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THE PRINCIPLE
OF THE SPECIFIC INTERACTION
OF IONS

BY

J. N. BRØNSTED



KØBENHAVN

HOVEDKOMMISSIONÆR: ANDR. FRED. HØST & SØN, KGL. HOF-BOGHANDEL
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1. Introduction.

While on the basis of the theory of complete dissociation of the strong electrolytes¹ 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 measurements² has shown the activity of ions to depend very markedly on their individual nature and also to be distinctively influenced by the nature of the salt solution serving as solvent. 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 MAC INNES³ and HARNED⁴ have given interesting contributions to the question of the activities of separate ions. The first principles introduced by MAC INNES that the activity of the cation and anion in the same solution may differ from one another does not conflict

¹ For literature see *Journ. Amer. Chem. Soc.* **42**, 761 (1920).

² Brønsted og Agnes Petersen, *ibid.* **43**, (1921).

³ Mac Innes, *ibid.* **41**, 1086 (1919).

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

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 a certain ion dissolved in slight amounts in various salt solutions of the same concentration should possess the same activity coefficients independent of the nature of the solvent. This, however, can not 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 in two uni-univalent solvents to amount in many cases to 10 p. ct. 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, appears 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

$$\sum n_1 d \ln \xi_1 = \sum n_1 d \ln n_1 + \sum n_1 d \ln f_1 = 0$$

holds thermodynamically¹, and the numbers of molecules being constant is reduced to

$$\sum n_1 d \ln f_1 = 0.$$

This equation shows that when a salt solution is gradually changed into another salt solution of the same concentration and the activity coefficients, 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, end in the assumption of equal activity coefficients for all ions. This thermodynamic result shows clearly that this principle can not be true².

¹ See section 8 of this paper.

² In a recent interesting paper LEWIS and RANDALL (Journ. Amer. Chem. Soc. **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 Brønsted and Agnes Petersen (Journ. Amer. Chem. Soc. **43**, (1921) 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 only possible 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 f. inst. the solubility of which is 0.016 in pure water, the apparent steep convergence of the curves corresponding to the various solvents (Fig. 4 p. 1134) 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 supposed much less soluble modification of $TlCl$ could be employed we would certainly find appreciable

The principle of the independent activity coefficients is based on a conjectured relation between activity and electric 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 electric interaction of the ions and their salting out effect.

The possibility of interpreting the properties of salt solution from this point of view has already been touched in a previous article¹. The object of the present paper is to prove that the activity coefficient of an ion is made up of several factors, partly depending upon properties belonging to the medium 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 picture of the changing peculiarities. On the other hand a thorough treatment of this problem must include the effect of changing 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 unvariably in the case of the generalised principles.

¹ Journ. Amer. Chem. Soc. **42**, 761 (1920).

centration 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 publication.

2. The Complex Nature of the Activity Coefficients.

In a recent article¹ 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 oxalotetramine cobaltic tetranitro diammine cobaltiate the following solubilities s were found at 0°:

Solvent	s
0.1 <i>n</i> Na-formate.	0.00128
0.1 <i>n</i> K-formate.	0.00132
0.1 <i>n</i> K-chloride	0.00137
0.1 <i>n</i> K-nitrate.	0.00141

where the first and the last numbers differ about 10 per cent.

The simplest way to account for such diversities would be to ascribe these diversities 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 quoted above. It also appears clearly from the fact that the solubilities of various sparingly soluble salts are influenced quite

¹ Brønsted and Agnes Petersen. Journ. Amer. Soc. **43**, (1921).

differently by the same solvent as exhibited for instance by the following data for oxalo tetrammine cobaltic tetranitrodiammine cobaltiate (*Ox-N*) and cesium tetrarhodanodiammine chromiate (*Cs-R*) at 20°:

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

s_0 and s here indicating the solubility in pure water and 0.1 *n* KNO_3 respectively. In spite of the nearly identical values of the solubilities of these two salts in water the solubilities in 0.1 KNO_3 -solutions differ largely.

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

Activity coefficients in general.....	f
— — of the ion K^+ in general.....	f_K
— — — K^+ in <i>NaCl</i> solution	$f_{K(NaCl)}$
Coefficients of interaction in general.....	f_i
— — — of the ion K^+ influenced	
— — — — by Na^+	$f_{K(Na)}$
— — — K^+ influenced by Cl^- ...	$f_{K(Cl)}$
Salting out coefficients in general.....	f_u
— — — of the ion K^+	$f_{(K)}$

Ratio of activity coefficients in general	r_f
— coefficients of interaction in general	r_i
— salting out coefficients general	r_u

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 express the activity coefficient for instance for the K -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 coefficients 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 unity. We then obtain the following fundamental equations as a complete statement of our principles:

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

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 forces¹ 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 one another.

Experimental indications of the validity of the above principles is furnished by some electric measurement² concerning the activity coefficient of the chloride ion in 0.1 n potassium chloride and potassium nitrate solutions. In spite of the chloride dissolving, on an average, about 4 p. ct. less of slightly soluble salts than the nitrate the activity coefficient of Cl^- by means of these measurements was found only 1 p. ct. higher in the chloride than in the nitrate solutions. From this result we draw the inference that the activity coefficient of anions vary very little when passed

¹ Brønsted, Journal Amer. Chem. Soc. **42**, 781 (1920).

