

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

THE VAPOR PRESSURE OF THE SATURATED AQUEOUS SOLUTIONS OF CERTAIN SALTSBY H. GENEVA LEOPOLD¹ AND JOHN JOHNSTON

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In the course of an investigation of the absorption of water by various materials, it was necessary to maintain atmospheres of constant humidity, which is best achieved by the use of a saturated salt solution. A survey of the literature on the vapor pressure of saturated salt solutions showed the data to be incomplete and of insufficient accuracy for our purpose; for much of the work consists of single measurements at a single temperature, and in many cases the several results differ by far more than the supposed experimental error. We undertook, therefore, a redetermination of the vapor pressure of some saturated solutions over the temperature range 20 to 50°, and believe that the uncertainty in the final results is not greater than 0.05 mm.; the salts used were sodium chloride, potassium chloride, sodium sulfate, potassium sulfate, potassium bichromate and, in addition, sodium chloride and potassium chloride together. Such data, apart from their practical utility, yield also a measure of the activity of both the salt and the water in these solutions, and this constitutes the best means of evaluating these quantities at temperatures other than in the freezing range of the solutions.

We have correlated our results with the data available on the vapor pressure of unsaturated solutions of the same salts by means of a sensitive method of plotting. This led us to observe that the vapor pressure of a saturated solution—presumably, therefore, also of some unsaturated solutions—attains to its final value only after the solution has been maintained at constant temperature for a period of 24 hours. This observation probably accounts for the lesser accuracy of many prior results, for it has been usual to record the pressure observed at the end of a period, at a given temperature, measured in minutes rather than in hours.

Experimental

The vapor pressure was measured directly, the form of apparatus used being that described by Johnston.² The essential feature is that between the bulb containing the solution and the main manometer, there is in a sort of double U-tube, a small mercury trap, the levels of which are adjusted by appropriate manipulation of stopcocks controlling the admission or extraction of air; after the whole apparatus has been thoroughly evacuated, this mercury is made the confining liquid and subsidiary manometer, and at pressures less than 60 mm. is the only manometer needed. The only modifications were the interposition of a bulb containing phosphorus pentoxide, to prevent access of

¹ From the dissertation presented to the Graduate School of Yale University, in June, 1926, by H. Geneva Leopold in candidacy for the degree of Doctor of Philosophy.

² Johnston, *Z. physik. Chem.*, **62**, 347 (1908).

water to the main manometer and the pump, and of a trap to prevent spattering of the solution over into the subsidiary manometer. The difference in level of the mercury columns was read by means of a depth gage,³ the vertical rod of which was set in bearings in a rigid brass frame; on its cross bar was mounted a small reading lens, at the center of which was glued a pointed piece of paper. When this is set up in front of, with a mirror at an equal distance behind, the manometer, the image of the paper point is in the plane of the manometer, and so errors due to parallax are avoided. With this simple form of cathetometer, the uncertainty in the readings is about 0.03 or 0.04 mm. The observed pressures were all reduced to their equivalent in terms of mercury at 0°.

The salt solution, previously heated to boiling, was introduced into the bulb, which was then sealed off; such air as had been retained by the solution was removed by continued pumping of vapor from the warm solution, this process being repeated until the observed final vapor pressure remained unchanged upon further pumping. The removal of the dissolved air is more difficult than we had anticipated; a period of 3 or 4 days is in many cases needed.⁴ Even so, when the temperature of the solution has been changed, the pressure does not attain to a new constant value until the lapse of several hours; consequently we use a thermometer and took readings, with frequent shaking of the solution bulbs, over a period of at least 24 hours. This gradual change to the equilibrium pressure, which may differ from the initial pressure by 0.2–0.3 mm., occurs after each evacuation of vapor from the solution, and is therefore due presumably to the slow equalization of some degree of undersaturation or supersaturation of the salt at the surface of the solution.

Each datum in Table I is the mean of 6 or more readings taken over an interval of at least 24 hours, and in many cases longer, during which the temperature was kept constant to $\pm 0.01^\circ$. The large number of observations made before we realized that a period of an hour at a given temperature is insufficient, have been omitted entirely; when plotted in the terms used in this paper, these points lie (along with those of previous workers) in a cluster so large that one could not determine in which direction to produce the curve.

TABLE I

THE OBSERVED VAPOR PRESSURES OF SATURATED AQUEOUS SALT SOLUTIONS

Temp., °C. <i>t</i>	Moles salt per 1000 g. water, <i>M</i>	Vapor pressure of water p_0	Vapor pressure of solution p	$\Delta = \frac{p_0 - p}{p_0 M}$
KCl				
21.42	4.664	19.14	16.23	0.03258
25.62	4.849	24.65	20.72	.03286
27.56	4.926	27.65	23.27	.03216
33.64	5.178	39.11	32.46	.03284
39.31	5.402	53.32	43.70	.03339
44.03	5.576	68.37	55.62	.03273
NaCl				
20.42	6.130	18.19	13.65	0.04073
25.49	6.148	24.45	18.35	.04057
29.96	6.167	31.75	23.80	.04060
36.92	6.201	46.86	35.03	.04070
40.55	6.220	56.96	42.54	.04070
50.00	6.277	92.51	68.84	.04077

³ Brown and Sharp depth gauge No. 605, with a range of 500 mm., capable of being read to 0.01 mm. Cf. Ferguson, *J. Wash. Acad. Sci.*, 10, 285 (1920). Another form is described by Lowry, *J. Opt. Soc. Am.*, 11, 645 (1925).

