The Raman Spectrum, Heat Capacities from 60 to 297° K.,

Heat of Fusion, Vapor-Pressures, and Entropy of

Monofluorotrichloromethane

Thesis Submitted by Darrell W. Osborne

in Partial Fulfillment of the Requirements

for the Degree of Doctor of Philosophy

California Institute of Technology

Pasadena, California

1938

The investigation of the Raman spectrum, vapor-pressures, and calorimetric properties of monofluorotrichloromethane (CCl_3F) between 60° and 297° K. has been carried out in order to permit comparison of the entropy calculated from electron diffraction and spectroscopic data with that obtained with the aid of the "third law" of thermodynamics. This compound is also of interest because of its relation to difluorodichloromethane, used extensively as a refrigerant.

The sample was kindly furnished by Dr. L. O. Brockway, who obtained it through the courtesy of Kinetic Chemicals, Inc., Delaware, New Jersey. The material was dried over calcium chloride and twice fractionally distilled through a column filled with glass helices. A small Hopkins condenser cooled with iced water was placed at the top of the column to maintain suitable refluxing. The boiling range of the major fraction was about 0.1° C. and the b. p. (corrected) 23.7±0.1° C. The middle fraction, about 130 ml., was then introduced into a bulb in the vacuum line connected with the calorimeter, the monofluorotrichloromethane frozen by means of liquid air, and the system evacuated with a mercury diffusion pump. A liquid air trap prevented contamination by mercury. Next the sample was completely dried by distillation through a tube filled with phosphorus pentoxide. The last traces of air were removed by repeating several times the cycle of operations melting, freezing, and pumping. A few ml. were pumped off and then about 80 ml. distilled into the next bulb. Again a little was pumped off, and finally about 70 ml. were condensed into the previously evacuated calorimeter, the temperature of the latter being kept above the m. p. of monofluorotrichloromethane so that the filling line would not

become plugged.

The Apparatus.

The apparatus was designed for vapor-pressure measurements and for low temperature calorimetry of condensed gases and volatile liquids. It was patterned after the apparatus used by Giauque and co-workers.[1]

The calorimeter assembly is shown in Fig. 1. The calorimeter, represented at 10 in the diagram, is constructed of copper. Its wall thickness is about 0.05 cm. and volume 118 ml. Equally spaced along the inside are ten horizontal, perforated copper discs 0.03 cm. thick, which make a spring fit with the walls and assist in establishing thermal equilibrium. The whole interior, including the discs, is gold plated. At 8 a small Pyrex glass tube is sealed directly to the calorimeter. This tube, 2, serves for filling and also can be connected with a manometer for vapor-pressure measurements.

A combined resistance thermometer and heater of No. 40 double-silk-covered copper wire nearly covers the outside of the calorimeter. Its resistance is 167 ohms at 0° C. It is baked on with Bakelite varnish and covered with gold leaf attached by another coat of lacquer. The gold leaf is to minimize radiation losses. No. 36 double-silk-covered copper wires are soldered to the No. 40 wires at the calorimeter. The No. 36 and No. 40 wires serve as current and potential leads respectively. Before use the thermometer-heater was seasoned by cooling in liquid air and warming to room temperature several times. It is calibrated concurrently with the heat capacity measurements by means of a standard copper-constantan thermocouple fastened to the
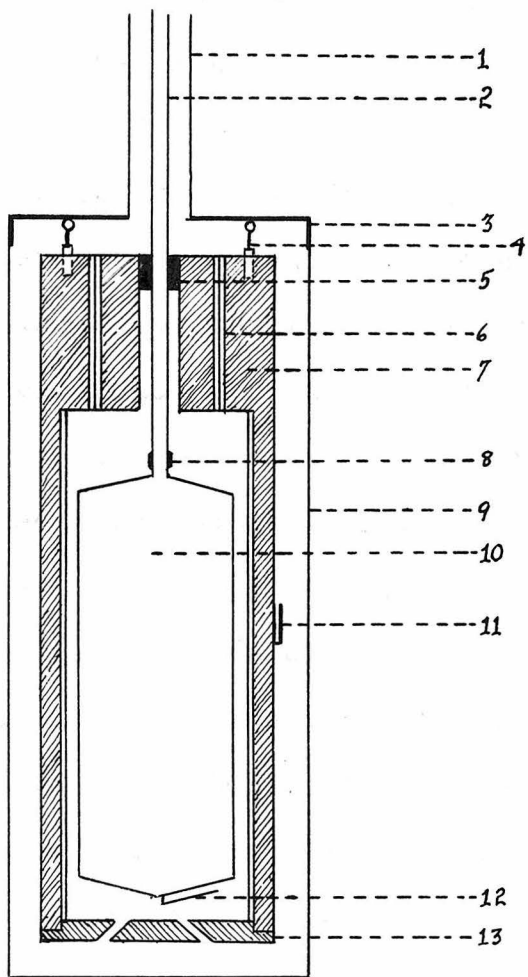
½ Actual Size

Fig. 1 Calorimeter Assembly

bottom of the calorimeter by Wood's metal in the small copper tube shown at 12 in Fig. 1.

By means of Wood's metal, 5, the calorimeter is suspended from the radiation shield, 7, a hollow cylinder of copper weighing about 2 kg. This heavy block is fitted with a constantan heater, 120 ohms resistance, wound on a closely fitting inner sleeve. The exterior is covered with gold foil. A calibrated thermocouple is soldered into the well at 11 with Wood's metal. Stout silk cords, 4, from the top of a vacuum-tight brass can, 9, support the radiation shield.

The wires from the calorimeter are led through Bakelite plugs, 6, paraffin being used for thermal contact. All the leads are wound around the radiation shield a number of times, bound with silk thread, and coated with paraffin. They then go up the German silver tube, 1, and are taken out through a picein joint 80 cm. above the top of the can. Also, the standard thermocouple is wound a number of times about the calorimeter; altogether about 80 cm. of it are around calori-meter and shield. Asbestos paper was wrapped around the wires in the lower portion of the tube in order to protect them when the can, 9, was soldered to its cover at 3. In addition, low melting bismuth solder was used and wet cloths put about the base of the tube.

The German silver tube connects with an oil-diffusion pump. Holes in the removable bottom of the radiation shield, 13, permit evacuation of the space between the calorimeter and radiation shield as well as that between radiation shield and calorimeter.

The assembly is suspended by the German silver tube in a Dewar flask 10 cm. wide and 36 cm. long, inside measure. A large brass can and a Bakelite cover through which the tube 1 passes enclose the calorimeter assembly and Dewar flask. This system can be made gas-tight and evacuated with a high capacity vacuum pump.

Various cooling baths were used in the Dewar flask. The lowest temperature, 57° K., was produced by boiling liquid air under reduced pressure. Between 90 and 200° K. the bath was liquid air under atmospheric pressure, between 200 and 275° K. carbon dioxide and alcohol, and between 275 and 300° K. ice and water.

All electrical measurements are made with a White Double Potentiometer with 100,000 microvolts range. The manufacturers, Leeds and Northrup, guarantee the instrument to 0.02%, and in addition an intercomparison of the coils was made. The standard cell was calibrated by Dr. Dunnington of the Physics Department in April, 1937, against a cell checked at the National Bureau of Standards seven months previously. It was of the unsaturated type, with negligible temperature coefficient, but inasmuch as there is likely to be hysteresis when the temperature is changed, it was kept in an air thermostat. The fixed resistances were of manganin (low temperature coefficient and low thermo-electric power against copper) and were compared potentiometrically with laboratory standards having Leeds and Northrup certificates about ten years old. Probably the standards and calibrations were good to 0.02%.

The galvanometer is a Leeds and Northrup H S type with an

all copper circuit. Its period is 10 sec. It is read with a telescope and a scale at 5 meters distance, and with this arrangement the sensitivity is 0.05 microvolt per mm. One can estimate the deflection to about 1/4 mm.

The electrical circuits for heating and temperature measurement are shown in Fig. 2. The thermocouples are not pictured; suitable switches connect them to the P potentiometer. All the connectors and switches are of copper. Most of the connectors are no. 14 or 16 wire, well insulated with rubber. The system is shielded against stray e. m. f.'s.

