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Phase Equilibria in the Condensed System Bromine–Bromine Trifluoride

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RECEIVED NOVEMBER 6, 1953

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 ± 0.5° and 60 ± 5 mole per cent. bromine (Br_2). The pure components are the only solid phases observed in the temperature range studied.

Ruff and Braida[1] 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.—J. T. Baker reagent grade bromine, whose melting point was in agreement with the literature value[2] as indicated in Table II, 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 in Table II, agreed with the literature value[3] within experimental error.

Apparatus.—In determining the liquid–liquid equilibria 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 pipet. 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 ±0.2°.

TABLE I

COMPOSITION OF CONJUGATE SOLUTIONS OF THE SYSTEM BROMINE–BROMINE TRIFLUORIDE

Temp., °C.	Mole per cent. Br_2 Upper phase	Mole per cent. Br_2 Lower phase
9.0[a]	13.9	95.4
16.1	16.2	94.8
25.0	17.7	92.9
28.7[a]	..	91.4
31.0[a]	20.6	91.1
35.3	22.2	90.0
39.4[a]	24.9	..
39.7	..	88.0
41.3[a]	..	87.9
42.2[a]	27.1	..
45.8	29.7	84.8
47.6[a]	32.2	82.8
49.1[a]	33.6	82.3
49.5	34.2	82.7
50.2[a]	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

[a] Equilibrium approached from a higher temperature.

TABLE II

SYSTEM BROMINE–BROMINE TRIFLUORIDE SOLID–LIQUID EQUILIBRIA

Melting points (literature values) bromine,[2] −7.3; bromine trifluoride[3] 8.77.

Mole per cent. Br_2	Univariant temp. Freezing curve	Univariant temp. Thaw curve	Invariant temp. Freezing curve	Invariant temp. Thaw curve	Eutectic temp. Freezing curve	Eutectic temp. Thaw curve	Solid phase
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	...	..	..

The freezing and thaw curves were determined in melting point tubes, made either of nickel or Monel metal. These tubes 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 a heating and cooling shield. 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 shield.

The temperatures of the 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

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(1) O. Ruff and A. Braida, *Z. anorg. allgem. Chem.*, **214**, 81 (1933).

(2) F. D. Rossini, *et al.*, "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards, 1952, p. 550.

(3) G. D. Oliver and J. W. Grisard, THIS JOURNAL, **74**, 2705 (1952).

the samples were taken were approached from both higher and lower temperatures as a check on the attainment of phase equilibria.

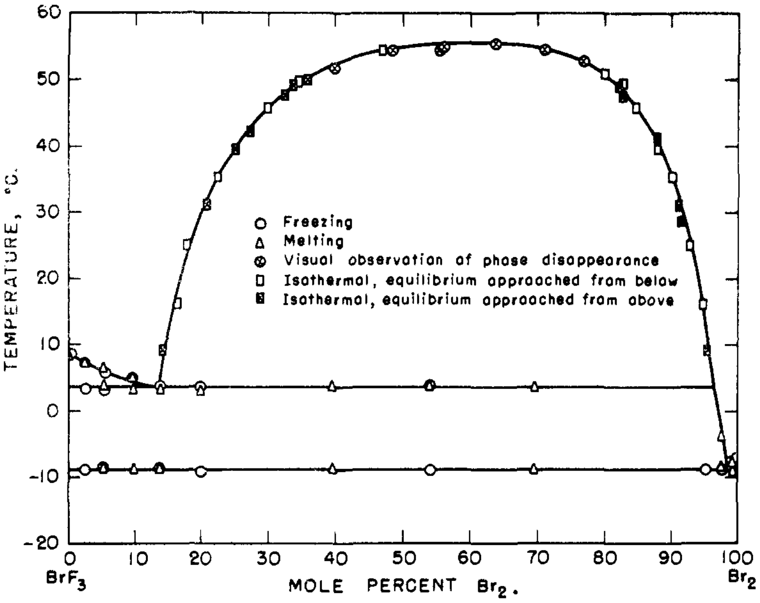

Fig. 1.—Liquid–liquid and solid–liquid equilibria of the system bromine–bromine trifluoride.

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, in a closed system. 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 I. These points were found to be reproducible within ±0.5°.

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 g.

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 I and II and are plotted in the usual fashion in Fig. 1. The consolute temperature is 55.5°. 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[5-8] 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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[4] I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," The Macmillan Co., New York, N. Y., 1947, p. 313.

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

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

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

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