TABLE XI

DISSOCIATION CONSTANT OF THE PbI^+ ION

a = molarity of lead perchlorate, b = molarity of potassium iodide, b = 0.002; measurements made at 290 mμ. $D' = 0$

a	I = 0.04 D	0.06 D	0.08 D	0.10 D
0.004	0.537	0.490	0.470	0.444
.006	.764	.703	.666	.628
.008	.962	.890	.849	.794
.010	1.137	1.060	1.008	.954
.012	1.303	1.209	1.156	1.089
K =	0.013	0.013	0.012	0.011

Av. K = 0.012

and to evaluate the activity coefficient term we used Davies' equation[19]

$$-\log \gamma = 0.5092\, z^2\sqrt{I}/(1 + \sqrt{I}) - 0.1zI$$

(19) C. W. Davies, *J. Chem. Soc.*, 2093 (1938).

that is to say, we put $z = 2$ for the lead ion and cancelled out the other two activity coefficients. Satisfactorily constant values of K were obtained over a range of total ionic strengths, the mean values being

$PbCl^+$, K = 0.027
$PbBr^+$, K = 0.017
PbI^+, K = 0.012

The result for $PbCl^+$ therefore favors the lower set tabulated by Garrels and Gucker[2] (their Table VII): it is in good agreement with the value of 0.026 calculated by James[1] from conductance data although somewhat higher than that of 0.023 which he obtained from e.m.f. data.

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The Condensed System Bromine Trifluoride–Antimony Pentafluoride

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RECEIVED MAY 14, 1955

Investigation of the system bromine trifluoride–antimony pentafluoride has shown the presence of two incongruently melting compounds, $3BrF_3{\cdot}SbF_5$ and $3BrF_3{\cdot}2SbF_5$, and two congruently melting compounds, $BrF_3{\cdot}SbF_5$ and $BrF_3{\cdot}3SbF_5$. The compound $BrF_3{\cdot}3SbF_5$ undergoes a solid phase transition at −22.6°.

Introduction

This system was investigated to determine the solubility of antimony pentafluoride in bromine trifluoride and to determine the solid phases formed in the system. This study was made by obtaining time–temperature cooling and thaw curves of synthetic complexes. Bromine trifluoride–antimony pentafluoride mixtures have been used as fluorinating agents.[1] The compound $BrF_3{\cdot}SbF_5$, which was reported to have a melting point at about 200°,[2] has been used by Sheft, Martin and Katz[3] as a fluorinating reagent for the quantitative determination of oxygen in inorganic oxides.

Experimental

Materials.—Bromine trifluoride obtained from the Harshaw Chemical Company was purified by distillation in a forty-inch nickel fractionation column, one-half inch in diameter and packed with one-eighth inch nickel helices. The melting point of the bromine trifluoride, as indicated in Table I, agreed with the literature value[4] within experimental error.

Antimony pentafluoride, also obtained from the Harshaw Chemical Company, was used without further purification. Spectrographic analysis for other metals, and nephelometric analysis for chloride and bromide showed negligible impurities. Melting points were taken of the antimony pentafluoride using a sample from the original container and a sample of a distilled portion. Both gave the same result. This value, as indicated in Table I, agreed closely with the literature value.[5]

Apparatus and Procedure.—The apparatus used for the thermal analysis was similar to one previously described.[6,7] The components were introduced under an atmosphere of helium through a one-fourth inch flared nickel fitting into nickel or Monel tubes three-fourths inch in diameter and six inches long. The temperatures were measured with copper–constantan thermocouples in conjunction with a multi-point Brown Recording Potentiometer. The thermocouples and recorder were calibrated against a standardized platinum resistance thermometer employing a Leeds-Northrup G-2 Mueller bridge.

Results and Discussion

The data, in terms of mole per cent. bromine trifluoride, are listed in Table I and are plotted in the usual fashion in Fig. 1. The values in Table I are the average of several determinations for any one mixture and are assumed to be accurate to within ±0.5°.

Supercooling phenomena were observed for all mixtures below 40°. Many samples would supercool as much as 40° and as a result it was impossible to obtain accurate, reproducible data from cooling curves where this occurred. Therefore, thaw curves were used below 40° and these proved to be quite reproducible. Above 40° good agreement was obtained when both freezing and thaw curves were obtained for a given complex.

The duration of the thermal effects was employed in a qualitative manner to aid in establishing the solid compositions. The compound $3BrF_3{\cdot}SbF_5$ is designated as such on the basis of the thermal halts obtained. The data, however, do not negate the possibility that this compound may be lower in bromine trifluoride content (*e.g.*, $2BrF_3{\cdot}SbF_5$).

(1) H. J. Emeleus and A. A. Woolf, *J. Chem. Soc.*, 164 (1950).
(2) A. A. Woolf and H. J. Emeleus, *ibid.*, 2865 (1949).
(3) I. Sheft, A. F. Martin and J. J. Katz, paper presented at the 127th National Meeting of the American Chemical Society, Cincinnati, Ohio, March 29 to April 7, 1955.
(4) G. Oliver and J. Grisard, THIS JOURNAL, **74**, 2705 (1952).
(5) O. Ruff, *Ber.*, **42**, 4021 (1909).
(6) J. Fischer and R. C. Vogel, THIS
(7) J. Fischer and R. C. Vogel, *ibid.*, **76**, 4829 (1954).

