

5. The overvoltage at a mercury meniscus in dil. sulfuric acid was found to *increase* as the large bubble at the top of the meniscus becomes larger, and to *decrease* suddenly when the bubble escapes.

CHICAGO, ILLINOIS

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[CONTRIBUTION FROM THE PHYSICO-CHEMICAL LABORATORY OF THE POLYTECHNICAL INSTITUTE OF COPENHAGEN]

## THE INDIVIDUAL THERMODYNAMIC PROPERTIES OF IONS

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RECEIVED SEPTEMBER 8, 1923

### The Principle of the Specific Interaction of Ions

The available information regarding the thermodynamic properties of salt solutions, as manifested through electrometric and freezing-point measurements and particularly through the measurement of the solubilities of sparingly soluble salts in salt solutions, leaves no doubt that these properties even at high dilution are largely dependent upon the nature of the solution considered. It is not a question here of the typical deviations depending upon the valence type of the various solutes, but of deviations shown by isotypic ions in dependency of their individual nature. In spite of the fact that these peculiarities have, at first sight, a rather random character, a closer examination has shown that an important simplicity prevails, which has been formulated by the writer as the *principle of the specific interaction of ions*.

The basis and the applicability of this principle have been elaborately presented in a previous article,<sup>1</sup> where emphasis was laid upon the possibility of splitting the activity coefficient into two factors, a coefficient of interaction and a salting-out coefficient, the latter of which should be a function of the solvent only. This deviation is valuable in cases where the possibility exists of determining separately the ratio of the two factors such as was shown in the previous article when salts of different valence type are used for saturating salts in solubility measurements. The calculation of these ratios requires a high degree of accuracy in the experimental determinations and but very slight deviations from the underlying principles because the equations for the calculations have such a form as to be highly sensitive towards such deviations.

The contents of the principles in question may, however, be expressed more simply without the above-mentioned division of the activity coefficient into its two factors. Let  $A_1B$  and  $A_2B$  represent two solvent salts with an anion (B) in common, and having the same equivalent concentration. Let X be an arbitrary cation and Y an arbitrary anion, present

<sup>1</sup> Brönsted, THIS JOURNAL, 44, 877 (1922).

in small amount in the two solvents. Then our principle can be stated by the following expressions.

$$\frac{f_X(A_1B)}{f_X(A_2B)} = F(A_1, A_2) \quad (1)$$

and

$$\frac{f_Y(A_1B)}{f_Y(A_2B)} = F(A_1, A_2, Y) \quad (2)$$

where  $F$  represents some indeterminate function. That is to say, the ratio of the activity coefficients of the same cation in two equally strong solutions having an anion in common is a function only of the nature of the two cations of the solvents. And the ratio of the activity coefficients of the same anion in two equally strong solutions having an anion in common is a function of the nature of the anion considered and the cations of the two solvents. In neither case does the nature of the common anion of the solvents enter.

It need hardly be added that the validity of the equations will remain unaffected if throughout the above statement the terms cations and anions be interchanged.

The meaning of this law appears clear by considering the accompanying diagram (Fig. 1). The ordinates indicate  $\ln f$ , that is, the logarithms of the activity coefficient of various cations and anions of the same type. From the two vertical lines indicated by  $\text{NaNO}_3$  ( $A_1B$ ) and  $\text{KNO}_3$  ( $A_2B$ ) the values of  $\ln f$  in the corresponding solution are read, reckoned from arbitrary standard values. The  $\ln f$  values for any particular ion in the two solvents are given by the intersections of the corresponding straight lines with the two axes. In accordance with Equation 1 the lines belonging to cations are all parallel, while in the case of anions, according to Equation 2 the slopes may be different. The shape of the curve remains unchanged when the anion of the solvent changes as, for example, in changing from potassium and sodium nitrate to potassium and sodium chloride solutions.

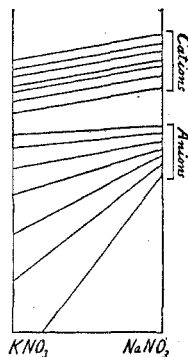


Fig. 1

In the verification of the principle of specific interaction, given in the previous paper the ion  $X$  in Equation 1 was changed not only in nature, its type being kept constant, but also in its general valence type. In fact, the assumption of the validity of Equation 1 under these conditions was the basis of the calculation of the ratios of interaction and salting-out effects. No experiments, however, have hitherto been available to show the applicability of Equation 1 to cases of different valence of the ions  $A_1$  and  $A_2$ . In the last part of the present paper evidence will be furnished which will show that Equation 1 is valid also for different valence of  $A_1$  and  $A_2$ , at least when  $X$  has a constant valence, and probably also when the valence of  $X$  changes.

Equations 1 and 2 and Fig. 1 furnish in reality a concise and adequate statement of what on the basis of the principle of specific interaction can be said regarding the influence of the natures of ions upon their thermodynamic properties.

It may be added that the change in the activity coefficients of a salt passing from  $A_1B$  to  $A_2B$  is given simultaneously when we remember that

$$\nu \ln f = \sum \nu' \ln f' \quad (3)$$

where  $f$  is the activity coefficient of the salt,  $f'f'' \dots$  the activity coefficient of the ions of the salt,  $\nu' \nu'' \dots$  the corresponding numbers of ions in one molecule and  $\nu = \sum \nu'$ .

