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**STUDIES ON SOLUBILITY. IV. THE PRINCIPLE OF THE
SPECIFIC INTERACTION OF IONS**

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1. Introduction

Although, according to the theory of complete dissociation of the strong electrolytes,¹ the thermodynamic properties of salt solutions are fairly satisfactorily accounted for by making the electrical forces arising from the net charges of the ions responsible for the deviations of such solutions from the ideal state, the total ion concentration here appearing as the predominating factor, a more detailed examination of activity coefficients, especially by means of solubility measurements,² has shown the activity of ions to depend very markedly on their individual natures and also to be distinctively influenced by the natures of the salt solutions serving as solvents. It seems to the writer, therefore, that further progress in this field can be expected only by a thorough study of those individual properties of the ions.

In recent papers MacInnes³ and Harned⁴ have made interesting contributions to the question of the activities of separate ions. The first prin-

¹ For literature see the first article of this series, *THIS JOURNAL*, **42**, 761 (1920).

² Brönsted and Agnes Petersen, *ibid.*, **43**, 2265 (1921).

³ MacInnes, *ibid.*, **41**, 1086 (1919).

⁴ Harned, *ibid.*, **42**, 1808 (1920).

ciples introduced by MacInnes that the activities of the cation and anion in the same solution may differ from one another does not conflict with previous views because the assumption of equality of the activity coefficients has been used only as a conscious approximation in order to simplify the question in hand. The second principle, that the activity of the chloride ion, at any given concentration, is independent of the cation associated with it, and especially the more generalized form of this principle suggested by Harned is, however, of much more questionable nature.

This principle stated by the authors as "the principle of the independent activity coefficients of the ions" involves the necessity that any ion dissolved in slight amounts in various dilute salt solutions of the same concentration should possess the same activity coefficient independent of the nature of the solvent. This, however, cannot be true because the solubility of a slightly soluble salt varies largely when passing from one solvent to another. Measurements made in this laboratory show the departure for a uni-univalent salt into uni-univalent solvents to amount in many cases to 10% in 0.1 *N* solutions. Of course if the concentration decreases, this departure will likewise decrease, but only for the reason that activity coefficients with decreasing concentration generally approach the same ideal value. It is a consequence of the results referred to above, that the activity coefficient of an ion is to a similar extent a function of the nature of this ion itself and of the solvent containing it.

The incorrectness of the principle, however, is brought out most strikingly by the following thermodynamic reasoning.

In a mixture of n_1, n_2, n_3, \dots molecules with the activities $\xi_1, \xi_2, \xi_3, \dots$ and the activity coefficients f_1, f_2, f_3, \dots the equation

$$\sum n_i d \ln \xi_i = \sum n_i d \ln \frac{n_i}{n} + \sum n_i d \ln f_i = 0$$

holds thermodynamically,⁵ n being the total number of molecules, and is easily reduced to

$$\sum n_i d \ln f_i = 0$$

This equation shows that when a dilute salt solution is gradually changed into another salt solution of the same concentration and the activity coefficients of the ions, according to the principle, remain constant, the same will be the case with the activity of the solvent. All salt solutions of the same concentration must, therefore, have the same freezing point, involving again the same activity coefficient for all ions, independent of their nature. The principle of the independent activity coefficients, therefore, ends in the assumption of equal activity coefficients for all ions in dilute solutions. This thermodynamic result shows clearly that this

⁵ See Section 8 of this paper.

principle cannot be true and that it indeed contradicts the first of the above principles.⁶

The principle of the independent activity coefficients is based on a conjectured relation between activity and electrical conductivity of ions. Without going into details respecting the availability of such a relation, the present writer wishes to emphasize the advantage of making thermodynamically related phenomena such as freezing points, solubilities and electromotive forces a basis for calculations of activity and osmotic coefficients. By associating experimental results from these various fields of investigation, it seems to be possible to reach a more detailed survey of the thermodynamic properties of solutions, particularly as regards the problem of the mutual electrical interaction of the ions and their salting-out effect.

The possibility of interpreting the properties of salt solutions from this point of view has already been touched in the first article of this series. The object of the present paper is to prove that the activity coefficient of an ion is made up of several factors, depending partly upon properties belonging to the medium, and partly upon an interaction between the ion concerned and the ions of the solvent; and it will show, moreover, that simple means are available for determining experimentally the ratio between these separate coefficients.

This problem is most simply attacked by confining ourselves to a consideration of solutions in which the total ion concentration is kept constant so that no change in the primary Milner-effect will confuse the pic-

⁶ In a recent interesting paper Lewis and Randall [THIS JOURNAL, 43, 1112 (1921)] have given a complete treatment of the theory of ion activities, in which the principle here in question is accepted and extended by introducing a new conception, the ionic strength. In spite of the obvious importance to be attached to the results resting upon the application of this conception, the conclusions of these authors as regards the problem here at hand are hardly compatible with the extensive amount of experimental material now available. It does not agree for instance with the fact found by Brönsted and Agnes Petersen (Ref. 2) that in the case of polyvalent ions the electric type is of marked influence upon the solubility. It seems as if this inconsistency may at least partly arise from the fact that the solubility of rather soluble salts was made a basis of the conclusions. Evaluating solubility data for activity determination in various solvents is possible only in a region of somewhat higher concentration than that corresponding to the solubility of the saturating salt in pure water. In the case of thallos chloride, for instance, the solubility of which is 0.016 in pure water, the apparent steep convergence of the curves corresponding to the various solvents [Lewis and Randall, *loc. cit.*, p. 1134, Fig. 4] does not involve a similar disappearance of the individualities of the solvents, but simply indicates the gradual approach of the composition of the saturated solutions to pure thallos chloride solutions. If a much less soluble modification of $TlCl$ could be employed we should certainly find appreciable differences at 0.016 *N* concentration. Not too much weight, therefore, can be given to the complete agreement of the low concentration data extrapolated in Table XIX. The above mentioned thermodynamic argument applies of course invariably in the case of the generalized principles.

ture of the changing peculiarities. On the other hand a thorough treatment of this problem must include the effect of changing concentration as well. In this respect the chief object will be to represent the peculiarities in such a form that they will vanish uniformly as the concentration approaches zero. This question of the concentration effect will, however, be reserved for a following article.

2. The Complex Nature of the Activity Coefficients

In the third article of this series⁷ a great number of examples showed that equally strong solutions of various uni-univalent salts dissolve slightly soluble metal-ammonia salts in largely varying proportions. For instance, in the case of oxalo-tetrammine cobaltic tetranitro-diammine cobaltiate the following solubilities, s , were found at 0°.

Solvent 0.1 N	s	Solvent 0.1 N	s
Na formate	0.00128	K chloride	0.00137
K formate	0.00132	K nitrate	0.00141

The first and the last numbers differ by about 10%.

The simplest way to account for such diversities would be to ascribe them to a certain dissolving power peculiar to each solvent, analogous to what has been assumed in the case of non-electrolytes dissolved in solutions of various salts. It is obvious, however, that conditions as simple as these do not prevail in the case of dissolved ions, because dissolving powers calculated in this way vary pronouncedly from one saturating salt to another.

This is shown by a good many data in the paper cited above.⁷ It also appears clearly from the fact that the solubilities of various sparingly soluble salts are influenced quite differently by the same solvent as exhibited, for example, by the following data for oxalo-tetrammine cobaltic tetranitro-diammine cobaltiate (Ox-N) and cesium tetrathiocyanato-diammine chromiate (Cs-R) at 20°.

	s_0	s	s/s_0
Ox-N	0.00266	0.00372	1.40
Cs-R	0.00263	0.00323	1.23

s_0 and s here indicating the solubility in pure water and 0.1 N potassium nitrate solution, respectively. In spite of the nearly identical values of the solubilities of these two salts in water the solubilities in 0.1 N potassium nitrate solutions differ largely.

These facts forced us to assume certain effects of interaction between the ions in addition to the effect of the dissolving power or salting-out effect, peculiar to each salt solution. We must again assume both of these effects to result from isolated causes due to the two ions constituting

⁷ THIS JOURNAL, 43, 2265 (1921).

the solvent salt. We must, therefore, represent the activity coefficient of a dissolved ion as a product of 4 separate coefficients, namely 2 coefficients of interaction and 2 salting-out coefficients.

