V_A, V_B = molal volumes of A and B, respectively, at their normal boiling points, cm^3/g mol

x_A, x_B = mole fractions of A and B in binary mixtures

X_B = association factor of the solvent B in Equation 5 (X_B = 1 for acetone and chloroform, 2.6 for water, and 1.5.for ethanol)

μ_A, μ_B = viscosity of pure liquids A and B, respectively; centipoises in Equations 5–8; poises in Equation 3

μ_{AB} = viscosity of binary mixture, poises

β = cell constant in Equation 1, cm^{-2}

ρ_{AB} = density of binary mixture, g/cm^3

α_A = $1 + (\partial \ln \gamma_A / \partial \ln x_A)$, thermodynamic factor

γ_A = activity coefficient

Subscripts

A = solute

B = solvent

AB = binary mixture of A and B

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Vapor Pressure-Temperature-Concentration Relationship for System Lithium Bromide and Water (40–70% Lithium Bromide)

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The vapor pressure of water over solutions containing 40, 50, 60, and 70 wt % lithium bromide was determined by direct static and gas transport methods. The data were fitted to the straight line relationship: Log $P_{(soln)}$ = B Log $P_{(water)}$ + C, where constants B and C are concentration dependent.

Accurate vapor-pressure data for aqueous lithium bromide solutions are necessary for developing and extending the performance range of absorption air conditioning machines (*1*). There are available in the literature vapor pressure-temperature-concentration diagrams for the system LiBr–H₂O; however, these *PTX* diagrams are constructed by extrapolating small sets of data determined over narrow temperature rang-

es (*2–4, 7, 8*). Hence, the smoothed values given by Uemura and Hasaba (*9*) over the range 34–65% LiBr and 20–160°C are not in complete agreement with Pennington's extrapolated values (*8*), especially at temperature and concentration extremes. The vapor-pressure values presented most likely lack correlation because generalized equations derived to represent data of a nonideal salt solution are extrapolated beyond experimental data limits.

This investigation was undertaken to determine the vapor pressure of aqueous lithium bromide solutions as a function of temperature at four concentrations to increase the degree of data reliability at temperature extremes. The two simplest and most direct procedures chosen for this study are the gas transport and static methods. Results obtained by these two methods were consistent to within ±1.9%.

Experimental

General. A number of methods for measuring the vapor pressure of aqueous lithium bromide solutions were consid-

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ered for reliability and simplicity. Two major considerations are accurate knowledge of the concentration of a hygroscopic lithium bromide solution in equilibrium with the water vapor and preventing water vapor from condensing in the measuring circuit of the apparatus at high water vapor partial pressure. Two independent methods chosen were the static and gas transport methods (6).

Static method. Direct vapor-pressure measurements were made via the static method by attaching a mercury manometer to a flask containing aqueous lithium bromide solution (Figure 1). All extraneous gases dissolved in the solution and in the apparatus were removed by repeated freezing and slight boiling under vacuum. Water vapor condensation and temperature gradients were eliminated by completely submerging the entire apparatus including the sample container and mercury manometer in a constant temperature bath. Temperature of the bath was controlled to within ±0.05°C. Vapor pressures measured by a mercury manometer at different temperatures were corrected to 0°C mercury and for mercury vapor pressure. Highest temperature limits of the apparatus were determined by the vapor pressure of mercury and size of the mercury manometer that could be submerged with the sample in the constant temperature bath employed. Distilled water was used to calibrate the manometer which was readable to ±0.2 mm Hg.

Gas transport method. The gas transport method uses the principle by which water is absorbed from an inert carrier gas after bubbling through a solution where the partial pressure of water in the gas phase has become equilibrated with the solution.

Figure 2 gives a schematic of the general configuration of the apparatus employed. Dry nitrogen is forced to flow through the system at point A. The prehumidifier (B) contains sulfuric acid solution at a concentration which has a water vapor pressure approximately equal to the water vapor pressure of the lithium bromide solution being examined. Preconditioning prevents removal of any significant quantity of water from the lithium bromide solution. Preconditioned gas is then bubbled through the lithium bromide solution (D) using a spiral gas washing bottle (Ace Glass, Catalog #7167) which gives maximum residence time between the liquid and gas phases. Total pressure over the lithium bromide solution is measured at E. Water absorption tubes (F and G) are placed in close proximity to the sample to minimize gas diffusion through the tubing and subsequent loss of water. The first absorption tube is located in a well inside the constant temperature bath (K) to prevent water from condensing prior to absorption at high water partial pressures. An absorber (G) is used as a check to ensure complete absorption of water. A wet gas test meter (H; Precision Scientific Co., Meter #TS63115) measured the dry nitrogen gas volume.