### The Linear Variation of the Activity Coefficients

The principle of the specific interaction of ions was based on the idea that ions of the same valence must be influenced uniformly by ions of their own sign. The individualities in salt solutions, therefore, ought to be attributed to the interaction of ions of opposite sign, varying with the nature of these ions, and to a more general effect upon all ions present, namely the salting-out effect or solvent effect, depending merely on the salt solutions serving as solvents. A continued study of the fundamental considerations of this principle has shown, however, that several of the results obtained for its corroboration can also be obtained by use of another simple principle, which we shall introduce in the theory of the dilute salt solutions as the principle of the *linear variation of the activity peculiarities*. This principle may be stated as follows. *In a dilute salt solution the osmotic deviations of the solutions and the activity deviations of any ion from an ideal value is, at constant composition of the dissolved salt mixture, a linear function of its total concentration and, at constant total concentration of an isotopic mixture, a linear function of its composition.*

In this statement the expression "activity deviations" from an ideal value is understood to mean  $\ln(f/f_i)$ , where  $f$  is the activity coefficient of the ion considered and  $f_i$  the ideal activity coefficient depending only upon the type of salt and the total concentration.

The first part of the above assumption, namely that at constant composition the osmotic and activity deviations are linear functions of the concentration, has already been advanced previously<sup>2</sup> for the case of pure salt solutions of univalent salts. The equation

$$1 - \varphi = \alpha \sqrt{c} + \beta c \quad (4)$$

was suggested to hold for solutions up to about 0.1  $N$  concentration. In this equation  $\alpha$  is a universal constant the value of which at  $0^\circ$  is about 0.32 and varies but little with the temperature, while  $\beta$  accounts for the individualities. The ideal value of the activity coefficient is

$$\ln f = -3\alpha \sqrt{c} \quad (5)$$

<sup>2</sup> Brönsted, THIS JOURNAL, 44, 938 (1922).

This part of the principle is, therefore, only an extension of the applicability of Equation 4 to valence types other than the uni-univalent, in which case it has already been verified. It remains to be shown that several of the results obtained previously on the basis of the principle of the specific interaction can be derived from the second part of the new principle.

For this purpose we shall introduce the thermodynamic equation<sup>3</sup>

$$x \, d \ln f_{\text{Na}} + (1-x) \, d \ln f_{\text{K}} + d \ln f_{\text{Cl}} = 2d\varphi \quad (6)$$

as applied to a mixture of sodium and potassium chloride solutions of constant total concentration. By introducing our assumption of a linear variation of the deviation coefficients with  $x$

$$\frac{d \ln f_{\text{Na}}}{dx} = a, \quad \frac{d \ln f_{\text{K}}}{dx} = b, \quad \frac{d \ln f_{\text{Cl}}}{dx} = c, \quad \frac{d\varphi}{dx} = d,$$

where  $a$ ,  $b$ ,  $c$  and  $d$  are constants, we obtain from Equation 6 when  $x = 0$ , the expression,  $b = 2d - c$ ; and when  $x = 1$ ,  $a = 2d - c$  and therefore for all values of  $x$

$$\frac{d \ln f_{\text{Na}}}{dx} = \frac{d \ln f_{\text{K}}}{dx} \quad (7)$$

in full conformity with Equation 1 and Fig. 1. By the same method as used in the previous paper<sup>3</sup> we then derive

$$\left. \begin{aligned} \varphi_{\text{NaCl}} - \varphi_{\text{KCl}} &= \ln \frac{f_{\text{NaCl(NaCl)}}}{f_{\text{NaCl(KCl)}}} \\ \varphi_{\text{NaCl}} - \varphi_{\text{KCl}} &= \ln \frac{f_{\text{KCl(NaCl)}}}{f_{\text{KCl(KCl)}}} \end{aligned} \right\} \quad (8)$$

and therefore:

$$\varphi_{\text{NaCl}} - \varphi_{\text{KCl}} = \ln \frac{f_{\text{HCl(NaCl)}}}{f_{\text{HCl(KCl)}}} \quad (9)$$

$$\varphi_{\text{NaCl}} - \varphi_{\text{KCl}} = \frac{1}{2} \ln \frac{S_{\text{AgCl(KCl)}}}{S_{\text{AgCl(NaCl)}}} \quad (10)$$

These equations, by means of which freezing points of the solvents with an ion in common are correlated to activity coefficient and solubilities of salts possessing the same common ion, are identical with the equations derived on the basis of the principle of the specific interaction of ions. Also, the solubility equation of salts in hetero-ionic solvents, namely,

$$\frac{S_{\text{AgCl(KNO}_3)}}{S_{\text{AgCl(NaNO}_3)}} = \frac{S_{\text{TiCl(KNO}_3)}}{S_{\text{TiCl(NaNO}_3)}} \quad (11)$$

is easily arrived at by using Equations 8 and 9. So far, the principle of linear variation and the principle of the specific interaction are quite equivalent. The equation<sup>4</sup>

$$\frac{S_{\text{AgCl(KNO}_3)}}{S_{\text{AgCl(NaNO}_3)}} = \frac{S_{\text{AgCl(KClO}_3)}}{S_{\text{AgCl(NaClO}_3)}} \quad (12)$$

and the more general.

$$\frac{f_{\text{HCl(NaNO}_3)}}{f_{\text{HCl(KNO}_3)}} = \frac{f_{\text{HCl(NaClO}_3)}}{f_{\text{HCl(KClO}_3)}} \quad (13)$$

<sup>3</sup> Ref. 1, p. 895. The notation used in that article will be followed here.

