Thermodynamic Properties of Gaseous Difluorodichloromethane (Freon-12)[1]

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The heat capacity of gaseous difluorodichloromethane (Freon-12) has been measured at −30, 0, 45 and 90° at pressures up to 1.5 atmospheres. The results, accurate within ±0.1%, have been used to obtain more accurate values of C_p^0 and $\Delta C_p/\Delta P$, the change of heat capacity with pressure, than hitherto available. Based on the experiments and on a recently published assignment of frequencies, new tables of the heat capacity, heat content, entropy and free energy function have been calculated. A new equation of state has been developed to conform to the values obtained for $\Delta C_p/\Delta P$.

Introduction

Measurements of heat capacities of gases, with an accuracy of one-tenth per cent., over a range of temperatures and low pressures, are of fundamental importance in at least two ways. First, the experimental values may be extrapolated to zero pressure at each temperature to yield values of the heat capacity of the hypothetical ideal gas. For most gases whose molecules have more than three atoms, the heat capacities thus obtained are more reliable than those calculated from molecular data and can frequently be used to decide questions of structure or frequency assignment. Second, the values obtained for the change in heat capacity with pressure are an order of magnitude more accurate than the same quantity calculated from data of state of good accuracy. Thus there is provided an opportunity to check or modify existing equations of state.

The flow calorimeter used in this Laboratory was recently shown[2] to have an accuracy of better than one-tenth per cent. The apparatus is a modification of a calorimeter described by Wacker, Cheney and Scott.[3]

The investigation of difluorodichloromethane ("Freon-12") was begun because of the scarcity of data in the literature from which to compile accurate tables of thermodynamic properties of both ideal and real gas for the series of "NBS-NACA Tables of Thermal Properties of Gases."[4] The recent work of Plyler and Benedict[5] on the infrared spectrum and the assignment of fundamental vibration frequencies, gives a calculated heat capacity of the ideal gas about 5% higher than the previous values of Thompson and Temple.[6] Most of the charts and tables[7] of thermodynamic properties which have been made available have resulted from the experimental work of Buffington, et al.[8-12]

Buffington and Gilkey[8] published data of state with an accuracy of about 1%, and Buffington and Fleischer[11] obtained three values of the gaseous heat capacity at one atmosphere with an estimated uncertainty of about 1%.

In the present research, heat capacities were measured with the flow calorimeter from the boiling point of CF_2Cl_2 up to 90°, and at pressures up to 1.5 atmospheres. The ranges covered were approximately those over which the apparatus could conveniently be operated.

New tables of thermodynamic properties of Freon-12 gas, both ideal and real, as a function of temperature and pressure, are being prepared for the NBS-NACA series.

Experimental

Material.—Ten pounds of CF_2Cl_2, specially purified by fractional distillation, was obtained from the Jackson Laboratory of E. I. du Pont de Nemours Company. The supplier furnished an infrared analysis which showed the CF_2Cl_2 to contain no detectable impurities. The most likely impurities were stated to be $CClF_3$, $CFCl_3$ and $CHClF_2$, and the minimum amounts detectable by infrared analysis were 0.02, 0.01 and 0.05%, respectively.

About one pound of the material was vented from the cylinder, then about two pounds was taken from the vapor phase for use. This sample was further purified by twice evaporating it at the boiling point and condensing it in a trap surrounded by liquid nitrogen, while pumping with a high-vacuum apparatus. Initial and final portions were discarded. Finally, the sample was repeatedly frozen and evacuated until a pressure of about 0.2 micron was observed at the temperature of liquid nitrogen.

A mass spectrograph analysis of the sample as used indicated presence of small amounts of one or more hydrogen-containing derivatives such as $CHClF_2$. The analysis was essentially qualitative, but seemed to indicate that the sample was 99.8% CF_2Cl_2 or better. The maximum possible error in heat capacity caused by impurities is estimated to be 0.05%.

Apparatus and Method.—The flow calorimeter and its operation have been described in detail elsewhere.[2] A brief resume is given here, with reference to Fig. 1.

The calorimeter was immersed in a stirred liquid bath to the level indicated by B. The bath was contained in a dewar flask, and had immersed in it the necessary heater, refrigeration, stirring apparatus and control thermometer, which are not shown in the figure. The bath temperature was automatically controlled and remained constant to ±0.001° for the period (20–40 minutes) of a heat capacity determination or longer.

The apparatus was made of metal. The center tube, where the gas was heated and the resulting temperature rise measured, was thin-walled monel. This part was protected as much as possible from heat leaks by polishing the various surfaces, by having high vacuum in the jacket and by maintaining the surrounding radiation shield S and the upper tube very near the temperature of the heated gas.