When all the switches in Fig. 2 are in the up position, the circuit is as shown in Fig. 2a, and temperature measurements can be made with the resistance thermometer-heater R. A very constant thermometer current is given by 16 Willard Low Discharge Batteries, Type DA 2-1, in series. The working cells for the potentiometer also are of the same kind. The resistance of the thermometer is obtained by comparing E_R, the potential drop across R, with E_I, the potential drop across a fixed 200 ohm resistance. The thermometer current, 0.0004 amp., is small enough for its heating effect to be neglected. The current is allowed to flow continuously through R, except during energy input, and then the batteries are kept in a steady state by discharge through practically the same total resistance (80,000 ohms). E_I was so constant that it was measured only near the beginning and end of each heat capacity determination. A copper plug box, r, with manganin resistances, is used to keep the galvanometer critically damped. The sensitivity of the thermometer is about 300 microvolts per degree over most of the range.
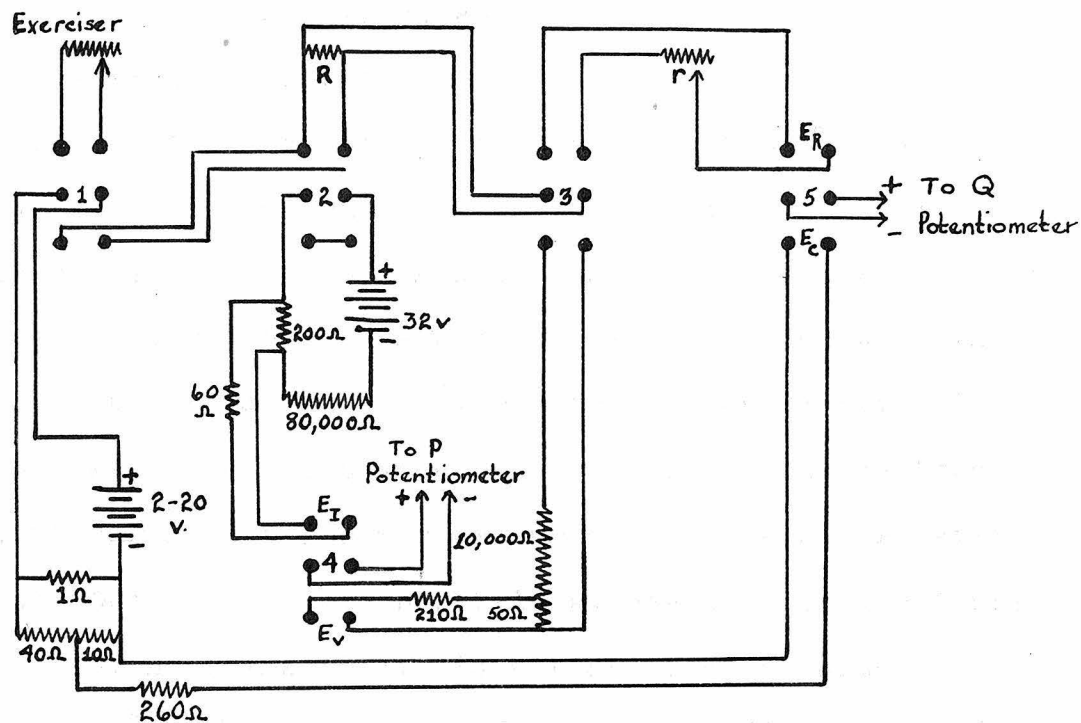
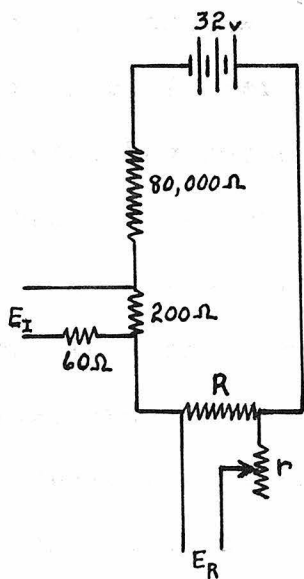Fig. 2   Heating and Temperature Circuits
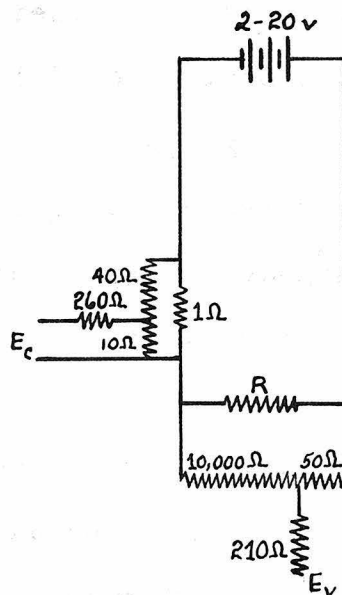

Fig. 2A Temperature Circuit

Fig 2B Heating Circuit

To add energy to the calorimeter, switches 2 to 5 are pulled down and at the proper time the rapid throw switch 1 also pulled down. The circuit is then as given in Fig. 2b. The voltage across the heater terminals is obtained by measuring E_V, the potential drop across a 50 ohm portion of the 10,050 ohms in parallel with R. The current through R and the resistance in parallel is obtained from E_C. All the individual resistors were accurately calibrated, and as a check E_C was compared with the potential drop across a standard 1 ohm resistance temporarily placed in series. The resistance of the potential leads from R to the 10,050 ohm resistance was measured with the calorimeter at 60 and at 290^0 K., radiation shield at nearly the same temperatures, and cooling baths of liquid air and ice and water, respectively, in the Dewar flask. These leads affect E_V by 0.1 to 0.2%. From E_V and E_C can of course be calculated the power, the resistance of the thermometer-heater, R, and the fraction of the current passing through the resistance in parallel with R. The source of energy is a battery of 1 to 10 lead storage cells. An exercising rheostat is provided for bringing the battery to a steady state before supplying energy to the calorimeter.

Time measurements are made with a small, synchronous motor geared to turn a Veeder-Root counter and to actuate a clicking device, made from a door bell, once per sec. The power comes from Boulder Dam, where the frequency is automatically controlled with high accuracy. The timer was found to give consistent results by comparison with a stop-watch. A reasonable estimate of the probable all-over error in timing, including any slight inaccuracy in manual switching is, $\pm$ 0.05%.

As mentioned before, a manometer can be connected to the calorimeter for vapor-pressure measurements. It is constructed of Pyrex tubing, 1.9 cm. i. d., and is enclosed in a wooden case with a plate glass window. A stream of compressed air from the laboratory supply, which changes temperature but slowly, is circulated in the case to eliminate temperature gradients in the mercury columns. The temperature inside the case is determined from two calibrated mercury thermometers. Gold foil in the line protects the calorimeter from mercury vapor.

Further details as to the construction of the apparatus may be found in the Doctorate Thesis of Mr. C. S. Garner (1938).

### Construction and Calibration of the Thermocouples

Each thermocouple consists of five No. 30 double-silk-covered constantan wires about three meters long, connected in parallel to average out small imperfections, and one No. 36 double-silk-covered copper soldered (with soft solder) to each junction, all bound together with silk thread and given a light coating of electrician's enameling fluid. The ice ends were inserted in small diameter, paraffin-filled, glass tubes about 45 cm. long. Similar bundles of constantan, taken from the spool just before these, were tested for inhomogeneities by the usual method of measuring the e. m. f. set up when different portions of the wire are immersed in liquid air, both ends of the loop being joined to copper leads and kept in an ice bath. The maximum e. m. f. found was 1.5 microvolts and the average 0.4 microvolt.

The thermocouples were compared with one calibrated in the investigation of Giauque, Johnston, and Kelley,[2] kindly lent to us by Dr. Hugh Huffman. Unfortunately, the copper wire to the

variable junction was accidentally broken; it was replaced by a new copper wire, which was found to differ from the old one by 2.4 microvolts at 85° K. This correction was equivalent to only 0.17° at 60° K. and was still smaller at higher temperatures.

