THE VAPOR PRESSURES OF AQUEOUS SOLUTIONS OF LITHIUM NITRATE AND THE ACTIVITY COEFFICIENTS OF SOME ALKALI SALTS IN SOLUTIONS OF HIGH CONCENTRATION AT 25°

BY J. N. PEARCE AND A. F. NELSON

Of all the colligative properties of solutions none are more accessible to thermodynamic treatment than the lowering of the vapor pressure of the solvent. Further, the advantages offered by this method are that it can be employed isothermally, that the vapor pressure can be measured over the entire range of concentration from pure solvent to the saturated solution in contact with the solid salt, and that the activity of the solvent can be obtained directly from vapor pressure measurements. An accurate knowledge of the vapor pressures of solutions permits us to calculate the free energy of dilution and the activities of both the solute and the solvent. It affords also a very valuable method for testing the theories of concentrated solutions.

The best obtainable chemically pure lithium nitrate was repeatedly recrystallized from pure distilled water. The purified salt was then dissolved at room temperature to form a stock solution just short of saturation and stored in a tight glass-stoppered bottle. The exact concentration of this solution was determined by a series of determinations in which accurately weighed portions were converted to the sulfate and heated to constant weight. All of the solutions were first prepared on a molar basis by diluting accurately weighed portions of the mother solution to one liter at 25°. The various solutions were made up with conductivity water which had been distilled from an alkaline solution of potassium permanganate.

The density of each solution at 25° was accurately determined, at least in duplicate, by means of large 35-cc. Ostwald pycnometers, using a similar pycnometer for counterpoise. An accurately calibrated set of precision brass weights was used. All weighings were made on a large precision balance by the oscillation method and were corrected for the buoyancy of the air. The weights of the solution taken in these density measurements are accurate to one part in 300,000.

The apparatus and experimental procedure employed in this research were those devised by Pearce and Snow.[1] The vapor pressure apparatus, exclusive of the generators, preheater and absorber, was immersed in a large Freas water thermostat maintained at 25 ± 0.005°.

The actual calculation of the vapor pressure of the solvent over the solution requires the knowledge of three values only: the corrected barometric pressure, P, and the weight of water vapor, W_W, taken up by the phos-

[1] Pearce and Snow, *J Phys. Chem*, **31**, 231 (1927).

phorus pentoxide absorber while W_S grams of silver are being deposited in the coulometer. The number of moles of water vapor, n_1, and the total number of moles of hydrogen and oxygen, n_2, electrolytically generated are calculated from W_W and W_S, respectively. The vapor pressure of the solvent, p, is calculated directly from these data by means of the simple relation

$$P = \frac{n_1}{n_1 + n_2} P$$

The essential vapor pressure data for solutions of lithium nitrate are collected in Table I. Here m is the molality of the solution, d is the density and p is the vapor pressure. Each vapor pressure recorded is the mean of at least three independently determined values. Only in one case did the pressure differ from the mean by more than 0.003 mm. We are including also data previously obtained for solutions of potassium chloride,[1] potassium iodide,[2] sodium chloride,[3] sodium bromide[2] and lithium chloride.[4] The data for these are collected in Tables II to VI. The vapor pressure data for all of the salts are graphically represented in Figs. 1 and 2. For all of these salts (Fig. 1) the vapor pressure of the solvent diminishes rapidly with increasing concentration and finally attains the value characteristic of the saturated solution at 25°. It will be observed that the vapor pressure of the lithium chloride solution at saturation ($m = 19.2$)