The gas entering the calorimeter at I was brought to bath temperature in the helix, its temperature was measured at N_1, electrical energy was added by means of the heater H_e and the temperature was again measured at N_2. N_1 and N_2 are nickel resistance thermometers. The power and rate of

(1) This work was supported in part by the National Advisory Committee for Aeronautics.

(2) J. F. Masi and B. Petkof, *J. Research Natl. Bur. Standards*, **48**, 179 (1942), RP 2303.

(3) P. F. Wacker, Ruth K. Cheney and R. B. Scott, *ibid.*, **38**, 651 (1947), RP 1804.

(4) Information about these tables may be obtained by writing Mr. Joseph Hilsenrath, Heat and Power Division, National Bureau of Standards, Washington 25, D. C.

(5) E. K. Plyler and W. S. Benedict, *J. Research Natl. Bur. Standards*, **47**, 202 (1951), RP 2245.

(6) H. W. Thompson and R. B. Temple, *J. Chem. Soc.*, 1422 (1948).

(7) For example, R. M. Buffington and W. K. Gilkey, Amer. Soc. Refrig. Engr., Circular No. 12 (1931).

(8) R. M. Buffington and W. K. Gilkey, *Ind. Eng. Chem.*, **23**, 254 (1931).

(9) W. K. Gilkey, F. W. Gerard and M. E. Bixler, *ibid.*, **23**, 364 (1931).

(10) F. R. Bichowsky and W. K. Gilkey, *ibid.*, **23**, 366 (1931).

(11) R. M. Buffington and J. Fleischer, *ibid.*, **23**, 1290 (1931).

(12) R. M. Buffington and W. K. Gilkey, *ibid.*, **23**, 1292 (1931).

flow were always chosen so that the rise in temperature was close to 10°.

The sample of Freon was contained in a steel cylinder in an ice-water bath (not shown in Fig. 1). Reduction in pressure was accomplished, and the rate of flow was accurately controlled, by means of a sensitive diaphragm valve. The mean pressure and pressure drop in the calorimeter were observed by means of a three-column manometer, two columns of which were connected to the calorimeter as shown in Fig. 1.

The gas was led from the calorimeter outlet at 0 to a receiver at liquid nitrogen temperature, through a snap-throw valve which was used to divert the flow, within 0.1 second, from one receiver to another.

A heat capacity experiment consisted of the data taken during a steady state period when the gas was removing heat at the same rate it was being added. Nearly continuous measurements were made of the exit temperature at N_2, and slight adjustments of the flow were made to keep that temperature as constant as possible. The experiment was begun and ended by directing the flow of gas to and away from a weighed receiver by means of the snap-throw valve. The readings of N_2 were identical at these two moments so that there was no gain or loss of energy by the calorimeter. Readings of the current and potential in the heater, the resistance of N_1 and a platinum resistance thermometer in the bath, height of the manometer columns, barometer, time interval to 0.01 second and weight of sample to 1 mg. were the other data obtained.

The electrical circuits used were similar to those previously described.[13] A G-2 Mueller Bridge was used for the measurement of resistances, and a sensitive five-dial potentiometer, with calibrated standard resistor and volt-box, was used for the energy measurements.

In order to eliminate, as far as possible, the effect of residual heat leaks, the heat capacity was determined at a number of different flow rates at each temperature and pressure of measurement, and extrapolated to zero reciprocal rate of flow. Also, "blank" determinations were made at several rates at each temperature and pressure, to measure the amount of cooling, δT, experienced by the gas in passing through the calorimeter when no heat was applied. The value of δT varied from 0.008 to 0.35°.

Results

Heat Capacity of the Ideal Gas.—If W is the power supplied to the heater, F is the rate of flow of the gas, ΔT is the observed rise in temperature, and δT is the fall in temperature in a corresponding blank experiment, the apparent heat capacity is calculated by

$$C = \frac{WF^{-1}}{\Delta T + \delta T} \tag{1}$$

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 corrected

TABLE I

HEAT CAPACITY OF GASEOUS DIFLUORODICHLOROMETHANE (SUMMARY OF RESULTS)

At press., atm.	−30.00°	0.00°	45.00°	90.00
	C_p, calories mole^{-1} degree^{-1}			
• 1.50		17.274	18.276	19.251
1.00		17.048	18.161	19.180
0.67	16.114			
.50		16.844	18.058	19.114
.33	15.893			
C_p^0, obsd.	15.672	16.650	17.946	19.045
$\Delta C_p/\Delta P$, cal. mole^{-1} deg.$^{-1}$ atm.$^{-1}$	0.664	0.410	0.218	0.137