In order to give these ideas a mathematical form the following notations will be used.

f_i	Activity coefficients in general.
f_{K^+}	Activity coefficients of the ion K^+ in general.
$f_{K(NaCl)}$	Activity coefficients of the ion K^+ in NaCl solution.
f_i	Coefficients of interaction in general.
$f_{K(Na)}$	Coefficients of interaction of the ion K^+ influenced by Na^+ .
$f_{K(Cl)}$	Coefficients of interaction of the ion K^+ influenced by Cl^- .
f_i	Salting-out coefficients in general.
$f_{(K)}$	Salting-out coefficients of the ion K^+ .
r_f	Ratio of activity coefficients in general.
r_i	Ratio of coefficients of interaction.
r_s	Ratio of salting-out coefficients.

Furthermore we put $\frac{f_{K(NaCl)}}{f_{K(LiCl)}} = r_{K(NaCl/LiCl)}$; $\frac{f_{K(Cl)}}{f_{K(NO_3)}} = r_{K(Cl/NO_3)}$; $\frac{f_{(K)}}{f_{(Na)}} = r_{(K/Na)}$.

By K , Na . . . and Cl , NO_3 . . . is here meant not only potassium, sodium . . . chloride and nitrate ions but generally various cations and anions respectively.

By means of the above assumption regarding the complex nature of the activity coefficient we can, for example, express the activity coefficient for the potassium ions as follows.

$$f_{K(NaCl)} = f_{K(Na)} f_{K(Cl)} f_{(Na)} f_{(Cl)} \quad (1)$$

While the coefficient of interaction is determined by the nature of the ions of both the solute and the solvent salt, the salting-out coefficient obviously has a more general character, as it depends merely upon the solvent itself.

3. The Principle of the Specific Interaction of Ions

Various considerations have led the writer to conclude that the above expression (1) for the activity coefficient of an ion can be largely simplified, namely, by introducing what we shall call the *principle of the specific interaction of ions*. This principle may be stated as follows.

In a dilute salt solution of constant total concentration, ions will be uniformly influenced by ions of their own sign.

We can therefore write

$$f_{K(K)} = f_{K(Na)} = f_{Cl(Cl)} = f_{Cl(NO_3)} = k \quad (2)$$

k being a constant depending only upon the concentration. For the present purpose, when we are comparing solutions of the same concentration, it can be equated to unity. We then obtain the following fundamental equations as a complete statement of our principles.

$$\left. \begin{aligned} f_{\mathbf{K}(\mathbf{KCl})} &= f_{\mathbf{K}(\mathbf{Cl})} f_{(\mathbf{K})} f_{(\mathbf{Cl})} \\ f_{\mathbf{K}(\mathbf{NaCl})} &= f_{\mathbf{K}(\mathbf{Cl})} f_{(\mathbf{Na})} f_{(\mathbf{Cl})} \end{aligned} \right\} \quad (3)$$

That this simplification is allowable becomes probable from a theoretical point of view when we remember that the individual deviations of salts in dilute solutions are mainly due to secondary electric forces⁸ determined by the size and structure of the ions and the number and positions of the separate electric charges of which the net charge is composed. In the case of ions of the same sign the repelling forces will tend to keep them apart and therefore, in dilute solution, to annihilate secondary effects perceptible only when the ions have sufficiently approached to one another.

Experimental indications of the validity of the above principle are furnished by electrical measurements⁹ concerning the activity coefficient of the chlorine ion in 0.1 *N* potassium chloride and potassium nitrate solutions. In spite of the chloride dissolving, on an average, about 4% less of slightly soluble salts than the nitrate, the activity coefficient of the chloride ion by means of these measurements was found to be only 1% higher in the chloride than in the nitrate solutions. From this result we draw the inference that the activity coefficients of anions vary very little when passed from one solution to another having the same cation. From these observations the above principle may be derived as a probable conclusion.

For fully establishing the principle, however, the simplest and the most direct way would be to utilize solubility data furnished by slightly soluble salts in salt solutions as solvents. It is the object of the following discussion to present the results achievable from such an examination and to show the conclusions they are leading to for the theory of solutions in general.

4. Introduction of the Theory of the Complex Nature of the Activity Coefficients and of the Principle of the Specific Interaction of Ions in the Theory of Solubility of Salts in Hetero-ionic Salt Solutions

In no other field are the individualities of salt solutions more pronouncedly exhibited than in the field of solubility of sparingly soluble salts in solutions of other salts as solvents. According to our theory these individualities are due partly to a peculiar avidity between ions of opposite sign represented by the coefficients of interaction, partly to a specific dissolving power exerted by the ions of the solvent and represented by the salting-out coefficients.

In order to avoid too much abstraction and complicated notations the principles stated above will be introduced by using, as far as possible, the symbols of well-known salts to represent the various types.

⁸ Brönsted, *THIS JOURNAL*, **42**, 781 (1920).

⁹ Brönsted, *K. Danske Vid. Selsk. Mat.-fys. Med.*, **3**, No. 9 (1920).

Thus, for instance, by AgCl and PbCl_2 we shall denote uni-univalent and univalent salts with a common anion; by KCl and KNO_3 , salts having a cation in common, etc.

Let s_{AgCl} , P_{AgCl} and Π_{AgCl} stand for solubility, stoichiometric solubility product and thermodynamic solubility product, respectively, of AgCl ; then using for the activity coefficients the notation suggested in the foregoing section we can write in the case of a potassium nitrate solution saturated with AgCl ,

$$\Pi_{\text{AgCl}} = P_{\text{AgCl}} f_{\text{Ag}(\text{KNO}_3)} f_{\text{Cl}(\text{KNO}_3)} \quad (4)$$

or introducing our principles by means of

$$\left. \begin{aligned} f_{\text{Ag}(\text{KNO}_3)} &= f_{\text{Ag}(\text{NO}_3)} f_{(\text{K})} f_{(\text{NO}_3)} \\ f_{\text{Cl}(\text{KNO}_3)} &= f_{\text{Cl}(\text{K})} f_{(\text{K})} f_{(\text{NO}_3)} \end{aligned} \right\} \quad (5)$$

the following equation,

$$\Pi_{\text{AgCl}} = s_{\text{AgCl}}^2 f_{\text{Ag}(\text{NO}_3)} f_{\text{Cl}(\text{K})} f_{(\text{K})}^2 f_{(\text{NO}_3)}^2 \quad (6)$$

In the case of an equally strong sodium nitrate solution as solvent we obtain analogously

$$\Pi_{\text{AgCl}} = s_{\text{AgCl}}^2 f_{\text{Ag}(\text{NaNO}_3)} f_{\text{Cl}(\text{Na})} f_{(\text{Na})}^2 f_{(\text{NO}_3)}^2 \quad (7)$$

and combining (6) and (7)

$$\frac{s_{\text{AgCl}(\text{KNO}_3)}}{s_{\text{AgCl}(\text{NaNO}_3)}} = \left(\frac{f_{\text{Cl}(\text{Na})}}{f_{\text{Cl}(\text{K})}} \right)^{1/2} \frac{f_{(\text{Na})}}{f_{(\text{K})}} \quad (8)$$

which by means of (5) can be rewritten as follows.

$$\frac{s_{\text{AgCl}(\text{KNO}_3)}}{s_{\text{AgCl}(\text{NaNO}_3)}} = \left(\frac{f_{\text{Cl}(\text{NaNO}_3)}}{f_{\text{Cl}(\text{KNO}_3)}} \right)^{1/2} \left(\frac{f_{(\text{Na})}}{f_{(\text{K})}} \right)^{1/2} \quad (9)$$

Introducing for the solubility ratio the symbol R and also the r from Section 2 (above), by means of

$$\frac{s_{\text{AgCl}(\text{KNO}_3)}}{s_{\text{AgCl}(\text{NaNO}_3)}} = R_{\text{AgCl}(\text{KNO}_3/\text{NaNO}_3)} \quad (10)$$