For the comparison the variable junctions of the standard and of five of our thermocouples were imbedded in Wood's metal in small copper receptacles soldered to the lower part of a solid cylinder of copper approximately the size of the calorimeter and in order to eliminate temperature gradients near the junctions, about 80 cm. of each couple wound around the cylinder, bound with silk thread, paraffined, and then wound with adhesive tape. This cylinder was suspended by stout silk casting line in the place later occupied by the calorimeter, and the thermocouple wires and leads to the constantan heater which was wound on the cylinder were led up through the radiation shield and taken out through picein at the top of the apparatus. The ice ends were immersed in a Dewar flask (to a depth of about 25 cm.) filled with distilled water and finely crushed ice. Comparisons were made at approximately ten degree intervals between 57 and 293° K., with radiation shield and copper cylinder at nearly the same temperature and the apparatus evacuated. Referring to the following diagram,
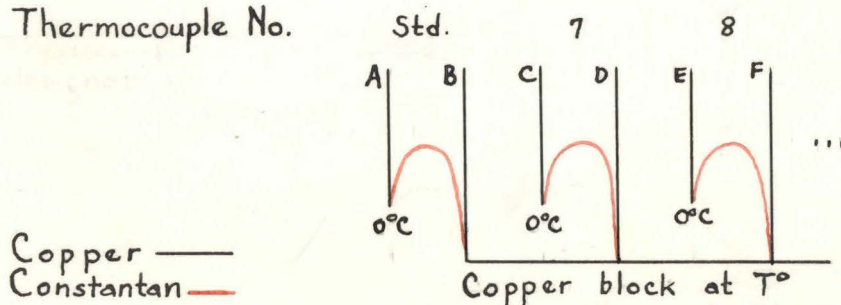
the large potential differences AC and CD were read on the White potentiometer and the small ones such as BD, CE, DF, and similar

quantities for the other thermocouples measured by double deflection of the galvanometer.

The calibration of the standard thermocouple was in terms of the table given by Giauque, Buffington, and Schulze[3] for their thermocouple 17. Inasmuch as our thermocouples differed from this table by about 270 microvolts at 60° K., it was necessary to construct our own conversion table. To do this, $E(17) - 1.04720 E(7)$ was plotted against $E(17)$, where $E(17)$ is the e. m. f. of thermocouple 17 of Giauque, Buffington, and Schulze, and $E(7)$ is the corresponding quantity for our thermocouple 7. This graph is shown on a small scale in Fig. 3, from which it can be seen that for many purposes it would be sufficiently accurate to take the ratio of $E(17)$ to $E(7)$ as a constant. The plot was used in conjunction with the temperature scale of Giauque, Buffington, and Schulze to obtain $E(7)$ at 50°, 60°, 70°, etc., up to 290° K. Linear interpolation between these values is not sufficiently precise, and hence it was decided to interpolate by the procedure of Southard and Andrews.[4] The data was fit approximately by the equation $\log (6401.80 - E) = -0.3233500 + 1.695000 \log T$, then $E - E(7)$ plotted against $E(7)$ on a large scale, and a smooth curve drawn which missed no point by more than 0.1 microvolt. With the aid of this curve the temperatures corresponding to $E(7)$ were calculated to 0.001° at intervals of 10 microvolts between 50 and 273.1° K. and of 20 microvolts between 273.1 and 300° K. It should be pointed out that the analytical expression alone does not fit the data at all well, deviating as much as 5.5 microvolts, but with the plot of $E - E(7)$ it served very well for interpolation.

After the calorimeter was installed, with thermocouple 7 in place on the bottom, the temperature scale was compared with the
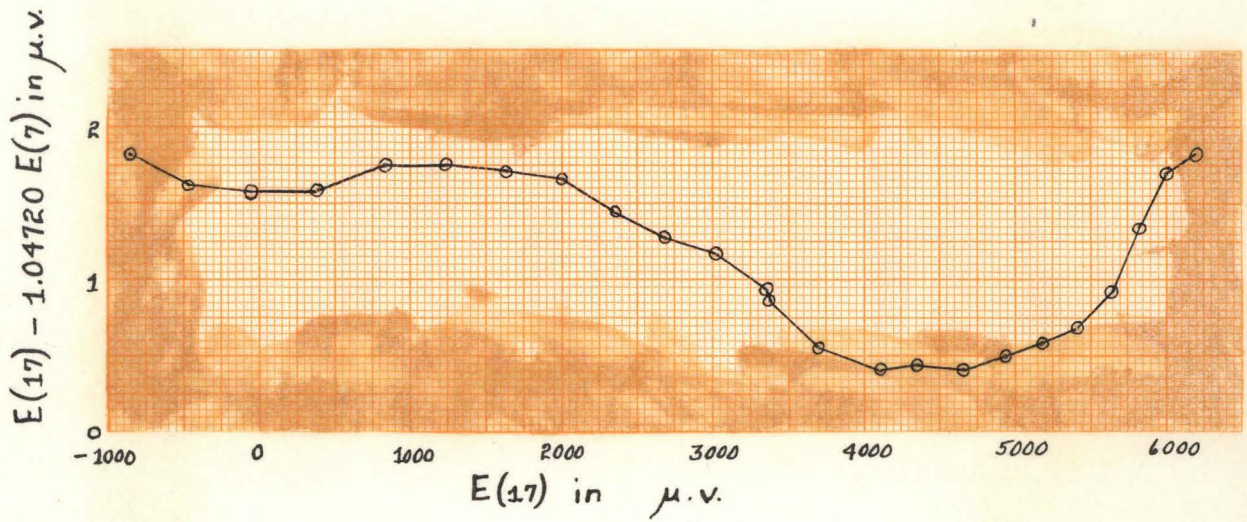
Fig. 3   Deviation   of   E(7) from E(17) in μ.v.

oxygen vapor-pressure thermometer. The oxygen was prepared by heating c. p. potassium permanganate in a well evacuated, glass system, dried by passage through a tube filled with phosphorus pentoxide, liquefied by means of liquid air, and fractionated, a middle portion being distilled into the calorimeter. Pressure measurements were made with a calibrated Henson comparator and the manometer described previously. Simultaneously another observer read E(7). Data from the International Critical Tables[5] were used to correct the readings to international cms. of mercury. No correction was necessary for capillary depression. The acceleration of gravity was taken as 979.57 cm./sec.^{2}, as determined by the Coast Geodetic Survey at this location. Table I gives the results of the comparison. The measurements are given in the order in which they were made. About 2 liters of oxygen gas were pumped off following the thirteenth reading and again after the the seventeenth. In the first column are the temperatures obtained from the thermocouple, and in column two are the pressures calculated from the equation of Cath,[6]

$$\log_{10} P \text{ (cm.)} = -419.31/T + 7.1173 - 0.00648 \, T,$$

assuming the temperatures coming from the thermocouple are correct. The third column lists the observed pressures, and column four gives the temperatures calculated from the observed pressures of oxygen less the temperatures obtained from thermocouple 7. The satisfactory agreement with the oxygen vapor-pressure thermometer gives me confidence that our temperature scale, assuming 0° C. to equal 273.10° K., is good to $\pm 0.05^\circ$, which is the accuracy claimed for the thermocouples of Giauque, Buffington, and Schulze. It is true that the last ten degrees or so below 300° K. are extrapolated, but since the e. m. f. is nearly a linear function of temperature

in that range, probably little error was introduced.

Table I Comparison of Thermocouple 7 with Oxygen Vapor-Pressures

T from thermocouple 7 ^{o}K.	P calculated cm. of Hg.	P observed cm. of Hg.	Δ T ^{o}K.
70.923	5.566	5.556	−0.010
70.941	5.584	5.559	−0.026
73.954	9.294	9.263	−0.021
73.968	9.315	9.276	−0.026
73.987	9.344	9.330	−0.009
74.734	10.527	10.523	−0.003
74.742	10.540	10.518	−0.013
80.578	24.624	24.665	+0.012
80.584	24.644	24.672	+0.008
84.575	40.870	40.866	−0.001
84.580	40.895	40.903	+0.002
89.853	73.87	74.004	+0.017
89.857	73.90	74.036	+0.017
86.255	49.785	49.696	−0.016
86.258	49.801	49.738	−0.011
90.083	75.66	75.630	−0.004
90.086	75.68	75.656	−0.003
90.327	77.60	77.538	−0.008
90.331	77.63	77.56	−0.009

