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THE CONSTANT VOLUME HEAT CAPACITIES OF GASEOUS TRIFLUOROMETHANE, CHLORODIFLUOROMETHANE AND DICHLOROFLUOROMETHANE

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TABLE OF CONTENTS

TABLE OF CONTENTS (CONT'D)

LIST OF TABLES

LIST OF TABLES (CONT'D)

LIST OF FIGURES

LIST OF FIGURES (CONT'D)

LIST OF FIGURES (CONT'D)

LIST OF APPENDICES

NOMENCLATURE

A	Work content, Helmholtz free energy
A,B,C	Arbitrary constants in various equations
A_1, B_1, C_1 A_2, B_2, C_2 A_3, B_3, C_3 A_4, B_4, C_4 A_5, B_5, C_5	Constants used in Martin's Equation of State
b	Constant used in Martin's Equation
c	Speed of sound or speed of light or speed of molecules
C_{calr}	Heat capacity of the calorimeter
C_p	Constant pressure heat capacity
C_v	Constant volume heat capacity
$C_v{}^*$	Constant volume heat capacity at zero pressure
C_{gross}	Gross heat capacity of calorimeter and contents
$C^{g,l}_{sat}$	Heat capacity of two phase mixture at constant volume
C^{l}_{sat}	Heat capacity of the saturated liquid
d	Differential operator
exp	Exponential operator
E	EMF
f g h	Functions
I	Electric current

K	Constant used in Martin's equation
k	Boltzman constant
ln	Natural logarithm
m	Mass
P,p	Pressure
Q	Quantity of energy
q	Rate of energy input
R	Resistance
R	Universal gas constant
r	Radius
S	Entropy
T	Temperature, Kinetic Energy
t	Temperature or time
U	Potential energy
V	Volume
Z	Compressibility factor

Greek Letters

	Arbitrary constants used in various equations
Δ	Finite increment
Θ	Time
ρ	Density
Ω	Ohms
ν	Vibrational frequency
$\bar{\nu}$	Wave number
δ	Partial differential operator

Subscripts

c	Critical
Corr	Correction
i	Summation index
mean	Mean value over some period
r R	Reduced
sat	Saturated
1	At the start of the heating period
2	At the end of the heating period

Superscripts

*	At the zero pressure
g	Gas phase
l	Liquid phase

ABSTRACT

A light-weight thin-walled stainless-steel spherical calorimeter, surrounded by a radiation shield within an evacuated chamber, was constructed to determine the constant-volume heat capacities of gases. The calorimeter was 8 inches in diameter and had a wall thickness of 0.0085 inches. Platinum heating coils, which also served as a resistance thermometer, were arranged inside the sphere to give uniform heating. The temperature differential between the calorimeter and the radiation shield was maintained within ± 0.2°C .

Constant-volume heat capacities of trifluoromethane, chlorodifluoromethane and dichlorofluoromethane were determined in the density region of 0.01 gm/c.c. and a temperature range of 40 to 140°C. Because of the low density, the measured heat capacity is that of the ideal gas, C_V^*, which can be compared with the heat capacity predicted by statistical mechanics using fundamental vibrational frequencies from molecular spectroscopy. For trifluoromethane and dichlorofluoromethane, the measured and predicted values of C_V^* are almost identical at 100°C, while at 40°C the measured values are about 3% higher than the predicted and at 140°C they are 3% lower. For chlorodifluoromethane, the agreement between the measured and predicted values is also nearly perfect at 100°C. The measured values are, however, 1.5% lower than the predicted at 40°C and 1.5% higher than the predicted values at 140°C. These results lend support to the accepted fundamental frequency assignments, but fail to explain the difference in the effect of temperature on the ideal-gas heat capacity.

I. INTRODUCTION

Experimental measurements of constant-volume heat capacity over a wide range of density and temperature are of great importance for the understanding of physical phenomena in terms of molecular physics and the development of an equation of state.

Constant volume heat capacity, C_V , at any temperature T and density ρ can be calculated as the sum of the zero-density heat capacity, C_V^* , at the same temperature, and the increase of heat capacity due to compression, i.e. $(\frac{\partial C_V}{\partial \rho})_T \, d\rho$. Therefore, direct measurements of the heat capacity at constant volume of gases are useful in two ways: (a) Experimental data can be extrapolated to zero pressure at any given temperature to determine ideal-gas heat capacity values, which may again be used to decide questions of structure or vibrational frequency. (b) The constant-volume heat capacity may be used to determine the change of heat capacity with density and then compared with the same values calculated from some equation of state of good accuracy. Thus, with the help of experimental C_V values, an equation of state can be tested and, if necessary, modified.

I-1 Constant-Volume Heat Capacity Calculated from Principles of Statistical Mechanics

The ideal-gas constant-volume heat capacity, C_V^* , can be determined by the method of statistical mechanics if the fundamental vibrational frequencies are available (Appendix G, page 117, Appendix H, page 121). It may be calculated over a wide temperature range assuming the usual three contributions to the energy of a molecule due to its translational, rotational and vibrational motions. The translational and rotational components are equal to R/2 per degree of freedom and have a total value of 3R for non-linear molecules. The vibrational component is calculated as the sum of all individual degrees of freedom due to vibrational motion, each corresponding to a fundamental frequency, ν , and can be represented as follows:

$$(C_v^*)_{\omega_i} = R \sum_{i=1}^{3n-6} \frac{x_i^2 e^{x_i}}{(e^{x_i}-1)^2} \qquad (1\text{-}1)$$

where,

$x_i = \frac{h\nu_i}{KT} = \frac{hc\omega_i}{KT}$

n = number of atoms in the molecule

ν_i = the fundamental frequency in sec^{-1}

ω_i = wave number in cm^{-1}

T = temperature in degrees Kelvin

K = Boltzmann constant

c = velocity of light in cm/sec.

The equation above assumes harmonic vibrations and, therefore, corrections using empirical equations(2,40) are sometimes made for anharmonicity, particularly at higher temperatures. When the molecule is complex in structure, assignment of fundamental frequencies is a difficult problem and often involves educated guesses. Accurate experimental C_v^* or C_p^* values can, therefore, be helpful in the proper selection of fundamentals.

I-2 Constant-Volume Heat Capacity and the Equation of State

The increase of heat capacity at constant volume with density is given by the following equation:

$$\Delta C_V = \int_{\infty}^{V_T} \left(\frac{\partial^2 P}{\partial T^2}\right)_V dV = - \int_{0}^{\rho} \frac{T}{\rho^2} \left(\frac{\partial^2 P}{\partial T^2}\right)_\rho d\rho \qquad (1\text{-}2)$$

With this equation, C_V can be calculated if C_V^* and highly accurate PVT data are available. If, however, $\left(\frac{\partial^2 P}{\partial T^2}\right)_\rho$ is not known precisely, calculated C_V values cannot be good and one must resort to the direct measurement of the constant-volume heat capacity at higher density. Experimental C_V data can then be used to determine $\left(\frac{\partial^2 P}{\partial T^2}\right)_\rho$ and modify an equation of state representing the PVT data.

I-3 Objectives of this Work

The objectives of this research were: (a) to design a calorimeter of very low heat capacity for direct measurement of C_V^* values in the density region of 0.01 gm/c.c. and temperature range of 40 to 140°C for gaseous trifluoromethane, chlorodifluoromethane and dichlorofluoromethane (b) to compare experimental C_V^* values with the statistical predictions.

II. LITERATURE REVIEW

In order to develop tables of thermodynamic properties for a substance, one must know its heat capacity. Methods to measure heat capacities reported in the literature are:

(a) Constant volume calorimetry, (b) Flow calorimetry, (c) heat exchanger with the same and different fluid, (d) explosion, (e) isentropic expansion, (f) resonance, (g) velocity of sound, (h) molecular spectroscopy. Partington and Shilling(54) review all measurement techniques prior to 1924.

II-1 Constant Volume Calorimetry:

In 1894, Joly(28) published experimental C_V values for air and carbon dioxide. In his method two identical copper spheres were used as a differential calorimeter, one was evacuated and the other filled with with a known quantity of gas. Starting from an arbitrary temperature, steam was blown against the two calorimeters until the temperature was uniformly 100°C. The heat capacity of the gas was calculated from the amount of water condensed on the two spheres.

Bennewitz and Splittgerber(5) measured the heat capacity of carbon dioxide near the critical point. Their method was to heat a steel calorimeter by means of an electrically heated coil. The calorimeter was placed in the evacuated space and surrounded by a constant-temperature water bath.

In 1938, Pall, Broughton and Maass(52) published experimental C_V values of ethylene near the critical point with an essentially improved technique. The calorimeter was heated electrically and by parallel heating of the calorimeter and its surrounding heat losses were minimised and adiabaticity was attained.

In 1950, Hoge(25) measured the heat capacities of oxygen through the critical region. His apparatus was designed for vapor pressure work, but could be used as an adiabatic calorimeter.

Sage and various co-workers(11) reported measurements of $C^{g,\ell}_{sat}$ to determine saturated-liquid heat capacity C^{ℓ}_{sat}. For the first time mechanical stirring was used in a calorimeter to keep the temperature uniform. In one of the calorimeters used by Sage et al., a stirrer was driven by an external motor whose shaft entered the calorimeter through a rotary seal; in another the calorimeter was rocked to mix the liquid within the calorimeter.

In 1952, Michels and Strijland(48) reported measurement of C_V values for carbon dioxide over a considerable range of temperature and density. They used a differential calorimeter consisting of two identical containers, one of which was filled with the gas.

De Nevers and Martin(14) reported measurement of constant volume heat capacities of gaseous perfluorocyclobutane and propylene over a considerable range of temperatures and densities with a new type of adiabatic calorimeter. It had very thin walls and was equipped with an internal motor stirrer to assure temperature uniformity.

Yu-Tang Hwang(26) reviews all experimental C_V measurements. He, however, in 1961, carried out experimental measurements of halogenated methanes at low densities with a thin-walled adiabatic calorimeter. His measurements on chloropentafluoromethane, chlorodifluoromethane, dichlorotetrafluoromethane, and tetrafluoromethane were the first measurements at constant volume with sufficient accuracy to allow a comparison with spectroscopic predictions.

In 1963, Schwing(57) designed a magnesium calorimeter of very low heat capacity to study constant volume heat capacities in the density region of 0.01 gm/c.c. Constant volume heat capacities were obtained for gaseous trifluoromethane, chlorodifluoromethane and dichlorofluoromethane as a function of temperature in the range of 25-100°C. His extrapolated C_V* values are generally 2.5% lower than those calculated from spectroscopic measurements.

11-2 Flow Calorimetry:

In 1931, Buffington and Fleischer(8) directly measured the heat capacity of dichlorofluoromethane using a flow calorimeter. Their accuracy was ± 4% and hence could not be used to compare with spectroscopic predictions.

In 1940, Benning, McHarness and Smith(4) used a flow calorimeter to determine the heat capacity of some halogenated methanes. Their data were taken at sufficiently low density and hence could be compared with C_p* values from spectroscopic predictions.

In 1952, Masi(44) measured the heat capacity of dichlorodifluoromethane using a flow calorimeter. His accuracy of ± 0.1% is by far the most accurate measurement to date of constant pressure heat capacity. The spectroscopic heat capacity for dichlorodifluoromethane agrees with his measurements. His data are accurate enough so that it is possible to determine the effect of anharmonicity on heat capacity at moderate temperatures. However, his method cannot be used for direct experimental determination of C_V*.

Faulkner(20) and Jones(29) give a review of the techniques involved in flow calorimetry for determining heat capacity.

11-3 Wire Ribbon Method:

In 1939, Eucken and Bertram(19) in Germany and Kistiakowsky, Lacher, and Stitt(33) in the United States determined heat capacities to check spectroscopic vibrational frequencies by a wire ribbon method.

Van der Kooi and De Vries(63) also developed a wire ribbon method for determining the accommodation coefficients and heat capacities of gases in the region of one micron of mercury pressure. The rate at which a gas at low pressure conducts energy away from a heated surface such as a wire ribbon, is a function of the number of molecules striking the surface per second $\frac{n\bar{c}}{4}$, the temperature difference between the surface and the gas (T_s-T), the heat capacity at constant volume, and the thermal accommodation coefficient which Knudsen defined as $a = \frac{(T_1-T)}{(T_s-T)}$ where T is the temperature of gas molecules approaching the surface at T_s , and T_1 , is that of the molecules leaving the surface. According to Knudsen(35) and Schafer(56) the energy conducted away from the surface in the form of translation energy is proportional to 4/3 times the translational component of heat capacity since the faster molecules strike the surface more frequently and thus conduct away more energy per second than the slow ones do, while the energy conducted away in the form of rotational and vibrational energy is directly proportional to their components of the heat capacity. From this and the relationships,

$$\frac{n}{N} = \frac{P}{RT} , \quad \bar{c} = \left(\frac{8RT}{\pi M}\right)^{1/2}$$

and $\frac{1}{3} C_V = \frac{R}{2}$, a general equation for the power dissipation of a heated surface by gaseous molecular conduction is obtained directly as:

$$q = Ka(C_V + 1/2\ R)(T_s-T)P(MT)^{-1/2} \qquad (2-2)$$

where K includes the area of the surface, the constant terms and unit conversion factors.

II-4 Isentropic Compression:

Kistiakowsky and Rice$^{(34)}$ measured heat capacities for air, carbon dioxide, ethane and deuterated ethane from the study of isentropic compression. The thermodynamic relation is

$$\left(\frac{\partial T}{\partial P}\right)_S = -\frac{(\partial S/\partial P)_T}{(\partial S/\partial T)_P} = \frac{T}{C_p}\left(\frac{\partial V}{\partial T}\right)_P \qquad (2\text{-}3)$$

Using an equation of state which is valid at low pressure $\left(\frac{\partial V}{\partial T}\right)_P$ can be evaluated and upon integration C_p can be expressed as a function of initial and final conditions.

If an equation of state such as $V = \frac{RT}{P} + B$, where B is a function of temperature, is chosen, we can write

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P} + \frac{dB}{dT} \qquad (2\text{-}4)$$

and

$$C_p \cdot \frac{dT}{T} = \left(\frac{R}{P} + \frac{dB}{dT}\right) dP \qquad (2\text{-}5)$$

On integration and assuming C_p is independent of T and P , we obtain

$$C_p = R\,\frac{\ln(P_i/P_f)}{\ln(T_i/T_f)} + \frac{dB}{dT}\,\frac{(P_i - P_f)}{\ln(T_i/T_f)} \qquad (2\text{-}6)$$

where P_i , P_f are the initial and final pressures, respectively, and T_i , T_f are the corresponding temperatures.

II-5 Speed of Sound:

Various authors have used the speed of sound measurement to determine C_v values. From the theory of propagation of sound, the speed of sound in a medium is given by the relation:

$$c^2 = -\frac{V^2}{M}\left(\frac{\partial P}{\partial V}\right)_S \tag{2-7}$$

Using thermodynamic relations

$$\left(\frac{\partial P}{\partial V}\right)_S = \left(\frac{\partial P}{\partial V}\right)_T + \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_S \tag{2-8}$$

and

$$\left(\frac{\partial T}{\partial V}\right)_S = -\frac{(\partial S/\partial V)_T}{(\partial S/\partial T)_V} = -\frac{T}{C_V}\left(\frac{\partial P}{\partial T}\right)_V \tag{2-9}$$

and combining Equations (2-7), (2-8) and (2-9), we have

$$c^2 = -\frac{V^2}{M}\left\{\left(\frac{\partial P}{\partial V}\right)_T - \left(\frac{\partial P}{\partial T}\right)_V^2 \frac{T}{C_V}\right\} \tag{2-10}$$

or,

$$C_V = \frac{V^2\, T\left(\frac{\partial P}{\partial T}\right)_V^2}{Mc^2 + V^2\left(\frac{\partial P}{\partial V}\right)_T} \tag{2-11}$$

When a sound wave is passed through a medium, it causes reversible adiabatic expansions and contractions. At low intensities thermal equilibrium is attained with respect to various degrees of freedom of the molecules and hence C_V values can be measured. However uncertainties in the attainment of thermal equilibrium and in the derivative of pressure with respect to T or V put limitations in accurate determination of C_V values.

