

364. *Vapour Pressures of Saturated Solutions. Lithium Chloride and Lithium Sulphate.*

By MALCOLM P. APPLEBEY, FRANZO H. CRAWFORD, and KENNETH GORDON.

THE boiling points of saturated solutions of a large number of alkali salts were determined by Lord Berkeley and one of us by a modification of the Landsberger apparatus (*Phil. Trans.*, 1904, **203**, A, 189; *Proc. Roy. Soc.*, 1911, **85**, A, 477), and hence the osmotic pressures of these solutions were calculated by means of Porter's well-known relation.

Subsequently, Applebey and Hughes (J., 1915, **107**, 1798) devised a static method of measurement by which the earlier results were substantially confirmed for the more soluble salts. The static method is capable of greater accuracy than the original method especially with very soluble salts, and at the same time allows determinations to be made over a range of temperatures and pressures which may be considerably extended by the use of subordinate manometers. The original series of determinations included the chlorides, nitrates, and sulphates of sodium, potassium, rubidium, and caesium, but no lithium salts were investigated. Determinations of the vapour pressures of lithium chloride and sulphate have now been made by the static method, and although the calculation of osmotic pressure of the chloride solutions can only be a rough approximation owing to the high solubility of the salt, the measurements are thought to be of some interest. This communication also embraces determinations of solubility and density of saturated solutions carried out for the osmotic calculations but enabling the transition points of lithium chloride hydrates to be fixed with some degree of precision.

EXPERIMENTAL.

Purification of Materials.—Lithium sulphate obtained from Kahlbaum showed only traces of impurities, and was satisfactorily purified by three recrystallisations of the monohydrate from water, the crystals being separated from mother-liquor by centrifuging in a platinum basket. Since the solubility diminishes with rise of temperature, the salt was separated by evaporation of the solution at about 80° in a flask through which a current of filtered air was passed.

Three different samples of lithium chloride were used. Two, obtained from Kahlbaum and Harrington respectively, were almost free from soluble impurity and were used after three recrystallisations as the monohydrate. The third sample, obtained later from Harrington's, contained, in addition to a small amount of insoluble matter, appreciable quantities of sulphate and nitrate. After three recrystallisations it gave no sign of a precipitate with barium chloride and only a very faint brown ring test for nitrate. A fourth batch of material was prepared from the mother-liquors by precipitation of the lithium with excess of ammonium carbonate, boiling the precipitated carbonate with three successive small portions of distilled water, igniting it to dispel the last traces of ammonium salts, dissolving it in hydrochloric acid, crystallising, and finally igniting it in air to remove hydrogen chloride. The salt so obtained was quite free from sulphate and nitrate, and showed only a faint spectroscopic indication of sodium. All

four preparations of the chloride gave results which were concordant in the physical measurements.

Density and Solubility Measurements.—Densities and solubilities were determined in the borosilicate pipettes designed for this work, and already described by Miss Farrow (J., 1926, 49). These (of capacity about 5 c.c. and stem-capacity 0.008 c.c. per division) are free from the inaccuracies which accompany the use of earlier forms. They were calibrated by means of redistilled mercury, the calibrated volumes showing in different experiments departures of only 0.0001 c.c. from the mean at 25°, and 0.0004 c.c. at 150°. Three pipettes on recalibration after 3 months' use showed values agreeing to 0.0001 c.c. with the original values at 25°.