TABLE I

THE VAPOR PRESSURE, ACTIVITY COEFFICIENT AND FREE ENERGY DATA FOR AQUEOUS SOLUTIONS OF LITHIUM NITRATE AT 25°

m	d	p, mm.	a_1	$\gamma_\pm$	$-\Delta \bar{F}_1$, cal.	$-\Delta \bar{F}_2^{0,\prime}$, cal.
0.00000	0.99707	23.752	1.000	1.000	...	..
.10058	1.00116	23.676	0.997	0.766	1.92	12
.20179	1.00494	23.593	.993	.726	3.98	772
.40594	1.01295	23.431	.986	.697	8.07	1548
.61264	1.02074	23.256	.979	.688	12.51	2026
.82194	1.02847	23.071	.971	.696	17.24	2388
1.0339	1.03616	22.882	.963	.718	22.12	2704
2.1115	1.07507	21.823	.919	.969	50.11	3899
3.3106	1.11303	20.518	.864	1.275	86.76	4757
4.5706	1.15094	19.028	.801	1.600	131.45	5396
5.9276	1.18825	17.481	.736	1.938	181.71	5924
7.3940	1.22515	15.843	.667	2.239	240.0	6378
8.9836	1.26183	14.128	.597	2.546	306.2	6776
10.7055	1.29886	12.403	.541	2.891	364.2	7100
11.8331	1.32024	11.359	.478	3.174	437.6	7353
12.8639[a]	1.33885	10.456	.442	3.415	484.1	7532

[a] Saturated.

[2] Pearce, Taylor and Bartlett, THIS JOURNAL. 50, 2951 (1928).
[3] Fred Fordemwalt, Master's thesis, Iowa.
[4] Donald Tilden, Master's thesis Iowa

is only a little more than one-half of the vapor pressure of pure water at $0°$. The relative positions of the vapor pressure curves and the relative magni-

TABLE II

THE VAPOR PRESSURE, ACTIVITY COEFFICIENT AND FREE ENERGY DATA FOR AQUEOUS SOLUTIONS OF POTASSIUM CHLORIDE at $25°$

m	p, mm.	a_1	$\gamma_\pm$	$-\Delta\overline{F}_1$, cal.	$-\Delta\overline{F}_2^{0,1}$, cal.
0.0	23.752	1.000	1.000	...	..
.2	23.597	0.993	0.708	3.88	733
.4	23.448	.988	.655	7.63	1463
.6	23.296	.981	.627	11.49	1892
.8	23.155	.975	.607	15.09	2195
1.0	23.017	.969	.595	18.63	2436
1.5	22.620	.952	.576	28.94	2878
2.0	22.243	.936	.536	38.90	3192
2.5	21.877	.921	.557	48.74	3444
3.0	21.497	.905	.557	59.13	3660
3.5	21.089	.888	.557	70.62	3843
4.0	20.696	.871	.564	81.64	4016
4.81[a]	20.021	.843	.576	101.29	4260

[a] Saturated.

TABLE III

THE VAPOR PRESSURE, ACTIVITY COEFFICIENT AND FREE ENERGY DATA FOR AQUEOUS SOLUTIONS OF POTASSIUM IODIDE AT $25°$

m	p, mm.	a_1	$\gamma_\pm$	$-\Delta\overline{F}_1$, cal.	$-\Delta\overline{F}_2^{0,1}$, cal.
0.0	23.752	1.000	1.000	...	..
.1	23.686	0.997	0.734	1.65	0
.2	23.620	.994	.666	3.30	707
.4	23.486	.988	.597	6.68	1399
.6	23.384	.983	.558	10.17	1799
.8	23.211	.976	.535	14.31	2091
1.0	23.072	.971	.519	17.22	2319
1.5	22.702	.957	.496	26.21	2746
2.0	22.316	.940	.483	36.97	3062
2.5	21.922	.923	.479	47.52	3311
3.0	21.516	.906	.480	59.60	3526
3.5	21.100	.888	.486	70.17	3727
4.0	20.681	.871	.492	82.07	3900
4.5	20.253	.853	.498	94.52	4054
5.0	19.822	.834	.511	107.2	4209
5.5	19.392	.816	.546	120.0	4401
6.0	18.966	.799	.577	133.4	4569
6.5	18.529	.780	.608	147.2	4726
7.0	18.082	.761	.644	161.7	4883
7.5	17.635	.742	.680	176.5	5029
8.0	17.190	.724	.709	191.6	5155
8.5	16.750	.705	.748	207.1	5290
8.938[a]	16.370	.689	.783	220.6	5404

[a] Saturated.