<sup>4</sup> Ref. 1, p. 883.

are, however, not derivable from the principle of the linear variation of the activity peculiarities. For their derivation is required the validity of the principle of the specific interaction, as given by

$$\left. \begin{aligned} \frac{f_{\text{Cl}(\text{NaCl})}}{f_{\text{Cl}(\text{KCl})}} &= \frac{f_{\text{Cl}(\text{NaNO}_3)}}{f_{\text{Cl}(\text{KNO}_3)}} = \frac{f_{\text{Cl}(\text{NaClO}_3)}}{f_{\text{Cl}(\text{KClO}_3)}} = \dots\dots\dots \\ \frac{f_{\text{K}(\text{KCl})}}{f_{\text{K}(\text{KNO}_3)}} &= \frac{f_{\text{K}(\text{NaCl})}}{f_{\text{K}(\text{NaNO}_3)}} = \frac{f_{\text{K}(\text{HCl})}}{f_{\text{K}(\text{HNO}_3)}} = \dots\dots\dots \end{aligned} \right\} \quad (14)$$

Since in the previous paper Equations 5-10 have already been verified, we must assume that the fundamental considerations underlying them, as given by the two principles and Equation 1, are correct.

Equation 8 combined with Equation 15,

$$\varphi_{\text{NaCl}} - \varphi_{\text{KCl}} = \frac{1}{2} \ln \frac{f_{\text{NaCl}(\text{NaCl})}}{f_{\text{KCl}(\text{KCl})}} \quad (15)$$

which is identical with Equation 24 in the previous paper, yields an important correlation between the activity coefficients of two salts with a common ion, namely

$$f_{\text{NaCl}(\text{NaCl})} f_{\text{KCl}(\text{KCl})} = f_{\text{NaCl}(\text{KCl})}^2 = f_{\text{KCl}(\text{NaCl})}^2 \quad (16)$$

and

$$f_{\text{NaCl}(\text{KCl})} = f_{\text{KCl}(\text{NaCl})} \quad (17)$$

The activity coefficient of sodium chloride, present in a small amount in a solution of potassium chloride is then seen to be identical with the activity coefficient of potassium chloride present in a small amount in a solution of sodium chloride of the same strength, this value being the geometrical mean of the activity coefficients of the two salts in their own solutions. The meaning of this is clearly illustrated by the accompanying diagram, Fig. 2, where the abscissa indicates the composition  $x$  of the mixture, and the ordinate  $\varphi$  and  $\ln f$ , and where, for instance, Salt 1 = NaCl, Salt 2 = KCl and Salt 3 = HCl. The four lines  $\varphi$ ,  $\ln f$ ,  $\ln f_2$  and  $\ln f_3$  are drawn parallel, and  $\ln f_{1(2)} = \ln f_{2(1)}$ .

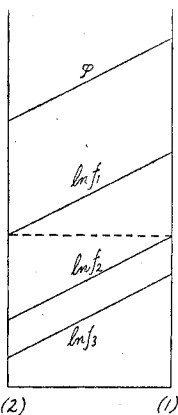


Fig. 2

This result is reached by means of the principle of the linear variation only. This principle also leads to corresponding equations for mixtures of salts with no ion in common.

For this purpose we first use Equation 15

$$\varphi_{\text{NaCl}} - \varphi_{\text{KCl}} = \frac{1}{2} \ln \frac{f_{\text{NaCl}(\text{NaCl})}}{f_{\text{KCl}(\text{KCl})}}, \quad \varphi_{\text{KCl}} - \varphi_{\text{KNO}_3} = \frac{1}{2} \ln \frac{f_{\text{KCl}(\text{KCl})}}{f_{\text{KNO}_3(\text{KNO}_3)}}$$

and thus

$$\varphi_{\text{NaCl}} - \varphi_{\text{KNO}_3} = \frac{1}{2} \ln \frac{f_{\text{NaCl}(\text{NaCl})}}{f_{\text{KNO}_3(\text{KNO}_3)}} \quad (18)$$

Moreover, from Equation 8,

$$\varphi_{\text{NaCl}} - \varphi_{\text{KCl}} = \ln \frac{f_{\text{XCl}(\text{NaCl})}}{f_{\text{XCl}(\text{KCl})}}, \quad \varphi_{\text{KCl}} - \varphi_{\text{KNO}_3} = \ln \frac{f_{\text{KY}(\text{KCl})}}{f_{\text{KY}(\text{KNO}_3)}}$$

where X is an arbitrary cation and Y an arbitrary anion, we obtain

$$\varphi_{\text{NaCl}} - \varphi_{\text{KNO}_3} = \ln \frac{f_{\text{XCl}(\text{NaCl})} f_{\text{KY}(\text{KCl})}}{f_{\text{XCl}(\text{KCl})} f_{\text{KY}(\text{KNO}_3)}} \quad (19)$$