⁴ Cf. Lovelace, Frazer and Sease, *THIS JOURNAL*, 43, 102 (1921).

TABLE I (Concluded)

Temp., °C. <i>t</i>	Moles salt per 1000 g. water, <i>M</i>	Vapor pressure of water p_0	Vapor pressure of solution p	$\Delta = \frac{p_0 - p}{p_0 M}$
NaCl and KCl				
22.19	20.06	14.41
25.53	24.52	17.50
27.60	27.70	19.79
27.60	27.70	19.72
27.62	27.73	19.80
31.08	33.83	23.98
Na ₂ SO ₄				
20.83	1.427	18.44	16.01	0.09221
25.02	1.953	23.78	20.44	.07276
28.46	2.552	29.12	25.17	.05310
32.38	3.473	36.44	31.47	.03885
35.02	3.473	42.22	36.74	.03991
42.88	3.371	64.39	57.03	.03390
50.55	3.283	95.06	84.39	.03418
K ₂ SO ₄				
18.90	0.6256	16.37	15.91	0.04507
22.25	.6620	20.13	19.55	.04350
24.73	.6884	23.38	22.60	.04857
25.58	.6974	24.59	23.89	.04203
31.55	.7600	34.77	33.61	.04408
35.96	.8052	44.47	42.90	.04371
43.42	.8825	66.23	63.74	.04261
48.41	.9333	85.46	82.11	.04208
52.30	.972	103.60	99.13	.04444
K ₂ Cr ₂ O ₇				
23.66	0.482	21.92	21.43	0.04627
26.40	.545	25.93	25.30	.04522
32.82	.698	37.35	36.05	.04999
36.21	.790	45.08	43.42	.04672
40.85	.920	57.88	55.48	.04510
50.77	1.210	96.10	91.55	.03917

Table I, Col. 2 contains the molality (M) of the saturated solution at t , as derived from the "best" curve drawn through a large-scale plot of the solubility data available.⁵ Cols. 3 and 4 list the vapor pressure at t° of water⁶ (p_0) and of the solution

⁵ Some points on the curve chosen may be found in Table IV. The individual references are: Potassium chloride: Berkeley, *Trans. Roy. Soc. (London)*, **203A**, 189 (1904); Brønsted, *Z. physik. Chem.*, **80**, 208 (1912); **82**, 621 (1913); Andreae, *J. prakt. Chem.*, [2] **29**, 456 (1884); de Coppet, *Ann. chim. phys.*, [5] **30**, 426 (1883); Tilden and Shenstone, *Proc. Roy. Soc. (London)*, **35**, 345 (1883); Meusser, *Z. anorg. Chem.*, **44**, 79 (1905); Foote, *Amer. Chem. J.*, **35**, 238 (1906); Sudhaus and Miner, *Jahrg. Beil. Bd.*, **37**, 18 (1914); Amadori and Pampanini, *Atti. accad. Lincei*, **20**, II, 475 (1911). Sodium chloride: Berkeley, *Trans. Roy. Soc. (London)*, **203A**, 189 (1904); Andreae, *J. prakt. Chem.*, [2] **29**, 456 (1884); Raupenstrauch, *Monatsh.*, **6**, 563 (1885); Taylor, *J. Phys. Chem.*, **1**, 718 (1897); Moller, *Pogg. Ann.*, **117**, 386 (1862); de Coppet, *Ann. chim. phys.*,

(p), expressed in millimeters of mercury at 0° ; and the last column lists the molal relative vapor pressure lowering, calculated from these data, a quantity which is plotted against the molality in the figures.

A Graphical Method of Evaluating Vapor-Pressure Data on Solutions.—The accuracy of vapor-pressure data has commonly been estimated from their regularity; but this criterion fails in the presence of a constant, or regular, error such as the presence of air or the use of an inaccurate thermometer. A much better criterion is the ratio of the vapor pressure of the solution to that of water (solvent) at the same temperature; in other words, to compare the relative humidity (p/p_0) which is affected differently at different temperatures by a constant error in p . The use of this ratio also shows up chance errors in p —since p/p_0 must vary regularly with temperature—provided that the vapor-pressure curve of the solvent has been accurately determined. A still more sensitive criterion, since for most salt solutions p/p_0 is not far from unity, is $1 - p/p_0$ or $(p_0 - p)/p_0$, the relative lowering of vapor pressure; and if this quantity is divided by the molality (M), the relative molal lowering of vapor pressure (Δ) so derived is found to change quite slowly with change in the salt concentration. Therefore a plot, even on quite a small scale, of this function (Δ) against the molality shows up the degree of accuracy of the experimental results; indeed, with all except the very best data, the points are so scattered that one finds difficulty in deciding just how the curve should be drawn.

As an instance of the fact that Δ changes slowly with concentration, the values of Δ derived from the measurements of Lovelace, Frazer and Sease⁴ in solutions of potassium chloride above 1 M are as follows:

M	1.2461	1.5099	1.7072	1.9938	2.2450	2.4916	3.0017	3.5783	4.0070
$\Delta \times 10^5$	3159	3166	3167	3169	3173	3180	3200	3220	3233

This regularity, which shows that these results are accurate to 0.001 mm., as claimed by the authors, contrasts with the irregular values of Δ lying between 0.30 and 0.33 as derived from the work of other authors in this same range of concentration.