(13) R. B. Scott, C. H. Meyers, R. D. Rands, Jr., F. G. Brickwedde and N. Bekkedahl, *J. Research Natl. Bur. Standards*, **35**, 39 (1945), RP 1661.
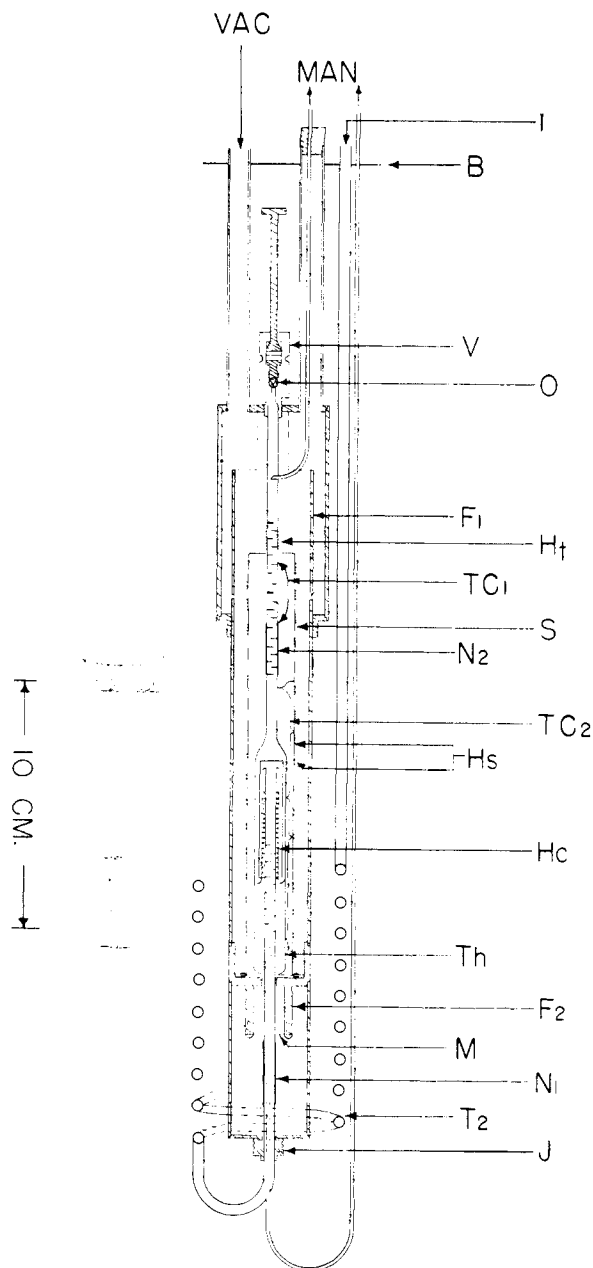

Fig. 1.—Scale drawing of flow calorimeter: B, constant temperature bath level; F_1 and F_2, flanges; H_c, calorimeter heater; H_s, shield heater; H_t, tube heater; I, inlet; J, bellows seal; M, mica spacer; MAN, manometer tubes; N_1 and N_2, nickel thermometers; O, outlet; S, radiation shield; T_2, helical tube; TC_1, tube thermel; TC_2, shield thermel; Th, metal thimble; V, throttle valve; VAC, vacuum line.

heat capacity, called C_p(observed), for all of the experiments with CF_2Cl_2, are plotted in Fig. 2 against the reciprocal of the rate of flow.

The straight lines drawn through the points in Fig. 2 were determined by the method of least squares. The average standard deviations from these lines was ±0.03%. The intercepts are taken as the true heat capacities and are reproduced in Table I.