Putting X = K and Y = Cl, this equation is reduced to

$$\varphi_{\text{NaCl}} - \varphi_{\text{KNO}_3} = \ln \frac{f_{\text{KCl}(\text{NaCl})}}{f_{\text{KCl}(\text{KNO}_3)}} \quad (20)$$

and for the reason of symmetry we also are allowed to write:

$$\varphi_{\text{NaCl}} - \varphi_{\text{KNO}_3} = \ln \frac{f_{\text{NaNO}_3(\text{NaCl})}}{f_{\text{NaNO}_3(\text{KNO}_3)}} \quad (21)$$

By combining (18), (20) and (21) we obtain

$$\frac{f_{\text{NaCl}(\text{NaCl})}}{f_{\text{KNO}_3(\text{KNO}_3)}} = \frac{f_{\text{KCl}(\text{NaCl})}}{f_{\text{KCl}(\text{KNO}_3)}} = \frac{f_{\text{NaNO}_3(\text{NaCl})}}{f_{\text{NaNO}_3(\text{KNO}_3)}} \quad (22)$$

or

$$\frac{f_{\text{Na}(\text{NaCl})} f_{\text{Cl}(\text{NaCl})}}{f_{\text{K}(\text{KNO}_3)} f_{\text{NO}_3(\text{KNO}_3)}} = \frac{f_{\text{K}(\text{NaCl})} f_{\text{Cl}(\text{NaCl})} f_{\text{Na}(\text{NaCl})} f_{\text{NO}_3(\text{NaCl})}}{f_{\text{K}(\text{KNO}_3)} f_{\text{Cl}(\text{KNO}_3)} f_{\text{Na}(\text{KNO}_3)} f_{\text{NO}_3(\text{KNO}_3)}}$$

or

$$f_{\text{KNO}_3(\text{NaCl})} = f_{\text{NaCl}(\text{KNO}_3)} \quad (23)$$

corresponding to Equation 17 for salts with a common ion.

### Some Recent Work on Activity Coefficients

The question of the activity coefficients of salts has been discussed in a recent paper by Harned and Brumbaugh.<sup>5</sup> To represent the concentration effect they use the equation

$$\ln f = A_c - Bc^m \quad (24)$$

of a form similar to that proposed by the writer,<sup>2</sup> namely,

$$\ln f = a\sqrt{c} + bc \quad (25)$$

The two equations are, however, entirely different in that in (25)  $a$  is a universal constant, the peculiarities of the various salts being accounted for solely by the coefficient  $b$ , while in (24)  $A$ ,  $B$ , and  $m$  are allowed to vary from one salt to another. As pointed out previously, an equation such as (24) does not fulfil the requirement, necessary from a theoretical point of view, of a uniform convergence of the values of  $\ln f$  for all salts, when the concentration approaches zero.

Equation 24, therefore, is to be looked upon as an empirically established expression by means of which, on account of the relatively great number of constants that may be varied independently, a rather close approximation to experimental results may be reached. The actual numerical values inserted for the constants in the equation exclude, however, its application at great dilution. Even if such an expression may be found to be helpful in some cases, it seems of more immediate importance to establish a theoretically corroborated formula for dilute solutions where

<sup>5</sup> Harned and Brumbaugh, THIS JOURNAL, 44, 2729 (1922).

the factors influencing the activity are still moderate in number. Equation 25 has no pretention of applicability at such high concentration, its limit being at about 0.1 *N* concentration for uni-univalent salts, and is not objectionable, therefore, that the minima for activity coefficients at high concentration cannot be computed with its help.<sup>6</sup>

In the important question of the change of the activity coefficients in salt solutions of constant total concentration the ideas advanced by Harned are obviously in no agreement with the theory developed in this and previous articles on this subject by the writer.

It should be of some general interest to subject these ideas to a detailed discussion in order to make clear the thermodynamic or experimental requirements to be observed in developments of this kind.

In a series of solutions of the same concentration containing salts with a common ion, the activity coefficient of that ion is assumed by Harned to be constant. Accordingly, in 0.1 *N* solutions of sodium, potassium, hydrogen chloride, . . . and in mixtures of such chlorides the chlorine ion should possess the same activity coefficient. As replacement of potassium ion by hydrogen ion or another cation is assumed to exert no influence on the chloride ion, it is obvious on this basis that a partial replacement of the chloride ion by a nitrate ion would also have no influence, because we must assume that the greatest effect exists between ions of different sign. According to this point of view acceptance of the principle of Harned, namely, "the principle of the independent activity coefficients," would result in the assumption that all activity coefficients, at constant total concentration, depend only upon their own nature and not upon the nature of the solution containing them. This, indeed, was the conclusion drawn by Lewis and Randall.<sup>7</sup> For thermodynamic reasons this conclusion, however, can be true only at ideal dilution, and in this region is included in the much simpler law that all activity coefficients are equal.

