$$H + O_2 + H_2 = H_2O + OH$$
$$OH + H_2 = H_2O + H$$

puts up a strong case for this mechanism. However, some experiments recently published by Pease[9] are very difficult to explain if hydrogen peroxide can be formed only through Reaction 2.

Pease found a considerable yield of hydrogen peroxide on passing a mixture of hydrogen and oxygen through a Pyrex tube at 550°, amounting in some experiments to as much as one molecule of hydrogen peroxide for four molecules of water formed. Reaction 2 cannot be held responsible for this result for the following reason. Reaction 1 has a collision yield of 1.8 × 10^{-4} at 550°. In order for Reaction 2 to be the source of hydrogen peroxide, one of these should take place for every *ca.* 10^4 collisions of OH with H_2, which means that the concentration of OH would have to be of the order of the H_2 concentration, namely, *ca.* 10^{19} per cc. This is obviously impossible. We are compelled for these reasons to assume with Pease, who experimented in the non-explosive region, that some other mechanism for the formation of hydrogen peroxide must be in operation.

[9] Pease, THIS JOURNAL, **52**, 5106 (1930); **53**, 3188 (1931).

PITTSBURGH, PENNSYLVANIA

ACTIVITY COEFFICIENTS OF SALTS IN ACETIC ACID SOLUTIONS FROM SOLUBILITY MEASUREMENTS

By RALPH P. SEWARD AND CLEMENT H. HAMBLET

Measurement of the solubility of salts in the presence of other salts, although complicated by the introduction of a third component, offers the most exact method of measuring changes in the activity coefficients of salts at low concentration in non-aqueous solutions. Previous research in this field includes the work of Williams[1] on methyl alcohol solutions, Hansen and Williams[2] on ethyl alcohol–water mixtures, Kraus and Seward[3] on isopropyl alcohol and acetone, Robinson[4] on acetone and Seward and Schumb[5] on ethyl alcohol. The results of these investigations have been compared in each case with those predicted by the interionic attraction theory of Debye and Hückel.[6] If the observed activity coefficient changes are

[1] Williams, THIS JOURNAL, **51**, 1112 (1929).
[2] Hansen and Williams, *ibid.*, **52**, 2759 (1930).
[3] Kraus and Seward, *J. Phys. Chem.*, **32**, 1294 (1928).
[4] Robinson, *ibid.*, **32**, 1089 (1928).
[5] Seward and Schumb, THIS JOURNAL, **52**, 3962 (1930).
[6] Debye and Hückel, *Physik. Z.*, **24**, 185 (1923).

plotted against the square root of the ionic strengths of the solutions, curves are obtained which for salts of higher valence type in methyl alcohol and for all salts in the solvents of lower dielectric constant have a markedly greater slope than the limiting slope which the Debye–Hückel theory requires for dilute solutions.   To account for this on the basis of the original Debye–Hückel approximation introduction of a negative value for the ion diameter is necessary.

Gronwall, La Mer and Sandved[7] have shown that the complete development of the equations used by Debye and Hückel gives a series of terms of which the original Debye and Hückel approximation is the first.   They have calculated values for the higher terms at different concentrations.

These authors as well as La Mer and Parks and Cowperthwaite and La Mer[8] have obtained, using these values, quantitative agreement between the complete equation and the measured activity coefficients of salts of higher valence type in aqueous solutions.   Their equation also predicts curves for non-aqueous solutions which are, qualitatively at least, in agreement with the experimental curves if a reasonable positive value for the ion diameter is assumed.   Bjerrum,[9] by treating ions within a certain arbitrary distance as undissociated, has developed values for the activity coefficients which also agree in predicting curves with positive deviations from the Debye–Hückel limiting slope for salts of higher valence type and for solutions of low dielectric constant.

