[Contribution from the Physical Chemistry Laboratory of the State University of Iowa]

THE VAPOR PRESSURES OF AQUEOUS SOLUTIONS OF POTASSIUM IODIDE AND SODIUM BROMIDE AT 25°[1]

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In the study of the colligative properties of solutions use has been made of methods involving the lowering of the freezing point, the lowering of the vapor pressure and the elevation of the boiling point of the solvent by the solute, and the application of electromotive-force methods. Because of the ease and the accuracy of the measurements, most of the work hitherto has been confined to the freezing point and electrometric methods. Of all of the properties of solutions, however, none are more accessible to thermodynamic treatment than the vapor pressure. While the vapor pressure method is free from all of the disadvantages, and in addition possesses many advantages over the others named, chiefly in that it can be used at any temperature, the results obtained have not been all that could be desired.

Four general methods have been employed for measuring the vapor pressures of solvents and solutions: (1) static, (2) indirect, (3) differential and (4) dynamic. The principles involved and the difficulties met with in their application have been discussed in a previous paper.[2] Of these the most convenient and rapid is the dynamic, or air-saturation method; moreover, it is based on a simple application of Dalton's Law of partial pressures. The essential features of the method as commonly used are: (1) a measured volume of air is saturated with vapor by passing it over the surface of, or bubbling it through the liquid contained in the saturator; (2) the weight of the solvent evaporated is determined by the loss in weight of the saturator, or by the gain in weight of the absorber which removes the solvent vapor from the effluent air; (3) the total pressure exerted by the gaseous mixture in contact with the liquid is obtained from barometer and manometer readings. From the data thus obtained the vapor pressure of the solvent may be calculated.

A survey of the vapor pressure data obtained by the dynamic method shows not only a wide variation in the values reported by different investigators for a single liquid, but also very frequently a considerable variation in the data given by a single investigator. The chief reasons for these deviations are few, but they have been difficult to overcome. The Earl of Berkeley and Hartley[3] have concluded that the failure of the original Walker-Ostwald method is due to variations in the hydrostatic pressure in the several vessels. They also suggest that liquid spray is carried mechanically

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[1] In memory of Ira Remsen.

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

[3] Earl of Berkeley and Hartley, *Proc. Roy. Soc.*, **77**, 156 (1906).

from the solution to the pure solvent. Attempts to eliminate both of these sources of error have been made by a number of men.[2] Another difficulty is our inability to measure accurately, and at the same time conveniently, the large volume of air required for a single determination. The error thus introduced will be greater or less, depending upon the magnitude of the vapor pressure of the liquid studied. Owing to the surface film effect any form of apparatus which requires the passing of air over the surface of the solvent or solution must present a large liquid surface. Moreover, the surface should be in constant motion. Forms of apparatus involving the bubbling of air through the liquid are obviously more compact, but they introduce error for the reason that while a bubble may be saturated with vapor in the depth of the liquid, it will expand on rising and may leave the surface without becoming entirely saturated. Again, the mathematical formulas which have been used heretofore are often highly complicated; slight errors of observation are highly magnified in calculating the vapor pressures.

Pearce and Snow[2] have devised a rapid method which apparently eliminates all of the previous sources of error. The method introduces the following new features. Instead of measuring the volume of air which passes through the solution, hydrogen and oxygen are generated electrolytically and the volume of the mixed gases, as well as the number of moles of each, is calculated from the weight of silver deposited in a coulometer. The actual calculation of the vapor pressure requires the knowledge of three values only: the corrected barometric pressure, P, and the weight of vapor, W_W, taken up by the P_2O_5-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 generated, n_2, are calculated from W_W and W_S, respectively. From these data the vapor pressure of the solvent can be calculated by means of the simple relation $p = [n_1/(n_1 + n_2)]P$.

Experimental Results

The experimental procedure is described in detail in the previous paper.[2] It need only be said that the utmost care was taken to insure purity in all materials used. The pure "Analyzed" salts were repeatedly crystallized from conductivity water distilled from a large still containing a strong alkaline solution of potassium permanganate. The solutions were accurately made up on the weight molal basis. The entire vapor pressure apparatus, except for the generators, preheaters and absorbers, was immersed in a large Freas water thermostat maintained at 25 ± 0.01° throughout the two-hour run.

The essential data are given in Tables I and II. Each vapor pressure value is the mean of at least three independently determined values which do not differ over all by more than a few 0.001 mm. The symbols used at the top of each column are self-explanatory.

