2. Equilibrium constants have been computed for each of the pressure-temperature conditions studied. These "constants" were found to increase with an increase in pressure.

3. By means of empirical formulas the percentage of ammonia at equilibrium has been calculated for a temperature range of 200–1000°, and a pressure range of 10–100 atmospheres.

Washington, D. C.

[Contribution from the Chemical Laboratory of the Johns Hopkins University]

VAPOR PRESSURES OF LITHIUM CHLORIDE SOLUTIONS AT 20°

By B. F. Lovelace, W. H. Bahlke and J. C. W. Frazer

Received September 22, 1923

This paper is a continuation of a series of studies of the vapor pressures of aqueous solutions begun by Frazer and Lovelace[1] using an accurate static method which depends upon the measurement of the difference in pressure between pure solvent and solution contained in bulbs immersed in the same accurately regulated water thermostat by means of a Rayleigh manometer. The error involved in measuring the pressure differences by this method is approximately 0.0006 mm. The measurements were made at 20° and in the concentration range from 0.1 to 1.0 *M*.

Experimental Details

A detailed description of the apparatus used in this work is given by Frazer and Lovelace,[1] and by Lovelace, Frazer and Miller.[2] No change in the apparatus was made except to replace the Gaede pump with a Langmuir pump using a three-stage rotary oil pump as auxiliary.

The solutions of lithium chloride were prepared from a carefully standardized stock solution, the salt for which was purified as follows. A commercial c. p. grade of lithium chloride was dissolved in distilled water, a small amount of ammonium carbonate solution added and the mixture heated and stirred for four hours to precipitate any magnesium, calcium, barium, iron or aluminum possibly present, then filtered. The ammonium carbonate used in the preparation left no residue on sublimation. To the filtered lithium chloride solution, ammonium carbonate solution was added in slight excess and the lithium carbonate filtered off and washed thoroughly with hot water. It was then heated in a platinum dish at a sufficiently high temperature to volatilize any ammonium carbonate possibly present. The salt was then suspended in a small amount of distilled water and pure hydrochloric acid added until the solution was neutral to rosolic acid. Analyses of the solution for lithium and for chlorine checked within 0.04%.

In previous investigations the removal of dissolved air from the solutions has been quite a time-consuming operation. Tests for air in the solution or solvent were made by allowing it to come to equilibrium with a large

---

[1] Frazer and Lovelace, This Journal, **36**, 2439 (1914).

[2] Lovelace, Frazer and Miller, *ibid.*, **38**, 515 (1916).

volume of vapor above it for hours.[3] The vapor was then trapped off and absorbed in phosphorus pentoxide for 20 minutes and the residual pressure measured on a McLeod gage. No solution was considered air-free unless the vapor showed a residual pressure less than 0.0001 mm. Usually the solutions had required from four to six 12-hour expansions before they were air-free. In the present investigation it was found that the air could be removed in a minimum of time, that is, one 12-hour expansion. This was accomplished by introducing the solution as nearly air-free as possible into the bulb which had been previously pumped air-free, and rapidly distilling a small portion of the solvent at the pressure of its vapor into a bulb containing phosphorus pentoxide.

In detail the method is as follows.

The solutions were made up in a flask shaped like that shown in Fig. 1. The required amount of the concentrated lithium chloride solution was introduced with a pipet into the flask which had been weighed empty. Water sufficient to bring the solution to the desired concentration was then introduced, the level marked, and a small excess added which was later removed by boiling the solution in the flask in order to remove air. The upper tube of the flask was then constricted at the portion "*a*" and a clean rubber tube fixed over the end of the glass and fitted with a pinchcock. The lower limb of the flask was then cautiously heated with a Bunsen flame in order to expel from this portion of the solution as much air as possible. The flame was then applied to the sides of the flask and the solution vigorously boiled for 30 minutes or more until the level was down nearly to the mark on the flask. The pinchcock was then closed and the flame removed simultaneously, the solution allowed to cool slightly and the flask sealed off at the constriction. The flask was then weighed and the weight of the solution noted, in order to determine approximately the concentration. Usually about 3 g. more water than that required for the concentration desired was present. This excess allowed for removal of water by distillation after the solutions were in the bulbs in the bath.

