

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE POLYTECHNICAL INSTITUTE OF COPENHAGEN]

CALCULATION OF THE OSMOTIC AND ACTIVITY FUNCTIONS IN SOLUTIONS OF UNI-UNIVALENT SALTS

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Received August 1, 1921

1. Introduction

For the theory of solutions it is of the greatest importance to find an expression which, as the concentration approaches infinite dilution, shows a uniform convergence towards an ideal state and is still able to account for the peculiarities of the various salts at higher concentration. For a long time work has been in progress, mostly on an empirical basis, to establish the laws governing the anomalies of the strong electrolytes. A particularly successful research in this line is the critical study of Noyes and Falk¹ who found the osmotic properties of salt solutions to be represented by the well-known equation,

$$2-i = K\sqrt{c}, \text{ or } 1-\varphi = \alpha\sqrt{c} \quad (1)$$

where φ indicates the osmotic coefficient² and α a constant peculiar to the salt in question. This equation enabled us to account approximately for the thermodynamic properties of salt solutions within a rather considerable range of concentrations, and with its aid we were in a position to calculate³ approximately ion activities and solubilities based on the modern view of salt solutions as being completely ionized.

It is obvious, however, that Equation 1 does not fulfil the requirement of a uniform convergence with decreasing concentration, because the function $1-\varphi$ which we shall term *the osmotic deviation* is directly proportional to the constant α peculiar to any salt. When comparing two salts, the equation

$$\frac{(1-\varphi)_1}{(1-\varphi)_2} = \frac{\alpha_1}{\alpha_2}$$

evidently holds, even at the greatest dilutions.

In an interesting paper,⁴ Lewis and Linhart have proposed the expression

$$1-\varphi = \alpha c^n \quad (2)$$

in the place of Equation 1 and have shown that this expression conforms very closely to available accurate measurements of freezing-point lowerings. It is not surprising that this expression can be better satisfied than Equation 1 because it contains two independent constants α and n to be varied when

¹ Noyes and Falk, *THIS JOURNAL*, **32**, 1011 (1910).

² For notation see Brönsted, *ibid.*, **42**, 761 (1920).

³ Bjerrum, *Z. Elektrochem.*, **24**, 321 (1918). Brönsted, Ref. 2.

⁴ Lewis and Linhart, *THIS JOURNAL*, **41**, 1955 (1919).

passing from one salt to another. It lacks, however, as does Equation 1, the property of a uniform convergence with decreasing concentration.

From the point of view of the complete dissociation of the strong electrolytes it was previously pointed out by the writer,⁵ that the separate or individual behavior of ions may be accounted for by attributing to them a secondary power beside the primary *Milner* effect, and some possible reason for the appearance of such a secondary power was mentioned. The leading idea of the present paper assumes that the osmotic deviation is determined by two such separate influences, one of which—namely, the pure *Milner* effect—being the only one perceptible at small concentrations, while for the secondary effect laws similar to those governing non-electrolytes dissolved in salt solutions must be assumed. As will appear from the following discussion a very satisfactory expression of thermodynamic properties of salt solutions can be derived from this point of view.

2. The Osmotic Deviation: A General Formula

As a good many earlier investigations have shown, addition of salts to a solution of a non-electrolyte causes a change, mostly an increase, in the activity of the non-electrolyte. This effect known as the "salting-out effect" is generally directly proportional to the concentration of the salt added. The assumption of a similar influence of salts upon the activity of ions in spite of the very different total effect in the two cases appears reasonable, because the sequence in which the influence manifests itself is generally the same.⁶

On the ground of this view we must assume the osmotic deviation of a salt solution to be represented by an equation of the following form

$$1 - \varphi = f(c) + \beta c \quad (3)$$

where $f(c)$ is a universal function and β a coefficient peculiar to the salt considered.

Inspection of the best measurements of osmotic and activity coefficients now shows Equation 3 to be satisfied for uni-univalent salts by introducing $f(c) = \alpha\sqrt{c}$ where α is a universal constant possessing at least approximately the value 0.32 at 0°. We can then write

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

as presumably of universal validity; and

$$1 - \varphi = 0.32\sqrt{c} + \beta c \quad (5)$$

as valid at 0° or in the neighborhood of this temperature.