TABLE IV

THE VAPOR PRESSURE, ACTIVITY COEFFICIENT AND FREE ENERGY DATA FOR AQUEOUS
SOLUTIONS OF SODIUM CHLORIDE AT 25°

m	p, mm.	a_1	$\gamma_\pm$	$-\Delta\bar{F_1}$, cal.	$-\Delta\bar{F_2}^{0.1}$, cal.
0.0	23.752	1.000	1.000	...	..
.2	23.594	0.992	0.732	4.74	782
.4	23.444	.987	.659	7.74	1480
.6	23.286	.980	.641	11.77	1928
.8	23.127	.974	.633	15.70	2254
1.0	22.969	.969	.630	18.74	2513
1.5	22.560	.949	.638	31.28	3009
2.0	22.134	.930	.657	43.11	3385
2.5	21.692	.914	.721	53.04	3759
3.0	21.227	.894	.788	66.71	4081
3.5	20.733	.868	.862	83.81	4370
4.0	20.210	.850	.944	96.38	4636
4.5	19.677	.828	1.087	111.6	4943
5.0	19.135	.803	1.136	129.9	5120
5.5	18.576	.782	1.182	145.7	5281
6.0	17.990	.758	1.238	164.7	5439
6.138[a]	17.825	.704	1.372	208.2	5587

[a] Saturated.

tudes of the vapor pressures at any given concentration are characteristic of the individual salts, as will be discussed later.

The plots of the fractional lowering of the vapor pressure against the molal concentrations of these uni-univalent salts are shown in Fig. 2. Theoretically, the fractional lowering of the vapor pressure of the solvent of an ideal solution is equal to the mole fraction of the solute. For non-electrolytes

$$\frac{p_0 - p}{p_0} = \frac{n_2}{n_1 + n_2}$$

If we assume complete dissociation of these binary salts, and if the ions behave as perfect solutes, the fractional lowering should be given by

$$\frac{p_0 - p}{p_0} = \frac{2n_2}{n_1 + 2n_2}$$

Here n_1 is the number of moles of water and $2n_2$ is the number of moles of ions from n_2 moles of the binary salt. If then, to repeat, we assume that the salts are completely dissociated and that their ions form perfect solutes, the curves representing the fractional lowering of the vapor pressure with the concentration of the salts should coincide exactly with the mole fraction–molality curve. While it is already a well-known fact, it is also very evident from Fig. 2 that solutions of these salts are far from ideal. While other causes may be effective, the position and slopes of these curves, especially in the more concentrated solutions, show, perhaps more than anything else, the rate of change in the apparent mole fraction of the water actually present as solvent.

TABLE V

THE VAPOR PRESSURE, ACTIVITY COEFFICIENT AND FREE ENERGY DATA FOR AQUEOUS
SOLUTIONS OF SODIUM BROMIDE AT 25°

m	p, mm.	a_1	$\gamma_\pm$	$-\Delta\bar{F}_1$, cal.	$-\Delta\bar{F}_2^{0,1}$, cal.
0.0	23.752	1.000	1.000	. . .	. .
.1	23.675	0.997	0.739	1.92	0
.2	23.608	.994	.693	3.60	746
.4	23.448	.987	.643	7.63	1479
.6	23.292	.981	.628	11.59	1932
.8	23.136	.974	.611	15.58	2240
1.0	22.973	.967	.607	19.77	2499
1.5	22.556	.950	.598	30.56	2960
2.0	22.128	.932	.633	41.98	3369
2.5	21.670	.912	.715	54.38	3778
3.0	21.181	.892	.812	67.90	4145
3.5	20.655	.870	.924	82.81	4481
4.0	20.094	.848	1.036	99.14	4775
4.5	19.501	.821	1.203	116.9	5092
5.0	18.876	.795	1.374	136.2	5374
5.5	18.242	.768	1.565	156.5	5641
6.0	17.603	.741	1.762	177.6	5885
6.5	16.934	.713	2.010	200.6	6136
7.0	16.234	.682	2.291	225.6	6379
7.5	15.570	.656	2.594	250.3	6607
8.0	14.888	.627	2.951	276.9	6838
8.5	14.231	.599	3.348	303.6	7059
9.0	13.582	.572	3.784	331.3	7277
9.131[a]	13.409	.565	3.895	338.9	7324