² Brønsted, K. Danske Vid. Selsk. Math.-fys. Medd. **3** Nr. 9 (1920).

from one solution to another having the same cation. These observations allow us to derive the above principle as a probable conclusion.

For fully establishing the principle, however, the most simple and the most direct way would be to utilize solubility data furnished by slightly soluble salts in salts solutions, as solvents. It is the object of the following chapters 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 Heteroionic 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.

Thus for instance by $AgCl$ and $PbCl_2$ we shall denote uni-univalent and uni-bivalent 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 KNO_3 -solution saturated with $AgCl$:

$$H_{AgCl} = P_{AgCl} f_{Ag(KNO_3)} f_{Cl(KNO_3)} \quad (4)$$

or introducing our principles by means of:

$$\left. \begin{aligned} f_{Ag(KNO_3)} &= f_{Ag(NO_3)} f_{(K)} f_{(NO_3)} \\ f_{Cl(KNO_3)} &= f_{Cl(K)} f_{(K)} f_{(NO_3)} \end{aligned} \right\} \quad (5)$$

the following equation:

$$H_{AgCl} = s_{AgCl(KNO_3)}^2 f_{Ag(NO_3)} f_{Cl(K)} f_{(K)}^2 f_{NO_3}^2 \quad (6)$$

In the case of an equally strong $NaNO_3$ -solution as solvent we obtain analogously:

$$H_{AgCl} = s_{AgCl(NaNO_3)}^2 f_{Ag(NO_3)} f_{Cl(Na)} f_{(Na)}^2 f_{(NO_3)}^2 \quad (7)$$

and combining (6) and (7):

$$\frac{s_{AgCl(KNO_3)}}{s_{AgCl(NaNO_3)}} = \left(\frac{f_{Cl(Na)}}{f_{Cl(K)}} \right)^{\frac{1}{2}} \frac{f_{(Na)}}{f_{(K)}} \quad (8)$$

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

$$\frac{s_{AgCl(KNO_3)}}{s_{AgCl(NaNO_3)}} = \left(\frac{f_{Cl(NaNO_3)}}{f_{Cl(KNO_3)}} \right)^{\frac{1}{2}} \left(\frac{f_{(Na)}}{f_{(K)}} \right)^{\frac{1}{2}} \quad (9)$$

Introducing for the solubility ratio the symbol R and also the r from section 2 by means of

$$\frac{s_{AgCl(KNO_3)}}{s_{AgCl(NaNO_3)}} = R_{AgCl(KNO_3/NaNO_3)} \quad (10)$$

Equations (8) and (9) are transformed into:

$$R_{AgCl(KNO_3/NaNO_3)} = r_{Cl(Na/K)}^{\frac{1}{2}} r_{(Na/K)} \quad (11)$$

$$R_{AgCl(KNO_3/NaNO_3)} = r_{Cl(NaNO_3/KNO_3)}^{\frac{1}{2}} r_{(Na/K)}^{\frac{1}{2}} \quad (12)$$

Since the coefficients belonging to the Ag^+ and NO_3^- -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 heteroionic salts 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:

$$\frac{S_{AgCl(KNO_3)}}{S_{AgCl(NaNO_3)}} = \frac{S_{AgCl(KClO_3)}}{S_{AgCl(NaClO_3)}} = \frac{S_{TlCl(KNO_3)}}{S_{TlCl(NaNO_3)}}.$$

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

$$\frac{S_{AgCl(KNO_3)}}{S_{AgCl(KClO_3)}} = \left(\frac{f_{Ag(ClO_3)}}{f_{Ag(NO_3)}} \right)^{\frac{1}{2}} \frac{f_{(ClO_3)}}{f_{(NO_3)}} = \left(\frac{f_{Ag(KClO_3)}}{f_{Ag(KNO_3)}} \right)^{\frac{1}{2}} \left(\frac{f_{(ClO_3)}}{f_{(NO_3)}} \right)^{\frac{1}{2}}.$$

OR

$$\frac{S_{AgCl(KNO_3)}}{S_{AgCl(KClO_3)}} = \frac{S_{AgCl(NaNO_3)}}{S_{AgCl(NaClO_3)}} = \frac{S_{AgIO_3(KNO_3)}}{S_{AgIO_3(NaNO_3)}}.$$

