

[CONTRIBUTION FROM THE RESEARCH LABORATORY, K-25 PLANT, CARBIDE AND CARBON CHEMICALS DIVISION, UNION CARBIDE AND CARBON CORPORATION]

Thermal Data, Vapor Pressure and Entropy of Bromine Trifluoride¹

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The heat capacity of bromine trifluoride was measured over the temperature range of 14 to 320°K. Three heat of fusion measurements gave an average value of 2874.6 ± 3 cal./mole at the triple point, 281.93°K. Vapor pressure measurements up to 1800 mm., which cover the temperature range 38 to 155° are represented by the equation $\log_{10} P_{\text{mm.}} = 7.74853 - 1685.8/(t + 220.57)$. The calculated heat of vaporization at the boiling point, 125.75°, is 10.2 kcal./mole. The entropy of the liquid and ideal gas at 298.16°K. are 42.57 ± 0.10 and 71.57 cal./deg. mole, respectively.

In continuation of the program to investigate the thermodynamic properties of fluorocarbon and interhalogen compounds, thermal, vapor pressure and entropy data have been determined on bromine trifluoride. This compound was first prepared in 1900 when Moissan² discovered that fluorine combined violently with bromine vapors. Later Ruff and co-workers³ prepared bromine trifluoride and studied many of its physical and chemical properties. Recently, this compound, as well as other interhalogens, has gained prominence in the chemical industry as an excellent oxidizing and fluorinating agent; consequently, further characterization was needed.

Experimental

Material.—The bromine trifluoride was prepared in this Laboratory by passing fluorine into liquid bromine at 15°. It was necessary to purify this material by distillation in a nickel column using a vacuum of 27 inches to prevent decomposition. First, the bromine was removed by distillation to yield a sample containing 0.36 mole % impurity; then by distilling the residue under similar vacuum conditions, a sample having only 0.09 mole % impurity was obtained. During the course of measurements, heat capacity runs were made periodically in the premelting temperature region; since no change in heat capacity could be detected, it was assumed that the purity of the sample remained constant, even though it was in the calorimeter at room temperature for more than a week.

Apparatus and Procedure.—All thermal measurements were made with an adiabatic calorimetric cryostat and accessory equipment which have been described.⁴ Typical heat capacity and fusion measurements were made by supplying a precisely measured amount of electrical energy to the calorimeter and measuring the temperature rise with a certified platinum resistance thermometer. Energy measurements made in terms of the absolute joule were converted to calories by dividing by 4.1840. The precision of the measurements was 0.1% and the estimated accuracy was about 0.2% except in the heat capacity measurements below 30°K. where it approached 1%.

Since free bromine attacks copper more readily than nickel and it is likely that a small amount of bromine was present, a calorimeter made of nickel, including the perforated conducting disc, and welded together replaced the usual copper calorimeter. After 0.5 mole of bromine trifluoride was distilled directly into the calorimeter, the filling tube was pinched flat and sealed by burning the flat portion in two with a welding torch.

The vapor pressure of bromine trifluoride was measured by the ebulliometric method in the apparatus referred to in a previous publication⁴ and described in detail elsewhere.⁵

(1) This document is based on work performed for the Atomic Energy Commission by Carbide and Carbon Chemicals Division, Union Carbide and Carbon Corporation, Oak Ridge, Tennessee.

(2) H. Moissan, "Le fluor et ses composés," G. Steinheil, Paris, 1900, p. 123.

(3) O. Ruff, *et al.*, *Z. anorg. allgem. chem.*, **202**, 49 (1931); *ibid.*, **206**, 63 (1932); *ibid.*, **214**, 91 (1933).

(4) G. D. Oliver and J. W. Grisard, *THIS JOURNAL*, **73**, 1688 (1951).

(5) J. W. Grisard and George D. Oliver, *Chemistry K-613*, Carbide and Carbon Chemicals Company, K-25 Plant, Oak Ridge, Tennessee, June 23, 1950.

Briefly, the sample was contained in a nickel boiler connected to a mercury manometer by helium filled lines. A Wild cathetometer was used in conjunction with a mirrored glass scale and barometer for measuring pressure. The temperatures were measured with a certified platinum resistance thermometer through a Mueller G-2 bridge and galvanometer.

Results and Discussion

Before proceeding with heat capacity measurements, the purity of the bromine trifluoride was established by the fractional melting point method. The equilibrium temperatures, 281.720, 281.807, 281.852 and 281.879°K., correspond, respectively, to the following melted fractions of the best sample, 0.222, 0.403, 0.649 and 0.863. These and similar data for another less pure sample are plotted in Fig. 1 as curves A and B, respectively.

