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[CONTRIBUTION FROM ARGONNE NATIONAL LABORATORY]

Pressure Studies of the Reaction of Fluorine with Bromine[1]

BY LAWRENCE STEIN

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The reaction of fluorine with bromine vapor was studied over the temperature range 25 to 300°. The reaction first produced bromine monofluoride, which was converted chiefly to bromine trifluoride on further addition of fluorine. At 25°, a small amount of bromine pentafluoride was also formed, as shown by the fluorine-to-bromine ratio of the "titration endpoint." At higher temperatures the amount of pentafluoride increased, and the reaction of fluorine with the trifluoride after the end-point became more rapid. The pressure changes in the bromine–fluorine reaction were correlated with the vapor-liquid phase diagram of the bromine–bromine trifluoride system at 25°. An equation of state for bromine vapor at 25° was derived from vapor density measurements: $P\bar{V} = RT - 0.377P$, where P is the pressure in atmospheres and $\bar{V}$ is the molar volume in liters.

Introduction

Although the direct combination of bromine and fluorine has been used by numerous experimenters for the preparation of the bromine fluorides,[2-5] the stoichiometry of the reaction and the variation of the product with experimental conditions has not been adequately described. The trifluoride is sometimes prepared by mixing fluorine with bromine vapor in a stream of nitrogen at room temperature, but purification of the trifluoride by distillation is then necessary, indicating that other fluorides are formed as well. The monofluoride, first reported by Ruff and Braida[6] to be unstable at temperatures above 50°, is now known to be quite stable at elevated temperatures, although it exists only in equilibrium with bromine and bromine trifluoride[7] and cannot be isolated as a pure liquid or vapor. The pentafluoride is a well-characterized compound, obtained by combination of the elements at 200° or higher and purified by distillation. The composition regions in which the various bromine fluorides can exist together or in the presence of free bromine or fluorine are determined not only by thermodynamic considerations but to a large extent by the kinetics of competing reactions. At room temperature, for example, the reaction between bromine and bromine trifluoride rapidly produces bromine monofluoride and a small amount of bromine pentafluoride, whereas a mixture of bromine and bromine pentafluoride shows no evidence of reaction within a 1 hr. period. Separate mixtures can therefore be made up, each having the same over-all composition expressed as a fluorine-to-bromine ratio but showing quite different phase behavior, and obviously not both in thermodynamic equilibrium. At 300°, bromine reduces bromine pentafluoride rapidly, and it is probable that equilibrium is attained within a few minutes in any mixture at this temperature. The present research is primarily a study of the compounds produced by the bromine–fluorine reaction at 25°. It was undertaken to determine the feasibility of combining the elements in a calorimeter to measure directly the heat of formation of bromine trifluoride, since several investigators recently have reported conditions under which only the trifluoride was produced.[8,9] Although bromine pentafluoride was formed with the trifluoride in every instance in the present research, the reaction still appears suitable for calorimetric study with appropriate corrections for the pentafluoride.

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[1] Based on work performed under the auspices of the U. S. Atomic Energy Commission.

[2] P. Lebeau, *Compt. rend.*, **141**, 1015 (1905).

[3] E. B. R. Prideaux, *J. Chem. Soc.*, 316 (1906).

[4] O. Ruff, A. Braida, O. Bretschneider, W. Menzel and H. Plaut, *Z. anorg. allgem. Chem.*, **206**, 59 (1932).

[5] A. G. Sharpe and H. J. Emeleus, *J. Chem. Soc.*, 2135 (1948).

[6] O. Ruff and A. Braida, *Z. anorg. allgem. Chem.*, **202**, 81 (1931).

[7] R. K. Steunenberg, R. C. Vogel and J. Fischer, THIS JOURNAL, **79**, 1320 (1957).

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

[9] J. Fischer, J. Bingle and R. C. Vogel, THIS JOURNAL, **78**, 902 (1956).