TABLE I

VAPOR PRESSURE DATA FOR AQUEOUS SOLUTIONS OF SODIUM BROMIDE AT 25° (R.M.B.)

M	p, mm.	p_0-p, mm.	$(p_0-p)/p_0$	P, atm.	a_1	a_1/N_1	$\gamma_2\pm$	$-\Delta F_1$, cal.	$-\Delta F_2$, cal.	$-\Delta F_2^{0.1}$, cal.
0.0	23.752	...	....	....	1.000	1.000	1.000	....	....	..
.1	23.675	0.077	0.003241	4.42	0.997	0.999	0.782	1.92	−3020	0000
.2	23.608	.144	.006062	8.27	.994	.997	.752	3.77	−2246	773
.4	23.448	.304	.012799	17.53	.987	.994	.731	7.68	−1457	1562
.6	23.292	.460	.019360	26.57	.980	.992	.724	11.71	− 987	2032
.8	23.136	.616	.025935	35.70	.972	.986	.711	15.65	− 657	2362
1.0	22.973	.779	.032798	45.37	.968	.985	(.697)	19.49	− 428	2592
1.5	22.556	1.196	.050353	70.15	.948	.973	.721	31.35	+ 94	3114
2.0	22.128	1.624	.068373	96.03	.929	.962	.754	43.68	+ 488	3508
2.5	21.670	2.082	.087656	124.37	.919	.960	.794	56.55	724	3744
3.0	21.181	2.571	.10824	155.21	.886	.934	.863	71.96	1125	4145
3.5	20.655	3.097	.13039	189.17	.861	.915	.943	88.89	1416	4436
4.0	20.094	3.658	.15401	226.25	.836	.896	1.020	105.87	1662	4682
4.5	19.501	4.251	.17902	266.59	.804	.889	1.170	129.24	1967	4987
5.0	18.876	4.876	.20524	309.60	.772	.841	1.329	153.04	2244	5264
5.5	18.242	5.510	.23202	356.11	.739	.812	1.528	179.07	2524	5544
6.0	17.603	6.149	.25888	403.83	.706	.782	1.740	206.35	2735	5755
6.5	16.934	6.818	.28705	455.54	.667	.745	2.086	240.65	3091	6111
7.0	16.234	7.518	.31652	511.77	.629	.708	2.443	274.25	3366	6386
7.5	15.570	8.182	.34448	567.28	.591	.671	2.911	311.28	3655	6675
8.0	14.888	8.864	.37319	626.70	.551	.630	3.500	352.96	3950	6970
8.5	14.231	9.521	.40081	686.28	.512	.590	4.224	396.52	4245	7265
9.0	13.582	10.170	.42817	747.97	.473	.550	5.111	442.77	4539	7559
9.131[a]	13.409	10.343	.43546	764.85	.462	.538	5.432	457.21	4626	7646

[a] Saturated.

TABLE II

VAPOR PRESSURE DATA FOR AQUEOUS SOLUTIONS OF POTASSIUM IODIDE AT 25° (M.D.T.)

M	p, mm.	p_1-p, mm.	$(p_0-p)/p_0$	P, atm.	a_1	a_1/N_1	$\gamma_2\pm$	$-\Delta F_1$, cal.	$-\Delta F_2$, cal.	$-\Delta F_2^{0.1}$, cal.
0.0	23.752	...	....	....	1.000	1.000	1.000	....	....	..
.1	23.686	0.066	0.002778	3.85	0.997	0.999	0.917?	1.65	−2819	0000
.2	23.620	.132	.005557	7.58	.994	.998	.813?	3.31	−2153	266
.4	23.486	.266	.011199	15.31	.988	.996	.740	6.71	−2443	1376
.6	23.348	.404	.017009	23.32	.983	.996	.687	10.10	−1051	1768
.8	23.211	.541	.02385	31.31	.977	.991	.662	13.82	− 753	2065
1.0	23.072	.680	.02863	39.46	.971	.988	(.649)	17.47	− 512	2306
1.5	22.702	1.050	.04421	61.31	.955	.980	.633	27.42	− 61	2758
2.0	22.316	1.436	.06046	84.42	.938	.972	.623	38.15	+ 261	3080
2.5	21.922	1.830	.07704	108.74	.920	.961	.639	49.48	556	3375
3.0	21.516	2.236	.09414	134.02	.901	.950	.656	61.60	803	3622
3.5	21.100	2.652	.11165	160.40	.882	.937	.678	74.50	1024	3854
4.0	20.681	3.071	.12929	187.46	.862	.924	.707	88.02	1232	4051
4.5	20.253	3.499	.14731	215.66	.841	.909	.732	102.41	1413	4232
5.0	19.822	3.930	.16546	244.61	.820	.894	.765	117.53	1591	4409
5.5	19.392	4.360	.18356	274.10	.798	.878	.800	133.28	1756	4576
6.0	18.966	4.786	.20150	303.93	.777	.861	.839	149.59	1816	4635
6.5	18.529	5.223	.21990	335.19	.754	.843	.868	167.10	2051	4870
7.0	18.082	5.670	.23872	367.90	.731	.823	.937	185.89	2230	5049
7.5	17.635	6.117	.25754	401.39	.707	.802	.993	205.62	2381	5199
8.0	17.190	6.562	.27627	435.52	.683	.781	1.049	226.29	2528	5347
8.5	16.750	7.002	.29480	470.11	.658	.759	1.120	247.82	2672	5491
8.938[a]	16.370	7.382	.31079	500.67	.637	.739	1.180	267.32	2793	5512

