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PHASE EQUILIBRIA IN THE CONDENSED
SYSTEM BROMINE - BROMINE TRIFLUORIDE

by

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ABSTRACT

Investigation of the system bromine - bromine trifluoride has shown a liquid immiscibility gap, which intersects the bromine trifluoride solubility curve. A study of the condensed system indicates that the consolute point is $55.5^{\circ} \pm 0.5^{\circ}\text{C.}$ and 60 ± 5 mole per cent bromine (Br_2). The pure components are the only solid phases observed in the temperature range studied.

INTRODUCTION

Ruff and Braida¹ reported that equilibrium mixtures of bromine and bromine trifluoride show limited miscibility and that an unstable intermediate species, bromine monofluoride, is present. To this date a satisfactory isolation of bromine monofluoride has not been reported.

In order to characterize the phases involved in the heterogeneous equilibria between bromine and bromine trifluoride, the condensed system involving these components was studied.

EXPERIMENTAL

Materials - Baker's reagent grade bromine, whose melting point was in agreement with the literature value² as indicated in Table 1, was used without further purification. The bromine trifluoride obtained from Harshaw Chemical Co. was purified by distillation in a 40-inch nickel fractionation column 1/2 inch in diameter and packed with 1/8-inch nickel helices. The melting point of the bromine trifluoride, as indicated on Table 2, agreed with the literature value³ within experimental error.

¹O. Ruff and A. Braida, Z. anorg. u. allgem. Chem., 214, 91 (1933).

²F. D. Rossini, et al., Selected Values of Chemical Thermodynamic Properties, National Bureau of Standards, 1952, page 550.

³G. Oliver and J. Griswald, J. Am. Chem. Soc., 74, 2705 (1952).

Table 1

COMPOSITION OF CONJUGATE SOLUTIONS OF THE SYSTEM
BROMINE - BROMINE TRIFLUORIDE

Temp., °C.	Mole Per Cent Br ₂	
	Upper Phase	Lower Phase
9.0*	13.9	95.4
16.1	16.2	94.8
25.0	17.7	92.9
28.7*	-	91.4
31.0*	20.6	91.1
35.3	22.2	90.0
39.4*	24.9	-
39.7	-	88.0
41.3*	-	87.9
42.2*	27.1	-
45.8	29.7	84.8
47.6*	32.2	82.8
49.1*	33.6	82.3
49.5	34.2	82.7
50.2*	35.6	-
50.8	-	80.0
53.9	46.8	-

Temperature at Visual Observation of Second Phase Disappearance:

Mole Per Cent Br ₂	Temp., °C.	Mole Per Cent Br ₂	Temp., °C.
39.6	51.8	55.7	54.9
48.4	54.5	71.1	54.7
55.6	54.8	76.9	52.8

*Equilibrium approached from a higher temperature.

Table 2

SYSTEM BROMINE - BROMINE TRIFLUORIDE
SOLID-LIQUID EQUILIBRIA

Mole Per Cent Br ₂	Univariant Temp.		Invariant Temp.		Eutectic Temp.		Solid Phase
	Freezing Curve	Thaw Curve	Freezing Curve	Thaw Curve	Freezing Curve	Thaw Curve	
0.0	-	-	8.7	8.6	-	-	BrF ₃
2.58	7.4	7.4	-	3.4	-8.8	-	BrF ₃
5.36	6.0	6.3	3.3	3.6	-8.6	-8.6	BrF ₃
9.80	4.7	5.0	-	3.6	-	-9.0	BrF ₃
13.88	-	-	3.8	3.6	-9.0	-8.9	BrF ₃
19.87	-	-	3.6	3.5	-9.1	-	BrF ₃
39.61	-	-	-	3.7	-9.0	-8.9	BrF ₃
54.08	-	-	3.8	3.8	-8.8	-	BrF ₃
69.55	-	-	-	3.5	-8.7	-8.8	BrF ₃
95.22	-	-	-	-	-8.8	-	BrF ₃
97.65	-	-3.7	-	-	-8.8	-8.6	BrF ₃
99.20	-8.0	-7.9	-	-	-	-8.6	Br ₂
100.0	-	-	-7.3	-7.1	-	-	-

Melting Points - Literature Values

Bromine² -7.3

Bromine Trifluoride³ 8.77

Apparatus - The apparatus used in determining the liquid-liquid equilibria is shown in Figure 1. The samples were contained in a 3/4-inch Kel-F (polychlorotrifluoroethylene) tube, 6 inches in length, which was flared at the top so that it could be closed with a nickel fitting. The fitting was provided with a 1/4-inch nickel thermocouple well which extended into the liquid, and a 3/8-inch tube provided access to the system so that samples could be removed with a Kel-F pipette. The temperature of the system was controlled by placing the tube in an aluminum block which was heated electrically and was cooled with circulating water. Sight ports in the block permitted observation of the interface between the two liquid layers. A strong light behind the tube was necessary owing to the intense color in both layers. The aluminum block and the tubes extending out of the apparatus were insulated with asbestos and glass wool to reduce temperature gradients within the system. Temperatures of the block and the liquid sample were measured with copper-constantan thermocouples and a Rubicon "type B" potentiometer. The temperature of the system was controlled within $\pm 0.2^\circ\text{C}$.

