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THE EFFECT OF SALTS ON THE SOLUBILITY OF OTHER SALTS. I.

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A. INTRODUCTION.

B. PRELIMINARY NOTE ON THE EFFECT OF SALTS ON THE SOLUBILITY OF UNI-BIVALENT SALTS.

A. Introduction.

It is the purpose of the following articles to describe the researches on the effect of salts on the solubility of other salts, which have been in progress in this laboratory for a number of years with the object of investigating the principles underlying this phenomenon. These investigations were carried out in large part with the aid of grants from the Carnegie Institution of Washington, to which we wish to acknowledge our great indebtedness.

The following well-known solubility principles were originally formulated upon the basis of the law of mass action:

I. The product of the concentration of the ions of a salt present as solid phase has the same value in dilute solutions of other salts as it has when it is present alone.[1]

II. The concentration of the un-ionized portion of a salt present as solid phase has the same value in dilute solutions of other salts as it has when present alone.[2]

It was, however, early recognized that both of these principles can not hold true accurately, since the ionization of salts (as derived from the conductance-ratio or freezing-point lowering) does not change with the concentration in accordance with the law of mass action. The first one has been generally employed, since it was shown by Arrhenius[3] that the second of the above principles is not even approximately true. Thus with the aid of his own data on the effect produced on the solubility of certain silver salts of organic acids by salts with a common ion, he found that the concentration of the un-ionized portion decreased rapidly with increasing ion-concentration, in some cases to such an extent that the total solubility became less than the concentration of the un-ionized portion in pure water. From a further study of the same data, Stieglitz[4] concluded that the first principle expressing the constancy of the product of the ion-concentrations is approximately true for these uni-univalent silver salts, and suggested that this might be adopted

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[1] Nernst, *Z. physik. Chem.*, **4**, 379 (1889).

[2] A. A. Noyes, *Ibid.*, **6**, 243 (1890).

[3] Arrhenius, *Ibid.*, **31**, 224 (1899).

[4] Stieglitz, THIS JOURNAL, **30**, 946 (1908).

for the present as an approximate empirical principle. Recent computations have shown, however, that the first principle is also subject to considerable deviations, and that these lie in a direction opposit to that of the deviations from the second principle. Thus, it has been computed[1] that in a solution saturated at 40° both with thallous chloride and thiocyanate, where the total concentration is about 0.04 normal, the concentration of the un-ionized TlCl is about 15 per cent. less, and the product of the concentration of the Tl^+ and Cl^- ions about 5 per cent. greater than it is in a solution of thallous chloride alone.

Any such computations necessarily involve some principle in regard to the ionization of salts in mixtures. Assuming that the conductance-ratio Λ/Λ_0 is an accurate measure of ionization, the following principle, first stated by Arrhenius,[2] has been well established in the case of uni-univalent salts through the study of the conductance of mixtures of them:[3] In a mixture of two salts with a common ion each salt has a degree of ionization equal to that which it has when alone present in a solution in which its ions have a concentration equivalent to that of the common ion in the mixture. This principle when combined with the empirical law, which has been found to express the change of the ionization $\gamma = \Lambda/\Lambda_0$ of single salts, with the concentration (C),

$$(C\gamma)^n/C(1-\gamma) = K \qquad (1)$$

may be expressed mathematically by the following equation:[4]

$$C_{B+}C_{A-}/C_{BA} = K(\Sigma C_i)^{2-n} \qquad (2)$$

where K is a constant characteristic of the salt, C_{B+} and C_{A-} are the concentrations of the positive and negative ions, of a salt BA, C_{BA} that of the un-ionized portion of the salt, and ΣC_i denotes the sum of the equivalent concentrations of all the positive or negative ions present in the solution, a quantity which will hereafter be called the total ion-concentration. The exponent n has a value lying almost always between 1.40 and 1.60.

In applying this equation (2) to any special mixture the values of γ, ΣC_i, n and K are first determined for each salt from the conductance data for the salt, and the values of C_{B+}, C_{A-} and C_{AB} for each salt in the mixture and of ΣC_i are then computed from the equation by a method of approximation.[5] In mixtures with a common ion it is only necessary to know the relation between γ and ΣC_i for each salt, since the above ionization rule may then be applied directly. In mixtures without a common ion the relation of the function $C_{B+}C_{A-}/C_{BA}$ to

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[1] Noyes, *Tech. Quart.*, **17**, 305 (1904); *Z. physik. Chem.*, **52**, 636 (1905).

[2] *Z. physik. Chem.*, **2**, 285 (1888); **31**, 218 (1899).

