The major impurity in the calorimetric sample was 0.79 wt. % of free carbon. The apparent heat capacities were adjusted for this contaminant using the heat capacity data for graphite (*3*). This adjustment was only 0.5 to 2.5% of the apparent heat capacity of the sample over the range of the measurement even though the molal composition of sample corresponds to 85.49% thorium dicarbide and 14.51% free carbon.

RESULTS AND DISCUSSION

Heat Capacities and Thermal Properties. The experimental heat capacities are presented in chronological order at the mean temperatures of the determinations in Table I. These data are based upon a defined thermochemical calorie equal to 4.1840 j., an ice point of 273.15° K., and a gram formula mass (g.f.m.) of 256.060 for thorium dicarbide. These data have been corrected for curvature—i.e., for the difference between $\Delta H/\Delta T$ and the corresponding derivative. The approximate values of ΔT used in the heat capacity determinations can usually be estimated from the increments between adjacent mean temperatures given in Table I. These heat capacity values are considered to have a probable error decreasing from about 10% at 5° K. to 1% at 10° K. and to less than 0.1% above 30° K.

The heat capacities and thermodynamic functions at selected temperatures, presented in Table II, are obtained from the heat capacity data by integration of a least squares-fitted curve (carefully compared with a large-scale plot of the data). Both the fitting and quadrature are performed by high-speed digital computers using programs previously described (*6, 7*). The thermodynamic functions are considered to have a precision corresponding to a probable error of less than 0.1% above 100° K. Additional digits beyond those significant are given in Table II for internal consistency and to permit interpolation and differentiation. The entropies and Gibbs energies have not been adjusted for nuclear spin and isotope mixing contributions and hence are practical values for use in chemical thermodynamic calculations. The present values of C_p and S may be compared with estimates by Krikorian (*8*), 10.25 ± 1.44 and 15.1 ± 3 cal. (g.f.m. °K.)$^{-1}$, respectively, at 298.15° K.

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Saturated Liquid Density of Carbon Tetrafluoride from 90° to 150° K.

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The saturated liquid density of carbon tetrafluoride has been measured at 16 temperatures between 90° and 150° K. The data can be represented by the equation

$$d(\text{grams/cm.}^3) = 2.254 - 3.64 \times 10^{-3} T - 5.40 \times 10^{-6} T^2$$

with a standard deviation of 7.1×10^{-4} grams/cm.^{3}

MEASUREMENTS of the saturated liquid density of carbon tetrafluoride (Freon-14) have been reported by Chari (*2*), whose work apparently forms the basis of the table of smoothed values obtainable from Du Pont (*5*). In a study of the optical properties of liquid CF_4, the authors observed seemingly anomalous behavior which could be attributed to inaccuracies in these density values. Moreover, a survey of the literature brought to light isolated measurements of the density and of the coefficient of thermal expansion (*3, 7*) which were more consistent with the optical results. The present measurements were performed to resolve this discrepancy.

EXPERIMENTAL

The pycnometer, a cylindrical copper vessel with a volume at 20° C. of 22.45 cm.^{3}, is essentially a low-temperature adiabatic calorimeter. It is equipped with a 25-ohm platinum thermometer mounted in a tapered copper plug which fits snugly into a re-entrant well. The thermometer has been calibrated at the National Bureau of Standards. Within the vessel four 0.005-inch sheet copper fins extend radially outward from the thermometer well at the center

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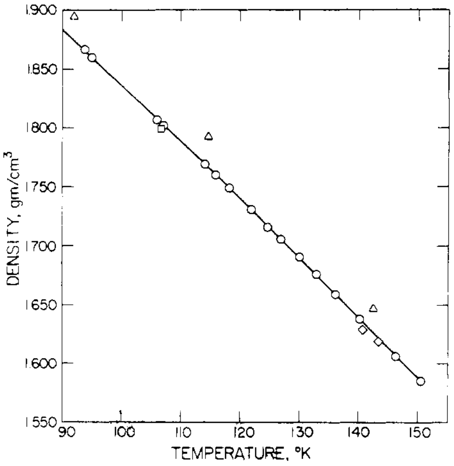