TABLE I

SOLID–LIQUID EQUILIBRIA OF THE SYSTEM BROMINE TRIFLUORIDE–ANTIMONY PENTAFLUORIDE

Melting points, lit. values: bromine trifluoride[4] 8.77; antimony pentafluoride[5] 7; A = BrF_3; B = $3BrF_3 \cdot SbF_5$; C = $3BrF_3 \cdot 2SbF_5$; D = $BrF_3 \cdot SbF_5$; E = $BrF_3 \cdot 3SbF_5$; F = SbF_5.

Compn., mole % BrF_3	Univariant point Cooling curve	Univariant point Thaw curve	Solid phase	Invariant point Thaw curve	Phase transition Thaw curve
100.0	...	...	(A)	8.7	...
92.7	...	− 1.2	(A)	−33.8	...
87.6	...	−14.6	(A)	−32.7	...
82.1	...	−26.8	(B)	−32.9	...
80.3	...	−20.2	(B)	−32.9	...
77.5	...	−14.1	(B)	−36.7	...
74.9	...	1.0	(C)	−17.1	...
73.7	...	10.1	(C)	−16.3	...
70.7	...	25.5	(C)	−17.5	...
68.4	...	30.5	(C)	−17.0	...
66.4	...	...	(D)	−17.4, 30.8	...
63.9	62.8	...	(D)	−21.2, 29.6	...
61.2	85.9	...	(D)	−21.8, 29.7	...
59.2	98.4	98.5	(D)	23.2	...
56.7	110.2	...	(D)	21.5	...
52.3	123.0	122.5	(D)	...	...
49.0	129.6	129.3	(D)	...	...
43.8	109.9	110.1	(D)	11.9	−22.7
38.6	71.2	...	(D)	12.4	−20.6
35.5	40.8	...	(D)	15.9	−22.5
31.4	...	21.8	(E)	16.7	−22.4
28.8	...	31.1	(E)	15.2	−22.8
26.2	...	30.9	(E)	...	−22.8
24.3	...	33.2	(E)	...	−22.6
22.8	...	34.1	(E)	...	−22.9
21.2	...	29.0	(E)	...	−23.9
20.7	...	30.3	(E)	−10.8	−23.3
18.4	...	29.8	(E)	− 4.4	−22.8
17.1	...	30.2	(E)	− 5.2	−23.3
15.6	...	25.4	(E)	− 1.2	−22.4
14.0	...	22.3	(E)	− 2.5	−22.2
12.3	...	24.2	(E)	1.7	−22.1
9.8	...	24.3	(E)	1.4	−22.5
6.7	...	19.1	(E)	0.3	−22.3
5.2	...	20.0	(E)	1.9	−22.5
3.4	...	...	(E)	3.0	...
2.5	...	7.6	(E)	5.1	...
1.2	...	8.6	(E)	5.9	...
0.8	...	11.1	(E)	5.7	...
0	...	...	(F)	5.9	...

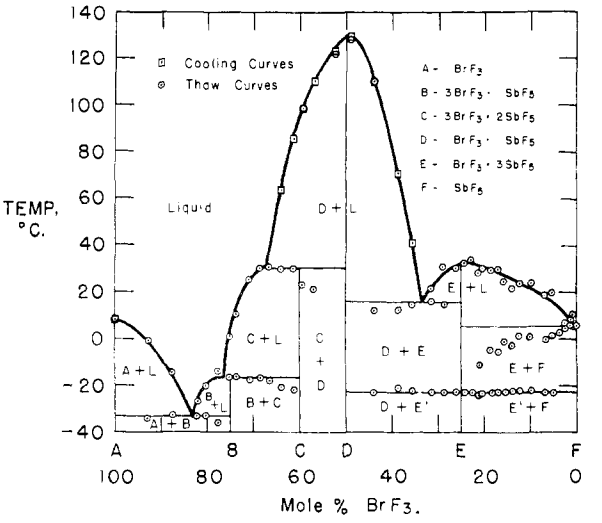

Fig. 1.—The condensed system bromine trifluoride–antimony pentafluoride.

From Fig. 1 it can be seen that there are two incongruent compounds, $3BrF_3 \cdot SbF_5$ and $3BrF_3 \cdot 2SbF_5$, which, respectively, decompose at $-16.3 \pm 0.5°$ and $30.8 \pm 0.5°$, and two congruent compounds, $BrF_3 \cdot SbF_5$ and $BrF_3 \cdot 3SbF_5$, which, respectively, melt at $129.8 \pm 0.5°$ and $33.5 \pm 0.5°$. The compound $BrF_3 \cdot 3SbF_5$ undergoes a solid phase transition at $-22.6 \pm 0.5°$.

From the shape of the solubility curve in the region in which the solid phase is the binary compound $BrF_3 \cdot SbF_5$, it is evident that the compound is stable and shows little tendency to dissociate in the liquid phase.

It was noted that the solutions, even for very low concentrations of bromine trifluoride, have deep red colors. This made it impossible to obtain any data by visual means.

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