⁵ Ref. 2, p. 781.

⁶ This rule has been verified in this laboratory using as non-electrolyte the substance trinitro-tri-ammine cobalt, which according to Werner's theory is an undissociated compound. In this case the solubility is strongly increased by most salts, contrary to the usual salting-out effect. A marked parallelism between the influence upon the non-electrolyte and the isomeric salt, flavo cobaltic tetranitro-di-ammine cobaltate by various salts was noted.

While the second term in these equations accounts for such effects as are peculiar to each solution, the square-root term represents the influence of the simple inter-ionic forces due to the electrical net charge. It is interesting to note that Milner's calculation of this electrical effect also leads to a square-root expression even if the α -values calculated in this way do not agree with that given here.⁷

Of the properties belonging to Equations 4 and 5 we may mention the fulfilment of the requirement referred to above, that as concentration decreases the same ideal curve for all electrolytes of the type considered is approached. This is due to the fact that as the concentration approaches zero the term βc accounting for the individuality of the solutions becomes infinitely small compared with the general term $\alpha\sqrt{c}$.⁸

The concentration at which this ideal form of our equation, namely,

$$1 - \varphi = \alpha\sqrt{c} \quad (6)$$

or

$$1 - \varphi = 0.32\sqrt{c} \quad (7)$$

is applicable depends upon the value of β . This coefficient, being usually of the same order of magnitude as α , the simple form of our equation will usually become applicable from 0.01 or 0.001 *N* solution downwards.

The following sections contain the experimental basis of our Equations 4 to 7. In the first of them is given the most direct verification by means of freezing-point measurements. In the subsequent sections expressions for the activity coefficients and verification procured by means of electrometric and solubility measurements with and without the help of the principle of the specific interaction⁹ of ions are developed.

3. Verification by Means of Freezing-point Measurements

Only very few measurements of freezing-point lowerings at 0.01 *N* and lower concentrations are sufficiently accurate to secure a reliable basis for a theory of salt solutions. The best existing freezing-point measurements are those of Adams¹⁰ on potassium chloride and potassium nitrate and those of Harkins and Roberts¹¹ on sodium chloride. The osmotic coefficients φ calculated from these measurements at rounded concentrations are given in Table I.

⁷ The results of Milner's calculations can be given in the form $1 - \varphi = 0.25 c^{0.49}$.

⁸ In a recent paper by Lewis and Randall [THIS JOURNAL, 43, 1121 (1921)] it is suggested that n in the Lewis and Linhart expression (Equation 2) may equal $1/2$ in the case of uni-univalent salts. If we make this assumption the expression of Lewis and Linhart conforms with the above Equation 6, but the individual properties of the substances are then not accounted for as in Equation 4 and the expression obtained, therefore, is valid only at high dilution.

⁹ Brönsted, THIS JOURNAL, 44, 877 (1921).

¹⁰ Adams, *ibid.*, 37, 492 (1915).

¹¹ Harkins and Roberts, *ibid.*, 38, 2676 (1916). The figure at 0.0836 *N* has been omitted in the following treatment as evidently erroneous.

TABLE I
OSMOTIC COEFFICIENT φ OF KNO_3 , KCl AND NaCl AT VARIOUS CONCENTRATIONS
 $c(t=0^\circ)$

c	φ_{KNO_3}	φ_{KCl}	φ_{NaCl}
0.005	0.976	0.980	0.982
0.01	0.968	0.971	0.973
0.02	0.954	0.961	0.958
0.05	0.923	0.943	0.945
0.1	0.889	0.927	0.934

The values of β computed from these data are $+0.10$, -0.28 and -0.35 for KNO_3 , KCl and NaCl , respectively. Introducing these values in Equation 4 we obtain

$$\left. \begin{aligned} (1-\varphi)_{\text{KNO}_3} &= 0.32\sqrt{c} + 0.10c \\ (1-\varphi)_{\text{KCl}} &= 0.32\sqrt{c} - 0.28c \\ (1-\varphi)_{\text{NaCl}} &= 0.32\sqrt{c} - 0.35c \end{aligned} \right\} \quad (8)$$

The osmotic deviations $1-\varphi$ calculated from these equations are given in Table II together with those calculated from the experimental φ -values in Table I. In the last column the values of $0.32\sqrt{c}$ are given.

