated in this way lies far beyond the domain of the established formulae. 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 neighbourhood 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 perspicuous 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 11—13 and the accompanying diagrams.

Table 11. The solubility ratio s/s_0 for $a = \frac{1}{3}$.
Homoionic solvent.

c	s/s_0	c	s/s_0	c	s/s_0
0.0001	0.108	0.01	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 12. The solubility ratio s/s_0 for $a = \frac{4}{3}$.
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 13. 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 the 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. By small α -values or [uni-uni-valent salts the solubility

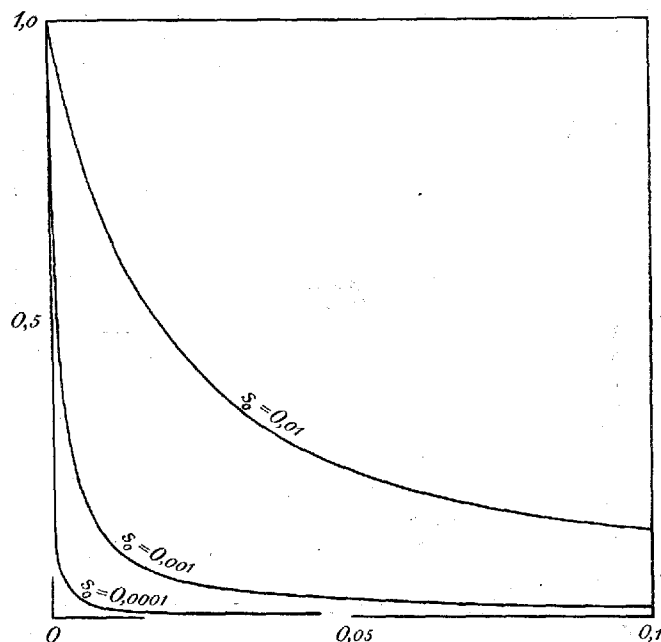


Fig. 7. Uni-univalent salts

exhibits a pronounced and steady decrease by increasing concentration of the added salt. By medium values of α or bi-bi-valent 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. To a large value of α or tri-tri-valent salts, finally, curves correspond showing pronounced minima and, by 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-tri-valent salt, as mentioned above, that the decreasing portion of the curve will disappear and the curve start rising.

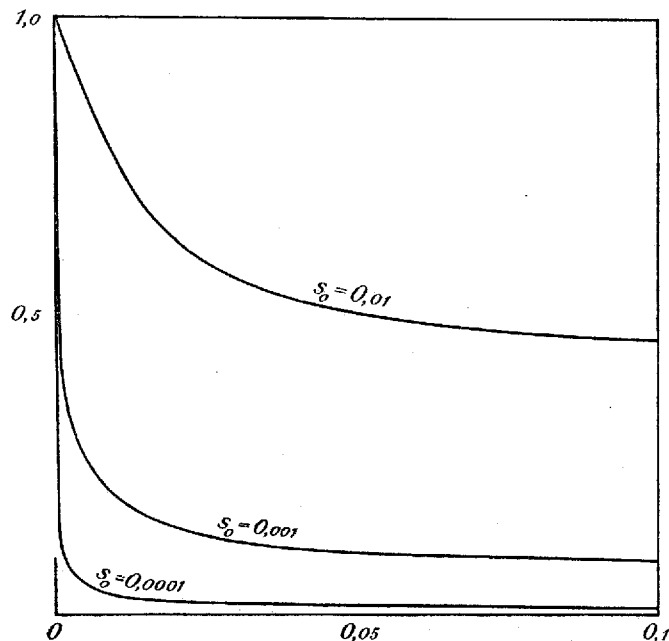
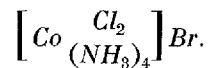


Fig. 8. Bi-bivalent salts.