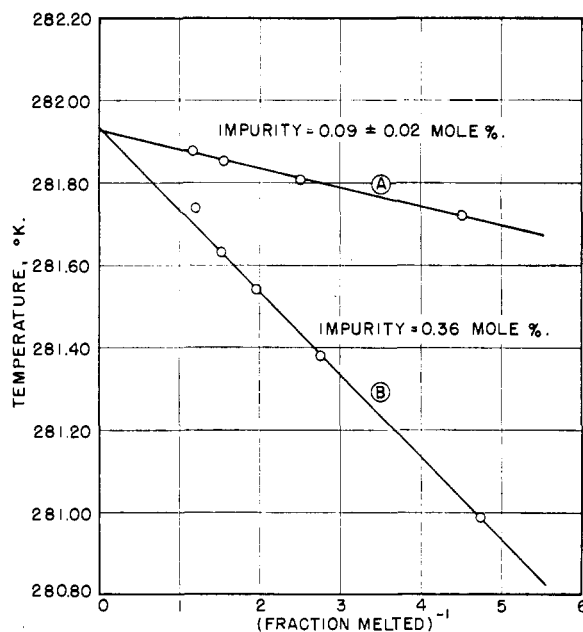


Fig. 1.—Bromine trifluoride melting point.

Assuming ideal solution of impurity in the liquid fraction, a plot of the equilibrium temperature against the reciprocal of the fraction melted should give a straight line. These data follow the theoretical linear relationship to the extent that both curves extrapolate to the same intercept and triple point, $281.93 \pm 0.05^\circ\text{K}$. It is interesting to note that samples of chlorine trifluoride⁶ containing similar amounts of impurities also appeared to follow Raoult's law. The experimental melting point data were used in the expression, $N_x = KAT$,

(6) J. W. Grisard, H. A. Bernhardt and George D. Oliver, *THIS JOURNAL*, **73**, 5725 (1951).

to calculate the mole fraction impurity, N_x , with the cryoscopic constant $K = 0.0182$.

Approximately 70 heat capacity measurements, made over the temperature range 14.5 to 320°K., are given in columns 3 and 6 of Table I. Columns 2 and 5 contain the temperature change for each observation. The liquid heat capacities were not corrected for vapor saturation as the vapor pressure is very low over the temperature range involved.

TABLE I
MOLAL HEAT CAPACITY OF BROMINE TRIFLUORIDE IN CAL./DEG.

| Molecular wt. = 136.916. 0°C. = 273.16°K. | | | | | |
|---|-------|--------------------|--------|--------|--------------------|
| T, °K. | ΔT | C _{satd.} | T, °K. | ΔT | C _{satd.} |
| 15.32 | 1.339 | 1.279 | 159.37 | 9.250 | 17.23 |
| 16.68 | 1.079 | 1.590 | 168.48 | 8.968 | 17.75 |
| 17.77 | 0.878 | 1.800 | 175.73 | 8.533 | 18.15 |
| 18.91 | 3.396 | 2.005 | 177.32 | 8.726 | 18.22 |
| 19.88 | 3.017 | 2.256 | 184.84 | 9.692 | 18.62 |
| 22.33 | 3.323 | 2.709 | 185.93 | 8.500 | 18.70 |
| 22.99 | 3.119 | 2.886 | 194.26 | 8.145 | 19.12 |
| 26.14 | 4.256 | 3.513 | 198.09 | 7.995 | 19.34 |
| 26.64 | 4.150 | 3.595 | 202.97 | 9.291 | 19.57 |
| 30.91 | 4.362 | 4.466 | 212.17 | 9.095 | 20.00 |
| 31.17 | 5.758 | 4.486 | 215.42 | 10.318 | 20.16 |
| 35.49 | 4.789 | 5.263 | 225.63 | 10.094 | 20.60 |
| 37.07 | 5.986 | 5.572 | 235.62 | 9.885 | 21.05 |
| 40.96 | 6.163 | 6.188 | 239.02 | 9.784 | 21.22 |
| 41.98 | 3.812 | 6.385 | 245.39 | 9.672 | 21.54 |
| 47.45 | 6.828 | 7.182 | 248.71 | 9.584 | 21.70 |
| 53.27 | 4.735 | 8.155 | 253.21 | 5.957 | 21.87 |
| 58.25 | 5.207 | 8.661 | 256.61 | 8.937 | 22.13 |
| 63.99 | 6.277 | 9.351 | 260.29 | 8.214 | 22.22 |
| 70.34 | 6.425 | 10.02 | 262.74 | 6.974 | 22.32 |
| 76.63 | 6.154 | 10.70 | 264.74 | 7.310 | 22.49 |
| 80.31 | 3.775 | 11.13 | 267.29 | 5.778 | 22.59 |
| 85.18 | 5.953 | 11.65 | 269.25 | 6.841 | 22.70 |
| 89.88 | 7.072 | 12.05 | 270.66 | 4.539 | 22.82 |
| 91.22 | 6.131 | 12.20 | 273.51 | 6.640 | 23.90 |
| 97.06 | 7.543 | 12.68 | | Liquid | |
| 104.17 | 6.776 | 13.28 | 285.55 | 5.936 | 29.65 |
| 105.37 | 7.870 | 13.40 | 286.82 | 5.598 | 29.61 |
| 108.69 | 6.526 | 13.65 | 287.65 | 4.720 | 29.66 |
| 113.55 | 8.497 | 14.06 | 292.41 | 5.570 | 29.70 |
| 115.59 | 7.278 | 14.19 | 293.53 | 7.043 | 29.77 |
| 121.91 | 8.235 | 14.71 | 295.80 | 7.102 | 29.71 |
| 130.61 | 9.165 | 15.35 | 300.56 | 7.012 | 29.81 |
| 140.18 | 9.977 | 16.05 | 308.14 | 8.147 | 29.92 |
| 149.96 | 9.570 | 16.69 | 316.27 | 8.117 | 30.00 |