The salt and solution were stirred together for periods varying from 12 to 24 hours before the pipette was introduced with the glass-wool filter attached. After a further 4 hours' stirring, the solid was allowed to settle. Up to this point no solution enters the pipette. The rod stopper of the pipette is now cautiously loosened, and the solution, freed from solid particles by the filter, enters the pipette. If necessary, a slight positive pressure can be applied to the solution in order to make it enter. When the pipette is filled to some position on the graduated stem, the rod stopper is thrust home, and the filter removed by a wire loop while the pipette is still immersed. The pipette is then removed, quickly wiped, closed with the cap, then thoroughly cleaned on the outside and prepared for weighing in the usual manner. Only at the lower temperatures was any difficulty experienced with air bubbles; chloride solutions at 25° are very viscous and this circumstance appears to favour entrainment of air bubbles contained in the glass-wool filter. The difficulty was overcome at these temperatures by first saturating the filter with solution by suction just before it was attached to the pipette. After weighing, the contents of the pipette are carefully washed out, and the content of solute determined; lithium sulphate was directly weighed after evaporation and ignition in a current of purified air; chloride was determined by titration with silver nitrate. At least three determinations were made at each temperature, and in general the density results obtained are concordant to ± 0.0005 , the solubilities to 0.05 unit.

Vapour-pressure measurements were made by the static method of Applebey and Hughes (*loc. cit.*), an auxiliary manometer outside the thermostat enabling the determinations with the chloride to be carried out over a wide range of temperature. At temperatures below 100°, direct-reading manometers were used, the vacuous arm being exhausted by a Sprengel pump. The sulphate results were also supplemented by differential-tensimeter measurements, in order to extend the range. The tensimeters, which contained pure water in the compensation bulb, were filled in the same manner and with the same precautions as the Applebey and Hughes apparatus.

The phenomenon noticed by Applebey and Hughes with sodium sulphate was repeated in the tensimeters containing lithium sulphate: the surface of the glass in the solution bulb was slowly attacked, and in some experiments became detached in flakes. Analysis showed that no appreciable impurity of a soluble kind was added to the solution from this cause.

Temperature control in the baths filled with medicinal paraffin was secured by a thermostatically controlled lamp, the heat effect of which supplemented the current through a main heater of nichrome ribbon. Constancy of temperature to $\pm 0.03^\circ$ was obtained for several hours before each measurement. Temperatures were read on Anschütz thermometers standardised on the air scale by the N.P.L., and are accurate to 0.05°.

In Table I are given the density and solubility (S ; g./100 g. of solution) for the two salts; Table II contains the vapour pressure of the saturated solutions, expressed in mm. of mercury at 0°, T denoting the absolute temperature.

TABLE I.
Densities and Solubilities.

(a) *Lithium chloride.*

$t.$	D_{4}°	$S.$	$t.$	D_{4}°	$S.$	$t.$	D_{4}°	$S.$	$t.$	D_{4}°	$S.$
1.05°	1.2678	40.90	24.15°	1.2962	45.47	80.85°	1.3312	52.94	120.2°	1.344	56.9
10.05	1.2789	42.71	40.05	1.3034	47.09	89.55	1.3418	54.82	140.3	1.339	57.6
15.70	1.2875	44.06	50.20	1.3080	48.23	95.15	1.3471	55.83	155.6	1.338	58.3
18.25	1.2926	44.86	64.95	1.3173	50.26	100.2	1.347	56.3			

(b) *Lithium sulphate.*

94.90	1.182	23.4	100.15	1.179	23.5	102.5	1.174	23.56	104.0	1.176	23.55
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TABLE II.

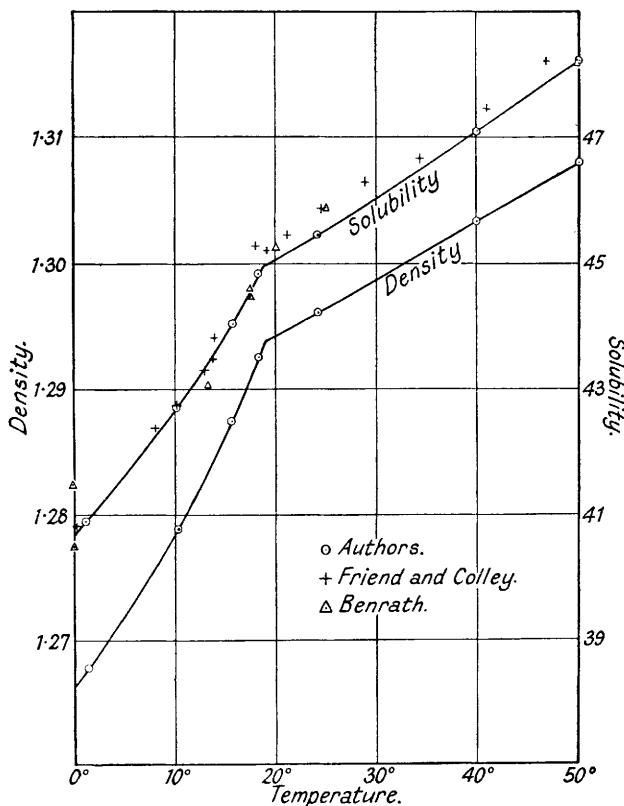
Vapour Pressures of Saturated Solutions.