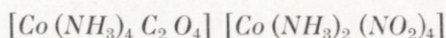
It is not difficult to extend these results to cases in which the saturating salt is of a higher type. If we consider Luteo cobaltic chromate for instance, the symbol of which is $L_2(CrO_4)_3$ (L standing for the Luteo ion $Co(NH_3)_6$) the following equations are obtained:

$$\left. \begin{aligned} \frac{S_{L_2(CrO_4)_3(KNO_3)}}{S_{L_2(CrO_4)_3(NaNO_3)}} &= \left(\frac{f_{CrO_4(Na)}}{f_{CrO_4(K)}} \right)^{\frac{3}{5}} \frac{f_{(Na)}}{f_{(K)}} \\ \frac{S_{L_2(CrO_4)_3(KNO_3)}}{S_{L_2(CrO_4)_3(NaNO_3)}} &= \left(\frac{f_{CrO_4(NaNO_3)}}{f_{CrO_4(KNO_3)}} \right)^{\frac{3}{5}} \left(\frac{f_{(Na)}}{f_{(K)}} \right)^{\frac{3}{5}} \\ \frac{S_{L_2(CrO_4)_3(KNO_3)}}{S_{L_2(CrO_4)_3(KCl)}} &= \left(\frac{f_{L(Cl)}}{f_{L(NO_3)}} \right)^{\frac{5}{2}} \frac{f_{(Cl)}}{f_{(NO)}} \\ \frac{S_{L_2(CrO_4)_3(KNO_3)}}{S_{L_2(CrO_4)_3(KCl)}} &= \left(\frac{f_{L(KCl)}}{f_{L(KNO_3)}} \right)^{\frac{5}{2}} \left(\frac{f_{(Cl)}}{f_{(NO_3)}} \right)^{\frac{3}{5}} \end{aligned} \right\} \quad (13)$$

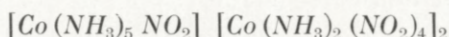
$$\text{or } \left. \begin{aligned} R_{L_2(Cr O_4)_3(KNO_3/Na NO_3)} &= r_{Cr O_4(Na/K)}^{3/2} r_{(Na/K)} \\ R_{L_2(Cr O_4)_3(KNO_3/Na NO_3)} &= r_{Cr O_4(Na NO_3/KNO_3)}^{3/2} r_{(Na/K)}^{3/2} \\ R_{L_2(Cr O_4)_3(KNO_3/K Cl)} &= r_{L(Cl/NO_3)}^{3/2} r_{(Cl/NO_3)} \\ R_{L_2(Cr O_4)_3(KNO_3/K Cl)} &= r_{L(K Cl/KNO_3)}^{3/2} r_{(Cl/NO_3)}^3 \end{aligned} \right\} (14)$$

From the form of these equations we learn that the above rule for uni-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 salts 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.

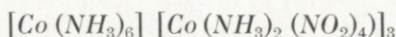
We preferably carry out this calculation by means of a special example applying for instance Equation (14) to the three salts 1. oxalotetrammine cobaltic tetranitrodiammine cobaltate (OxN):



2. Xantho cobaltic tetranitrodiammine cobaltate (XN_2):



and 3. Luteo cobaltic tetranitrodiammine cobaltate (LN_3):



each containing the same univalent anion and a uni-, bi- and trivalent cation respectively. Application of Equation (14) gives in the three cases for the solubility ratio R using KNO_3 and $NaNO_3$ as solvents:

$$R_I = R_{OxN(KNO_3/Na NO_3)} = r_{N(Na/K)}^{1/2} r_{(Na/K)} \quad (15)$$

$$R_{II} = R_{XN_2(KNO_3/NaNO_3)} = r_{N(Na/K)}^{\frac{2}{3}} r_{(Na/K)} \quad (16)$$

$$R_{III} = R_{LN_3(KNO/NaNO_3)} = r_{N(Na/K)}^{\frac{3}{4}} r_{(Na/K)} \quad (17)$$

From two of these equations the ratio of interaction $r_{N(Na/K)}$ and the salting out ratio $r_{(Na/K)}$ 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:

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

and for the salting out ratio:

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

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 $r_f = \frac{f_{N(NaNO_3)}}{f_{N(KNO_3)}}$ 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.

By 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 (19) or analogous equations should obtain also in the case of non-electrolytes as saturating substances 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. EULER¹ neutral

¹ Zeitschr. f. phys. Ch. **31**, 360 (1899), Zeitschr. f. Electrochemie **23**, 192 (1917).

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 we are therefore necessitated to assume a kind of interaction between ions and neutral molecules too. This however is generally slight, compared with the action between ions of opposite sign.

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

5. Experiments Covering Solubilities in Heteroionic Solvents.

a) Experiments 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 concerning some xantho cobaltic and chloropentammine cobaltic salts namely:

Xantho-cobaltic tetrarhodano diamminechromiate..	($X R_2$)
— — nitro — cobaltiate ..	($X N_2$)
Chloropentammine cobaltic tetrarhodano diammine chromiate.....	($P R_2$)
Chloropentammine cobaltic tetranitro diammine cobaltiate	($P N_2$)

using uni-univalent salt solutions as solvents. The results are given in Tabela I and II.

Table I. Solubility of XR_2 and XN_2 in 0.2 Molal Salt Solutions at 0° and 20° .

Solvent	$XR_2, t = 0^\circ$	$XR_2, t = 20^\circ$	$XN_2, t = 0^\circ$	$XN_2, t = 20^\circ$
H_2O	0.000392	0.001284	0.000311	0.000992
$Na CHO_2$	629	1950	570	1692
$K CHO_2$.	667	2040	629	1824
$Na Cl$. . .	680	2097	621	1823
$K Cl$	723	2193	682	1952
$Na NO_3$.	746	2228
$K NO_3$. .	790	2325

Table II. Solubility of PR_2 and PN_2 in 0.2 Molal Salt Solutions at 0° and 20° .