[a] Saturated.

It has been shown[5] long ago that the hydrating power of a salt in solution is primarily a function of the cation, that the hydration of an ion is an inverse function of its volume, and that the magnitude of hydration of the ions is a periodic function of the atomic weights. It is interesting to note, Fig. 2, that the curves for the fractional lowering of the vapor pressure produced by the two potassium salts are practically superimposed, the one on the other. Just above them lie the curves for the two sodium salts; the fractional lowering produced by the sodium bromide is at all concentrations greater than that for the corresponding solutions of sodium chloride. Of the two, sodium bromide exhibits the greater hydrating power. Still higher on the plot lie the curves for the lithium salts with the most highly hydrated lithium chloride on top.

The order of increasing fractional lowering of the vapor pressure of water produced by the different salts at any one concentration is exactly that to be predicted on the basis of the hydrate theory. In the hydration of the ions part of the water molecules are removed from the field of action as solvent.

[5] Jones and Pearce, *Am. Chem. J.*, **38**, 683 (1907); see also Washburn and Millard THIS JOURNAL, **37**, 694 (1915).

TABLE VI

THE VAPOR PRESSURE, ACTIVITY COEFFICIENT AND FREE ENERGY DATA FOR AQUEOUS
SOLUTIONS OF LITHIUM CHLORIDE AT 25°

m	p, mm.	a_1	$\gamma_\pm$	$-\Delta\bar{F}_1$, cal.	$-\Delta\bar{F}_2^0$, cal.
0.0	23.752	1.000	1.000	....	....
.1004	23.724	0.999	0.755	0.70	3
.2185	23.633	.995	.710	2.98	853
.4040	23.492	.989	.678	6.53	1527
.6082	23.349	.983	.678	10.14	2012
.8142	23.166	.975	.689	14.80	2377
1.0216	22.992	.968	.711	19.28	2683
1.5471	22.399	.943	.895	34.76	3448
2.0845	21.751	.916	1.155	52.17	3583
2.6327	21.110	.889	1.457	69.90	4656
3.1940	20.370	.858	1.827	91.05	5154
3.7687	19.594	.825	2.284	114.1	5615
4.3576	18.787	.791	2.849	139.0	6049
4.9582	17.687	.745	3.550	174.8	6450
5.5749	16.574	.697	4.467	213.3	6875
6.2074	15.592	.657	5.472	249.4	7243
6.8567	14.562	.613	6.713	290.0	7603
7.5199	13.337	.562	8.180	342.1	7947
8.2002	12.274	:517	9.986	391.3	8286
9.6109	10.260	.432	14.545	497.5	8920
11.0955	8.046	.339	19.972	641.7	9467
12.6577	6.388	.269		778.6	
14.3221	5.054	.214		915.0	
16.0508	4.003	.168		1055.7	
17.8635	3.203	.135		1187.8	
19.2186^a	2.770	.117		1273.8	

^{a} Saturated.

According to the Mass Law, the hydration per single ion should be greatest in the most dilute solutions and it should decrease in magnitude as the concentration of the ions is increased. In spite of this decrease in the magnitude of ionic hydration with increase in concentration, the total amount of water removed from the field of solvent by hydration should be greatest in the most concentrated solution. The greater the number of molecules taken up as hydrate water, the greater will be the decrease in the effective value of n_1, and, correspondingly, the greater will be the mole fraction of the solute. It follows, therefore, that if the value of the mole fraction of the solute is thus abnormally increased by the formation of hydrates in the solution, the fractional lowering of the vapor pressure will be increased correspondingly. This is fully borne out by the relative positions and slopes of the curves in Fig. 2.

