Iodine pentafluoride is therefore probably an associated liquid.[12]

Acknowledgment.—This investigation was made possible by a grant from the Atomic Energy Commission (Contract AT (11-1)-151).

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(12) NOTE ADDED IN PROOF.—The electric moment of iodine pentafluoride in the vapor phase has been determined in this laboratory and the value 2.24 ± 0.1 debye found: M. T. Rogers, R. D. Pruett and J. L. Speirs, unpublished results. The refractive indices and molar refractions of chlorine trifluoride and iodine pentafluoride have been measured in the vapor phase in this laboratory: M. T. Rogers, J. G. Malik and J. L. Speirs, unpublished results. From the known liquid densities, the squares of the refractive indices n^2 are then estimated to be 1.761 and 2.126 for liquid chlorine trifluoride and iodine pentafluoride, respectively. These observations do not alter the argument presented in this article.

EAST LANSING, MICHIGAN

[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE COLLEGE]

Iodine Pentafluoride, Freezing and Boiling Point, Heat of Vaporization and Vapor Pressure–Temperature Relations[1]

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RECEIVED APRIL 30, 1954

The freezing point of pure iodine pentafluoride is 9.43 ± 0.01° and the vapor pressure is given as a function of temperature by the equation $\log p(\text{mm.}) = 8.6591 - 2159.0/T$. The calculated boiling point is 100.5° and the heat of vaporization is 9.88 kcal./mole.

Introduction

As a part of an investigation of the physical properties of several halogen fluorides, we have redetermined the freezing point and the vapor pressure–temperature relations of purified iodine pentafluoride. No reports of these properties have appeared since the original paper of Ruff and Braida.[2] Their pioneering work was handicapped by the lack of suitably resistant materials for the construction of apparatus. The availability of fluorinated plastics now permits the preparation and preservation of material of higher purity. Apparatus used in the present work was therefore specially constructed, largely from Fluorothene and Teflon.[3]

The earlier value of the freezing point of iodine pentafluoride, 9.6°, given by Ruff and Braida, was obtained on material having an implied purity between 99.2 and 99.9%. The method and limits of error were not stated. In Table I our freezing point results are given for a number of samples of varying degrees of purity as determined from their freezing curves by the method of White.[4] These samples were prepared and measured using several different techniques over an extended period of time. Based on the samples of higher purity, we report 9.43 ± 0.01° as our most reliable value for the freezing point of pure iodine pentafluoride.

The values given by Ruff and Braida for the vapor pressure of iodine pentafluoride as a function of temperature are essentially confirmed by our results, although the latter show considerably better internal consistency over the measured range of approximately 30 to 140 mm. pressure. The Ruff and Braida data for the range from 15 to 70 mm. pressure may be expressed in the form (recalculated)

$$\log p(\text{mm.}) = 8.82 - 2205/T$$

with an approximate uncertainty of ±2 mm. A calculated value of the boiling point from this expression would be 97.8° rather than the value of 98.5 ± 1.5° given by Ruff and Braida. Their calculated value of the heat of vaporization is 9.02 kcal./mole. Our result, in equation form, for the vapor pressure–temperature relationship of pure iodine pentafluoride in the range from 30 to 150 mm. pressure is

$$\log p(\text{mm. at } 0°) = 8.6591 - 2159.0/T$$

The equation is based on measurements at thirteen different pressures and the r.m.s. deviation of calculated from experimental values was 0.15 mm. Our calculated value of the heat of vaporization is 9.88 kcal./mole. The calculated boiling point is 100.5°, an extrapolated value which is suggested as a more accurate substitute for the original Ruff and Braida value.

TABLE I

FREEZING POINTS OF IODINE PENTAFLUORIDE SAMPLES

Sample	t_f,[a] °C.	t_x, °C.	m_i	t_0, °C.
A	9.398	9.376	0.0025	9.420
B	9.408	9.386	.0025	9.430
C	9.336	9.245	.0086	9.427

[a] t_f, extrapolated freezing point of original sample; t_x, temperature of half-frozen sample; m_i, the molal concentration of impurity in the original sample; t_0, freezing point of pure solvent calculated by method of Witschonke.[4]

Experimental

Purification of Material.—Commercially available iodine pentafluoride (General Chemical Co.) was pretreated at room temperature to remove dissolved iodine by agitating with a mixture of dry air and chlorine trifluoride (Harshaw Chemical Co.) in a Fluorothene beaker using a magnetic stirrer. The mixture, containing a considerable quantity of chlorine trifluoride and some non-volatile impurities, was transferred to the pot of the fractionating column and the more volatile impurities were pumped off as the pressure fell below 40 mm. Considerable chlorine trifluoride was evolved as the pot and jacket were heated to raise the pressure to 40 mm. Even after flooding the column and operating under total reflux for as long as two hours it was found advisable to discard at least the first 10% of the product as it still contained demonstrable traces of chlorine trifluoride.