II-6 Molecular Spectroscopy

Chloro-fluoro derivatives of methane have been investigated spectroscopically. Pitzer et.al.(22), Bernstein and Pullin(7), Cleveland *et al.*(13), Edgell and May(17), and Plyer(55) have made spectroscopic predictions of fundamental frequencies on compounds triflurormethane, chlorodifluoromethane and dichlorofluoromethane.

III. EXPERIMENTAL APPARATUS

III-1 General Discussion:

In gas calorimetry, the heat capacity of the container is generally several times greater than the heat capacity of the gas itself. Consequently, comparatively small errors in the heat capacity measurement can be magnified to a large error in the specific heat being determined. Denevers(14) and Hwang(41) have shown that their calorimeters could be used to obtain ± 1% C_V data over a certain density below which their data become less and less reliable due to the unfavorable ratio of the heat capacity of the calorimeter and the gas. Schwing(57) points out that at low pressures any given calorimeter cannot be used to determine simultaneously reliable values of C_V^* and $C_V - C_V^*$. This is because the uncertainty in C_V values increases with decreasing density. Thus, the design of a calorimeter is solely dictated by the investigator's objectives.

On a close examination of the generalized plot by Hwang(26) of $C_V - C_V^*$ values against reduced density with reduced temperature T_r as parameters, it is observed that in the reduced density range of 0.00 to 0.02 and reduced temperature range of 0.95 to 1.07, $C_V - C_V^*$ has a maximum value of 0.1 cal/gm mole °C i.e. 0.0012 cal/gm°C for gaseous chlorodifluoromethane. Hence any calorimeter designed to work in this reduced temperature and density range will turn out C_V values which can be reliably used as C_V^* values. Such a calorimeter was built in this research to determine C_V^* values for trifluoromethane, chlorodifluoromethane and dichlorofluoromethane from experimental measurements of constant volume heat capacities in the density region of 0.01 gm/c.c. and temperature range of 40 to 140°C .

III-2 Calorimeter Shell:

The calorimeter shell, Figure 3-1 was made of 301 stainless steel, 0.0085 inches thick and approximately 8 inches inside diameter. The spherical shape was chosen because for any given volume and allowable stress it resulted in the lowest mass of the container. The sphere was fabricated from hemispheres by the Spinform Corporation of Livonia, Michigan. Spheres were drawn out of stainless steel sheets by hydroforming process which retained a uniform thickness from the equator to the pole.

For loading and unloading the calorimeter, a valve core, of the type used in automobile tires, was mounted in a brass fixture of 1/8 inch pipe thread. In order to reduce the effect of the brass fixture as a possible source of heat sink, it was machined to about 10 grams from the original weight of about 20 grams. This also helped in the reduction of the heat capacity of the calorimeter by about 1 cal/°C or approximately 3% . The brass fixture was silver soldered to the wall of the calorimeter. The valve cores were supplied by Schrader Company of Brooklyn, New York with specially made Teflon seats for freon refrigerants. A metal cap was screwed on the brass fixtures to prevent loss of gas in case of leaks through the valve core. Inside the sphere a brass deflector was silver soldered near the valve to act as a baffle when the calorimeter

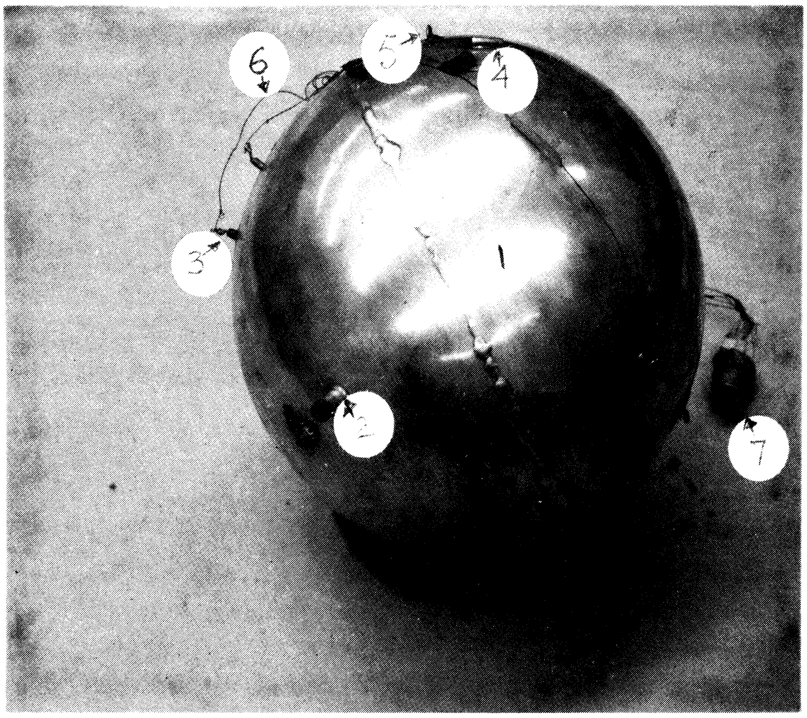

Figure 3-1. The Calorimeter.

(1) The Calorimeter Shell.
(2) Brass Valve.
(3) Stupakoff Terminals.
(4) Thermocouple Wells.
(5) Mounting Rings.
(6) Lead Wires.
(7) Coaxial Plug.

was loaded and thus the delicate electrical system inside the sphere was protected from mechanical disturbance.

Six Stupakoff terminals (Kovar glass seals) Part No. 95.0001 Figure 1-1 , were silver soldered into the wall of the calorimeter with their flanges pressing against the inside surface of the sphere. Four terminals were placed in the upper hemisphere and two in the lower.

The two hemispheres were silver soldered with a back up ring (1/4 inch wide) inside. The calorimeter was then silver plated to improve the heat transfer by radiation.

Three brass rings were silver soldered to the wall of the calorimeter for mounting purposes. Three 20-gauge copper tubings (0.125 in. o.d., 0.0635 inch i.d., and 1/2 inch long) were silver soldered to the calorimeter to be used as thermocouple wells.

On the basis of the yield strength of 40,000 p.s.i. for 301 stainless steel, the calorimeter was designed for a working pressure of 170 p.s.i. However, during silver plating an accidental mishap resulted in the calorimeter popping out of the silver cyanide bath and bumping against an electrode rod with considerable force. The damaged area squeezed inside and the calorimeter was brought back to the spherical shape by pressurizing. But a permanent V-shaped dent remained on the wall of the calorimeter. For fear of collapse because of this dent, the calorimeter was never evacuated in open atmosphere. For safety reasons, therefore, it was decided not to operate the calorimeter beyond 125 p.s.i. and a temperature of 150°C.

The volume of the calorimeter was determined by measuring the temperature, pressure, and mass of nitrogen gas charged. The volume was found to be 4530 c.c.

III-3 Calorimeter Heaters and Thermometer:

Since the success of the experiment depended much upon the reduction of the weight and hence the heat capacity of the calorimeter, the design of Schwing(57) for uniform heating was chosen instead of a heating system with an internal motor stirrer of Hwang(41) and DeNevers.(14)

In order to design a uniform heating system which would result in small temperature gradients around the sphere, the power input per unit volume of the calorimeter i.e. $I^2R/(4\pi r^2)(dr)$ should be maintained constant. This means that the resistance of the heating wire would increase as the square of the radius from the center of the sphere. This was achieved in practice by winding the platinum heating wire around a mica cross with a linear increase in the length of each coil and a linear increase in the frequency of winding. Using a template, triangles were cut with a base of two inches and a height of four inches from mica sheets. Using the same template, holes were drilled on, the mica sheets on both sides of the triangle as shown in Part B, Figure 3-3. Four holes were drilled for the first inch, six holes were drilled for the second inch, eight holes were drilled for the third inch and four holes were drilled for the last half inch. Notches were made by cuts from the sides up to each hole.

For each heater assembly, two mica triangles were used. Both triangles were incised about two inches through the vertical, one from the center of the base and the other from the vertex. A pyramidal shape was made by locking the two triangles through the incisions. The mica pyramid was put on a rig and thermocouple grade platinum ribbon, 0.0005 inch by 1/32 inch, was wound around the notches, Figure 3-2 .

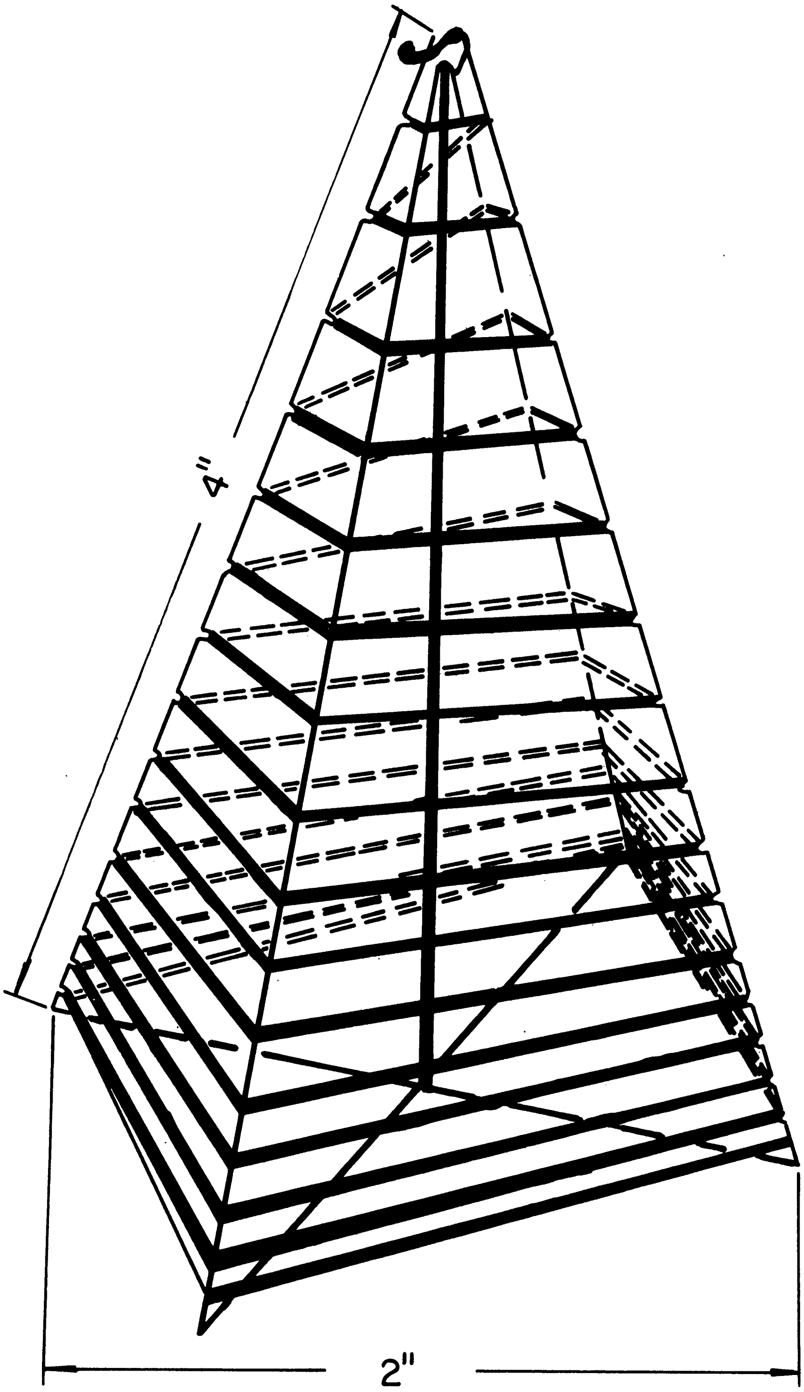

Figure 3-2. Platinum Resistance Ribbon Coiled on Mica Cross.

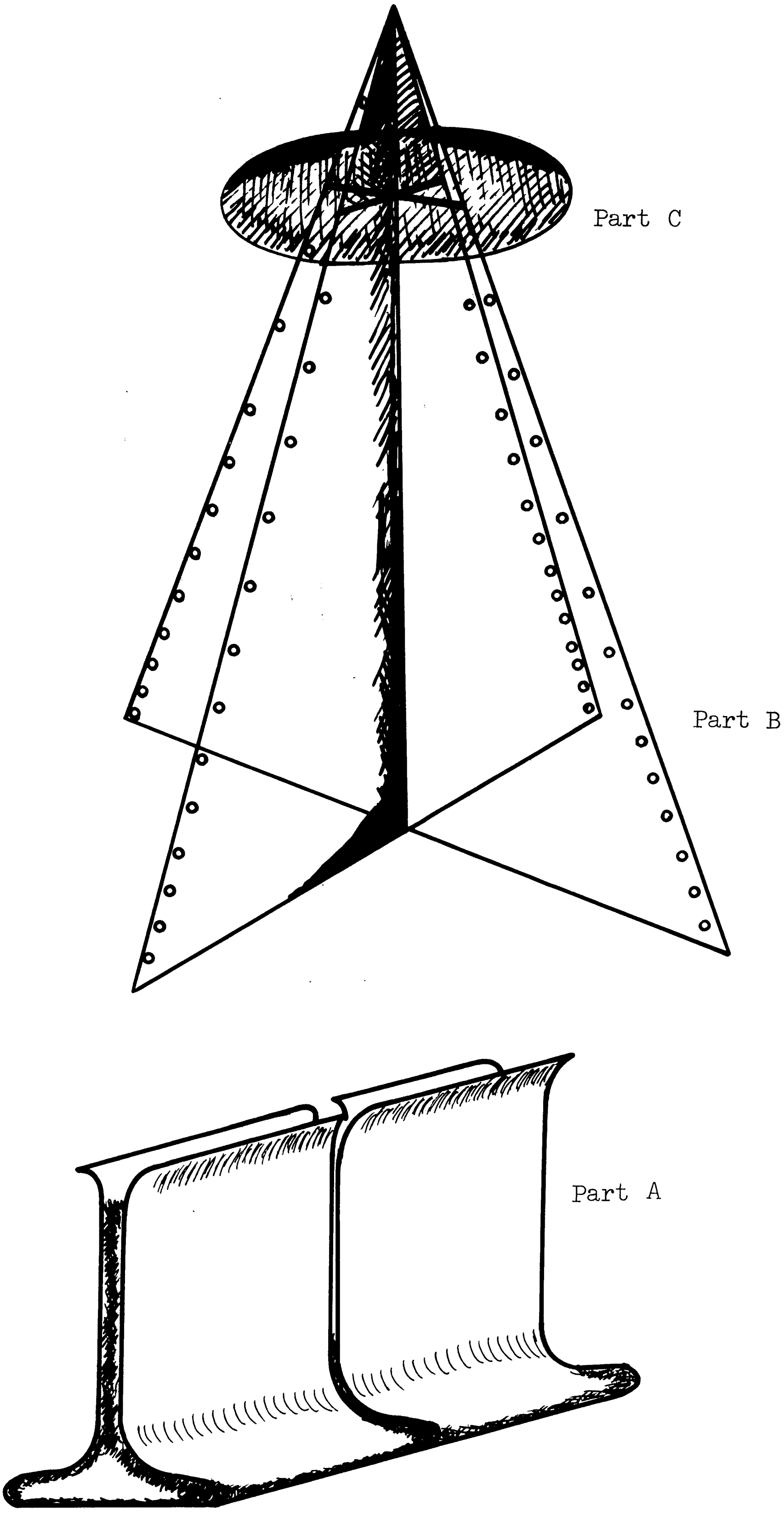

Figure 3-3. Assembly of Heaters.

