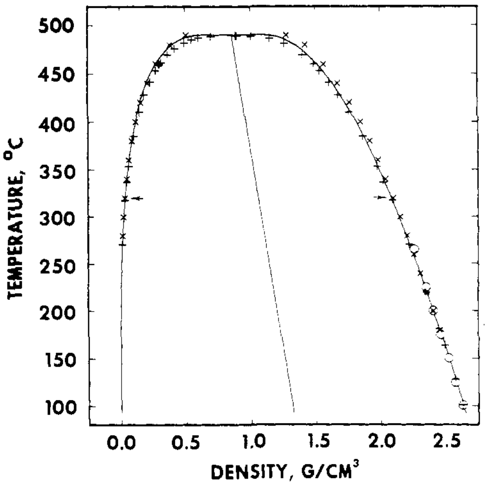

Figure 1. Coexistence curve for aluminum bromide
——, Calculated from Equations 10 and 11; O, Biltz and Voight (*1*); ×, Zhuravlev (*10*); +, Johnson et al. (*4*). Arrows indicate highest experimental temperature reached in present work

temperature. Indeed, the experimental points observed by Johnson et al. lie slightly below Equation 10 at temperatures above our highest temperature. Similarly, Zhuravlev's liquid density data lie slightly above our Equation 10, also above our highest temperature. These data are shown in Figure 1.

Safety

The same precautions should be taken as were reported previously (*5*) for the containment of liquids above their normal boiling points in glass vessels.

Nomenclature

a_i = empirical coefficients
A = constant, a function of a_2 and a_3
b_i = empirical coefficients
B = constant, a function of a_3
d = density of $AlBr_3$ vapor
D = density of $AlBr_3$ liquid
m_i = mass of $AlBr_3$ in *i*th tube
n = number of individual experimental measurements
Q = positive difference between rectilinear diameter and d or D
T_i = total enclosed volume in *i*th tube
t = temperature in degrees centigrade
t_c = critical temperature
V_i = liquid $AlBr_3$ volume in *i*th tube
z_i = residual; function to be treated by least-squares fitting
ρ = overall tube average density; i.e., m/T
ρ_c = density at critical temperature
ρ_m = rectilinear diameter; i.e., $(d + D)/2$
σ = standard deviation in Q
τ = distance from critical temperature, i.e., $t_c - t$
ϕ = fraction of total tube volume occupied by liquid; i.e., V/T

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X-Ray Powder Data and Unit Cell Parameters of $MgCl_2 \cdot 6H_2O$

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Detailed X-ray powder data for $MgCl_2 \cdot 6H_2O$ were obtained by diffractometry by use of CuK_α radiation at 22°C. The data were indexed on a bimolecular monoclinic unit cell, space group C2/m, with a = 9.858 ± 0.001 Å; b = 7.107 ± 0.001 Å; c = 6.069 ± 0.001 Å; β = 93° 47′ ± 10′. Calculated density was 1.591 g/cm³, compared with a measured density of 1.593 ± 0.003 g/cm³.

The structure of magnesium chloride hexahydrate, $MgCl_2 \cdot 6H_2O$, was determined by Andress and Gundermann (*1*), who reported a bimolecular unit cell, space group C2/m, with a = 9.90 ± 0.03 Å; b = 7.15 ± 0.03 Å; c = 6.10 ± 0.03 Å; β = 94° ± 20′. The only available X-ray powder data appeared in the original Hanawalt et al. compilation (*3*) and was subsequently included in the "Powder Diffraction File" (*5*). Comparison of the structure factors calculated by Andress and Gundermann with the powder data indexed by J. V. Smith indicates the incomplete nature of the powder data. This, coupled with the relatively low precision of the reported unit cell parameter measurements, prompted acquisition of the data reported in this work.

X-Ray Procedures

Powder data were acquired at 22°C by conventional methods by use of a General Electric XRD-700 recording diffractometer with CuK_α radiation generated at 50 kVp and 20 Ma. Flat recessed sample holders machined from Lucite were used. Samples containing approximately 20% high-purity rock crystal quartz as an internal standard were scanned from 2° to 60° 2 θ at a rate of 0.2° per min, which permitted measurement of 2 θ values to the nearest 0.01°. Samples containing no internal standard were then scanned, following alignment on the (020) line of the chloride, to provide complete interplanar spacing and intensity data.

