[CONTRIBUTION FROM THE THERMODYNAMICS SECTION, NATIONAL BUREAU OF STANDARDS]

Heat Capacity of Gaseous Perfluorocyclobutane[1]

BY JOSEPH F. MASI

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The heat capacity of gaseous perfluorocyclobutane has been measured with an accuracy of 0.1% with a constant-flow calorimeter at three pressures at each of the temperatures 10, 50 and 90°. Values of $C_p^{\circ 1}$, believed reliable to 0.15%, were obtained by extrapolation of the measurements to zero pressure. These are 36.19, 39.23 and 42.01 cal. mole^{-1} degree^{-1}, respectively, at the three temperatures. The corresponding values of the pressure coefficient of heat capacity are 0.84, 0.47 and 0.28 cal. mole^{-1} degree^{-1} atmosphere^{-1}.

Introduction

Perfluorocyclobutane can be obtained by dimerizing tetrafluoroethylene and also by pyrolyzing Teflon. It is an extremely stable compound. Its structure is of interest because of the question of planarity in the simpler cyclic compounds generally, and because of the present-day practical interest in fluorocarbons and their polymers. Analyses of the spectra of perfluorocyclobutane have been based on a symmetrical structure with a planar ring (symmetry group D_{4h}).[2,3] There is evidence, however, of less symmetry.[4-6]

Accurate values of the heat capacity of the ideal gas, particularly over a range of temperatures, are helpful in deciding such questions of structure. Accordingly, the heat capacity of the real gas C_4F_8 was measured at three pressures at each of three temperatures with an accuracy of about 0.1%; the values at each temperature were extrapolated to zero pressure.

Experimental

Material.—Specially purified samples of perfluorocyclobutane were very kindly furnished by the Jackson Laboratories of the E. I. du Pont de Nemours Co. and the Central Research Department of the Minnesota Mining and Manufacturing Company. The latter sample was thought by the supplier to have small quantities of two of the completely fluorinated butenes as possible impurities. The du Pont sample was thought to have possibly some n-C_4F_{10} as impurity. Each sample was evaporated near its boiling point (−5°) and condensed in a cold (liquid N_2) trap beyond which a high vacuum was maintained. First and last portions were discarded. The two lots of purified material were combined into one sample of about 450 g., large enough for efficient operation of the flow calorimeter.

A mass spectrograph analysis of the material as used in this investigation indicated presence of about 0.1% n-C_4F_{10} and small amounts of other, unidentified, C_4 fluorinated compounds. These impurities should have little effect on the measured heat capacities.

Apparatus and Method.—The flow calorimeter used for these measurements has been described previously.[7] The method of controlling the flow of gas, however, needs to be mentioned. The sample was contained as a liquid in a brass cylindrical boiler having copper radial vanes. The boiler had a capacity of about 500 ml. and had a long monel tube for a neck. It was wound with a heater, which was covered with a copper envelope soldered to the boiler. The latter arrangement helped with heat distribution and also protected the heater insulation from attack by liquids in which the boiler was immersed. During operation of the apparatus, the boiler was hung in a tall dewar which was kept cold by a small amount of ethanol–Dry Ice slush, contained in the bottom. The rate of flow was maintained constant by manually adjusting the power supplied to the heater, so that the pressure drop and mean pressure in the calorimeter were constant.

The receivers for the gas after leaving the calorimeter, and the valve for diverting the flow from one receiver to the other, have been described.[7] A special by-pass was constructed for rapidly returning the sample to the boiler.

Results

Determinations of the heat capacity of perfluorocyclobutane were made at three pressures at each of three temperatures. In accordance with established practice[7] the measurements were made at a number of different flow rates so that by extrapolation to infinite rate of flow, the principal effects of heat leakage could be eliminated. Fifty-two determinations were made in all. Also, about forty-eight "blank" determinations were made in which the gas was passed through the unheated calorimeter at the mean temperatures and pressures and at the various rates of flow of the heat capacity experiments, and the fall in temperature, δT, measured. A graph of δT against the pressure drop was prepared for each pressure and temperature. The value of δT varied from zero to 0.2°.

