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Vapor Pressures of Hydrated Barium Chloride

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Vapor pressures of water over the monohydrate and over the dihydrate of barium chloride were measured from 17 °C to 72 °C in a glass apparatus from which air had been evacuated. Equilibrium was approached from higher as well as lower pressures. Vapor pressures for the dihydrate were found to be somewhat lower than previously published values. Vapor pressures for the monohydrate confirm a few published values but are much lower than the values published later in the International Critical Tables. The enthalpies of dehydration of the dihydrate and of the monohydrate were found to be 59 ± 2 kJ·mol^{-1}and 56 ± 3 kJ·mol^{-1}, respectively.

Introduction

These measurements were initiated to test a new apparatus on a known material before using it on a radioactive material of interest. When results on the monohydrate were found to be much different from values in the International Critical Tables,[1] the work was expanded into a complete study.

Experimental Section

Baker's "analyzed, meets ASC specifications" barium chloride dihydrate, $BaCl_2·2H_2O$, was used without further purification or sizing. The claimed purity includes a minimum of 99.0% $BaCl_2·2H_2O$ and not more than 0.15% alkaline earth elements. Tests on fresh material showed a weight loss of 12.7% on heating at 300 °C, indicating some dehydration during years of storage in the local environment, even though in a seemingly closed bottle. Grain sizes were estimated to be ≤0.5 mm. Sample sizes were (1 to 2) g.

Equipment and Procedures. The equipment is shown in Figure 1. The sample rested in a pan near the bottom of the 96-cm^3 glass tube. The part inside the dotted line was heated by an electric mantle when necessary to prevent condensation. Measurements of pressures below ~1.4 kPa were made with the manometer, which was filled with vacuum pump oil, found to have a density of 0.869 g·cm^{-3} at ~22 °C. The precision for differences in readings was estimated to be ±4 Pa. The uncertainties were generally larger than this and are given in Tables 1 and 2. For higher pressures, differences in the mercury column heights were needed, and the precision for these differences was ±40 Pa. The manometer was usually used by closing stopcock B so as to observe the approach to equilibrium precisely and/or to prevent water vapor from entering the part of the equipment outside the heating mantle and condensing there. Then the total water vapor pressure was the sum of the drop in the mercury column relative to its reading at full vacuum plus the manometer differences. The water tube allowed vapor to be introduced into the sample tube at the start of an experiment so that equilibrium could be approached from any desired initial pressure.

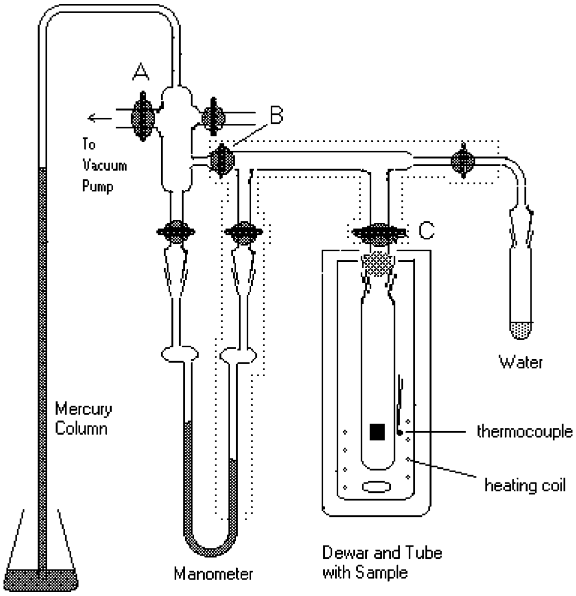

Figure 1. Apparatus for measuring vapor pressures. The space within the dotted line was insulated and heated when necessary. A thermoregulator outside the Dewar controlled the current to the heating coil.