Since both the development of Gronwall, La Mer and Sandved and that of Bjerrum predict greater deviations from the Debye–Hückel limiting slope the lower the dielectric constant, assuming a constant ion diameter, the present investigation was undertaken to determine whether agreement with the theory would be found in solvents with dielectric constants less than ten.   Glacial acetic acid was selected as the solvent.   Measurements of freezing points of acetic acid solutions have been made by Webb,[10] and e. m. f. measurements by Conant and Werner and by Hutchison and Chandlee.[11]   These investigators agree in concluding that the Debye–Hückel theory may be applied to the solutions studied if a rather large value for the ion diameter is assumed.

In the present investigation the solubilities of potassium perchlorate in glacial acetic acid in the presence of ammonium perchlorate, sodium nitrate, and sodium bromide and of potassium nitrate in the presence of ammonium chloride and ammonium nitrate have been measured.

[7] Gronwall, La Mer and Sandved, *Physik. Z.*, **29**, 358 (1928).

[8] La Mer and Parks, THIS JOURNAL, **53**, 2040 (1931); Cowperthwaite and La Mer, *ibid.*, **53**, 4333 (1931).

[9] Bjerrum, *Det. Kgl. Danske Videnskab. Selskab, Math-fys. Medd.*, [9] **7**, 1 (1926).

[10] Webb, THIS JOURNAL, **48**, 2266 (1926).

[11] Conant and Werner, *ibid.*, **52**, 4436 (1930); Hutchison and Chandlee, *ibid.*, **53**, 2881 (1931).

Preparation of Materials

Acetic Acid.—"Reagent quality" acid melting at about 15.65° was refluxed for forty hours with acetic anhydride equivalent to 80% of the water calculated to be present. It was then distilled using a Vigreux column arranged so that the hot vapors were in contact only with glass. In this way large quantities of acid were obtained melting from 16.5 to 16.6°. No acid melting lower than 16.5° was used. If water is assumed to be the impurity present,[12] a melting point of 16.5 corresponds to 0.05% water.

After various methods of purification recommended in the literature had been applied to c. p. acetic acid, without entirely satisfactory results, it was decided to employ "reagent" quality acid, fractional distillation of which yielded suitable material.

Salts.—The salts used were c. p. salts, further purified by recrystallization and carefully dried before use.

Determination of Solubilities.—The method was, in general, that used by Kraus and Seward. To insure equilibrium an excess of the saturating salt was rotated in a large bath with one to two liters of solvent (acetic acid containing various quantities of added salt) for sixteen hours or longer at about 30° and then at 25 ± 0.02° for at least eight hours. After being allowed to stand without removal from the bath for three hours, the clear solution was siphoned off and analyzed. In some cases filtration was necessary.

The concentration of the added salt was calculated from the total weight of acetic acid used and the weight of solid salt added. In calculating concentrations the densities of the pure solvent were used. The value of 1.044 from the "International Critical Tables" for the density of acetic acid at 25° was used. The concentration of the saturating salt was determined by distilling the acetic acid from a known weight of solution and analyzing the residue.

The number of salts whose solubility is of the magnitude desired is very limited. Considerable time was wasted in an attempt to get consistent values for the solubility of sodium iodate. Apparently equilibrium was not reached even in six days of rotation as the values obtained varied from 0.00036 to 0.00060 mole per liter. This seems to agree with the observations of Hill and Donovan[13] on the solubility of iodates in water. Potassium perchlorate was finally chosen although its analytical determination is not so favorable. The measurements on the solubility of potassium nitrate have been included since the e. m. f. and freezing point measurements referred to have been made in this range of concentrations. In the case of potassium perchlorate in the presence of ammonium perchlorate, and also in the case of potassium nitrate in the presence of ammonium chloride and of ammonium nitrate, the solubility of the saturating salt was determined by adding an excess of concentrated sulfuric acid to the residue left after evaporation of the solvent and igniting in a platinum dish, the po-

[12] DeVisser, *Rec. trav. chim.*, **12**, 101 (1893).
[13] Hill and Donovan, THIS JOURNAL, **53**, 934 (1931).