TABLE II
OSMOTIC DEVIATIONS $1-\varphi$ FOUND (f) AND CALCULATED (c)

c	KNO_3		KCl		NaCl		$0.32\sqrt{c}$
	$(1-\varphi)_f$	$(1-\varphi)_c$	$(1-\varphi)_f$	$(1-\varphi)_c$	$(1-\varphi)_f$	$(1-\varphi)_c$	
0.005	0.024	0.023	0.020	0.021	0.018	0.020	0.022
0.01	0.032	0.033	0.029	0.029	0.027	0.028	0.032
0.02	0.046	0.047	0.039	0.040	0.042	0.038	0.045
0.05	0.077	0.077	0.057	0.058	0.055	0.054	0.072
0.1	0.111	0.111	0.073	0.073	0.066	0.066	0.101

The agreement between the values of $1-\varphi$ found and calculated leaves nothing to be desired. It is of particular interest that our equation holds equally in the case of positive and negative β -values, representing respectively negative and positive salting-out effects exerted by the salts on their own ions.

Other measurements of high value are those of Hall and Harkins¹² on potassium and sodium iodates. They agree approximately with the expression

$$(1-\varphi) = 0.32\sqrt{c} + 0.17c$$

Slight deviations between the values found and calculated are compatible with the assumption of experimental errors of the order of magnitude 0.0002° in the freezing points of the most dilute solutions.

On turning to the application of our formula to other freezing-point measurements as a rule we no longer find such agreement as in the cases mentioned. This, however, is no serious objection to its validity, because most earlier investigations lack that high degree of precision necessary

¹² Hall and Harkins, THIS JOURNAL, 38, 2658 (1916).

to secure reliable results at the lower concentrations. This, for instance, is clearly demonstrated when the values collected by Noyes and Falk are introduced in the above calculations. We find in this case no agreement at all with our formula. Most previous experimental material in this field is therefore unserviceable for the establishment or verification of a theory of solution.

Fortunately the freezing-point method is not the only way of obtaining information about thermodynamic properties of solutions. For the use of other methods, however, it is necessary to develop the relationship between the osmotic deviation as dealt with in this section and the activity functions on the basis of our theory as given by Equation 4.

4. Calculation of Activity Coefficients

When Equation 4 is connected with the general relation between osmotic and activity coefficients¹³ the following equation results,

$$\ln f = -3\alpha\sqrt{c} - 2\beta c \quad (9)$$

where f stands for the activity coefficient of the salt. Corresponding equations hold for the activity coefficients f' and f'' for the cation and anion, respectively, namely

$$\left. \begin{aligned} \ln f' &= -3\alpha\sqrt{c} - 2\beta'c \\ \ln f'' &= -3\alpha\sqrt{c} - 2\beta''c \end{aligned} \right\} \quad (10)$$

the three activity coefficients being correlated by $f^2 = f'f''$, and the β -coefficients, therefore, by $2\beta = \beta' + \beta''$.

Introducing into Equations 9 and 10 the value $\alpha = 0.32$ found in the foregoing section, we obtain

$$\left. \begin{aligned} \ln f &= -0.96\sqrt{c} - 2\beta c \\ \ln f' &= -0.96\sqrt{c} - 2\beta'c \\ \ln f'' &= -0.96\sqrt{c} - 2\beta''c \end{aligned} \right\} \quad (11)$$

We see thus that the activity coefficients of salts are determined by two terms, one of which is universal, independent of the nature of the salt concerned, while the other accounts for its individual property. As the latter is directly proportional to the concentration we shall find the same to be true when comparing 2 different salts, as is clearly shown by the following simple equation.

$$\ln \frac{f_1}{f_2} = -2(\beta_1 - \beta_2)c \quad (12)$$

Equation 11 allows a direct calculation of activity coefficients from osmotic measurements, by which the value of the β -coefficient is furnished. At high dilution the equation assumes the simple form,

$$\ln f = \ln f' = \ln f'' = -3\alpha\sqrt{c} \quad (13)$$

and at 0°

$$\ln f = \ln f' = \ln f'' = -0.96\sqrt{c} \quad (14)$$

¹³ Ref. 2, p. 765.

showing the activity coefficients of all salts and ions to be uniformly determined by the concentration.