Equations 8 and 9 are transformed into

$$R_{\text{AgCl}(\text{KNO}_3/\text{NaNO}_3)} = r_{\text{Cl}(\text{Na}/\text{K})}^{1/2} r_{(\text{Na}/\text{K})} \quad (11)$$

$$R_{\text{AgCl}(\text{KNO}_3/\text{NaNO}_3)} = r_{\text{Cl}(\text{NaNO}_3/\text{KNO}_3)}^{1/2} r_{(\text{Na}/\text{K})}^{1/2} \quad (12)$$

Since the coefficients belonging to the silver and nitrate ions do not enter into these equations we are obviously justified in making the following deduction, that *when using as solvents equally strong solutions with an anion in common the solubility ratio shown by a slightly soluble uni-univalent and hetero-ionic salt depends only on the anion of the saturating salt and the cations of the two solvents.* According to this theory we shall therefore find, for instance,

$$\frac{s_{\text{AgCl}(\text{KNO}_3)}}{s_{\text{AgCl}(\text{NaNO}_3)}} = \frac{s_{\text{AgCl}(\text{KClO}_3)}}{s_{\text{AgCl}(\text{NaClO}_3)}} = \frac{s_{\text{TlCl}(\text{KNO}_3)}}{s_{\text{TlCl}(\text{NaNO}_3)}}$$

As an analogous rule it is evident that when the two solvents possess a common cation we can also write

$$\frac{S_{\text{AgCl(KNO}_3)}}{S_{\text{AgCl(KClO}_3)}} = \left(\frac{f_{\text{Ag(ClO}_3)}}{f_{\text{Ag(NO}_3)}} \right)^{1/2} \frac{f_{\text{(ClO}_3)}}{f_{\text{(NO}_3)}} = \left(\frac{f_{\text{Ag(KClO}_3)}}{f_{\text{Ag(KNO}_3)}} \right)^{1/2} \left(\frac{f_{\text{(ClO}_3)}}{f_{\text{(NO}_3)}} \right)^{1/2}$$

or

$$\frac{S_{\text{AgCl(KNO}_3)}}{S_{\text{AgCl(KClO}_3)}} = \frac{S_{\text{AgCl(NaNO}_3)}}{S_{\text{AgCl(NaClO}_3)}} = \frac{S_{\text{AgClO}_3(\text{KNO}_3)}}{S_{\text{AgClO}_3(\text{KClO}_3)}$$

It is not difficult to extend these results to cases in which the saturating salt is of a higher type. If we consider luteo cobaltic chromate, for instance, the symbol of which is $L_2(\text{CrO}_4)_3$ (L standing for the luteo ion $\text{Co}(\text{NH}_3)_6$) the following equations are obtained.

$$\left. \begin{aligned} \frac{S_{L_2(\text{CrO}_4)_3(\text{KNO}_3)}}{S_{L_2(\text{CrO}_4)_3(\text{NaNO}_3)}} &= \left(\frac{f_{\text{CrO}_4(\text{Na})}}{f_{\text{CrO}_4(\text{K})}} \right)^{3/6} \frac{f_{\text{(Na)}}}{f_{\text{(K)}}} \\ \frac{S_{L_2(\text{CrO}_4)_3(\text{KNO}_3)}}{S_{L_2(\text{CrO}_4)_3(\text{NaNO}_3)}} &= \left(\frac{f_{\text{CrO}_4(\text{NaNO}_3)}}{f_{\text{CrO}_4(\text{KNO}_3)}} \right)^{3/6} \left(\frac{f_{\text{(Na)}}}{f_{\text{(K)}}} \right)^{2/6} \\ \frac{S_{L_2(\text{CrO}_4)_3(\text{KNO}_3)}}{S_{L_2(\text{CrO}_4)_3(\text{KCl})}} &= \left(\frac{f_{\text{L(Cl)}}}{f_{\text{L(NO}_3)}} \right)^{2/6} \frac{f_{\text{(Cl)}}}{f_{\text{(NO}_3)}} \\ \frac{S_{L_2(\text{CrO}_4)_3(\text{KNO}_3)}}{S_{L_2(\text{CrO}_4)_3(\text{KCl})}} &= \left(\frac{f_{\text{L(KCl)}}}{f_{\text{L(KNO}_3)}} \right)^{2/6} \left(\frac{f_{\text{(Cl)}}}{f_{\text{(NO}_3)}} \right)^{2/6} \end{aligned} \right\} \quad (13)$$

or

$$\left. \begin{aligned} R_{L_2(\text{CrO}_4)_3(\text{KNO}_3/\text{NaNO}_3)} &= r^{3/6}_{\text{CrO}_4(\text{Na/K})} r_{\text{(Na/K)}} \\ R_{L_2(\text{CrO}_4)_3(\text{KNO}_3/\text{NaNO}_3)} &= r^{3/6}_{\text{CrO}_4(\text{NaNO}_3/\text{KNO}_3)} r^{2/6}_{\text{(Na/K)}} \\ R_{L_2(\text{CrO}_4)_3(\text{KNO}_3/\text{KCl})} &= r^{2/6}_{\text{L(Cl/NO}_3)} r_{\text{(Cl/NO}_3)} \\ R_{L_2(\text{CrO}_4)_3(\text{KNO}_3/\text{KCl})} &= r^{2/6}_{\text{L(KCl/KNO}_3)} r^{2/6}_{\text{(Cl/NO}_3)} \end{aligned} \right\} \quad (14)$$

From the form of these equations we learn that the above rule for univalent saturating salts holds true also when saturating salts of higher types are employed. The solubility ratio is obviously independent of the common ion of the solvents and also of the nature of the ion of opposite sign in the saturating salt as far as saturating salts of the same type are considered. It is very important to note, however, that the form of the equations varies with the type of the saturating salt, as this fact enables us to compute the values of r_i and r_u separately.

We carry out this calculation preferably by means of a special example, applying for instance Equation 16 to the three salts (1) oxalo-tetrammine cobaltic tetranitro-diammine cobaltiate (symbol OxN), $[\text{Co}(\text{NH}_3)_4\text{C}_2\text{O}_4][\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]$, (2) xantho cobaltic tetranitro-diammine cobaltiate (symbol XN_2), $[\text{Co}(\text{NH}_3)_5\text{NO}_2][\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]_2$, and (3) luteo cobaltic tetranitro-diammine cobaltiate (LN_3), $[\text{Co}(\text{NH}_3)_6][\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]_3$, each containing the same univalent anion and a uni-, bi- and trivalent cation, respectively. Application of Equation 16 gives in the three cases

for the solubility ratio R , using potassium and sodium nitrates as solvents,

$$R_I = R_{\text{OXN}(\text{KNO}_3/\text{NaNO}_3)} = r^{1/2}_{\text{N}(\text{Na}/\text{K})} r_{(\text{Na}/\text{K})} \quad (15)$$

$$R_{II} = R_{\text{XN}_2(\text{KNO}_3/\text{NaNO}_3)} = r^{2/3}_{\text{N}(\text{Na}/\text{K})} r_{(\text{Na}/\text{K})} \quad (16)$$

$$R_{III} = R_{\text{LN}_3(\text{KNO}_3/\text{NaNO}_3)} = r^{3/4}_{\text{N}(\text{Na}/\text{K})} r_{(\text{Na}/\text{K})} \quad (17)$$

From two of these equations the ratio of interaction $r_{\text{N}(\text{Na}/\text{K})}$ and the salting-out ratio $r_{(\text{Na}/\text{K})}$ can obviously be determined by means of the experimentally found solubility ratios R_I , R_{II} and R_{III} . For the ratio of interaction we obtain

$$r_i = r_{\text{N}(\text{Na}/\text{K})} = \left(\frac{R_{II}}{R_I}\right)^6 = \left(\frac{R_{III}}{R_I}\right)^4 = \left(\frac{R_{III}}{R_{II}}\right)^{12}; \quad (18)$$

and for the salting-out ratio,

$$r_u = r_{(\text{Na}/\text{K})} = \frac{R_I^4}{R_{II}^3} = \frac{R_I^8}{R_{III}^2} = \frac{R_{II}^9}{R_{III}^8} \quad (19)$$

showing the ratios R_I , R_{II} and R_{III} to be correlated also.