(a) Lithium chloride.							
<i>t.</i>	$10^6/T.$	<i>p.</i>	$\log p.$	<i>t.</i>	$10^6/T.$	<i>p.</i>	$\log p.$
60.45°	3000	14.9	1.173	91.00°	2747	53.5	1.728
61.35	2991	15.9	1.201	95.25	2716	62.2	1.794
70.00	2915	26.6	1.425	100.30	2679	78.3	1.894
70.45	2912	26.2	1.418	99.95	2681	80.0	1.903
80.15	2832	37.9	1.579	109.75	2613	115.6	2.063
85.15	2792	46.0	1.663	119.85	2545	173.9	2.240
90.10	2754	51.2	1.709				

(b) Lithium sulphate.							
<i>t.</i>	$10^6/T.$	<i>p.</i>	$\log p.$	<i>t.</i>	$10^6/T.$	<i>p.</i>	$\log p.$
25.30	3352	20.85	1.319	69.40	2921	197.3	2.295
30.65	3293	28.5	1.455	84.30	2799	349.9	2.544
45.65	3138	64.5	1.810	89.65	2757	458.0	2.661
60.15	3002	129.6	2.113	99.50	2685	657.7	2.812

The values of the solubility and density of lithium chloride are represented in Figs. 1 and 2, and the vapour-pressure results are given in the form of graphs of $\log p$ against $10^6/T$ in Fig. 3.

FIG. 1.

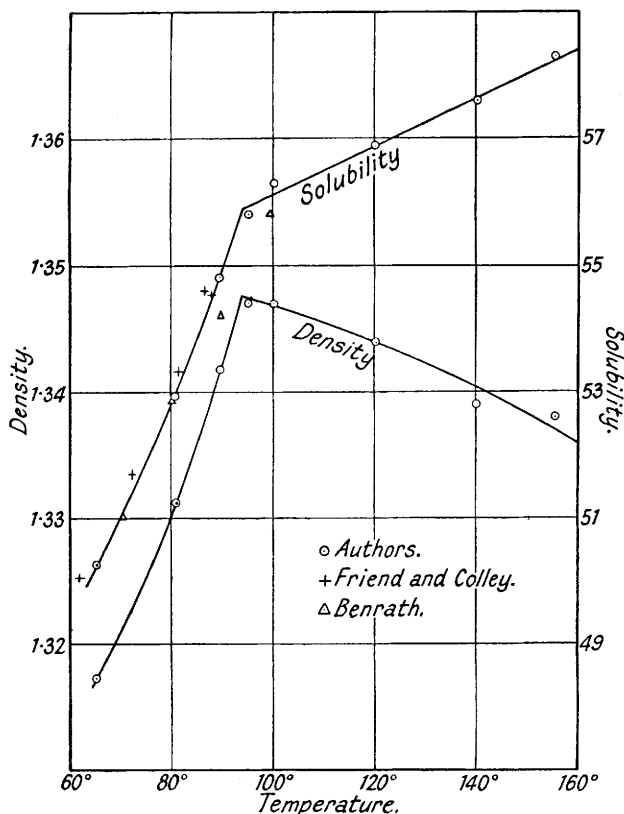


DISCUSSION OF RESULTS.