For vapor pressures measured above 75°C, an oven was used (Precision Scientific Co., Model 114) instead of an oil constant temperature bath. A large fan installed inside the oven eliminated temperature gradients and reduced the temperature variation of the oven to less than ±0.1°C. Temperatures were measured using a narrow-range precision thermometer supplied with Bureau of Standards calibration. The apparatus was calibrated against distilled water. The vapor pressure of water above the lithium bromide solution was calculated according to Dalton's law by use of the following equations:

$$N_{H_2O} = \frac{\text{weight water absorbed}}{18.016} \qquad (1)$$

$$N_{N_2} = \frac{(P_{atm} - P_{H_2O} \text{ meter}) \, V \text{ meter}}{R \, K \text{ meter}} \qquad (2)$$

$$P_{total} = P_{atm} + P_{system} \qquad (3)$$

$$P_{H_2O} = \frac{N_{H_2O}}{N_{H_2O} + N_{N_2}}(P_{total}) \qquad (4)$$

where N_{H_2O} = moles of water, $N(N_2)$ = moles of nitrogen, P_{atm} = atmospheric pressure, P_{H_2O} meter = partial pressure of water in wet test gas meter, V meter = volume nitrogen read on wet test gas meter, R = gas constant, K meter = absolute temperature of wet gas test meter, P_{total} = total gas pressure over lithium bromide solution, P_{system} = gauge pressure over lithium bromide solution, and P_{H_2O} = partial pressure of water over lithium bromide solution.
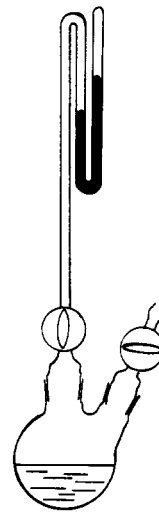

Figure 1. Static vapor-pressure apparatus
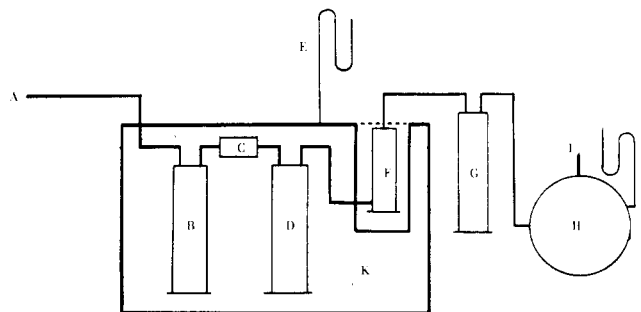
Figure 2. Gas transport vapor-pressure apparatus
A. Dry nitrogen gas input
B. Prehumidifier (H_2SO_4 soln)
C. Gas line filter
D. LiBr solution
E. Manometer
F. Water absorption tube
G. Water absorption tube
H. Precision wet test gas meter
I. Gas meter exit
J. Manometer
K. Constant temperature bath or oven

Table I. Vapor Pressure (Torr) of Lithium Bromide Solutions as Determined by Static Method

Temp, °C	Wt % LiBr		
	40	50	60
0	2.98	...	...
10	5.43	...	...
25	13.74	...	1.99
40	31.84	15.74	5.00
50	54.20	26.91	9.53
60	84.33	44.56	...
75	158.5	90.00	34.51

Table II. Vapor-Pressure Data Determined by Gas Transport Method (Unsmoothed)

Av temp, °C	Concn, wt %	$P_{(soln)}$, torr	P_{H_2O},[a] torr
24.98	40.00	14.39	23.7
50.00	40.00	56.23	92.5
75.07	40.00	166.7	289.9
100.23	40.00	483.5	766.4
24.98	50.00	6.138	23.7
50.00	50.00	27.99	92.5
75.07	50.00	88.71	289.9
100.23	50.00	248.3	766.4
125.01	50.00	587.5	1741
24.98	60.00	1.799	23.7
50.00	60.00	8.241	92.5
75.07	60.00	33.81	289.9
125.01	60.00	277.3	1741
149.95	60.00	625.2	3566
125.01	70.27	101.8	1741
149.95	70.27	279.9	3566
175.08	70.27	631.4	6707

[a] Water vapor pressure taken from 1967 ASME Steam Tables.