The bath surrounding the sample tube was heated by a coil just inside the lower part of the Dewar and thermostated to within ±0.5 °C by an Omega regulator with a thermocouple sensor, the junction placed on the outside of the sample tube at the level of the sample. The thermocouple and readout were calibrated together at the ice point and the boiling point of water and at the transition points of the hydrates of sodium sulfate, manganous chloride, and sodium bromide. One test of temperature inhomogeneity was made by placing a second thermocouple on the sample tube joint, which is between the top of the liquid and the lid. At a temperature of ~60 °C, this thermocouple read 0.3 °C lower than the thermocouple at the sample level. Thus, it is concluded that the thermocouple placed opposite the sample measured the sample temperature to within ±0.2 °C.

Air was pumped from the entire apparatus before an experiment to accelerate equilibration. In a few tests with a McLeod gauge, the mechanical vacuum pump was found to draw to about 1 Pa or less. Leakage in the part of the

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Table 1. Vapor Pressures of Barium Chloride Monohydrate and Their Uncertainties

t/°C	initial pressure/kPa	final pressure/kPa	equilibration time
17.3	0.20	0.086 ± 0.01	5 d
31.0	0.20	0.173 ± 0.004	3 d
31.3	0.17	0.146 ± 0.003	3 d
32.1	0.13	0.138 ± 0.02	2 d
34.1	0.11	0.133 ± 0.004	17 h
34.3	0.29	0.231 ± 0.01	13 h
34.6	0.49	0.244 ± 0.007	8 h
34.6	0.05	1.01 ± 0.007	3 h
34.8	0.23	0.170 ± 0.01	25 h
34.9	0.17	0.142 ± 0.007	27 h
35.3	0.40	0.248 ± 0.004	20 h
35.3	0.56	0.272 ± 0.01	1 d
35.5	0.13	0.241 ± 0.005	3 d
35.8	0	0.105 ± 0.004	19 h
35.9	0.13	0.195 ± 0.007	41 h
36.1	0.66	0.344 ± 0.004	3 h
37.0	0.13	0.199 ± 0.007	2 d
38.3	0	0.160 ± 0.007	26 h
39.8	0.20	0.24 ± 0.01	16 h
40.3	0.36	0.274 ± 0.004	14 h
42.2	0.24	0.35 ± 0.01	21 h
42.8	0.50	0.40 ± 0.01	16 h
43.0	0.88	0.76 ± 0.03	7 h
45.3	0.24	0.312 ± 0.01	5 d
49.7	0.40	0.60 ± 0.03	22 h
50.4	1.0	0.60 ± 0.01	19 h
61.3	1.3	1.04 ± 0.04	14 h
61.3	1.3	1.10 ± 0.01	8 h
61.7	0.90	1.01 ± 0.01	25 h
61.8	0.89	0.96 ± 0.03	8 h
62.3	1.4	1.26 ± 0.03	2.5 h
64.3	2.7	1.51 ± 0.01	1 d
64.5	2.5	1.47 ± 0.04	25 h
71.8	2.0	2.06 ± 0.05	3 h
72.1	2.0	2.05 ± 0.07	3 h

Table 2. Vapor Pressures of Barium Chloride Dihydrate and Their Uncertainties

t/°C	initial pressure/kPa	final pressure/kPa	equilibration time
22.3	0.54	0.50 ± 0.01	18 h
22.4	0.39	0.39 ± 0.004	24 h
22.4	0.46	0.53 ± 0.01	24 h
22.5	0	0.56 ± 0.01	3 d
24.2	0.27	0.31 ± 0.01[a]	23 h
31.1	1.7	1.22 ± 0.03	2.5 h
31.4	1.1	0.90 ± 0.05	22 h
33.2	variable	1.01 ± 0.01	1 h
33.8	1.27	1.31 ± 0.03	75 m
34.1	2.0	1.39 ± 0.04	24 h
34.2	1.3	1.04 ± 0.03	27 h
35.1	0.88	1.19 ± 0.01	25 h
36.3	1.8	1.30 ± 0.03	19 h
45.9	0	2.50 ± 0.07	1 h
48.0	0.4	2.66 ± 0.04	70 m
50.0	0	3.88 ± 0.07	24 h
50.3	4.4	3.85 ± 0.05	17 h
50.6	2.0	3.97 ± 0.04	18 h
51.0	5.0	4.05 ± 0.04	18 h
51.7	4.8	5.15 ± 0.04	20 h
52.4	3.9	5.10 ± 0.07	20 h
63.8	0	9.4 ± 0.1	0.5 h
70.5	0	13.59 ± 0.07	0.5 h