Calibration of the Resistance Thermometer

The resistance thermometer was calibrated during the heat capacity runs by comparison with thermocouple 7, on the bottom of the calorimeter. The absolute accuracy is of course no better than that of the thermocouple, $\pm 0.05^{o}$, but it is assumed that the absolute error does not vary appreciably over a small range, so that small temperature intervals can be determined with much higher accuracy. Measurements were made at intervals of approximately 2 to 6 degrees. The data was treated by making two plots, one of deviations of R from a linear function of temperature, and the other of dR/dT. The first curve was used to get the average temperature of the heat capacity determination. The second was on a very large scale and was used to convert the
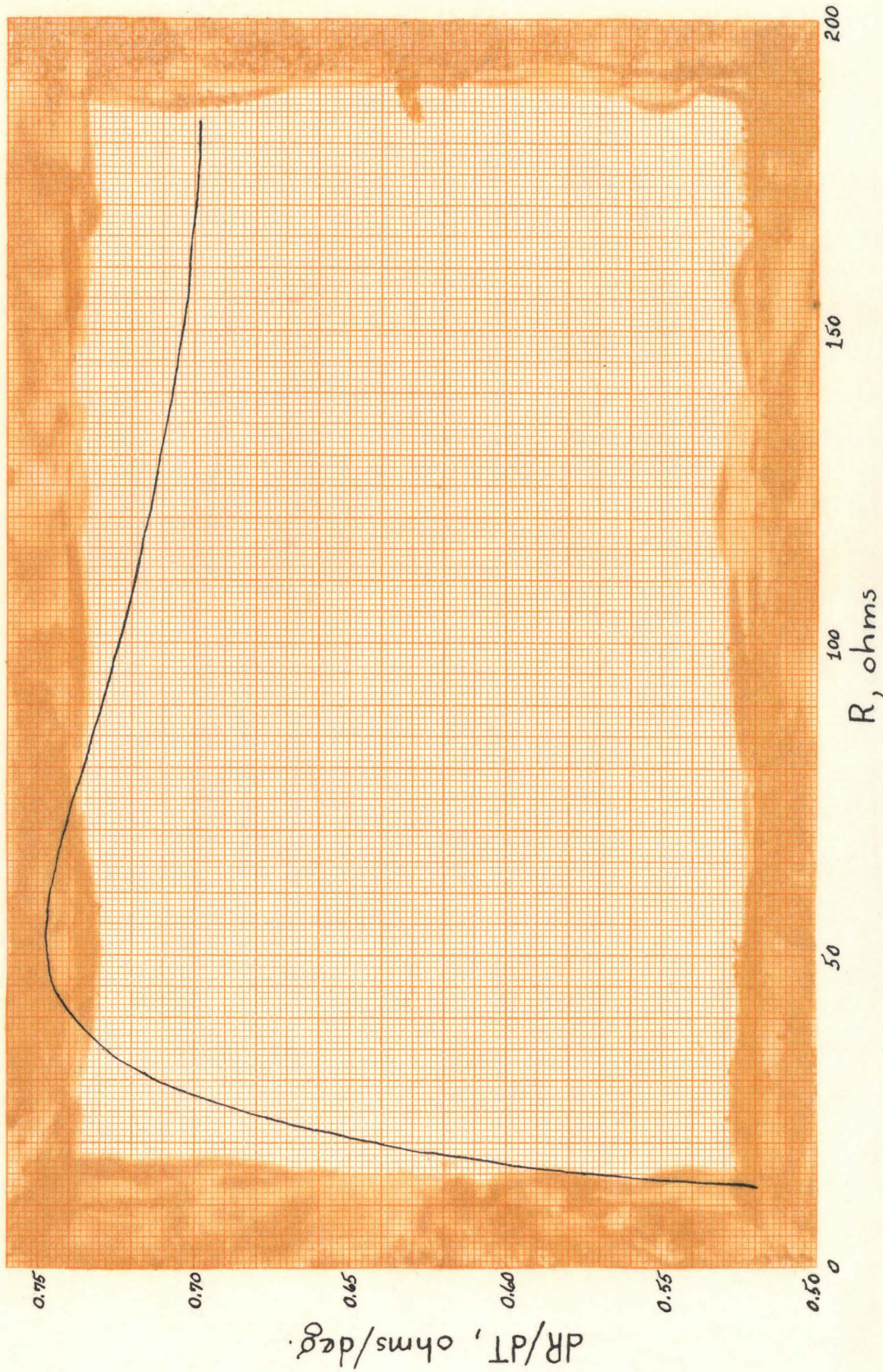
Fig. 4 Sensitivity of Resistance Thermometer

effective rise in resistance of the thermometer-heater into
the corresponding temperature rise. Fig. 4 shows this graph
much reduced, with the experimental points omitted since they
are too numerous. It was more convenient to have R rather than
T as abscissae; temperatures corresponding to a few points are
13 ohms--60.18° K., 50 ohms--113.80° K., 180 ohms--294.39° K.

Heat Capacity Measurements

The method is as follows: Hydrogen is admitted into the
calorimeter assembly and the calorimeter allowed to fall to the
temperature of the cooling bath. Then the container is evacuated.
The radiation shield is heated to a suitable temperature, and in
case it is much hotter than the cooling bath, a small current is
adjusted to keep its temperature constant during the run. Below
the m. p. of monofluorotrichloromethane the radiation shield was
between the initial and final temperatures of the calorimeter;
above the m. p. it was definitely hotter to prevent condensation
of the sample in the inlet tube with resulting heat effect which
would ruin the heat capacity run. The heating rate of the
calorimeter is then taken by measuring E_I once and then E_R at
50 sec. intervals for about 5 minutes. Then a current of 0.05 to
0.1 amp. is passed through the calorimeter heater for a pre-deter-
mined time of 5 to 15 minutes, producing a temperature rise of
3 or 4 degrees. For 10 minutes or more prior to the energy input
the battery has been discharging through a rheostat set equal to
the total resistance in the heater circuit. E_V and E_C are measured
at suitable intervals. After the end of the energy input, the
heating rate is again followed, usually for 20 or 25 minutes,
depending on how long is required to reach a steady state. The

usual time necessary was 10 or 20 minutes.

While the calorimeter is being heated, both current and voltage change due to the increase in resistance of the thermometer-heater. To avoid graphical integration an extension of the method of Gibson and Giauque[1] was employed. It can be shown that if a quantity changes quadratically with time, then the average over a period t equals the average of the values at 0.211 t and 0.789 t, and also equals the average of the values at 0.147 t, 0.500 t, and 0.853 t, regardless of the coefficients in the quadratic. This method was tested for E_C and E_V at the lowest temperature, where the percent change in R is greatest for a given temperature rise. In each case it was found that the average E_V or E_C obtained from frequent readings agreed to 0.01% with that calculated from the values at 0.211 t and 0.789 t, or 0.147 t, 0.500 t, and 0.853 t. This agreement is rather amazing in view of the fact that the change in E_C in the test was as high as 18%.

In calculating the energy supplied to the heater, a defined calorie equal to 4.185/1.0004 international joules was used. Allowance was made for the resistance of the potential leads (0.1 to 0.2%) and for the fraction of the current passing through the 10,050 ohm resistance in parallel with the heater. These could be calculated to a high degree of accuracy. A rather uncertain correction of 0.04% was added for the heat developed in the current leads between calorimeter and radiation shield. It was assumed that half the heat went to the calorimeter and half to the shield.

The correction for heat interchange with the surroundings was made on the assumption that over a range of 4 or 5 degrees the heat transfer varies linearly with the temperature of the exterior

of the calorimeter, the temperature of the radiation shield remaining constant. The major part of the correction was applied by linearly extrapolating to the middle of the heating period the measurements of E_R made before starting energy input and the measurements of E_R made after a steady state is reached following energy input. The difference in these extrapolated values of E_R, multiplied by $200/(E_I)_{avg}$., gives the effective rise in resistance of the thermometer, except for some supplementary corrections discussed in the following paragraphs.

The correction made as just described would take care of heat interchange if the change in E_R with time were really constant and if the average temperature of the heater-thermometer during energy input, which can be obtained from the energy measurements, were equal to the average of the initial and final temperatures of the calorimeter and contents. Deviations from the first of these were important only in the case of the empty calorimeter, giving rise to a correction to the heat capacity of the empty calorimeter which increased from about 0.1% at 130^0 K. to 2% at 295^0 K. Deviations from the second affected the heat capacity of the empty calorimeter by 0.2% and the total heat capacity by 0.4% near room temperature.

During the measurements of resistance before and after energy input there is a slight thermal head between the resistance thermometer and the average location of heat capacity, since the temperature of the calorimeter and contents is changing mostly due to thermal flow through the resistance thermometer. The correction for the difference in this thermal head turns out to be equal to that due to the increased temperature of the exterior during energy input.

