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THE VAPOR PRESSURE AND HEAT OF VAPORIZATION OF BROMINE TRIFLUORIDE

J. W. Grisard and George D. Oliver

Work Supervised by
E. A. Bernhardt
Laboratory Division
F. W. Hurd, Superintendent

CARBIDE AND CARBON CHEMICALS COMPANY
UNION CARBIDE AND CARBON CORPORATION
K-25 Plant
Oak Ridge, Tennessee

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A B S T R A C T

The vapor pressure of bromine trifluoride has been measured over the range 39 to 155°C. and the following equation was derived by methods of least squares to represent the experimental data.

$$\log_{10} P_{\text{mm}} = 7.74853 - 1685.8/(t + 220.57)$$

The heat of vaporization was estimated from the following equation which is based upon the Clausius-Clapeyron relation.

$$\Delta H_{\text{cal/mole}} = 7714 \left[(t + 273.16)/(t + 220.57) \right]^2$$

THE VAPOR PRESSURE AND HEAT OF VAPORIZATION OF BROMINE TRIFLUORIDE

In continuation of the program to measure the physical properties of interhalogens, the vapor pressure of bromine trifluoride has been determined. Ruff and Braida (4) measured some of the physical and chemical properties including the vapor pressure over a limited range, 4 to 136 mm. The present investigation extends the vapor pressure data to 2 1/2 atmospheres on material of high purity.

EXPERIMENTAL

Material. The sample of bromine trifluoride was the same as that used for thermal measurements (3). It was prepared by passing fluorine into dry liquid bromine held at 15°C. After purification by distillation, the material had a purity of 99.91 mole per cent (3). No further purification was made except that of flashing off to a vacuum trap any higher volatile materials formed in the vapor pressure boiler during operation.

Apparatus and Procedure. The boiling point apparatus and method of measurement has been described in detail in previous reports (1,2). Briefly, the apparatus was composed of a nickel boiler connected to a mercury manometer by helium-filled lines. A Wild cathetometer, readable to ± 0.01 mm. over an 800 mm. range, was used in conjunction with a mirrored glass scale and a barometer for measuring pressures. A certified platinum resistance thermometer and Mueller G-2 bridge were used in making the temperature measurements. The observed boiling point pressures were converted to standard millimeters of mercury by the usual corrections for capillarity, gravity and temperature (2).

DATA AND DISCUSSION

Vapor pressure measurements made from 17 to 1800 mm. of mercury covering a temperature range from 38.7 to 154.8°C. are listed in table I. These experimental data were fitted by a method of least squares (5) with the following Antoine equation: $\log_{10} P_{\text{mm}} = 7.74853 - \frac{1685.8}{t + 220.57}$ (1)

Column 3 and 7 of table I show the difference between observed and calculated pressures, and column 4 and 8 express the 95% confidence limits for each point. The unusually large uncertainties of these data are attributed to decomposition of the material while undergoing measurement in the boiling point apparatus. After an unsuccessful attempt to measure the pressure at 165°C., it was discovered that most of the 60 g. sample had decomposed and diffused into an adjacent liquid nitrogen cold trap (2).

Ruff and Braida (1) reported a boiling point of 127.6°C. for bromine trifluoride which is somewhat higher than $125.75 \pm 0.05^\circ\text{C.}$ calculated from the above equation.

By combining the vapor pressure and Clausius-Clapeyron equations, one obtains equation, 2,

$$\Delta H_v = 7714 \left[(t + 273.16)/(t + 220.57) \right]^2 \quad (2)$$

which may be used to estimate the heat of vaporization of bromine trifluoride. Of course, the accuracy of the results depends on how closely the compound follows the ideal gas laws.

TABLE I
THE VAPOR PRESSURE OF BROMINE TRIFLUORIDE

Temp., °C.	Pressure, mm.	Obs.-Calc., mm.	Precision, ±mm.	Temp., °C.	Pressure, mm.	Obs.-Calc., mm.	Precision, ±mm.
38.716	17.67	0.02	0.02	111.848	475.93	0.32	0.32
49.097	31.46	0.11	0.04	121.961	671.68	0.30	0.48
57.000	47.25	-0.08	0.05	126.841	787.57	0.35	0.62
66.226	74.07	-0.15	0.06	131.857	923.3	0.3	0.8
76.355	117.80	0.08	0.08	137.301	1092.1	0.8	1.0
84.935	170.05	0.01	0.11	148.295	1507.0	-0.7	1.5
91.837	225.05	-0.07	0.15	154.822	1808.0	-2.5	1.9
101.748	330.15	0.28	0.21				

SUMMARY

The vapor pressure of bromine trifluoride has been measured over the pressure range of 17 to 1800 mm. and an equation representing the data was calculated. An approximate equation for calculating the heat of vaporization was developed by use of the Clausius-Clapeyron and the vapor pressure equations.

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Experimental work was completed February 6, 1951.