an over-all purity of 99.3% for the fluorine used in these measurements. All the data have been corrected by this factor.

The addition of nitrogen to the fluorine caused no observable effect on the absorption spectrum. In one case 600 mm. of nitrogen was added to 100 mm. of fluorine, and in a second experiment an equal pressure of nitrogen was added to 300 mm. of fluorine. In both cases a decrease of only 0.01 l. mole^{-1} cm.$^{-1}$ was found, which is well within the experimental uncertainty.

In order to determine the extent of the reaction between the fluorine and the cell, measurements were made over time periods much longer than the normal 20 minutes. These showed that the cell windows were very slowly etched at a rate generally less than 0.001 absorbance unit per hour, as indicated by blank measurements. In addition, the fluorine was consumed at a rate of about 0.7% per hour. For the usual observation period of 20 minutes, both effects were negligible.

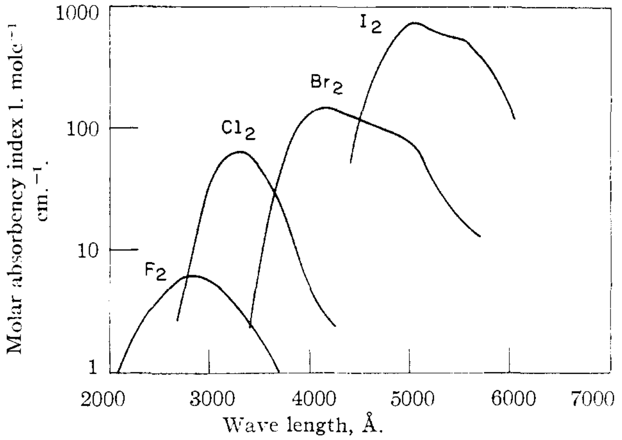

Fig. 1.—Absorption spectra of the halogens.

Higher temperature measurements at 50, 75 and 100° indicated no large differences in the absorption peak. Decreases of 2.1, 2.8 and 3.1%, respectively, were observed, but these values are subject to some uncertainty due to the appreciable etching of the cell windows at these temperatures.

Discussion

The continuous absorption peak height and location for fluorine are in agreement with those found by von Wartenberg[4,5] and Bodenstein,[6] falling between their results. There is little doubt as to the existence of this absorption of fluorine, but it is small in comparison with those of the other halogens.[11,12,13] The position of this peak, with its lower region extending into the violet part of the visible spectrum suggests the very pale yellow color frequently reported for gaseous fluorine. The relation of the absorption spectrum of fluorine to those of the other halogens is apparent in Fig. 1.

(11) G. E. Gibson and N. S. Bayliss, *Phys. Rev.*, **44**, 188 (1933).

(12) A. P. Acton, R. G. Aickin and N. S. Bayliss, *J. Chem. Phys.*, **4**, 474 (1936).

(13) E. Rabinowitch and W. C. Wood, *Trans. Faraday Soc.*, **32**, 540 (1936).

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[Contribution from the Chemical Engineering Division, Argonne National Laboratory[1]]

Liquid-Vapor Equilibria in the System Bromine–Bromine Trifluoride

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The 75 and 100° isotherms of the system bromine–bromine trifluoride have been determined. At both temperatures the system exhibits azeotropes at pressures greater than the sum of the pressures of pure bromine and bromine trifluoride. This suggests another molecular species in the vapor phase coexistent with bromine and bromine trifluoride.

The presence of bromine monofluoride as a species in mixtures of bromine and bromine trifluoride was suggested by Ruff and Braida.[2] Fischer, Steunenberg and Vogel[3] showed that there is a marked positive deviation from ideality with the formation of a liquid immiscibility gap in the condensed system bromine-bromine trifluoride. There was no evidence for the formation of solid bromine monofluoride.

It had been observed at temperatures around −10° by Ruff and Braida that the pressures over mixtures of bromine and bromine fluorides were in excess of those predicted from the properties of the known pure compounds using reasonable assumptions. Similar excesses of pressure for liquid mixtures of bromine and bromine trifluoride at temperatures from 25 to 125° have been noted in this Laboratory. In order to obtain further information about the occurrence of bromine fluoride and to evaluate the feasibility of the bromine-bromine trifluoride separation, 75 and 100° isotherms of the bromine–bromine trifluoride system were studied. Apparent molecular weights calculated from vapor densities at 75 and 100° for the system bromine–bromine trifluoride were obtained.