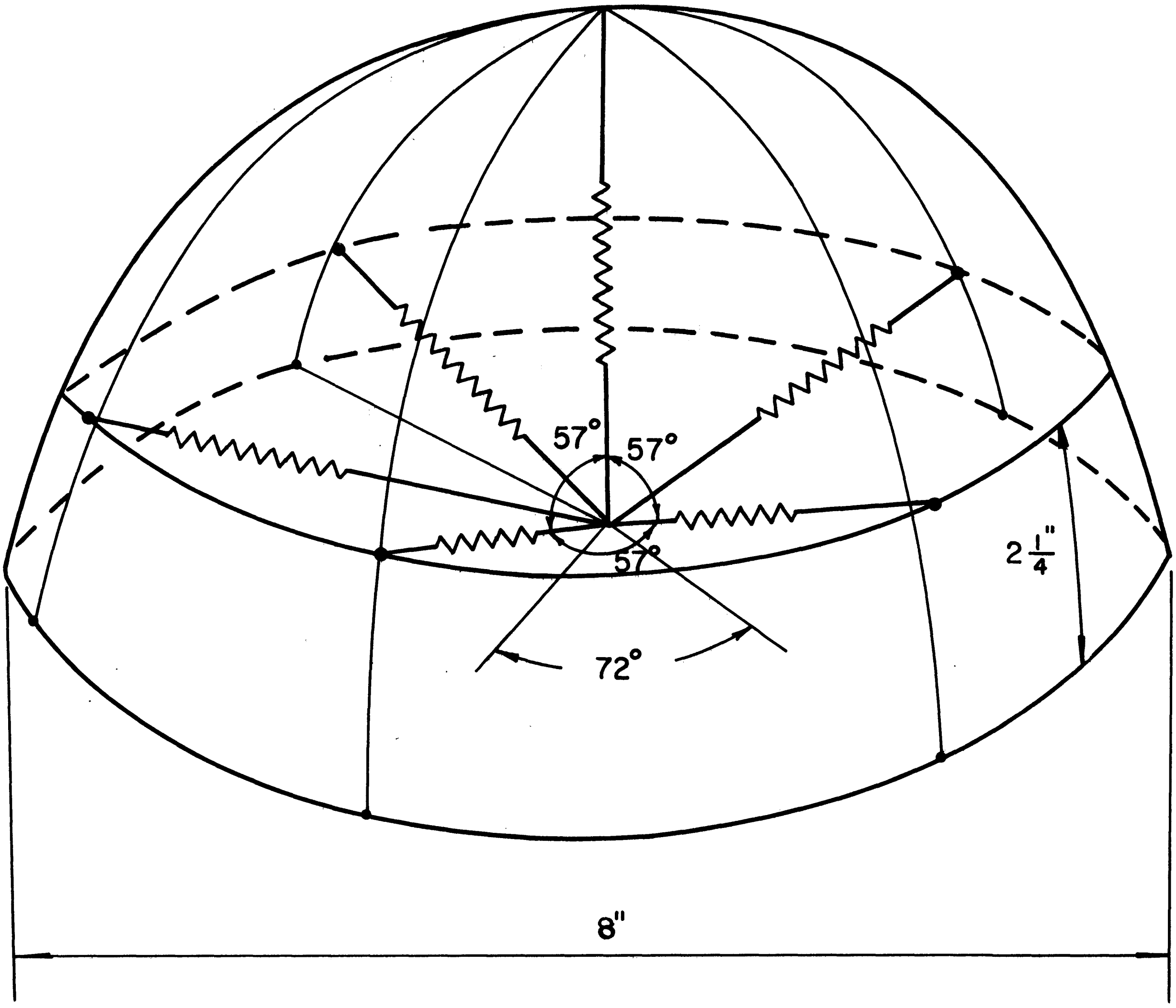

Figure 3-4. Schematic Location of Heaters in Each Hemisphere.

The specially made ribbon was supplied by the Baker Platinum Division of New Jersey. Each heater required approximately six feet of ribbon and had a resistance of about 24 ohms at room temperature.

Twelve such heaters were erected, six in each hemisphere. One heater was on the pole and five others along the circumference in equal spacings. In each hemisphere, the solid angle between each heater and its three neighbors was approximately equal to 57°, Figure 3-4. Each heater was first annealed at a temperature of 1100°F before being installed in the sphere. The whole heating system after being installed was further annealed by passing about 500 watts overnight.

The uniform heating system worked satisfactorily during the entire experiment. With proper manual control of the shield, the temperature gradient between the top and the bottom of the sphere could be maintained, on the average, within ± 0.5°C.

III-4 General Fabrication and Circuitry:

In each hemisphere, where the heaters were placed, six holders 0.003 inch thick, Part A, Figure 3-3, made out of heat treated phosphor-bronze sheet, were silver soldered to the wall of the calorimeter. The heaters were inserted into the holders and were firmly held in position by supporting copper wires which were knotted to the mica structure of the heater and then silver soldered to the wall of the calorimeter. A notched mica disc followed by a notched platinum disc, Part C, were then cemented over the heater at the pole of the hemisphere, Figure 3-3. The wire endings of the heaters were then silver soldered to the wall of the calorimeter and the platinum disc. The same technique was used for the other hemisphere. Electrical connections were made between the

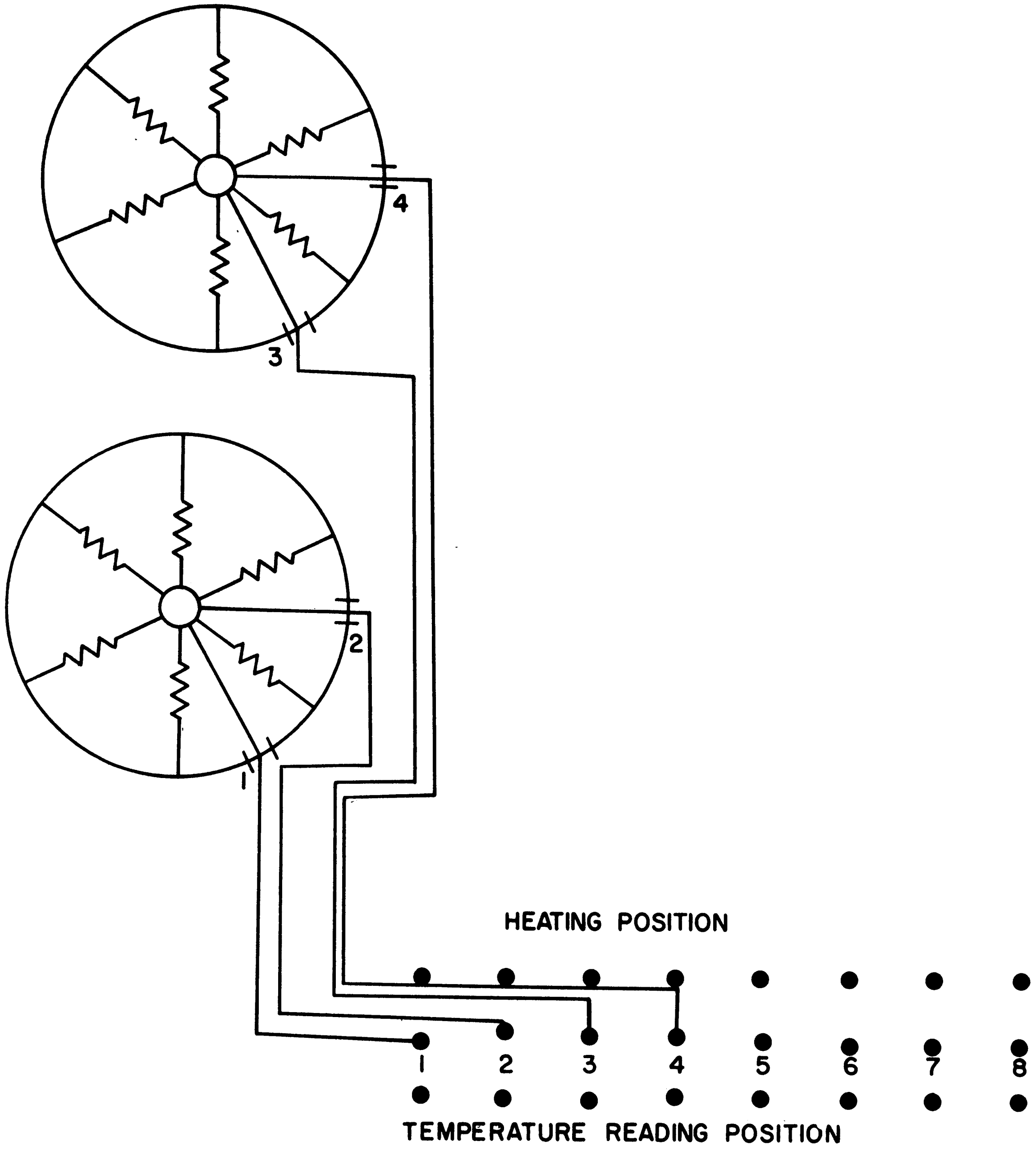

Figure 3-5. Schematic Representation of the Electrical Circuitry of the Calorimeter.

platinum disc and the Stupakoff terminals with copper wires. The electrical circuitry is schematically shown in Figure 3-5 . The circuitry is such that all the heaters acted as a single resistance thermometer. This resulted in an integral temperature measurement of the calorimeter and its contents. This also gave a fair estimate of the average temperature of the calorimeter and its contents during the heating period.

III-5 Radiation Shield:

The radiation shield for minimizing the heat losses to the surroundings and improving the adiabaticity of the calorimeter comprised of two 12 inch i.d., 1/4 inch thick copper hemispheres. Three baffle plates, made of copper sheets, 1 1/2 inch wide by 2 1/2 inch long and 1/16 inch thick, were placed in front of three 7/8 inch diameter holes on the contact the edges of the hemispheres to facilitate evacuation. The baffle plates were shaped in a way that the clearance between the shield and the baffle was approximately 3/8 inch. The base of the baffle plate was held by two 1/8 inch brass screws. Each baffle plate had 1/8 inch diameter hole near the top for suspending the calorimeter. Three brass legs of 1/2 inch diameter were brazed to the lower shield to position the shield in the center of the vacuum container. Three small pieces of copper blocks, held to the bottom hemisphere with 1/8 inch screws, were used to center the upper hemisphere.

The outside of each shield was bonded with two electric heaters, Type No. 5220 from Electrofilm, Incorporated. The heaters were made up of a wire mesh designed and fabricated by Electrofilm. The variation in wattage in each shield was less than ± 10% . The power capacity was over 5000 watts. Any variation in wattage was largely damped by the 1/2 inch thick copper shell.

To minimize heat-leakage to the vacuum container through the three brass legs a single heating tape was wound around the three legs.

Two variacs, 0-110 volt, 15 amp., supplied the power to the two shield heaters and one variable transformer, 0-110 volt, 8 amp was used for the leg heater.

III-6 The Thermocouples

For the accuracy in experimental measurements, temperature control between the calorimeter and the shield heater was absolutely necessary. As in the works of Hwang(41) and Schwing(57), three control points (top, side, and bottom) were used along the surface of the calorimeter. Also on the radiation shield corresponding points were selected. Since the radiation shield consisted of two hemispheres, two points were chosen, one in each hemisphere but closely located.

Seven copper-constantan differential thermocouples indicated the temperature difference between any two points. All the constantan wires were brought to a common junction within the vacuum container junction board. The temperature difference between any two control points was indicated by the deflection of a light beam through a moving coil galvanometer, Leeds and Northrup No. 1193782. The circuitry consisted of an eleven point, double pole, rotary switch, Leeds and Northrup Type 8240, No. 1210525, and the galvanometer. The deflection of the light beam was read on a frosted glass scale, graduated from 0-30 cm to the left and to the right. A deflection of 1 cm corresponded to 0.02°C temperature difference. Two resistors (1000 and 10,000 ohms) were put in series with the galvanometer to control the sensitivity of the galvanometer, if necessary. The circuit diagram for the entire thermocouple

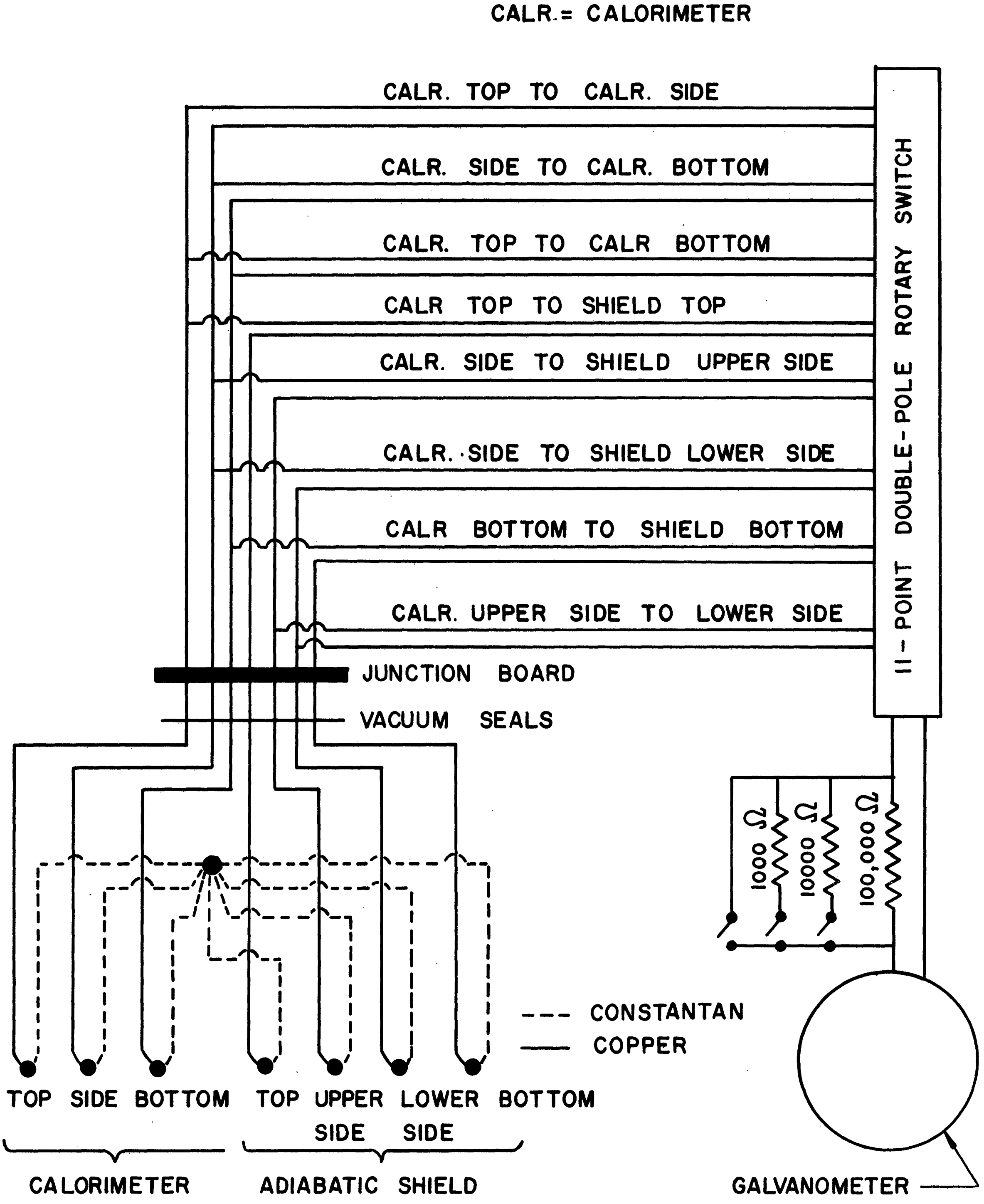

Figure 3-6. Circuit Diagram of Thermocouples.

system is shown in Figure 3-6. The thermocouples were placed in thermal but not electrical contact with various surfaces for which insulated thermocouple wells were used at various control points. The wells were made of 20 gage copper tubing (0.125-in. o.d., 0.0635 in i.d., and 1/2 in. long), and were silver soldered to the radiation shield or calorimeter. The thermocouples were insulated with Teflon tubing (0.052 in., o.d. and 0.030 in. (i.d.)) and were coated with vacuum grease and forced into the copper tube.

III-7 The Vacuum Container

With a view to reducing the heat transfer by convection, the calorimeter and the radiation shield were housed in a vacuum chamber which also was a safety provision in case of explosion of the calorimeter.

Each half of the vacuum container was fabricated by welding a "Taylor Forge" 16 inch schedule 80 welding cap to a "Taylor Forge" 16 inch 300# slip-on flange. The flange was 2 1/4 inches thick and the container 0.843 inches thick. The vacuum container weighed about 680 pounds. After welding it was found that the flanges were slightly warped and gave about 3/16 inches clearance at the outer edge. Three legs, each made of 3 by 1 1/2 by 2 1/2 inch channel, were welded to the bottom of the vacuum container and bolted to a concrete slab.