5. Verification by Means of Electrical Measurements

The best experimental material available for checking the equations set up in the foregoing section is in the results of the electrometric measurements of Noyes and Ellis¹⁴ and Linhart¹⁵ on cells of the type, H | HCl | Ag-Cl.Ag, containing acid of various concentrations. By these measurements, however, only relative values of the activity coefficient of the hydrochloric acid are furnished. The comparison is made by assuming the solutions of lowest concentration to be *ideal dilute* solutions, *i. e.*, attributing to them the f -value appearing in Equation 14.

The values obtained in this way are given in the second column of Table III. The third column contains the values of f calculated from Equation 2, and in the last column are given the ideal values from Equation 14.

TABLE III
ACTIVITY COEFFICIENTS OF HCl, FOUND AND CALCULATED

c	f_{found}	$f_{\text{calc.}}$	f_{ideal}
0.0001	...	0.991	0.991
0.0002	...	0.987	0.987
0.0005	0.978	0.979	0.979
0.001	0.971	0.971	0.970
0.002	0.958	0.959	0.958
0.005	0.934	0.938	0.934
0.01	0.912	0.915	0.908
0.02	0.882	0.886	0.873
0.05	0.848	0.850	0.824
0.1	0.803	0.784	0.737

The β -value inserted in Equation 11 for the calculation of $f_{\text{calc.}}$ is -0.31 and the equation employed therefore:

$$\ln f = -0.96\sqrt{c} + 0.62c \quad (15)$$

When the highest concentration $0.1 N$ is dispensed with the agreement between f_{found} and $f_{\text{calc.}}$ is seen to be complete. Comparison with the figures in the last column shows the hydrochloric acid solutions to be *ideal*, at least up to $0.002 N$.

These electrometric measurements, therefore, fully verify our theory. The equation, $1 - \phi = 0.32\sqrt{c} - 0.31c$, derivable from (15) is very similar to Equation 8 obtained for potassium and sodium chlorides by using freezing-point data and shows that hydrochloric acid at the dilutions here considered exhibits no peculiar behavior such as previous experiments on this subject might lead us to suspect.

¹⁴ Noyes and Ellis, THIS JOURNAL, 39, 2532 (1917).

¹⁵ Linhart, *ibid.*, 41, 1175 (1919).

It is very remarkable that the value 0.32 of α derived from freezing-point measurements applies here at the temperature of the experiment, 25°. The assumption of an approximate independence of the temperature of the α -coefficient is, however, also corroborated by solubility measurements as referred to in the following sections.¹⁶

6. Verification by Means of Solubility Data

When a salt is dissolved in very small amount in a salt solution of the (total) concentration c , Equations 9 to 11 must hold for the dissolved salt, β , β' and β'' being constants which depend upon the nature of the dissolved salt as well as the salt solution serving as solvents. The theory is, therefore, directly applicable to the problem of calculating solubilities of slightly soluble salts in salt solutions of varying concentration.

Solubility in the Ideal Region of Concentrations.—In this region Equation 9 simplifies into

$$\ln f = -3\alpha\sqrt{c} \quad (13)$$

Since at constant temperature the solubility of a salt is inversely proportional to its activity coefficient, we can write

$$\ln s/s_0 = 3\alpha(\sqrt{c_t} - \sqrt{s_0}) \quad (16)$$

or by introduction of the value of α

$$\ln s/s_0 = 0.96(\sqrt{c_t} - \sqrt{s_0}) \quad (17)$$

In these equations s_0 is the solubility in pure water, s in a hetero-ionic salt solution of very low concentration c , and c_t the total concentration $c+s$.