tassium being weighed as potassium sulfate. The solubility of potassium perchlorate in the presence of sodium nitrate and sodium bromide was measured by the cobaltinitrite method using the procedure recommended by Van Rysselberge.[14] Since the composition of the cobaltinitrite precipitate varies with the conditions of precipitation, each series of determinations was accompanied by two or more determinations of a known weight of perchlorate of the same magnitude as that from the solutions being analyzed in order to determine the weight of potassium perchlorate corresponding to a given weight of cobaltinitrate precipitate. Two samples of solution were withdrawn from each bottle to give check analyses except for potassium chlorate in the presence of ammonium perchlorate. Since the solubility was decreased in this case, all of the solution from each bottle was required to give a large enough weight of potassium sulfate to give reasonable accuracy in weighing. The three values for the solubility of potassium perchlorate in pure acetic acid were obtained from three independent saturations.

Experimental Data.—The following tables give the solubilities of potassium perchlorate and of potassium nitrate in the presence of varying amounts of added salts in glacial acetic acid at 25°. For comparison with the theory the calculated values of $-\log P_{i_0}/P_i$ and the square roots of the total salt concentrations are included. All concentrations are expressed in moles of salt per liter of solution.

TABLE I

SOLUBILITY OF POTASSIUM PERCHLORATE IN THE PRESENCE OF OTHER SALTS IN GLACIAL ACETIC ACID AT 25°

(a) Added salt sodium nitrate

Concn. NaNO$_3$ $\times$ 10^4	Concn. KClO$_4$ $\times$ 10^4 (anal.)			Concn. KClO$_4$ $\times$ 10^4 (mean)	$-\dfrac{1}{2}\log\dfrac{P_{i_0}}{P_i}$	$\sqrt{C}\times 10^2$
0.00	1.98	1.93	1.95	1.95	0.000	1.40
1.68	2.53	2.54		2.53	.113	2.05
3.46	3.05	3.05		3.05	.193	2.55
6.33	3.57	3.58		3.57	.263	3.14
10.09	4.11	4.16		4.13	.325	3.77
15.50	4.82	4.85		4.83	.393	4.50
18.25	5.24	5.21		5.22	.427	4.84

(b) Added salt sodium bromide

Concn. NaBr $\times$ 10^4						
0.00	1.98	1.93	1.95	1.95	0.000	1.40
0.78	2.36	2.36	2.34	2.35	.080	1.77
1.20	2.71	2.70		2.70	.141	1.97
1.92	2.90	2.89		2.90	.170	2.19
2.10	2.88	2.88		2.88	.168	2.23
2.78	3.15	3.10	3.04	3.10	.200	2.42
5.90	3.76	3.85		3.79	.287	3.11

[14] Van Rysselberge, *Ind. Eng. Chem., Anal. Ed.*, **3**, 3 (1931).

TABLE I   (*Concluded*)

(c)   Added salt ammonium perchlorate

Concn. NH$_4$ClO$_4$ $\times$ 10^4		Concn. KClO$_4$ $\times$ 10^4 (anal.)		Concn., KClO$_4$ $\times$ 10^4 (mean)	$-\frac{1}{2}\log\frac{P_{i0}}{P_i}$	$\sqrt{C} \times$ 10^2
0.00	1.98	1.93	1.95	1.95	0.000	1.40
1.98	1.94				.150	1.98
3.16	1.76				.180	2.22
3.78	1.90				.226	2.38
5.09	1.71				.243	2.61
7.65	1.55				.287	3.03
9.83	1.55				.333	3.37
13.06	1.39				.362	3.80
20.93	1.41				.457	4.73

