The calculated 1-atm. diagram is compared with the experimentally observed data at 1 atm. in Figure 4. The activity coefficients calculated from the correlation are compared with the observed values in Figure 5. The coefficients for the more volatile bromine pentafluoride are in good agreement with the van Laar equations, while those for the trifluoride deviate somewhat at high pentafluoride concentrations. This is to be expected, however, because small errors in measuring the concentration of the less volatile trifluoride are magnified many times in the activity coefficients. Thus, if the van Laar equations are used to calculate the vapor and liquid concentrations, the results will agree very closely with the experiments.

NOMENCLATURE

x_1, x_2 = mole fraction of bromine pentafluoride and bromine trifluoride in liquid phase, respectively
y_1, y_2 = mole fraction of bromine pentafluoride and bromine trifluoride in vapor phase, respectively
P_1, P_2 = vapor pressure of pure bromine pentafluoride and bromine trifluoride, respectively, at temperature of solution
P = total pressure over solution
t = temperature, °C.
$\gamma_1 = Py_1/p_1x_1$, activity coefficient of bromine pentafluoride
$\gamma_2 = Py_2/p_2x_2$, activity coefficient of bromine trifluoride
A = limit ($\log_{10} \gamma_1$) as x_1 approaches zero, a constant of van Laar equations
B = limit ($\log_{10} \gamma_2$) as x_2 approaches zero, a constant of van Laar equations

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Heat Capacity of Saturated Liquid Perchloryl Fluoride above Its Boiling Point

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A program at the Pennsalt Chemicals Corp. has been concerned with determination of physical properties of perchloryl fluoride (ClO_3F) (*3,8*). The present report deals with the saturated heat capacity of the liquid from the boiling point to the critical region. No previous measurements of the heat capacity of perchloryl fluoride have been reported in the literature.

APPARATUS

Calorimeter and Cryostat. The calorimeter (Figure 1) was designed to be used at vapor pressures up to 60 atm. The calorimeter, *A*, was fabricated from a 4-inch length of 1-inch nickel pipe with all joints silver-soldered and had an internal volume of 58.79 cc. Radiation shield *B* was an 8-inch length of 2½-inch copper pipe, with ⅛-inch plate ends. The outer container, *C*, was made from 4½-inch brass tubing of ⅛-inch wall with ⅛-inch end plates.

A 20-ohm length of B. & S. gage No. 36 double silk-covered Constantan wire, which served as a heater, was wound on the outer surface of the calorimeter. Also wrapped on the calorimeter was a 10-ohm length of B. & S. gage No. 40 double Formvar-coated copper wire to serve as a thermometer. Paired voltage and current leads of No. 36 B. & S. gage double silk-covered copper wire were attached to the heater and copper thermometer. The radiation shield was wound with approximately 100 ohms of No. 36 B. & S. gage Constantan wire, which served as a heater.

All leads and thermocouple wires, as well as the wires wrapped on the calorimeter and shield, were impregnated with Formvar lacquer and baked. The outer surface of the calorimeter, both surfaces of the radiation shield, and the inner surface of the outer container were covered with aluminum foil.

A tube connection, *F*, through the top plate of the outer container allowed passage of the wire leads. The seal at this point was made by a device developed by Johnston and Kerr (*4*). A standard 24/40 female ground-glass joint was fitted with a Lucite plug, in whose surface vertical grooves had been machined. The lead wires were laid in these grooves and carefully sealed in position with Apiezon W wax, so that the plug formed a vacuum-tight seal with the ground-glass joint. This was an easily prepared and excellent vacuum seal. A second tube connection, *H*, provided access to a vacuum system capable of 10^{-5} mm. of mercury or better and to a helium source.

The entire assembly was placed in a constant temperature bath which could be controlled to ±0.10° above 25° and to ±0.50° to −40°C.

Electrical Circuits. The general plan of electrical circuits for energy supply and for the resistance and thermocouple measurements was similar to that described by Gibson and Giauque (*2*), except that the thermometer and heater were separate units.