The vacuum seal between the two flanges was accomplished by a silicone rubber "O"-ring provided by Precision Rubber Products Corporation (PRP6543, i.d. 17.000 in., having a cross section of 0.275 in. and made out of a compound 1130-80). On the lower flange a groove was machined for the "O"-ring with the following dimensions: groove i.d. 17.000-.005 + .000 in., groove depth: .225 ± .005 in., groove width, approximately

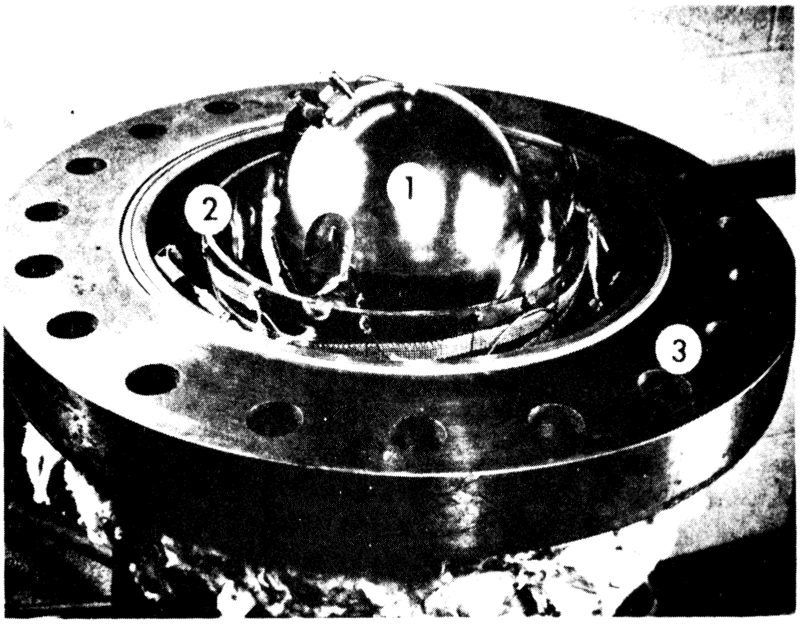

Figure 3-7. Calorimeter, Shield, and Vacuum Container in Their Relative Positions.

(1) Calorimeter.

(2) Adiabatic shield, showing three baffle pieces which also serve as the suspension frame for the calorimeter.

(3) Vacuum container, showing a silicone rubber "O"-ring in the groove, and Fiberglas insulation outside the container.

0.375 in. Seven-eighths inch copper tube connected the container to the vacuum system. Twenty 1-1 1/4 by 6 inch machined bolts were used to bolt the two flanges. A 1/2 ton chain hoist was used to lift the upper half of the container which had an iron ring welded to the top. It rolled on an overhead track made up of a 6 inch by 3 1/2 inch I-beam 6 feet long. Six leads of the shield heaters were taken out of the vacuum container through a Stupakoff multi-terminal heater, No. 25.4003 which was silver soldered to a two inch long stainless steel tube welded to the wall of the container. The thermocouple leads together with the calorimeter leads were led to the outside junction box through a six foot long tygon tubing. The lower half of the vacuum container was insulated by 2 inch thick Fiberglass and a removable mat of Fiberglass was placed on the top of the container before the start of the experiment.

The entire vacuum container, shield and the calorimeter, Figure 3-7 , were housed in a steel cabinet for additional safety measures. The steel cabinet, approximately 2 by 3 1/2 by 8 feet in size was bolted to the concrete slab, cast into the rectangular frame made of six by two inch channel. The frame of the cabinet consisted of 2 by 2 by 3/8 inch angles to which were attached 1/4 inch hot rolled steel sheets. Two doors each 4 by 8 feet, were fixed to the cabinet by four 1/2 inch hinges. Four 3/4 inch bolts were used to close the doors. Since the rear of the cabinet had no steel sheet, in case of rupture, pieces were expected to fly in the direction of the window to the outside.

III-8 Electrical Junction Box:

A separate electrical junction box was installed to avoid spurious thermal e.m.fs which could be produced by temperature gradients across the vacuum container. This was connected to the container wall through a six foot long piece of tygon tubing.

The junction box was a 500 c.c. stainless steel beaker. A piece of stainless steel tubing was silver soldered to the bottom and a 1/8 inch thick, one inch wide, steel flange was silver soldered to the top. The matching brass plate and the flange were held together with eight 1/4 inch bolts. An "O"-ring was used between the flanges as vacuum seal. Two Stupakoff eight terminal Kovar-glass headers, No. 95.4003, were soldered to the brass plate. Of the total 16 terminals, six were led to the calorimeter, seven were used for differential thermocouples, two for spare wires and one was not used. All the wires used were 30 gauge copper Formvar and Fiber glass insulated.

III-9 The Vacuum and Loading System:

Figure 3-8 is a schematic diagram of the vacuum system consisting of a Cenco Hyvac No. 2 pump which exhausted to the atmosphere and maintained an inlet pressure of about 50 microns of mercury. A pipe connected this pump to the outlet of a VMC diffusion pump for reducing the pressure to about one micron of mercury. For the measurement of the pressure, a Lippincot-McLeod gauge was connected to the vacuum container via flexibl "Tygon" tubing and copper tubing. 5/8 inch long pieces of glass tubing were inserted into the Tygon tubing to prevent it from collapsing during evacuation. In front of the Mcleod gauge, a "Lucite" shield, 8 inches b 12 inches by 14 inches thick was mounted to prevent flying glasses in case the calorimeter ruptured.

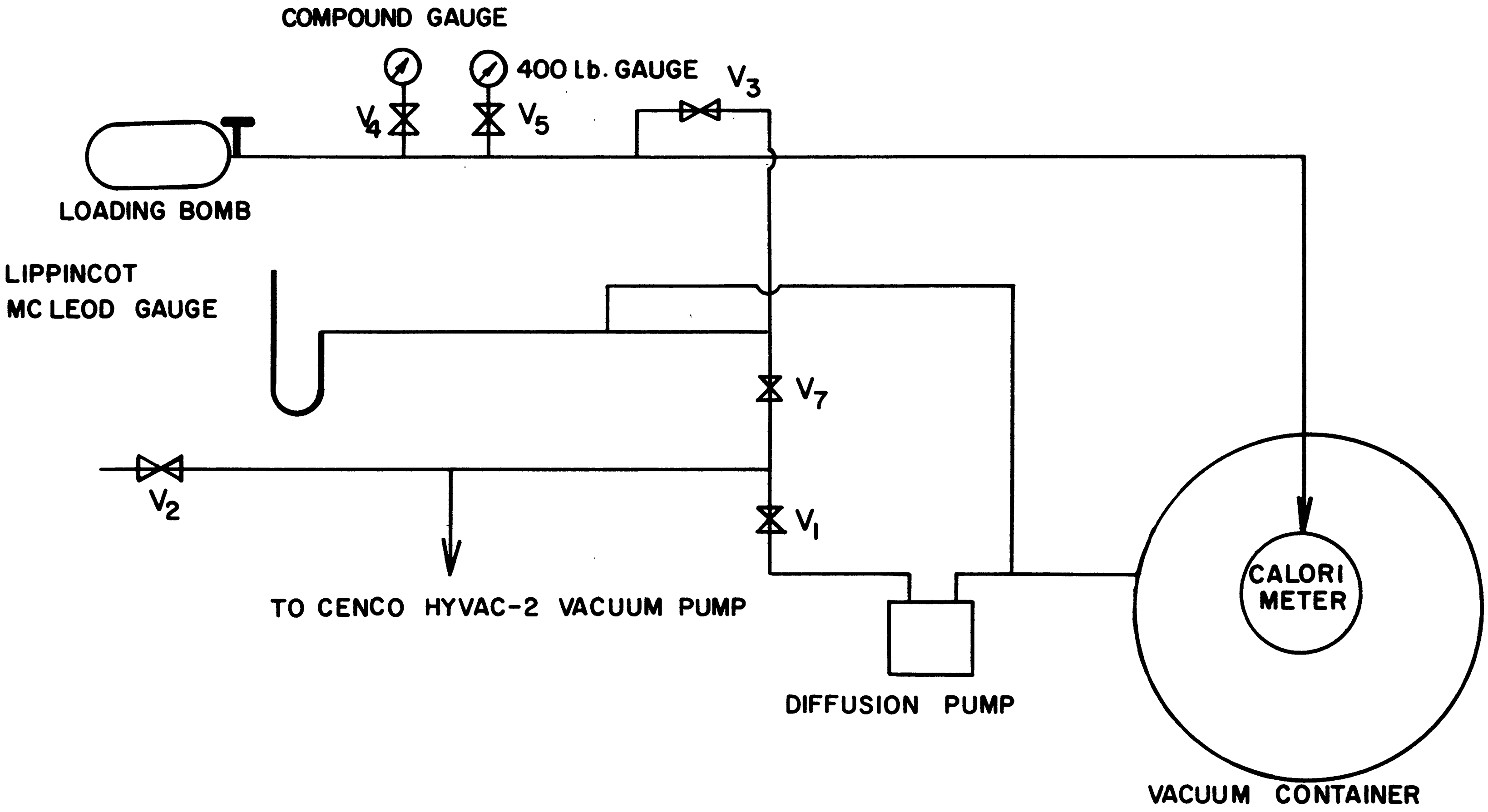

Figure 3-8. Schematic Diagram of the Vacuum and the Loading System.

Copper tubings, 1/4 inch and 7/8 inch nominal diameter, were used for the vacuum system. The valves were Imperial Diaphragm type vacuum valves.

With the valve V_2 closed and all other valves open, the mechanical pump was turned on. This evacuated the calorimeter and the vacuum container simultaneously since it was desired to evacuate the calorimeter in evacuated surroundings to avoid any collapsing of the calorimeter. Then with the valve V_7 closed, the diffusion pump was turned on. During loading the valves V_3 and V_7 were kept closed.

III-10 The Measuring System:

Two basic circuits were used for the measuring system as shown in Figure 3-9. One was for temperature measurement, and the other for measuring the power input to the calorimeter. Four electrical lead wires, about 18 inches long, were led from the calorimeter to a co-axial plug, the female part of which was mounted on the lower shield for attaining flexibility in the removal of the calorimeter for loading and weighing. From the female plug lead wires ran into the junction box described in Section III-8, and from there to the 8-pole double throw master switch which completed the power circuitry and temperature measurement circuitry in the "up" and "down" position respectively. Power was supplied by two 12 volt batteries put in parallel. A battery charger was used for recharging when not in use.

The power circuitry consisted of lead wires one and four, the balancing resistor, auto batteries, the resistance circuitry of the calorimeter, a two-amp fuse, milliammeter, and a 0.1 ohm standard resistor. Leads two and three were taken to a potential dividing circuit

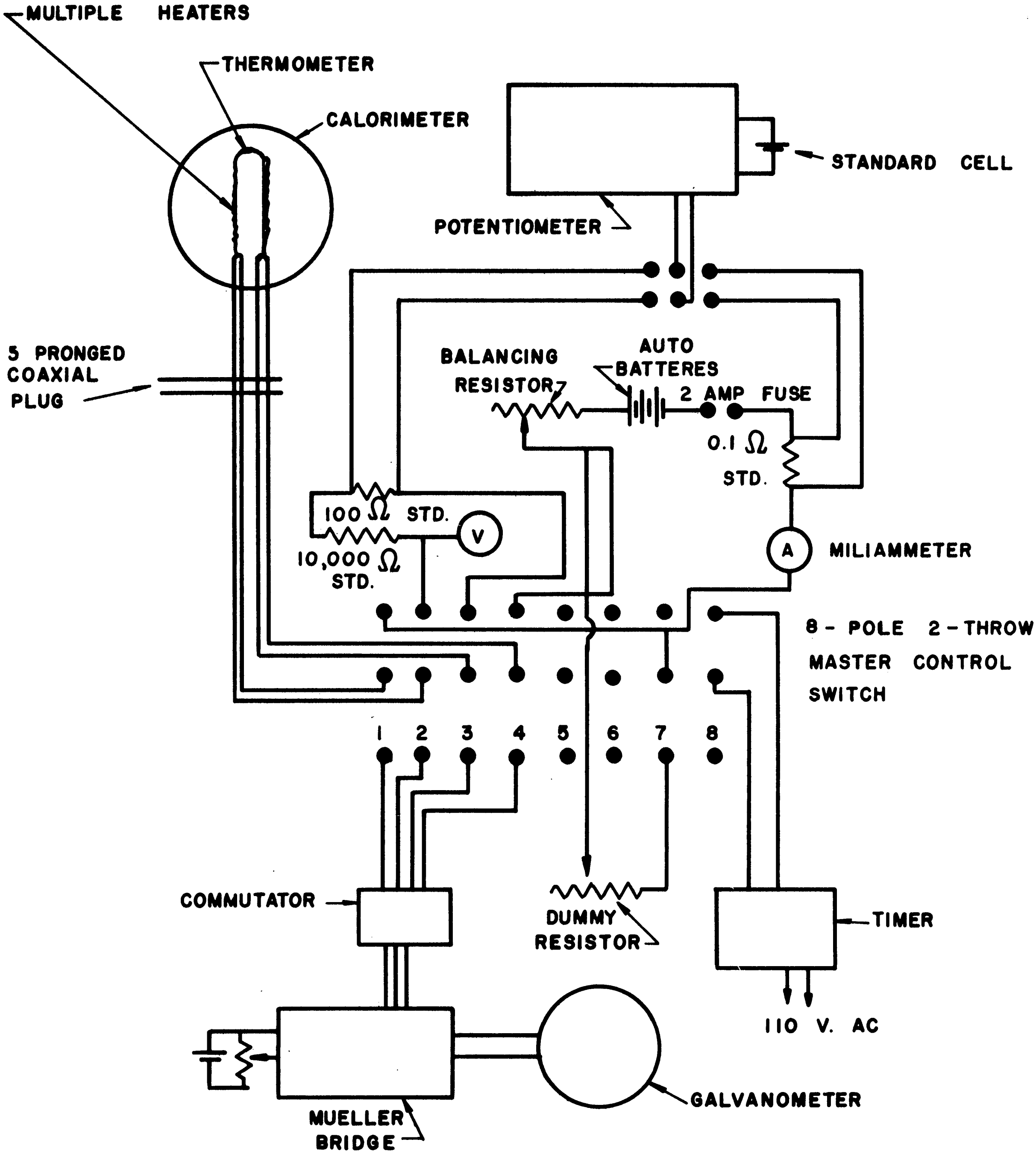

Figure 3-9. Circuit Diagram of the Measuring System.

consisting of a standard 100 ohm resistor, Leeds and Northrup Type No. 4030-B, Serial No. 1508856, a standard 10,000 ohm resistor, Leeds and Northrup Type No. 4040-B, Serial No. 1201941, and a volt meter. The 100 ohm resistor is accurate to within ±0.01% as certified in the spring of 1961 whereas the o.1 ohm and 10,000 ohm resistors were certified in the fall of 1956 with same accuracy. The voltage drop across the heater in the calorimeter was estimated by measuring the voltage drop across the 100 ohm resistor. All standard resistors were kept in an oil bath 10 inches by 7 inches by 5 inches, made of stainless steel pan filled with SAE 20 motor oil to avoid fluctuations in room temperature.

A Leeds and Northrup portable precision potentiometer, No. 8662 Serial No. A1272, was used for determining the voltage drop across the standard resistors. This potentiometer had a self-contained galvanometer and a standard cell which was calibrated against a Weston standard cell. 1 1/2 volt dry batteries were used for power requirements of the potentiometer. A two-pole double-throw switch connected the potentiometer either to the 0.1 ohm resistor or to the 100 ohm resistor according as the measurement of current and voltage was desired.

A 0-800 milliammeter and a 0-25 v. voltmeter, Figure 3-9, indicated approximately the current and voltage in the power circuitry.

A balancing resistor was connected in series with the thermometer-heater to minimize the fluctuations of power input to the calorimeter as suggested by Hoge.(25) The balancing resistor was a 10 ohm sliding-contact Ohmite No. 0145 resistor.