TABLE II

SOLUBILITY OF POTASSIUM NITRATE IN THE PRESENCE OF OTHER SALTS IN GLACIAL ACETIC ACID AT 25°

(a)   Added salt ammonium nitrate

Concn. NH$_4$NO$_3$ $\times$ 10^2		Concn. KClO$_4$ $\times$ 10^2 (anal.)		Concn. KClO$_4$ $\times$ 10^2 (mean)	$-\frac{1}{2}\log\frac{P_{i0}}{P_i}$	$\sqrt{C}$
0.000	1.828	1.830	1.827	1.828	0.0000	0.1352
0.437	1.854	1.853		1.853	.0519	.1514
0.740	1.899	1.897		1.898	.0877	.1634
1.083	1.855	1.852		1.853	.1057	.1714
1.917	1.937	1.940		1.938	.1747	.1964
2.542	1.955	1.965		1.960	.2107	.2122

(b)   Added salt ammonium chloride

Concn. NH$_4$Cl $\times$ 10^2						
0.000	1.828	1.830	1.827	1.828	0.0000	0.1352
0.182	2.106	2.092		2.099	.0599	.1510
0.364	2.196	2.183		2.194	.0791	.1599
0.757	2.437	2.438		2.437	.1249	.1787
1.132	2.727	2.724		2.725	.1734	.1964
1.221	2.804	2.791 ·		2.798	.1847	.2005

Discussion

The interionic attraction theory leads to an equation relating the value of minus the logarithm of the activity coefficient of the salt to the concentration of the solution.   The development of the theory by Debye and Hückel leads to the equation

$$-\log f = \frac{22.6\sqrt{C}}{1 + 1.166 \times 10^8 a \sqrt{C}} \tag{1}$$

for acetic acid at 25°, where C is the total salt concentration in moles per liter and a the average ion diameter in centimeters.   Since all the salts used are uni-univalent, the coefficients involving valence are omitted.

The development by Gronwall, La Mer and Sandved[15] leads to the equation

[15] Ref. 7, page 388 and Table V, page 387.

$$-\log f = \frac{19.4}{10^8 a} \cdot \frac{x}{1 + x} - \frac{307.8}{(10^8 a)^3} F_3(x) - \frac{24,460}{(10^8 a)^5} F_5(x) \qquad (2)$$

for univalent type salts in acetic acid at 25°, where $x = 1.166 \times 10^8 a \sqrt{C}$, a and C are the same as above, and $F_3(x)$ and $F_5(x)$ are functions of x whose values have been calculated and tabulated by these authors. The first term on the right in Equation 2 has the same value as $-\log f$ in Equation 1. The two equations, therefore, differ by the values of the second and third terms in Equation 2. The term involving change in dielectric constant with salt concentration has been omitted since its value is unknown. Hutchison and Chandlee,[16] however, conclude that, at concentrations somewhat larger than those of the perchlorate solutions in the present investigation, the effect of this term is less than 1% of the value of the first term in the expression for the activity coefficient.

Since different writers have used widely varying values for the dielectric constant of acetic acid, it was decided to measure it. This was done through the generous coöperation of Dr. J. Wyman of Harvard University. The values reported by Dr. Wyman for the glacial acetic acid employed in these experiments are: $\lambda = 8.586$ meters, $\epsilon = 6.274$; $\lambda = 8.590$ meters, $\epsilon = 6.279$; $\lambda = 3.792$ meters, $\epsilon = 6.236$; $\lambda = 3.791$ meters, $\epsilon = 6.234$. The mean of these values, 6.25, was used in calculation of the constants. This is in reasonably good agreement with the recent value of 6.16 obtained by Smyth.[17]

The activity coefficient of the salt saturating the solution is related to the measured solubilities by the equation

$$-\log f = -\tfrac{1}{2} \log P_{i_0}/P_i - \log f_0$$

where P_i is the product of the ion concentrations of the saturating salt in the mixtures and P_{i_0} is the same product for the salt in the absence of added salt. Since f_0, the activity coefficient of the salt in the pure solvent, is a constant, variations of the value of $-\tfrac{1}{2} \log P_{i_0}/P_i$ with concentration are equal to the variations of $-\log f$, and $-\log f_0$ may be calculated by extrapolation to zero concentration.