Experimental

Reagents.—Mallinckrodt reagent grade bromine was dried over phosphorus pentoxide and vacuum distilled, a middle fraction being collected and sealed off in a Pyrex bulb attached to a small Monel valve. The bromine was frozen and thawed under vacuum several times to remove air, then stored in the bulb until used.

Fluorine gas obtained from The Pennsylvania Salt Manufacturing Company was distilled from one U-tube to another at liquid nitrogen temperature to remove hydrogen fluoride, then stored in a Monel vessel. In most experiments, the purity of the fluorine was 98.4%, as determined by titration with mercury. In several instances, fluorine of greater than 99% purity was used. Carbon tetrafluoride was shown to be the chief impurity by infrared analysis.

Technical grade bromine trifluoride from Harshaw Chemical Company was purified in a nickel still by the Chemical Engineering Division of this Laboratory, then stored in a nickel or Monel vessel. Immediately before use it was distilled under vacuum in a Fluorothene test-tube until shown to be pure by its infrared spectrum.

Pressure Measurements.—The chief parts of the apparatus used for pressure measurements are shown in Fig. 1.

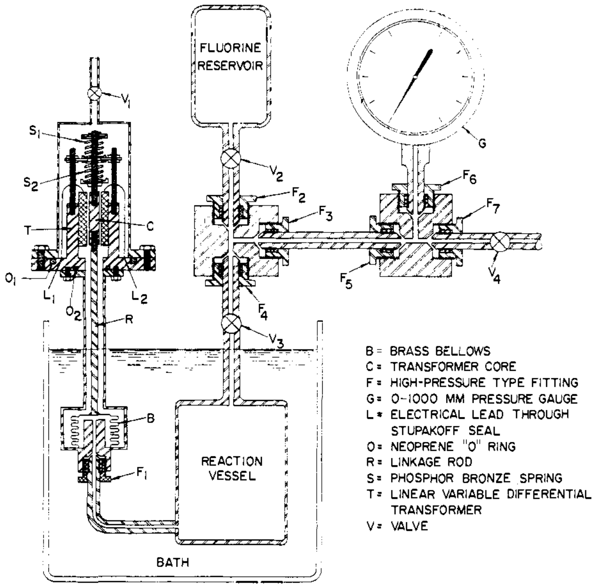

Fig. 1.—Apparatus for pressure measurements at 25°.

On the left is a differential pressure gauge designed for use with corrosive materials. It consisted of a linear variable differential transformer contained in a brass case which was connected by "O" ring seals to another case containing a bellows. The motion of the bellows was transmitted by a metal rod to the movable core of the transformer. The pressure of the gas inside the bellows and reaction vessel was balanced by an equal pressure of helium inside the transformer housing. Valve V_1 was connected to a mercury manometer made of 20 mm. i.d. glass tubing and to needle valves leading to vacuum and pressurized helium. An input of 6.3 v. 60 cycle a.c. was used with the transformer, which was of type 033 SS-LT manufactured by Schaevitz Engineering. The output was measured on the most sensitive scale of a Model 400 AB Hewlett-Packard vacuum tube voltmeter. Before each experiment, the output at balance was determined by connecting both sides of the bellows to a common helium supply and varying the pressure stepwise from 0 to 760 mm. The output at balance usually shifted less than 0.05 mv. over this pressure range. The sensitivity of the gauge was 1.57 mv./mm., allowing pressure changes as small as 0.03 mm. to be detected with the Model 400 AB voltmeter. The manometer pressures were measured to ±0.02 mm. with a Wild cathetometer.

The Monel reaction vessel and the bellows assembly were immersed in a carbon tetrachloride bath regulated at 25.0 ± 0.1°. A precision mercury thermometer certified by The National Bureau of Standards was used to adjust the bath temperature, and calibrated thermocouples were used with a Rubicon potentiometer, Model 2732, to measure temperatures at various other parts of the apparatus.

The ratio of the volume of the reaction vessel and bellows to that contained between valves V_2, V_3 and V_4 was found to be 7.78 by expansion of helium, using the ideal gas equation. The 0 to 1000 mm. Helicoid pressure gauge comprising part of the smaller volume was read to the nearest mm., and corrections for the gauge readings were determined by calibration with the manometer. Valve V_4 was connected through a liquid nitrogen trap to a vacuum line.