[a] Not included in least-squares fit because of the large disagreement with other values measured here.

apparatus to the right of B (Figure 1) was checked periodically by noting any change in the oil manometer with valve A open and B and C shut. Leakage into the sample tube was checked occasionally by noting any slow change in the oil manometer with the sample at 0 °C or after the fact by noting the pressure in the sample bulb after condensing the water there with an ice + salt bath. Leakage into the water tube was checked occasionally by measuring its pressure in an ice bath. As a precaution, the apparatus was pumped out at the beginning of the day and at other times when the experiment permitted. For all but the dihydrate at the higher temperatures, that part of the apparatus to the left of valve B was pumped continuously so that minor leakage there was not an issue.

To start experiments at a new temperature below 60 °C, short trials (<1 h) from various initial vapor pressures established the approximate value of the equilibrium pressure. The water vapor pressure in the sample tube was then adjusted to somewhere near the expected final pressure, and the sample tube was closed off at stopcock C. After an equilibration period of (1 to 3) d, the space contained between stopcocks B and C and the right side of the manometer was filled with water vapor at the expected vapor pressure. Then the sample tube stopcock was opened. A correction was made for any pressure change noted on the manometer, based on the relative volumes of the sample tube and the air-filled space. An uncertainty of 10% due to temperature differences and miscellaneous volume uncertainties is assigned to this correction. Because only the initial and final vapor pressure were measured, there is no proof of equilibrium for a single experiment. Proof of equilibrium at these lower temperatures rests on the agreement or average of several measurements made from initial pressures both lower and higher than the final pressure. However, at temperatures above 60 °C, equilibrium could be attained in a few hours with constant observation of the manometer and barometer.

Each of the two equilibria for barium chloride hydrates involves two degrees of hydration. Some of each material must be present to allow equilibrium to be approached from either direction. The relative masses present were measured a few times by comparison of the total mass to the initial mass of the fresh sample. Significant amounts of both hydrates were found to be present for both the dihydrate and the monohydrate studies. Actual amounts were assumed to be unimportant. Only tiny amounts of a particular hydrate are needed to absorb or evolve sufficient vapor to attain equilibrium. For example, a calculation shows that 7 mg of anhydrous barium chloride is sufficient to absorb an excess of 1 kPa of vapor from the 96-cm^3 sample tube.

Results

The vapor pressures measured here are presented in Tables 1 and 2, along with the uncertainties, and in Figure 2. These uncertainties include the precision of scale readings and the uncertainties involved in deciding when equilibration had been reached (≥60 °C) or in the correction for the final measurement when the sample bulb had been isolated (<60 °C), as discussed above. Literature values[2–6] are included in Figure 2 for comparison. The present values and the literature values for the dihydrate were fit to straight lines of the logarithm of pressure versus the reciprocal of absolute temperature according to $\ln P = a\{(1/298.15) - (1/T)\} + b$. The best fit lines for the present data are included in Figure 2.

From the Clausius–Clapeyron equation, $\ln P = -\Delta H/(RT)$, the enthalpy change for the equilibrium between hydrate forms and vapor is then $\Delta H = -aR$, where R is the molar gas constant. The term $a/298.15$ allows ΔG_{298} to be calculated simply from b, according to $\Delta G_{298} = 298.15R(\ln P^\circ - b)$.[7] Standard deviations of a and b were calculated by the usual statistical formulas.[8] By the reverse procedure,