In order to see whether either Equation 1 or Equation 2 is applicable to the observed solubility changes, values of $-\tfrac{1}{2} \log P_{i_0}/P_i$ for the potassium perchlorate solutions have been plotted in Fig. 1 against the square roots of the total salt concentrations.

It may be noted that there is little difference between the curves obtained with three different added salts, two without and one with an ion common to the saturating salt. The curves closely approach the limiting slope of Equation 1 at the lower concentrations. This was not anticipated since comparable results in solvents of higher dielectric constant show consistent

[16] Hutchison and Chandlee, THIS JOURNAL, 53, 2887 (1931).

[17] Smyth, *ibid.*, 52, 1825 (1930). For the method used by Dr. Wyman see *ibid.*, 53, 3292 (1931).

positive deviations.   A fair agreement with the experimental data may be obtained with Equation 1 if a value of a of 9×10^{-8} is assumed.   The curvature of the theoretical curve, however, is markedly less than those of the experimental curves.

Since Equation 2 has been shown to account for the positive deviations from the limiting slope which have been observed in other solvents, it might be expected to prove less satisfactory than Equation 1 in the present
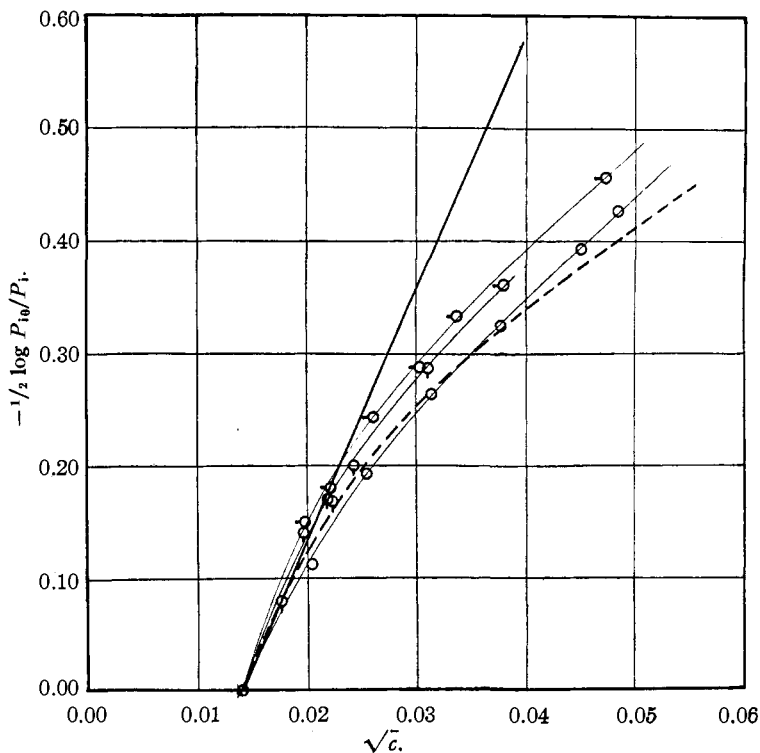

Fig. 1.—O, $KClO_4$ + $NaNO_3$; -O, $KClO_4$ + NH_4NO_3; ♀, $KClO_4$ + NaBr.
————, Limiting slope, Equation 1; – – –, Equation 2, $a = 9 \times 10^{-8}$.

case where in a solvent of much lower dielectric constant no such deviations are observed.   This is not the case, however, for with $a = 9 \times 10^{-8}$ the curve obtained from Equation 2 gives a somewhat better agreement with the experimental curves.   There is, however, a marked deviation at the higher concentrations.   This curve is shown in the figure.