Let us now consider the effect of change of temperature upon the function [5] 30, 426 (1883); Gay-Lussac, *Ann. chim. phys.*, [2] 11, 310 (1819). Sodium sulfate: Richards and Yngve, *THIS JOURNAL*, 40, 164 (1918); Takenchi, *Mem. Coll. Kyoto*, 1, 249 (1915); Wuite, *Z. physik. Chem.*, 86, 349 (1914); Berkeley, *Trans. Roy. Soc. (London)*, 203A, 189 (1904); Tilden and Shenstone, *Proc. Roy. Soc. (London)*, 35, 345 (1883); Loewel, *Ann. chim. phys.*, [3] 49, 50 (1857); Gay-Lussac, *Ann. chim. phys.*, 11, 312 (1819). Potassium sulfate: Berkeley, *Trans. Roy. Soc. (London)*, 203A, 189 (1904); Trevor, *Z. physik. Chem.*, 7, 468 (1891); Andreae, *J. prakt. Chem.*, [2] 29, 456 (1884); Tilden and Shenstone, *Proc. Roy. Soc. (London)*, 35, 345 (1883). Potassium dichromate: Koppel and Blumenthal, *Z. anorg. Chem.*, 53, 263 (1906); Kremers, *Pogg. Ann.*, 92, 499 (1854); Alluard, *Compt. rend.*, 59, 500 (1864); Sherrill and Eaton, *THIS JOURNAL*, 29, 1643 (1907); Le Blanc and Schmandt, *Z. physik. Chem.*, 77, 621 (1911).

⁶ Taken from the Reichsanstalt "Wärmetabellen," by Holborn, Scheel and Henning, 1909, Vieweg and Son, Braunschweig.

tion Δ . If we calculate, from measurements at a series of temperatures of the vapor pressure of a solution of constant composition, the values of Δ —or what suffices in this case, the relative humidity p/p_0 —we find that the values at adjacent temperatures differ by as much as those at the highest and lowest temperature. In other words, *within the accuracy of the data available*, the relative humidity—and hence Δ —may be regarded as independent of temperature. This is the principle, first stated by Princesps, commonly known as Babo's law;^{7a} and is equivalent to the statement that the activity of water in a solution of constant concentration is substantially independent of the temperature. It is quite clear, however, that if there were measurements of sufficient accuracy, on a solution of constant molality at a series of temperatures, we would observe a slight increase in relative humidity with increase of temperature.^{7b} This rate of increase would be parallel to the rate at which the average degree of "hydration" of the ions of the salt decreases with rising temperature, and it would seem that this trend should be most marked for those salts which ordinarily form the largest hydrates, a view which is substantiated by the results for sodium sulfate.

The fact that, for a solution of constant molality, the relative humidity, and hence the function Δ , is independent of temperature *within the limits of accuracy of existing data*, enables us to omit temperature from further consideration, and so to bring together on a single plane diagram all of the data upon solutions of a salt from freezing range to the boiling point of a saturated solution. On this diagram the coördinates are molality and Δ , the relative lowering of vapor pressure of water per mole of solute. In the few cases in which the vapor pressure of a single solution was measured at a series of temperatures, we used the average value of Δ ; in general, for a given value of M , there is available only a single value of Δ , but these may refer to quite different temperatures. This plot thus allows one to correlate results from various sources, to estimate their relative accuracy and to derive throughout the range of concentration definitive values of higher accuracy than have hitherto been available. It is much more sensitive than the method proposed by Bencowitz,⁸ namely, to plot $\log p/p_0$ against $1/T$; for on this basis he is able to represent by straight lines data which our figures indicate are of doubtful accuracy.

^{7a} Recent data which confirm this principle, *within the accuracy of the measurements*, are those on cane sugar solutions by Perman and Saunders (*Trans. Faraday Soc.*, **19**, 112 (1923)). This is further exemplified by a comparison of the work of Sidgwick and Ewbank (*J. Chem. Soc.*, **125**, 2268 (1924)) on solutions of potassium chloride, sodium chloride and potassium sulfate at 5°, with that of Tammann (*Ann. Physik*, **24**, 523, (1885)) on the solutions of these salts at 100°.

^{7b} See, for example, in the very recent results of Perman and Lovett (*Trans. Faraday Soc.*, **22**, 1 (1926)) on urea solutions over the range 40–80°.

⁸ Bencowitz, *J. Phys. Chem.*, **29**, 1432 (1925).

Solutions of Potassium Chloride (Fig. 1).—The data made use of in the preparation of this figure are listed in the following tabular statement with respect to author (with the abbreviated designating letter), temperature range (*s* denoting the saturated solution), general method of measurement, and reference.