[a] Saturated.

In the present paper we intend only to show briefly the results obtained in the study of two salt solutions by the new dynamic method recently devised in this Laboratory. The general discussion of the theories involved will be left for a later paper.

The change in the vapor pressure, p, and in the fractional lowering $(p_0 - p)/p_0$ with increasing concentration, are shown graphically in Fig. 1. These curves show at once the influence of hydration upon the vapor pressure of solutions. The p-curve for sodium bromide is at all concentrations below that for potassium iodide; its curvature toward the concentration axis becomes more and more pronounced as the concentration increases. On the other hand, the curve for the fractional lowering, $(p_0 - p)/p_0$, produced by the sodium bromide lies at all concentrations above that given for potassium iodide. Solutions formed by such salts are far from ideal solutions; the positions and the slopes of the $(p_0 - p)/p_0$ curves show, perhaps more than anything else, the rate of change in the apparent mole fraction of the water actually present as solvent. Lewis defines an ideal solution as one which obeys Raoult's law at all concentrations and pressures, that is, $(p_0 - p)/p_0 = n/(N + n)$. A plot of the mole fraction

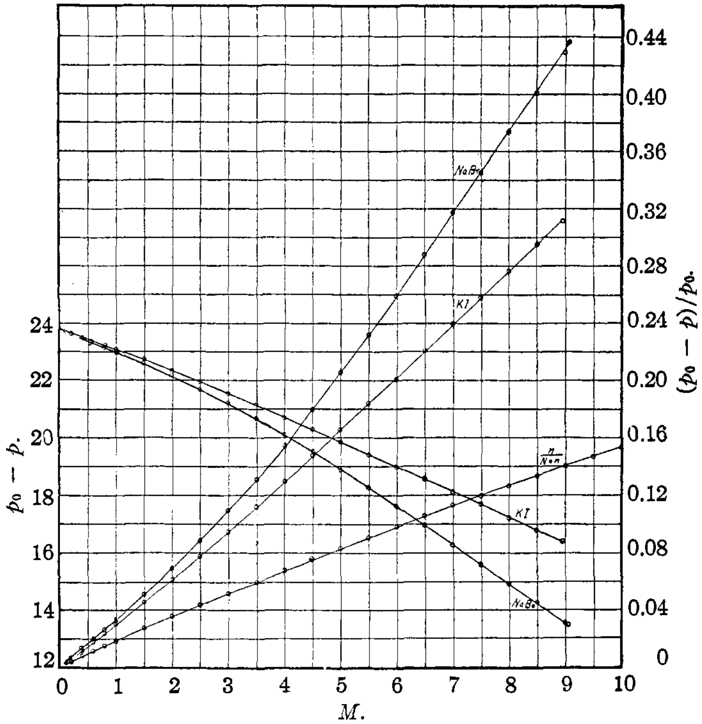

Fig. 1.

of the solute against the corresponding molalities should give us graphically the change in the fractional lowering with increase in concentration for an ideal solution. Such a plot is included in Fig. 1. As should be expected the curve shows a slight bend toward the concentration axis as the concentration increases.