Solvent	$PR_2, t = 0^\circ$	$PR_2, t = 20^\circ$	$PH_2, t = 0^\circ$	$PN_2, t = 20^\circ$
H_2O	0.001731	0.000637
$Na CHO_2$	0.000477	0.001516	325	1100
$KC HO_2$.	510	1592	363	1207
$Na Cl$. . .	524	1627	353	1187
$K Cl$	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 XR_2 , XN_2 , PR_2 , and PN_2 , in Various 0.2 Molal Solvents.

Solvent	$t = 0^\circ$		$t = 20^\circ$	
	XR_2	PR_2	XR_2	PR_2
$KCHO_2/Na CHO_3$.	1.060	1.069	1.046	10.50
$K Cl/Na Cl$	1.063	1.046	1.046	1.046
$KNO_3/Na NO_3$. . .	1.059	..	1.044	...
K^+/Na^+ mean . . .	1.059		1.046	

Solvent	t = 0°		t = 20°	
	XN ₂	PN ₂	XN ₂	PN ₂
<i>K CHO</i> ₂ / <i>Na CHO</i> ₂	1.103	1.119	1.078	1.099
<i>K Cl</i> / <i>Na Cl</i>	1.098	1.115	1.071	1.088
<i>K</i> ⁺ / <i>Na</i> ⁺ mean	1.109		1.084	
	XR ₂	XN ₂	XR ₂	XN ₂
<i>Na Cl</i> / <i>Na CHO</i> ₂ . . .	1.081	1.090	1.076	1.077
<i>K Cl</i> / <i>K CHO</i> ₂	1.083	1.087	1.075	1.070
<i>Cl</i> ⁻ / <i>CHO</i> ₂ ⁻ mean	1.085		1.075	
	XR ₂		XR ₂	
<i>Na NO</i> ₃ / <i>Na CHO</i> ₂ . .	1.186		1.143	
<i>K NO</i> ₃ / <i>K CHO</i> ₂	1.183		1.140	
<i>NO</i> ₃ ⁻ / <i>CHO</i> ₂ ⁻ mean	1.184		1.142	
	PR ₂	PN ₂	PR ₂	PN ₂
<i>Na Cl</i> / <i>K CHO</i> ₂	1.098	1.086	1.073	1.079
<i>K Cl</i> / <i>K CHO</i> ₂	1.074	1.084	1.071	1.070
<i>Cl</i> ⁻ / <i>CHO</i> 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°	t = 20°
$r_{R(Na/K)}^{Na/K}$ $r_{(Na/K)}$	1.059	1.046
$r_{N(Na/K)}^{Na/K}$ $r_{(Na/K)}$	1.109	1.084
$r_{X(HCOO/Cl)}^{HCOO/Cl}$ $r_{(HCOO/Cl)}$	1.085	1.075
$r_{X(HCOO/NO_3)}^{HCOO/NO_3}$ $r_{(HCOO/NO_3)}$	1.184	1.142
$r_{P(HCOO/Cl)}^{HCOO/Cl}$ $r_{(HCOO/Cl)}$	1.086	1.073

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

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

Table V. Solubility of CsR and CsN in Various Solvents at 0° .

Solvent	CsR	CsN
H_2O	0.000789	0.00532
$NaCHO_2$, 1 mol. . . .	831	785
$NaNO_3$, 1 mol	1365	1268
$Mg(NO_3)_2$, 0,5 mol.	1356	1113
$MgSO_4$, 0,5 mol. . . .	973	815

Table VI. Ratios of Solubility of CsR and CsN in Various 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 verifies closely the rule of the specific action of the ions and the ab-

sence 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 *Cs* tetra-rhodano chromiate (*CsR*), *Co*-tetranitro-cobaltiate (*CsN*) and the corresponding oxalotetramine 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 0.1 Salt Solutions at 20°

Solvent	<i>CsN</i>	<i>OxN</i>	<i>CsR</i>	<i>OxR</i>
H_2O	0.01713	0.002659	0.002629	0.001366
0.1 KNO_3 . . .	2092	3723	3233	1813
0.1 $NaNO_3$. . .	2055	3615	3182	1786
0.1 KCl	2021	3647	3110	1771
0.1 $NaCl$	1987	3531	3072	1737

Table VIII. Solubility Ratios of *CsN*, *CsR*, *OxN* and *OxR* in 0.1 Mol. Solutions of Alkali Nitrates and Chlorides and Water at 20°.