Experimental

Materials.—Reagent grade bromine was purified by distilling off a large portion, about one-quarter of the original volume at room temperature to remove any chlorine present. The remainder was passed over phosphorus pentoxide in order to remove traces of water. The sample to be used was condensed in a Fluorothene trap cooled with liquid nitrogen. Approximately 15- to 20-ml. portions were collected in the trap at a time. Each portion was frozen, evacuated and thawed several times to remove non-condensable gases. A 3- to 4-ml. portion of the bromine in the trap was distilled off to remove any further impurities more volatile than bromine. The residual amount of bromine was then distilled into the equilibrium cell of the apparatus.

Reagent grade bromine trifluoride was purified by dis-

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(1) Work performed under the auspices of the U. S. Atomic Energy Commission.

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

(3) J. Fischer, R. K. Steunenberg and R. C. Vogel, This Journal, **76**, 1497 (1954).

tillation in a 40-inch, nickel fractionation column $^1/_2$-inch in diameter, packed with $^1/_8$-inch nickel helices. It was freed of non-condensable gases when dispensed to the apparatus in the manner described below.

Apparatus.—The liquid-vapor equilibria were attained by pumping the vapor in a cyclic fashion through the liquid until equilibrium was reached. The liquid and vapor phases were then sampled. The apparatus was of nickel and Monel construction. The volume of the equilibrium cell was approximately 260 ml. and could be used with liquid volumes from 45 to 140 ml. The vapor sampling vessels had volumes between 905 and 910 ml. and were calibrated to ±0.1 ml. using helium at determined temperatures and pressures. Teflon gaskets served to seal the system at appropriate flares. The temperatures of the vapor and liquid in the equilibrium cell were measured by copper constantan thermocouples in contact with the bottom of the thermocouple wells, with a type K2 Leeds and Northrup potentiometer. The thermocouples were calibrated to ±0.01° against a standard resistance thermometer, employing a Leeds and Northrup G2 Mueller bridge. Calibrated thermocouples were also placed in contact with the gas sampling vessel and the pressure transmitter. The pressure within the system was measured with a 3800 mm. well type mercury manometer, obtained from the Meriam Instrument Company of Cleveland, Ohio, employing a Booth-Cromer pressure transmitter[4] in conjunction with a self-balancing relay. A thin nickel diaphragm, which served as a sensing element in the pressure transmitter, separated the vapor in the system from the helium in the balancing system connected to the mercury manometer. The vapor in the system was cycled through the liquid by means of a magnetically operated nickel and Monel pump described by Rosen.[5] The liquid was sampled by draining a portion of it into a $^3/_8$-inch Fluorothene sample tube which was cooled with liquid nitrogen. The entire apparatus was contained in a constant temperature air box. The temperature of the liquid and vapor in the equilibrium cell would be held constant to ±0.01° at 75 and 100°. The baffles in the box were so arranged that the pressure transmitter, gas sampling vessels, vapor pump and the lines were held a few hundredths of a degree above the temperature of the equilibrium cell in order to prevent condensation in these parts and to obtain a true reading of the vapor pressure in the equilibrium cell.

Procedure.—The distilled bromine trifluoride, which was stored under a helium atmosphere, and the bromine were distilled into the previously evacuated apparatus and then evacuated several times with alternate freezing and melting in order to remove traces of dissolved gases. The constant temperature box was heated to 75 or 100°. The vapor was circulated through the liquid with the use of the magnetically operated pump until equilibrium was reached, as indicated by constant pressure at constant and equal temperature of liquid and vapor. Liquid and vapor samples were then taken and weighed using an empty sample container as a tare in the weighing of the vapor sample.