Correction was also made for change in the temperature of the radiation shield during a few of the runs. This can be made negligible by proper adjustment of the current through the shield heater.

The heat capacity of the empty calorimeter, about one-third the total heat capacity with the size of sample used, was measured by the method described, about 2 cm. of hydrogen being inside the calorimeter to aid in the distribution of heat. The results are shown graphically in Fig. 5. The smooth curve actually used was on a scale much larger, and the average deviation was about 0.1%.

A correction was necessary for vaporization of monofluorotrichloromethane at temperatures above 180° K. The volume of the calorimeter and inlet tube was measured accurately by an expansion method and the volume of the liquid calculated from the mass and density of the substance. Ruff and Keim[7] have reported the density to be 2.08 - 0.00185 T gm./ml. between 180° and 201° K., and 1.4944 at 17.2° C. Linear interpolation was used to get the density at other temperatures. The vapor-pressure and heat of vaporization were calculated from the vapor-pressure equation given later in this paper. The correction amounted to about 2% near the boiling point, and probably it was good to about 10% of its value.

It was intended to measure the amount of material in the calorimeter by distilling it into a bulb, connected to the inlet tube by means of a vacuum-tight, ground-glass joint, and weighing it. Unfortunately, the line broke during this operation, and some was lost. Hence the sample was dried and fractionated on the
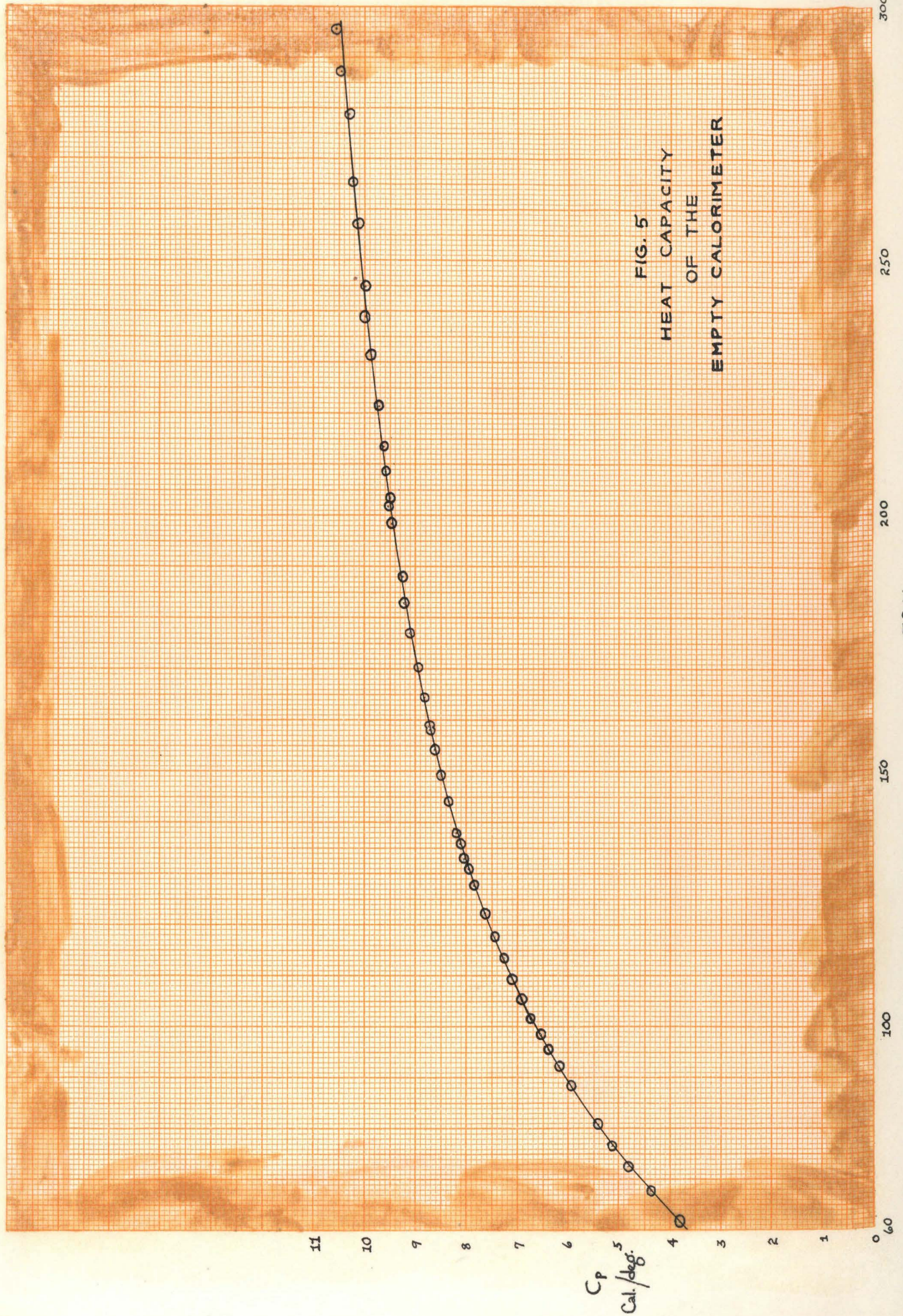
FIG. 5

HEAT CAPACITY

OF THE

EMPTY CALORIMETER

vacuum bench once more, weighed in the bulb, and condensed in the calorimeter. Several heat capacity measurements were made in a range where the previous results were particularly consistent. The amount present in the first series was then calculated to be 0.7660 mole, using 137.38 as the molecular weight. The estimated uncertainty was about 0.1%. Weights were corrected to vacuum.

The molal heat capacities of monofluorotrichloromethane are given in Table II and Fig. 6. The mean deviation from a smooth curve is about 0.2% for the solid and 0.3% for the liquid. The probable error is about 0.3% for the solid and 0.6% for the liquid.

Table II   Molal Heat Capacities of Monofluorotrichloromethane

T $^{o}K.$	$\tilde{C}_p$ cal./deg./mole	Run number
62.22	11.68	1
65.25	12.09	2
68.08	12.34	3
70.53	12.56	4
75.85	12.90	5
79.85	13.22	6
85.37	13.69	7
89.02	13.94	8
89.29	13.96	59
92.86	14.28	9
96.36	14.53	10
99.68	14.82	11
103.0	15.12	12
106.6	15.46	13
110.3	15.75	14
114.0	16.12	15
117.9	16.46	16
122.4	16.85	63
126.2	17.30	17
131.2	17.77	18
135.3	18.13	19
137.3	18.38	64
139.1	18.58	20
141.0	18.83	65
141.9	18.92	60
143.2	19.06	21

Table II, continued. Molal Heat Capacities of Monofluoro-
trichloromethane.

T °K.	C_p cal./deg./mole	Run number
144.7	19.32	66
145.9	19.36	61
147.0	19.49	22
148.3	19.75	67
152.0	19.97	68
156.4	21.66	23
156.5	21.12	28
157.1	21.92	69
159.5	25.90	24
160.0	26.74	29
160.1	28.20	27
162.54	melting point	
165.9	26.10	30
169.2	26.11	25
171.2	26.10	31
173.0	26.18	26
175.8	26.29	32
180.2	26.45	33
183.3	26.37	70
190.9	26.59	36
196.4	26.66	37
201.7	26.63	38
207.0	26.70	39
212.9	26.93	71
222.0	27.05	73
225.0	27.19	74
231.8	27.17	72
241.3	27.42	75
247.9	27.55	76
254.7	27.70	77
260.2	27.73	78
261.0	27.87	49
266.3	27.91	79
272.5	28.07	80
279.3	28.21	81
283.5	28.38	83
285.6	28.41	82
290.5	28.60	55
291.8	28.56	84
296.88	boiling point	

In a number of runs there was condensation in the inlet tube,
giving high results. These have been rejected and do not appear
in Table II.