Three heat of fusion measurements made on bromine trifluoride are summarized in Table II. An average value of the heat of fusion is 2874.6 ± 3.0 cal./mole. Premelting corrections were not made since each measurement was started at low enough temperature to include practically all pre-melting.

TABLE II
HEAT OF FUSION OF BROMINE TRIFLUORIDE

| Temperature interval, °K. | Cor. heat input, cal./mole | $\int C_p dT$, cal. | ΔH , cal./mole |
|---------------------------|----------------------------|----------------------|------------------------|
| 270.185-286.124 | 3270.4 | 394.7 | 2875.7 |
| 268.391-285.288 | 3286.0 | 410.7 | 2875.3 |
| 266.228-283.90 | 3293.6 | 420.7 | 2872.9 |
| Mean | | | 2874.6 ± 3 |

Vapor pressure measurements were determined on the sample after completion of the thermal measurements. Experimental data covering the pressure range of 17 to 1800 mm. and listed in Table III were fitted with the following Antoine equation by methods of least squares.⁷

$$\log_{10} P_{\text{mm.}} = 7.74853 - 1685.8/(t + 220.57) \quad (1)$$

Deviations of experimental data from this equation are given in columns 3 and 6 of Table III. As usual, the precision of the results was established by calculating 95% limits which varied from 0.02 to 0.04° over the experimental temperature range.

TABLE III
THE VAPOR PRESSURE OF BROMINE TRIFLUORIDE

| $t_{\text{obsd.}}$, °C. | $P_{\text{obsd.}}$, mm. | $P_{\text{obsd.}} - P_{\text{calcd.}}$ | $t_{\text{obsd.}}$, °C. | $P_{\text{obsd.}}$, mm. | $P_{\text{obsd.}} - P_{\text{calcd.}}$ |
|--------------------------|--------------------------|--|--------------------------|--------------------------|--|
| 38.72 | 17.67 | 0.02 | 111.85 | 475.93 | 0.32 |
| 49.10 | 31.46 | .11 | 121.96 | 671.68 | .30 |
| 57.00 | 47.25 | -.08 | 126.84 | 787.57 | .35 |
| 66.23 | 74.07 | -.15 | 131.86 | 923.3 | .3 |
| 76.36 | 117.80 | .08 | 137.30 | 1092.1 | .8 |
| 84.94 | 170.05 | .01 | 148.30 | 1507.0 | -.7 |
| 91.84 | 225.05 | -.07 | 154.82 | 1808.0 | -2.5 |
| 101.75 | 330.15 | .28 | | | |

The unusually large uncertainties in these data at the higher temperatures were attributed to the decomposition of the material while undergoing measurements. After an unsuccessful attempt to measure the pressure at 165°, it was discovered that most of the 60-g. sample apparently had decomposed and diffused through the condenser into an adjacent liquid nitrogen trap. Ruff and Braida⁸ reported a boiling point of 127.6° for bromine trifluoride which is somewhat higher than 125.75 $\pm 0.05^\circ$ as calculated from equation (1).