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 cobalt bromide or praseo bromide



Trans dinitrotetrammine cobalt chloride or croceo chloride

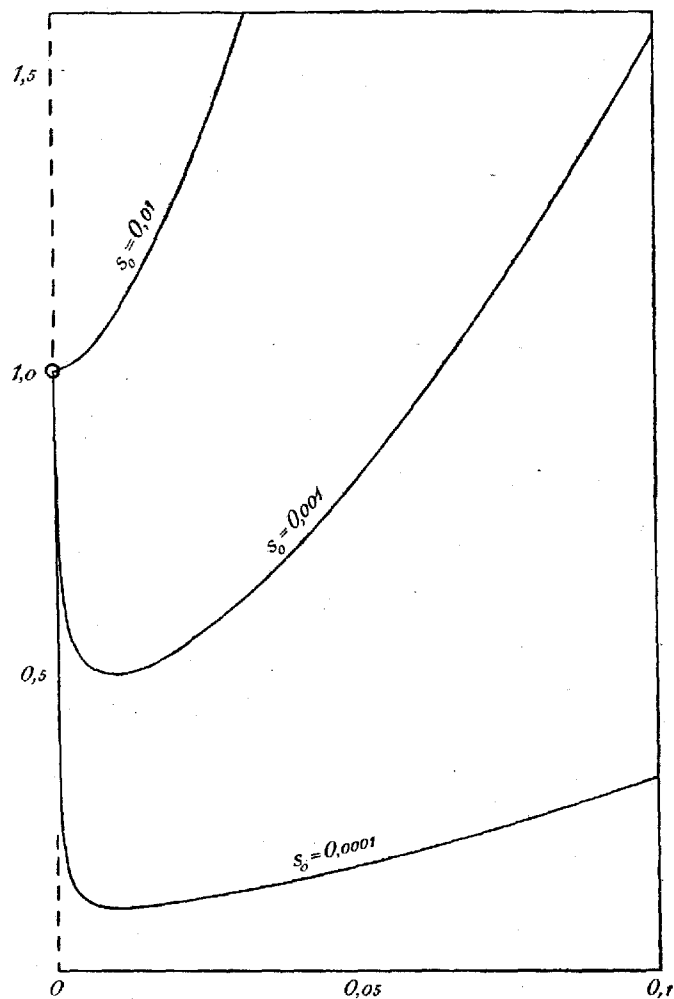
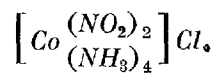


Fig. 9. Tri-trivalent salts.

Isorhodanopentammine cobalt sulphate

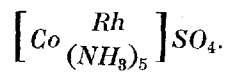


Table 14. The solubility of praseo bromide in kalium bromide solutions at $t = 0^\circ$. $\alpha = 0.355$.

c	$s_{exp.}$	$s_{theor.}$
0.00	0.00635	—
0.02	0.00212	0.00212
0.05	0.00107	0.00107
0.1	0.000635	0.000634

Table 15. The solubility of croceo chloride in kalium chloride solutions at $t = 0^\circ$. $\alpha = 0.38$.

c	$s_{exp.}$	$s_{theor.}$
0.00	0.02216	—
0.02	0.01515	0.01516
0.05	0.01005	0.00991
0.1	0.00640	0.00647

Table 16. The solubility of isorhodanopentamine cobalt sulphate in magnesium sulphate solutions at $t = 0^\circ$. $\alpha = 1.73$.

c	$s_{exp.}$	$s_{theor.}$
0.00	0.01177	—
0.02	0.01005	0.0096
0.05	0.00980	0.0099
0.1	0.01034	0.0116

Table 17. The solubility of thallous chloride in kalium chloride solutions at $t = 25^\circ$. $\alpha = 0.40$.

c	$s_{exp.}$	$s_{theor.}$
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 WINNINGHOFF¹ for thallic chloride are given in Tables 14—17.

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 by employment of 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.

6. The Liquid-Liquid Equilibrium.

Some interesting phenomena whose occurrence may be suspected from the established formulae, say (30), in the case of polyvalent ions, may 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 great 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 addition of a homoionic salt. The solubility s is plotted against the total concentration c_t . The point R corresponds to the mentioned point R in fig. 6. We have here

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

¹ Journ. Am. Chem. Soc. 33, 1663 (1911).