There is still another way of explaining the abnormally high fractional lowering of the vapor pressure produced by these salts. According to the present views, strong electrolytes in aqueous solution are completely, or

practically completely, dissociated at all concentrations. All deviations of the colligative properties of these solutions from the behavior demanded by the classical theory are considered to be due to the influence of interionic attraction.[6] Because of the electrical attraction between the positive and negative ions, there are on an average in the neighborhood of any given ion more ions of unlike than of like sign. Consequently, with increase in concentration of the ions accompanying the addition of the salt the attraction between the ions will increase and will attain a maximum value at
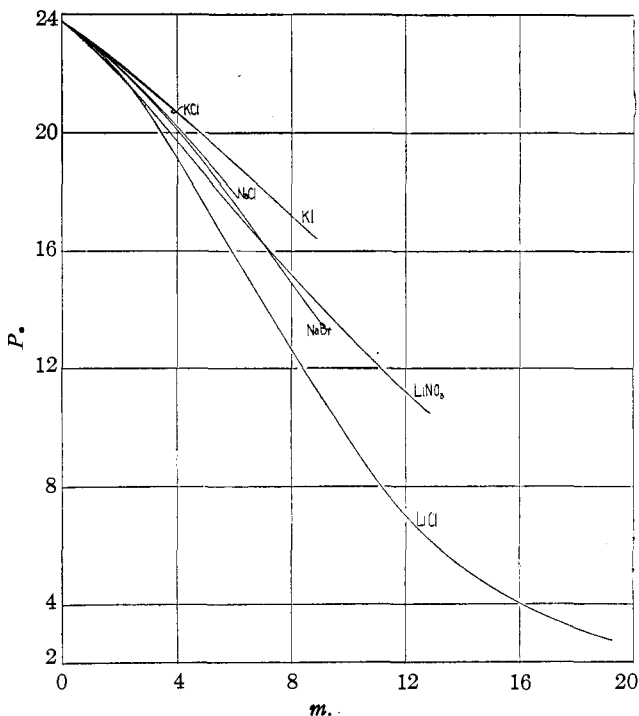
Fig. 1.

saturation. At saturation when the ions are at their closest approach they will assume, doubtless, within the solvent a more or less mobile, lattice-like structure. Further, the molecules of the polar solvents possess a dipole structure. Hence, if we consider the ions in solution as point charges, the molecules of the solvent will not be unaffected by the presence of the strong electric fields of the ions. Some of the dipole water molecules will be attracted to and oriented by the electrically charged ions. Because of this attraction and orientation these molecules will lose a part, if not all, of their characteristic fugacity. Hence, the vapor pressure of the solution will be less than it would be if no such attraction existed. It is obvious, therefore,

    6 Debye and Hückel, *Physik. Z.*, **24**, 185 (1923).

that with increasing concentration of the ions the number of water dipoles thus affected and removed from the field of solvent as such will be increased. At saturation the concentration of the ions, and hence the attractive influence of their charges, is fixed. The system becomes invariant and the vapor pressure is constant for a given temperature. The ultimate effect will be the same as that which would be produced by ionic hydration in the ordinary sense.
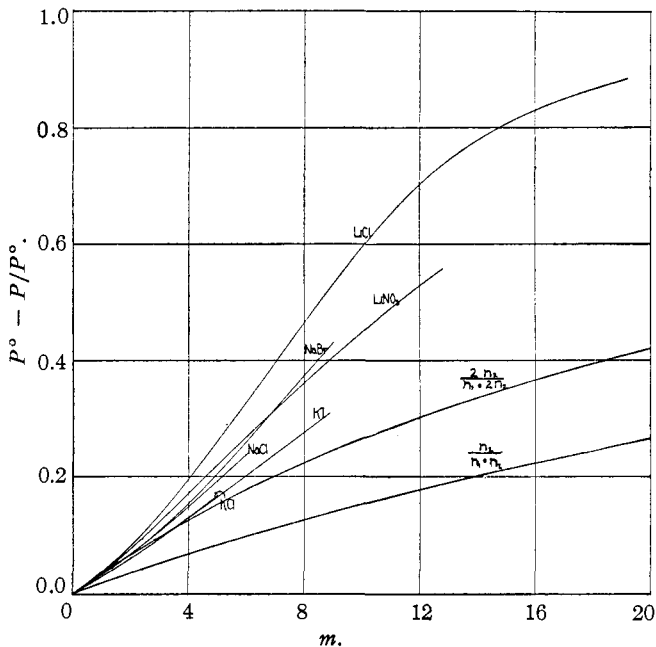