Table 3. Enthalpies and Gibbs Energies of Reaction and Vapor Pressures at 25 °C for Barium Chloride Equilibria from Straight Line Fits to Measured Vapor Pressures or Obtained from Literature Values of the Pure Substances[a]

	monohydrate-anhydride			dihydrate-monohydrate		
	ΔH	ΔG_{298}	P_{298}	ΔH	ΔG_{298}	P_{298}
	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$	kPa	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$	kPa
this work	56 ± 3	17.3 ± 0.2	94 ± 8	$59. \pm 2.$	12.7 ± 0.5	620 ± 30
		$a = 6697 \pm 340$, $b = -2.37 \pm 0.60$			$a = 7102 \pm 210$, $b = -0.514 \pm 0.015$	
Schottke[2]	52 ± 2	16.6 ± 0.5	123 ± 4			
		$a = 6215$, $b = -2.10$				
refs 2−4				56.6 ± 1.2	12.2 ± 0.1	727 ± 12
					$a = 6812 \pm 140$, $b = -0.319 \pm 0.003$	
NBS[8]	60.	16.7	126	58.	12.1	757

[a] Constants a and b are for the best fits. The standard state of water is taken as the vapor at 0.10133 MPa (a standard atmosphere) and 25 °C.

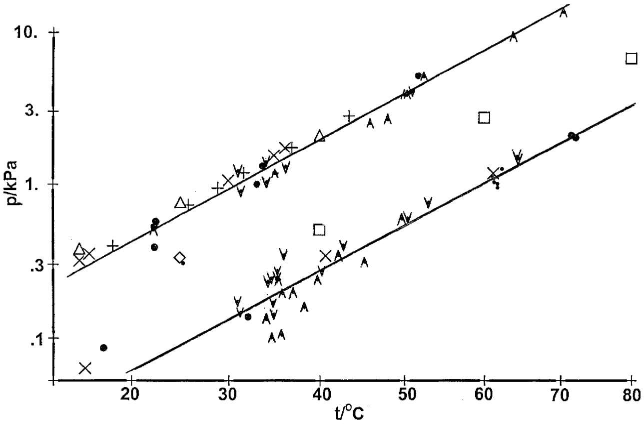

Figure 2. Water vapor pressure of barium chloride hydrates, scaled as the logarithm of pressure versus reciprocal Kelvin temperature. ∧, v, and · are for the present data and indicate the direction of change, if any, from the initial conditions. The solid lines are fitted to them. Literature values for the dihydrate (upper points): ×, Schottky; +, Frowein; Δ, Baxter. Literature values for the monohydrate (lower points): ×, Schottky; □, Lescoeur; ◇, Foote.

the free energies and entropies of formation for the pure substances in ref 9 were used to calculate the enthalpy and free-energy changes for the two reactions and then the expected equilibrium vapor pressures at 25 °C. All of this is presented in Table 3.

The vapor pressures measured here for the dihydrate are consistently somewhat lower than the previous experimental values[2−4] over the range where these latter values exist (i.e., below ~43 °C), as seen in Figure 2. Note from the standard deviations in Table 3 that the literature values, taken together, have a greater precision than the values measured here.

Vapor pressures measured for the monohydrate are somewhat lower than Schottky's[2] and much lower than those of Lescoeur[5] and Foote.[6] It is possible that Lescoeur did not thoroughly remove the dihydrate, the form normally present, because he states that it easily loses water at 60°−65 °C, whereas I found (30−60) min of pumping to be required at these temperatures.

Both Baxter and Cooper[3] and Schottky[2] discussed the special difficulty of obtaining equilibrium with the hydrates of barium chloride. Baxter and Cooper[2] measured evaporation into a very slow air flow over a 280-cm-long column of dihydrate. Schottky[2] demonstrated that the approach to vapor equilibrium from either hydrate is typically erratic and not always monotonic. For his monohydrate measurements, he used an all-glass system containing an oil manometer and a monohydrate + anhydride mixture. After air evacuation, he melted all openings shut, leaving no stopcocks or other joints for possible air leakage. He allowed 10 d for equilibration. His measurements are undoubtedly the most accurate available for the monohydrate.

Acknowledgment

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