According to Equation 3 the ratio of the two activity coefficients r_f = $\frac{f_{\text{N}(\text{NaNO}_3)}}{f_{\text{N}(\text{KNO}_3)}}$ is given by

$$r_f = r_i r_u \quad (19a)$$

and is thus determinable from the same solubility ratios.

Corresponding results are easily obtained when other types of saturating salts are considered.

In these equations our principles have been given such a form that they can be subjected to a direct experimental test.

It may be expected, perhaps, that the r_u value derivable by means of Equation 24 or analogous equations would obtain also in the case of non-electrolytes, a saturating substance here representing directly the solubility ratio. This would indeed be the case if no interaction between ions and neutral molecules occurred. According to H. v. Euler¹⁰ neutral substances in many cases exhibit the same solubility ratio in two solvents, a fact which is found consistent with the above assumption. Further inquiry in this field, however, shows deviations to exist, which in certain cases are very considerable, and it is therefore necessary to assume a kind of interaction between ions and *neutral molecules*. This, however, is generally slight, compared with the action between ions of opposite sign.

When utilizing argon or another inert gas as saturating substance any peculiar interaction would probably be precluded, and we should therefore expect the ratio of solubility of such a substance in two salt solutions to be identical with the r_u for these solvents found in the way described.

¹⁰ Euler, *Z. physik. Chem.*, 31, 360 (1899); *Z. Elektrochem.*, 23, 192 (1917).

5. Experiments Covering Solubilities in Hetero-ionic Solvents

Experiment of Minor Accuracy.—Most of the experimental material referred to in this section was produced for other purposes than that of verifying the above principles, and it is but moderately accurate.

In the first place, experiments were available utilizing certain xantho cobaltic and chloro-pentammine cobaltic salts, namely:

Xantho cobaltic tetrathiocyanato-diammine chromiate.....	(XR ₂)
Xantho cobaltic tetranitro-diammine cobaltiate.....	(XN ₂)
Chloro-pentammine cobaltic tetrathiocyanato-diammine chromiate.....	(PR ₂)
Chloro-pentammine cobaltic tetranitro-diammine cobaltiate.....	(PN ₂)

using uni-univalent salt solutions as solvents. The results are given in Tables I and II. The figures here and in the following tables represent mols. per liter of the solution.

TABLE I
SOLUBILITY OF XR₂ AND XN₂ IN 0.2 M SALT SOLUTIONS AT 0° AND 20°

Solvent	XR ₂ , <i>t</i> = 0° × 10 ⁶	XR ₂ , <i>t</i> = 20° × 10 ⁶	XN ₂ , <i>t</i> = 0° × 10 ⁶	XN ₂ , <i>t</i> = 20° × 10 ⁶
H ₂ O	392	1284	311	992
NaCHO ₂	629	1950	570	1692
KCHO ₂	667	2040	629	1824
NaCl	680	2097	621	1823
KCl	723	2193	682	1952
NaNO ₃	746	2228
KNO ₃	790	2325

TABLE II
SOLUBILITY OF PR₂ AND PN₂ IN 0.2 M SALT SOLUTIONS AT 0° AND 20°

Solvent	PR ₂ , <i>t</i> = 0° × 10 ⁶	PR ₂ , 20° × 10 ⁶	PN ₂ , <i>t</i> = 0° × 10 ⁶	PN ₂ , <i>t</i> = 20° × 10 ⁶
H ₂ O	173	637
NaCHO ₂	477	1516	325	1100
KCHO ₂	510	1592	363	1207
NaCl	524	1627	353	1187
KCl	548	1702	393	1291

By means of these figures the solubility ratios have been calculated and are collected in Table III.

TABLE III
RATIOS OF SOLUBILITY OF XR₂, XN₂, PR₂ AND PN₂ IN VARIOUS 0.2 M SOLVENTS

Solvent	<i>t</i> = 0°		<i>t</i> = 20°	
	XR ₂	PR ₂	XR ₂	PR ₂
KCHO ₂ /NaCHO ₂	1.060	1.069	1.046	1.050
KCl/NaCl	1.063	1.046	1.046	1.046
KNO ₃ /NaNO ₃	1.059	1.046	1.044	1.046
K ⁺ /Na ⁺ , mean	1.059		1.046	
	XN ₂	PN ₂	XN ₂	PN ₂
KCHO ₂ /NaCHO ₂	1.103	1.119	1.078	1.097
KCl/NaCl	1.098	1.115	1.071	1.088
K ⁺ /Na ⁺ , mean	1.109		1.084	

	XR_2	XN_2	XR_2	XN_2
NaCl/NaCHO ₂	1.081	1.090	1.076	1.077
KCl/KCHO ₂	1.083	1.087	1.075	1.070
Cl ⁻ /CHO ₂ ⁻ , mean	1.085		1.075	
	XR_2		XR_2	
NaNO ₃ /NaCHO ₂	1.186		1.143	
KNO ₃ /KCHO ₂	1.183		1.140	
NO ₃ ⁻ /CHO ₂ ⁻ , mean	1.184		1.142	
	PR_2	PN_2	PR_2	PN_2
NaCl/NaCHO ₂	1.098	1.086	1.073	1.079
KCl/KCHO ₂	1.074	1.084	1.071	1.070
Cl ⁻ /CHO ₂ ⁻ , mean	1.086		1.073	

The figures in this table furnish a good verification of the principle of the specific interaction of the ions. The agreement of the figures within each group in the tables shows that the action between ions of the same sign hardly surmounts the possible experimental error. The results may be stated in the following way by means of Equation 14.

TABLE IV

	$t = 0^\circ$	$t = 20^\circ$
$r^{2/3}R(Na/K) \ r(Na/K)$	1.059	1.046
$r^{2/3}N(Na/K) \ r(Na/K)$	1.109	1.084
$r^{1/3}X(HCOO/Cl) \ r(HCOO/Cl)$	1.085	1.075
$r^{1/3}X(HCOO/NO_3) \ r(HCOO/NO_3)$	1.184	1.142
$r^{2/3}P(HCOO/Cl) \ r(HCOO/Cl)$	1.086	1.073

These figures show that the coefficients of interaction may differ very markedly from one another. The relative action of Na⁺ and K⁺ is thus seen to be about 7% higher for the N⁻ than for the R⁻ ion. The r -coefficients themselves cannot be calculated from these figures since salts of only a single type are employed as saturating salts. With the rise of temperature the peculiarity diminishes and the ratios approach unity.

In the following tables are the results of some further experiments covering cesium tetrathiocyanato-diammine chromiate and cesium tetranitro-diammine cobaltiate in various solvents.

TABLE V
SOLUBILITY OF CsR AND CsN IN VARIOUS SOLVENTS AT 0°

M	Solvent	CsR $\times 10^6$	CsN $\times 10^6$
	H ₂ O	789	532
1.0	NaCHO ₂	831	785
1.0	NaNO ₃	1365	1268
0.5	Mg(NO ₃) ₂	1356	1113
0.5	MgSO ₄	973	815

TABLE VI
RATIOS OF SOLUBILITY OF CsR AND CsN IN SOLVENTS AT 0°

Solvent	CsR	CsN	Mean
NaNO ₃ /NaCHO ₂	1.64	1.62	1.63
Mg(NO ₃) ₂ /MgSO ₄	1.39	1.37	1.38
NaNO ₃ /Mg(NO ₃) ₂	1.01	1.14	...

The agreement found here between the ratios in solvents with a common cation and the disagreement between the ratios in solvents with a common anion verify closely the rule of the specific action of the ions and the absence of any action between ions of the same sign. This is the more remarkable as in this case the increase in solubility is very high on account of the high concentration of the solvents employed.

The results of a series of measurements covering the four salts cesium tetrathiocyanato chromiate (CsR), cesium tetranitro cobaltiate (CsN) and the corresponding oxalo-tetrammine cobaltic salts (OxR and OxN) in which nitrates and chlorides of potassium and sodium were employed as solvents, are tabulated below.