In the experiments at 25°, bromine vapor was added to the reaction vessel to a measured pressure, the section between V_2, V_3 and V_4 was filled with fluorine at higher pressure, and V_3 was opened slightly for short periods to admit fluorine to the reaction vessel. The pressure of fluorine added was computed from the gauge pressures and the volume ratio, using small temperature corrections when necessary and assuming ideal gas behavior. After each addition, the pressure was balanced with the differential gauge until there was no further change with time, then the next fluorine addition was made.

In the few experiments done at higher temperatures, the differential gauge was not used, and an electrically heated reaction vessel, approximately 180 cc. in volume, was substituted for the one shown in the diagram. The temperature of the vessel, measured by thermocouples at several points, was uniform within ±0.5° to the top of valve V_3; beyond this there was a temperature gradient in a section of tubing approximately 18 cm. long between valve V_3 and fitting F_4. At each temperature of the vessel, helium was expanded from the section between valves V_2, V_3 and V_4 into the evacuated vessel to determine an empirical pressure ratio from the gauge readings. The reaction was studied by first filling the vessel with a measured pressure of bromine vapor, then adding each increment of fluorine by momentarily opening valve V_3 until there was no further pressure drop on the gauge. Some back diffusion of vapor out of the vessel probably occurred when the pressure on both sides of V_3 was the same, but this was minimized by opening V_3 only briefly. Pressure measurements of the reaction made by this method have an estimated accuracy of ±3 mm.

Vapor Density of Bromine.—A Pyrex bulb attached to a small valve and pressure-type fitting was used to determine vapor densities of bromine at 25°. The volume of the bulb at this temperature, obtained by calibration with distilled water, was 0.52912 liter. The bulb was immersed up to the valve in a water-bath at 25.0 ± 0.1°, evacuated and filled with bromine vapor to a pressure measured by the differential gauge and manometer. The pressures were corrected to 0° and standard gravity. The bulb was weighed on an analytical balance to 0.1 mg., using a tare bulb above the opposite pan. No corrections for air buoyancy were applied, since the difference in weight between the evacuated bulb and the bulb filled with bromine was small enough to require only movement of the rider and chain. When the bulb was wiped dry with a cloth, a static charge was produced which leaked off very slowly, even with a radioactive source in the balance case. Reproducible weighings were obtained, however, when the outside of the bulb was rinsed with reagent grade acetone and dried with a jet of air.

Vapor–Liquid Phase Studies.—Mixtures of bromine and bromine trifluoride were made up by weight to approximately 40 g. total weight in Fluorothene test-tubes attached to small valves, with air being excluded. The vapor pressure of each mixture was measured at 25.0° with the Helicoid gauge. The small change in composition of the liquid due to vaporization into the gauge was neglected.

The composition of the vapor in equilibrium with the liquid phases was determined by chemical analysis. Vapor samples of about 0.5 g. were withdrawn slowly through a partly opened valve into Fluorothene test-tubes cooled with liquid nitrogen, then weighed to 0.1 mg., hydrolyzed and analyzed. The pressure dropped by approximately 5 to 10 mm. during the sampling, as the composition changed, so the average pressure was taken for each sample. The liquid phase was kept in a bath at 25° and was shaken to ensure equilibrium with the vapor.