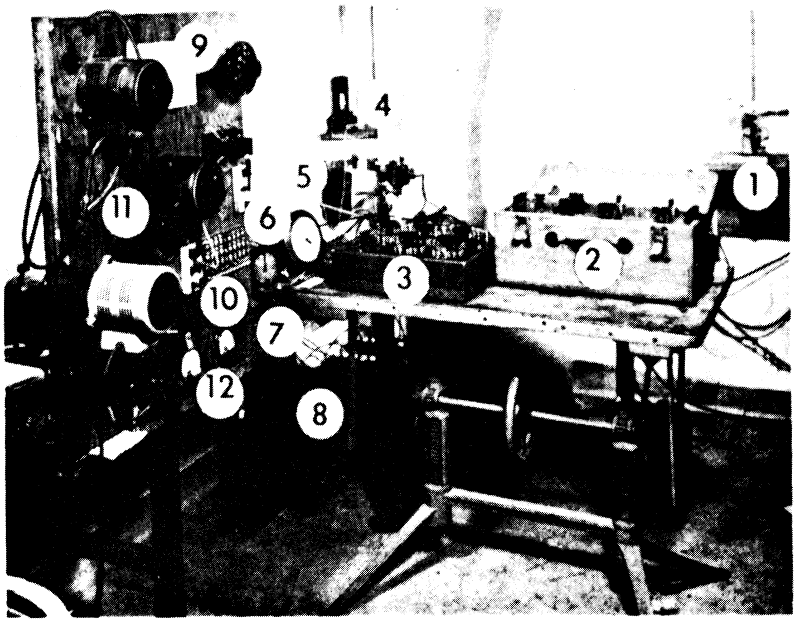

Figure 3-10. Control and Measuring Instruments.

(1) Lippincot-McLeod gauge.

(2) Potentiometer.

(3) Mueller bridge.

(4) Galvanometer, light and scale.

(5) Battery charger.

(6) Clock and timer.

(7) Balancing and dummy resistor.

(8) Lead storage batteries.

(9) 11-point 2-pole selector switch.

(10) 8-pole double-throw master control switch.

(11) Powerstats variable transformers.

(12) Milliammeter and voltmeter.

The time of heating the calorimeter was measured by a synchronous timer with an electrically actuated clutch (Standard Electric Time Company Model S-6). The 8-pole double throw switch engages and disengages the clutch of the timer.

Figure 3-10 illustrates the control and measuring instruments used in this experiment.

IV. EXPERIMENTAL PROCEDURE

IV-1 Loading the Calorimeter:

The calorimeter was placed in the vacuum container. A diffusion pump together with a roughing pump built a vacuum of 1 micron in the whole system including the loading lines that run from the gas shipping container. The gas was then forced into the calorimeter. The calorimeter was purged with small amounts of gases several times and was evacuated to about 5μ each time. Before the charge was made, the calorimeter was heated to approximately 100°C to take care of degassing problems. A high pressure gauge on the loading line approximately indicated the amount of charge in the calorimeter. In the case of dichlorofluoromethane, the shipping container was placed on a 2 Kg crude balance to get an idea of how much amount of gas had flown into the calorimeter. After charging the calorimeter was weighed and the weight is believed to be accurate to within ± .03 gms . After a series of runs at one density, the total weight of the calorimeter plus gas was checked.

The calorimeter and the radiation shields were polished to reduce radiant heat transfer. The calorimeter was positioned with fiberglass strings in the lower radiation shield. All thermocouples were put in respective control points. The top shield was then placed over the lower shield with the calorimeter in the right position. The heating leads of the radiation shields were electrically connected by means of co-axial plugs. The "O"-ring was then placed in the groove of the vacuum container and then the upper half of the vacuum container was lowered into position. Twenty 1 1/4 inch bolts were used to hold the flanges of the vacuum container. The Fiberglass insulation was put over the vacuum container and the system was then evacuated.

IV-2 Operating the Calorimeter:

When the system was evacuated to about 1 micron, a series of experimental measurements was started for a particular charge of gas, from a temperature of about 30°C. Each normal run was divided into three different periods: the temperature measuring period, the heating period and another temperature measuring period. In case of consecutive runs, the second temperature measuring period was used as the initial temperature measuring period of the next run.

During a particular run, the most important and difficult problem was the control of temperature differences between the shield and the calorimeter. Theoretically one desires zero temperature difference between the control points of the calorimeter and those of the shield. In practice, this was not true as indicated by the differential thermocouples. For various densities of charges and at various temperatures, the temperature difference between the control points was on the average 0.1°C during the temperature measuring periods and about 0.2°C during the heating period.

During the initial temperature measuring period, several resistance readings were taken with a Mueller bridge at five minute intervals and at the same time zero average temperature difference was maintained between the shield and the calorimeter. Connections to the resistance thermometer in the calorimeter were made through a Leeds Northrup mercury cup commutator for normal and reverse resistance readings. The average of these readings was the true temperature because the lead resistances were cancelled. Once the rate of change of temperature with respect to time, i.e. "drift," had been established, the heating period was started by switching the 8-pole double throw to the "up" position. This started the heating of the calorimeter, and engaged the clutch of the timer and disconnected the Mueller bridge to prevent any current flowing through it. The heating period lasted for 30 minutes and the temperature rise was generally on the order of 10 °C . A minute earlier of the heating period, a burst of power was given to the shield, considering its slow response, to match the calorimeter temperature when the heating period started. During the heating period, attentive manual control of the shield was maintained to have zero average temperature difference between the control points of the shield and the calorimeter. The differential thermocouple readings were taken every two minutes.

The heat input to the calorimeter was estimated by taking current and voltage readings in quick intervals every eighth minute from the start of the heating period. Two current readings, before and after the voltage reading, established the average current reading at the time of voltage measurement. The current was determined by measuring the voltage across the 0.1000-ohm standard resistor and the voltage by measuring the potential drop across the voltage dividing circuit consisting of 100.00 ohms and 10,000.00 ohms standard resistors.

The 8-pole double-throw master switch was placed in the temperature measuring position to terminate the heating period. This disengaged the timer and the Mueller bridge was put into circuitry. The time was read from the timer which was reset to zero for the next run. The power to the shield was cut down appreciably just about a minute before the end of the heating period so that the temperature difference between the shield and the calorimeter did not go out of control.

The calorimeter was then allowed to equilibrate in temperature for ten minutes maintaining good control between the shield and the calorimeter. Then followed the final temperature measuring period. Resistance readings were noted every five minutes until the final drift rate was properly established. Usually eight resistance readings were taken. The final drift rate was used as the initial drift rate for the next run.

IV-3 Changing the Density:

After a series of runs at a given density, preparations were made for the next run. The old check-valve was replaced by a new one and the calorimeter was reloaded as outlined before. The calorimeter performed without leaks.

V. METHOD OF CALCULATION OF GROSS HEAT CAPACITY, ANALYSIS OF HEAT LOSS CORRECTION AND ESTIMATION OF ACCURACY

V-1 Method of Calculation of Gross Heat Capacity:

In the case of a perfectly adiabatic calorimeter, the gross heat capacity, C_{gross} can be expressed as:

$$\int_{T_1}^{T_2} C_{gross}\, dT = \int_{\theta_1}^{\theta_2} q\, d\theta \tag{5-1}$$

where q is the rate of heat input during the time interval from θ_1 to θ_2 and the temperature rise from T_1 to T_2. For a small temperature interval, (C_{gross}) mean may be defined at the mean temperature as

$$(C_{gross})_{mean} = \frac{\int_{\theta_1}^{\theta_2} q\, d\theta}{\int_{T_1}^{T_2} dT} = \frac{q_{mean}\, \Delta\theta}{\Delta T} \tag{5-2}$$

In actual calorimetric measurement such as this, there is always a definite heat leakage to the surroundings from the calorimeter. Therefore, for any reliable measurement an accurate estimation of the heat leakage is essential. Equation (5-2) can then be written as:

$$(C_{gross})_{mean} = (q_{mean} + q_{corr})\, \frac{\Delta\theta}{\Delta T} \tag{5-3}$$

The heat leakage can, however, be expressed in terms of an equivalent temperature change ΔT_{corr}, that is the temperature change that would have occurred had there been no heat loss to the surroundings. Equation (5-3) can then be modified as:

$$(C_{gross})_{mean} = \frac{q_{mean}\, \Delta\theta}{(\Delta T - \Delta T_{corr})} \tag{5-4}$$

In this experiment ΔT_{corr} is calculated from the average of the initial and final drift rates as explained fully in Section V-2. C_{gross} is calculated from Equation (5-4) as shown by a sample calculation in Appendix B.

V-2 Analysis of Heat Loss Correction:

As has been pointed out in the previous section, an accurate estimation of the term ΔT-ΔT_{corr} for heat losses is needed for the calculation of the gross heat capacity. It is, therefore, considered mandatory to fully explain that term and its physical implications. In the experimental set-up shown in Figure 3-7, as soon as the temperature of the calorimeter was higher than that of the vacuum container and the surroundings outside it, the radiation shield being at approximately the same temperature as that of the calorimeter, it is noted that the calorimeter started losing heat as shown by its temperature drop with time. The heat loss was believed to be mainly by conduction through the wires leading from the calorimeter to the surroundings and partly by convection and radiation because the shield could not be maintained at perfect thermal equilibrium with the calorimeter. The rate of temperature change of the calorimeter or drift rate was experimentally observed to follow Newton's law of thermal leakage i.e. at any temperature the rate of heat loss from the calorimeter to the surroundings was found to be proportional to the temperature difference between the calorimeter and the surroundings.

Mathematically, it can be formulated as:

$$-\left(\frac{dQ}{d\Theta}\right)_{loss} = \kappa(T-T_s) \qquad (5\text{-}5)$$

where $-\left(\frac{dQ}{d\Theta}\right)_{loss}$ is the rate of heat loss, κ is the thermal leakage modulus, T the temperature of the calorimeter and T_s the temperature of the surroundings.

On the basis of the assumptions that (a) the calorimeter and its contents are at a uniform temperature T, and (b) the radiation shield is always near thermal equilibrium with the calorimeter (i.e. $T_{shield} \cong T$), the following differential equation can be written from an energy balance of the calorimeter:

$$C_{gross} \frac{dT}{d\Theta} + \kappa(T-T_s) = q \qquad (5\text{-}6)$$

where C_{gross} is the gross heat capacity of the calorimeter and its contents and q is the rate of heat input. The above Equation (5-6) can also be written in the form of an integral equation as:

$$(C_{gross})_{mean}\, \Delta T + \kappa \int_0^{\Theta} (T-T_s)\, d\Theta = q_{mean}\, \Delta\Theta \,. \qquad (5\text{-}7)$$

where the term $\kappa \int_0^{\Theta} (T-T_s) d\Theta$ accounts for the total heat loss to the surroundings. Had there been no such heat loss, i.e. the calorimeter was perfectly adiabatic, the temperature of the calorimeter and its contents would rise by an amount, say ΔT_{corr}. Therefore it follows:

$$-\,(C_{gross})_{mean}\, \Delta T_{corr} = \kappa \int_0^{\Theta} (T-T_s)\, d\Theta \qquad (5\text{-}8)$$

For a small temperature rise of about 10°C of the calorimeter during the heating period, if one assumes that T_s does not significantly change and $(C_{gross})_{mean}$ and q_{mean} can be used in the Equation (5-6), the analytical solution of the Equation (5-6) can be expressed as:

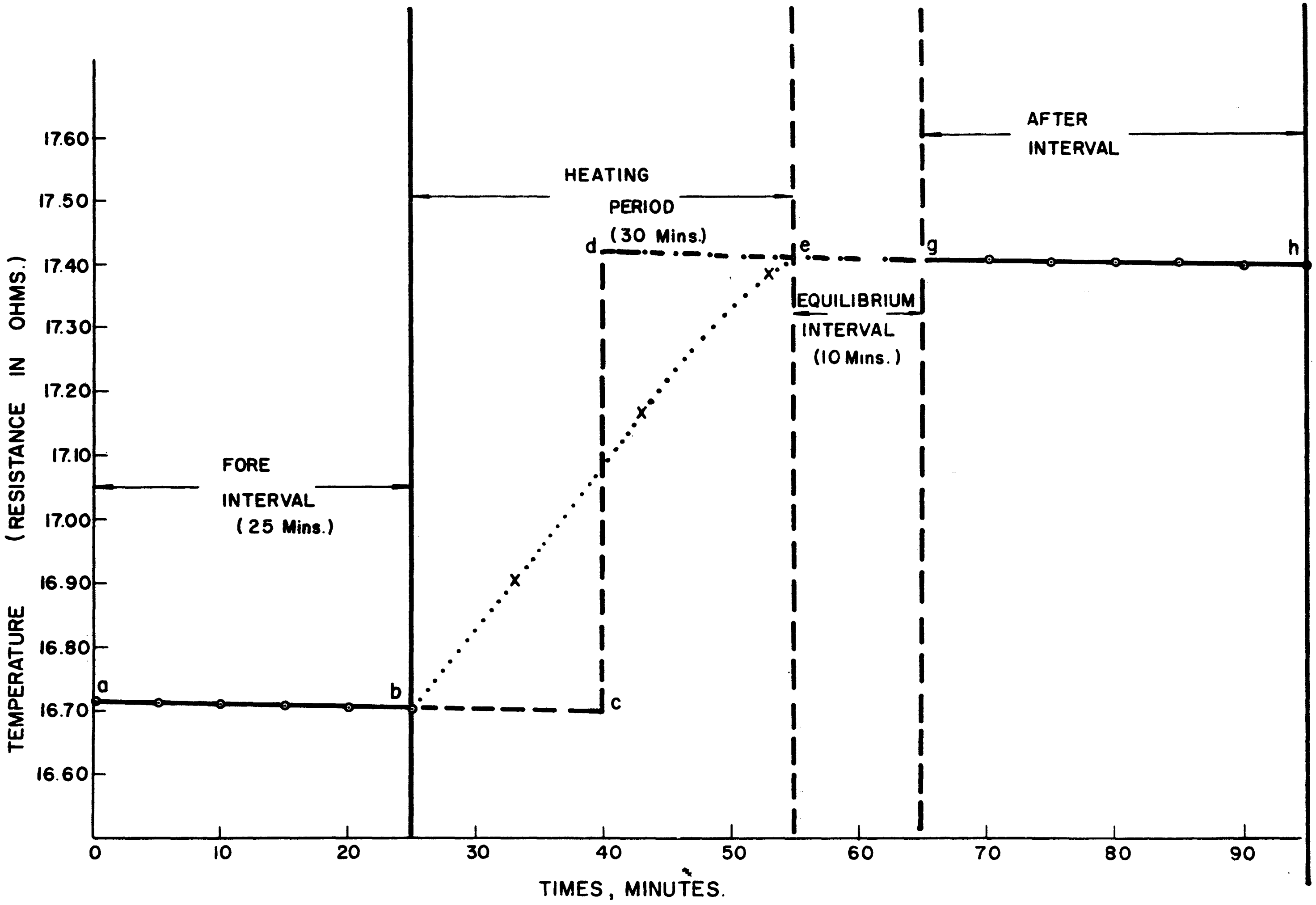

Figure 5-1. Temperature Versus Time Plot for the Calorimeter.
(Run No. F-22-G-2)

$$T-T_s = \frac{q_{mean}}{\kappa} + (T_b-T_s-\frac{q_{mean}}{\kappa})\, e^{-\frac{\kappa}{(C_{gross})_{mean}}\theta} \qquad (5\text{-}9)$$

where T_b is the initial temperature of the calorimeter and its contents. The Equation (5-9) describes the temperature profile of the calorimeter as a function of time during the heating period. For an accurate estimation of $(C_{gross})_{mean}$, Equation (5-9) has very limited use because (a) the physical quantities κ and T_s are not known from experimental measurements (b) the calorimeter and its contents are not at a uniform temperature (c) no accurate measurement of the temperature of the calorimeter and its contents is made during the heating period, although from the voltage and current measurements one can calculate such a temperature with fair approximation.