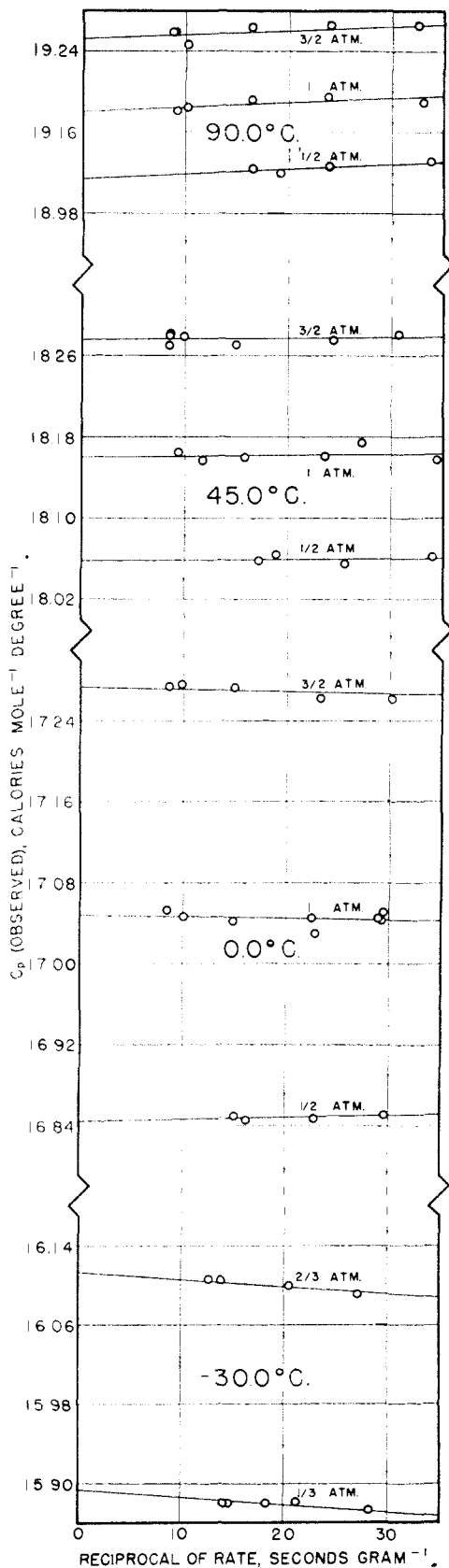**Thermodynamic Functions of the Ideal Gas.**— The final values of heat capacity at finite pres-

Fig. 2.—Heat capacity data for CF₂Cl₂.

sures in Table I were extrapolated linearly to zero pressure at each temperature, and the results are

given as "C_p^0, observed." It is believed that these heat capacity values for the ideal gas CF_2Cl_2 are reliable to better than $\pm 0.15\%$.

For comparison with these results there were calculated C_p^0 values over the same temperature range using the harmonic-oscillator, rigid-rotator approximation and the frequency assignment of Plyler and Benedict.[5] These were found to be too low by 0.6 to 0.8%. In order to correct this deficiency, the following procedure was adopted: The frequency assigned to one fundamental in the 425–475 cm.$^{-1}$ range, where the spectroscopic observations are ambiguous, was lowered, while an approximate average anharmonicity correction, after the method of Stockmayer, Kavanaugh and Mickley,[14] was applied to the calculation of C_p^0. Since these two corrections change the temperature coefficient of heat capacity in opposite directions, it was possible to adjust them relative to each other to obtain the best agreement with the observed C_p^0. Finally adopted for the calculation of the thermodynamic properties were the frequencies assigned by Plyler and Benedict, except that ν_9 was changed from 473 to 450 cm.$^{-1}$. Anharmonicity constants were included of the form

$$X_{ij} = a(\nu_i + \nu_j)$$

where a has the value 7.5×10^{-4}.

The comparisons of the ideal gas heat capacity values are summarized in Fig. 3, in which the base line is the final calculated values of this paper. The values attributed to Buffington and Fleischer[11] are their experimental values at one atmosphere (thought to be accurate to 1%) after correction for non-ideality by the equation of state of Buffington and Gilkey.[8] The value of Eucken and Bertram[15] was obtained by the "hot-wire" comparison method.
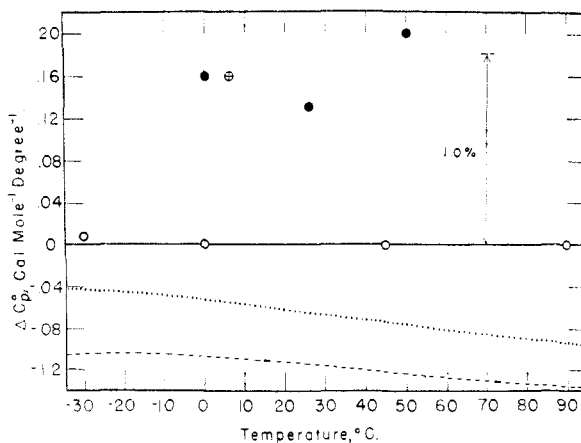

Fig. 3.—Heat capacity of ideal gas CF_2Cl_2: the base line (zero ordinate) is the calculated heat capacity as given in Table II; O, this research; ●, Buffington and Fleischer[11]; ⊕, Eucken and Bertram,[15] ----, calculated from assignment of Plyler and Benedict[5] (without anharmonicity correction); ......, same, changing ν_9 from 473 to 450 cm.$^{-1}$.