The measured flow rate F, power W, temperature rise ΔT and blank correction δT, for each experiment were combined to give the heat capacity

$$C = WF^{-1}/(\Delta T + \delta T) \qquad (1)$$

The values of C were corrected for the deviation of the observed mean pressure and mean temperature from the nominal values. These corrections were small, never larger than 0.1%. The correction to be applied to equation 1 for the curvature of the heat capacity–temperature function was calculated to be negligible. The corrected values of heat capacity called C_p (observed), for all of the experiments with C_4F_8, are plotted in Fig. 1 against the reciprocal of the rate of flow.

The straight lines drawn through the points in Fig. 1 were initially determined by the method of least squares, then adjusted slightly where necessary to give constant slope at each temperature. The lines obtained by this method are essentially those that would result from a least-square treatment of all the points of one temperature simultaneously. For each line there was calculated the quantity $\sigma = \sqrt{\Sigma d^2/(n-1)}$ where d is the vertical deviation of each point from the line. The average of all the values of σ was ±0.03%.

The value of ΔT was kept near 10° except for two points at 50° and 1 atmosphere, which had

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[1] This work was supported by the Ordnance Corps, Department of the Army.

[2] W. F. Edgell, THIS JOURNAL, **69**, 660 (1947).

[3] H. H. Claassen, *J. Chem. Phys.*, **18**, 543 (1950).

[4] W. F. Edgell and D. G. Weiblen, *ibid.*, **18**, 571 (1950).

[5] H. P. Lemaire and R. L. Livingston, *ibid.*, **18**, 569 (1950).

[6] H. P. Lemaire and R. L. Livingston, THIS JOURNAL, **74**, 5732 (1952).

[7] J. F. Masi and B. Petkof, *J. Research Natl. Bur. Standards*, **48**, 179 (1952) RP 2303.

ΔT values of about 5°. No effect of changing the temperature rise was observed.

The calorie used in this work is the defined calorie, equal to 4.1840 absolute joules; 0° = 273.16°K.

The zero intercepts of the lines in Fig. 1 are summarized in Table I. These results have been linearly extrapolated to zero pressure at each temperature to give the tabulated values of "C_p°, obsd." Based on the precision of the individual experiments, as indicated by the value of σ given above, and on the previous use[7] of the calorimeter with a gas (oxygen) of known heat capacity, the author feels that the values of C_p at finite pressure are uncertain by no more than 0.1%. The probable error of the values of C_p°, is therefore considered to be about 0.15%.

The experimental values of C_p° are compared in Table I with values calculated on the basis of the harmonic-oscillator, rigid-rotator approximation from the frequency assignment made by Claassen,[3] on the assumption of a planar ring with D_{4h} symmetry. The calculated values appear to be too high by 1.3 to 1.7%. The entire question of the spectra and molecular constants is being critically investigated in another project at the National Bureau of Standards.

The equation of state at low pressures was assumed to be

$$PV = RT + BP \qquad (2)$$

where

$$B = b - ce^{a/T} \qquad (3)$$

as suggested by Hirschfelder, McClure and Weeks.[8] The observed pressure coefficients of heat capacity, given in the last line of Table I, were set equal to

$$\frac{\partial C_p}{\partial P} = -T\frac{\partial^2 B}{\partial T^2} \qquad (4)$$

in order to obtain values of a and c. There was obtained

$$B = b - 120.6e^{620/T} \text{ cm.}^3 \text{ mole}^{-1} \quad (5)$$

The values of $\partial C_p/\partial P$ calculated from eq. 5 are 0.84, 0.46 and 0.28 cal. mole^{-1} degree^{-1} atmosphere^{-1} at 10, 50 and 90°, respectively. The corresponding values calculated from an equation of state used by E. I. du Pont de Nemours Co.[9] for this compound as