A new hydrolyzing technique was employed, in which the frozen sample in an open Fluorothene test-tube was suspended by a Nichrome wire above 100 cc. of aqueous solution in a 1-liter round bottom flask. A stopcock with a Teflon plug was attached to the flask with a standard taper joint; no grease was used on either the stopcock or joint. After most of the air in the flask was removed with a water aspirator (pumping for about 20 seconds), the stopcock was closed, and the flask was shaken vigorously for several minutes. The hydrolyzed solution then was transferred to a 250-ml. volumetric flask, together with several rinses of the flask, sample tube and stopcock, and the solution was made up to 250 ml. Although the round bottom flask was taped as a precaution against internal pressure, it was found that with samples containing 1 g. or less of bromine trifluoride, the pressure inside the flask always remained below one atmosphere. The hydrolyzing solution consisted of 0.2 *M* aluminum nitrate and 0.2 *M* hydrazine sulfate. Aliquots of 50 or 100 ml. of the hydrolyzed solution were analyzed for bromine by the gravimetric silver bromide method.[10] Fluorine was determined by difference, the total bromine weight being subtracted from the weight of sample. Known mixtures of bromine and bromine trifluoride were analyzed by this method, and the total bromine found was correct to within 0.1%.

Discussion

In Fig. 2 some of the experimental pressure curves are shown for the addition of fluorine to bromine at 25°. Total pressure is plotted against pressure of added fluorine, both being corrected for the inert impurities in the fluorine. Curves 1 through 6 were obtained with initial pressures of bromine of 51.9, 83.2, 113.4, 148.9, 177.8 and 209.8 mm. in the reaction vessel. Curve 7 was obtained with saturated bromine vapor and several grams of bromine liquid present initially. At the low initial pressures of bromine, the addition of fluorine first produced an increase in pressure to a maximum at B, then a decline to point C, and an abrupt rise again beyond C. In the region from A to C, care was taken to add the fluorine slowly, since small explosions occurred if the addition was made rapidly. The pressures measured in this region were very steady, equilibrium apparently being established five minutes or less after each fluorine addition. Beyond point C, however, the pressure rose during each fluorine addition, then fell slowly afterwards and did not reach a steady value even in periods longer than one hour. The points beyond C were therefore taken immediately after the fluorine additions and linearly extrapolated back to the intersection with the descending pressure curve.

The initial slope at A of curves 1 through 4 was almost unity, indicating that bromine monofluoride was the chief product formed in the region from A to B. Bromine trifluoride also was produced in lesser amount, as required by the equilibrium[7] for the reaction

$$BrF_3 + Br_2 \rightleftarrows 3BrF \qquad (1)$$

At B the saturation pressure of the trifluoride was reached, and a liquid phase appeared. The pressure then dropped as the bromine and bromine monofluoride were converted to the trifluoride, which continued to condense. At C the bromine and bromine monofluoride were depleted, and the pressure then rose as excess fluorine was added. Until point C was reached, there was essentially no unreacted fluorine present in any of the equilibrium mixtures. Beyond C, fluorine was present in large amount, and the observed slow drop in pressure with time in the region between C and D was due to the slow reaction of the fluorine with bromine trifluoride to form bromine pentafluoride.

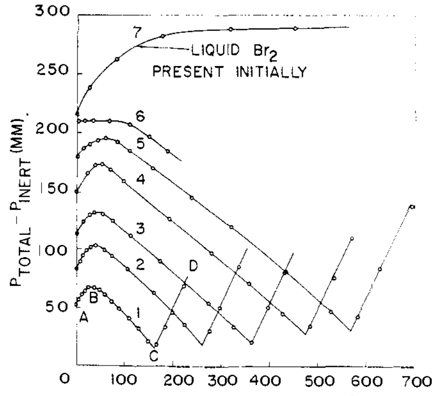

Fig. 2.—Pressure curves for the addition of fluorine to bromine at 25°.

Point C has the appearance of a "titration end-point," and it has been used as such,[8,9] with bromine trifluoride reported to be the only product formed. In the present research, the amount of fluorine (corrected for inert impurities) added up to point C always exceeded the theoretical amount for the formation of the trifluoride, the excess varying from 3.2 to 6.5%. The amounts of fluorine added to point C for curves 1 through 5, were 160, 261, 360, 474 and 566 mm., respectively, after correction for impurities. Also, the corrected minimum pressure at point C was never as low as the vapor pressure of pure bromine trifluoride, but increased regularly from curve 1 to 5, as would be expected for increasing amounts of the pentafluoride. The conclusion therefore was reached that the pentafluoride was formed as well as the monofluoride and trifluoride in the region between A and C.