Analysis for Bromine in Bromine Trifluoride.—The mixtures of bromine in bromine trifluoride were analyzed for bromine by titrating the bromine with fluorine to form bromine trifluoride. A similar procedure has been reported by Sheft, Hyman and Katz,[6] except that in this investigation the end-point was determined from a pressure *vs.* moles fluorine added plot, while Sheft, *et al.*, used the disappearance of the bromine color. As the bromine in the sample is converted to bromine trifluoride by the slow addition of fluorine, maintaining the temperature at 25° or below, the pressure in the system falls to a minimum when the stoichiometric amount of fluorine has been added and then rises as excess fluorine is admitted to the system. The pressure over liquid bromine–bromine trifluoride mixtures at about 25° is approximately 285 mm. while the pressure of pure bromine trifluoride is about 8 mm. The mole per cent. of bromine and bromine trifluoride in the sample was calculated from the quantity of fluorine used and the known weight of the sample. This analytical method does not, of course, distinguish between bromine and bromine monofluoride. If bromine monofluoride was present, it titrates on an equimolar basis while bromine requires three moles of fluorine per mole. The fluorine additions were made slowly, to prevent a rise in temperature and with frequent halts to obtain the pressures in the fluorine measuring vessel and in the vessel containing the sample. The analytical accuracy found for several synthetic standards is shown in Table I, indicating a mean error of ±0.9%.

TABLE I

TITRATION OF BROMINE STANDARDS WITH FLUORINE

Moles bromine in standard	Moles bromine trifluoride in standard	Moles bromine found	Error, %
0.005246	0	0.005197	−0.94
.006462	0	.006450	−0.20
.03492	0	.03486	−0.17
.002275	0.034	.002251	−1.05
.007275	0.010	.007367	+1.26
.01319	0	.01298	−1.59

The fluorine, assayed for purity by the method of Aoyana and Kanda,[7] employing the quantitative reaction between mercury and fluorine, was found to be at least 99% fluorine by volume. In the titration of bromine with fluorine, the pressure at the end-point in excess of that of pure bromine trifluoride was a measure of gaseous impurities in the fluorine. These impurities were shown to be less than 0.5% by volume.

A few liquid samples containing small amounts of bromine were analyzed by colorimetric comparisons with synthetic standards.

Results and Discussion

The data for the 75 and 100° isotherms of the bromine–bromine trifluoride system are shown in Table II and III, respectively, and plotted in the usual fashion in Fig. 1. It is emphasized that the values indicated in the tables and figure express

TABLE II

LIQUID–VAPOR EQUILIBRIA OF BROMINE–BROMINE TRIFLUORIDE AT 75.00 ± 0.01°

Vap. press. in mm.	Mole % Br_2 in liquid	Mole % Br_2 in vapor	Density vapor samples g. per G.M.V.
111	0.0	0.0	143
202	...	22.6	114
309	...	39.7	110
514	2.3 1.5[a]	...	..
517	1.5[a]	50.5	118
554	1.9[a]	...	..
932	5.5 3.9[a]	...	..
963	4.1[a]	67.1	128
1287	10.0	72.9	135
1509	...	75.9	139
1671	26.9	...	..
1727	33.3	79.4	140
1808	61.7	81.4	143
1802	71.7	81.0	146
1817	90.5	83.1	143
1799	93.6	85.4	143
1723	...	86.7	150
1695	...	89.6	162
1630	...	91.3	171
1561	98.5	91.6	153
1330	...	97.5	161
1250	100.0	100.0	168

[a] Analyzed colorimetrically.

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(4) S. Cromer, "The Electronic Pressure Transmitter and Self-Balancing Relay," SAM Laboratories, Columbia University, MDDC-803, 1947.

(5) F. D. Rosen, "Magnetic Pumps for Corrosive Gases and Liquids," Carbide and Carbon Chemical Company, K-25 Plant, October 31, 1951 (K-833).

(6) I. Sheft, H. Hyman and J. Katz, *Anal. Chem.*, **25**, 1877 (1953).

(7) A. Aoyana and E. Kanda, *Bull. Chem. Soc. Japan*, **12**, 409 (1937).