TABLE VII
SOLUBILITY OF CsN, OxN, CsR AND OxR IN 0.1M SALT SOLUTIONS AT 20°

Solvent	CsN × 10 ⁶	OxN × 10 ⁶	CsR × 10 ⁶	OxR × 10 ⁶
H ₂ O	17130	2659	2629	1366
KNO ₃	20920	3723	3233	1813
NaNO ₃	20550	3615	3182	1786
KCl	20210	3647	3110	1771
NaCl	19870	3531	3072	1737

TABLE VIII
SOLUBILITY RATIOS OF CsN, CsR, OxN AND OxR IN 0.1M SOLUTIONS OF ALKALI NITRATES AND CHLORIDES, AND WATER AT 20°

Solvent	CsN	OxN	CsR	OxR
KNO ₃	1.222	1.400	1.230	1.327
NaNO ₃	1.200	1.360	1.210	1.307
KCl	1.180	1.372	1.183	1.296
NaCl	1.162	1.328	1.168	1.271

TABLE IX
SOLUBILITY RATIOS OF CsN, OxN, CsR AND OxR IN ALKALI NITRATES AND CHLORIDES AT 20°

Solvents	CsN	CsR		
KNO ₃ /KCl	1.036	1.040	}	$r^{1/2}_{Cs(Cl/NO_3)} r_{(Cl/NO_3)} = 1.036$
NaNO ₃ /NaCl	1.033	1.036		
	OxN	OxR	}	$r^{1/2}_{Ox(Cl/NO_3)} r_{(Cl/NO_3)} = 1.024$
KNO ₃ /KCl	1.021	1.024		
NaNO ₃ /NaCl	1.024	1.028		
	CsN	OxN	}	$r^{1/2}_{N(Na/K)} r_{(Na/K)} = 1.030$
KNO ₃ /NaNO ₃	(1.018)	1.030		
KCl/NaCl	(1.016)	1.030		
	CsR	OxR	}	$r^{1/2}_{R(Na/K)} r_{(Na/K)} = 1.016$
KNO ₃ /NaNO ₃	1.017	1.015		
KCl/NaCl	1.013	1.019		

The two numbers in parentheses are evidently too low, perhaps due to the fact that the solid cesium tetranitro cobaltate takes up some potassium salt from the solution to form a solid mixture. Such a behavior may be expected because the crystals are very similar, certainly isomorphic, and the solubility is of the same order of magnitude. This, however, will not interfere with the other values if, as we must assume, potassium nitrate and potassium chloride behave uniformly. In the case of the corresponding tetrathiocyanato chromiates an analogous phenomenon is precluded by the widely differing solubilities of the potassium and cesium salts of this anion.¹¹

Otherwise, as shown by Table X, the agreement between the figures in each group justifies the conclusion that in this case also we have a good verification of the principles to be tested.

Finally, we may add the results of some measurements with praseo salts.

As the purity of these salts could not be tested in the usual way on account of their instability the data in question are of minor value. Still, a conclusion confirming our principle may be drawn from them. Pi^- indicates the picrate ion and Rh^- the thiocyanate ion.

TABLE X
SOLUBILITY OF PRASEO SALTS IN VARIOUS SOLVENTS AT 0°

Solvent <i>M</i>	PrRh $\times 10^4$	PrNO ₃ $\times 10^4$	PrIO ₃ $\times 10^4$	PrPi $\times 10^4$
0.1 KCl	3580	5000	5710	295
0.1 NaCl	3530	4835	5680	285.5
0.1 KClO ₃	3645	5790
0.1 NaClO ₃	3605	5760
0.05 KCl	3355	5480	5250	274
0.05 NaCl	3320	4510	5240	266
0.05 KClO ₃	3390	5310	...
0.05 NaClO ₃	3370	5280	...
H ₂ O	2820	3860	4410	212

TABLE XI
RATIOS OF SOLUBILITY OF PRASEO SALTS IN 0.1M ALKALI CHLORIDES AND CHLORATES AT 0°

Solvents	PrRh	PrIO ₃		
KClO ₃ /KCl	1.017	1.013	}	$r^{1/2}_{\text{Pr}(\text{Cl}/\text{ClO}_3)} r_{(\text{Cl}/\text{ClO}_3)} = 1.016$
NaClO ₃ /NaCl	1.021	1.013		
KCl/NaCl	1.014	}	}	$r^{1/2}_{\text{Rh}(\text{Na}/\text{K})} r_{(\text{Na}/\text{K})} = 1.011$
KClO ₃ /NaClO ₃	1.008			
KCl/NaCl	1.005	}	}	$r^{1/2}_{\text{IO}_3(\text{Na}/\text{K})} r_{(\text{Na}/\text{K})} = 1.005$
KClO ₃ /NaClO ₃	1.005			

¹¹ Later experiments have shown that a similar effect is still perceptible in this system. The ratios 1.017 and 1.013 in Table IX are therefore certainly somewhat too low.

The very slight difference found between the solubility of PrIO_3 in K^+ and Na^+ solvents agrees with the fact that solutions of potassium and sodium iodates are materially alike in respect to their osmotic properties as shown by Jahn¹² and Hall and Harkins.¹³ The relation here referred to between osmotic coefficients and activity is derived on the basis of our principle in Section 8.

Experiments of Higher Accuracy.—A series of experiments has been begun in this laboratory for the purpose of securing very accurate data for verifying our principles. All these data will be reserved for a special article. Only a few results may be stated here in order to show the accuracy obtainable and the exactness with which our principles hold.

Tenth normal solutions of potassium and sodium nitrate served as solvents. The saturating salts contained the univalent tetranitro cobaltiate anion $\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4^-$. The cations and the corresponding solubility ratio are given in the following table.

TABLE XII
SOLUBILITY RATIOS $s_{\text{KNO}_3}/s_{\text{NaNO}_3}$ OF VARIOUS TETRANITRO-DIAMMINE COBALTIATES AT 20°.

Cation	$s_{\text{KNO}_3}/s_{\text{NaNO}_3}$
Oxalo-tetrammine cobaltic.....	1.0339
Silver.....	1.0343
Tetramethyl-ammonium.....	1.0340
Carbonato-tetrammine cobaltic.....	1.0324
	R = 1.0339
Chloro-pentammine cobaltic.....	1.0411
Xantho cobaltic.....	1.0414
	R = 1.0413
Triethylene-diammine cobaltic.....	1.0450
Aquo-pentammine cobaltic.....	1.0465
	R = 1.0458

By means of Equations 15–17 we can compute the R when introducing $r_i = 1.0476$ and $r_u = 1.0101$. The R values thus calculated are given in Table XIII together with those found.

TABLE XIII

	R found	R calculated
R_I	1.0339	1.0339
R_{II}	1.0413	1.0419
R_{III}	1.0458	1.0460

The agreement leaves nothing to be desired.

¹² Jahn, *Z. physik. Chem.*, **59**, 37 (1907).

¹³ Hall and Harkins, *THIS JOURNAL*, **38**, 2669 (1916).

6. Application of the Theory to Solutions in Homo-ionic Solvents

The solubility of a uni-univalent salt in a homo-ionic salt solution is determined by

$$\Pi_{AgCl} = P_{AgCl(KCl)} f_{Ag(K)} f_{Ag(Cl)} f_{Cl(K)} f_{Cl(Cl)} f^2_{(K)} f^2_{(Cl)} \quad (20)$$

where the same notation is used as in Section 3. Introducing the principles of the specific interaction we can write

$$\left. \begin{aligned} \Pi_{AgCl} &= P_{AgCl(KCl)} f_{Ag(Cl)} f_{Cl(K)} f^2_{(K)} f^2_{(Cl)} \\ \Pi_{AgCl} &= P_{AgCl(NaCl)} f_{Ag(Cl)} f_{Cl(Na)} f^2_{(Na)} f^2_{(Cl)} \end{aligned} \right\} \quad (21)$$

and therefore

$$\left(\frac{P_{AgCl(KCl)}}{P_{AgCl(NaCl)}} \right)^{1/2} = \left(\frac{f_{Cl(Na)}}{f_{Cl(K)}} \right) \frac{f_{(Na)}}{f_{(K)}} \quad (22)$$

Putting

$$\left(\frac{P_{AgCl(KCl)}}{P_{AgCl(NaCl)}} \right)^{1/2} = R_{AgCl(KCl/NaCl)} \quad (23)$$

and introducing the same r -coefficients as in the foregoing section we obtain,

$$R_{AgCl(KCl/NaCl)} = r^{1/2}_{Cl(Na/K)} r_{(Na/K)} = r^{1/2}_{Cl(NaCl/KCl)} r^{1/2}_{(Na/K)} \quad (24)$$

in full analogy to the corresponding Equation 12 in the case of hetero-ionic solvents.