Fig. 2.

In this discussion we have assumed that the univalent ions of smaller ionic volume will have the greater charge densities. For this reason they will attract and orient a greater number of water dipoles than will the univalent ions of large ionic volume. The relative positions of the mole fraction–molality curves for these salts must, therefore, be the same as those described above.

The above considerations apply equally well in explaining the positions of the vapor pressure curves of the various solutions, Fig. 1. As we might expect, the positions of the vapor pressure–molality curves assume an order exactly the reverse of that taken by those for the fractional lowering. Briefly stated, the greater the degree of hydration of the ions of a salt at a given concentration, the smaller will be the amount of water present as solvent and, hence, the lower will be the vapor pressure of the solution. It would seem to follow, therefore, that any theory of interionic attraction

must take into account the influence of the solvent dipoles which, in their attraction by the charged ions, must modify to some degree the attraction between the ions themselves.

At all concentrations above 4 m the fractional lowering of the vapor pressure produced by these salts is greater than that calculated for the completely dissociated salt. At the lower concentrations, however, the fractional lowering curves appear to lie slightly below the theoretical curve. The concentrations at which the two intersect extend to higher concentrations as the hydrating power of the ions increases.

The activity of the solvent has been calculated by means of the series relation[7]

$$\ln a_1 = - \left(\frac{p_0 - p}{p_0}\right) - \frac{1}{2}\left(\frac{p_0 - p}{p_0}\right)^2 - \frac{1}{3}\left(\frac{p_0 - p}{p_0}\right)^3 \cdots$$

In very dilute solutions only the first term is of any significance, but more terms must be added as the concentration is increased. In our calculations of $\ln a_1$ terms have been added until the effect of an additional term becomes negligible.

The activity coefficients of the ions, $\gamma_{\pm}$, were calculated by means of the relation of Randall and White[8]

$$\ln y_{\pm} = - \frac{h}{2.303} - \frac{2}{2.303} \int_0^{m^{1/2}} \frac{h}{m^{1/2}} \, dm^{1/2}$$

where $h = 1 + 55.51 \ln a_1/vm$, and v is the number of ions formed from one molecule.
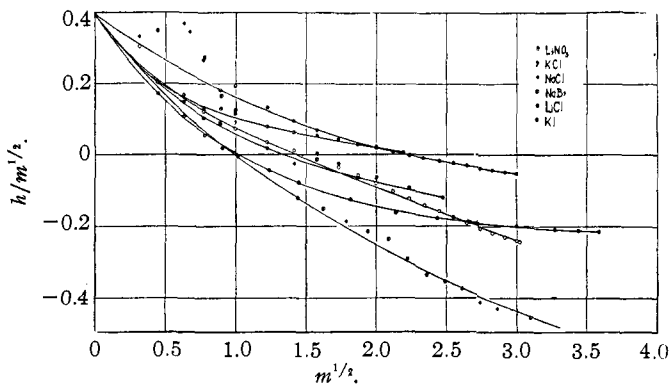

Fig. 3.