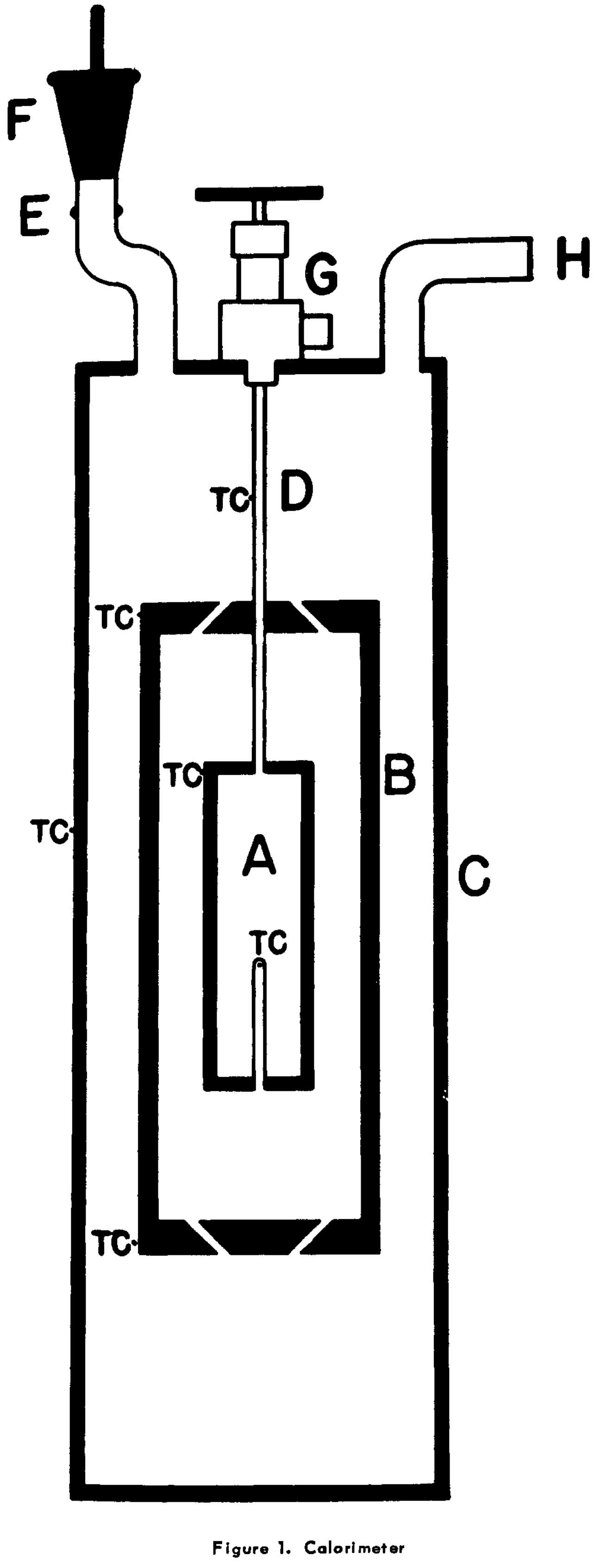

Figure 1. Calorimeter

A. Calorimeter
B. Radiation shield
C. Outer container
D. ⅛-inch tubing
E. Kovar glass-to-metal seal
F. Johnston-Kerr seal
G. Valve
H. Vacuum connection
TC. Thermocouple

A White single potentiometer having a 100,000-μv. range was used for the thermocouple and thermometer readings. A suitable standard resistor was used for current measurements in the thermometer circuit. A 1.5-volt instrument-type low drain battery operating through an 8000-ohm resistor supplied the current for the thermometer.

The electrical energy for heating the calorimeter was supplied by a 6-volt lead storage battery, which was brought to a steady state by a preliminary discharge through a resistance approximately equal to that of the heater. A resistance of 5000 ohms was connected in parallel with the calorimeter heater through one set of leads and the voltage drop across a small known fraction of this resistance was measured. In the other set of leads a 0.1-ohm standard resistance allowed current to be measured by the voltage drop on a Rubicon Type B potentiometer.

Temperature Scale. The temperature scale was based on a National Bureau of Standards calibrated platinum resistance thermometer below 0°C. and an NBS calibrated mercury-in-glass thermometer above that temperature. Measurements were actually made with the thermocouples and copper thermometer, which were compared during each measurement with the temperature standards. The *dR/dT* of the thermometer was 0.0435 ohm per °K. The resistance was consistent during each series to ±0.0004 ohm (0.01°K.) and was stable between series to ±0.001 ohm (0.025°K.).

Source of Perchloryl Fluoride. The material used had been prepared and purified in this laboratory. It was of the same batch used in previous work (*3,8*). Purity was assayed by infrared and mass spectrometric analysis and was stated to be 99.9^{+}%.

PROCEDURE

The perchloryl fluoride was condensed into the calorimeter from a storage cylinder and the quantity distilled obtained by weight difference. The amounts used were such that the liquid did not completely fill the calorimeter at the critical point. The inner assembly (calorimeter and shield) was then isolated by producing a vacuum of 10^{-5} mm. of mercury or better in the outer container. With all elements of the assembly at approximately the same temperature, the shield and bath were heated to about 1° above the temperature expected on the calorimeter following the heat input. The usual temperature rise of the calorimeter was 3° to 5°. At this point, the drift rate of the calorimeter was taken. It was considered constant when the same rate was obtained for a 5-minute period. The calorimeter heating cycle was then initiated. Voltage readings were taken across the heater and voltage divider network at periodic intervals. An afterdrift was taken following the heating cycle in the same manner as the foredrift. With these data the drift rates were extrapolated to the midpoint of the heating period to obtain the initial and final temperatures.