[3] For references, see Sherrill, THIS JOURNAL, **32**, 741 (1910).

[4] Arrhenius, *Z. physik. Chem.*, **31**, 218 (1899). Sherrill, *Loc. cit.*

[5] For examples see THIS JOURNAL, **32**, 741 (1910); **31**, 754 (1909).

ΣC_i is determined for the separate salts, and is then applied for calculating the concentrations in the mixture.

It is important to note that the only evidence in favor of equation (2) is that the specific conductances of mixtures calculated with its aid are in good agreement with the experimental values. It therefore will furnish correct values of the ion-concentrations only in case the commonly accepted principle is correct, that the conductance ratio Λ/Λ_0 is a reliable measure of the degree of ionization of a single salt, a principle which can be true only in case the mobilities of the ions do not vary with the concentration.

In the case of salts of the uni-bivalent type, there is, furthermore, the uncertainty as to whether intermediate ions (such as KSO_4^- or NO_3Ba^+) are present in considerable proportions. Certain remarkably simple principles have, however, been established, which have been thought to indicate that the complications which would arize from ionization in two successive stages do not exist. Namely: 1. The conductance-ratio of such salts changes with the concentration according to the same exponential law (expressed by equation (1) above) that holds in the case of uni-univalent salts.[1] 2. The conductance of mixtures of such salts can be approximately calculated from the conductance of the constituents by the same principle (expressed by equation (2)) that holds for uni-univalent salts.[2] 3. The transference numbers of uni-bivalent salts (except those of the bivalent metal halides) change only slightly with increasing concentration.[3] 4. Simple mixed salts (such as $BaClNO_3$) scarcely ever separate in the solid state when solutions of the constituent salts are evaporated. In view of these facts we have assumed provisionally, in this first discussion of the data, that intermediate ions do not exist and that the concentration of the ions and of the un-ionized portion of uni-bivalent salts, whether present alone or in mixtures, can be calculated with the help of the same principles as are applicable to uni-univalent salts. The hypothetical character of this assumption is, however, fully recognized, and it is hoped that the nature of the results in the case of uni-bivalent salts will throw some light upon this question.

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[1] Cf. Noyes, Melcher, Cooper and Eastman, THIS JOURNAL, **30**, 335 (1908). Noyes and Johnston, THIS JOURNAL, **31**, 987 (1909).

[2] Cf. Noyes, *Tech. Quart.*, **17**, 293 (1904); *Science*, 20, 584 (1904); *Z. physik Chem.*, **52**, 635 (1905). Sherrill, *Loc. cit.*

[3] Cf. Falk, THIS JOURNAL, **32**, 1569 (1910). It should be noted that this author mentions a hypothesis, suggested by Lewis, which requires that the intermediate ion have such a conductance that its presence would not influence the value of the transference number. Under this hypothesis the conductance of the intermediate ion is in general much smaller than that of the corresponding bivalent ion. It follows from this that the concentration of the univalent ion calculated as usual under the assumption that no intermediate ion is present would be too small.

By applying the above principles, there have, accordingly, been calculated in this series of papers the concentration of the un-ionized portion and the product of the concentration of the ions of the salt with which the solution is saturated, and in this way the character and magnitude of the deviations from the two solubility principles derived from the mass-action law have been determined.

In dealing with these deviations, it is convenient to make use of the concept of *activity*, proposed by Lewis.[1] Without citing the fundamental definitions of this quantity, or its thermodynamic relations to other quantities, it will suffice for our purpose to state that the activities of a substance in two phases in equilibrium with each other are equal, that activity has the same dimensions as concentration, and that the activity of each substance in any solution always has such a value that all mass-action relations are valid. Thus in any aqueous or non-aqueous solution in equilibrium with the solid salt BA, the two solubility principles are necessarily true, when expressed in activities:

$$A_{B+} \times A_{A-} = \text{const. and } A_{AB} = \text{const.}$$

For each substance in solution, as the concentration is decreased, the ratio of activity to concentration, the *activity coefficient* (A/C), approaches a constant value, which in aqueous solutions may for convenience be assumed to be unity at infinit dilution.