We now learn from the latest article by Harned and Brumbaugh that the Harned principle is to be interpreted somewhat differently. In equally strong solutions of sodium, potassium, hydrogen chlorides . . . and in their mixtures the chlorine ion is assumed to possess the same activity, but in their mixtures the activity coefficients of the constituent cations are assumed to vary. Furthermore, the activity coefficients of other cations introduced in small amounts are also assumed to vary from one solution to another. This assumption of Harned, although thermodynamically possible, is in peculiar contrast to the principle of the specific interaction of ions. For the theoretical reasons already stated, it is highly improbable, and furthermore it does not agree with experimental facts.

<sup>6</sup> Ref. 5. The minima found by Harned and Brumbaugh and by M. Chow [THIS JOURNAL, 42, 488 (1920)] in mixtures of potassium chloride and hydrochloric acid at low acid concentrations can hardly be looked upon as sufficiently established.

<sup>7</sup> Lewis and Randall, *ibid.*, 43, 1137 (1921).

Let us take, for example, solutions of sodium and potassium chlorides of equal concentration. Thallous chloride shows different solubility in these two solutions. This is possible with constant chlorine-ion activity if the thallous ion is affected differently by the sodium and the potassium ions. But if this influence is the only reason for the difference in solubility, such as the Harned theory assumes, then the same solubility ratio should be shown by *all* sparingly soluble thallous salt when using the corresponding sodium and potassium salt solutions as solvents. That is to say, we should expect

$$\frac{S_{TlCl}(KCl)}{S_{TlCl}(NaCl)} = \frac{S_{TlX}(KX)}{S_{TlX}(NaX)} = \frac{S_{TlY}(KY)}{S_{TlY}(NaY)} = \dots\dots\dots (26)$$

where X, Y... represent various anions. This equation, however, is clearly erroneous.

This is indicated, for instance, by the fact that oxalotetrammine-cobaltic chloride and nitrate give the following values for 0.1 *N* solution of the solvents.

$$\frac{S_{OxCl}(KCl)}{S_{OxCl}(NaCl)} = 1.020 \qquad \frac{S_{OxNO_3}(KNO_3)}{S_{OxNO_3}(NaNO_3)} = 1.051$$

and chloropentammine-cobaltic chloride and nitrate,

$$\frac{S_{P_{Cl_2}}(KCl)}{S_{P_{Cl_2}}(NaCl)} = 1.029 \qquad \frac{S_{P(NO_3)_2}(KNO_3)}{S_{P(NO_3)_2}(NaNO_3)} = 1.092$$

These values differ widely. Similar results have been found in this Laboratory in a number of cases. The principle in question is thus clearly seen to be inconsistent with experimental facts.

Moreover, if the change of the activity coefficient of a cation, when passing from a NaX solution into a KX solution of the same strength, should be independent of the nature of X while the activity of X keeps its activity coefficient unchanged, then, as can be easily shown thermodynamically, the difference in osmotic coefficients, and therefore in freezing points, of the NaX and KX solutions should be the same independently of X; or, generally, the difference in freezing points of two salt solutions with a common ion should be independent of the nature of that common ion. This result, too, is in conflict with experimental facts. For 0.1 *N* solutions, for instance, we have the following markedly varying differences in the molar freezing-point lowerings,  $\Delta_1 - \Delta_2$ .

| Salt <sub>1</sub> | Salt <sub>2</sub> | $\Delta_1 - \Delta_2$ | Difference |
|-------------------|-------------------|-----------------------|------------|
| NaNO <sub>3</sub> | KNO <sub>3</sub>  | 0.090                 | } 0.063    |
| NaCl              | KCl               | .027                  |            |
| KCl               | KNO <sub>3</sub>  | .148                  | } .063     |
| NaCl              | NaNO <sub>3</sub> | .085                  |            |

It would be of no assistance to make the high concentrations in the above examples responsible for the failure of the principle, because this carries meaning only if the deviations from it are small, *compared with the*



deviations from the ideal values generally exhibited by the ions. Decrease in concentration would, therefore, mean no improvement in applicability.

The principle of independent activity coefficients, whether taken in the sense of Lewis and Randall,<sup>7</sup> or as the modification proposed by Harned and Brumbaugh, is thus clearly seen to fail in accounting for the individual properties of salt solutions. It can be stated as a general and obvious conclusion that the thermodynamic and experimental evidence which has been found to be strongly confirmatory of the principle of the specific interaction of ions at the same time excludes the possibility of describing the phenomena in question by means of any theory in which "independent" activity coefficients are involved, since it is the most marked feature of this principle that the activity coefficient of an ion is, to a similar extent, a function of the nature of the ion itself and of the nature of the solution containing it.<sup>8</sup>

### Experimental Part. Solubility of Cobalt Ammonia Salts in Sodium Sulfate and Sodium Chloride Solutions<sup>9</sup>

Only uni-univalent salts were used for solvents in the earlier experimental verification of the principle of the specific interaction. As it would be of interest to try to broaden the experimental basis of the principle, experiments were performed in which solutions of sodium sulfate and chloride were used as solvents. The dissolving powers of these two solvents differ by a greater amount than in the case of two uni-univalent salt solutions and a more rigid verification is, therefore, possible with them.