Some few results obtained in this laboratory in order to verify Equation 17 are tabulated below. The sparingly soluble salts examined were as follows: (1) oxalo-cobaltic tetrathiocyanato-diammine chromiate, $[\text{Co}(\text{NH}_3)_4\text{C}_2\text{O}_4] [\text{Cr}(\text{NH}_3)_2(\text{CNS})_4]$; (2) croceo-cobaltic tetranitro-diammine cobaltiate, $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2] [\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]$; (3) croceo-cobaltic tetrathiocyanato-diammine chromiate, $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2] [\text{Cr}(\text{NH}_3)_2(\text{CNS})_4]$;

TABLE IV

SOLUBILITY OF METAL AMMONIA SALTS IN VERY DILUTE SALT SOLUTIONS. $t=20^\circ$

c	c_t	$(s/s_0)_{\text{found}}$	$(s/s_0)_{\text{calc.}}$
	1. Oxalo-chromiate. $s_0=0.00137$		
0.000	0.00137	1.000	1.000
0.001	0.00239	1.011	1.012
0.002	0.00340	1.023	1.021
	2. Croceo-cobaltiate. $s_0=0.000370$		
0.000	0.00037	1.000	1.000
0.001	0.00138	1.021	1.019
0.002	0.00238	1.035	1.029
	3. Croceo-chromiate. $s_0=0.000143$		
0.000	0.000143	1.000	1.000
0.001	0.00115	1.025	1.021

¹⁶ Regarding the influence of changing temperature on activity coefficients, see Brönsted, *Z. physik. Chem.*, **100** (1922).

solutions of sodium chloride, potassium chloride and potassium nitrate were used as solvents. The highest concentration used being 0.002 *N*, no difference in solvent power of the three solvents could be observed, and so only the mean values are given in the table.

The agreement between the values of s/s_0 found and calculated is satisfactory and proves that the square-root expression holds in the region of concentration 0.00014 *N* to 0.002 *N* used here.

Experiments are in progress in this laboratory to secure accurate solubility data at still lower concentrations.

Solubility at Higher Concentrations.—When, in the general equation for the solubility equilibrium in hetero-ionic solvent

$$s^2 f' f'' = s_0^2 f_0^2 \quad (18)$$

the f -values as given in Equations 9 and 10 are introduced, we obtain

$$\ln s/s_0 = 3\alpha(\sqrt{c_i} - \sqrt{s_0}) + \beta c \quad (19)$$

where β is a constant depending upon the ionic interaction and salting out effect of the solvent and α has the usual value 0.32.

In the case of a homo-ionic solvent we have in the place of (18)

$$s c_i f' f'' = s_0^2 f^2, \quad (20)$$

and thus in the same way

$$\frac{1}{2} \ln \frac{s c_i}{s_0^2} = 3\alpha(\sqrt{c_i} - \sqrt{s_0}) + \beta c \quad (21)$$

A considerable amount of experimental material from a recently published investigation¹⁷ on solubility of metal ammonia salts is available for checking these equations. A series of examples taken from this source has been recalculated with the aid of Equation 19 inserting $3\alpha = 0.96$, and for β that value which gives the closest agreement with the experimental results. The data concerned, valid at 0°, are given in Table V.

The agreement between the values of s/s_0 found and calculated as exhibited by this table is in most cases very close, which is the more remarkable as the β -values introduced vary extraordinarily. Equation

TABLE V
SOLUBILITY RATIO s/s_0 FOUND AND CALCULATED FOR METAL AMMONIA SALTS IN VARIOUS SOLVENTS

c	$(s/s_0)_{\text{found}}$	$(s/s_0)_{\text{calc.}}$
1. Praseo cobaltic iodate in potassium chloride, $s_0 = 0.00441$, $\beta = +0.20$		
0.00	1.000	1.000
0.02	1.104	1.097
0.05	1.191	1.187
0.1	1.295	1.307

¹⁷ Brønsted and Agnes Petersen, THIS JOURNAL, 43, 2265 (1921).

TABLE V (continued)

c	$(s/s_0)_{\text{found}}$	$(s/s_0)_{\text{calc.}}$
2. Praseo cobaltic bromide in potassium formate, ^a $s_0 = 0.00632$, $\beta = -0.58$		
0.00	1.000	1.000
0.02	1.082	1.072
0.05	1.143	1.132
0.1	1.198	1.198
0.2	1.280	1.280
3. β -Croceo cobaltic nitrate in potassium formate, $s_0 = 0.00494$, $\beta = -0.16$		
0.00	1.000	1.000
0.02	1.086	1.085
0.05	1.164	1.162
0.1	1.258	1.258
0.2	1.404	1.403
4. Croceo cobaltic perchlorate in potassium formate, $s_0 = 0.0124$, $\beta = +0.14$		
0.00	1.000	1.000
0.05	1.148	1.154
0.1	1.264	1.263
5. Croceo cobaltic dioxalo-tri-amine cobaltate in potassium chloride, $s_0 = 0.000593$, $\beta = +0.78$		
0.00	1.000	1.000
0.02	1.186	1.158
0.05	1.332	1.311
0.1	1.546	1.546

^a The mean values of the data for potassium formate, tri-, di- and monochloroacetate have been taken.