The apparatus used in obtaining freezing and thaw curves is shown in Figure 2. The melting point tubes, made either of nickel or Monel metal, were 3/4 of an inch in diameter and 6 inches long. The sample was introduced through the 1/4-inch flared fitting. The tube was placed in the heating and cooling shield as indicated in Figure 2.

The rate of temperature change of the system was controlled by electrical heating and flow of cold nitrogen gas through the copper coils surrounding the stainless steel shield.

The temperatures of the aluminum shield and of the sample in contact with the thermocouple well were measured with iron-constantan thermocouples in conjunction with a multipoint Brown recording potentiometer. The thermocouples and recorder were calibrated against a standard platinum resistance thermometer employing a G-2 Mueller bridge.

Procedure - The liquid-liquid portion of the phase diagram was determined by both the isothermal method and the synthetic method. The solid-liquid portion of the phase diagram was determined from cooling and thawing curves. In the determination of the liquid-liquid equilibria by the isothermal method, an approximately equimolar mixture of bromine and bromine trifluoride was used. About 15 ml. was placed in a Kel-F tube which was in turn held in the aluminum block for proper temperature control. The mixture was shaken vigorously and allowed to stand overnight. After being allowed to equilibrate for about 18 hours, the tube was shaken again. As soon as the two phases had separated, each phase was sampled. The temperatures at which the samples were taken were approached from both higher and lower temperatures as a check on the attainment of phase equilibria.

Samples of about 1 ml. from the conjugate solutions were placed in weighed nickel tubes, capped, and reweighed, giving the total sample weight. Owing to the violence of the reaction, the samples were hydrolyzed in a 250-ml. nickel bomb with 100 ml. of solution 0.27 M in aluminum nitrate and 0.23 M in hydrazine sulfate. All the bromine in the hydrolyzed sample was reduced to bromide, which was determined as silver bromide by a standard gravimetric procedure.⁴ The fluorine content was obtained as the residuum of the total weight.

In the upper temperature ranges, sampling became difficult owing to the volatility of the material. Observations in this region were made using the synthetic method. Bromine and bromine trifluoride were weighed into the Kel-F tube, and the mixture was shaken in the block during temperature cycling. The temperatures of the interface appearance and disappearance were measured in several such cycles. The average values of appearance and disappearance of the second phase are given in Table 1. These points were found to be reproducible within $\pm 0.5^\circ\text{C}$.

In the determination of the solid-liquid equilibria, synthetic complexes were prepared by weighing bromine and bromine trifluoride, under an atmosphere of helium, in the nickel melting point tubes previously described. The total weight of complex was approximately 50 grams.

The melting point tube was shaken and placed in the heating and cooling shield (Figure 2). The maximum cooling rate employed was 0.5 degree/minute. Thaw curves were obtained in some instances when supercooling effects caused unsatisfactory cooling curves.

Supercooling was particularly troublesome in complexes falling within the immiscibility gap and containing 39.61, 54.08, and 69.55 mole per cent bromine. In order to obtain the upper invariant point, the temperature was lowered to the approximate temperature of the invariant point, which was obtained with complexes of lower mole percentages of bromine. The tubes were vigorously shaken and then allowed to supercool. After the solid precipitated, as indicated by sudden increases in temperatures, the temperatures were slowly raised, and the thaw curves were obtained. In one determination, for the complex of 54.08 mole per cent bromine, the supercooling was not bad, and a satisfactory freezing point, which agreed with the melting point, was obtained.

RESULTS AND DISCUSSION

The data, in terms of mole per cent bromine, are listed in Tables 1 and 2 and are plotted in the usual fashion in Figure 1. The consolute

⁴I. M. Kolthoff and E. B. Sandell, Textbook of Quantitative and Inorganic Analysis, Macmillan Company, 1947, page 313.

temperature is 55.5°C. Because the upper portion of the immiscibility curve is very flat, it is difficult to assign a precise value for the consolute composition, which is approximately 61 mole per cent bromine.

Although spectroscopic examinations^{5,6,7,8} have indicated that intermediate species such as bromine monofluoride do exist, our data do not show their presence in the solid phase. Only the two components, bromine and bromine trifluoride, were observed in the solid phase within the temperature range covered by this work.

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⁵D. F. Smith, M. Tidwell, and D. Williams, Phys. Rev., 77, 420 (1950).

⁶P. H. Brodersen and H. J. Schumacher, Z. Naturforsch., 2a, 358 (1947).

⁷P. H. Brodersen and H. J. Schumacher, Anales asoc, quim. argentina, 38, 52 (1950).

⁸Private communication with H. Hyman of Argonne National Laboratory concerning spectral absorption in the visible range for mixtures of bromine and bromine trifluoride.

FIGURE 1
TUBE AND HEATING BLOCK.

FIGURE 2
COOLING CURVE APPARATUS.

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FIGURE 3
LIQUID-LIQUID AND SOLID-LIQUID EQUILIBRIA
OF THE SYSTEM BROMINE-BROMINE TRIFLUORIDE.