Author	Symbol	Temp. range, °C.	Molality range	Method
Adams ⁹	A	<0	0.005-0.117	Freezing temp.
Berkeley ^{10a}	B	107.4	7.788(<i>s</i>)	Boiling temp.
Berkeley and Appleby ^{10b}	BA	108	7.828(<i>s</i>)	Boiling temp.
Brönsted ¹¹	B'	100	7.535(<i>s</i>)	Boiling temp. (indirect)
Dieterici ¹²	D	0	1.0-3.82	Differential
Edgar and Swan ¹³	ES	19-30	4.56(<i>s</i>)-5.03(<i>s</i>)	Static
Emden ¹⁴	E	14-95	1.35-4.02	Static
Hovorka and Rodebush ¹⁵	H	<0	0.001-0.01	Freezing temp.
Lovelace, Frazer and Sease ⁴ ..	F	20	0.05-4.00	Differential
Nicol ¹⁶	N	70-95	1.11-5.55	Indirect
Pearce and Snow ¹⁷	P	25	0.20-4.81(<i>s</i>)	Dynamic
Rodebush ¹⁸	R	<0	0.95-3.30	Freezing temp.
Sidgwick and Ewbank ^{7a}	SE	5	1.28-3.82	F. p. depression of nitrobenzene
Speranski ¹⁹	S	25-51	4.74-5.82	Differential
Tammann ^{7a}	T	45-100	1.85-3.67	Static
Harrison and Perman ²⁰	P	40-80	0.44-6.90	Static
This paper.....	L	21-44	4.66(<i>s</i>)-5.58(<i>s</i>)	Static

It will be noticed that we have included three sets of measurements of depression of freezing point (δ), this having been done mainly to enable us to continue the curve to zero concentration. These data, for the more dilute solutions, were transformed to our variable by means of the equation²¹ $\log p/p_0 = \log a = -0.004211\delta - 0.0000022\delta^2$, in which a , the relative activity of the water in the solution, is the same as p/p_0 . The foregoing equation is applicable only to solutions so dilute

⁹ Adams, *THIS JOURNAL*, **37**, 481 (1915).

¹⁰ (a) Berkeley, *Trans. Roy. Soc. (London)*, **203A**, 189 (1904). (b) Berkeley and Appleby, *Proc. Roy. Soc. (London)*, **85A**, 489 (1911).

¹¹ Brönsted, *Z. physik. Chem.*, **82**, 621 (1913).

¹² Dieterici, *Ann. Physik*, **42**, 513 (1891).

¹³ Edgar and Swan, *THIS JOURNAL*, **44**, 570 (1922).

¹⁴ Emden, *Ann. Physik*, **31**, 145 (1887).

¹⁵ Hovorka and Rodebush, *THIS JOURNAL*, **47**, 1614 (1925).

¹⁶ Nicol, *Phil. Mag.*, **22**, 502 (1886).

¹⁷ Pearce and Snow, *J. Phys. Chem.*, **31**, 231 (1927).

¹⁸ Rodebush, *THIS JOURNAL*, **40**, 1204 (1918).

¹⁹ Speranski, *Z. physik. Chem.*, **70**, 519 (1910).

²⁰ Harrison and Perman, *Trans. Faraday Soc.*, **23**, 1 (1927).

²¹ Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., **1923**, p. 284;

that the heat of dilution is negligible; otherwise, one must take this factor into account and correct the foregoing results by means of the equation^{21a}

$$\log \frac{a''}{a'} = -\bar{L} \frac{T'' - T'}{2.303RT'T''} + (\bar{C} - \bar{C}_0) \left[\frac{T''(T'' - T')}{2.303RT'T''} - \frac{1}{R} \log \frac{T''}{T'} \right]$$

in which T'' is the temperature chosen for the calculations (in our case 298.1°) and T' is $273.1 - \delta$; \bar{L} is the molal heat of dilution at T'' , and \bar{C} and \bar{C}_0 , respectively, the partial molal heat capacity of the solvent in the solution and of the pure solvent; a' is calculated from the simple equation above, and the corrected value a'' is set equal to p/p_0 .

In the application of this equation to the data of Rodebush, the value of \bar{L} was taken from the work of Wüst and Lange,²² and \bar{C} was evaluated from the results of Randall and Bisson²³ by plotting the specific heat of the solution against the concentration in terms of moles of water per mole of salt, and taking the slope of this curve at the several molalities. These values, together with the uncorrected (from a') and corrected values of Δ , are given in Table II.

TABLE II

THE RELATIVE MOLAL VAPOR-PRESSURE LOWERING (Δ) OF SOLUTIONS OF POTASSIUM CHLORIDE, DERIVED FROM THE FREEZING-POINT DATA OF RODEBUSH, CORRECTED FOR THE HEAT OF DILUTION

Moles KCl per 1000 g. H ₂ O M	(Cal. per mole H ₂ O) \bar{L}	\bar{C}	$\frac{p_0 - p}{p_0 M}$	Corr. $\Delta = \frac{p_0 - p}{p_0 M}$
0.0	0.0	17.98
.951	— 2.32	17.96	0.03089	0.03136
1.445	— 5.53	17.93	.03064	.03142
2.331	—13.20	17.86	.03024	.03149
3.043	—19.35	17.77	.03005	.03159
3.192	—20.54	17.75	.03004	.03162
3.300	—21.55	17.74	.02992	.03154

It may be mentioned that we also attempted to derive Δ from the freezing-point data by means of the consideration that the vapor pressure of the solution is the same as that of the ice with which it is in equilibrium. But the values calculated from this basis and the most recent vapor-pressure table²⁴ for ice and water below 0° were not compatible with other data and, indeed, were inconsistent among themselves.

Fig. 1 shows the molal relative vapor-pressure lowering (Δ) caused by potassium chloride in solution as a single curve over the range from extremely dilute to boiling saturated solutions. From 0.3 to 0.8 molal the

²² Wüst and Lange, *Z. physik. Chem.*, **116**, 161 (1925).