Table III. Constants B and C for Equation 6 for Vapor Pressure of Water Above Lithium Bromide Solutions Using Least-Squares Method for Combining Static and Gas Transport Experimental Data

Wt %	40.00	50.00	60.00	70.27
Mole fraction	0.1215	0.1718	0.2373	0.3290
Slope B, Eq. 6	0.9941	1.0553	1.1605	1.3547
Constant C, Eq. 6	−0.2318	−0.6464	−1.3247	−2.3772
SD of B	0.0113	0.0058	0.0100	0.0354
SD of C	0.0225	0.0135	0.0254	0.0355
r^a	0.9993	0.9999	0.9999	0.9960

[a] Linear correlation coefficient.

Table IV. Partial Pressure of Water over Lithium Bromide Solutions (Values Obtained Using Equation 6)

Temp, °C	Wt % LiBr				
	0^a	40.00	50.00	60.00	70.27
10	9.20	5.33	[b]	[b]	[b]
20	17.52	10.10	4.63	[b]	[b]
30	31.81	18.28	8.70	2.63	[b]
40	55.31	31.67	15.59	4.99	[b]
50	92.52	52.82	26.82	9.06	[b]
60	149.4	85.05	44.48	15.80	[b]
70	233.7	132.7	71.33	26.56	[b]
80	355.2	201.2	110.9	43.18	[b]
90	525.8	297.1	167.8	68.07	[b]
100	760.0	428.5	247.5	104.4	33.53
110	1074	(604.6)[c]	356.8	156.0	53.61
120	1489	(836.2)	505.4	227.8	83.42
130	2026	(1136)	696.7	325.7	126.5
140	2710	(1517)	(947.2)[c]	456.5	187.8
150	3570	(1994)	(1266)	628.5	272.7
160	4636	(2585)	(1669)	851.1	388.5
170	5940	(3309)	(2167)	(1135)	543.6
180	7520	(4183)	(2780)	(1492)	748.2
190	9414	(5229)	(3524)	(1936)	(1014)[c]
200	11662	(6470)	(4417)	(2483)	(1355)

[a] Water vapor pressure taken from 1967 ASME Steam Tables.
[b] Liquid and solid phases present at this temperature. [c] Extrapolated values from Equation 6 are shown in parentheses.

Chemical Preparation and Analytical

Lithium bromide solutions were prepared by slowly adding purified lithium carbonate to certified reagent grade 48% hydrobromic acid. The neutral endpoint was reached by final adjustment with lithium hydroxide. Samples at specific concentrations were prepared by evaporation and analyzed by titration with silver nitrate. The average difference for samples titrated was ±0.12% lithium bromide. Samples were analyzed before and after each vapor-pressure determination to check any concentration variation owing to water loss during vapor-pressure determinations.

Results and Discussion

Literature values for vapor pressure of lithium bromide solutions are represented by equations which express vapor pressure as a function of temperature and concentration; i.e., $\text{Log } P = A + B/T + C/T^2$, where A, B, and C are functions of the concentration. The basic vapor-pressure equation
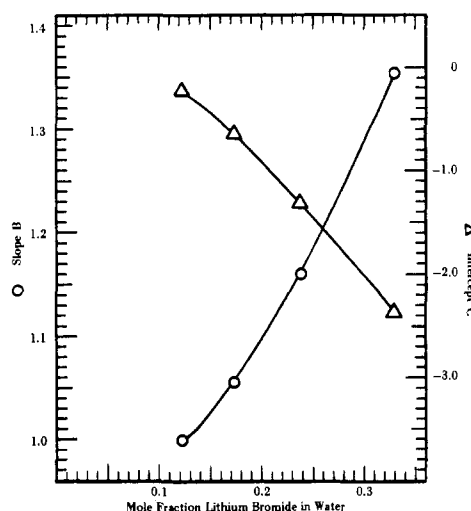
$$\text{Log } P = H/T + C \qquad (5)$$