As saturating substances the following three uni-univalent cobalt salts were employed: (1) oxalotetramminecobaltic-tetrathiocyanato-diammine chromiate,  $[\text{Co}(\text{NH}_3)_4\text{Ox}][\text{Cr}(\text{NH}_3)_2(\text{CNS})_4] = \text{OxR}$ ; (2) oxalotetramminecobaltic-oxalodinitrodiammine cobaltiate,  $[\text{Co}(\text{NH}_3)_4\text{Ox}][\text{Co}(\text{NH}_3)_2(\text{NO}_2)_2\text{Ox}] = \text{OxN}$ ; (3) nitrothiocyanato-tetramminecobaltic-oxalodinitrodiammine cobaltiate,  $[\text{Co}(\text{NH}_3)_4(\text{CNS})(\text{NO}_2)][\text{Co}(\text{NH}_3)_2(\text{NO}_2)_2\text{Ox}] = \text{RnN}$ ; of these 1 and 2 have a cation, and 2 and 3 an anion in common. Furthermore, two oxalotetrammine cobaltic salts with a bivalent anion were employed, namely, (4) oxalotetramminecobaltic persulfate,  $[\text{Co}(\text{NH}_3)_4\text{Ox}]_2\text{S}_2\text{O}_8 = \text{Ox}_2\text{S}_2\text{O}_8$ , and (5) oxalotetramminecobaltic dithionate,  $[\text{Co}(\text{NH}_3)_4\text{Ox}]_2\text{S}_2\text{O}_6 = \text{Ox}_2\text{S}_2\text{O}_6$ . All of these compounds are well-crystallizing salts, rather stable in solution and very slightly soluble in water. The solubility data for pure water as solvent at 20° are (1) OxR, 0.00139 *M*; (2) OxN, 0.000670 *M*; (3) RnN, 0.000449 *M*; (4) Ox<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, 0.000755 *M*; (5) Ox<sub>2</sub>S<sub>2</sub>O<sub>6</sub>, 0.000201 *M*.

Table I gives the solubilities in the salt solutions, *c* being the equivalent

<sup>8</sup> Ref. 1, p. 878.

<sup>9</sup> Experiments by Kirsten Volqvartz.

concentration of the solvent solutions and  $s$  the molar solubility, using for each salt its solubility in pure water as unity.

TABLE I  
SOLUBILITY OF O<sub>x</sub>R, O<sub>x</sub>N AND R<sub>n</sub>N IN Na<sub>2</sub>SO<sub>4</sub> AND NaCl SOLUTIONS AT 20°

|                  | $c$   | $s_{\text{Na}_2\text{SO}_4}$ | $s_{\text{NaCl}}$ | $\frac{s_{\text{Na}_2\text{SO}_4}}{s_{\text{NaCl}}}$ |
|------------------|-------|------------------------------|-------------------|--|
| O <sub>x</sub> R | 0.005 | 1.086                        | 1.040             | 1.040  |
|                  | .01   | 1.143                        | 1.071             | 1.068  |
|                  | .02   | 1.228                        | 1.118             | 1.099  |
|                  | .05   | 1.369                        | 1.183             | 1.157  |
|                  | .1    | 1.527                        | 1.260             | 1.212  |
| O <sub>x</sub> N | .005  | 1.107                        | 1.065             | 1.039  |
|                  | .01   | 1.176                        | 1.103             | 1.067  |
|                  | .02   | 1.268                        | 1.153             | 1.099  |
|                  | .05   | 1.459                        | 1.266             | 1.153  |
|                  | .1    | 1.688                        | 1.403             | 1.202  |
| R <sub>n</sub> N | .005  | 1.071                        | 1.060             | 1.010  |
|                  | .01   | 1.111                        | 1.090             | 1.016  |
|                  | .02   | 1.144                        | 1.125             | 1.018  |
|                  | .05   | 1.230                        | 1.203             | 1.022  |
|                  | .1    | 1.307                        | 1.272             | 1.028  |

A glance at the solubility ratios  $\left(R_I = \frac{s_{\text{Na}_2\text{SO}_4}}{s_{\text{NaCl}}}\right)$  in the last columns of this table shows that there is very close agreement between the values for the two salts with a common cation and a very striking deviation between the values for the two salts with a common anion. This is also shown by the accompanying graph, Fig. 3, in which the solubility ratios are plotted against the concentrations of the solvents.

These facts, however, are in full conformity with the principle of the specific interaction, as seen from the following thermodynamic equations,

$$R^2_{\text{OxR}} = \left[ \frac{s_{\text{OxR}}(\text{Na}_2\text{SO}_4)}{s_{\text{OxR}}(\text{NaCl})} \right]^2 = \frac{f_{\text{Ox}}(\text{NaCl}) f_{\text{R}}(\text{NaCl})}{f_{\text{Ox}}(\text{Na}_2\text{SO}_4) f_{\text{R}}(\text{Na}_2\text{SO}_4)} \quad (27)$$

$$R^2_{\text{OxN}} = \left[ \frac{s_{\text{OxN}}(\text{Na}_2\text{SO}_4)}{s_{\text{OxN}}(\text{NaCl})} \right]^2 = \frac{f_{\text{Ox}}(\text{NaCl}) f_{\text{N}}(\text{NaCl})}{f_{\text{Ox}}(\text{Na}_2\text{SO}_4) f_{\text{N}}(\text{Na}_2\text{SO}_4)} \quad (28)$$