TABLE III

LIQUID–VAPOR EQUILIBRIA OF BROMINE–BROMINE TRIFLUORIDE AT 100.00 ± 0.01°

Vap. press. in mm.	Mole % Br_2 in liquid	Mole % Br_2 in vapor	Density vapor samples g. per G.M.V.
309	0.0	0.0	144
789	0.7[a]	36.1	117
1763	4.5 3.2[a]	63.9	129
2956	13.8	74.4	139
3849	51.0	76.9	145
3888	71.6	78.6	145
3888	82.3	79.4	143
3757	93.6	86.4	172
3247	98.3	89.5	154
2483	100.0	100.0	169

[a] Analyzed colorimetrically.

analytical compositions in terms of bromine and bromine trifluoride and in no way indicate the molecular species present in the system.

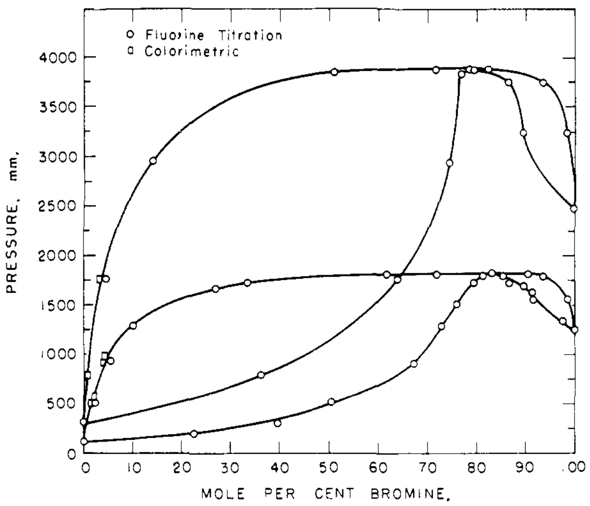

Fig. 1.—Liquid-vapor equilibrium for the system bromine–bromine trifluoride at 100° (upper curves) and 75°.

A comparison of our values of the vapor pressures of the pure components with previous data helps to establish confidence in the apparatus used in these experiments. This comparison at 75° is as follows

	Our values, mm.	Lit. values, mm.
Br_2	1250	1286[8]
BrF_3	111	110.91[9]
BrF_5	2247	2249.2[9]

A similar comparison at 100° is as follows

Br_2	2483	2553[8]
BrF_3	309	308.87[9]

The vapor pressures of the maxima in Fig. 1 greatly exceed the sum of the pressures of the pure components. Therefore, it is likely that at least one other compound is formed in the vapor as a result of a reaction between bromine and bromine trifluoride. Theoretically, the formation of bromine monofluoride as a product will result in such increases in pressure as are observed in the system. One cannot exclude the simultaneous occurrence of other reactions which may decrease the pressure but may yield an increase in total pressure for the over-all reaction. It can also be inferred from the apparent molecular weights, calculated from the densities of the saturated vapor samples shown in Tables II and III, that bromine monofluoride is present as a molecular species in the vapor.

Attempts to calculate the pressure equilibrium constant

$$K_p = \frac{(P_{BrF})^3}{P_{BrF_3}\,P_{Br_2}} \qquad (1)$$

where P is the partial pressure of the indicated species for the reaction

$$BrF_3(g) + Br_2(g) \rightleftarrows 3BrF(g) \qquad (2)$$

employing the partial pressures calculated from the total pressures and the analytical composition of the vapors in equilibrium with mixtures of bromine and bromine trifluoride, failed to give a constant value. It is believed that the accuracy of the data is not great enough to be used in calculating an equilibrium constant in which the partial pressures of the species formed is cubed.

The shift in the maximum vapor pressure point in going from the 75° isotherm to the 100° isotherm of the system, as indicated in Fig. 1, eliminated any contention that such a maximum point represents the presence of another pure compound in the system and lends further support to the theory that the vapor is at least a mixture of bromine, bromine trifluoride and bromine monofluoride. The evidence that such a molecule as bromine monofluoride exists in the vapor is not sufficient to infer that such a species exists in the liquid. The stoichiometry of the reaction and the equilibrium constant are being determined for the reaction of the components of this system in the vapor phase from spectroscopic studies.

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LEMONT, ILLINOIS

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(8) F. E. C. Scheffer and M. Voogd, *Rec. trav. chim.*, **45**, 214 (1926).

(9) R. D. Long, Argonne National Laboratory, Document ANL-5405.