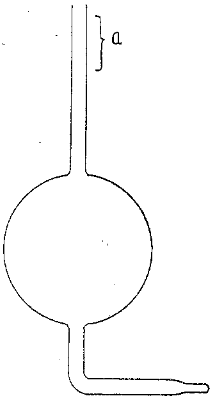

Fig. 1

The sealed flask was then fixed to a mercury reservoir as shown in Fig. 2, the tube broken at "*a*" by pressure of the fingers and the mercury allowed to complete the filling of the flask, the flow being regulated by a pinchcock. The tube was then fitted with a capillary filled with mercury and the tip broken at *b*, some of the solution being wasted to replace the mercury in the capillary. The solution was then introduced into the bath in the usual manner.[4]

It was necessary to have the system free from air before introducing the solutions; this was accomplished quite readily by beginning the evacuation while the bulb and mercury seal were still wet. In this way a layer of water preceded the mercury up the tube leading to the bulb. The water was then removed by exposure to phosphorus pentoxide. The system was evacuated until no gain in pressure could be measured on the McLeod gage after the system had stood for 12 hours.

---

[3] Lovelace, Frazer and Rogers, [THIS JOURNAL, **42,** 1794 (1920)] showed that 12 hours was necessary to establish equilibrium between solution and vapor.

[4] Ref. 3, p. 1797.

After the solutions had been introduced into the system they were exposed to phosphorus pentoxide for a definite length of time until about 1 g. of water had been removed. It had been previously determined by experiment that the water distilled at a practically constant rate so that it was unnecessary to weigh the water removed.

The solution was then trapped off and the system evacuated to remove air given up by the solution. After distilling and evacuating the solutions thrice they were usually air-free, the whole operation requiring about 24 hours. By the method formerly used it required from four to ten days to remove the dissolved air.

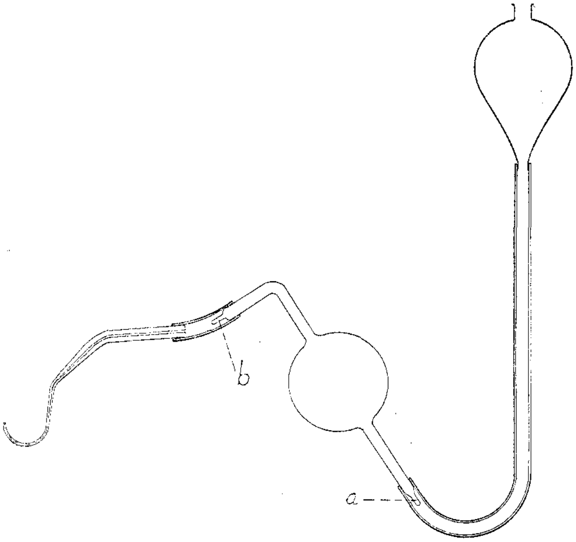

Fig. 2

In making readings of the vapor-pressure lowering, the accurate regulation of the temperature described in former articles was followed. Usually three readings of the zero point of the gage were made, three readings of the solution in the first bulb, three readings of the second solution and then two more readings of the zero. No readings were regarded as sufficiently accurate unless the zero before and after checked within 0.1 mm. scale deflection. Readings were made by two different observers extending over two or three days until four reliable sets of readings were obtained on each solution.

After the solutions were measured they were removed from the bath and placed in clean, glass-stoppered flasks and analyzed for chlorine. Concentrations (Table I) are expressed in moles of lithium chloride per 1000 g. of water.

Results

The results of the measurements are given in Table I. Col. 1 gives the room temperature, Col. 2 the concentration, Col. 3 the lowering as measured, Col. 4 the lowering corrected to millimeters of mercury at 0° and Col. 5 the lowering per mole.