In actual practice, it was, therefore found more convenient to calculate $(C_{gross})_{mean}$ from the Equation (5-10), which is obtained by substituting the Equation (5-8) into the Equation (5-7) and rewriting as:

$$(C_{gross})_{mean}\, \Delta\tau = q_{mean}\, \Delta\theta \qquad (5\text{-}10)$$

where $\Delta\tau$ i.e. $\Delta T-\Delta T_{corr}$ is the effective rise in temperature of the calorimeter and its contents in the absence of any heat loss to the surroundings. ΔT is the observed temperature rise. The physical significance of $\Delta\tau$ is best explained from the temperature time plot, Figure 5-1, which also describes the principles involved in the experimental method for the calculation of the gross heat capacity, Appendix B. The slopes of the lines ab and gh represent the initial and final drift rates. T_b is the initial temperature of the calorimeter and its contents. T_e represents the equilibrium temperature of the calorimeter and its contents at the end of the heating period and is obtained by extrapolation of the line gh . T_e-T_b is the observed temperature difference ΔT . T_d-T_c is ΔT-ΔT_{corr} i.e. $\Delta \tau$.

V-3 Method of Calculation of Constant Volume Heat Capacity and Ideal Gas Heat Capacity

The gross heat capacity, C_{gross} calculated from Equation (5-4) is the sum of the heat capacity of the calorimeter itself with its accessories plus the heat capacity of the gas charged. It can be expressed as:

$$C_{gross} = C_{calr} + mC_V \text{ (gas) at any temperature} \qquad (5\text{-}11)$$

Equation (5-11) can also be rewritten as:

$$C_{gross} = C_{calr} + m(C_V - C_V^*) + mC_V^* \qquad (5\text{-}12)$$

If the correction term C_V-C_V^* is negligible, Equation (5-12) reduces to

$$C_{gross} = C_{calr} + mC_V^* \qquad (5\text{-}13)$$

in which case C_{gross} becomes a linear function of mass.

In this research gross heat capacity measurements have been made for gaseous trifluoromethane, chlorodifluoromethane and dichlorofluoromethane in the density region of 0.01 gm/c.c. or 0.0002 gm-mole/c.c. Figure D-1 of Hwang(26) is the generalized plot of C_V-C_V^* versus reduced density with reduced temperature T_r as parameter. From the generalized plot it is noted that C_V-C_V^* is approximately 0.10 cal/gm-mole°C at a reduced density of 0.02 and reduced temperature of 0.95. Thus in the reduced density range of 0.00 to 0.02 and reduced temperature range of 0.95 to 1.07, $C_V-C_V^*$ values are always on the average within 1% of C_V^* values. For chlorodifluoromethane at 40°C i.e. at about $T_r = 0.85$ and density of 0.0136 gm/c.c. i.e. at about $\rho_r = 0.026$, $C_V-C_V^*$ is approximately 0.2 cal/gm-mole°C (obtained by linear extrapolation from Figure E-14. Thus even at the lowest temperature and highest density of this study where $C_V-C_V^*$ has the maximum value, C_V differs from C_V^* by about 2.00% . From Martin's[(39)] equation of state, the values of $\left(\frac{\partial C_V}{\partial m}\right)_T$ at 40°C and 140°C are $(0.705)(10^{-4})$ cal/gm^2°C and $(0.249)(10^{-4})$ cal/gm^2°C respectively. In order to evaluate these quantities with an accuracy of ± 100% , the experimental smoothed gross heat capacity data should be better than 0.07 cal/°C and 0.025 cal/°C at 40°C and 100°C respectively. Even the calibration curve for the calorimeter is not believed to be known with such precision. On the basis of the above considerations, it is reasonable to use Equation (5-13) for the calculation of C_V or C_V^* values.

The method of calculation of C_V values at any temperature for an unknown gas involves the following steps:

(1) C_{calr} is determined from the calibration curve discussed in (VI-1).

(2) The gross heat capacity data for each mass of charge are expressed as a function of temperature by a least square straight line.

(3) The smoothed gross heat capacity values (at any particular temperature) for various masses together with the value of C_{calr} are expressed as a function of mass by a least square straight line. The value of C_{calr} is weighted four times. The slope of the line represents the experimental C_V or C_V^* value.

V-4 Estimation of the Accuracy

The gross heat capacity value is a function of the experimental variables, time t , voltage E , current I , temperature difference of ΔT-ΔT_{corr} . Mathematically this can be expressed as

$$C_{gross} = \frac{Q}{\Delta T} = f(t,E,I,\Delta T,\Delta T_{corr}) = \frac{t(EI-E^2/2018)}{\Delta T-\Delta T_{corr}} \tag{5-11}$$

Therefore the variation in C_{gross} can be represented as:

$$dC_{gross} = \frac{\partial f}{\partial t}\,dt + \frac{\partial f}{\partial E}\,dE + \frac{\partial f}{\partial I}\,dI + \frac{\partial f}{\partial(\Delta T)}\,d(\Delta T) + \frac{\partial f}{\partial(\Delta T_{corr})}\,d(\Delta T_{corr}) \tag{5-12}$$

$$= \frac{(EI)_{mean}-E^2_{mean}/2018}{\Delta T-\Delta T_{corr}}\,dt + \frac{t(I-2E_{mean}/2018)}{(\Delta T-\Delta T_{corr})}\,\Delta E$$

$$+ \frac{(t)(E_{mean})}{(\Delta T-\Delta T_{corr})}\,\Delta I + \frac{((t)(EI)_{mean}-E^2_{mean}/2018)}{(\Delta T-\Delta T_{corr})^2}\,(\Delta(\Delta T_{corr}-\Delta T)) \tag{5-13}$$

The time was read with an electric timer which was accurate to ± 0.001 minute. Since the heating period was about thirty minutes, the error due to time measurement in C_{gross} heat capacity measurement is considered negligible.

Voltage was measured with an accuracy of ± 0.002 and its magnitude was about 3 volts. Current measurement had an uncertainty of ±0.0002 and its magnitude was about 0.4 amps. The average of three instantaneous power readings resulted in Q_{mean} which was within ± 0.5% of any instantaneous power. The power consumed in the voltage measuring circuit was about 0.5% of instantaneous power. The uncertainty in the over all accuracy estimation due to this is 0.025% .

The resistance thermometer inside the calorimeter had an average accuracy of ±0.015°C . But since the calibration was internally consistent, the temperature difference, ΔT, is believed to have much greater accuracy. ΔT , however, depended on the final temperature T_2 which was not directly measured but was estimated using the final drift rate for the elapsed time during the equilibrium period. The drift rate at an average temperature of 100°C was about 0.012°C/min. The drift rate on the average was also known with an accuracy of ± 10% . So during the ten-minute equilibrium period an uncertainty of 0.012°C could possibly result.

ΔT_{corr} , the heat leakage correction term, had uncertainties in its estimation. This term was calculated by determining the initial and final drift rate when there is no radiation heat transfer between the radiation shield and the calorimeter and then applying a correction to account for imperfect control between the shields and the calorimeter resulting in radiation heat interchange between the two. The average value of ΔT_{corr} was about 0.36°C and drift rates and control correction were known to ± 10% .

TABLE 5-1

ACCURACY OF MEASURED VARIABLES

Variable	Approximate Average Value	Accuracy
t	30.0 min	±0.001 min
E	3.0	±0.002 volts
I	0.35	±0.0002 amp
T	12°C	±0.012°C
ΔT_{corr}	0.36	±0.036°C

Approximate values of measured variables and the possible maximum error are shown in Table 5-1. Substituting these values into Equation (5-13), an approximate estimation of the variation in C_{gross} at 100°C is made as follows:

$$\frac{\Delta C_{gross}}{14.4837} = \frac{((3)(3.5)-3^2/2018)}{12.36}(0.001) + \frac{(30)(0.35-(2)(3)/2018)}{12.36}(0.002) + \frac{(30)(3)}{12.36}(0.0002) + \frac{(30)((3)(0.35)-3^2/2018)}{(12.36)^2}(0.048)$$

or $\Delta C_{gross} = \pm 0.1705$ cal. During the entire experiment, the reproducibility of data was found to be ±0.15 calories. The calibration of the calorimeter with several gases had an average variation of ±0.05 calories. In general, it could be said C_{gross} data on the average had fluctuations of the order of ± 0.3% .

The volume of the calorimeter was determined by means of nitrogen gas within ± 0.5% . The mass of the contents of the calorimeter was known to ± 0.3% . The volume variation over the temperature and pressure range is considered negligible. The maximum possible error in the density is ±0.5% .

VI. CALIBRATION OF THE HEAT CAPACITY OF THE CALORIMETER

VI-1 Calibration of the Calorimeter (1964) Heat Capacity with a Known Gas (Nitrogen)

This research had been designed to take gross heat capacity measurements of various gases at extremely low densities of the order of 0.01 gm/c.c. or approximately .0002 gm-mole/c.c. It was necessary, therefore, to establish accurately the calibration curve of the heat capacity of the calorimeter in this density range. Nitrogen gas was chosen for this purpose because: (a) Nitrogen gas has been studied extensively by various investigators and its heat capacity is believed to be known with an accuracy of ± 0.3% (b) The gas behaves ideally in the ranges of temperature and density for study so that the second partial of pressure with respect to temperature is vanishingly small and hence the correction term $C_V - C_V^*$ is negligible.

The gross heat capacity, C_{gross}, calculated from Equation (5-10), is the sum of the heat capacity of the calorimeter itself with its accessories plus the heat capacity of the gas charged. It can be expressed as:

$$C_{gross} = C_{calr} + mC_V \text{ (gas) at any temperature} \qquad (6\text{-}1)$$

The method of determination of C_{calr} values from Equation (6-1) with Nitrogen gas whose heat capacity is known accurately, involved the following procedures: (a) Gross heat capacity measurements were carried out at four different densities as shown in the C_{gross} versus temperature curves in Figure E-6 and presented in Table E-3. The curves drawn are least square lines as given in Table 6-2. (b) The smoothed gross heat capacity values were then cross-plotted against mass with temperature as parameter. They were fitted with straight lines of the form a+bm subject to least squares criterion where b represents the known heat capacity values of nitrogen, Figure 6-1. The heat capacity values of nitrogen shown in Table 6-1 were compiled from the book by F. Din.(15) Figure 6-1 shows the plot of C_{gross} versus mass with temperature as parameter. Table 6-6 and Figure 6-3 give the calibration of the heat capacity of the calorimeter.

TABLE 6-1

HEAT CAPACITY VALUES OF NITROGEN

Temperature °C	C_V, Cal/gm°C
40	0.1758
60	0.1760
80	0.1762
100	0.1764
120	0.1766
140	0.1768

VI-2 Recalibration of the Calorimeter

The calorimeter was first calibrated with nitrogen gas and heat capacity values were measured for gaseous dichlorodifluoromethane, chlorodifluoromethane, dichlorofluoromethane and trifluoromethane. From the data of chlorodifluoromethane, it was decided about a year later to run some more gross heat capacity measurements for that compound. The calorimeter was recalibrated with nitrogen gas as shown in Figures 6-2 and 6-3 and Tables 6-3 and 6-7. The 1966 calibration line can be represented by $34.3147 + 0.031147T$ where T is in degree Centigrade as compared to the previous 1964 calibration line given by $33.8257 + 0.032512T$. From the comparison of the two calibration lines, it appears that the 1966

TABLE 6-2

SMOOTHED GROSS HEAT CAPACITY VALUES WITH NITROGEN FOR THE CALIBRATION OF THE CALORIMETER (1964)

Run No.	Mass gms	C_{gross} cal/°C						Least Square Line
		40°C	60°C	80°C	100°C	120°C	140°C	
N_2-A	21.31	38.9758	39.5904	40.2050	40.8196	41.4342	42.0488	37.7466 + 0.030730T
N_2-B	18.23	38.4690	39.1212	39.7734	40.4256	41.0778	41.7300	37.1645 + 0.032613T
N_2-C	11.62	37.1856	37.8163	38.4470	39.0777	39.7084	40.3391	35.9242 + 0.031534T
N_2-D	6.50	36.0115	36.7265	37.4415	38.1565	38.8715	39.5865	34.5815 + 0.035749T

TABLE 6-3

SMOOTHED GROSS HEAT CAPACITY VALUES WITH NITROGEN FOR THE CALIBRATION OF THE CALORIMETER (1966)

Run No.	Mass gms	C_{gross} cal/°C						Least Square Line
		40°C	60°C	80°C	100°C	120°C	140°C	
N_2-E	17.50	38.6390	39.2454	39.8518	40.4582	41.0646	41.6710	37.4621 + 0.030322T
N_2-F	15.40	38.3443	39.0356	39.7269	40.4182	41.1095	41.8008	36.9618 + 0.034563T
N_2-G	10.60	37.3306	37.9595	38.5884	39.2173	39.8463	40.4751	36.0747 + 0.031447T

TABLE 6-4

SMOOTHED GROSS HEAT CAPACITY VALUES WITH DICHLORODIFLUOROMETHANE

Run No.	Mass gms	C_{gross} cal/°C						Least Square Line
		40°C	60°C	80°C	100°C	120°C	140°C	
F-12-A	74.70	45.4405	46.2344	47.0283	47.8222	48.6164	49.4100	43.8527 + 0.039695T
F-12-B	70.00	44.8073	45.6980	46.5887	47.4794	48.3701	49.2608	43.0255 + 0.044539T
F-12-C	47.50	41.4479	42.2598	43.0717	43.8836	44.6955	45.5074	39.8241 + 0.040595T

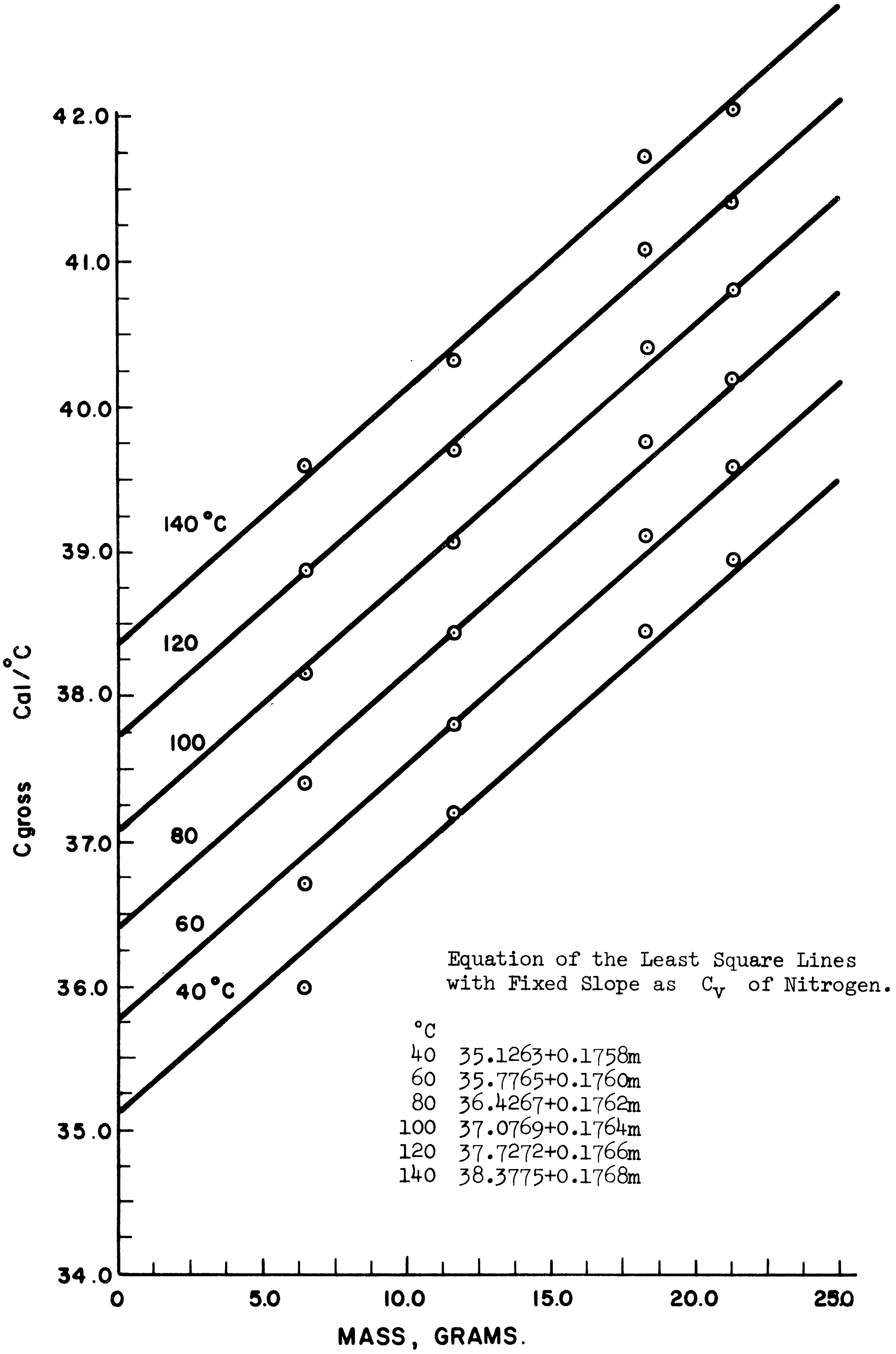

Figure 6-1. Calibration of the Heat Capacity of the Calorimeter (1964) with Nitrogen from C_{gross} Versus Mass Plot.