The distilled product was colorless indicating the absence of colored metallic salts. The presence of iodine in even small traces is apparent as a distinct coloration, passing

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(1) Physical Properties of the Halogen Fluorides. I.

(2) O. Ruff and A. Braida, *Z. anorg. allgem. Chem.*, **220**, 43 (1933).

(3) Trademark of E. I. du Pont de Nemours and Co., Inc.

(4) W. P. White, *J. Phys. Chem.*, **24**, 393 (1920); C. R. Witschonke, *Anal. Chem.*, **24**, 350 (1952).

through the stages of straw yellow to red to red-black with increasing concentration. This furnished a sensitive indication as to the presence of any hydrogen fluoride contamination produced in subsequent handling by reaction with adsorbed or atmospheric moisture. Conversely the failure to show an immediate coloration on deliberate exposure to moisture or traces of iodine was a sensitive test for chlorine trifluoride impurity.

We found that it was essential to remove free or dissolved iodine prior to the distillation step, since it was sufficiently volatile that iodine crystals formed in the condensing head of the column with resultant contamination of the product. No deterioration of the purified product was noted during indefinitely long periods of storage in closed Fluorothene containers exposed to ordinary room temperature and light. Most of the distillations were made at approximately 50 mm. pressure and 50% reflux ratio.

Apparatus and Procedure.—The fractionating assembly consisted of a Monel pot (approximately 400-ml. capacity) connected by a tapered joint to a packed Monel column, approximately 0.75″ i.d. by 15″ long, surrounded by a heated and insulated metal jacket and an outer copper tubing shell. Protruded nickel packing (Scientific Development Co.), 0.16″ by 0.16″, was used. The column had an efficiency of at least seven theoretical plates on the simpler standard mixtures.

The condensing head assembly, constructed entirely of Fluorothene, was connected by a taper joint to the top of the column. The take-off assembly connected to the condensing head was constructed of Fluorothene. Three valves were incorporated performing the functions of take-off rate control, isolation of the self-contained product reservoir from the product receiver, and preconditioning or evacuation of the product receiver. These valves, using phosphor-bronze bellows (Hoke Type 1132-15), were adapted so that liquid product did not contact the small metal area which was exposed only to vapor.

The product was either received directly in Fluorothene tubes for the freezing point determinations, or passed through a short nickel inlet pipe and Monel valve (Hoke Type 1132) into closed storage vessels. These were standard Fluorothene beakers with lids, held together by clamping means, the only exposed metal being the Monel inlet and outlet fittings located on the lid above the liquid level. All receiving vessels and other apparatus were preconditioned by chlorine trifluoride treatment, flushing with dry air, and evacuation to remove adsorbed moisture.

The column operation was only directly observable through thin transparent Fluorothene sections of the condenser and takeoff assemblies. Copper–constantan thermocouples were located on the jacket, near the top and bottom of the inner Monel column, and in the condensing head just below the take-off. The latter couple was directly exposed to the vapor over a length of several inches (in spiral form) to avoid thermal conduction error. It was located about 2″ above the top of the packing and in a region free of cold condensate return from the condenser cold finger.

Temperature differentials were recorded with reference to a cold junction maintained at nearly the same temperature in a heated and stirred Dewar flask. The reference temperature was measured (±0.01°) by a calibrated thermometer and the temperature differential was recorded (to a maximum sensitivity of approximately 0.005°) by use of a combination of Leeds and Northrup "Speedomax" potentiometer–recorder and Type 9835-B d.c. amplifier.