The effect of non-ideality of fluorine and bromine vapor on these measurements also was considered. One early literature value for the density of fluorine at 0° and one atmosphere pressure[11] indicated close adherence of fluorine to the ideal gas law. More recently, the second virial coefficients of fluorine at various temperatures have been reported.[12] At the low pressures of fluorine used in the present research, the difference between the *PV* product computed from the ideal gas equation and the virial equation with the second coefficient equal to −19 cc. was less than 0.1% at 25°. The ideal gas equation was therefore considered sufficiently accurate for fluorine in the present research.

The only data found in the literature on the density of bromine vapor[13-16] were either ob-

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[10] I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," The Macmillan Co., New York, N. Y., 1947, p. 313.

[11] "International Critical Tables," Vol. III, McGraw-Hill Book Co., Inc., New York, N. Y., 1926, p. 3.

[12] D. White, J. H. Hu and H. L. Johnston, *J. Chem. Phys.*, **21**, 1149 (1953).

[13] J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. II, Longmans, Green and Co., London, 1922, p. 48.

[14] H. B. Baker, *J. Chem. Soc.*, 1051 (1928).

[15] "Gmelins Handbuch der Anorganischen Chemie," Verlag Chemie G.m.b.H., Leipzig-Berlin, 1926, Section 7, p. 72.

[16] J. A. Lasater, S. D. Cooley and R. C. Anderson, THIS JOURNAL, **72**, 1845 (1950).

tained at high temperatures or else were discordant, so the density at 25° was determined by the Regnault method with the results shown in Table I. Three of the measurements were made with reagent grade bromine not dried or redistilled, but within the experimental error of 0.1% no difference was noted from the remainder of the measurements. The equation of state for bromine vapor at 25° was obtained

$$P\bar{V} = RT - 0.377P \qquad (2)$$

where

P = pressure in atm.
$\bar{V}$ = molar volume in liters
R = 0.082054 liter atm./deg. mole
T = 298.16°K.

In deriving this virial equation, the intercept was forced through RT, and only the slope was determined by least squares.

TABLE I

DENSITY OF BROMINE VAPOR AT 25.0°

Pressure (atm.)	Density (g./l.)	$(P\bar{V})$ Exp. (l. atm.)	$(P\bar{V})$ Eq. (l. atm.)
0.04899	0.3201	24.46	24.447
.06996	.4570	24.45	24.439
.07937	.5192	24.44	24.435
.09556	.6252	24.43	24.429
.10956	.7172	24.42	24.424
.12186[a]	.7970[a]	24.44[a]	24.419
.13614	.8909	24.43	24.414
.14296	.9363	24.41	24.411
.16399	1.0738	24.41	24.403
.18066[a]	1.1840[a]	24.39[a]	24.397
.19196	1.2570	24.41	24.393
.21624	1.4167	24.40	24.384
.23462	1.5386	24.37	24.377
.26416[a]	1.7348[a]	24.34[a]	24.366

[a] Reagent grade bromine used without further purification.

The effect of the non-ideality of bromine vapor on the theoretical end-point of the reaction, assuming bromine trifluoride to be the only product, proved to be quite small. In curve 5, for example, correction of the bromine to the ideal gas state increased the initial pressure from 177.8 to 178.2 mm. The theoretical pressure of fluorine required for the conversion to the trifluoride was thus shifted from 533.4 to 534.6 mm., which was still much less than that found experimentally, due to the formation of some pentafluoride.

In Fig. 2 it also can be seen that the maximum at B diminished and finally disappeared as the initial pressure of bromine approached the saturation pressure. When saturated vapor and liquid were both present initially, the pressure rose continuously as fluorine was added, asymptotically approaching a value of approximately 290 mm. This is shown in curve 7, which was not carried to completion.