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Table I. X-Ray Powder Diffraction Data for $MgCl_2 \cdot 6H_2O$ at 22°C

hkl	$2\theta_{obsd}$	d_{obsd}	d_{calcd}	I/I_1
110[a]	15.38	5.760_9	5.7607	14
$11\bar{1}$	20.87	4.256_2	4.2569	9
111[a]	21.70	4.095_3	4.0954	100
$20\bar{1}$	22.52	3.948_0	3.9476	13
201	24.05	3.700_2	3.6999	4
020[a]	25.06	3.553_3	3.5535	26
021	29.14	3.064_4	3.0648	1
002	29.50	3.027_8	3.0279	2
310[a]	30.01	2.977_5	2.9772	23
220[a]	31.05	2.880_1	2.8803	58
$31\bar{1}$ $11\bar{2}$[a]	32.78	2.732_0	2.7377 2.7240	39
$20\bar{2}$ $22\bar{1}$[a] 112[a]	33.88	2.645_7	2.6580 2.6411 2.6385	69
311	34.35	2.610_6	2.6105	3
221[a]	35.01	2.562_9	2.5629	6
202	35.83	2.506_1	2.5055	1
400[a]	36.53	2.459_7	2.4591	6
$40\bar{1}$	38.59	2.333_0	2.3328	5
022 130[a]	39.08	2.304_8	2.3047 2.3031	39
401[a]	40.48	2.228_3	2.2277	27
$31\bar{2}$	41.23	2.189_5	2.1896	2
$13\bar{1}$	41.76	2.162_9	2.1639	3
131[a]	42.18	2.142_3	2.1417	9
$22\bar{2}$	42.50	2.127_0	2.1285	2
312	43.91	2.061_9	2.0619	6
222[a]	44.21	2.048_6	2.0477	11
330 $20\bar{3}$	47.48	1.914_8	1.9202 1.9123	6
421	48.23	1.886_8	1.8874	4
$13\bar{2}$[a]	49.36	1.846_2	1.8469	23
203	49.96	1.825_4	1.8255	2
331	50.39	1.810_9	1.8103	4
040[a]	51.40	1.777_6	1.7768	19
023	52.08	1.756_0	1.7552	3
$42\bar{2}$[a]	53.15	1.723_2	1.7255	10
$22\bar{3}$	54.49	1.683_9	1.6840	2
422	56.08	1.639_9	1.6409	2
$24\bar{1}$[a]	56.76	1.621_8	1.6202	4
332[a]	57.86	1.593_9	1.5940	4

[a] Lines reported by "Powder Diffraction File," No. 1-0431.

Sample Preparation

Initial measurements were made with Fisher ACS Certified $MgCl_2 \cdot 6H_2O$ crystals covered with plastic wrap (Dow Handi-Wrap) to prevent absorption of atmospheric water. It proved to be impossible, however, to grind the crystals to a sufficiently small particle size, less than 270 mesh, necessary for reliable intensity measurements without excessive absorption of water. Detailed measurements were made, therefore, with Dow flake $MgCl_2 \cdot 6H_2O$, consisting of aggregates of fine crystals. Measured 2 θ values for the two materials were identical. Integrated intensities were obtained from the diffractometer recording chart by counting squares.

Density Measurements

Density of Dow flake $MgCl_2 \cdot 6H_2O$ was measured by suspension in liquid mixtures at 22°C. Densities of the pure liquids and mixtures were determined by pycnometric comparison with water. Flakes were floated on bromoform (ρ = 2.865); xylene (ρ = 0.863) was added a few drops at a time, and the mixture was agitated. When a few of the flakes remained suspended with all others floating because of included air, the density of the liquid was determined by pycnometer. When flakes were placed in carbon tetrachloride (ρ = 1.585), some floated, some sank, and some remained suspended because of differences in porosity. Bromoform was added a drop at a time, the mixture was agitated, and the flakes were observed. When none remained on the bottom and some were in suspension, the density of the liquid was determined by pycnometer.

Results

Measured diffraction angles, 2 θ, interplanar spacings, d_{obsd}, and relative intensities, I/I_1, are given in Table I.

Initial indexing was accomplished by comparing observed interplanar spacings with those calculated from the unit cell parameters of Andress and Gundermann (*1*). After identification of the (400), (020), and (002) lines and the (201) ($20\bar{1}$) pair, precise lattice parameters were calculated by Ito's method (*2*, *4*). Diffraction angles and interplanar spacings were then recalculated, and all lines in the pattern were identified. Agreement between calculated and observed values is excellent. The revised lattice parameters are a = 9.858 ± 0.001 Å; b = 7.107 ± 0.001 Å; c = 6.069 ± 0.001 Å; β = 93° 47′ ± 10′.

Indexing is in agreement with the reported space group, C2/m, in that $h + k = 2n$ for all lines. Relative intensities are reasonably close to reported values (*3*). The unit cell volume is 424.27 Å^3, and the calculated density, ρ_x, is 1.591 g/cm^3. Densities determined by suspension in xylene–bromoform and carbon tetrachloride–bromoform mixtures were 1.593 and 1.594, respectively. Within reasonable experimental limits, therefore, the density data are in agreement. The value obtained, 1.593 ± 0.003, is considerably higher than that obtained from the X-ray data of Andress and Gundermann (*1*), 1.568, and that reported in the "Handbook of Chemistry and Physics" (*6*), 1.569.

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