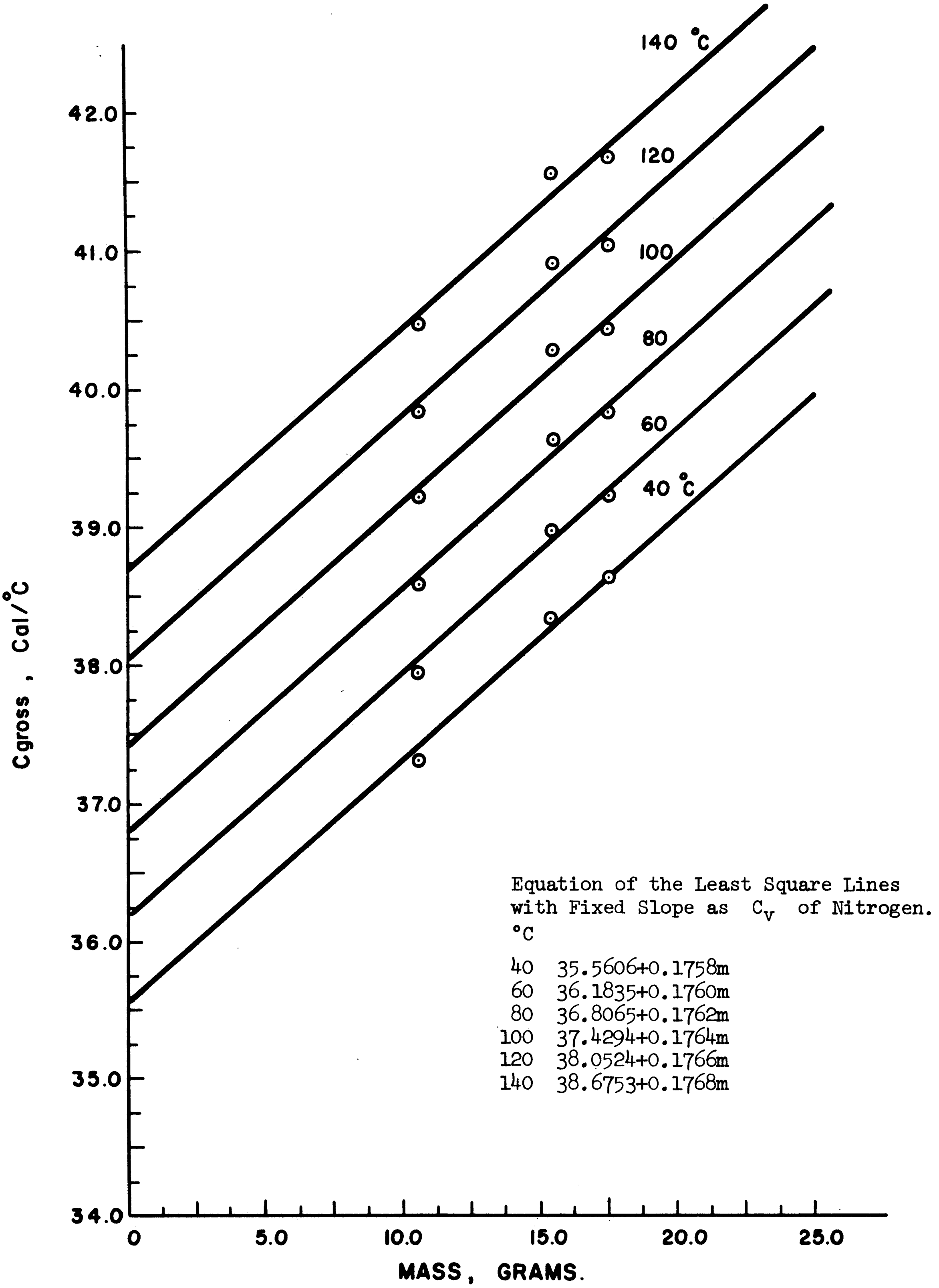

Figure 6-2. Calibration of the Heat Capacity of the Calorimeter (1966) with Nitrogen From C_{gross} Versus Mass Plot.

calibration line differs from the 1964 calibration line over the temperature range of 40°C to 140°C by an amount of about + 0.35 Cal/°C or approximately + 1.0% . Although no quantitative analysis can be put forward to account for this shift, it is conjectured that the following facts may be the "cause." (a) Because of a faulty diaphragm valve near the diffusion pump, the 1964 vacuum system was modified with the elimination of the diffusion pump. Cenco Hyvac Pump No. 7. was used for evacuating the whole system and vacuum of five micron pressure was maintained instead of one micron previously attained with a diffusion pump. This might have caused a change in the adiabaticity of the system. (b) Before starting the 1966 series of experiments, all the thermocouple wirings and connections were inspected and some of the thermocouple tips were resoldered. The thermocouple junction boxes were covered with Fiber glass insulation to protect them from air currents in the room. The thermocouple wires leading to the calorimeter and the shield were allowed to run a more substantial length inside the shield and the lead wires from the calorimeter were kept in closer contact with the inner surface of the lower shield before reaching the vacuum container. During the 1966 experiment no measurement variables were observed to be unusually different from the 1964 experiment. However, this experiment being extremely sensitive to the heat transfer characteristics between the calorimeter and the surroundings, it is believed that the slight changes in the physical surroundings of the calorimeter mentioned above could have affected the final calibration as observed.

TABLE 6-5

GROSS HEAT CAPACITY VALUES WITH DICHLORODIFLUOROMETHANE TO CHECK THE CALIBRATION OF THE HEAT CAPACITY OF THE CALORIMETER (1964)

Mass gms	Temp. °C	C_v^* cal/gm°C	$C_v-C_v^*$ cal/gm°C	$m(C_v-C_v^*)$ cal/°C	C_{gross} cal/°C	$C_{gross}-m(C_v-C_v^*)$ cal/°C
74.7	40	0.1314	0.00451	0.3369	45.4405	45.1036
	60	0.1352	0.00356	0.2659	46.2344	45.9685
	80	0.1390	0.00287	0.2144	47.0283	46.8139
	100	0.1428	0.00231	0.1726	47.8222	47.6496
	120	0.1466	0.00187	0.1397	48.6164	48.4767
	140	0.1504	0.00147	0.1098	49.4100	49.3000
70.0	40	0.1314	0.00417	0.2919	44.8073	44.5154
	60	0.1352	0.00335	0.2345	45.6980	45.4635
	80	0.1390	0.00270	0.1890	46.5887	46.3997
	100	0.1428	0.00217	0.1519	47.4794	47.3275
	120	0.1466	0.00172	0.1204	48.3701	48.2497
	140	0.1504	0.00133	0.0931	49.2608	49.1677
47.5	40	0.1314	0.00295	0.1401	41.4479	41.3078
	60	0.1352	0.00231	0.1097	42.2598	42.1501
	80	0.1390	0.00179	0.0850	43.0717	42.9807
	100	0.1428	0.00146	0.0694	43.8836	43.8142
	120	0.1466	0.00116	0.0551	44.6955	44.6404
	140	0.1504	0.00093	0.0442	45.5074	45.4632

TABLE 6-6

CALIBRATION OF THE HEAT CAPACITY OF THE CALORIMETER (1964) BY NITROGEN

Temp. °C	$C_{calr.}$ cal/°C	Equation of the Calibration Line
40	35.1263	33.8257 + 0.032512T
60	35.7765	
80	36.4267	
100	37.0769	
120	37.7272	
140	38.3775	

TABLE 6-7

CALIBRATION OF THE HEAT CAPACITY OF THE CALORIMETER (1966) BY NITROGEN

Temp. °C	$C_{calr.}$ cal/°C	Equation of the Calibration Line
40	35.5606	34.3147 + 0.031147T
60	36.1835	
80	36.8065	
100	37.4294	
120	38.0524	
140	38.6753	

TABLE 6-8

CALIBRATION OF THE HEAT CAPACITY OF THE CALORIMETER (1964) (Checked by Dichlorodifluoromethane)

Temp. °C	$C_{calr.}$ cal/°C	Equation of the Calibration Line
40	35.2378	33.9920 + 0.031145T
60	35.8607	
80	36.4836	
100	37.1065	
120	37.7294	
140	38.3523	

VI-3 Check of the Calibration of the Calorimeter with Dichlorodifluoromethane

In order to check the calibration of the heat capacity of the calorimeter with nitrogen (VI-1), and also to establish the feasibility of the equipment for the determination of the spectroscopic heat capacity of unknown compounds, gaseous dichlorodifluoromethane was chosen for study. Masi(44) studied this gas extensively and his experimental spectroscopic heat capacity values $(C_V{}^*)$ are claimed to be accurate within ± 0.1% and agree very well with spectroscopic heat capacity values predicted by statistical mechanics.

Gross heat capacity measurements were carried out in the density range of 0.006 gm/c.c. Three different masses were charged as shown in Table 6-4. The smoothed gross heat capacity values from 40°C to 140°C at temperature intervals of 20°C were obtained from the raw data, Figure E-12, by fitting with least square lines as presented in Table 6-4. $C_V-C_V{}^*$ values based on Martin's equation of state were used to calculate the quantity C_{gross} (smoothed) - $m(C_V-C_V{}^*)$ shown in Table 6-5 which was used for the determination of the intercept for any isotherm by least square method with the slope as $C_V{}^*$ values given by Masi.(44) The intercepts were fitted with a least square line which is the calibration curve for the heat capacity of the calorimeter. The calibration curve is plotted in Figure 6-3, and presented in Table 6-8. The calibration of the heat capacity of the calorimeter by dichlorodifluoromethane agrees well with that by nitrogen. For the determination of C_V of unknown gases, nitrogen calibration, however, was chosen in preference to dichlorodifluoromethane calibration because C_V values of nitrogen are known more accurately than those of dichlorodifluoromethane.

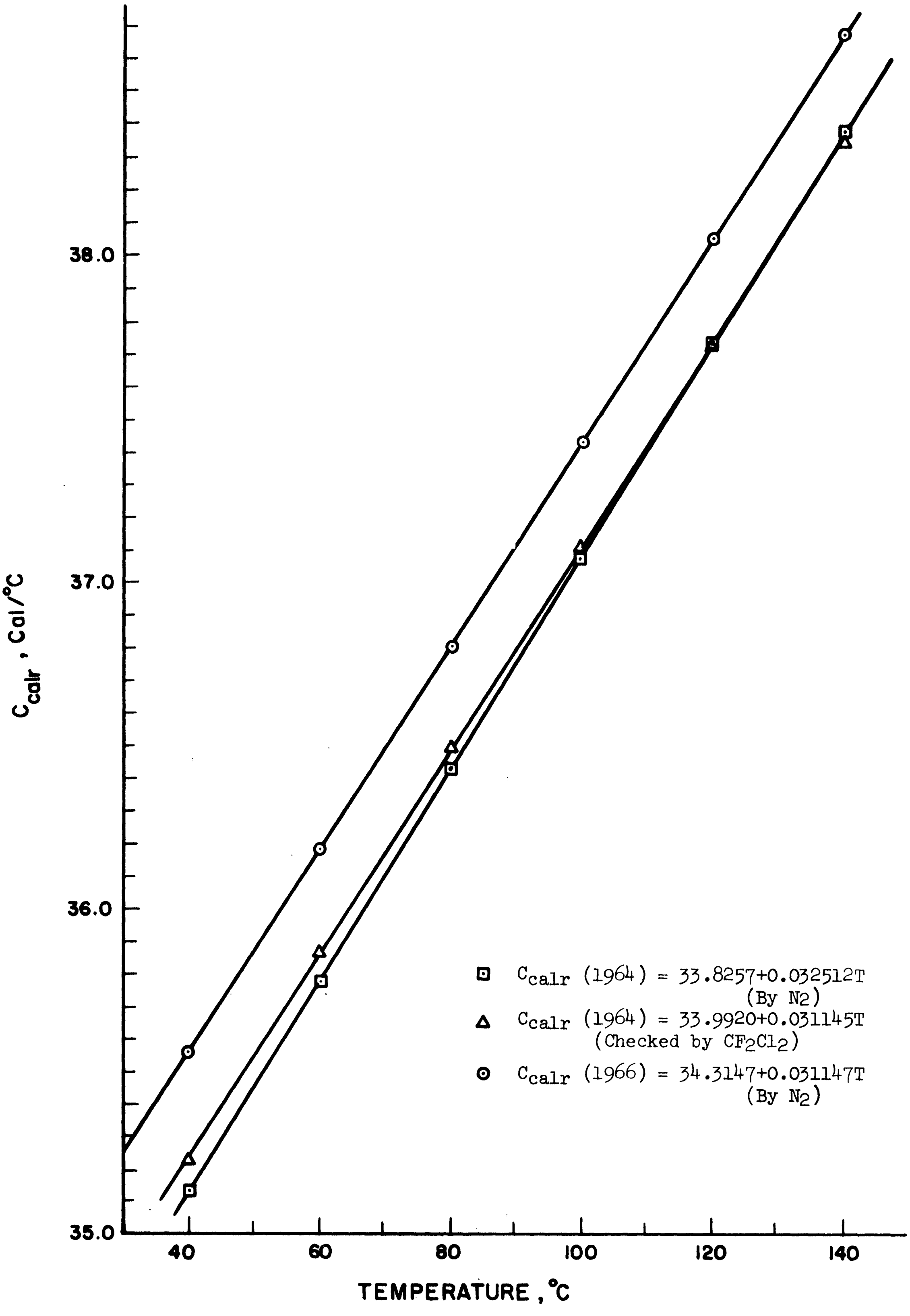

Figure 6-3. Calibration of the Calorimeter Heat Capacity.

VII. EXPERIMENTAL RESULTS

VII-1 Constant Volume Heat Capacity of Trifluoromethane

Gross heat capacity measurements were carried out using the calorimeter (1964) for three different masses of gaseous trifluoromethane in the density region of 0.0067 gm/c.c. to 0.0106 gm/c.c. and temperature range of 40°C to 140°C .