Solvent	<i>CsN</i>	<i>OxN</i>	<i>CsR</i>	<i>OxR</i>
0.1 KNO_3 . . .	1.222	1.400	1.230	1.327
0.1 $NaNO_3$. . .	1.200	1.360	1.210	1.307
0.1 KCl	1.180	1.372	1.183	1.296
0.1 $NaCl$	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	<i>CsN</i>	<i>CsR</i>	
KNO_3/KCl . . .	1.036	1.040	} $r_{Cs(Cl/NO_3)}^{1/2} r_{Cl/NO_3} = 1.036$
$NaNO_3/NaCl$. . .	1.033	1.036	

Solvents	<i>OxN</i>	<i>OxR</i>	
KNO_3/KCl . .	1.021	1.024	} $r_{Ox(Cl/NO_3)}^{1/2} r_{(Cl/NO_3)} = 1.024$
$NaNO_3/NaCl$	1.024	1.028	
	<i>CsN</i>	<i>OxN</i>	
$KNO_3/NaNO_3$	(1.018)	1.030	} $r_{N(Na/K)}^{1/2} r_{(Na/K)} = 1.030$
$KCl/NaCl$. . .	(1.016)	1.030	
	<i>CsR</i>	<i>OxR</i>	
$KNO_3/NaNO_3$	1.017	1.015	} $r_{R(Na/K)}^{1/2} r_{(Na/K)} = 1.016$
$KCl/NaCl$. . .	1.013	1.019	

The two figures in brackets are evidently too low, perhaps due to the fact that the solid *CsN* takes up some *KN* from the solution to form a solid mixture. Such a behaviour may be expected because the crystals are very similar, certainly isomorphic and the solubility of the same order of magnitude. This, however, will not interfere with the other values if, as we must assume, KNO_3 and *KCl* behave uniformly. In the case of the corresponding tetra-rhodano chromiates an analogous phenomenon is precluded by the widely differing solubilities of the potassium and caesium salt of this anion¹.

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

Finally we may add the results of some measurement 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 confirmatory to

¹ 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.

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 $t = 0^\circ$

Solvent	$Pr Rh$	$Pr NO_3$	$Pr JO_3$	$Pr Pi$
0.1 KCl	0.00358	0.00500	0.00571	0.000295
0.1 $NaCl$. . .	353	4835	568	2855
0.1 $KClO_3$. .	3645	...	579	...
0.1 $NaClO_3$.	3605	...	576	...
0.05 KCl . . .	0.003355	0.00458	0.00525	0.000274
0.05 $NaCl$. . .	332	451	524	266
0.05 $KClO_3$. .	339	...	531	...
0.05 $NaClO_3$	337	...	528	...
H_2O	0.00282	0.00386	0.00441	0.00212

Table XI. Ratios of Solubility of Praseo Salts in 0.1 Molal Alkali Chlorides and Chlorates at 0° .

Solvents	$Pr Rh$	$Pr JO_3$	
$KClO_3/KCl$	1.017	1.013	} $r_{Pr(Cl/ClO_3)}^{1/2} r_{(Cl/ClO_3)} = 1.016$
$NaClO_3/NaCl$	1.021	1.013	
	$Pr Rh$		
$KCl/NaCl$	1.014		} $r_{Rh(Na/K)}^{1/2} r_{(Na/K)} = 1.011$
$KClO_3/NaClO_3$. . .	1.008		
	$Pr JO_3$		
$KCl/NaCl$	1.005		} $r_{JO_3(Na/K)}^{1/2} r_{(Na/K)} = 1.005$
$KClO_3/NaClO_3$. . .	1.005		

The very slight difference found between the solubility of $PrJO_3$ 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 Jahn¹ and Hall and Harkins². The relation here referred to between osmotic coefficients and activity is derived on the basis of our principle in section 8.

b. Experiments of higher accuracy. A series of experiments is 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 publication. Only a few results may be stated here in order to show the accuracy obtainable and the exactness with which our principles hold.

0.1 *N* solutions of potassium and sodium nitrate served as solvents: The saturating salts contained the univalent tetranitro cobaltate anion $Co(NH_3)_2(NO_2)_4^-$. The cations and the corresponding solubility ratios are given in the following table.

Table XII. Solubility Ratios s_{KNO_3}/s_{NaNO_3} of Various Tetranitrodiammine Cobaltates at 20°.

Cation	s_{KNO_3}/s_{NaNO_3}
Oxalo tetrammine cobaltic.....	1.0339
Silver	1.0343
Tetramethyl-ammonium	1.0340
Carbonato-tetrammine cobaltic	1.0324
	$R_I = 1.0339$
Chloropentammine cobaltic	1.0411
Xantho cobaltic	1.0414
	$R_{II} = 1.0413$
Triethylene diammine cobaltic	1.0450
Aquo pentammine cobaltic.....	1.0465
	$R_{III} = 1.0458$

¹ Z. physik. Chem. **59**, 37 (1907).

² Journ. Amer. Chem. Soc. **38**, 2669 (1916).

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} . . .	1.0459	1.0460

The agreement leaves nothing to be desired.

6. Application of the Theory to Solutions in Homoionic Solvents.

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

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

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

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

and therefore

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

Putting

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

and introducing the same coefficients as in the foregoing section we obtain:

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

in full analogy to the corresponding equation (12) in the case of heteroionic 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

$$\left(\frac{P_{L_2(CrO_4)_3(K_2CrO_4)}}{P_{L_2(CrO_4)_3(Na_2CrO_4)}} \right)^{\frac{1}{5}} = \left(\frac{f_{CrO_4(Na)}}{f_{CrO_4(K)}} \right)^{\frac{3}{5}} \frac{f_{(Na)}}{f_{(K)}} \quad (25)$$

or

$$\left. \begin{aligned} R_{L_2(CrO_4)_3(K_2CrO_4/Na_2CrO_4)} &= r_{CrO_4(Na/K)}^{\frac{3}{5}} r_{(Na/K)} = \\ &= r_{CrO_4(Na_2CrO_4/K_2CrO_4)}^{\frac{3}{5}} r_{(Na/K)}^{\frac{3}{5}} \end{aligned} \right\} \quad (26)$$

also fully analogous to the corresponding equation (14).