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

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

which was used to calculate the heat of vaporization, the value at the boiling point being 10,235 cal./mole.

The experimental data have been utilized to calculate the entropy for the liquid and vapor state of bromine trifluoride at 298.16°K. The heat of vaporization value at 298.16°K., calculated by

TABLE IV
THE ENTROPY OF BROMINE TRIFLUORIDE IN CAL./DEG. MOLE

| | |
|--|------------------|
| S_{14° (Debye, 4° freedom, $\theta = 115.58$) | 0.357 |
| $\Delta S_{14-281.93^\circ}$ solid, graphical | 30.359 |
| $\Delta S_{281.93^\circ}$ fusion, 2874.7/281.93° | 10.197 |
| $\Delta S_{281.93-298.16^\circ}$ liquid, graphical | 1.660 |
| $S_{298.16^\circ}$ of liquid | 42.57 ± 0.10 |
| $\Delta S_{298.16^\circ}$ vaporization, 11,370/298.16° | 38.14 |
| $\Delta S_{298.16^\circ}$ compression, $R \ln P/760$ | -9.14 |
| Entropy of the ideal gas at 1 atm. and 298.16°K. | 71.57 |

(7) C. B. Willingham, W. J. Taylor, J. M. Pignocco and F. D. Rossini, *J. Research Natl. Bur. Standards*, **35**, 219 (1945).

means of equation 2, was 11,370 cal./mole and the entropy of vaporization was 38.14 cal./deg. mole. Because of the low vapor pressure (7.65 mm.) at 298.16°K. and the lack of other pertinent data, a gas imperfection correction was not estimated; however, a correction for entropy of compression

was included. The results of the calculations are summarized in Table IV.

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OAK RIDGE, TENNESSEE

[CONTRIBUTION FROM THE DEPARTMENT OF INDUSTRIAL CHEMISTRY, THE FACULTY OF ENGINEERING, KYOTO UNIVERSITY]

The Relative Rates of Chromic Acid Oxidation of Toluenes in Acetic Acid

BY YOSHIRO OGATA, ATSUO FUKUI AND SADA O YUGUCHI

The rates of oxidation of toluene and ring-substituted toluenes by chromium trioxide in acetic acid at 70° have been estimated iodometrically. The rates are first-order with respect to the concentration of toluenes and second-order with respect to that of chromium trioxide. Chromic acetate produced exhibits a retarding action which is probably due to its ability to decrease the acidity of the medium. In general, electron-attracting groups in the benzene ring diminish the rate in the order: None > *p*-Br > *p*-Cl > *p*-CN > *p*-NO₂. The above results are explicable by a tentative mechanism which involves a rate-determining attack of two molecules of chromium trioxide and a subsequent elimination of chromic oxide from the intermediate with or without an attack of other molecules of chromium trioxide. In the latter case, carbon dioxide is evolved probably as a result of an induced oxidation. The rate constants tend to decrease with increased initial concentration of toluenes.

Kinetic studies on the chromic acid oxidation of ethanol,¹ isopropyl alcohol² and carboxylic acids³ in aqueous media, and of aromatic aldehydes⁴ in a mixture of acetic acid and sulfuric acid⁴ have been reported. Slack and Waters⁵ have observed, in the initial reaction of chromic acid oxidation of diphenylmethane in acetic acid, that the rate is first-order with respect to diphenylmethane and second-order with respect to chromium trioxide, the rate being retarded by the presence of chromic acetate or water. But little appears to have been reported regarding the oxidation of toluene.

The present paper deals with a kinetic investigation upon the oxidation of toluene and ring-substituted toluenes in acetic acid with chromium trioxide. Rates were estimated iodometrically. A characteristic feature of this reaction is the retardation by chromic acetate and the induced oxidation producing carbon dioxide the amount of which was also measured.

Experimental

Materials.—Glacial acetic acid was rectified by successive distillations from chromium trioxide added with acetic anhydride and then from chromium trioxide alone.⁶ It was

free from oxidizable substances and water, m.p. 16.6°. Chromium trioxide was of best grade free of sulfate and chloride, its purity of 100% being confirmed iodometrically. Toluene and substituted toluenes were purified by duplicate distillations; those which were solid exhibited melting points in agreement with the literature and those which were liquid showed constant boiling points. About 20% of chromium trioxide was reduced during its solution in acetic acid at 60° for about eight hours. Therefore, it was necessary to determine the amount of chromic acetate from the difference between the dissolved weight of chromium trioxide and the amount found by the iodometric titration of the solution. In general, the concentration of the chromium trioxide solution was ca. 0.4 mole/l.