If the saturating salt has the composition $L_2(CrO_4)_3$ and is dissolved in the two solvents K_2CrO_4 and Na_2CrO_4 the following equation is obtained

$$\left(\frac{P_{L_2(CrO_4)_3(K_2CrO_4)}}{P_{L_2(CrO_4)_3(Na_2CrO_4)}} \right)^{1/6} = \left(\frac{f_{CrO_4(Na)}}{f_{CrO_4(K)}} \right)^{2/6} \frac{f_{(Na)}}{f_{(K)}} \quad (25)$$

or

$$R_{L_2(CrO_4)_3(K_2CrO_4/Na_2CrO_4)} = r^{2/6}_{CrO_4(Na/K)} r_{(Na/K)} = r^{2/6}_{CrO_4(Na_2CrO_4/K_2CrO_4)} r^{2/6}_{(Na/K)} \quad (26)$$

also fully analogous to the corresponding Equation 14.

The ratios of interaction and the salting-out ratios are of course determinable from Equations 25 and 26 in just the same way as from Equations 13 and 14 in the case of hetero-ionic solvents. Equations 15–19 are therefore also valid for homo-ionic solvents, the only difference being that when hetero-ionic solvents are used R represents directly the solubility ratio, (p. 892) while in the case of homo-ionic solvents as stated above it means the n th root of the ratio of solubility products, n being the total number of ions contained in one molecule of the saturating salt. As in Equations 22–26 all coefficients belong to the ions of the solvent itself; dissolution of homo-ionic solutes leads directly to a determination of the interaction of ions in the salt solutions employed as solvents.

7. Experiments Covering Solubilities in Homo-ionic Solvents

In order to examine the theoretical results reached in the foregoing

section a series of measurements was carried out with cobalt ammonia salts dissolved in homo-ionic solvents. The saturating salts employed contained the following complex ions: oxalo-tetrammine cobaltic, (symbol, Ox), $[\text{Co}(\text{NH}_3)_4\text{C}_2\text{O}_4]$; chloro-pentammine cobaltic (symbol, [Cl]), $[\text{Co}(\text{NH}_3)_5\text{Cl}]$; bromo-pentammine cobaltic, (symbol, [Br]), $[\text{Co}(\text{NH}_3)_5\text{Br}]$; luteo cobaltic, (symbol, L), $[\text{Co}(\text{NH}_3)_6]$; oxalo-dinitro-diammine cobaltate ion, (symbol, On), $[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_2\text{C}_2\text{O}_4]$; and the solvents were 0.1 *M* solutions of potassium nitrate, sodium nitrate, potassium chloride and sodium chloride. The temperature of the experiment was 0° and the same method was used as stated in an earlier communication.² The results of the measurements are given in the following tables.

TABLE XIV

SOLUBILITY OF NITRATES IN POTASSIUM NITRATE AND SODIUM NITRATE SOLUTIONS AT 0°

Saturating Salt	0.1 <i>M</i> KNO_3 $\times 10^4$	0.1 <i>M</i> NaNO_3 $\times 10^4$	$P_{\text{KNO}_3}/P_{\text{NaNO}_3}$	<i>R</i>
Ox NO_3	816	777	1.051	1.025
[Cl](NO_3) ₂	3970	3670	1.092	1.030
L(NO_3) ₃	4930	4500	1.131	1.031

TABLE XV

SOLUBILITY OF CHLORIDES IN POTASSIUM CHLORIDE AND SODIUM CHLORIDE SOLUTIONS AT 0°

Saturating Salt	0.1 <i>M</i> KCl $\times 10^4$	0.1 <i>M</i> NaCl $\times 10^4$	$P_{\text{KCl}}/P_{\text{NaCl}}$	<i>R</i>
OxCl	5810	5700	1.020	1.010
[Cl]Cl ₂	610	593	1.029	1.010
[Br]Cl ₂	220	213	1.033	1.008

TABLE XVI

SOLUBILITY OF KON IN POTASSIUM NITRATE AND POTASSIUM CHLORIDE SOLUTIONS AT 0°

	0.1 <i>M</i> KNO_3 $\times 10^4$	0.1 <i>M</i> KCl $\times 10^4$	$P_{\text{KNO}_3}/P_{\text{KCl}}$	<i>R</i>
KOn	3800	3510	1.086	1.042

TABLE XVII

SOLUBILITY OF NaON IN SODIUM NITRATE AND SODIUM CHLORIDE SOLUTIONS AT 0°

	0.1 <i>M</i> NaNO_3 $\times 10^4$	0.1 <i>M</i> NaCl $\times 10^4$	$P_{\text{NaNO}_3}/P_{\text{NaCl}}$	<i>R</i>
NaOn	9720	9280	1.051	1.025

R denotes, as explained the *n*th root of the ratio of solubility products, *n* being the number of ions of each salt. In order to calculate the ratios of interaction and the salting-out ratios from these data we use Equations 18 and 19 shown to be valid in the case of homo-ionic solvents also, *R*_I, *R*_{II} and *R*_{III} corresponding to di-ionic, tri-ionic and tetra-ionic solutes, respectively.

A. Calculation of the Ratio of Interaction and the Salting-out Ratio for 0.1 *M* Potassium and Sodium Nitrate Solutions.—We have found (Table XIV) that *R*_I = 1.025, *R*_{II} = 1.030, and *R*_{III} = 1.031.

Introducing these values into Equations 18 and 19, $r_i = r_{\text{NO}_3(\text{Na/K})} = \left(\frac{R_{\text{II}}}{R_{\text{I}}}\right)^6 = \left(\frac{R_{\text{III}}}{R_{\text{I}}}\right)^4$ and $r_u = r_{(\text{Na/K})} = \frac{R_{\text{I}}^4}{R_{\text{II}}^3} = \frac{R_{\text{I}}^3}{R_{\text{III}}^2}$ we obtain as the most fitting values $r_i = 1.028$ and $r_u = 1.011$.

Again inserting these values into Equations 20, 21 and 22 we calculate the R values tabulated below together with the experimental values of R .

TABLE XVIII

COMPARISON OF R VALUES FOR POTASSIUM NITRATE AND SODIUM NITRATE SOLUTIONS

	R_{I}	R_{II}	R_{III}
Calc.	1.025	1.030	1.032
Found	1.025	1.030	1.031

showing that the adopted values of r_i and r_u agree excellently with the experiment.

B. Calculation of the Ratio of Interaction and the Salting-out Ratio for 0.1 M Solutions of Potassium and Sodium Chlorides.—The calculation is carried out quite similarly. Introducing the most fitting values: $r_i = r_{\text{Cl}(\text{Na/K})} = 1.000$; $r_u = r_{(\text{Na/K})} = 1.010$; we obtain the figures in Table XIX.

TABLE XIX

COMPARISON OF R VALUES FOR POTASSIUM AND SODIUM CHLORIDE SOLUTIONS

	Found	Calc.
R_{I}	1.010	1.010
R_{II}	1.009	1.010

The value for R_{II} , 1.009, is taken as the mean of the values 1.010 and 1.008 for $[\text{Cl}]\text{Cl}_2$ and $[\text{Br}]\text{Cl}_2$, respectively. On account of the higher solubility of $[\text{Cl}]\text{Cl}_2$, the corresponding R_{II} value is certainly more accurate in these cases and using this value the agreement between R values found and calculated becomes complete.