The vapor–liquid phase diagram of the bromine–bromine trifluoride system at 25° was useful in interpreting these results. The data for this system are given in Table II, and the diagram is given in Fig. 3. Composition was expressed as a molar ratio of fluorine to bromine, since bromine and bromine trifluoride were not the only species present in the mixtures. In the region where two immiscible liquid phases appeared, the lower phase was designated by "Liquid I" and the upper phase by "Liquid II."

TABLE II

VAPOR–LIQUID EQUILIBRIA OF Br_2–BrF_3 MIXTURES AT 25°

Liquid phases		Vapor phase	
$\frac{F}{Br}$ Mole ratio	Pressure (mm.)	$\frac{F}{Br}$ Mole ratio	Pressure (mm.)
Liquid 1		Vapor in equilibrium with Liquid I	
0.000	215		
.009	232	0.114	242
.055	262	.148	268
.080	279	.162	277
.110[a]	290	.180	290
Liquid II		Vapor in equilibrium with Liquid II	
2.10[a]	290		
2.25	275	0.180	290
2.43	252	.183	255
2.54	234	.204	228
2.66	200	.258	182
2.80	151	.418	135
2.82	143	.606	93
2.89	98	.976	56
2.95	60	1.59	31
2.97	43	1.92	20
3.00	8	2.61	14
		3.00	8

[a] Computed from data in reference 17.

The phase diagram largely explained the observed pressure changes of the bromine–fluorine reaction. The maximum at B in Fig. 2 corresponded to the first appearance of liquid II, and the region between B and C corresponded to the descending equilibrium mixture of vapor and liquid II as the fluorine-to-bromine ratio increased. When liquid bromine was present initially, the addition of fluorine produced the bromine-rich phase, liquid I, rather than the bromine trifluoride-rich phase, liquid II. The pressure then rose as the fluorine-to-bromine ratio increased, until the immiscible region was reached, when both liquid phases were present. Further additions of fluorine then converted some of liquid I into liquid II, the total pressure remaining constant, as required by the phase rule. The fluorine additions were not continued to the point where the pressure would have descended again upon depletion of liquid I. The agreement between the observed pressures in the bromine–fluorine reaction and those predicted from the bromine–bromine trifluoride phase diagram was only fair, the differences probably arising from the bromine pentafluoride which also was formed.

The pressure changes on adding fluorine to bromine vapor at 100, 200 and 300° are shown in Fig. 4 for initial bromine pressures of 98 to 102 mm. In each experiment, the pressure rose to approximately twice the initial pressure as bromine monofluoride was chiefly formed, then remained almost constant as the monofluoride was converted to the trifluoride and pentafluoride. On depletion of the monofluoride at point C, the pressure rose

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(17) J. Fischer, R. K. Steunenberg and R. C. Vogel, THIS JOURNAL, **76**, 1497 (1954).

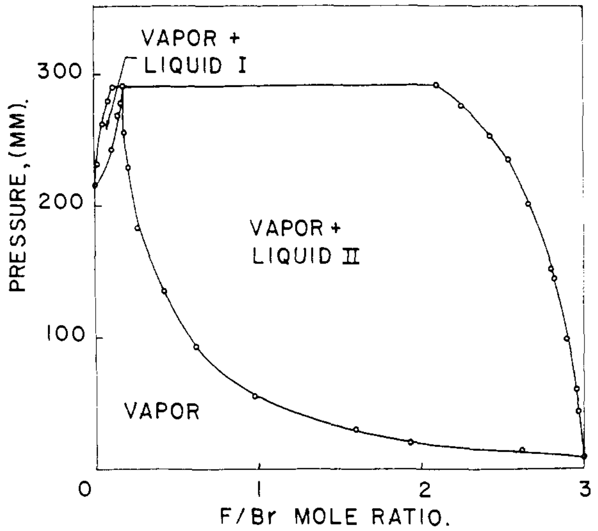

Fig. 3.—Vapor–liquid phase diagram of the system Br_2–BrF_3 at 25°.