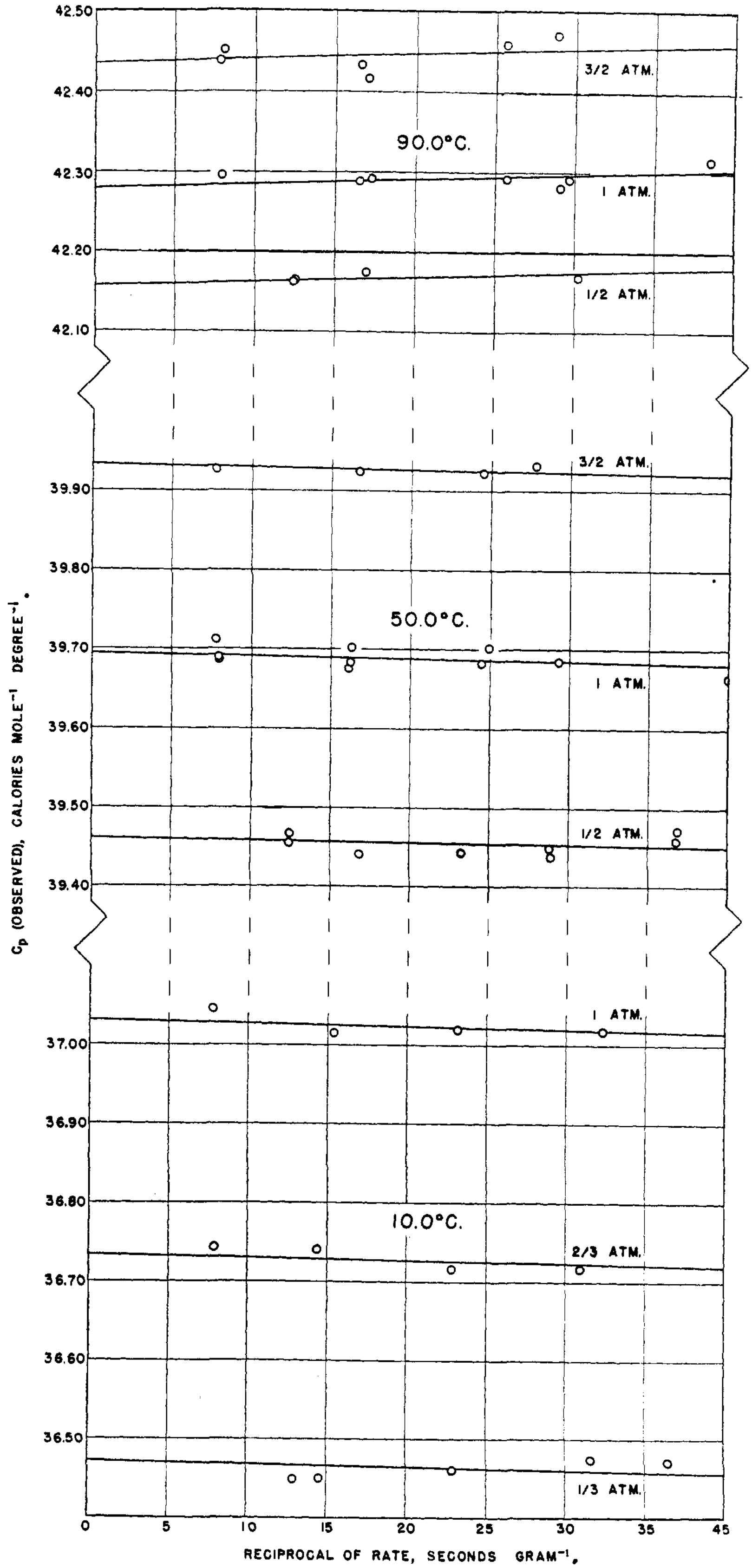

Fig. 1.—Heat capacity data for perfluorocyclobutane.

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[8] J. O. Hirschfelder, F. T. McClure and I. F. Weeks, *J. Chem. Phys.*, **10**, 201 (1942).

[9] Private communication, Dr. E. G. Young, Kinetic Chemicals Incorporated, Wilmington, Delaware.

TABLE I

HEAT CAPACITY OF GASEOUS PERFLUOROCYCLOBUTANE (C_4F_8) SUMMARY OF RESULTS

Pressure, atm.	10.00°	50.00°	90.00°
	C_p, cal.	mole^{-1}	degree^{-1}
1.50		39.93	42.43
1.00	37.03	39.69	42.28
0.67	36.74		
.50		39.46	42.16
.33	36.47		
C_p°, obsd.	36.19	39.23	42.01
C_p°, spec.[a]	36.80	39.82	42.56
$\Delta C_p/\Delta P$, cal. mole^{-1} deg.$^{-1}$ atm.$^{-1}$	0.84	0.47	0.28

[a] From assignment by H. H. Claassen, *J. Chem. Phys.*, **18**, 543 (1950).