Pressure measurements (±0.1 mm.) were made with a cathetometer and absolute mercury manometer. The mercury was protected by a minimum flow of dry air purge gas past the manometer to the column take-off assembly which was maintained at a slightly lower pressure by a vacuum system. A sensitive Fluorolube[5] oil manometer and two isolating valves were located between the mercury manometer and distilling column. These permitted determination of the proper balance of purge gas and column take-off pressures. Pressure measurements were corrected for any unbalance (not more than 0.1 mm.). Fundamental control of column pressure was obtained by a Cartesian Diver Manostat (Emil Greiner Co.) operating to hold the purge gas pressure constant against a continuous dry air leak and the air demand of the column. We were not able to measure pressure directly using a Fluorolube oil absolute manometer because of loss of vacuum in the closed end caused by excessive solubility of gases in the oil. The production of non-condensable gas from the column was observed to be negligible, therefore no correction was made for the pressure differential between the column and the take-off assembly.

The vapor pressure–temperature measurements were made under conditions of total reflux on the latter half of a charge of iodine pentafluoride. After reaching apparently constant head temperature each measurement at a particular pressure was made over a period of at least 30 to 60 minutes, followed by a trial of higher and lower jacket temperatures to check their effect on the possible contribution of superheating due to non-adiabatic operation, flooding or surging. Under best conditions variations were held to approximately ±0.02°; however, a minimum probable over-all temperature error of ±0.05° must be assumed due to known causes such as reading and instrumental errors, and variations due to slight pressure fluctuations.

Freezing Point Assembly.—Freezing point measurements were made in a thin-walled 1″ × 6″ Fluorothene test-tube, using samples of about 100 g. Agitation was obtained by either rotary or reciprocating motion of a grooved cylindrical stirrer, the shaft of which was supported by a central bearing post extending down from the tube closure. All parts exposed to iodine pentafluoride were constructed of Teflon or Fluorothene except the thermocouple. About 20″ lengths of the copper and constantan thermocouple wires were wound on a helical double thread on the central bearing post and, in actual operation, at least a 10″ length of the wires was exposed to the liquid to prevent thermal conduction errors. The moving shaft at the upper bearing was sealed, for rotation by a little Fluorolube oil, for reciprocating motion by a flexible Fluorothene hood, or by a flow of dry purge gas.

Controlled cooling was obtained in some runs by using an intermediate dead air space between the sample container and a glass tube surrounded by a suitable constant temperature freezing bath (such as a carbon tetrachloride solid–liquid mixture). In other cases a controlled variable-temperature bath surrounded the sample container. The tendency of high purity samples to freeze on the walls of the tube gave trouble with all the methods of agitation and cooling tried.

For the freezing-point measurements of highest accuracy the ice-point error was determined immediately prior to use. The combination of a Type K-2 Leeds and Northrup potentiometer and each thermocouple pair (from the same lots of copper and constantan wire), was directly calibrated against a Leeds and Northrup platinum resistance thermometer and Type G-1 Mueller bridge assembly certified by the National Bureau of Standards. A modification of White's apparatus[6] was used to maintain the reference temperature at 0° during calibration and measurement operations. Because of the proximity of the ice point to the working temperature, better than normal accuracy was possible. The experimental r.m.s. deviation from an e.m.f.–temperature relation of the form $E = at + bt^2$ corresponded to approximately 0.005° over the range 0–10° (maximum deviation 0.008°).

During freezing the thermocouple output was recorded by a Brown "Elektronik" potentiometer–recorder used with a Leeds and Northrup Type 9835-B d.c. amplifier at a sensitivity of approximately 1.5° per inch. Marker pips were superimposed on the chart record at points at which the differential was measured by the manually balanced Type K-2 potentiometer.

The difference between the freezing point T_f of each sample and T_0, the freezing point of the pure liquid, was in each case estimated by Witschonke's[4] method. The amount of impurity in the final measured sample (Table I), partially introduced by handling, was estimated from the cooling curve assuming that hydrogen fluoride was the impurity. The value of 3.80 kcal. mole^{-1} for the heat of fusion of iodine pentafluoride was calculated from the data of Ruff and Braida.[2]

Acknowledgment.—The generous support of this work by the Atomic Energy Commission is gratefully acknowledged (Contract AT (11-1)-151).

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[5] Trade-mark of Hooker Electrochemical Co.

[6] W. P. White, THIS JOURNAL, **56**, 20 (1934).