The heat capacities for several degrees below the melting
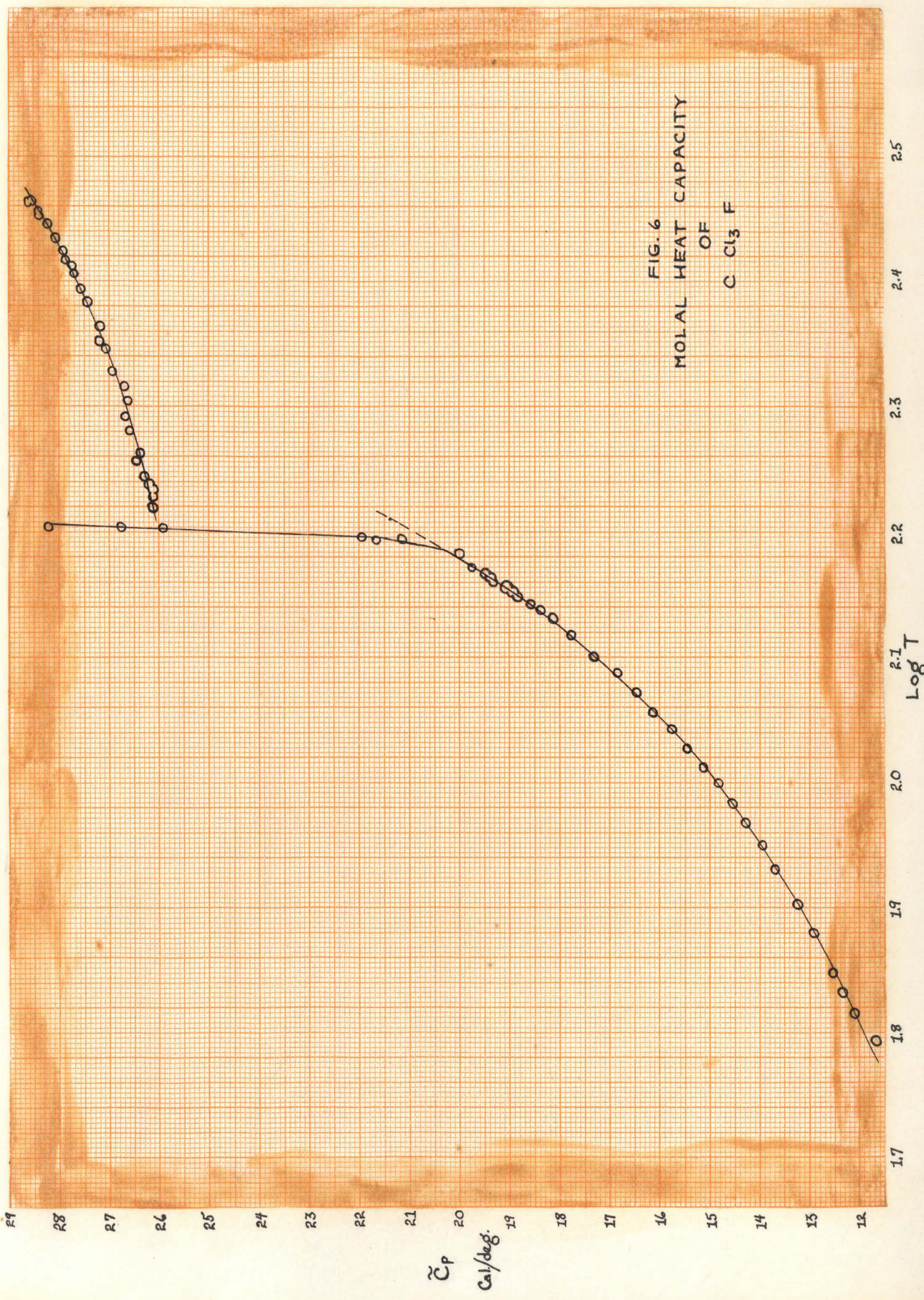point are high due to premelting. The area between the heat

FIG. 6

MOLAL HEAT CAPACITY

OF

C Cl₃ F

capacity curve through the observed points and that obtained by extrapolation from below where premelting is appreciable can be used with the heat of fusion and m. p. to calculate the mol-percent of impurity which is soluble in the liquid and insoluble in the solid, assuming that the solution formed is perfect. Thus, at 159.5° K. this heat effect amounts to about 15 cal. per mole; hence one calculates that there is 0.09 mol-percent liquid soluble, solid insoluble impurity in the monofluorotrichloromethane sample.

Heat of Fusion

The heat of fusion was determined in practically the same way as the heat capacities. The same amount of material, 0.7660 mole, was in the calorimeter. The radiation shield was heated to a fraction of a degree above the melting point and then the current through its heater adjusted to hold the temperature constant. The calorimeter was brought to about 150° K., and after a steady state was reached, the heating rate was observed. Then about 0.1 amp. was passed through the heater-thermometer until all the solid was melted. The time necessary was about 4500 sec. Readings of E_c and E_V, from which the current and voltage could be calculated, were taken at intervals. Then after the heating period the drift was again followed until it became constant. The results are summarized in Table III. The first column gives the temperature interval through which the calorimeter and contents rose. Column two gives the energy added electrically, and column three lists the heat received from the surroundings. The fourth column gives the heat required to raise the temperature of the calorimeter and the 0.7660 mole of the solid to the m. p. (corrected for premelting) plus the heat to raise the calorimeter and the liquid to the final

temperature. The last column gives the molal heat of fusion. The probable error is about 0.2%.

Table III   Heat of Fusion of Monofluorotrichloromethane

Temp. interval $^oK.$	Energy input cal.	Interchange cal.	$\int C_p dT$ cal.	$\Delta \tilde{H}_f$ cal./mole
150.73-166.35	1652.3	4.0	399.3	1641.0
150.59-163.90	1585.1	5.2	332.0	1642.7
			Mean	1641.8 ± 3.2

Melting Point Determination

The melting point was determined by observing the equilibrium temperatures with different amounts melted, calculated from the amount of energy added and the heat of fusion. The results are presented in Table IV. The change of melting point with percent melted indicates about 0.01 mol-percent of impurity, in contrast with the estimate of 0.09 mol-percent obtained from the premelting effect. Perhaps there was lack of equilibrium in the premelting range. The melting point of the pure compound from our measurements is 162.54 ± 0.05^o K. Ruff and Keim[7] give -111° C.

Table IV   Melting Point of Monofluorotrichloromethane

% melted	T ($^oK.$) from thermocouple 7	T ($^oK.$) from res. thermometer
20	162.493	--
32	162.523	162.531
45	162.538	162.539
58	162.542	162.540
71	162.543	162.540
84	162.541	162.542

Vapor-Pressures

The vapor-pressures of monofluorotrichloromethane were measured in the manner described for the comparison of thermocouple 7 with the oxygen vapor-pressure thermometer. The observations are shown in Table V along with the pressures calculated from the equation

$$\log_{10} P \text{ (cm.)} = 8.21671 - (1610.04)/T - 0.0030743\ T,$$

in column three. Temperatures, column one, were obtained from thermocouple 7 and are given to 0.001° because of the high relative accuracy. The observed pressures are in column two. All the pressures are expressed in international cms. of mercury.

Table V Vapor-Pressures of Monofluorotrichloromethane

T $^{\circ}K.$	P observed cms. of Hg	P calculated cms. of Hg	$P_{obs.} - P_{calc.}$ cms. of Hg.
236.640	4.854	4.848	+ 0.006
236.680	4.851	4.858	− 0.007
239.742	5.781	5.807	− 0.026
239.812	5.781	5.830	− 0.049
251.489	11.019	11.003	+ 0.016
251.526	11.040	11.024	+ 0.016
251.571	11.052	11.050	− 0.002
265.183	21.398	21.381	+ 0.017
265.229	21.410	21.426	− 0.016
274.799	32.509	32.578	− 0.069
274.809	32.510	32.592	− 0.082
280.918	41.869	41.853	+ 0.016
280.938	41.884	41.887	− 0.003
280.945	41.894	41.901	− 0.007
282.229	44.120	44.088	+ 0.032
282.268	44.192	44.156	+ 0.036
285.980	51.027	51.006	+ 0.021
285.987	51.035	51.019	+ 0.014
291.103	61.802	61.793	+ 0.009
291.109	61.840	61.807	+ 0.033
291.211	62.046	62.040	+ 0.006
293.844	68.205	68.253	− 0.048
293.893	68.376	68.371	+ 0.005
295.330	71.937	71.962	− 0.025
295.381	72.125	72.093	+ 0.032