²³ Randall and Bisson, *THIS JOURNAL*, **42**, 347 (1920).

²⁴ Washburn, *Monthly Weather Rev.*, **52**, 488 (1924); based upon a critical examination of all available data.

curve has been dotted as there is some uncertainty on account of the hump in the curve expressing the results of Lovelace, Frazer and Sease alone, which over the rest of the range are clearly the best available; this hump may well be real, for they claim that the irregularity is greater than the possible experimental error, 0.001 in Δ corresponding to 0.0175 in the measured depression. The points listed in Table II lie below the curve, but the difference corresponds to less than 0.05 mm. in p ; this slight discrepancy is probably due to the fact that the heat values used refer to 25° (there being no others available), whereas one should use thermal data which refer to the same temperature as the results to be transformed and corrected.

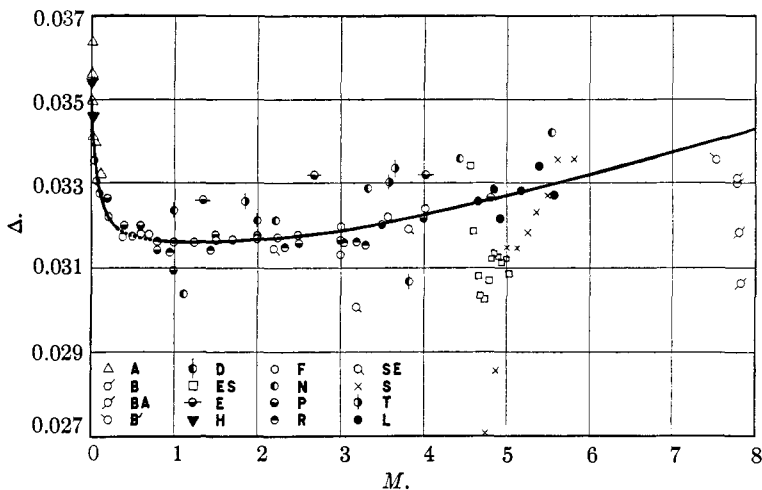


Fig. 1.—The relative molal vapor-pressure lowering of solutions of potassium chloride.

Altogether we venture to believe that this curve gives the best representation of the vapor-pressure data of solutions of potassium chloride now available, it tends to exaggerate the discrepancies, many of the points being off by no more than 0.1 mm. It may be pointed out that the points derived from the measured boiling temperature of the saturated solution all lie considerably below the natural prolongation of the curve—and the same is true for each one of the salts investigated; this corresponds to a somewhat too high vapor pressure or too low surface concentration, and is in line with our repeated observation that the vapor pressure of a saturated solution only attains to its definitive equilibrium value after an interval measured in hours.

Solutions of Sodium Chloride (Fig. 2).—The data made use of are listed below, as in the previous case.

Author	Symbol	Temp. range, °C.	Molality range	Method
Berkeley ^{10a}	B	107.5	6.760(s)	Boiling temp.
Berkeley and Appleby ^{10b}	BA	108	6.766(s)	Boiling temp.
Bousfield and Bousfield ²⁵	B ²	18	0.56-6.113(s)	Isopiestic solns.
Brönsted ¹¹	B'	100	6.690(s)	Boiling temp.
Dieterici ²⁶	D	0	0.07-0.96	Differential
Emden ¹⁴	E	18-95	0.85-5.13	Static
Harkins and Roberts ²⁷ ...	HR	<0	0.005-0.136	Freezing temp.
Johnston, S. M. ²⁸	J	>100	0.1-2.9	Boiling temp.
Nicol ¹⁶	N	70-95	0.11-0.44	Indirect
Rodebush ¹⁸	R	<0	1.04-5.20	Freezing temp.
Sidgwick and Ewbank ^{7a} ..	SE	5	1.13-5.48	F.-p. depression of nitrobenzene
Smits ²⁹	S'	0	0.04-3.35	Differential
Speranski ^{19,30}	S	24-95	6.14(s)-6.64(s)	Differential
Tammann ^{7a}	T	49-100	2.56-5.13	Static
This paper.....	L	20-50	6.130(s)-6.277(s)	Static

In this case again two sets of freezing data were employed and converted as before into the variable Δ by means of the heat data as determined by Randall and Bisson, and computed by Lewis and Randall.³¹ The uncorrected and corrected values of Δ for the several molalities investigated by Rodebush are:

<i>M</i>	1.045	1.526	2.429	3.057	3.806	4.739	5.201
$\Delta \times 10^5$ (uncorr.)	3181	3212	3279	3339	3432	3535	3596
$\Delta \times 10^5$	3254	3317	3434	3520	3645	3769	3835

These points again lie slightly below our best curve, and probably for the same reason as in the case of potassium chloride.

The experimental work of Bousfield and Bousfield consisted essentially in a comparison of the concentrations of isopiestic solutions of the chlorides of potassium, sodium and lithium. The numerical results, as given by them, are based upon a vapor-pressure curve for sodium chloride solutions (particularly at the lower concentrations) as standard, but this curve is not in satisfactory agreement with the best of the other data cited in Fig. 2 nor do their values for potassium chloride fit the curve in Fig. 1. On the contrary, if their results are recomputed on the basis of the curve (Fig. 1) as standard, the results for sodium chloride lie very close to the curve in Fig. 2, the difference corresponding to only 0.0015 mm. at the

²⁵ Bousfield and Bousfield, *Proc. Roy. Soc. (London)*, **103A**, 429 (1923).