It is evident, if solutions in one solvent are alone considered, that the activity of a substance can be defined as the "effective" concentration which would enable mass-action relations to hold accurately,[2] and that the activity coefficient of a substance at high concentration is a relative measure of its effectiveness in influencing any chemical equilibrium in which it is involved compared with its effectiveness at very small concentrations, where its activity coefficient is taken as unity. Thus, if, as above stated, the concentration of un-ionized TlCl is 15 per cent. less in a saturated solution in the presence of TlSCN than it is in a saturated solution in pure water, the activity coefficient of the un-ionized TlCl must be 15 per cent. larger in the former than in the latter solution, since it is in both cases in equilibrium with the same solid phase. Similarly, if the ion-concentration product, $C_{Tl^+}C_{Cl^-}$, is 5 per cent. larger in the former solution, the product of the activity coefficients of the two ions must be 5 per cent. smaller; and, if the two ions deviate equally from normal activity, the activity coefficient of each is 2.5 per cent. smaller

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[1] *Z. physik. Chem.*, 61, 129 (1907); *Proc. Am. Acad.*, 43, 259 (1907).

[2] Thus defined, the term "activity" is substantially identical with the term "active mass," which has been used, often somewhat vaguely, by earlier investigators. A great advantage of Lewis' treatment is that it shows how this quantity is related thermodynamically to other quantities, such as distribution coefficient, electromotive force of concentration cells, osmotic pressure, etc.

in the TlSCN solution than in the saturated solution in pure water.[1]

We may, therefore, hope, with the aid of the solubility data, not only to study the deviations from the solubility principles, but also to determin in what measure the well-known deviation from the theoretical dilution law is due to abnormal behavior of the ions and in what measure to abnormal behavior of the un-ionized substance. A substance dissolved in water is considered to be normal when its activity (as defined above) is equal to its concentration.

The results of this investigation will be presented in a series of articles. The second part of the present article will consist of a brief discussion of the data already published in regard to solubility effect in cases where a uni-bivalent salt is present as solid phase, the matter being there considered only in its general aspects, but not with reference to the detailed method of treatment described in the preceding pages. In the second and third articles will be presented the results of several new series of solubility determinations made in this laboratory with uni-univalent substances present as the solid phases. Article IV will contain the theoretical discussion of these and some other previously obtained results with uni-univalent salts, along the lines above indicated. In article V, VI and VII the results of new experimental investigations of the solubility of various uni-bivalent salts in the presence of other salts will be described and discussed.

B. Preliminary Note on the Effect of Salts on the Solubility of Uni-bivalent Salts.

It is our purpose in this note to call attention to a certain effect uniformly observed when the solubility of uni-bivalent salts is studied in the presence of another salt having the bivalent ion in common, since the general character of this effect does not seem to have been previously recognized.

In all the cases of moderately soluble uni-bivalent salts (B_2A or A_2B) thus far investigated, it has been found namely, that, though the solubility is reduced in at least rough conformity with the requirements of

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[1] In order to avoid misunderstanding with regard to the use of the activity concept, it seems desirable to point out that it may be considered merely a simple method of expressing the results obtained with a given set of assumptions. It assists in comparing the results obtained with different substances, and does not interfere with the adoption of some more concrete explanation of these. Thus, a change in the activity coefficient of a dissolved substance may be due to a "change in the nature of the solvent" or to a "solvent action" produced by the added salt. Such an effect must undoubtedly be taken into account in concentrated solutions (compare Kendall, *Proc. Roy. Soc.*, 85, 200 (1911)), and it is extremely improbable that it is negligible in solutions as concentrated as 0.1 normal. Or, to take another example, a marked change in the apparent activity coefficient of a bivalent ion (such as $SO^=$) might be caused by the conversion of a certain proportion of it into an intermediate ion (such as $AgSO_4^-$).

the solubility-product principle ($C^2_{B+}C_{A=}$ = const., or $C_{B++}C_{A-}^2$ = const.) when a salt is added having the *uni*-valent ion (B^+ or A^-) in common, this is by no means the case when a salt is added having the *bi*-valent ion ($A^=$ or B^{++}) in common. In the latter case, the decrease of the solubility caused by the addition of an equivalent quantity of the second salt with a common bivalent ion does not exceed a few per cent. even when the solubility is as small as 0.04 molal, and the addition of a larger quantity causes the solubility to increase. Thus in the case of lead chloride there is a slight initial decrease on the first addition of lead nitrate but on further addition the solubility soon becomes greater than that in pure water. In the case of much more soluble salts, such as barium hydroxide in the presence of barium nitrate and barium nitrate in the presence of barium hydroxide,[1] even a small addition of the second salt causes an increase of the solubility.

These statements are illustrated by the accompanying figure in which the solubilities of lead chloride,[2] thallous oxalate,[3] silver sulfate,[4] and calcium hydroxide[5] are plotted as ordinates and the concentration of the added salts as abscissas.[6] The solubilities are expressed in formula weights per liter, and the concentrations of the added salts in equivalents per liter. In a similar diagram at the end of the second article of this series it is shown that the effect of sodium sulfate on the solubility of thallous sulfate is similar to the effect of lead nitrate on the solubility of lead chloride.