$$R^2_{\text{RnN}} = \left[ \frac{s_{\text{RnN}}(\text{Na}_2\text{SO}_4)}{s_{\text{RnN}}(\text{NaCl})} \right]^2 = \frac{f_{\text{Rn}}(\text{NaCl}) f_{\text{N}}(\text{NaCl})}{f_{\text{Rn}}(\text{Na}_2\text{SO}_4) f_{\text{N}}(\text{Na}_2\text{SO}_4)} \quad (29)$$

where  $s_{\text{OxR}}(\text{Na}_2\text{SO}_4)$  means the solubility of O<sub>x</sub>R in the Na<sub>2</sub>SO<sub>4</sub> solution,  $f_{\text{Ox}}(\text{NaCl})$  the activity coefficient of the Ox ion in the sodium chloride solution, etc. Now, dividing (27) by (28), and (28) by (29), we obtain

$$\left(\frac{R_{\text{OxR}}}{R_{\text{OxN}}}\right)^2 = \frac{\frac{f_{\text{R}}(\text{NaCl})}{f_{\text{R}}(\text{Na}_2\text{SO}_4)}}{\frac{f_{\text{N}}(\text{NaCl})}{f_{\text{N}}(\text{Na}_2\text{SO}_4)}} \quad (30)$$

$$\left(\frac{R_{\text{OxN}}}{R_{\text{RnN}}}\right)^2 = \frac{\frac{f_{\text{Ox}}(\text{NaCl})}{f_{\text{Ox}}(\text{Na}_2\text{SO}_4)}}{\frac{f_{\text{Rn}}(\text{NaCl})}{f_{\text{Rn}}(\text{Na}_2\text{SO}_4)}} \quad (31)$$

Since in (30) (but not in (31)) the right hand side of the equation according to our principle equals unity, the solubility ratios  $R_{OxR}$  and  $R_{OxN}$  but not  $R_{OxN}$  and  $R_{RnN}$ , accordingly, should be equal. The values in Table I furnish, therefore, a complete verification of the theory.

In an earlier communication<sup>10</sup> it was concluded that the solubility of uni-univalent salts was mainly governed by the equivalent concentration of the solvent, independent of its type; that is, that the shape of the solubility curves of such salts suffered no general or typical alteration when passing from one solvent to another of different type. The data now

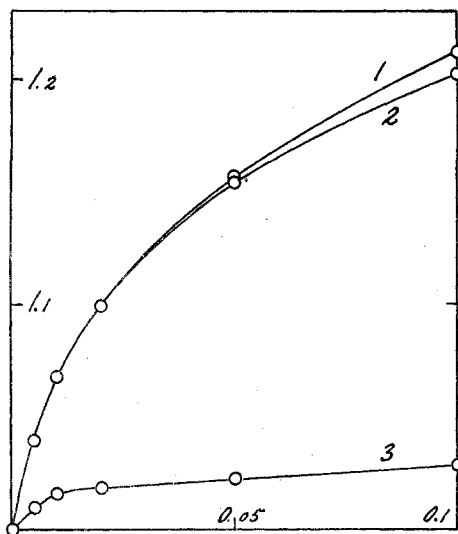


Fig. 3

available at low concentration show that this conclusion must be abandoned. The  $R$ -curves in the case of sodium sulfate and chloride are not rectilinear but exhibit a curvature particularly pronounced at high dilution. We infer that univalent ions are influenced by oppositely charged ions to an extent that is systematically dependent on their valence.

The values in the second and third columns of Table I confirm the earlier finding regarding the marked individualities of the activity coefficients of salts even at great dilution. It is of particular

interest that the principle of the specific interaction holds in spite of very great difference in the individual values of the activity coefficients in the various solvents.

TABLE II  
SOLUBILITIES OF  $OxR$  AND  $OxN$  IN SOLUTIONS OF SODIUM SULFATE AND SODIUM CHLORIDE OF HIGH CONCENTRATIONS AT 20°

|       | $c$ | $^sNa_2SO_4$ | $^sNaCl$ | $\frac{^sNa_2BO_4}{^sNaCl}$ |
|-------|-----|--------------|----------|-----------------------------|
| $OxR$ | 0.1 | 1.527        | 1.260    | 1.212                       |
|       | 0.2 | 1.719        | 1.367    | 1.256                       |
|       | 0.5 | 1.957        | 1.525    | 1.283                       |
|       | 1.0 | 1.993        | 1.626    | 1.224                       |
| $OxN$ | 0.1 | 1.688        | 1.403    | 1.202                       |
|       | 0.2 | 2.000        | 1.612    | 1.239                       |
|       | 0.5 | 2.657        | 2.149    | 1.238                       |
|       | 1.0 | 3.448        | 3.060    | 1.130                       |

<sup>10</sup> Brönsted and Petersen, *THIS JOURNAL*, 43, 2280 (1921).

The principle of the specific interaction may be expected to hold true only in dilute solution. Some measurements were made with the two oxalotetrammine salts at higher concentrations in order to determine the limits for its validity. The results are recorded in Table II.