Apparatus and General Procedure.—In one glass-stoppered erlenmeyer flask was placed 10 cc. of the solution of chromium trioxide and in the other a solution of toluene in acetic acid. The two flasks were dipped in an electrically-controlled thermostat maintained at 70.0 ± 0.1°. After reaching the temperature equilibrium, 5 cc. of the solution of toluene was added to the solution of chromium trioxide. One-cc. aliquots were pipetted out at known intervals of time and titrated with 0.05 *N* thiosulfate after being added to 5 cc. of 10% aqueous sulfuric acid and 3 cc. of 25% aqueous potassium iodide. The pipets were calibrated at the temperature.

The determination of the amount of carbon dioxide, evolved by the induced oxidation and identified as barium carbonate, was carried out as follows. In a flask equipped with a ground-glass reflux condenser and dipped in a thermostat at 70°, an acetic acid solution of chromium trioxide was mixed with that of toluene. The carbon dioxide was drawn out by passing air, which is free of oxygen, with alkaline hydrosulfite solution and carbon dioxide with solid potassium hydroxide. After being freed of acetic acid with aniline and of water with calcium chloride, the carbon dioxide was absorbed by 40% aqueous caustic potash. The increase in weight of the potash bulb corresponds to that of carbon dioxide liberated. The reliability of this procedure was proved by a test with a known amount of carbon dioxide produced from calcium carbonate and hydrochloric acid. If oxygen in the air or a trace of acetic anhydride in the acetic acid was not removed, a little larger amount of carbon dioxide was produced. The final concentration of chromium trioxide was consistent with that expected from the kinetic data. The decrease in chromium trioxide content with pure acetic acid was calculated by the weight of carbon dioxide, which was in agreement with that observed in the kinetic experiment. No carbon dioxide was detected by employing water in place of acetic acid as solvent.

The ether extracts of the oxidation products of toluene and *p*-nitrotoluene gave benzoic acid, m.p. and mixed m.p. 122–123°, and *p*-nitrobenzoic acid, m.p. and mixed m.p. 239–240°, respectively. No indication of the other product was observed.

(1) (a) M. Bobtelsky and C. Radovinsky-Cholatnikow, *Z. anorg. allgem. Chem.*, **199**, 241 (1931); M. Bobtelsky and R. Cohn, *ibid.*, **210**, 225 (1933); (b) M. G. Lejeune, *Compt. rend.*, **182**, 694 (1926).

(2) (a) F. H. Westheimer and A. Novick, *J. Chem. Phys.*, **11**, 506 (1943); W. Watanabe and F. H. Westheimer, *ibid.*, **17**, 61 (1949); F. H. Westheimer and N. Nicolaides, *This Journal*, **71**, 25 (1949); F. Holloway, M. Cohen and F. H. Westheimer, *ibid.*, **73**, 65 (1951); (b) F. H. Westheimer, *Chem. Revs.*, **45**, 419 (1949).

(3) (a) H. C. S. Sneath, *Rec. trav. chim.*, **54**, 651 (1935); **56**, 873 (1937); **59**, 111 (1940); **60**, 199, 710, 877 (1941); **61**, 213 (1942); (b) N. R. Dhar, *J. Chem. Soc.*, **111**, 707 (1917); **123**, 1856 (1923); *Ann. chim.*, [9] **11**, 130 (1919); R. M. Purkayostha and N. R. Dhar, *Z. anorg. allgem. Chem.*, **121**, 156 (1922); R. C. Banerji and N. R. Dhar, *ibid.*, **134**, 172 (1924); A. K. Bhattacharya and N. R. Dhar, *ibid.*, **169**, 381 (1928); A. N. Dey and N. R. Dhar, *Z. Elektrochem.*, **32**, 586 (1928).

(4) E. Lucchi, *Boll. sci. facoltà chim. ind. Bologna*, 208 (1940); 333 (1940); 165, 176 (1941); *Gazz. chim. ital.*, **71**, 729, 752 (1941) [*C. A.*, **36**, 8880 (1942); **37**, 2252 (1943); **37**, 4293 (1943); **36**, 7012 (1942)].

(5) R. Slack and W. A. Waters, *J. Chem. Soc.*, 1666 (1948); 599 (1949).

(6) For the purification of acetic acid see K. J. P. Orton and A. E. Bradfield, *J. Chem. Soc.*, 960 (1924); 983 (1927); A. Weissberger and E. Proskauer (translated by R. G. A. New), "Organic Solvents," Clarendon Press, Oxford, 1935, p. 146.