The quantity of heat applied to the calorimeter was calculated by the standard method with a correction applied for the energy lost in the network.

TREATMENT OF DATA

The effect of the heat of vaporization and heat content of the gas was taken into account in calculating the saturated heat capacity. The method of calculation outlined by Osborne and Van Dusen (*7*) makes it unnecessary to know the heat capacity of the saturated vapor, a quantity not usually known. The equation used to calculate the saturated liquid molar heat capacity was:

$$C_s = \frac{(Q - N) + n_g \dfrac{\Delta H}{T} \times dT - d(n_g \Delta H)}{n_T \times dT}$$

Table I. Molar Heat Capacity of Saturated Liquid Perchloryl Fluoride

Series I, 0.3670 mole; Series II, 0.3656 mole; 0 °C. = 273.16 °K.; 1 cal. = 4.1840 abs. joules

T, °K.	C_s, Cal./Deg. Mole	Series	T, °K.	C_s, Cal./Deg./ Mole	Series
226.10	23.00	I	278.69	26.00	I
227.59	23.23	I	285.12	26.10	I
233.85	23.63	I	292.02	26.66	I
238.73	23.80	I	298.87	27.19	I
240.26	24.04	I	306.01	27.63	I
243.87	23.97	I	311.42	28.37	I
249.43	24.25	I	318.17	29.05	I
249.54	24.27	I	325.41	29.97	II
253.75	24.65	I	332.89	30.98	II
255.13	24.60	I	339.92	32.92	II
260.20	24.81	I	340.88	33.68	II
260.77	24.84	I	345.00	35.77	II
261.24	24.92	I	348.00	37.03	II
265.10	25.07	I	356.50	44.99	II
272.32	25.54	I	357.95	46.59	II
277.34	25.88	I	360.19	62.57	II
278.70	25.95	I			

where

C_s = molar heat capacity of liquid
Q = heat added, calories
N = heat capacity of calorimeter, calories
ΔH = molar heat of vaporization, calories per mole, under saturation conditions
n_g = moles of vapor phase
n_T = moles of perchloryl fluoride in calorimeter
T = temperature, degrees Kelvin
dT = interpolated temperature interval for heating cycle

Values of ΔH were obtained by calculation using vapor pressure data (*3*) and liquid and vapor densities obtained from the work of Engelbrecht and Atzwanger (*1*). The heat capacity of the empty calorimeter, which was about 70% of the total measured heat capacity, was calculated by means of a quadratic equation based on a separate set of determinations.

EXPERIMENTAL RESULTS

Table I lists the heat capacity of the saturated liquid from 226° to 360°K. The corresponding vapor pressures are 1 and 45.8 atm. The corrections described above for the heat of vaporization and heat capacity of the vapor were about −1.5% at the boiling point and −4% at 330°K.; at higher temperatures the correction became positive, reading + 6.9% at 360°K.

These data show the expected steep rise of the value of heat capacity as the temperature approached the critical temperature, 368.33°K. The uncertainty in the results is estimated to be 0.5% up to 340°K., and to increase to about 3% at the highest temperature. For internal consistency the results are reported to four figures.

Table II. Physical Properties of Perchloryl Fluoride

		Lit. Ref.
Melting point, °K.	127	(*1*)
Boiling point (760 mm.), °K.	226.40	(*3*)
Density of liquid, g./cc., 131° to 234°K.	$d = 2.266 - 1.603 \times 10^{-3} T - 4.080 \times 10^{-6} T^2$	(*3*)
Density of gas, g./cc. at Tc	0.637	(*1*)
Critical temperature, °K.	368.33	(*3*)
Critical pressure, atm. abs.	53	(*3*)
Heat of vaporization, kcal. at b.p.	4.6	(*3*)
Viscosity of liquid, centipoise, 207° to 327°K.	$n = 299 T^{-1} - 1.755$	(*8*)
Surface tension, dynes/cm. at 198°K.	24.05	(*8*)
Vapor pressure		
To 2 atm.	$\log P\,(\text{mm.}) = 18.90112 - \frac{1443.467}{T} - 4.09566 \log_{10} T$	(*3*)
To critical region	$\log P\,(\text{atm.}) = 4.46862 - \frac{1010.81}{T}$	(*3*)
Heat of formation, kcal./mole 298.16°K.	−5.12	(*5*)
Dipole moment, debye unit	<0.09	(*6*)

A summary of the reported physical properties of perchloryl fluoride is given in Table II.

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