19 obviously applies much better than the cube-root expression used in the previous papers.

The results given here lend strong support to the applicability of the formulas applied for these calculations and therefore to the underlying theory as represented by the fundamental Equations 5 and 9.

7. Application of the Theory of the Specific Interaction of the Ions

When Equation 4 is applied to two salt solutions with a common ion, sodium chloride and potassium chloride, for instance, we can write

$$\begin{aligned}(1 - \varphi)_{\text{NaCl}} &= \alpha\sqrt{c} + \beta_{\text{NaCl}}c \\ (1 - \varphi)_{\text{KCl}} &= \alpha\sqrt{c} + \beta_{\text{KCl}}c\end{aligned}$$

and so

$$-(\varphi_{\text{NaCl}} - \varphi_{\text{KCl}}) = (\beta_{\text{NaCl}} - \beta_{\text{KCl}})c \quad (22)$$

Furthermore we have according to Equation 9

$$\begin{aligned}-\ln f_{\text{NaCl}} &= 3\alpha\sqrt{c} + 2\beta_{\text{NaCl}}c \\ -\ln f_{\text{KCl}} &= 3\alpha\sqrt{c} + 2\beta_{\text{KCl}}c\end{aligned}$$

and so

$$-\frac{1}{2} \ln \frac{f_{\text{NaCl}}}{f_{\text{KCl}}} = (\beta_{\text{NaCl}} - \beta_{\text{KCl}})c. \quad (23)$$

Combining Equations 22 and 23 we obtain,

$$\varphi_{\text{NaCl}} - \varphi_{\text{KCl}} = \frac{1}{2} \ln \frac{f_{\text{NaCl}}}{f_{\text{KCl}}} \quad (24)$$

In a recent paper⁹ the writer has shown, on the basis of the principle of the specific interaction of the ions, the following equation to hold.

$$\varphi_{\text{NaCl}} - \varphi_{\text{KCl}} = \frac{1}{2} \ln \frac{f_{\text{Cl}(\text{NaCl})} f_{(\text{Na})}}{f_{\text{Cl}(\text{KCl})} f_{(\text{K})}} \quad (25)$$

where $f_{\text{Cl}(\text{NaCl})}$ and $f_{\text{Cl}(\text{KCl})}$ denote the activity coefficients of the chlorine ion in NaCl and KCl solutions respectively, and $f_{(\text{Na})}$ and $f_{(\text{K})}$ what are called the salting-out coefficients. Now combining Equations 24 and 25 the following relation results,

$$\frac{f_{\text{NaCl}}}{f_{\text{KCl}}} = \frac{f_{\text{Cl}(\text{NaCl})} f_{(\text{Na})}}{f_{\text{Cl}(\text{KCl})} f_{(\text{K})}} \quad (26)$$

Bearing in mind that $f^2 = f'f''$ or $f_{\text{NaCl}}^2 = f_{\text{Na}(\text{NaCl})} f_{\text{Cl}(\text{NaCl})}$ and that $f_{\text{Na}(\text{NaCl})} = f_{\text{Na}(\text{Cl})} f_{(\text{Na})} f_{(\text{Cl})}$ etc., $f_{\text{Na}(\text{Cl})}$ indicating the coefficient of interaction of the sodium ion in a chloride solution, Equation 26 may be rewritten as follows.