In the usual manner, the heat capacity, heat content, entropy and free energy function have

(14) W. H. Stockmayer, G. M. Kavanaugh and H. S. Mickley, J. Chem. Phys., 12, 408 (1944).

(15) A. Eucken and A. Bertram, Z. physik. Chem., B31, 361 (1936)

been calculated, including the anharmonicity corrections noted above, and are given to 1500°K. in Table II. The product of the moments of inertia was obtained by the method of Hirschfelder,[16] using the bond distances and angles given by Brockway.[17]

TABLE II

THERMODYNAMIC FUNCTIONS OF THE IDEAL GAS, CF_2Cl_2

T, °K.	C_p^0, cal. mole^{-1} deg.$^{-1}$	S^0, cal. mole^{-1} deg.$^{-1}$	$H^0 - E_0^0$, kcal. mole^{-1}	$-(F^0 - E_0^0)/T$, cal. mole^{-1} deg.$^{-1}$
200	14.043	65.648	2.0100	55.598
273.16	16.654	70.430	3.1372	58.945
298.16	17.407	71.920	3.5628	59.971
300	17.456	72.027	3.5948	60.044
400	19.831	77.394	5.4664	63.728
500	21.469	82.004	7.5354	66.933
600	22.605	86.024	9.7419	69.788
700	23.411	89.571	12.044	72.366
800	24.003	92.742	14.418	74.719
900	24.448	95.599	16.845	76.883
1000	24.791	98.194	19.308	78.886
1100	25.060	100.57	21.800	80.751
1200	25.277	102.76	24.317	82.495
1300	25.454	104.79	26.853	84.132
1400	25.602	106.68	29.406	85.676
1500	25.728	108.45	31.973	87.136

Equation of State.—At the low pressures of the heat capacity measurements, it was assumed that the term involving P^2 in the virial equation

$$PV = RT + BP + CP^2 \tag{2}$$

could be neglected. The values of $\Delta C_p/\Delta P$ listed in the last line of Table II were set equal to

$$\frac{\partial C_p}{\partial P} = -T \frac{\partial^2 B}{\partial T^2} \tag{3}$$

and B was assigned the form proposed by Hirschfelder, McClure and Weeks[18]

$$B = b - ce^{a/T} \tag{4}$$

The values of c and a were then chosen to fit the experimental data.

Then, for all the experimental $P-V-T$ data obtained by Buffington and Gilkey,[8] the values of the left-hand side of the equation

$$V - \frac{RT}{P} + ce^{a/T} = b + CP \tag{5}$$

(16) J. O. Hirschfelder, *J. Chem. Phys.*, **8**, 431 (1940).

(17) L. O. Brockway, *J. Phys. Chem.*, **41**, 747 (1937).

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

were calculated and plotted against P. It was found that a better fit of the $P-V-T$ data could be obtained if b was a linear function of temperature rather than a constant. C was assumed to be inversely proportional to the temperature. The final expressions for the virial coefficients to be used in eq. 2 were

$$B = 216 + 0.391T - 152e^{445/T} \text{ cc. mole}^{-1}$$

and

$$C = 14.6 - \frac{9.603}{T} \text{ cc. mole}^{-1} \text{ atm.}^{-1} \tag{6}$$

From eqs. 6 the derivative of heat capacity with respect to pressure was calculated at one atmosphere and plotted as the solid curve in Fig. 4.
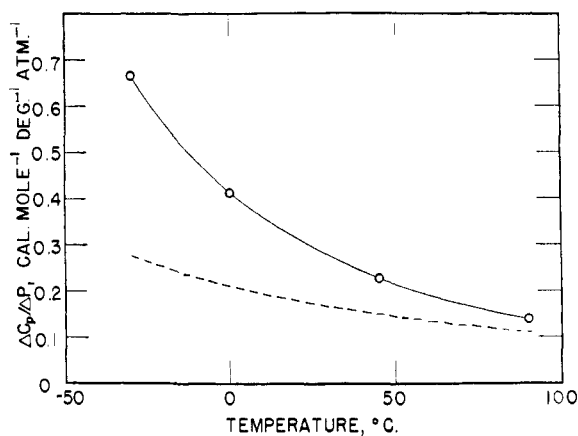

Fig. 4.—Pressure coefficient of heat capacity of CF_2Cl_2: O, this research; —, equations 6; ----, equation of Buffington and Gilkey.[8]

The same quantity calculated from the equation of state of Buffington and Gilkey is shown by the dashed curve. The virial coefficients of eqs. 6 reproduce all of the data of state of Buffington and Gilkey with a root-mean-square deviation of ±0.5% compared with ±0.4% deviation from the equation derived by those authors.

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