The ratios of interaction and the salting out ratios are of course determinable from Equations (25)–(26) in just the same way as from Equations (13) and (14) in the case of heteroionic solvents. Equations (15)–(19) are therefore also valid for homoionic solvents, the only difference being that when heteroionic solvents are used R represents directly the solubility ratio while in the case of homoionic 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 homoionic solutes leads directly to a determination of the interaction of ions in the salt solutions employed as solvents.

7. Experiments Covering Solubilities in Homoionic 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 homoionic solvents. The saturating salts employed contained the follow-

ing complex ions: oxalo-tetrammine cobaltic (*Ox*): $[Co(NH_3)_4 C_2O_4]^+$, chloropentammine cobaltic (*[Cl]*): $[Co(NH_3)_5 Cl]^{++}$, bromo-pentammine cobaltic (*[Br]*) $[Co(NH_3)_5 Br]^{++}$, luteo cobaltic (*L*) $[Co(NH_3)_6]^{+++}$, oxalo dinitro diammine cobaltate ion (*On*) $[Co(NH_3)_2(NO_2)_2 C_2O_4]^-$, and the solvents were 0.1 molal solutions of KNO_3 , $NaNO_3$, KCl and $NaCl$. The temperature of the experiment was 0° and the same method was used as stated in the earlier communication. The result of the measurements are given in the following tables.

Table XIV. Solubility of Nitrates in KNO_3 - and $NaNO_3$ -Solutions at 0° .

Saturating Salt	0.1 KNO_3	0.1 $NaNO_3$	P_{KNO_3}/P_{NaNO_3}	<i>R</i>
<i>OxNO</i> ₃	0.000816	0.000777	1.051	1.025
<i>[Cl]</i> (NO_3) ₂ . . .	0.00397	0.00367	1.092	1.030
<i>L</i> (NO_3) ₃	0.00493	0.00450	1.131	1.031

Table XV. Solubility of Chlorides in KCl - and $NaCl$ -Solutions at 0° .

Saturating Salt	0.1 KCl	0.1 $NaCl$	P_{KCl}/P_{NaCl}	<i>R</i>
<i>OxCl</i>	0.00581	0.00570	1.020	1.010
<i>[Cl]</i> Cl_2	0.000610	0.000593	1.029	1.010
<i>[Br]</i> Cl_2	0.000220	0.000213	1.033	1.008

Table XVI. Solubility of *KOn* in KNO_3 and KCl -Solutions at 0° .

	0.1 KNO_3	0.1 KCl	P_{KNO_3}/P_{KCl}	<i>R</i>
<i>KOn</i>	0.00380	0.00351	1.086	1.042

Table XVII. Solubility of *NaOn* in $NaNO_3$ and $NaCl$ -Solutions at 0° .

	0.1 $NaNO_3$	0.1 $NaCl$	P_{NaNO_3}/P_{NaCl}	<i>R</i>
<i>NaOn</i>	0.00972	0.00928	1.051	1.025

R denotes — as explained p. 25 — 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 homoionic solvents also, R_I , R_{II} , and R_{III} corresponding to biionic, triionic and tetraionic solutes respectively.

1. Calculation of the ratio of interaction and the salting out ratio for 0.1 molal KNO_3 and $NaNO_3$ solutions. We have found (Table XIV)

$$R_I \dots = 1.025$$

$$R_{II} \dots = 1.030$$

$$R_{III} \dots = 1.031$$

Introducing these values in (18) and (19):

$$r_i = r_{NO_3(Na/K)} = \left(\frac{R_{II}}{R_I}\right)^6 = \left(\frac{R_{III}}{R_I}\right)^4$$

and

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

we obtain as the most fitting values of r_i and r_u

$$r_i = 1.028$$

$$r_u = 1.011$$

Again inserting these values in Equation (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 KNO_3 and $NaNO_3$ solutions.

	Found	Calcul.
$R_I \dots$	1.025	1.025
$R_{II} \dots$	1.030	1.030
$R_{III} \dots$	1.031	1.032

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

2. Calculation of the ratio of interaction and the salting out ratio for 0.1 molal solutions of *KCl* and *NaCl*. The calculation is carried out quite similarly. Introducing the most fitting values:

$$r_i = r_{Cl(Na/K)} = 1.000$$

$$r_u = r_{(Na/K)} = 1.010$$

we obtain the figures in Table XIX.

Table XIX. Comparison of *R*-values for *KCl* and *NaCl*-Solutions.