The value of h was calculated for each concentration and the values of $h/m^{1/2}$ were then plotted against the square roots of the corresponding molalities. A smooth curve, Fig. 3, was then drawn through the points to

[7] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York, 1923, p. 274.

[8] Randall and White, THIS JOURNAL, 48, 2514 (1926).

the limiting value[9] of $h/m^{1/2}$ (0.394) for $m = 0$ at 25°.   The integral in the equation is the area under the curve.   This was measured by means of a polar planimeter.

The activity coefficients calculated in this manner have been plotted against the square roots of the corresponding concentrations, Fig. 4.   For the sake of convenience in plotting, five of the curves have been displaced upward successively by increments of 0.025.   For each salt the values of the activity coefficients pass through a minimum value and then rise more or less rapidly with increase in concentration of the salt.   Here again we observe that the increase in the value of the activity coefficients at the
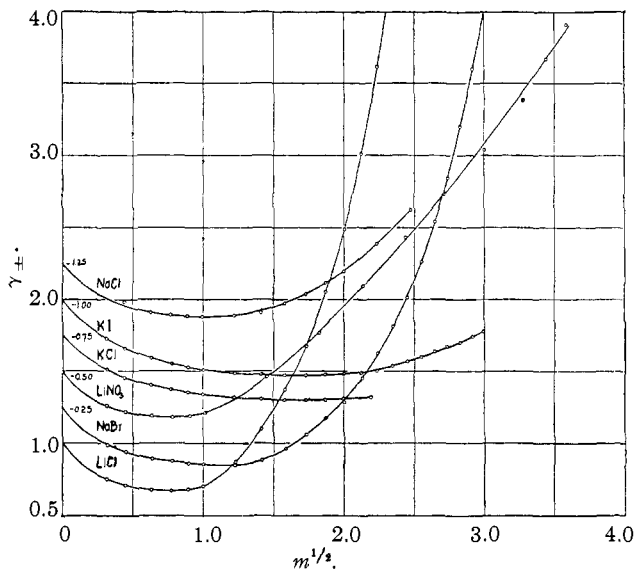

Fig. 4.

higher concentrations is the most rapid for those salts which are the most highly hydrated in solution.   The curves for the slightly hydrated potassium salts are practically superimposed the one on the other.   Owing to the sensitivity of the h function to slight errors, the values of the activity coefficients of lithium chloride above 11.0 m have not been included.   It is needless to say that they are very high.

Alluring as it might be, any attempt to apply the Debye–Hückel equation,[6] or any of its subsequent modifications, to solutions of the concentrations here used would be futile indeed.

The accuracy attainable by our vapor pressure method is to be seen by a comparison of the activity coefficients of potassium chloride determined by different methods, Table VII.   The values given by Randall and White[8]

⁹ Randall, THIS JOURNAL, 48, 2512 (1926).

TABLE VII

A COMPARISON OF THE ACTIVITY COEFFICIENTS OF POTASSIUM CHLORIDE OBTAINED BY DIFFERENT METHODS

m	V. p. (R.-W.)[10]	F. p. (Harned)[11]	E. m. f. (Harned)[12]	V. p. (P.-S.)[1]
0.001		0.965	0.965	0.965
.005		.926	.926	.926
.010		.899	.899	.900
.050		.809	.815	.813
.100	0.772	.762	.764	.763
.200	.715		.712	.708
.500	.651		.644	.638
1.000	.651		.597	.595
1.500			.576	.576
2.000	.570		.569	.563
2.500			.568	.557
3.000			.571	.557
3.500			.571	.557
4.000			.581	.564
4.810				.574

are calculated from the vapor pressure data of Frazer, Lovelace and Sease[10] at 20°. The data for freezing point[11] and electromotive[12] force methods are taken from compilations by Harned. For comparable concentrations the agreement is excellent indeed.