The vapor pressures of solutions give us immediately a means of calculating osmotic pressures. The theories and the relations involved in the consideration of osmotic pressure have been most admirably discussed in a recent paper by Bancroft and Davis.[4] Of the many relations which have been suggested for calculating osmotic pressure from vapor pressure data, we shall mention only two for the present. The first is the one presented by Fraser,[5]

$$p_1 = \frac{RT}{V_0} \ln \frac{p_0}{p} \tag{1}$$

In this V_0 is the volume of one mole of the solvent, which, as we have used it, is the volume occupied by 18.016 g. of water at 25°. Fraser states that this is an exact expression even at large concentrations, provided the perfect gas laws apply to the vapor and the effect of pressure on the molal volume V_0 is negligible.

By thermodynamic means Lewis has derived a relation which holds more rigidly over a very wide range of concentration, namely

$$P - \frac{\beta}{2} P_2 = \frac{RT}{V_0} \ln \frac{p_0}{p} \tag{2}$$

Here β is the coefficient of compressibility of the water and V_0 is the molecular volume as before. For small values of P the effect due to the compressibility term vanishes and (2) becomes equivalent to (1). We have calculated the osmotic pressures by both equations. Within limits of error the osmotic pressures by the two formulas agree to within 0.01 atm. up to 0.8 M, but from this point on they begin to diverge. At saturation the value of P (1) for sodium bromide is 13.3 atm. greater than for P by (2); P by (1) for potassium iodide is 5.27 atm. greater than that calculated by (2). For the sake of brevity we are inserting only those osmotic pressures calculated by (2). The value of β for water at 25° was interpolated from compressibility data[6] at 20° and 30°.

The vapor pressure apparatus used makes possible the rapid determination of thermodynamic data. The activity of the solvent α_1 in a solution may be calculated from the fractional lowering of the vapor pressure by means of the series relation.[7]

[4] Bancroft and Davis, *J. Phys. Chem.*, **32,** 1 (1928).

[5] Taylor, "Treatise on Physical Chemistry," D. Van Nostrand Company, Inc., New York, **1924,** p. 275.

[6] "International Critical Tables," Vol. III, p. 40.

[7] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, **1923,** p. 274.

$$\ln \alpha_1 = -\frac{p_0 - p}{p_0} - \left(\frac{p_0 - p}{p_0}\right)_2 - \left(\frac{p_0 - p}{p_0}\right)_3 - \ldots$$

In very dilute solutions only the first term is of importance; in making our calculations of α_1 other terms were added until the influence of an added term became negligibly small. The values of α_1 and α_2/N_1 are given in Cols. 6 and 7, Tables I and II. For pure water $\alpha_1/N_1 = 1$ and the departure of α_1/N_1 from unity is the measure of the variation from a perfect solution.

Further, to calculate the activities of the solute α_2 and from these the activity coefficients, $\gamma\pm$, we made use of the thermodynamic relation

$$\int d \ln \alpha_2 = -\int \frac{N_1}{N_2} d \ln \alpha_1$$

To this end we plotted the values of N_1/N_2 against log α_2 and from the area under the curve, measured by means of a planimeter, determined the difference between the values of log α_2 at given different concentrations and the value of log α_2 for a molality whose activity coefficient had been determined previously by other means. From these we have obtained quantities which are proportional to α_2. Upon taking the square roots of these and dividing by M we found another series of quantities, $k\gamma$, which are proportional to γ. To evaluate γ it was necessary to find the value of k. We did this by assuming the values of γ obtained by Harned and Douglas[8] for the two 1 M solutions. Dividing the value of k thus found for each salt into each of the products, $k\gamma$, we obtained the values of the activity coefficients given in Col. 8. These activity coefficients have been plotted against the corresponding values of M, Fig. 2. The agreement between the values of γ for sodium bromide and those calculated by Harned and Douglas for the same concentration range is exceptionally good; that between the values of γ for solutions of potassium iodide at the three

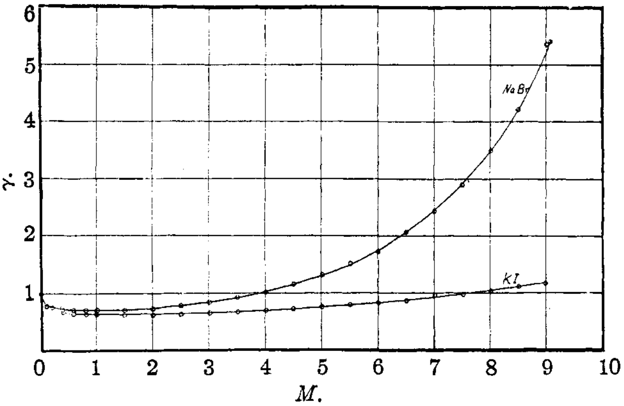

Fig. 2.