Solubility.—The solubility of lithium chloride has been determined by Friend and Colley (J., 1931, 3148; which see for record of earlier workers' results) over the range 0—88°, and by Benrath (Z. anorg. Chem., 1932, 205, 417) from 0° to 99.5°. These two sets of observations are plotted for comparison with our own measurements in Figs. 1 and 2. The values given by Benrath appear to be somewhat irregular; five of his points lie in close

agreement with our curve, two are well above, and two below. There are also two rather widely differing values at 0° . His paper contains no experimental details of the measurements. The curve of Friend and Colley's determinations is more regular. It agrees closely with our measurements below 15° , but above that temperature it diverges somewhat widely and shows results nearly a whole unit higher than ours. Friend and Colley determined the content of their solutions by evaporation and weighing the solid residue, whereas we employed a carefully standardised silver titration procedure by the chromate method, working always at night and with the use of tinted yellow goggles which made the results more precise. We also checked our method by titrating a solution made up from lithium chloride which had been evaporated to dryness in a dry air stream (LiCl taken, 2.4956 g.; found by titration, 2.504 g.). The difficulty of dehydrating a very deliquescent salt such as lithium chloride without decomposition is well known, and we consider it likely that the

FIG. 2.



discrepancy between our results is probably to be so explained. We are confirmed in this opinion by the evidence which can be adduced from the determinations of the densities of unsaturated solutions by the authors whose results are collected in Table III. These determinations have been made with great care and give density-concentration curves which are nearly linear and, in most cases, only need short extrapolation to reach the conditions of saturation. The concentrations corresponding to the densities of the saturated solutions determined by us thus give the solubilities with a considerable degree of precision. Where the conditions for accurate extrapolation are favourable, the results obtained agree closely with our experimental values.

Density.—The determination of the density of solid lithium chloride by Haigh (*J. Amer. Chem. Soc.*, 1912, **34**, 1142) enables calculation to be made for the volume change on solution at 20° . In the saturated solution this amounts to an expansion of 0.42 c.c. per mol. of

TABLE III.

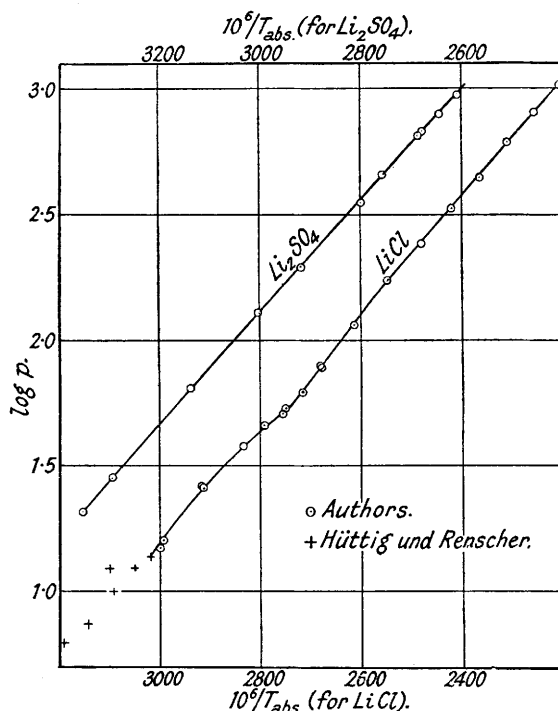
Observer.	Temp.	% Satn. of highest point.	No. of obsns. above 70% satn.	Density.	Solubility.	
					Extra-polated.	Deter-mined.
Kohlrausch and Tollingen ¹	18°	91	1	1.2920	44.71	44.72
Green and Masson ²	18	94	4	1.2920	44.67	44.72
	25	94	4	1.2966	45.45	45.56
Baxter and Wallace ³	0	63	0	1.2667	41.0	40.65
	25	99.7	1	1.2966	45.83	45.56
	50	94	1	1.3079	48.25	48.20
	70.2	50	0	1.3216	51.3	51.15
	100	71	1	1.3468	56.0	56.15

¹ *Wied. Ann.*, 1879, **6**, 38.