²⁶ Dieterici, *Ann. Physik.*, **67**, 859 (1899).

²⁷ Harkins and Roberts, *THIS JOURNAL*, **38**, 2676 (1916).

²⁸ Johnston, S. M., *Trans. Roy. Soc. (Edinburgh)*, **45**, 855 (1908).

²⁹ Smits, *Z. physik. Chem.*, **51**, 33 (1905).

³⁰ Speranski, *ibid.*, **84**, 160 (1913).

³¹ Ref. 21, p. 350.

lowest concentration and to 0.011 mm. at the highest. Accordingly, this basis was used to evaluate their results for both sodium chloride and for lithium chloride, which also now show excellent agreement with the best curve based on the other data available.

Solutions Saturated with Both Potassium and Sodium Chloride.—In this the method of plotting could not be used, because the molality of these saturated solutions has not been accurately determined.

Solutions of Lithium Chloride (Fig. 3).—Although we did no experimental work on solutions of lithium chloride, it seemed worth while to exhibit its curve for comparison with the other halides. The only data available are those of Lovelace, Bahlke and Frazer³² (F) at 20° for the range 0.097–1.032 *M*, using a differential method; the isopiestic results of

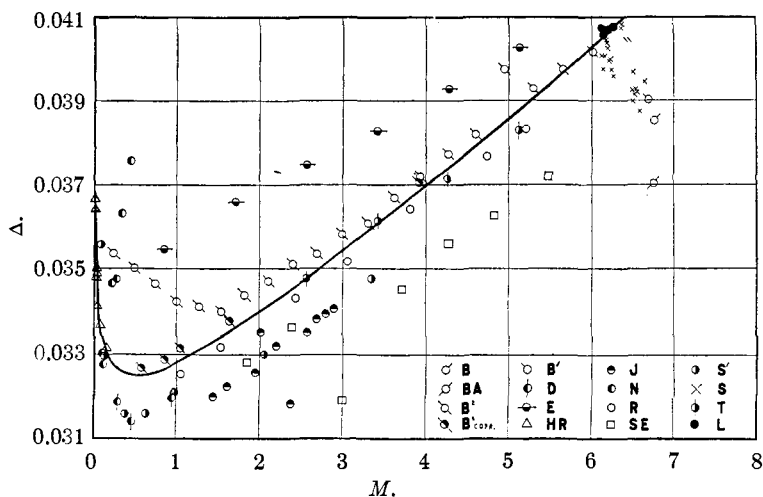


Fig. 2.—The relative molal vapor-pressure lowering of solutions of sodium chloride.

Bousfield and Bousfield (B^2) already alluded to; and the freezing-point depression at 0.01 and 0.02 *M* as given by Noyes and Falk³³ (NF). The first-named results are again obviously of a high order of accuracy, and the others are in excellent accord with them.

Comparison of the Curves for the Alkali Halides.—The three curves all start from the same point, Δ for zero concentration of a uni-univalent salt being 0.0355; all three drop sharply to a minimum and then rise again, the most rapid rise corresponding to the minimum at the lowest concentration, and conversely. It is significant that, at concentrations beyond that at which the minimum occurs, the slope is greatest for lithium chloride,

³² Lovelace, Bahlke and Frazer, *THIS JOURNAL*, 45, 2930 (1923).

³³ Noyes and Falk, *ibid.*, 32, 1011 (1910).

which forms a monohydrate stable between 13 and 98°; less for sodium chloride, which appears as hydrate only below 0°; and least for potassium chloride with no known solid hydrates. If hydrates form in solution, the net concentration of the water will be less than its gross concentration, and the observed vapor pressure less than it would otherwise be; this divergence increases with concentration as the relative amount of water

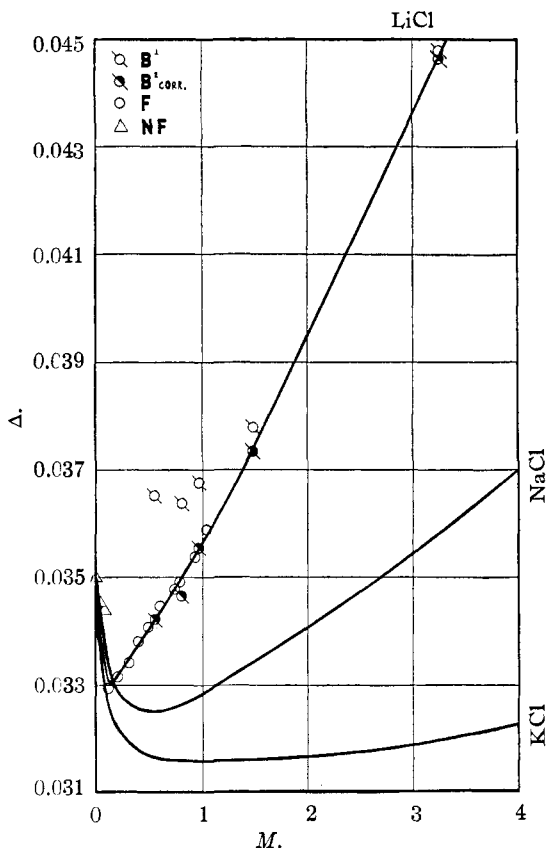


Fig. 3.—The relative molal vapor-pressure lowering of solutions of the chlorides of potassium, sodium and lithium.

decreases. On this basis Δ would, with increasing concentration, increase most rapidly in the case of the salt which we would expect to be hydrated in solution to the greatest extent; this is in harmony with the results for the three halides, and also for the two alkali sulfates.