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[8] Harned and Douglas, THIS JOURNAL, **48**, 3095 (1926).

lowest concentrations is not good. This is not surprising when we consider the roundabout way in which γ is calculated. Even very slight errors in the vapor pressure readings are highly magnified when working with vapor pressures at concentrations less than 1 M.

From the activities of the solvent and the solute it is possible to calculate also three other important thermodynamic quantities. Thus the relation $-\Delta\bar{F}_1 = \bar{F}_1 - F_1^0 = RT \ln \alpha_1$ gives the increase in free energy accompanying the transfer of one mole of water from the pure solvent to a solution of the given molality. Likewise, $-\Delta\bar{F}_2 = \bar{F}_2 - F_2^0 = RT \ln \alpha_2$ gives the corresponding change in free energy for the solute. The values of $-\Delta F_1$ and $-\Delta F_2$ thus calculated are given in Cols. 9 and 10. In making these calculations we have taken $R = 1.9885$ cal. and $T = 298.12°$. In the last column of each table under $-\Delta F_2^0$ is tabulated the increase in free energy accompanying the dilution from any concentration M to one exactly 0.1 M.

In this paper we have made all of our calculations on the basis of "weight molal" concentrations, that is, moles per 1000 g. of water. While we have attributed the deviations from the laws of ideal solutions to hydration, we have not been oblivious to the newer development of the solution theory brought out by Debye and Hückel. More recently Hückel[9] has extended the interionic attraction theory to concentrated solutions and he states that the interionic attraction theory provides a better explanation for these deviations than does hydration. He also states that the variation of the activity coefficient with the concentration can be expressed by the relation

$$\log f = -\frac{0.354\sqrt{2c}}{1 + A\sqrt{2c}} + B\cdot 2c$$

where A and B are constants and c represents the concentration in moles per liter.

The experimental method presented makes it possible to determine vapor pressures for all concentrations from 0.1 M up to saturation. The data obtainable should give us a good opportunity to test the validity and range of application of the Hückel equation to saturated solutions. Unfortunately, no accurate density data are available for converting our concentrations to the molar concentration basis used by Hückel. We are now determining the densities of these solutions and will report our test of the Hückel equation in a forthcoming paper.

Summary

1. The vapor pressure of solutions of sodium bromide and potassium iodide have been determined at 25° for concentrations lying between 0.1 M and the saturated solutions.

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[9] Hückel, *Physik. Z.*, **26**, 93 (1925).

2. From the data obtained we have calculated the osmotic pressures, the activities of the solute and solvent, the activity coefficients and various changes in free energy accompanying change in concentration.

3. For all concentrations the magnitude of these solution values is greater for solutions of sodium bromide than for solutions of potassium iodide.

IOWA CITY, IOWA

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

A NEW METHOD FOR MEASURING OSMOTIC PRESSURE[1,2]

BY R. V. TOWNEND

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Introduction

In the past the study of osmotic pressure has been hampered by the experimental difficulties involved in making exact measurements. At least partly for this reason, the possibilities of osmotic pressure as a means for investigating the nature of solutions of electrolytes have been largely overlooked. The subject is treated briefly in many textbooks of chemistry, although its fundamental importance in other lines, such as plant and animal nutrition, has long been recognized by botanists and others. As a means for determining the activity of dissolved substances it ranks with such methods as vapor pressure lowering, freezing point lowering, and boiling point raising. With the exception of vapor pressure measurements, it is the only method of directly measuring activity at any and all temperatures. The osmotic method also has certain advantages over that which depends on the estimation of difficultly soluble substances in the presence of other salts. In the latter case it is necessary to make certain assumptions, such as the "ionic strength principle," whereas this is unnecessary in the case of the osmotic method. Moreover, the fact that a thousandth molal potassium chloride solution has a freezing point lowering of about 0.00368°, whereas the same solution has an osmotic pressure of about 36 mm., indicates clearly that as a means for investigating dilute solutions it would be of unsurpassed value provided certain experimental difficulties could be overcome.

The Measurement of Osmotic Pressure

The ordinary method for measuring osmotic pressure and the only one which has so far given satisfactory results consists in the use of a porous

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[1] In memory of Ira Remsen.

[2] The substance of this paper was presented by the author to the Board of University Studies of The Johns Hopkins University as part of the requirement for the degree of Doctor of Philosophy.