Figure 1. Saturated liquid density of CF_4 vs. temperature

△ Chari (2); ◇ Ruff and Keim (7); ☐ Croll and Scott (3); ○ This work, experimental; — This work, Equation 1. Ruff and Keim (6) also reported a value of density of 1.93 at 93° and 94° K.

to the pycnometer walls. The pycnometer hangs on nylon threads within a copper radiation shield, and the whole is enclosed in a vacuum jacket. The lower end of the stainless steel capillary filling line is joined to a short length of 0.15-mm. i.d. borosilicate glass capillary by a Kovar seal; a similar seal joins the capillary to the calorimeter. The lower Kovar and glass sections of the pycnometer have a volume of about 0.1 cm.³ The glass capillary, which has etched graduations, protrudes from the top of the radiation shield, and the level of the liquid in it may be viewed from outside the cryostat through a series of right-angle prisms and a telescope.

Both the pycnometer and the shield are equipped with heaters, and a copper-constantan differential thermocouple between them acts as the sensing element for a commercial controller which maintains the shield temperature to within ±0.05° C. of that of the pycnometer. A bath of liquid nitrogen serves as the refrigerant.

The number of moles of gas condensed in the pycnometer is determined by the change in pressure in a calibrated 6.5-liter bulb kept near room temperature in a foam plastic enclosure. The bulb temperature is known to within 0.05° C. A fused quartz Bourdon gage (Texas Instrument Co.) which reads directly to 0.001 inch of Hg is used to determine the pressure.

In the calculation of the density from the pressure change in the bulb, corrections have been applied for gas imperfection (*4*), the thermal contraction of the pycnometer (*1*), and the amount of gas in the dead space. At the highest filling pressure, the correction caused by the second virial coefficient changes the number of moles by 0.6%. At the lowest temperature, the volume of the pycnometer is diminished by 0.1%. That portion of the liquid situated outside the radiation shield never exceeds 0.03 cm.³ At all but the highest temperatures, the dead space corrections are negligible. The estimated accuracy of the density determination is 0.1%.

Batch analysis of the CF_4 sample indicated as impurities 0.02 mole % Freon-12 and Freon-13, 0.24 mole % air, and 10 p.p.m. water.

Table I. Density of CF_4

T°, K.	d, Grams/Cm.³, Measured	d, Grams/Cm.³, Equation 1
93.72	1.867	1.866
94.99	1.860	1.860
106.00	1.807	1.808
107.12	1.802	1.803
114.11	1.769	1.769
115.91	1.760	1.760
118.22	1.749	1.749
121.95	1.731	1.730
124.70	1.716	1.717
126.95	1.706	1.706
130.04	1.691	1.690
132.95	1.676	1.675
136.17	1.659	1.659
140.20	1.638	1.638
146.32	1.606	1.607
150.43	1.585	1.585

RESULTS

Sixteen experimentally determined values of the saturated liquid density of CF_4 in the temperature range 94° to 105° K. are listed in Table I. Also included are density values calculated from the equation,

$$d(\text{grams/cm.}^3) = 2.254 - 3.64 \times 10^{-3}T - 5.40 \times 10^{-6}T^2 \qquad (1)$$

which has been obtained from the experimental values by the method of least squares. T is the absolute temperature in degrees Kelvin. The standard deviation of the points from the smooth curve is 7.1×10^{-4} grams/cm.³ The data and the fitted curve are plotted in Figure 1 in which, for comparison, the results of other investigations are included.

Croll and Scott (*3*) also report a value of $2.59 \pm 0.04 \times 10^{-3}/°$ K. for α, the coefficient of thermal expansion in the temperature range 94° to 107° K. From the analytic representation of the data, values of $2.49 \pm 0.10 \times 10^{-3}$ and $2.67 \pm 0.10 \times 10^{-3}/°$ K. at 94° K. and 107° K. are derived. The average value of α is in good agreement with their results.

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