C. Significance of the Above Agreement.—The above calculations led to two independent determinations of $r_u = r_{(\text{Na/K})}$ at 0° namely: $r_{(\text{Na/K})} = 1.011$, and $r_{(\text{Na/K})} = 1.010$, using nitrates and chlorides respectively as solvents. In the previous section the same value 1.010 was found at 20° by means of tetranitro-diammine cobaltiate dissolved in alkali nitrate solutions. We find thus through these measurements that the sodium ion has a salting-out effect about 1.0% larger than the potassium ion in 0.1 N solution. It is very desirable to test the scope of the present theory by further examinations in the same direction using as solvents various salt solutions with a common ion and salts of various types as solutes. It is interesting to note that the salting-out effects of 0.1 N solutions of potassium and sodium ions towards non-electrolytes differ in several cases by about the same amount. However, as

explained above, by using non-electrolytes as saturating substances we cannot assume the $r_{(\text{Na}/\text{K})}$ to be precisely determined.

For the ratio of interaction we found $r_{\text{NO}_3(\text{Na}/\text{K})} = 1.028$, and $r_{\text{Cl}(\text{Na}/\text{K})} = 1.000$. While the chlorine ion is acted upon equally by potassium and sodium ions we see that the nitrate ion has an almost 3% higher avidity for the potassium ion than for the sodium ion.

The ratio of activity coefficients can now be calculated by means of Equation 19a

$$r_f = r_i r_u$$

yielding for the activity ratio of the nitrate ion

$$r_{\text{NO}_3(\text{NaNO}_3/\text{KNO}_3)} = 1.028 \times 1.011 = 1.039$$

while for the chlorine ion correspondingly:

$$r_{u(\text{NaCl}/\text{KCl})} = 1.000 \times 1.011 = 1.011.$$

The activity coefficient of the nitrate ion is thus about 4% higher in a 0.1 *N* solution of sodium nitrate than in a potassium nitrate solution of the same concentration, while in the case of the chlorides the corresponding value for the chlorine ion is about 1%.

8. Interrelation between Activity and Osmotic Coefficients and the Solubility and Freezing Point

Already in the first paper an interrelation between solubility and freezing point was suspected, because a solvent having a small freezing-point lowering generally proved of high dissolving power towards a slightly soluble salt and *vice versa*. A simple relation, however, could not be found, because the ratio of dissolving power of two solvents varies with the nature of the saturating salt. This problem is readily solved by introducing the principle of the specific interaction of ions in connection with a general thermodynamic treatment of the relation between activity and osmotic coefficients in a mixed solution of constant total concentration.

The general relation¹⁴

$$\sum c_i d \ln \xi_i = d\eta \quad (27)$$

where c_i and ξ_i stand for the concentration and the activity of the first ion, η for the osmotic concentration and $\sum c_i = c$ is the total ion concentration, forms a basis for such treatment.

Introducing in this equation $\xi_i = c_i f_i$ and $\eta = c\varphi$ and assuming c to be constant we obtain

$$\sum c_i d \ln c_i + \sum c_i d \ln f_i = c d\varphi \quad (28)$$

or

$$\sum c_i d \ln f_i = c d\varphi \quad (29)$$

¹⁴ Ref. 8, p. 761.

If we now consider a mixed solution of potassium and sodium chlorides in which $\frac{c_{\text{NaCl}}}{c_{\text{KCl}}} = \frac{x}{1-x}$ we can write

$$c_{\text{NaCl}} = \frac{c}{2}x; \quad c_{\text{KCl}} = \frac{c}{2}(1-x); \quad c_{\text{Cl}} = \frac{c}{2}$$

and thus

$$x \, d \ln f_{\text{Na}} + (1-x) \, d \ln f_{\text{K}} + d \ln f_{\text{Cl}} = 2d\varphi \quad (30)$$

by which the activity coefficients of the ions in the mixed solution are thermodynamically correlated to the osmotic coefficients.

We shall now introduce the principle of the specific interaction of ions. Since, according to this, the coefficients of interaction of the cations are unchanged when the solution gradually changes from a potassium to a sodium chloride solution because the only interacting ion, Cl^- , is present in constant concentration, the change in f_{K} and f_{Na} is due to the changing salting-out effect alone. We, therefore, can put

$$d \ln f_{\text{K}} = d \ln f_{\text{Na}} = d \ln f_u \quad (31)$$

and

$$d \ln f_u + d \ln f_{\text{Cl}} = 2d\varphi; \quad (32)$$

or in integrated form

$$\varphi_{\text{NaCl}} - \varphi_{\text{KCl}} = \frac{1}{2} \ln \frac{f_{(\text{Na})}}{f_{(\text{K})}} + \frac{1}{2} \ln \frac{f_{\text{Cl}(\text{NaCl})}}{f_{\text{Cl}(\text{KCl})}} \quad (33)$$

or by means of (5)

$$\varphi_{\text{NaCl}} - \varphi_{\text{KCl}} = \frac{1}{2} \ln \frac{f_{\text{Cl}(\text{Na})}}{f_{\text{Cl}(\text{K})}} + \ln \frac{f_{(\text{Na})}}{f_{(\text{K})}} \quad (34)$$

These equations can also be written

$$\varphi_{\text{NaCl}} - \varphi_{\text{KCl}} = \ln [r^{1/2}_{\text{Cl}(\text{Na}/\text{K})} r_{(\text{Na}/\text{K})}] = \frac{1}{2} \ln [r_{\text{Cl}(\text{NaCl}/\text{KCl})} r_{\text{Na}/\text{K}}] \quad (35)$$

In the more general case of the two salts aluminum sulfate and ferric sulfate we obtain by quite similar calculations,

$$2 \, d \ln f_u + 3 \, d \ln f_{\text{SO}_4} = 5d\varphi \quad (36)$$

or

$$\varphi_{\text{Al}_2(\text{SO}_4)_3} - \varphi_{\text{Fe}_2(\text{SO}_4)_3} = \frac{2}{3} \ln \frac{f_{\text{SO}_4(\text{Al}_2(\text{SO}_4)_3)}}{f_{\text{SO}_4(\text{Fe}_2(\text{SO}_4)_3)}} + \frac{2}{3} \ln \frac{f_{(\text{Al})}}{f_{(\text{Fe})}} \quad (37)$$

and

$$\varphi_{\text{Al}_2(\text{SO}_4)_3} - \varphi_{\text{Fe}_2(\text{SO}_4)_3} = \frac{2}{3} \ln \frac{f_{\text{SO}_4(\text{Al})}}{f_{\text{SO}_4(\text{Fe})}} + \ln \frac{f_{(\text{Al})}}{f_{(\text{Fe})}} \quad (38)$$

yielding, for instance, for magnesium and calcium chlorides

$$\varphi_{\text{MgCl}_2} - \varphi_{\text{CaCl}_2} = \frac{2}{3} \ln \frac{f_{\text{Cl}(\text{MgCl}_2)}}{f_{\text{Cl}(\text{CaCl}_2)}} + \frac{1}{3} \ln \frac{f_{(\text{Mg})}}{f_{(\text{Ca})}} = \frac{2}{3} \ln \frac{f_{\text{Cl}(\text{Mg})}}{f_{\text{Cl}(\text{Ca})}} + \ln \frac{f_{(\text{Mg})}}{f_{(\text{Ca})}} \quad (39)$$

and for potassium and sodium sulfates

$$\varphi_{\text{Na}_2\text{SO}_4} - \varphi_{\text{K}_2\text{SO}_4} = \frac{1}{3} \ln \frac{f_{\text{SO}_4(\text{Na}_2\text{SO}_4)}}{f_{\text{SO}_4(\text{K}_2\text{SO}_4)}} + \frac{2}{3} \ln \frac{f_{(\text{Na})}}{f_{(\text{K})}} = \frac{1}{3} \ln \frac{f_{\text{SO}_4(\text{Na})}}{f_{\text{SO}_4(\text{K})}} + \ln \frac{f_{(\text{Na})}}{f_{(\text{K})}} \quad (40)$$