Vidensk. Selsk. Math.-fysiske Medd. II, 10.

$$\text{or} \quad d \ln s = d \ln c_t = d \ln c. \quad (36)$$

Introducing here $s = \frac{\xi_1}{f}$ and $c = \frac{\xi_2}{f}$, 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

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

or, since $\xi_1 = \text{constant}$ on account of the solution being saturated with s_1

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

At concentrations corresponding to the point of contact R the activity of s_2 will thus remain constant by rising con-

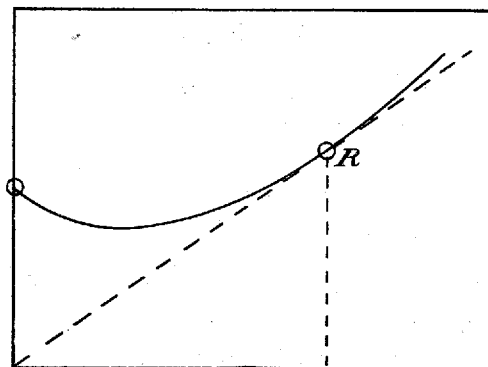


Fig. 10.

centration. 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 solu-

tion. 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

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

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 by increasing concentration in dilute solution, by 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 involved formulae. Introducing in (39) the values of a which are used above as fitted to represent the behaviour of the various types of salts, we shall calculate the following values of c_R .

Table 18.

Type of salt	a	c_R
uni-univalent	$\frac{1}{3}$	59
bi-bivalent	$\frac{4}{3}$	0.93
tri-trivalent	3	0.082

Only in the case of tri-tri-valent salts, as seen from the figures, the calculation of c_R affords some trustworthy

result, as only in this case the magnitude of c_R calculated is small enough for rendering the applied formulae to a certain degree valid. Even the concentration 0.08 computed for such salts may be regarded as a rough estimation, on account of the deviation from the used formulae increasing rapidly with increasing valency 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 is 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 is able to exist only owing to the insufficient velocity of crystallization, the tendency of the concentrated layer to separate the solid phase thereby being obscured.

According to this view the solubility of salts of higher types may remain far below the solubility of the liquid layer¹ or a fortiori far below the critical concentration c_R . In fact the solubility determinations with such salts, carried out in connection with the mentioned investigation on metal ammonia salts, clearly confirms this conclusion, as in all cases solubilities not surpassing 0.001 molal was found.

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 with different sign. The separation is in all cases studied by mixing two samples of the solutions concerned under the

¹ See J. N. BRØNSTED: Zeitschrift f. physik. Chemie 56, 683 (1906).

microscope. Usually the separation occurs instantaneously forming clouds of minute particles gradually joining to greater liquid drops. The change of the liquid salt into the solid phase usually takes place rapidly. Notably in the case of the tri-valent triethylene-diamine cobalt ion the liquid system, however, may be fairly stable, and the procedure of the growth of the drops and their ultimate crystallization furnish a proper 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 solutions, 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 Fig. 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 instable or hypothetical character.

By employment of homoionic solvents a limiting curve of similar meaning 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 thermo-

dynamic base 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, f. inst. in mixed solutions of kalium chloride and kalium bromide of slight concentration. Solutions of such a kind will behave in a markedly simple manner by 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 are not able to vary independently but, as mentioned in section 2 of this article, are subjected to thermodynamical correlations. In a following paper we shall deal with these correlations more thoroughly.

Like our chief assumption concerning the activity coefficient, the employed cube root expression for $\log f$ is also an approximation. It is clear, therefore, that all the formulae derived in the preceeding chapters represent only the general shape of the solubility curves, but are not able to explain the peculiar behaviour of a selected system. In order to ascertain whether the hypothesis advanced may, properly modified, be able to form the base of a more minute theory of solubility, it must preferably be looked upon in the light of the theory of the complete electrolytic dissociation supported by BJERRUM¹ and MILNER².

In a recent paper³ I have shown that this theory may

¹ Proc. of the 7. intern. Congress of appl. Chemistry London 1909. Sec. X. Zeitschr. f. Elektrochemie 24, 321 (1918).

² Phil. Mag. 6, 23, 553 (1912), 6, 25, 742 (1913).

³ Meddelanden från K. Vetenskabsakademien's Nobelinstitut 5 Nr. 25.