$$\frac{f_{\text{Na}(\text{NaCl})} f_{\text{Cl}(\text{NaCl})}}{f_{\text{K}(\text{KCl})} f_{\text{Cl}(\text{KCl})}} = \left(\frac{f_{\text{Cl}(\text{NaCl})} f_{(\text{Na})}}{f_{\text{Cl}(\text{KCl})} f_{(\text{K})}} \right)^2$$

or

$$\frac{f_{\text{Na}(\text{NaCl})}}{f_{\text{K}(\text{KCl})}} = \frac{f_{\text{Cl}(\text{NaCl})}}{f_{\text{Cl}(\text{KCl})}} \left(\frac{f_{(\text{Na})}}{f_{(\text{K})}} \right)^2 \quad (27)$$

or

$$\frac{f_{(\text{Na})}}{f_{(\text{K})}} = \frac{f_{\text{Cl}(\text{Na})}}{f_{\text{Cl}(\text{K})}} \left(\frac{f_{(\text{Na})}}{f_{(\text{K})}} \right)^2 \quad (28)$$

Since the right-hand side of Equations 27 and 28, as shown in the paper quoted is determinable from solubility measurements we are in a position by means of these two equations to calculate the ratio of the activity coefficients and the ratio of interaction of the potassium and sodium ions or generally of two different ions with the same sign.

In the case of the alkali chlorides and nitrates we have found in the previous paper at 0°

$$\frac{f_{(\text{Na})}}{f_{(\text{K})}} = 1.010, \quad \frac{f_{\text{Cl}(\text{Na})}}{f_{\text{Cl}(\text{K})}} = 1.000, \quad \frac{f_{\text{NO}_3(\text{Na})}}{f_{\text{NO}_3(\text{K})}} = 1.028$$

and are so able to calculate the activity ratios of the alkali ions as follows.

$$\begin{aligned} \frac{f_{\text{Na}(\text{Cl})}}{f_{\text{K}(\text{Cl})}} &= 1.000 \cdot 1.010^2 = 1.020 \\ \frac{f_{\text{Na}(\text{NaCl})}}{f_{\text{K}(\text{KCl})}} &= 1.010 \cdot 1.010^2 = 1.030 \\ \frac{f_{\text{Na}(\text{NO}_3)}}{f_{\text{K}(\text{NO}_3)}} &= 1.028 \cdot 1.010^2 = 1.049 \\ \frac{f_{\text{Na}(\text{NaNO}_3)}}{f_{\text{K}(\text{KNO}_3)}} &= 1.038 \cdot 1.010^2 = 1.059 \end{aligned}$$

In the question of activity coefficients the theory here presented leads clearly a step further than the mere application of the principle of the specific interaction. Equation 28 obviously shows that the coefficients of interaction and the salting-out coefficients are correlated by an equation into which the nature of the common ion does not enter. In case an additional inquiry into this matter should prove Equation 28 to be generally valid, it would certainly contribute to the solution of the question of the mechanism of bringing about an effect of electrical interaction between ions, such as was shown in the paper referred to as necessary in order to be able to account for the peculiarities of salt solutions.

Summary

From the point of view that the individualities of salt solutions have an origin similar to that of the individual salting-out effect in the case of non-electrolytes, equations were set up to govern the osmotic and activity functions of uni-univalent salts in pure and mixed solutions.

These equations were found to be strongly supported by the most accurate experimental results including measurements of freezing-point lowerings, electromotive force and solubilities.

Ratios of activity coefficients were calculated on the ground of these equations in conjunction with the principle of the specific interaction of ions.

COPENHAGEN, DENMARK

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE NATIONAL BISCUIT COMPANY, No. 7]

THE USE OF PHTHALATE SOLUTIONS FOR HYDROGEN ELECTRODE STANDARDS

BY EARLE T. OAKES AND HENRY M. SALISBURY

Received August 5, 1921

The recent proposals to replace the calomel electrode by phthalate solutions as standard hydrogen electrodes led the present authors to investigate the reliability of such solutions.

A buffer solution of potassium hydrogen phthalate and sodium hydroxide was made up as described by Clark and Lubs.¹ Fifty cc. of 0.2 *M* potassium hydrogen phthalate solution and 45.45 cc. of 0.2 *M* sodium hydroxide were mixed and diluted to 200 cc. with conductivity water. This solution was made up to give a Sørensen value of 6.0 and when tested by indicators this value was obtained.

Using the method described by Beans and Oakes² a quantity of this solution was tested by the hydrogen electrode. Measurements were taken

¹ Clark and Lubs, *J. Biol. Chem.*, **35**, 3, 504 (1916).

² Beans and Oakes, *THIS JOURNAL*, **42**, 2116 (1920).