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The System Magnesium Bromate-Water

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The eutectic of the system $Mg(BrO_3)_2$–H_2O lies at −13.0° and 38.5% $Mg(BrO_3)_2$ with ice and $Mg(BrO_3)_2\cdot 6H_2O$ as saturating solids. The transition from hexa- to dihydrate occurs at 80.0°. A saturated solution boils at 134° and contains 74.6% $Mg(BrO_3)_2$.

With the exception of a single determination by Kohlrausch,[1] no solubility data for the system $Mg(BrO_3)_2$–H_2O are available. The only solid phase that has been prepared previously is the hexahydrate.

Materials and Methods

Magnesium bromate hexahydrate was prepared by the addition of $MgSO_4$ solution to a hot suspension of $Ba(BrO_3)_2\cdot H_2O$. When the resulting solution gave no test for Ba^{++} and $SO_4^{=}$ ions the precipitate was allowed to digest overnight and then removed by filtration. The solution was evaporated by boiling until it became rather sirupy (at about 140°), but no solid precipitated. Upon cooling, however, the mass solidified completely. This salt was recrystallized twice and then air-dried. Analysis for bromate by iodometry and for magnesium by precipitation of the oxime showed 72.03 wt. % $Mg(BrO)_2$ to be present, indicating that the solid was the hexahydrate (theory = 72.15%).

It was found that 8-hydroxyquinoline is oxidized by BrO_3^- even in alkaline solution. Magnesium-oxine precipitates which were formed in the presence of BrO_3^- varied erratically in weight. This interference was eliminated by reducing the BrO_3^- prior to the addition of the oxine. KBr or KI plus HCl were added, and the solution was boiled to expel the liberated halogen.

Magnesium bromate dihydrate was prepared by heating the hexahydrate to 50–60°. A typical sample which attained constant weight in this temperature range contained 88.67% $Mg(BrO_3)_2$ by iodometry (theory for $Mg(BrO_3)_2\cdot 2H_2O$ = 88.61%). The salt was stored at 60° until used.

Anhydrous magnesium bromate was obtained by heating either hydrate to 105°.

The solubility determinations below 80° were made in a water thermostat constant to ±0.05°. Above 80° a vapor bath[2] was used, and the maximum variation was ±0.5°. All samples were stirred internally. Repeated analysis showed that equilibrium was attained within an hour in every case. In a few cases equilibrium was checked by approach from supersaturation. Each reported value is the average of at least two independent determinations which agreed within 2 parts per thousand.

Data on the ice curve are the freezing points of solutions prepared by mixing known weights of the components, and were reproducible to ±0.1°. Boiling points of similarly known solutions were determined with a small percolator apparatus.[3] They were reproducible to ±0.3° in dilute and ±1° in concentrated solutions. The melting point of the hexahydrate was found (±0.1°) by the usual capillary method.

The densities of solutions saturated with hexahydrate were determined in small pycnometers. The results were plotted and the tabulated data were read from the average curve. They are probably correct to 2 parts per thousand.

Discussion

The solubility of $Mg(BrO_3)_2\cdot 6H_2O$ increases linearly from the eutectic (−13.0°) to 65°, and can be represented by the equation

$$S = 42.4 + 0.300t$$

over this range with an average deviation of 0.1 from the experimental values. Above 60° the solubility increases more rapidly, and the hexahydrate melts to a clear liquid at 80.5°. Upon scratching this liquid yields the dihydrate, which is the stable phase from 80.0° to the boiling point of a saturated solution (134°). The transition from hexa- to dihydrate is slow enough to permit the observation of the metastable melting point of the hexahydrate. The solubility of the dihydrate may be expressed as

$$S = 65.1 + 0.064t$$

with an accuracy of ±0.1.

The boiling point of a saturated solution was difficult to determine. When an unsaturated solu-

TABLE I

THE SYSTEM $Mg(BrO_3)_2$–H_2O

Temp., °C.	Saturated solution		Temp., °C.	Satd. soln. Mg $(BrO_3)_2$, wt. %
	$Mg(BrO_3)_2$, wt. %	Density		
	Ice		$Mg(BrO_3)_2\cdot 6H_2O$ +	
− 1.6	9.34	...	$Mg(BrO_3)_2\cdot 2H_2O$	
− 4.2	20.94	...	80.0^a	70.1^a
−10.1	34.66	...	$Mg(BrO_3)_2\cdot 2H_2O$	
			81	70.1
Ice + $Mg(BrO_3)\cdot 6H_2O$			90	70.8
−13.0	38.5^a	1.448	100	71.9
			117	72.6
	$Mg(BrO_3)_2\cdot 6H_2O$		130	73.3
0	42.34	1.512	$134^{a,b}$	73.6^a
10	45.58	1.562		
20	48.66	1.609	B.p. of unsaturated solns.	
30	51.4	1.662		
40	54.5	1.722	101.0	15.15
50	57.3	1.787	102.6	27.2
65	62.5	1.900	106.5	44.3
75	66.8	2.013	116	60.9
78	68.3	2.070	131	72.2
80.5^c	70.15	...		

[a] Estimated graphically. [b] Boiling point. [c] Metastable melting point.