Although the curves predicted by Equations 1 and 2 are very nearly alike in the concentration range studied, a study of more dilute solutions where they differ more should show which is the more reliable.   The experimental uncertainties make this very difficult.   An empirical relationship which seems to hold quite generally for non-aqueous solutions may

throw some light on the question.   This is that a very nearly linear rela-
tionship exists between the square root of the ion product and the square
root of the total concentration.   In Fig. 2 the solubilities of potassium
perchlorate (equal to $\sqrt{P_i}$ in mixtures without a common ion) have been
plotted against the square roots of the total salt concentrations in the
sodium nitrate mixtures.   The points are seen to lie on a straight line.
Extrapolation of this line to zero concentration gives a value of $0.625 \times$
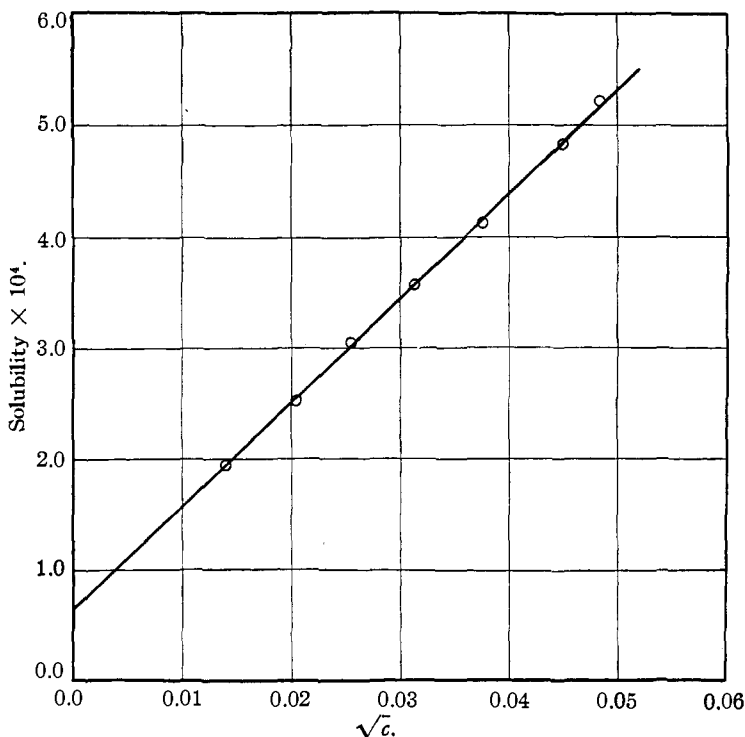10^{-4} for the hypothetical solubility of potassium perchlorate in a solution

Fig. 2.—Solubility of potassium perchlorate in the presence of sodium
nitrate.

of zero ionic strength.   From this value the value of $-\log f_0$ can be calcu-
lated and is found to be 0.488.   This is in much better agreement with the
value of 0.450, obtained for $-\log f$ from Equation 2, using $a = 9 \times 10^{-8}$,
than with the value 0.275 obtained from Equation 1 using $a = 9 \times 10^{-8}$.
The maximum value, with a equal to zero, obtainable from Equation 1 is
0.312.   With $a = 8.5 \times 10^{-8}$ in Equation 2 an almost exact check would
be obtained.

The changes of activity coefficients with concentration in more con-
centrated solutions may be calculated from the measurements of the solu-