	Found	Calcul.
R_I	1.010	1.010
R_{II}	1.009	1.010

The figures for R_{II} , 1.009 is taken as the mean of the values 1.010 and 1.008 for $[Cl]Cl_2$ and $[Br]Cl_2$ respectively. On account of the higher solubility of $[Cl]Cl_2$ the corresponding R_{II} -value is certainly more accurate with this salt and considering this fact the agreement between *R*-values found and calculated becomes complete.

3. Significance of the above agreement. The above calculations led to two independent determinations of $r_u = r_{(Na/K)}$ at 0° namely:

$$r_{(Na/K)} = 1.011$$

$$r_{(Na/K)} = 1.010$$

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 nitrates solutions. We find thus through these measurements that the sodium ion has a salting out effect about 1.0 p. ct. larger than the potassium ion at 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 effect of 0.1 N solutions of *K*- and *Na*-ion towards non-electrolytes differ in several cases by about the same amount. However, as explained in the foregoing by using non-electrolytes as saturating substances we can not assume the $r_{(Na/K)}$ to be precisely determined.

For the ratio of interaction we found:

$$\begin{aligned} r_{NO_3(Na/K)} &= 1.028 \\ r_{Cl(Na/K)} &= 1.000 \end{aligned}$$

While the chlorine ion is acted upon equally by *K*- and *Na*-ions we see the nitrate ion to have an almost 3 p. ct. higher avidity for K^+ than for Na^+ .

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

$$r_{NO_3(NaNO_3/KNO_3)} = 1.028 \cdot 1.011 = 1.039$$

while for the chlorine ion correspondingly:

$$r_{Cl(NaCl/KCl)} = 1.000 \cdot 1.011 = 1.011.$$

The activity coefficient of the nitrate ion is thus about 4 p. ct. higher in a 0.1 N solution of $NaNO_3$ than in a KNO_3 -solution of the same concentration, while in the case of the chlorides the corresponding figure for the chlorine ion is about 1 p. ct.

8. Inter-Relation between Activity and Osmotic Coefficients and between Solubility and Freezing Point.

Already in the first paper quoted above an interdependency between solubility and freezing point was suspected based on the fact that solvents having a small freezing point lowering generally proved of high dissolving power towards slightly soluble salts and vice versa. A simple relation, however, could not be found, because the ratio of dissolving power of two solvents vary with the nature of the saturating salt. This question 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 relation¹

$$\sum c_1 d \ln \xi_1 = d\eta \quad (27)$$

where c_1 and ξ_1 stand for the concentration and the activity of the first ion, η for the osmotic concentration, and $\sum c_1 = c$ is the total ion concentration, forms a basis for such treatment.

Introducing in this equation $\xi_1 = c_1 f_1$ and $\eta = c\varphi$ and assuming c to be constant we obtain

$$\sum c_1 d \ln c_1 + \sum c_1 d \ln f_1 = cd\varphi \quad (28)$$

or

$$\sum c_1 d \ln f_1 = cd\varphi \quad (29)$$

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

$$c_{NaCl} = \frac{c}{2}x,$$

¹ Brønsted. Journ. Amer. Chem. Soc. **42**, (761) 1920.

$$c_{KCl} = \frac{c}{2} (1-x),$$

$$c_{Cl} = \frac{c}{2}$$

and thus

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

by which the activity coefficient of the ions in the mixed solutions are thermodynamically correlated to the osmotic coefficient.

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 *KCl* to a *NaCl*-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

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

and

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

or in integrated form

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

or by means of (5)

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

These equations can also be written:

$$\left. \begin{aligned} \varphi_{NaCl} - \varphi_{KCl} &= \ln [r_{Cl(Na/K)}^{\frac{1}{2}} r_{(Na/K)}] = \\ &= \frac{1}{2} \ln [r_{Cl(NaCl/KCl)} r_{(Na/K)}] \end{aligned} \right\} \quad (35)$$

In the more general case of the two salts $Al_2(SO_4)_3$ and $Fe_2(SO_4)_3$ we obtain by quite similar calculations:

$$2d\ln f_u + 3d\ln f_{SO_4} = 5d\varphi \quad (36)$$

$$\text{or } \varphi_{Al_2(SO_4)_3} - \varphi_{Fe_2(SO_4)_3} = \frac{3}{5} \ln \frac{f_{SO_4(Al_2(SO_4)_3)}}{f_{SO_4(Fe_2(SO_4)_3)}} + \frac{2}{5} \ln \frac{f_{(Al)}}{f_{(Fe)}} \quad (37)$$

$$\text{and } \varphi_{Al_2(SO_4)_3} - \varphi_{Fe_2(SO_4)_3} = \frac{3}{5} \ln \frac{f_{SO_4(Al)}}{f_{SO_4(Fe)}} + \ln \frac{f_{(Al)}}{f_{(Fe)}} \quad (38)$$

yielding for instance for $MgCl_2$ and $CaCl_2$:

$$\left. \begin{aligned} \varphi_{MgCl_2} - \varphi_{CaCl_2} &= \frac{2}{3} \ln \frac{f_{Cl(MgCl_2)}}{f_{Cl(CaCl_2)}} + \frac{1}{3} \ln \frac{f_{(Mg)}}{f_{(Cl)}} = \\ &= \frac{2}{3} \ln \frac{f_{Cl(Mg)}}{f_{Cl(Ca)}} + \ln \frac{f_{(Mg)}}{f_{(Ca)}} \end{aligned} \right\} (39)$$