Sodium Sulfate Solutions (Fig. 4).—The most complete work is that of Wuite³⁴ (W) who made static measurements on solutions saturated

³⁴ Wuite, *Z. physik. Chem.*, **86**, 349 (1914).

with the anhydrous salt at 19.4–50.4° (3.728–3.283 *M*) and with the decahydrate at 21.6–32.4° (1.447–3.510 *M*), and supplemented these by solubility determinations. There are also data by Tammann^{7a} over the unsaturated range 0.94–3.44 *M*, and freezing-point data on dilute solutions (0.025–0.25 *M*) are given by Noyes and Falk³³ (NF). Some other considerations³⁵ led us to believe that Wuite's value at the transition point is rather low, as indeed we found it to be by 0.9 mm.; and the measurements at other temperatures indicate that most of Wuite's values are low—this being another illustration of the necessity of maintaining the solution for a period of hours at the temperature before the definitive observation is made. We believe that our points are the more accurate, but have drawn a dotted curve through Wuite's. A few of Tammann's points have been inserted, as well as the values calculated from the freezing data, but no attempt was made to draw a single continuous curve for the decahydrate.

In this case it is obvious that the relative vapor pressure of a solution of constant composition cannot be independent of temperature, for there are two branches of the curve with divergent values of Δ (at different temperatures) for the same molality of solution.

Solutions of Potassium Sulfate and of Potassium Dichromate (Fig. 5).—For potassium sulfate there are data by Berkeley^{10a} and Berkeley and Appleby^{10b} on the boiling temperature (101°, 101.39°) of the saturated solution (1.396, 1.399 *M*); a similar observation by Brönsted¹¹ (100°, 1.388 *M*); freezing data by Hovorka and Rodebush¹⁵ (0.001–0.001 *M*) and from Noyes and Falk³³ (0.045–0.25 *M*); together with our own direct measurements.

The curve is similar to that for lithium chloride, though Δ is of course

³⁵ See Norton and Johnston, *Am. J. Sci.*, **12**, 467 (1926),

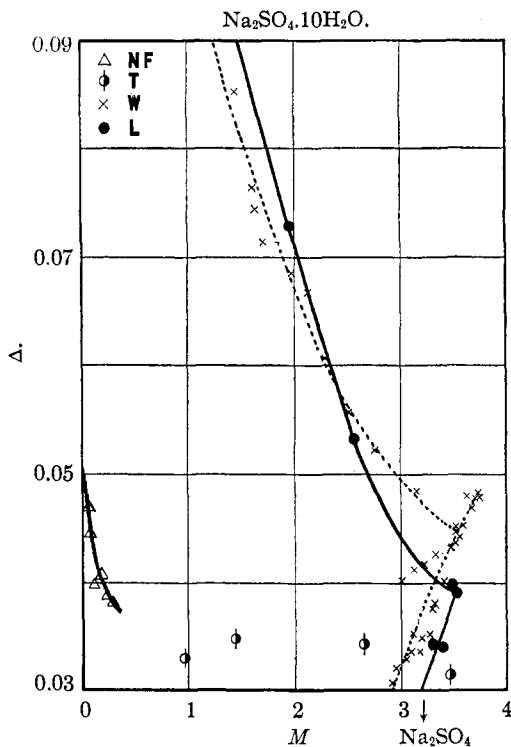


Fig. 4.—The relative molal vapor-pressure lowering of solutions of sodium sulfate.

higher, being above 0.055 at zero concentration. It will be observed that the boiling data again lie considerably below the probable course of the curve.

For potassium dichromate there are no data except ours; in this case the curve appears to have a negative slope over the range investigated. This implies that the complete curve from zero concentration would first fall, then rise and then fall again; but the data are insufficient to decide this question; this course, it may be remarked, would in effect be similar to that of the curve for potassium chloride if the "hump" is real.

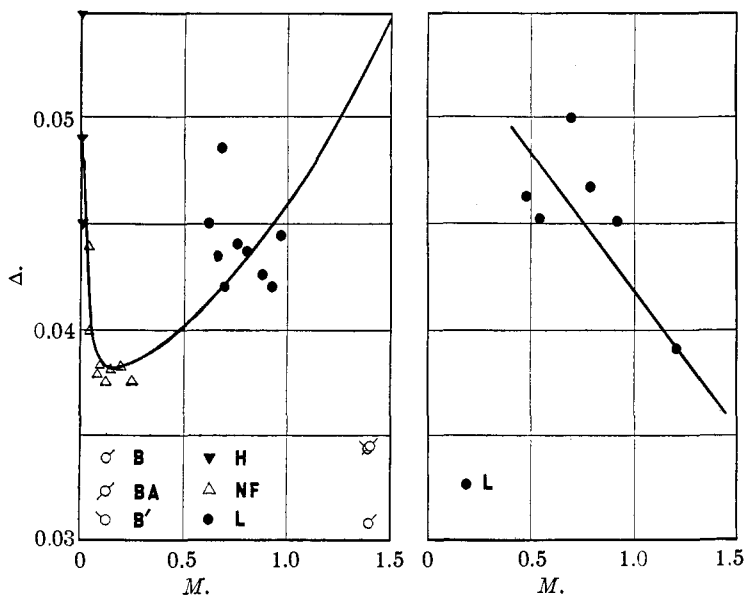


Fig. 5.—The relative molal vapor-pressure lowering of solutions of potassium sulfate (left) and potassium dichromate (right).