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 raised 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 chapter 2 and reckoned with through 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, in order 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 behaviour which is appreciable already at fairly small concentrations. From the usual point of view this individuality should be ascribed to diversities in the degree of dissociation. On the base of the theory of complete dissociation it becomes necessary to attribute to any separate ion a secondary power beside the primary MILNER effect

able to exert a peculiar 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 mass points, and no regard being paid to the contingency of hydration of the ions. When the ions are considered as particles of finite sizes, and appointed with electrical charges in finite distance 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, that the theory of Milner is not able to give an exact picture of the behaviour 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 specially 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 in the solution to take place. Of course in many cases this opinion may be true. The solubility of silver cyanide in kalium cyanide f. inst., 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 α 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 raised solubility. In a solution of hexamine cobalt sulphate f. inst., we have no reason for believing the ions tending to form complexes. Nevertheless the solubility of this salt increases rapidly by increasing concentration of a sodium sulphate 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 BRAY¹. 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. HARKINS² emphasizes 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, f. inst. lead chloride. Let s_1 and s_2 be the solubility in

¹ l. c.

² Journ. Am. Chem. Soc. 33, 1807 (1911).

equivalents in a solution of kalium 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 coefficient 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

$$s_1 c_t = s_2^2. \quad (40)$$

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 well 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 $s_1 c_t = k$ and s_2 consequently will not be constant but decrease slightly. By increasing concentration the fall in s_1 may gradually diminish, corresponding to s_2 passing through a minimum and thereafter increasing. The effect observed is thus no abnormal one but contrarily in full concordance with what would be expected from the standpoint adduced.

The significance of the valency of the ions is accounted for by assigning different values to the coefficient a in the employed formulae according to the type of the salts. The relationship between valency and activity coefficient is suggested by BJERRUM¹ and explained through the attracting

¹ Zeitschr. f. Elektrochemie 24, 321 (1918).

forces operating between the ions, these forces changing 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 applies most profitably in the formulae. At any rate, the rapid rise in the electric forces by increasing valency manifests itself very distinctly by the solubility measurements.

As shown in the foregoing there will be a fall in the activity by rising 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 concentration 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 breach of continuity by 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 HILDEBRAND¹ is sensibly dependent upon the difference in internal pressure of the liquids concerned, we must suggest the supercooled liquid salts of high valency to be in possession of extremely high internal pressure, as exactly to be expected from the conception of the salts being, in solid and liquid state, also more or less completely dissociated. At any rate the assumption of a decreasing dissociation of the salts by

¹ Journ. Am. Chem. Soc. 38, 1452 (1916).

rising 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, namely, that the effect, which is here assumed to render the solubility of a salt increasing 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 firstly 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 hydroxyle-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,

Table 19. The dissociation product of water in salt solutions of the concentration c .

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

calculated by means of (27), may be expressed approximately by the following figures.

The alteration in the dissociation product is thus very considerable. In a 0.1 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 obscured¹.

As in the case of water, we shall find an effect of the same kind by other weak electrolytes. We may establish quite generally that any equilibrium in aqueous solution involving incompletely dissociating electrolytes may be influenced correspondingly by addition of salts. By consideration of such cases, however, the phenomenon known as the "salting out" effect must not be disregarded. This effect will cause the activity of a non-electrolyte, or of the undissociated portion of a weak electrolyte, to rise by rising salt concentration. The solubility of a slightly soluble weak acid f. inst., 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 a. LANGBECK² with weak acids have given results which are confirmatory to this view.

¹ If the H^+ and the OH^- ions are hydrated to a different extent, rising 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 (*Zeitschr. f. Elektrochemie* 21, 418 (1915)) are to be interpreted in this way.

² HOFFMANN a. LANGBECK, *Zeitschr. f. physik. Chemie* 51, 385 (1905).

For the treatment of solubility phenomena of the strong electrolytes the results obtained with non-electrolytes or weak electrolytes, however, are of wide consequence. Then 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 dissolving power, may be found to be in close connection with the salting out effect. As an illustration may be noted that kalium 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 respect¹. This fact has caused A. E. HILL² to surmise without paying attention to the exceptional character of the employed substance that the solubility generally diminish on addition of heteroionic solvents.

Having now in the present paper advanced the general points of view from which the solubility equilibrium in salt solutions supposedly ought to be considered, we may in the following articles of this series turn to a more detailed treatment of the whole problem in connection with the publication of the remaining part of the experimental results.

¹ J. N. BRØNSTED, *Meddelanden fr. K. Vetenskapsakademiens Nobel-institut* Bd. 5, Nr. 25 (1919).

² A. E. HILL, *Journ. Amer. Chem. Soc.* 32, 1186 (1910).

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