bility of potassium nitrate. In Fig. 3 the values of $-\frac{1}{2} \log P_{i_0}/P_i$ have been plotted against the square roots of the total salt concentration. It is seen that even at these concentrations, up to 0.045 mole per liter, the effect of adding different salts, one with and the other without a common ion, is the same within the limit of experimental uncertainties. Since Equations 1 and 2 differ less at higher concentrations, the theoretical curve for Equation 1 only is shown and with an a value of 9.5×10^{-8} agrees well with the results of our experiments without the introduction of a term involving change of dielectric constant.
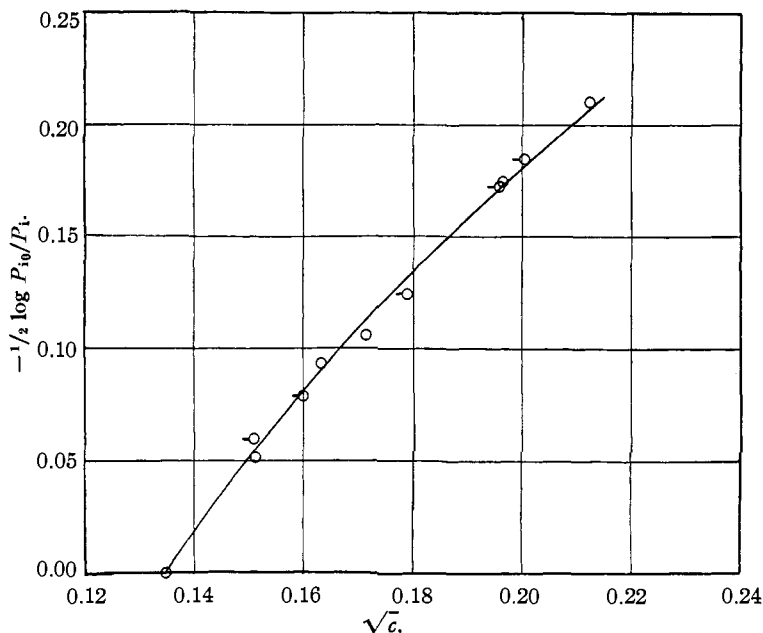

Fig. 3.—O, KNO₃ + NH₄NO₃; -O, KNO₃ + NH₄Cl. ——, Equation 1, $a = 9.5 \times 10^{-8}$.

The fact that the properties of solutions of the same salts in water and in other solvents may be explained by the interionic attraction theory when much smaller values for the ion diameters are employed indicates that the a values assumed for the acetic acid solutions cannot be the true ion diameters independent of solvation. That this is not peculiar to acetic acid solutions is indicated by some preliminary solubility measurements made by the authors in ethyl acetate, with about the same dielectric constant, where the curves were found to have an even smaller slope than those for the acetic acid solutions. Apparently some property of the solvent in addition to the dielectric constant is necessary in order to explain the properties of solutions of salts in it.

Summary

The solubilities of potassium perchlorate and potassium nitrate have been measured in the presence of several added salts in pure glacial acetic acid.

The observed solubilities agree with those predicted by the interionic attraction theory if a sufficiently large ion diameter is assumed.

An empirical relationship from which the value of the activity coefficient may be calculated has been pointed out.

A somewhat better agreement is obtained with the extended theory of Gronwall, La Mer and Sandved than with the original Debye–Hückel development.

It is concluded that explanation of the properties of salt solutions requires that other properties of the solvent in addition to its dielectric constant must be considered.

CAMBRIDGE, MASSACHUSETTS

THE VAPOR PRESSURES OF SATURATED AQUEOUS SOLUTIONS OF CERTAIN SALTS

BY H. W. FOOTE, BLAIR SAXTON AND J. K. DIXON

RECEIVED OCTOBER 7, 1931   PUBLISHED FEBRUARY 5, 1932

The literature of this subject has been summarized by Johnston and Leopold,[1] who pointed out, as have others, the difficulties of the usual static methods. One of the chief difficulties is in completely removing air from the saturated solution and another is in obtaining a solution for measurement which is neither supersaturated nor undersaturated. The above-mentioned writers found that equilibrium was established very slowly in their apparatus after removal of air by pumping, due presumably to difficulty in reaching complete saturation.

An apparatus which has been developed for another purpose has been found to avoid the difficulties mentioned above and to be suitable for determining the vapor pressure of saturated solutions from about 0° to somewhat above room temperature with an accuracy of approximately ±0.05 mm. The apparatus eliminates the error caused by air dissolved in the solution by forming the solution in the absence of air, and as the conditions are such that a saturated solution is formed very rapidly, equilibrium is established in a very short period of time.

Apparatus, Procedure and Materials

A diagram of the apparatus, not drawn to scale, is shown in Fig. 1. In its essentials, it consists of a bulb A, for holding the salt and solution, connected to the bulb B con-

---

[1] Johnston and Leopold, THIS JOURNAL, **49,** 1974 (1927).