A relation between solubility and osmotic coefficients of the solvents is now easily arrived at by writing Equation 22 as follows.

$$\frac{1}{2} \ln \frac{P_{\text{AgCl}(\text{KCl})}}{P_{\text{AgCl}(\text{NaCl})}} = \frac{1}{2} \ln \frac{f_{\text{Cl}(\text{Na})}}{f_{\text{Cl}(\text{K})}} + \ln \frac{f_{(\text{Na})}}{f_{(\text{K})}} \quad (41)$$

which by comparison with (34) gives

$$\varphi_{\text{NaCl}} - \varphi_{\text{KCl}} = \frac{1}{2} \ln \frac{P_{\text{AgCl}(\text{KCl})}}{P_{\text{AgCl}(\text{NaCl})}} \quad (42)$$

The corresponding relations for the more general case of $\text{L}_2(\text{SO}_4)_3$ dissolved in aluminum sulfate and ferric sulfate solutions give

$$\varphi_{\text{Al}_2(\text{SO}_4)_3} - \varphi_{\text{Fe}_2(\text{SO}_4)_3} = \frac{1}{3} \ln \frac{P_{\text{L}_2(\text{SO}_4)_3(\text{Fe}_2(\text{SO}_4)_3)}}{P_{\text{L}_2(\text{SO}_4)_3(\text{Al}_2(\text{SO}_4)_3)}} \quad (43)$$

The difference in osmotic coefficients, and therefore in freezing points, of two solutions with a common ion, may thus be computed from the solubility ratio of a sparingly soluble salt possessing also the common ion of the solvents; and *vice versa*, solubility ratios can be calculated from freezing-point measurements.

In a quite similar way solubility measurements in hetero-ionic solvents may be utilized for the same purpose. According to Equations 8 and 14

$$\ln \frac{S_{\text{AgCl}(\text{KNO}_3)}}{S_{\text{AgCl}(\text{NaNO}_3)}} = \frac{1}{2} \ln \frac{f_{\text{Cl}(\text{Na})}}{f_{\text{Cl}(\text{K})}} + \ln \frac{f_{(\text{Na})}}{f_{(\text{K})}} \quad (44)$$

and

$$\ln \frac{S_{\text{L}_2(\text{CrO}_4)_3(\text{Fe}_2(\text{SO}_4)_3)}}{S_{\text{L}_2(\text{CrO}_4)_3(\text{Al}_2(\text{SO}_4)_3)}} = \frac{3}{5} \ln \frac{f_{\text{CrO}_4(\text{Al})}}{f_{\text{CrO}_4(\text{Fe})}} + \ln \frac{f_{(\text{Al})}}{f_{(\text{Fe})}} \quad (45)$$

and thus

$$\ln \frac{S_{\text{AgCl}(\text{KNO}_3)}}{S_{\text{AgCl}(\text{NaNO}_3)}} = \varphi_{\text{NaCl}} - \varphi_{\text{KCl}} \quad (46)$$

and

$$\ln \frac{S_{\text{L}_2(\text{CrO}_4)_3(\text{Fe}_2(\text{SO}_4)_3)}}{S_{\text{L}_2(\text{CrO}_4)_3(\text{Al}_2(\text{SO}_4)_3)}} = \varphi_{\text{Al}_2(\text{CrO}_4)_3} - \varphi_{\text{Fe}_2(\text{CrO}_4)_3} \quad (47)$$

Equation 42 can be tested by means of the solubility data from Tables XIV to XVII and available data of the freezing-point lowerings of alkali nitrates and chlorides taken from the critical study of Noyes and Falk. The figures are collected in Table XX.

TABLE XX
COMPARISON OF FREEZING-POINT AND SOLUBILITY DATA

Salt ₁	Salt ₂	$\Delta_1 - \Delta_2$	$\varphi_1 - \varphi_2$	P_2/P_1	$1/2 \ln(P_2/P_1)$
NaNO ₃	KNO ₃	0.090	0.024	1.051	0.025
NaCl	KCl	0.027	0.008	1.020	0.010
KCl	KNO ₃	0.148	0.039	1.086	0.041
NaCl	NaNO ₃	0.085	0.023	1.051	0.025

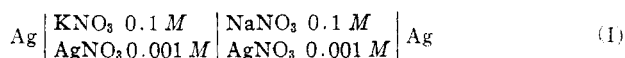
According to Equation 42 we have $\varphi_1 - \varphi_2 = 1/2 \ln (P_2/P_1)$.

The figures in the second and fourth columns show this relation to be fulfilled very exactly and thus lend strong support to the theory on which these calculations are based.

9. Determination of the Liquid-junction Potential on the Basis of our Principles

The principles established in the preceding sections can clearly be utilized for estimating the liquid junction potential in a galvanic cell.

If we wish to determine the potential π_d at the liquid junction, 0.1 M KNO_3 | 0.1 M NaNO_3 , we add a little silver nitrate and measure the cell



the electromotive force of which is given by the equation

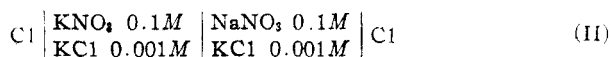
$$\pi_1 = RT \ln \frac{f_{\text{Ag}(\text{NaNO}_3)}}{f_{\text{Ag}(\text{KNO}_3)}} + \pi_d \quad (48)$$

or according to our principles

$$\pi_1 = RT \ln r_{(\text{Na}/\text{K})} + \pi_d \quad (49)$$

Since $r_{(\text{Na}/\text{K})}$, as shown, may be determined from solubility measurements we are in a position to calculate π_d from the electromotive force of the cell found.

Adding a little chloride to the two nitrate solutions we can build the following cell



yielding the electromotive force

$$\pi_2 = RT \ln \frac{f_{\text{Cl}(\text{KNO}_3)}}{f_{\text{Cl}(\text{NaNO}_3)}} + \pi_d$$

or

$$\pi_2 = -RT \ln [r_{(\text{Na}/\text{K})} r_{\text{Cl}(\text{Na}/\text{K})}] + \pi_d \quad (50)$$

equally usable for estimation of π_d .

Combining Equations 49 and 50 we obtain

$$\frac{\pi_1 - \pi_2}{2} = RT \ln [r^{1/2}_{\text{Cl}(\text{Na}/\text{K})} r_{(\text{Na}/\text{K})}] \quad (51)$$

or by introduction of (II)

$$\frac{\pi_1 - \pi_2}{2} = RT \ln \frac{S_{\text{AgCl}(\text{KNO}_3)}}{S_{\text{AgCl}(\text{NaNO}_3)}} \quad (52)$$

showing an important relation to hold between solubility and electromotive force.

It is obvious that when r_u has been determined from solubility measurements and therefore π_d can be computed by means of Equation 49 from measurements of the cell (I) then Equation 49 can be generally utilized for the determination of r_i , the ratios of interaction, inserting in the solutions various electrodes and adding small amounts of the corresponding salts.

Since for $r_{(\text{Na}/\text{K})}$ the value 1.010 has been found above, the liquid junction potential in a cell like (I) containing potassium and sodium associated with the same anion is given by $\pi_d = \pi_1 - 0.00025$ volt at 20° . The two π 's are here reckoned in the direction from K^+ to Na^+ solution.

Summary

1. The activity coefficient of an ion may be determined by two factors, one of which is due to the salting-out effect of the salt solution serving as solvent and the other to electrical interaction between the said ion and the ions of the solvent.

2. Ions are uniformly influenced by ions of their own sign. Their activity coefficients depend, therefore, only upon the action of ions of opposite sign and the salting-out effect of the solvent.

3. The salting-out effect of a salt solution can be represented as a product of the salting-out effects of the separate ions.

4. Simple relations regarding solubility in salt solutions at constant concentration are derived.

5. Methods for determining the ratios of salting-out coefficients, coefficients of interaction and activity coefficients are given.

6. A thermodynamic relation between activity coefficients and osmotic coefficients in solutions of constant total concentration, and a relation between solubility and freezing point are derived.

7. A method for estimating liquid-junction potentials is found.

8. The theoretical conclusions in the paper are experimentally verified.

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