"Freon C318" are 0.22, 0.16 and 0.13. The equation of state referred to is

$$PV = RT + (0.0019425T - 2.570)/V + (0.02878 - 0.00002247T)/V^2 \quad (6)$$

where P is in p.s.i.a., T is in degrees Rankine, and V is in ft.^{3}/lb.

The determination of the value of the constant b awaits precise vapor density measurements at low pressure.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, ST. LOUIS UNIVERSITY]

Analysis of Lead Dithizonate by the Method of Continuous Variations[1]

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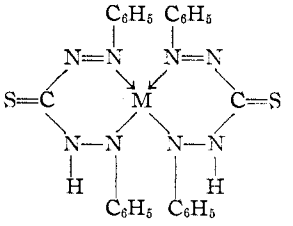
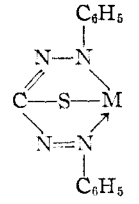
The formulas PbDz and $PbDz_2$ have been proposed for the complex between divalent lead and dithizone. All previous analyses of this complex have employed photometric calibration curves based upon weighed amounts of dry reagent; however doubt exists as to the purity of dithizone in the dry form. Purified dithizone–carbon tetrachloride solutions, of concentrations established by molar extinction coefficient data, were used in this investigation. Purity was checked by a criterion based upon the optical density at 620 and 450 mμ. The formula $PbDz_2$ was confirmed by Job's method of continuous variations. The significance of the relative magnitudes of the molar extinction coefficients necessary to the method is presented for the general case.

Since its introduction by Fischer[2] in 1929, diphenylthiocarbazone ("dithizone," Dz) has been applied extensively as a reagent for the determination of small amounts of lead. The structure of the divalent lead–dithizone complex at *p*H 8–10 was proposed by Fischer to be $PbDz_2$ (I), involving the keto form of the reagent.



I, keto complex



II, enol complex

Liebhafsky and Winslow[3] investigated the structure of the complex experimentally, and concluded the formula to be PbDz (II), involving the enol form of the reagent. The method employed was to extract known amounts of lead into a carbon tetrachloride–dithizone phase, from which the excess reagent was removed by extraction with an aqueous solution of potassium cyanide; the complex left in the organic phase was destroyed with dilute perchloric acid, and the dithizone liberated was determined photometrically by reference to a standard curve. Clifford,[4] in an attempt to resolve the disagreement, pursued a line of investigation similar to that of Liebhafsky and Winslow. Solutions of dithizone in carbon tetrachloride were shaken with a twofold excess of lead, and the dithizonate formed was extracted into the organic phase. Portions of the dithizonate solution were analyzed for lead electrolytically. Other portions of the same solutions were shaken with dilute acid to destroy the dithizonate, which reverted to the green dithizone color, and the amount of dithizone equivalent to the lead present was determined photometrically with reference to a calibration curve. As a result of this work, Clifford arrived at the formula $PbDz_2$.

The formula $PbDz_2$ was also obtained by Irving[5] through his "reversion" procedure.

These methods suffer from the difficulty that a calibration curve, based upon weighed amounts of "purified," dry dithizone, must be determined. It is questionable whether dithizone has ever been obtained pure in the dry state.[4]

In an attempt to provide further evidence for a resolution of the disagreement on the formula of the lead–dithizone complex, Job's method of continuous variations,[6] which is quite different in principle from previous methods employed, was applied to the problem. The work of Tipton[7]

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[1] (a) Based upon a thesis submitted by J. O. Hibbits to the faculty of St. Louis University in partial fulfillment of the requirements for the Degree of Bachelor of Science. (b) To whom correspondence should be addressed.

[2] H. Fischer, *Z. angew. Chem.*, **42**, 1025 (1929).

[3] H. A. Liebhafsky and E. H. Winslow, THIS JOURNAL, **59**, 1966 (1937).

[4] P. A. Clifford, *J. Assoc. Offic. Agr. Chemists*, **26**, 26 (1943).

[5] H. Irving, E. I. Risdon and G. Andrew, *J. Chem. Soc.*, 537 (1949).

[6] P. Job, *Ann. Chem.*, **9**, 113 (1928).

[7] G. M. Tipton, S.J., Dissertation, St. Louis University, 1949 (to be published).