TABLE II

SOLUBILITY OF $Mg(BrO_3)_2$ IN $Mg(NO_3)_2$ SOLUTIONS AT 85°

Original complex, wt. %		Saturated soln., wt. %		% H_2O in solid by extrapolation
$Mg(NO_3)_2$	$Mg(BrO_3)_2$	$Mg(NO_3)_2$	$Mg(BrO_3)_2$	
..	...	0	70.4^a	...
3.38	71.91	4.72	64.30	10.93
3.86	70.91	6.00	62.99	12.54
5.11	69.15	7.35	61.12	11.71
5.83	68.57	8.85	59.62	12.33
5.83	70.48	9.50	58.04	10.91
			Av.	11.68
			Theory for $Mg(BrO_3)_2\cdot 2H_2O$:	11.39

[a] Estimated graphically.

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[1] F. Kohlrausch, *Sitzb. K. Akad. Wiss. (Berlin)*, i, 90 (1897).

[2] W. F. Linke, *J. Chem. Ed.*, **29**, 492 (1952).

[3] R. L. Shriner and R. C. Fuson, "Identification of Organic Compounds," 2 Ed., John Wiley and Sons, Inc., New York, N. Y., 1944, p. 92.

tion is boiled in open air the boiling point rises steadily, but the dihydrate does not precipitate. The liquid becomes very viscous and can be heated to about 150° before precipitation occurs. When the solid separates the boiling point decreases markedly but continued heating again causes the solution to superheat. Seeding with the dihydrate has no effect. An attempt to boil a solution which was first brought to equilibrium at 130° with a large quantity of dihydrate yielded similar superheating. Evidently the rate of loss of water vapor was too fast, and the viscosity of the solution too high, to permit the attainment of equilibrium throughout the mixture.

A test-tube containing solution and dihydrate was placed in a thermostat at 140° and stirred for about an hour. When the stirring was stopped, bubbles rose constantly in the solution, indicating that it was boiling. The bath temperature was then lowered in 1 or 0.5° intervals with about 15 minutes stirring at each step. Bubbling decreased markedly at 134° and stopped entirely at 132.5°. The graphical estimate of the boiling point is 134 ± 1°, in agreement with these observations.

When $Mg(BrO_3)_2{\cdot}6H_2O$ is heated to 50–60° in open air it is converted to $Mg(BrO_3)_2{\cdot}2H_2O$. Heating at 105° yields the anhydrous salt. However, direct analysis of the solid in contact with saturated solutions above 80° did not prove that it was the dihydrate. Attempts to separate and dry the solid invariably led to some retention of the solution and crystallization of the hexahydrate. For example, a sample which was filtered by suction at 100° and then centrifuged, contained 85.0% $Mg(BrO_3)_2$, corresponding to 2.7 moles of water per mole of salt.

The identity of the dihydrate as the saturating phase was established by determining the change in the solubility of the salt upon the addition of $Mg(NO_3)_2$. Complexes were prepared from $Mg(BrO_3)_2{\cdot}2H_2O$, a solution of $Mg(NO_3)_2$ of known concentration, and water, and were stirred for from 1 to 5 hours at 85°. The solutions were then filtered and analyzed for bromate and for total magnesium. Algebraic extrapolation of the tie lines yielded the composition of the saturating (di) hydrate. Graphical extrapolation of the ternary solubility curve to zero % $Mg(NO_3)_2$ showed the solubility of the dihydrate in water at 85° to be 70.4%. This is the same solubility found in the binary system $Mg(BrO_3)_2$–H_2O, and proves that the phase stable above 80° is the dihydrate.

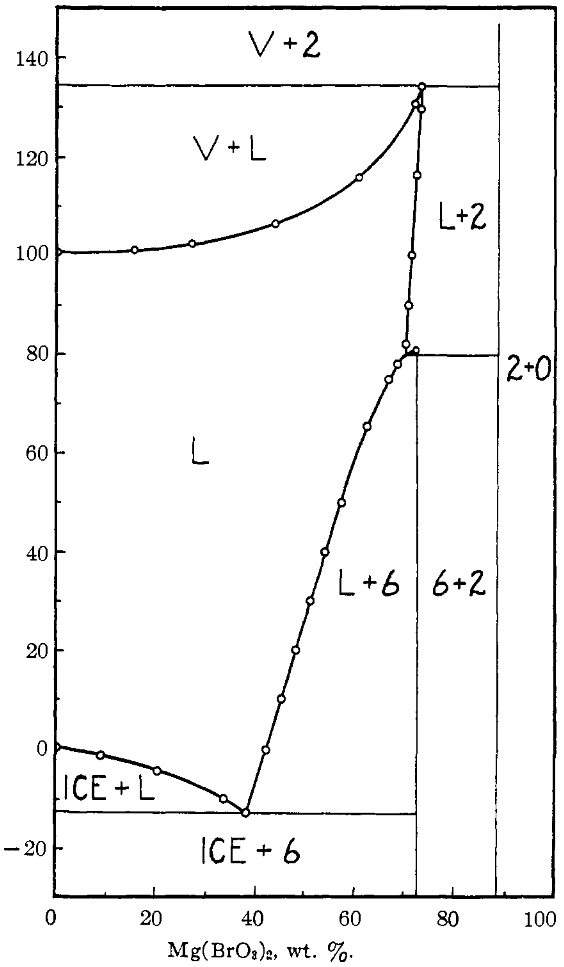

Fig. 1.—The system $Mg(BrO_3)_2$–H_2O at 1 atm.

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