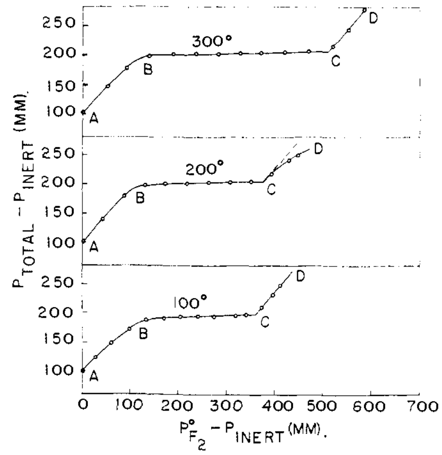

Fig. 4.—Pressure curves for the addition of F_2 to Br_2 at 100, 200 and 300°.

again as excess fluorine was added. At 100°, the reaction between fluorine and bromine trifluoride was still slow enough to allow the points between C and D to be determined, although the pressures were falling. At 200°, the excess fluorine reacted so rapidly with the trifluoride that the points between C and D could hardly be determined and no longer yielded a straight line. The relative amount of pentafluoride present at point C increased with temperature, as expected. At 300°, the plateau extended all the way to the bromine pentafluoride end-point, and the pressures measured between C and D were stable, since no higher fluoride than the pentafluoride was formed by the excess fluorine.

Acknowledgment.—The author wishes to thank Dr. Bernard M. Abraham, Mr. Howard E. Flotow and Mr. Roger D. Carlson for suggestions regarding the design of the differential pressure gauge and for the loan of a variable differential transformer; Mr. Irving Sheft for the provision of bromine trifluoride; and members of the Chemical Engineering Division for the distillation of the bromine trifluoride.

LEMONT, ILLINOIS

[CONTRIBUTION FROM ARGONNE NATIONAL LABORATORY]

Infrared Studies of the Bromine Fluorides[1]

BY LAWRENCE STEIN

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The infrared absorption spectra of bromine monofluoride, trifluoride and pentafluoride were obtained in the vapor phase at approximately 25°. The reaction of bromine with bromine trifluoride was carried out in the infrared cell to produce the monofluoride, and it was found that small amounts of pentafluoride also were produced. A partial disproportionation of the trifluoride into monofluoride and pentafluoride was postulated. This was confirmed by the appearance of the pentafluoride in samples of the trifluoride which were heated to 150° or higher. The reactions of fluorine with bromine and fluorine with bromine trifluoride also were studied in the infrared cell.

Introduction

The infrared spectra of bromine trifluoride[2,3] and bromine pentafluoride[2,4] previously have been reported in the literature. In the present article, several new vibrational bands of bromine pentafluoride and the fundamental and second harmonic of bromine monofluoride are reported. A comparison of the infrared absorption spectra of the three bromine fluorides shows that the strongest bands all occur in the region between 600 and 700 cm.$^{-1}$; fortunately they do not coincide, so each compound can be identified in the presence of the others. By infrared analysis, bromine pentafluoride is found as one of the products of the reaction between bromine and bromine trifluoride. The disproportionation of bromine trifluoride into monofluoride and pentafluoride must therefore occur to a small extent. In the reaction of fluorine with bromine, the pentafluoride also appears, confirming the results of the pressure studies.[5] The rate of reaction of fluorine with bromine trifluoride liquid is shown to be appreciable even at 25°.

Experimental

Reagents.—Bromine, fluorine and bromine trifluoride of the same purity as in previous experiments[5] were used. Bromine pentafluoride from Harshaw Chemical Company was distilled several times in Fluorothene test-tubes until

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(1) Based on work performed under the auspices of the U. S. Atomic Energy Commission.

(2) H. M. Haendler, G. W. Bukata, B. Millard, E. I. Goodman and J. Littman, *J. Chem. Phys.*, **22**, 1939 (1954).

(3) H. H. Claassen, B. Weinstock and J. G. Malm, *ibid.*, **28**, 285 (1958).

(4) J. G. Burke and E. A. Jones, *ibid.*, **19**, 1611 (1951).

(5) L. Stein, THIS JOURNAL, **81**, 1269 (1959).