The deviations from the principle, as exhibited by the values of  $\frac{S_{\text{Na}_2\text{SO}_4}}{S_{\text{NaCl}}}$  for the two salts at equal concentrations of the solvents, are perceptible in 0.1 *N* solution and very pronounced at higher concentrations.

The results obtained with two uni-bivalent salts in dilute solutions are given in Table III, the same notation being used as above.

TABLE III  
SOLUBILITIES OF  $\text{Ox}_2\text{P}$  AND  $\text{Ox}_2\text{D}$  IN SOLUTIONS OF SODIUM SULFATE AND SODIUM CHLORIDE AT 20°

|                                   | <i>c</i> | $S_{\text{Na}_2\text{SO}_4}$ | $S_{\text{NaCl}}$ | $\frac{S_{\text{Na}_2\text{SO}_4}}{S_{\text{NaCl}}}$ |
|-----------------------------------|----------|------------------------------|-------------------|--|
| $\text{Ox}_2\text{S}_2\text{O}_8$ | 0.01     | 1.259                        | 1.157             | 1.087  |
|                                   | .02      | 1.409                        | 1.250             | 1.126  |
|                                   | .05      | 1.743                        | 1.445             | 1.199  |
|                                   | .1       | 2.175                        | 1.716             | 1.269  |
| $\text{Ox}_2\text{S}_2\text{O}_6$ | .01      | 1.292                        | 1.185             | 1.091  |
|                                   | .02      | 1.465                        | 1.294             | 1.133  |
|                                   | .05      | 1.850                        | 1.53              | 1.208  |
|                                   | .1       | 2.27                         | 1.81              | 1.284  |

The values in the last column of this table show that the solubility ratios ( $R_{II} = \frac{S_{\text{Na}_2\text{SO}_4}}{S_{\text{NaCl}}}$ ) in this case also are nearly identical for the two salts at the same concentrations of the solvents, as expected from our theory.

If the ratio of the solubilities of a salt in the two solvents is taken not at the same equivalent concentration as in all the above calculations, but at the same molar concentration or at the same ionic strength<sup>11</sup> this ratio will generally approach much closer to unity. When plotting the solubilities against the ionic strength, the curves tend to coincide at very low concentrations. The identity of the values of  $\frac{S_{\text{Na}_2\text{SO}_4}}{S_{\text{NaCl}}}$  found by comparing two isotopic salts with a common cation does, however, appear only when the equivalent concentration is used, that is, when the cation of the solvent is present in the same concentration in the two solutions compared, a fact which is in full conformity with the ideas underlying the principle of the specific interaction of ions.

Since the measurements here mentioned involve saturating salts of different type, but with an ion in common, the salting-out ratio,  $r_u = \frac{f(\text{Cl})}{f(\text{SO}_2)}$ , can be calculated according to the theory given in the previous

<sup>11</sup> Ref. 8, p. 1140.

article.<sup>12</sup> Applying the formula derived there  $r_u = R_I^4/R_{II}^3$  and introducing the values of  $R_I = RO \times N$  and  $R_{II} = RO \times_2 S_2 O_6$  from the tables, we find the values of  $r_u$  corresponding to the concentrations  $c$  as follows,

|             |       |       |       |       |
|-------------|-------|-------|-------|-------|
| $c$ .....   | 0.01  | 0.02  | 0.05  | 0.10  |
| $r_u$ ..... | 1.019 | 0.997 | 0.998 | 1.013 |

that is to say, values very near unity. As far as these experiments are concerned, the salting-out effects of the two solvents are then very nearly identical.

### Summary

1. The principle of the specific interaction of ions is presented in the form of a simple equation and a diagram.

2. The individualities of the thermodynamic properties of salts vary linearly with their concentration when the total concentration is kept constant. On the basis of this law several of the results obtained by means of the principle of the specific interaction may be derived.

3. Thermodynamic and experimental evidence to prove the invalidity of the principle of the independent activity coefficients has been adduced.

4. Solubility measurements embracing a series of cobaltic ammonia salts in solutions of sodium sulfate and sodium chloride have been carried out. The results were found in full agreement with the principle of the specific interaction.

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[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

## DETERMINATION OF SIZE AND DISTRIBUTION OF SIZE OF PARTICLE BY CENTRIFUGAL METHODS

BY THE SVEDBERG AND J. BURTON NICHOLS

RECEIVED SEPTEMBER 14, 1923

In the determination of size and distribution of size of particle through gravity sedimentation by Odén's method<sup>1</sup> one is limited to relatively coarsely grained sols of about 100  $\mu\mu$  radius or larger. Since this is due to the extremely slow rate of settling, if the effect of gravity be increased sols of true colloidal size might thus be determined. To this end we have employed centrifugal force, and since direct weighing becomes impracticable here we designed a special centrifuge so constructed that the sol may be observed as it is precipitated. Then for a uniform sol, size of particle may be determined by measuring the rate of movement outward of the boundary of the particles and applying a modified form of Stokes' law.

<sup>12</sup> Ref. 1, p. 885.

<sup>1</sup> Odén, *Bull. Geol. Inst. Upsala*, 16, 15 (1918).