Figure 3. Slope and intercept constants of vapor-pressure equation: $\text{Log } P_{(soln)} = B \text{ Log } P_{(water)} + C$
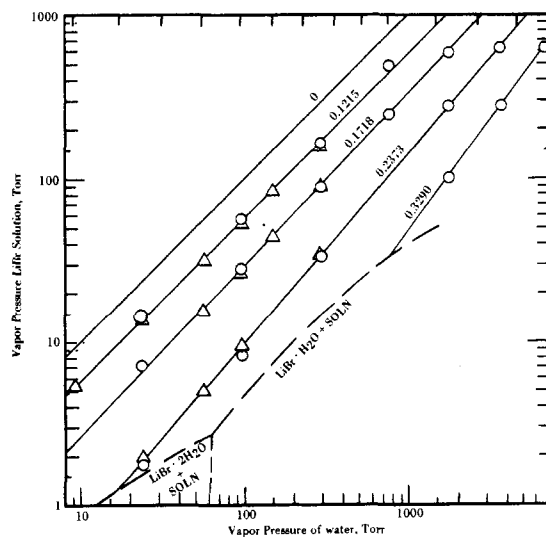
Figure 4. Vapor pressure of lithium bromide solutions (mole fractions)

△ Static method
○ Dynamic method

Table V. Comparison of Vapor-Pressure Data with Literature Values

Concn, wt %	Temp, °C	This work, torr	Uemura (9) torr	Pennington (8), torr
40.00	25	13.66	11.72	21.07[a]
40.00	50	52.81	48.87	78.27[a]
40.00	75	163.94	158.88	228.08[a]
40.00	100	428.47	423.31	551.86[a]
50.00	25	6.39	5.28	6.39
50.00	50	26.82	24.31	26.77
50.00	75	89.27	85.41	89.92
50.00	100	247.54	244.14	251.47
50.00	125	593.64	594.17	608.63
60.00	25	1.87	1.64	1.92
60.00	50	9.06	8.92	9.25
60.00	75	34.00	35.53	34.72
60.00	100	104.37	111.88	106.75
60.00	125	273.13	293.72	279.60
60.00	150	628.52	668.14	650.96[a]
70.27	100	33.53	39.52[a]	46.77[a]
70.27	125	103.08	114.41[a]	124.14[a]
70.27	150	272.71	280.22[a]	285.20[a]
70.27	175	639.03	601.05[a]	581.04[a]

Concn, wt %	Temp, °C	This work, torr	Int. Crit. Tables (2), torr	Peacock (7), torr	Löwer (3), torr
40	20	10.1	9.0[a]	9.6	9.3
40	100	428	431	420	435
50	20	4.63	4.9	7.1	4.1
50	100	247.5	256	248	248
60	20	1.31	1.9[a]	...	1.32
60	100	104.4	112.3[a]	111	108
60	64.3	19.84	Maust (4) 19.82		

[a] Extrapolated values.

shows the change of log P with respect to $1/T$ is related to the latent heat of vaporization (H). Because latent heat of vaporization is not constant but varies slightly over an extended temperature range, extrapolating for vapor pressures beyond experimentally determined points can lead to error. A more useful method has been demonstrated by plotting log P of so-lution vs. log P of water at the same temperature (Equation 6) (5).

$$\text{Log } P_{(soln)} = B \text{ Log } P_{(water)} + C \qquad (6)$$

This method eliminates the effect of the change in latent heat of vaporization of water and results in greater linearity. Slope B in Equation 6 is equivalent to the ratio of latent heat of vaporization of solution (L) to that of pure water (L_2) as shown by Equation 7.

$$\text{Log } P_{(soln)} = \frac{L_1}{L_2} \text{Log } P_{(water)} + C \qquad (7)$$

Vapor-pressure values determined by the static (Table I) and the gas transport (Table II) methods were in good agreement; therefore, these results were combined and used to calculate the constants for Equation 6 using the least-squares method. The constants and standard deviations are given in Table III, and a plot of Equation 6 constants vs. mole fraction is shown in Figure 3. The statistical treatment of the data as developed from Equation 6 shows a linear relationship for the vapor pressures of lithium bromide solution over the temperature and pressure range studies. Statistical curves and experimental data are plotted in Figure 4, and calculated values using Equation 6 are given in Table IV.

Vapor pressures as a function of concentration and temperature are compared with previously published data in Table V. Close agreement exists between results found and Pennington's (8) data, as opposed to data reported by Uemura (9). Also, the single vapor-pressure point determined by Maust (4) with an ebulliometer (the same method used by Pennington) is in close agreement with this study. Disagreement is evident when Pennington's values are extrapolated.

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