The boiling point calculated from the vapor-pressure equation is $296.88 \pm 0.05°$ K. $(23.78°$ C.), which is in agreement with the value obtained by distillation of the sample, $23.7 \pm 0.1°$ C. (corrected to 76 cm. of mercury by means of the vapor-pressure equation.) The equation of Ruff and Keim,[7]

$$\log_{10} P \text{ (cm.)} = 7.540 - 1385/T,$$

gives $24.1°$ C. as the boiling point, but since the highest pressure from which this equation was obtained was less than 60 cm., the fit should not be expected to be very close near the boiling point. The only other value of the boiling point recorded in the literature is $24.9°$ C.[8]

The heat of vaporization of monofluorotrichloromethane at its boiling point was calculated from the empirical vapor-pressure equation and the Clapeyron equation, using 1.48 gm./ml. as the density of the liquid and assuming that the vapor follows a modified Berthelot equation of state

$$p\tilde{v} = RT \left\{ 1 + 9pT_c(1 - 6T_c^2/T^2)/128p_cT \right\} .$$

The critical constants T_c and p_c have not been determined for this substance, but an estimate may be obtained from the fact that the ratio of critical temperature to boiling temperature for similar compounds is fairly constant. The average of the ratio for carbon tetrachloride,[9] 1.590, and for chloroform,[9] 1.603, was used to get $474.1°$ K. as T_c for monofluorotrichloromethane. A linear extrapolation to $474.1°$ K. on a plot of log P against $1/T$ for the four highest vapor-pressures measured gives $p_c = 50.0$ atm. This is nearly equal to p_c for carbon tetrachloride,[9] 45.0 atmospheres. The heat of vaporization calculated using these constants is 5905 cal./mole at the boiling point. The Berthelot correction amounts to -220 cal./mole.

Entropy from the Calorimetric Data

The calculation is summarized in Table VI. The greatest uncertainty lies in the extrapolation to 0° K. Several methods were considered, but no satisfactory one was found. Presumably one could fit the observed curve by a combination of Einstein and Debye functions; however, this procedure is extremely difficult. The n-formula of Lewis and Gibson[10] and the method of Kelley, Parks, and Huffman[11] were tested on the data for carbon tetrachloride;[12] the values of the entropy obtained were both about 15% low. The method actually used was to plot against log T the molal heat capacities of monofluorotrichloromethane (above 60° K.) and those of carbon tetrachloride given by Lord and Blanchard,[12] and then to shift the heat capacity curve for carbon tetrachloride along the axis of log T until it joined on to the other curve at 60° K. Graphical integration of the curve obtained in this manner gave the value 10.12 cal./deg./mole listed in Table VI.

The change in entropy between 60° and the m. p. and between the m. p. and the b. p. was calculated by graphical integration of a smooth curve through the experimental heat capacities (corrected for premelting in the interval just below the m. p.) plotted on a large scale against log T.

A small correction for gas imperfection was derived from the equation of state assumed for the calculation of the heat of vaporization together with one of Maxwell's relations,

$$(dS/dP)_T = - (dV/dT)_P .$$

In order to get the change in entropy of the gas between the b. p. and 298.10° K., at 1 atm. pressure, the molal heat capacity of the gas at constant pressure and these temperatures was calculated from the spectroscopic and electron diffraction data.

Table VI Entropy of Monofluorotrichloromethane from
the Calorimetric Data

	S cal./deg./mole
0 - 60.00° K., extrapolation	10.12 ± 1.5
60.00 - 162.54° K., graphical	15.26 ± 0.05
Fusion, 1641.8/162.54	10.10 ± 0.02
162.54 - 296.88° K., graphical	16.34 ± 0.10
Vaporization, 5905/296.88	19.89 ± 0.20
Entropy of actual gas at b. p.	71.71 ± 1.5
296.88 - 298.10° K.	0.07
Correction for gas imperfection	0.14
Entropy of ideal gas at 298.10° K., 1 atm.	71.92 ± 1.5

Raman Spectrum of Monofluorotrichloromethane

The Raman spectrum of liquid monofluorotrichloromethane was photographed, using a water-cooled mercury arc in Pyrex and a short-focus glass spectrograph with a dispersion of about 60 $\overset{o}{A}$. per mm. near 4400 $\overset{o}{A}$. The compound was distilled in vacuo into the Raman tube, which was of Pyrex and about 25 ml. capacity. An iron arc provided the comparison spectrum. An exposure of about one-half hour was sufficient.

In Table VII are listed the observed Raman shifts, together with the number of times each shift appeared on the plate (including both Stokes and anti-Stokes lines) and also the relative intensities. The accuracy for the frequencies was about 2 cm.$^{-1}$ except for the weakest line, which could not be measured with the comparator.

Table VII   Raman Spectrum of Monofluorotrichloromethane

$\Delta \tilde{\nu}$ in cm.$^{-1}$	No. of appearances	Relative intensity
246	3	6
351	3	6
398	4	6
536	5	10
838	2	4, broad
1072	2	2
1540	1	0

It should be remarked that the frequency 838 cm.$^{-1}$ shows some indication of being a doublet.

By the methods of group theory[13] it has been shown that a molecule such as $FCCl_3$ has six normal modes of vibration. Of these, three are single and three double, and all are active both in the Raman effect and in the infrared absorption spectrum. In the non-degenerate vibrations there is a change in the electric moment along the symmetry axis and in the doubly-degenerate ones a change perpendicular to the symmetry axis. The lines arising from the doubly-degenerate vibrations have the special depolarization ratio 6/7 for unpolarized and 3/4 for plane-polarized incident light.

In order to make the assignment, the non-degenerate frequencies of $FCCl_3$ were computed by the following procedure. Rosenthal and Voge have given a normal coordinate treatment for molecules of the type XYZ_3 and have derived a set of potential constants for the $-CCl_3$ group from the frequencies for CH_4, $ClCH_3$, and CCl_4. This potential function and a C-H bond constant obtained in the derivation are sufficient to calculate the three parallel fre-

quencies of $HCCl_3$ and $DCCl_3$ fairly accurately. To treat $FCCl_3$
I used Rosenthal and Voge's formulae and potential function for
the $-CH_3$ group plus the frequencies of FCH_3 to calculate a C-F
bond constant. Then this was used with the potential function
for the $-CCl_3$ group to get the following values for the parallel
frequencies of $FCCl_3$: 341, 499, and 1380 cm.$^{-1}$ Another value
for the C-F bond constant, given by Sutherland and Dennison,[15]
led to the values 339, 493, and 1276 cm.$^{-1}$ Now if one assumes
that the intense Raman lines observed are fundamentals and that
the calculation just sketched is reasonably accurate, then one
can assign 351, 536 and 1072 (or 1540) cm.$^{-1}$ to the non-degenerate
vibrations and 246, 398, and 838 cm.$^{-1}$ to the doubly degenerate
vibrations.

The fundamental frequencies of $HCCl_3$ and of $DCCl_3$ are also
useful in making the assignment. For $HCCl_3$ they are[16] 263 (2),
366 (1), 668 (1), 768 (2), 1222 (2), and 3025 (1), where the
numbers in parentheses are the degeneracies, obtained from
polarization measurements. For $DCCl_3$ they are[17] 262 (2), 366 (1),
651 (1), 736 (2), 908 (2), and 2256 (1) cm.$^{-1}$ Four of the fre-
quencies are shifted but little in going from $HCCl_3$ to $DCCl_3$,
and hence it seems reasonable that approximately these same
frequencies should appear for $FCCl_3$. These are 246 (2), 351 (1),
536 (1), and 838 (2) cm.$^{-1}$ The two highest frequencies for the
chloroforms apparently involve mainly the C-H bond, since they
depend so markedly upon the mass of the hydrogen. The frequencies
for $FCCl_3$ which involve mainly motions of the F against the CCl_3
pyramid are probably 398 and 1072 (or 1540) cm.$^{-1}$ Of these, the
first consists of bending and the second of stretching the C-F
bond, since the former is degenerate and the latter non-degenerate.

1072 cm.$^{-1}$ may possibly be an overtone of 536 cm.$^{-1}$, but the exact agreement with 2 x 536 is suspicious. The most intense Raman line, 536 cm.$^{-1}$ should be assigned to symmetrical stretching of the C-Cl bonds, and it may be noted that the frequency in the HCCl$_3$ spectrum with which we correlate it (668 cm.$^{-1}$) is also assigned to this mode of vibration.[16] The only other non-degenerate frequency is 351 cm.$^{-1}$; it must correspond to the symmetrical bending of the C-Cl bonds. As for the remaining frequencies, 246 and 838 cm.$^{-1}$ they may be assigned to degenerate bending and stretching of the C-Cl bond, respectively. It must be emphasized that this characterization of the modes of vibration is very approximate.