² *J.*, 1908, **93**, 2023.

³ *J. Amer. Chem. Soc.*, 1916, **38**, 80.

FIG. 3.



dissolved salt, a result in very good agreement with the value 0.435 c.c. obtained by Lamb and Lee (*ibid.*, 1913, **35**, 1686) for the most concentrated solution investigated (approximately 90% saturated). The absence of reliable data for the density of the solid at higher temperatures makes accurate calculation impossible, but if it be assumed that the coefficient of expansion derived from the measurements of Henglein (*Z. physikal. Chem.*, 1925, **117**, 286) remains valid for temperatures up to 160°, the following expansions can be calculated for the range of saturated solutions investigated by us :

<i>t</i>	20°	40°	60°	80°	100°	120°	140°	160°
Δv , c.c./mol.	0.42	0.52	0.62	0.72	0.88	0.71	0.47	0.34

These data, which are given with reserve, appear to show that, as the saturated solutions become more concentrated with increase of temperature, the expansion on solution of a mol. steadily increases; after the upper transition point at 94° is passed, however, the expansion shows a rapid falling off.

Transition Points.—For the dihydrate and the monohydrate of lithium chloride, the solubility curves intersect at 19.0°, and the density curves at 19.2°, from which we obtain a final value of 19.1° with a probable error of $\pm 0.25^\circ$. This is confirmed by cooling curves

obtained with pure specimens of the salt; two such determinations gave 19.01° and 19.28°. Determinations of this temperature by earlier investigators are as follows:

From solubility measurements	{	12.5°: Bogorodsky (based on Kremers's determinations) (<i>J. Russ. Phys. Chem. Soc.</i> , 1893, 25 , 316).
		18°: Friend and Colley (<i>loc. cit.</i>).
From cooling curves or temperatures of continued coexistence with saturated solution.	{	21.5°: Bogorodsky (<i>J. Russ. Phys. Chem. Soc.</i> , 1894, 26 , 209).
		20° (approx.): Benrath (<i>loc. cit.</i>).

The early work of Bogorodsky is discordant. The two modern determinations differ by a degree on either side of our measurements.

The upper transition temperature between the monohydrate and anhydrous salt is given with a fair degree of concordance by the solubility, density, and vapour-pressure curves, as 94.1°, 93.5°, and 93.4°, respectively. The most probable value is considered to be 93.5° ± 0.5°. The only previous value for this constant is 98° derived by Bogorodsky (*loc. cit.*) from Kremers's inaccurate solubility values. Our result is confirmed by cooling curves, which gave a very definite halt at 93°.

Vapour Pressure.—The logarithm of the vapour pressure of saturated solutions of lithium sulphate is within the error of experiment a linear function of the reciprocal of the temperature, and is given by the equation $\log p = -2230/T + 8.794$, or $\log_e p = -5135/T + 20.25$. The b. p. of the unsaturated solution at 760 mm. is 103.8°, and the temperature coefficient of the vapour pressure at this temperature is 27.49 mm./°C. From these data and the appropriate volumes, by the Clausius-Clapeyron equation, the heat of evaporation of 1 mol. of water from the saturated solution is 9981 cal. Subtracting 9590 cal. for the latent heat of 1 mol. of water vapour and 100 cal. for the external work in expansion of 1 mol. of water from its vapour pressure at the b. p. of the solution to 1 atm., we have 291 cal. evolved in the saturation of 1 mol. of water with monohydrate. Converting to 1 mol. of the monohydrate, we find its heat of solution to be -5500 cal., which may be compared with Thomsen's value of -3410 cal. in dilute solution.