The results are also shown graphically in Fig. 3 where the molecular lowering is plotted against the concentration. For comparison the data of Lovelace, Frazer and Sease[5] on potassium chloride are shown in the same

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

TABLE I

VAPOR PRESSURE LOWERING OF AQUEOUS SOLUTIONS OF LITHIUM CHLORIDE AT 20°

Moles LiCl per 1000 g. of water	Observed lowering Mm. Hg	Lowering corrected Mm. Hg at 0°	Molecular lowering Corrected observed lowering divided by Moles salt per 1000 g. of H_2O
0.0968	0.0562	0.0559	0.5775
0.1842	.1076	.1071	.5814
0.2952	.1738	.1730	.5860
0.3862	.2300	.2290	.5929
0.4782	.2871	.2858	.5977
0.5897	.3582	.3566	.6047
0.7257	.4448	.4428	.6101
0.7810	.4804	.4782	.6123
0.9268	.5775	.5749	.6203
1.0316	.6518	.6489	.6290

figure. The curve for lithium chloride is considerably higher owing to the fact that this salt is highly hydrated in solution while potassium chloride is not. Although the degree of hydration decreases with increasing concentration the apparent effect increases with concentration since the percentage of total solvent associated with the lithium chloride increases with the concentration.

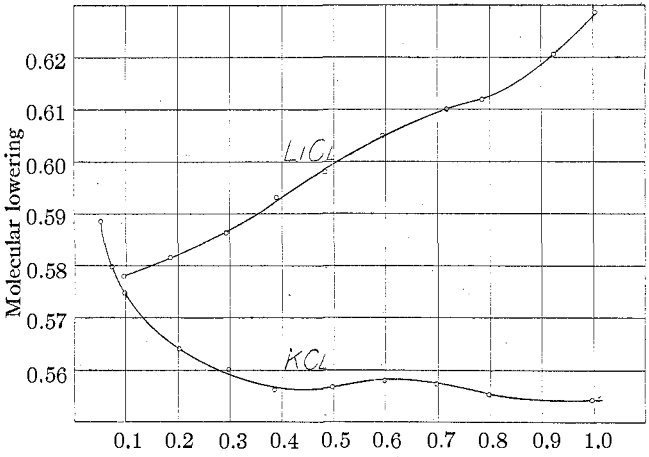

Fig. 3

An irregularity between 0.4 and 0.8 M similar to that found for potassium chloride[6] is also apparent in the lithium chloride curve, but is masked somewhat in the latter case by the comparatively large slope of the curve.

In Table II the observed vapor-pressure lowerings at 20° have been compared with those calculated from the freezing-point measurements of Washburn and MacInnes.[7] The ratio of the vapor pressure of the solution

---

[6] Ref. 5, p. 106.

[7] Washburn and MacInnes, THIS JOURNAL, **33,** 1701 (1911).

to that of the pure solvent at the freezing point was calculated by means of the equation[8]

$$\log \frac{N}{N+n} = \log \frac{P}{P_0} = \frac{\Delta C_p}{R} \log \frac{T_F}{T_0} \frac{-4343(L_F - \Delta C_p \Delta T_F)}{RT_F} + \frac{0.4343\ LF_0}{RT_{F_0}}$$

where $\frac{N}{N+n}$ is the mole fraction of solvent; P, the vapor pressure of the solution; P_0, the vapor pressure of pure solvent; T_F the freezing point of the solution in degrees A.; T_0, the freezing point of solvent in degrees A., = 273°; L_F, the molal heat of fusion of the solvent, = 1435.5 calories; ΔC_p, the difference between the molal heat capacities of the solvent in liquid and solid state, = 9.05 calories; ΔT_F, the lowering of the freezing point; R, the gas constant, = 1.985 calories.

Assuming that the ratio P/P_0 is independent of the temperature the values given in Col. 3 of Table II were calculated.

TABLE II

Moles of LiCl per 1000 g. of water	ΔT_F	$P_0 - P$		Difference f. p.—obs.
		From f.-p. measurements	Observed	
0.1	0.351	0.054	0.056	−0.002
0.2	0.694	.115	.117	− .002
0.3	1.049	.178	.175	+ .003
0.4	1.416	.239	.236	+ .003
0.5	1.791	.311	.300	+ .001
0.6	2.174	.365	.365	.000
0.8	2.966	.499	.485	+ .014
1.0	3.792	.633	.648	− .015

The agreement between the two is very good considering the fact that the salt is so highly hydrated in solution.

Summary

The lowering of the vapor pressure of water due to dissolved lithium chloride has been measured at 20° and in the concentration range of 0.1 M to 1.0 M.

An improved method for removing air from the solutions before measuring has been devised.

The observed vapor-pressure lowering has been compared with those calculated from freezing-point measurements.

BALTIMORE, MARYLAND

---

[8] *Mass. Inst. Tech. Quart.*, **21**, 372 (1908).