These results show that the solubility-product principle is not even approximately true in the cases when a salt with a common bivalent ion is added, for the ion-concentration-product $C_{B++}C_{A-}^2$ or $C_{B+}^2 C_{A--}$ evidently increases greatly, since the large addition of the bivalent ion is not compensated by any considerable decrease of the uni-valent ion of the salt with which the solution is saturated.

The suggestion has been made in specific instances of this kind that the increase or too small decrease of the solubility is due to the combi-

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[1] Parsons and Corson, THIS JOURNAL, 32, 1383 (1910).

[2] Noyes, *Z. physik. Chem.*, 9, 629 (1892). Von Ende, *Z. anorg. Chem.*, 26, 151 (1901).

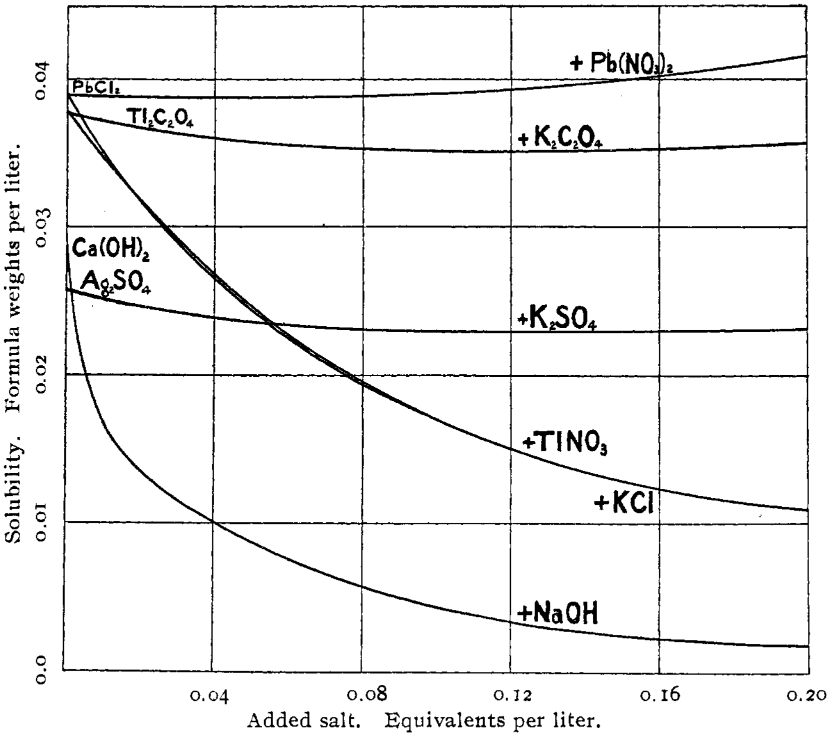
[3] Abegg and Spencer, *Z. anorg. Chem.*, 46, 406 (1905).

[4] Drucker, *Ibid.*, 28, 362 (1901).

[5] d'Anselme, *Bull. soc. chim.*, [3] 29, 938 (1903). According to Zahorsky, *Z. anorg. Chem.*, 3, 41 (1893), the solubility of calcium hydroxide in an approximately normal calcium chloride solution is practically the same as in water and is increased by further additions of calcium chloride. It therefore seems probable that the initial depressing effect of this salt on the solubility of calcium hydroxide is not very great.

[6] The data for these substances are in general not sufficient to permit of an exact quantitative study, and for this reason the positions of the curves are to be considered only approximate.

nation of the two salts with the formation of a specific complex cation or anion. We desire to call attention to the fact that the uniformity of the results with so many entirely different salts requires a more general explanation. Thus it is possible that the effect is due to the presence of the intermediate ion ($ClPb^+$, $AgSO_4^-$, etc.), since this may well be present in corresponding quantities in solutions of all uni-bivalent salts.[1] However this may be, we wish especially to emphasize the view that the effect in question is not specific or exceptional, but is the normal one in the case of salts of this type.



We will not, however, follow the matter further at this point, as Dr. W. D. Harkins has determined, in this laboratory, the solubility of several additional uni-bivalent salts in the presence of various other salts, and will discuss carefully all available data in the seventh article of this series.

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[1] This explanation has already been suggested to account for specific results, thus by Von Ende, *Loc. cit.*, in the case of lead chloride, and by Abegg and Spencer, *Loc. cit.*, in the case of thallous oxalate.