For lithium chloride, our values for the vapour pressures are in fair agreement with those of Hüttig and Renschler (*Z. anorg. Chem.*, 1924, **137**, 159), where these fall in the range of temperature covered by our experiments. With this salt, the logarithmic vapour-pressure curve is linear only at the higher temperatures (above 120°) where it follows the equation $\log p = -2293/T + 8.075$ or $\log_e p = -5280/T + 18.60$. By the same method as above, we have: b. p. of saturated solution, 168.6°; temperature coefficient of the vapour pressure at 168.6°, 20.58 mm./°C.; heat of vaporisation of solution, 10,400 cal. for 18 g. of water. Latent heat of water at 168.6°, 8835 cal.; external-work term (calculated), 1775 cal.; whence 210 cal. are absorbed in the saturation of 1 mol. of water with the salt, and heat of solution of 1 mol. of the salt in its saturated solution = 350 cal.; the result is correct in sign but has no claim to accuracy owing to the uncertainty of the volume and heat data for water at so high a temperature.

Tangents drawn to the vapour-pressure curves at the transition point similarly give the latent heat of evaporation of 1 mol. of water as 11,950 and 6500 cal. respectively for separation of anhydrous salt and monohydrate. From these values the heat of hydration may be approximately calculated as $\text{LiCl} + \text{H}_2\text{O} \longrightarrow \text{LiCl} \cdot \text{H}_2\text{O} + 4950$ cal. The difference in the heats of solution of the anhydrous salt (Thomsen) and monohydrate (Bogorodsky, *loc. cit.*) in dilute solution is 4323 cal.

Osmotic Pressures.—Calculation of the osmotic pressures by the Porter equation (cf. Lord Berkeley and Applebey, *loc. cit.*) gives for a saturated solution of lithium sulphate at the b. p. under normal pressure a value of 212.9 atm., or, since the molar concentration is 2.51 mols./litre, a pressure of 84.8 atm. per mol. per litre, which may be compared with other sulphates, for which the results are collected in the following table, P being the osmotic pressure (in atm.) and c the concentration (in mols./l.).

Salt.	B. p.	c .	P .	P/c .	Salt.	B. p.	c .	P .	P/c .
Li_2SO_4	103.8°	2.51	212.9	84.8	Cs_2SO_4	109.96°	4.01	545.4	135.8
Na_2SO_4	102.85	2.60	162.2	62.5	Ti_2SO_4	100.32	0.347	17.8	51.3
K_2SO_4	101.39	1.25	79.4	63.2	Cs alum.	100.53	0.300	21.2	70.1
Rb_2SO_4	103.51	2.50	197.0	78.6					

It is interesting to note that the lithium salt, whose solubility happens to be quite near those of the sodium and rubidium salts, gives a much higher value for P/c , which is in accordance with other observations indicating a higher osmotic activity for the lithium ion, probably owing to hydration.

Similar calculation for the chloride can only be regarded as giving the order of the osmotic pressure, since it involves the assumption that the compressibility of water remains unchanged when it is subjected to negative pressures far higher than it could possibly withstand. Such a calculation gives for the osmotic pressure at the b. p. 3050 atm., or, since the solubility is 18.50 mols./l., a pressure of 165 atm. per mol. per litre. These figures are very much higher than the values for any other salt investigated. Comparison of alkali chlorides is made in the following table.

Salt.	B. p.	c .	P .	P/c .	Salt.	B. p.	c .	P .	P/c .
LiCl	168.6°	18.50	3050	165	RbCl	113.51°	7.95	743.2	93.5
NaCl	108.67	5.65	476.8	84.4	CsCl	119.92	9.21	1055.0	114.5
KCl	108.60	5.98	473.3	79.1	TlCl	100.097	0.097	5.5	57.0

The numbers in the last column chiefly show the rapid increase of P/c with molecular concentration; with lithium chloride this is so great as to cover any minor effect such as is shown by the sodium and potassium salts, where the approximate agreement in solubility enables the higher osmotic activity of sodium to show itself.

ST. JOHN'S COLLEGE, OXFORD.

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