and for K_2SO_4 and Na_2SO_4

$$\left. \begin{aligned} \varphi_{Na_2SO_4} - \varphi_{K_2SO_4} &= \frac{1}{3} \ln \frac{f_{SO_4(Na_2SO_4)}}{f_{SO_4(K_2SO_4)}} + \frac{2}{3} \ln \frac{f_{(Na)}}{f_{(K)}} = \\ &= \frac{1}{3} \ln \frac{f_{SO_4(Na)}}{f_{SO_4(K)}} + \ln \frac{f_{(Na)}}{f_{(K)}} \end{aligned} \right\} (40)$$

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

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

which by comparison with (34) gives:

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

The corresponding relation for the more general case of $L_2(SO_4)_3$ dissolved in $Al_2(SO_4)_3$ and $Fe_2(SO_4)_3$ solutions is

$$\varphi_{Al_2(SO_4)_3} - \varphi_{Fe_2(SO_4)_3} = \frac{1}{5} \ln \frac{P_{L_2(SO_4)_3, Fe_2(SO_4)_3}}{P_{L_2(SO_4)_3, Al_2(SO_4)_3}} \quad (43)$$

The difference in osmotic coefficients, and therefore in freezing points, of two solutions with a common ion, is

thus computable from the solubility ratio of sparingly soluble salts 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 heteroionic solvents are utilizable for the same purpose. According to Equation (8) and (44)

$$\ln \frac{s_{AgCl(KNO_3)}}{s_{AgCl(NaNO_3)}} = \frac{1}{2} \ln \frac{f_{Cl(Na)}}{f_{Cl(K)}} + \ln \frac{f_{(Na)}}{f_{(K)}} \quad (44)$$

and

$$\ln \frac{s_{L_2(CrO_4)_3(Fe_2(SO_4)_3)}}{s_{L_2(CrO_4)_3(Al_2(SO_4)_3)}} = \frac{3}{5} \ln \frac{f_{CrO_4(Al)}}{f_{CrO_4(Fe)}} + \ln \frac{f_{(Al)}}{f_{(Fe)}} \quad (45)$$

and thus

$$\ln \frac{s_{AgCl(KNO_3)}}{s_{AgCl(NaNO_3)}} = \varphi_{NaCl} - \varphi_{KCl} \quad (46)$$

and

$$\ln \frac{s_{L_2(CrO_4)_3(Fe_2(SO_4)_3)}}{s_{L_2(CrO_4)_3(Al_2(SO_4)_3)}} = \varphi_{Al_2(CrO_4)_3} - \varphi_{Fe_2(CrO_4)_3} \quad (47)$$

Equation (42) can be tested by means of the solubility data from Tables (14)—(17) 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	$A_1 - A_2$	$\varphi_1 - \varphi_2$	P_2/P_1	$\frac{1}{2} \ln P_2/P_1$
$NaNO_3$	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:

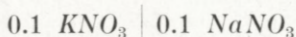
$$\varphi_1 - \varphi_2 = \frac{1}{2} \ln \frac{P_2}{P_1}.$$

The figures in the 2nd and 4th column show this relation to be fulfilled very exactly and thus lends strong support to the theory on which these calculations are based.

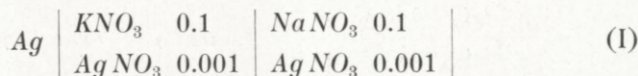
9. Determination of the Liquid-Junction Potential on the Basis of our Principles.

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

If we want to determine the potential at the liquid junction:



we add a little AgNO_3 and measure the cell:



the electromotive force of which is given by:

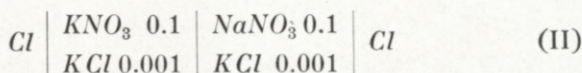
$$\pi_1 = RT \ln \frac{f_{\text{Ag}(\text{NaNO}_3)}}{f_{\text{Ag}(\text{KNO}_3)}} + \pi_d \quad (48)$$

or according to our principles:

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

Since $r_{(\text{Na/K})}$, as shown, is determinable 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

$$\pi_2 = RT \ln \frac{f_{Cl(KNO_3)}}{f_{Cl(NaNO_3)}} + \pi_d$$

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

equally usable for estimation of π_d

Combining (49) and (50) we obtain

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

or by introduction of (11):

$$\frac{\pi_1 - \pi_2}{2} = RT \ln \frac{s_{AgCl(KNO_3)}}{s_{AgCl(NaNO_3)}} \quad (52)$$

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 is computable 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 $r_{(Na/K)}$ the value 1.010 has been found above the liquid function potential in a cell like (I) containing potassium and sodium associated with the same anion is given by

$$\pi_d = \pi_1 - 0.00025 \text{ volt}$$

at 20°. The two π are here reckoned in the direction from K^+ to Na^+ -solution.

Summary.

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

Den polytekniske Lærestalts fysisk-kemiske Laboratorium.

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