Conclusion

From the curves for the several salts, plotted on a large scale, values at a series of concentrations were read off; they are presented in Table III. Similarly we have derived, and give in Table IV, values of the percentage humidity in equilibrium with saturated solutions of the several salts at a series of temperatures, and believe that these are more reliable than those hitherto available for these salts. We have also made use of the data to plot the molality of the solutions against that of the isopiestic solution of potassium chloride; from the curves, which are of gentle curvature (though they cannot be represented over the whole range by a single quadratic equation) we have read off the results listed in Table V for four of the salts.

TABLE III

INTERPOLATED VALUES OF THE RELATIVE MOLAL VAPOR-PRESSURE LOWERING (Δ) FOR THE SEVERAL SALTS

M	KCl	NaCl	LiCl	Na ₂ SO ₄ ^a	Na ₂ SO ₄ .10H ₂ O	K ₂ SO ₄	K ₂ Cr ₂ O ₇
0.01	0.03444	0.03500	0.03500	0.0481	0.0476
.02	.03416	.03464	.03468	.04680447
.04	.03364	.03420	.03420	.04500415
.08	.03296	.03355	.03326	.04280388
.10	.03277	.03338	.03305	.03900385
.2	.03220	.03285	.033210383
.4	.03182	.03253	.033780394	0.0498
.5	.03175	.03250	.034070402	.0485
.6	.03169	.03252	.034370411	.0472
.8	.03162	.03264	.035000434	.0445
1.0	.03160	.03283	.035670460	.0419
1.5	.03161	.03340	.03744	0.0895	.0548
2.0	.03169	.03404	.039400711
2.5	.03178	.03472	.041450547
3.0	.03192	.03545	.04355	0.0251	.0443
3.5	.03209	.03620	.04568	.0386	.0389
4.0	.03228	.03699
4.5	.03251	.03778
5.0	.03275	.03860
5.5	.03300	.03945
6.0	.03323	.04031
6.5	.03348	.04118
7.0	.03372
7.5	.03396
8.0	.03421

^a At 32.38° (tr. point) $M = 3.512$; $p = 31.47$ mm.; $(p_0 - p)/p_0 M = 0.03885$.

TABLE IV

THE ACTIVITY OF WATER AT REGULAR INTERVALS OF TEMPERATURE IN SOLUTIONS SATURATED WITH THE SEVERAL SALTS

Temp., °C.	KCl		NaCl		Na ₂ SO ₄		K ₂ SO ₄		K ₂ Cr ₂ O ₇	
	M	100 p/p ₀	M	100 p/p ₀	M	100 p/p ₀	M	100 p/p ₀	M	100 p/p ₀
10	4.150	86.58	6.108	75.29	0.526	97.88
20	4.603	85.01	6.128	75.16638	97.35	0.418	97.93
30	5.029	83.53	6.168	74.96744	96.82	.628	97.06
40	5.428	82.11	6.217	74.70	3.409	87.61	.847	96.28	.897	96.12
50	5.882	81.20	6.276	74.41	3.290	89.14	.949	95.70	1.201	95.28
60	6.117	79.64	6.344	74.05	3.180	90.43	1.044	95.14
70	6.476	78.33	6.420	73.65	3.089	91.47	1.138	94.53

TABLE V

MOLALITIES OF ISOPIESTIC SOLUTIONS

KCl	NaCl	LiCl	K ₂ SO ₄
0.010	0.010	0.010	0.008
.020	.020	.020	.018
.040	.040	.040	.036
.080	.080	.080	.070
.100	.098	.098	.088

TABLE V (Concluded)

KCl	NaCl	LiCl	K ₂ SO ₄
.2	.197	.188	.172
.4	.393	.373	.328
.5	.488	.465	.403
.6	.580	.558	.476
.8	.772	.724	.610
1.0	.964	.890	.736
1.5	1.425	1.284	1.020
2.0	1.873	1.660	1.247
2.5	2.303	2.011	1.464
3.0	2.730	2.343	...
3.5	3.145	2.665	...
4.0	3.559	2.976	...
4.5	3.960	3.273	...
5.0	4.367	3.562	...
5.5	4.756
6.0	5.139
6.5	5.514
7.0	5.888
7.5	6.260
8.0	6.608

Summary

The vapor pressure of the solution saturated with potassium chloride, sodium chloride, potassium sulfate, sodium sulfate, potassium dichromate, and with both potassium chloride and sodium chloride has been measured by a static method, with an accuracy of about 0.05 mm., over the temperature range 20 to 50°. Each solution was kept at constant temperature for at least 24 hours before the definitive reading was made; inattention to this necessary precaution by most previous authors has resulted in values which are slightly in error, as if the concentration of the solution at its surface was not precisely the saturation concentration. The various data for solutions of each salt up to saturation have been correlated by a sensitive method of plotting; the resulting curves are a more reliable picture of the vapor pressure of these solutions than has hitherto been available.

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