Entropy from Raman Spectrum and Electron Diffraction

The translational entropy was calculated from the Sackur-Tetrode equation. The computation of the rotational entropy was made with the electron diffraction data of Brockway[18] for monofluorotrichloromethane, assuming the molecule acts as a rigid, symmetric top. The effect of the isotopes of chlorine was taken into account merely by using the average atomic mass for chlorine; such a procedure in the case of carbon tetrachloride yields practically the same result as the more refined method used by Lord and Blanchard.[12] The product of the three principal moments of inertia is $(6.14 \pm 0.23) \times 10^{-113}$ gm. cm.^{2} A symmetry number of 3 was used, in accordance with the discussion of Lord and Blanchard regarding the effect of isotopes on the symmetry number.[12] The equation for the translational and rotational entropy, neglecting nuclear spin, is then

$$S_{\text{trans.+ rot.}} = 21.15 + 18.300 \log_{10} T - 4.5750 \log_{10} P_{\text{atm.}}$$

The vibrational entropy was calculated from the Raman frequencies, using the equation

$$S_{vib.} = R\sum_{i} p_i \left\{ x_i / (e^{x_i} - 1) - \ln(1 - e^{-x_i}) \right\},$$

where $x_i = hc\tilde{\nu}_i / kT$ and p_i is the degeneracy of the ith fundamental frequency. This relation is derived on the assumption that the normal modes of vibration are harmonic oscillators weakly coupled. Tables of the function under the summation sign may be found in several places.[19] No allowance was made for the different symmetry types due to the presence of isotopes of chlorine, for the isotope shift should be small.

The results are presented in Table VIII. The values of all natural constants used are those given in the International Critical Tables.[5]

Table VIII Entropy of Monofluorotrichloromethane at 298.10° K. and 1 Atmosphere from Spectroscopic and Electron Diffraction Data.

	S, cal./deg./mole
Translational and rotational	66.43
Vibrational	7.67
Total (neglecting nuclear spin)	74.10

Between the "calorimetric" and "spectroscopic" values for the entropy there is a discrepancy of 2.18 cal./deg./mole. Probably the chief reason for this divergence is the poor extrapolation below 60° K. No definite conclusion can be drawn as to whether or not there is agreement until the heat capacity measurements are extended to lower temperatures. There is, of course, the possibility that the Raman spectrum was incorrectly analyzed. However, it is only necessary to know the fundamental frequencies and their degeneracies. The highest non-degenerate frequency

can be either 1072 or 1540 cm.$^{-1}$ without much change in the entropy.

Acknowledgements

Summary

An apparatus for vapor-pressure measurement and low temperature calorimetry has been assembled.

The heat capacities of monofluorotrichloromethane have been measured between 60° K. and the b. p. The heat of fusion at the m. p., 162.54 ± 0.05° K. (-110.56° C.), is 1641.8 ± 3.2 cal./mole. The vapor-pressures between 5 and 72 cm. are well represented by the equation

$$\log_{10} P \text{ (cm.)} = 8.21671 - (1610.04)/T - 0.0030743\ T.$$

The b. p. from the vapor-pressure equation is 296.88 ± 0.05° K. (23.78° C.) and the heat of vaporization, including a Berthelot correction of -220 cal./mole, is 5905 ± 60 cal./mole. The entropy from the calorimetric data, making an extrapolation below 60° K. amounting to 10.12 cal./deg./mole, is for the ideal gas 71.92 ± 1.5 cal./deg./mole at 298.10° K and 1 atmosphere.

The Raman spectrum has been photographed and the following shifts observed, with the relative intensities indicated: 246 (6), 351 (6), 398 (6), 536 (10), 838 (4, broad), 1072 (2), and 1540 (0) cm.$^{-1}$ An assignment of the frequencies has been made

and with the aid of electron diffraction data the entropy of monofluorotrichloromethane at 298.10° K. and 1 atmosphere, neglecting nuclear spins, calculated to be 74.10 cal./deg./mole.

References

1 Gibson and Giauque, J. Am. Chem. Soc. 45, 93 (1923); Giauque and Wiebe, ibid. 50, 101 (1928).

2 Giauque, Johnston, and Kelley, ibid. 49, 2367 (1927).

3 Giauque, Buffington, and Schulze, ibid. 49, 2343 (1927).

4 Southard and Andrews, J. Franklin Inst., 207, 323 (1929).

5 International Critical Tables, McGraw-Hill Book Co., New York, (1926), vol. I.

6 Cath, Comm. Phys. Lab. Univ. Leiden, 152d, 1918.

7 Ruff and Keim, Z. anorg. allgem. Chem. 201, 245 (1931).

8 Swarts, Bull. Acad. Roy. Belg. (3) 24, 309 (1892).

9 International Critical Tables, vol. III, p. 248.

10 Lewis and Gibson, J. Am. Chem. Soc. 39, 2565 (1917).

11 Kelley, Parks, and Huffman, J. Phys. Chem. 33, 1802 (1929).

12 Lord and Blanchard, J. Chem. Phys. 4, 707 (1936).

13 Rosenthal and Murphy, Rev. Mod. Phys. 8, 317 (1936). Wilson, J. Chem. Phys., 2, 432 (1934)

14 Rosenthal and Voge, ibid. 4, 134 (1936). Voge and Rosenthal, ibid. 4, 137 (1936).

15 Sutherland and Dennison, Proc. Roy. Soc. 148, 250 (1935).

16 Kohlrausch, "Der Smekal-Raman Effekt," Springer, Berlin (1931) p. 116.

17 Wood and Rank, Phys. Rev. 48, 63 (1935). Redlich and Pordes, Naturwiss. 22, 808 (1934).

18 Brockway, J. Phys. Chem. 41, 185 (1937).

19 Gordon and Barnes, J. Chem. Phys. 1, 297 (1933).

Propositions Submitted for Oral Examination

1.   In calibrating a set of fractional weights against a brass standard to an accuracy of 0.01 mg. it is unnecessary to make buoyancy corrections, provided that when the weights are used the buoyancy corrections are applied as though the weights were brass.

2.   Precise measurements of specific heats of substances with low vapor-pressures can better be made by the adiabatic method than by the method in which the temperature of the environment is kept constant.

3.   For precise determination of temperatures and temperature intervals, strain-free resistance thermometers are superior to thermocouples.

4.   The method for auto-calibrating a White double potentiometer described by the manufacturers of the instrument (Leeds and Northrup) cannot be used without modification.

5.   Heat capacity data are of little value for determining symmetry numbers of molecules.

6.   The discrepancy of 7.2 calories per degree per mole between the spectroscopic and "third law" values for the entropy of tetramethyl-methane[1] at its normal boiling point may be due to
      (a)   "False equilibrium" in the crystal at the lowest
             temperatures reached in the experiments.
      (b)   Lack of free rotation of the methyl groups.
      (c)   Inadequacy of the symmetry number approximation.

7.   The Nernst Heat Theorem should be regarded as a useful generalization with some exceptions rather than as "always irrelevant and useless."[2]

8.   Graduate students working on structural, physical, or inorganic chemistry should be encouraged to take a course in qualitative organic analysis.

9.   A reasonable assignment for the Raman shifts of liquid CCl_3F is
$$\tilde{\nu}_1 = 351 \text{ cm.}^{-1} \quad ; \quad \tilde{\nu}_3 = 536 \quad ; \quad \tilde{\nu}_5 = 1072 \text{ (or perhaps 1540)}$$
$$\tilde{\nu}_2 = 246 \quad ; \quad \tilde{\nu}_4 = 838 \quad ; \quad \tilde{\nu}_6 = 398$$
where $\tilde{\nu}_1$, $\tilde{\nu}_3$, and $\tilde{\nu}_5$ are non-degenerate and $\tilde{\nu}_2$, $\tilde{\nu}_4$, and $\tilde{\nu}_6$ doubly-degenerate vibrations involving mainly bending of the C-Cl bonds, stretching of the C-Cl bonds, and stretching of the C-F bond respectively.

(1)   Aston and Messerly, J. Am. Chem. Soc. <u>58</u>, 2354 (1936).

(2)   Fowler and Sterne, Rev. Mod. Physics <u>4</u>, 707 (1932).