The free energy change involved in the transfer of one mole of water from the pure solvent to a solution of any molality m is given by $-\Delta F_1 = RT \ln 1/a_1$. These values have been calculated for each series of salt solutions and are to be found in the next to the last column of Tables I to VI. The values given in the last column in each table represent the change in free energy accompanying the transfer of one mole of solute from a solution of molality m to one which is exactly 0.1 m. Here again we find that for any given concentration the values of $-\Delta F_1$ and $-\Delta \overline{F}_2^{0.1}$ are always greater, the greater the hydrating power of the dissolved salt.

Summary

The vapor pressures of aqueous solutions of lithium nitrate and five alkali halides have been determined at 25° for concentrations ranging from 0.1 m up to saturation.

From these data there have been calculated the activity of the solvent, the geometric mean activity coefficients of the ions, and the free energy changes accompanying the transfer of solute and solvent.

[10] Frazer, Lovelace and Sease, THIS JOURNAL, **43**, 102 (1921).

[11] Harned, in Taylor, "A Treatise on Physical Chemistry," D. Van Nostrand Co., New York, 1931, p. 769.

[12] Harned, *ibid.*, p. 772.

A theoretical discussion of the vapor pressure relations of the various salts has been given.

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THE ALDEHYDE BISULFITE COMPOUNDS. II. THE EFFECT OF VARYING HYDROGEN ION AND OF VARYING TEMPERATURE UPON THE EQUILIBRIUM BETWEEN BENZALDEHYDE AND BISULFITE ION

By T. D. Stewart and L. H. Donnally

Elsewhere we have shown[1] that the specific rate of dissociation of benzaldehyde bisulfite

$$C_6H_5CH(OH)SO_3^- \longrightarrow C_6H_5CHO + HSO_3^- \qquad (1)$$

increases rapidly as the hydrogen-ion concentration is decreased from (H^+) 10^{-2} to 10^{-7}. Since the equilibrium at $(H^+) = 10^{-7}$ is still in favor of the bisulfite compound, the reverse of Reaction 1 is evidently even faster. Therefore it is not possible to use an ordinary titration method for the determination of the amounts of the substances in equilibrium. The method developed is as follows.

Experiment.—Benzaldehyde which had been distilled in an atmosphere of nitrogen was added mole per mole to c. p. sodium bisulfite. Distilled water which had been boiled and saturated with nitrogen was added and the reaction allowed to go to completion. All water used was boiled and saturated with nitrogen to expel both carbon dioxide and oxygen. The salt thus obtained was washed four times with water and finally dissolved in water to make an approximately 1 M solution of sodium benzaldehyde bisulfite; 5 cc. of this solution was diluted for each determination to one liter, making the initial concentration of benzaldehyde bisulfite about 0.005 M. These solutions were allowed to stand in the thermostat to reach equilibrium.

Except for determinations at P_H 1 and 13 where solutions of 1 N hydrochloric acid and 0.1 N sodium hydroxide were used, buffer solutions of standard or measured P_H values were employed for the dilution. In the range P_H 1.5 to 3 and P_H 6 to 7.5 a phosphate buffer, and P_H 1.5 to 3 and P_H 6, acetate buffer solutions were used, the acidities of which were determined against standard buffer solutions with a glass electrode. From P_H 9 to 12 Sörensen standard borate buffer solutions were used. For the phosphate and acetate buffer solutions it was determined by means of a glass electrode that the bisulfite compound, benzaldehyde and bisulfite ion in equilibrium had a negligible effect on the P_H values of the solution. With the borate buffer a hydrogen electrode was used for this purpose. In this case because of the doubtful effect of bisulfite on the electrode benzaldehyde alone of the constituents was used. A negligible effect was found.

Analysis.—Since the dissociation reaction is slow at P_H 2, the determination of ionic sulfite in equilibrium in the buffer solutions was made by rapidly acidifying the solution and simultaneously adding iodine in slight excess of the ionic sulfite. For this purpose an amount of 1 N hydrochloric acid sufficient to acidify the particular buffer

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[1] Stewart and Donnally, This Journal, 54, 2333 (1932).