Gross heat capacity data are shown in Figure E-8 and Table E-5. The data were smoothed with straight lines by least square method and the values are presented in Table 7-1. Smoothed gross heat capacity values were then cross plotted with the mass of gas charged as shown in Figure 7-1. Together with the calibration point at zero mass, these data were fitted with straight lines by least square method. The calibration point was weighted four times more than any smoothed gross heat capacity point because it has been determined from about four times more data points and hence is believed to be known with about four times more of accuracy. The slopes of these lines give directly the heat capacity values for each isotherm. The smoothed gross heat capacity values are scattered enough over the temperature range and hence do not permit the fitting of data with curved lines with any degree of confidence to determine the quantity $\left(\frac{\partial C_V}{\partial m}\right)_T$. From Martin's equation of state$^{(37)}$, at 40°C and 140°C the values of $\left(\frac{\partial C_V}{\partial m}\right)_T$ obtained are $(0.75)(10^{-4})$ Cal/gm^2°C and $(0.143)(10^{-4})$ cal/gm^2°C respectively. In order to establish the variation of heat capacity with density with an accuracy of ± 100% and then compare with the values obtained from the equation of state, it is required that each smoothed gross heat capacity value is known with a

TABLE 7-1

SMOOTHED GROSS HEAT CAPACITY VALUES WITH GASEOUS TRIFLUOROMETHANE USING THE CALORIMETER (1964)

Run No.	Mass gms	C_{gross} cal/°C						Least Square Line
		40°C	60°C	80°C	100°C	120°C	140°C	
F-23-A	47.90	42.9244	43.7177	44.5110	45.3043	46.0976	46.8909	41.3378 + 0.039667T
F-23-B	40.00	40.9149	41.8984	42.8819	43.8654	44.8489	45.8324	38.9480 + 0.049173T
F-23-C	31.30	40.1156	40.9057	41.6958	42.4859	43.2760	44.0661	38.5354 + 0.039504T

TABLE 7-2

HEAT CAPACITY VALUES OF GASEOUS TRIFLUOROMETHANE

Temp°C	C_v^* cal/gm°C
40	0.1564
60	0.1614
80	0.1663
100	0.1713
120	0.1762
140	0.1812

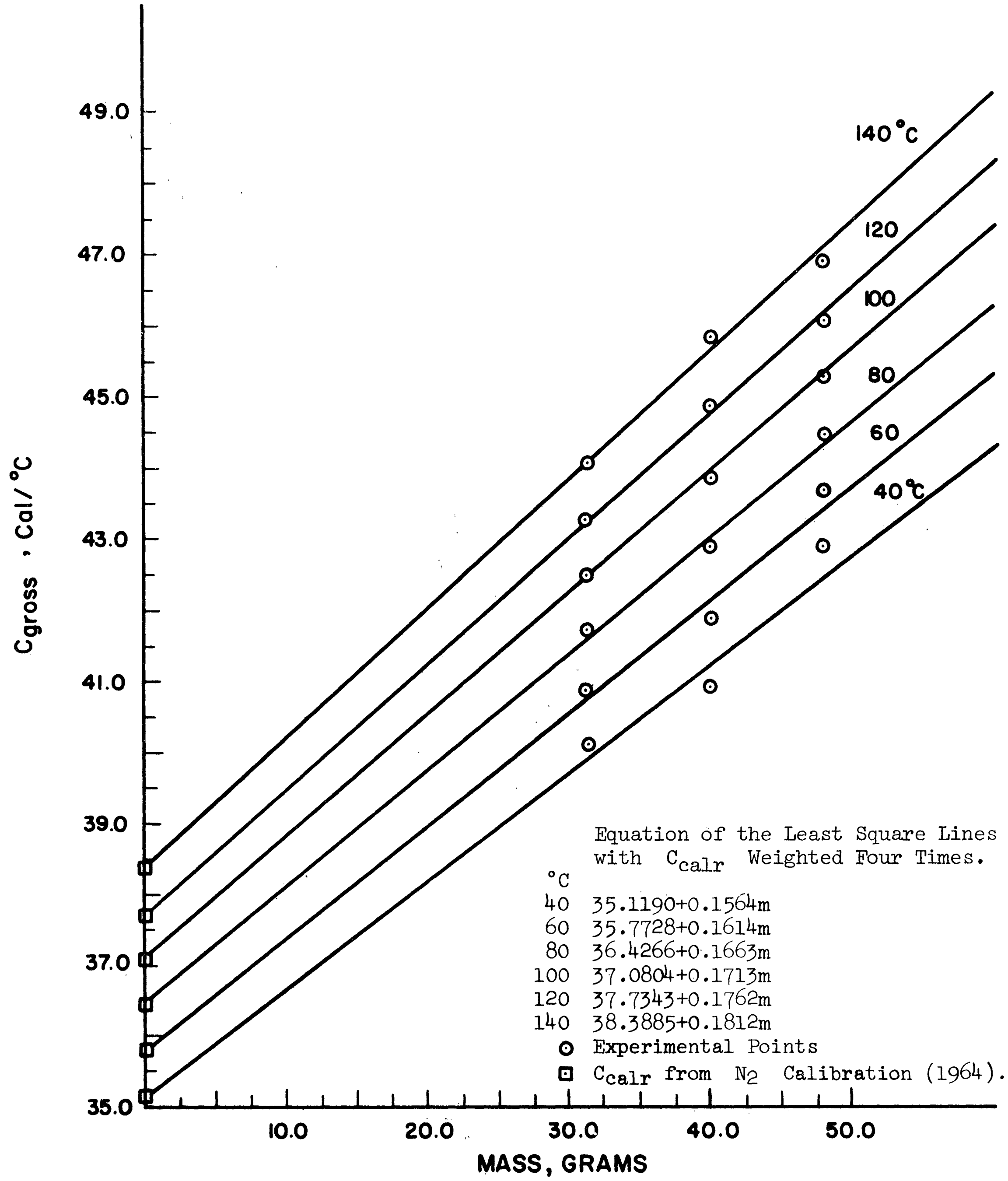

Figure 7-1. Gross Heat Capacities Versus Mass for Trifluoromethane Using Calorimeter (1964).

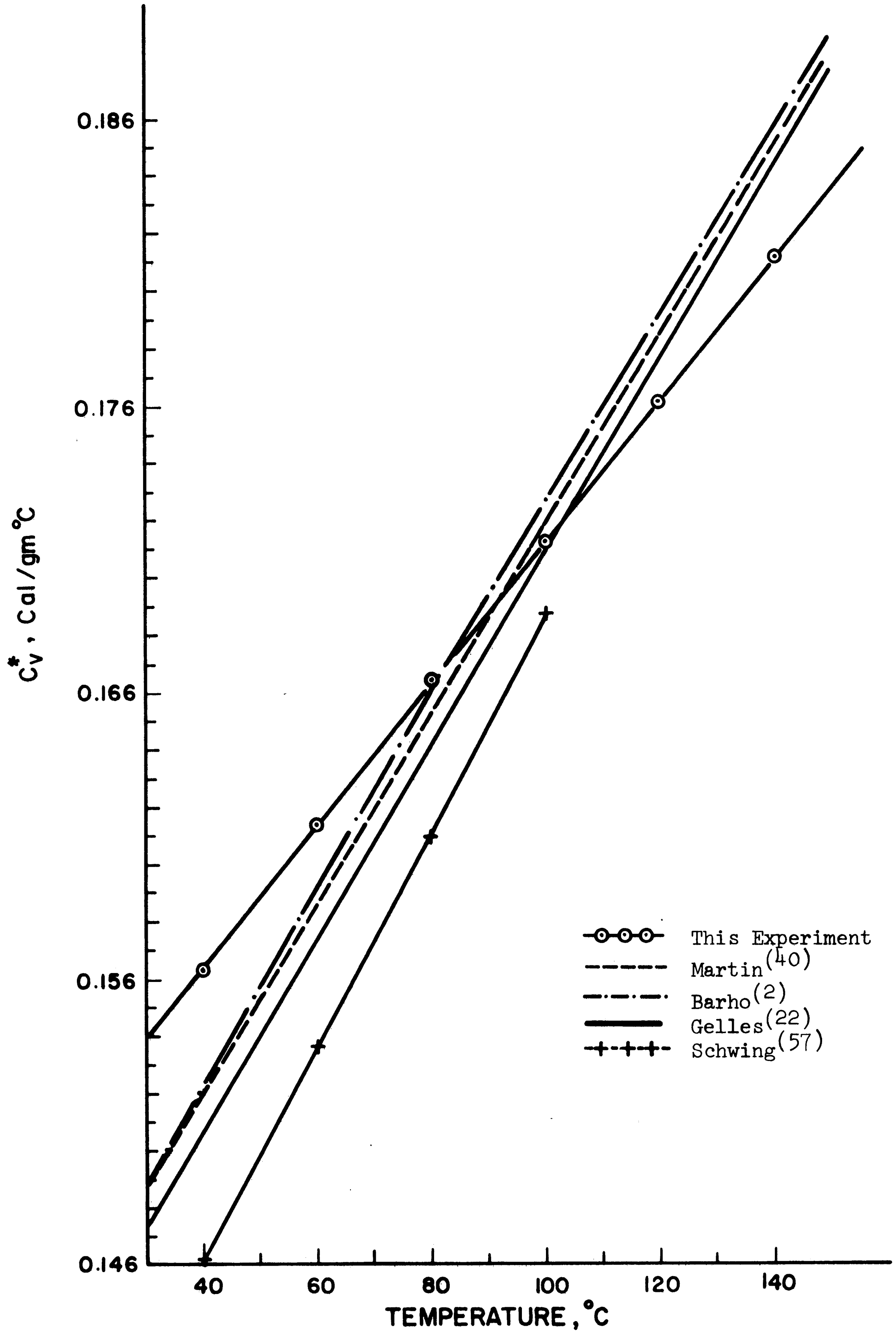

Figure 7-2. C_v^* values of Trifluoromethane Versus Temperature.

precision of ± 0.075 cal/°C at 40°C and ± 0.0143 cal/°C at 140°C . Let alone the smoothed gross heat capacity values, the calibration of the calorimeter is not believed to be known with such a precision.

The slopes of the lines in the C_{gross} versus mass plot are the heat capacity values for each isotherm in that density range and the best C_V^* values that could be reported from such data. The C_V^* values thus obtained are plotted against temperature as shown in Figure 7-2 and compared with values obtained from different sources in the literature. Vander Kooi and DeVries(63), reported experimental C_V^* value of 0.1465 cal/gm°C at 26.8°C which is identical to the value of Gelles and Pitzer(22) and Decker, Meister and Cleveland.(13)

The spectroscopic heat capacity values by Decker, Meister and Cleveland,(13) and Gelles and Pitzer,(22) contain no correction for the anharmonicity in the molecule. The upper curve has been calculated by Hou and Martin(40) with an arbitrary correction for anharmonicity of 0.54% at 30°C and 0.75% at 170°C varying linearly between these temperatures. The spectroscopic values theoretically predicted agree on the average within ± 2% with the experimental C_V^* values of this work.

VII-2 Constant Volume Heat Capacity of Chlorodifluoromethane

Gaseous chlorodifluoromethane has been studied intensively in this research and the work has been carried out in two phases. In the first phase with the calibration of the calorimeter (1964) given by Table 6-6, gross heat capacity measurements were made for four different charges of mass in the temperature range of 40°C to 140°C and density range of 0.0045 gm/c.c. to 0.0136 gm/c.c., Table E-6, Figure E-9. Almost a year later it was decided to carry out some more experimental

TABLE 7-3

SMOOTHED GROSS HEAT CAPACITY VALUES WITH GASEOUS CHLORODIFLUOROMETHANE USING THE CALORIMETER (1964)

		C_{gross} cal/°C						
Run No.	Mass gms.	40°C	60°C	80°C	100°C	120°C	140°C	Least Square Line
F-22-A	61.60	44.2568	45.1617	46.0666	46.9715	47.8764	48.7813	42.4470 + 0.045245T
F-22-B	39.16	40.6390	41.4215	42.2040	42.9865	43.7690	45.5515	39.0741 + 0.039123T
F-22-C	28.75	38.9163	39.7452	40.5741	41.4030	42.2319	43.0608	37.2 79 + 0.041461T
F-22-D	19.00	37.6347	38.4004	39.1661	39.9318	40.6975	41.4632	36.1034 + 0.038283T

CALIBRATION EQUATION FOR THE CALORIMETER 33.8257 + 0.032512T

TABLE 7-4

SMOOTHED GROSS HEAT CAPACITY VALUES WITH GASEOUS CHLORODIFLUOROMETHANE USING THE CALORIMETER (1966)

Run No.	Mass gms.	C_{gross} cal/°C						
		40°C	60°C	80°C	100°C	120°C	140°C	Least Square Line
F-22-E	47.0	42.0141	42.9029	43.7917	44.6805	45.5693	46.4581	40.2365 + 0.04444T
F-22-F	33.88	39.6224	40.5459	41.4694	42.3929	43.3164	44.2399	37.7754 + 0.046174T
F-22-G	21.50	38.2301	39.0505	39.8708	40.6912	41.5116	42.3319	36.5894 + 0.041018T

CALIBRATION EQUATION FOR THE CALORIMETER 34.3147 + 0.031147T

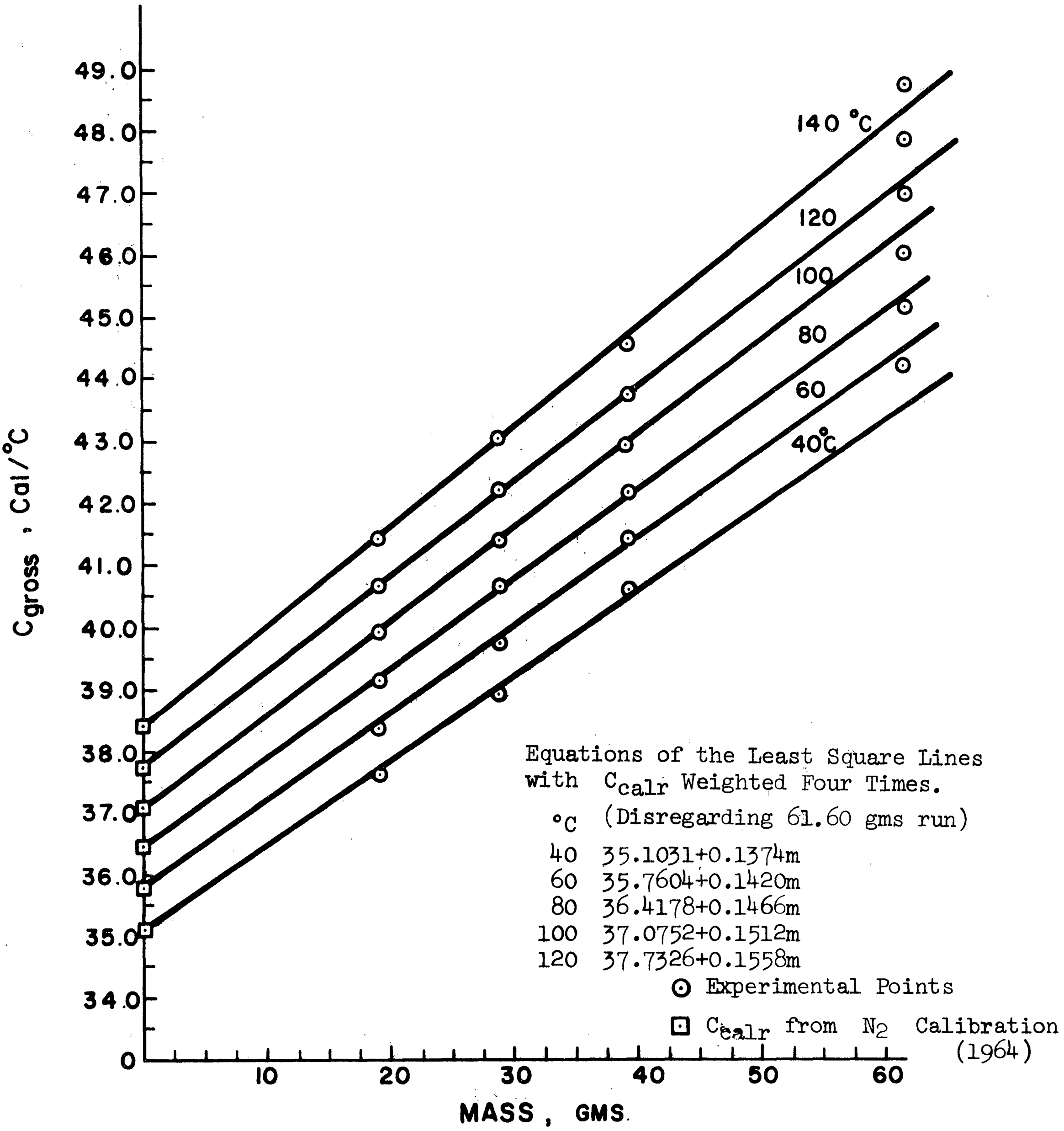

Figure 7-3. Gross Heat Capacities Versus Mass for Chlorodifluoromethane Using Calorimeter (1964).

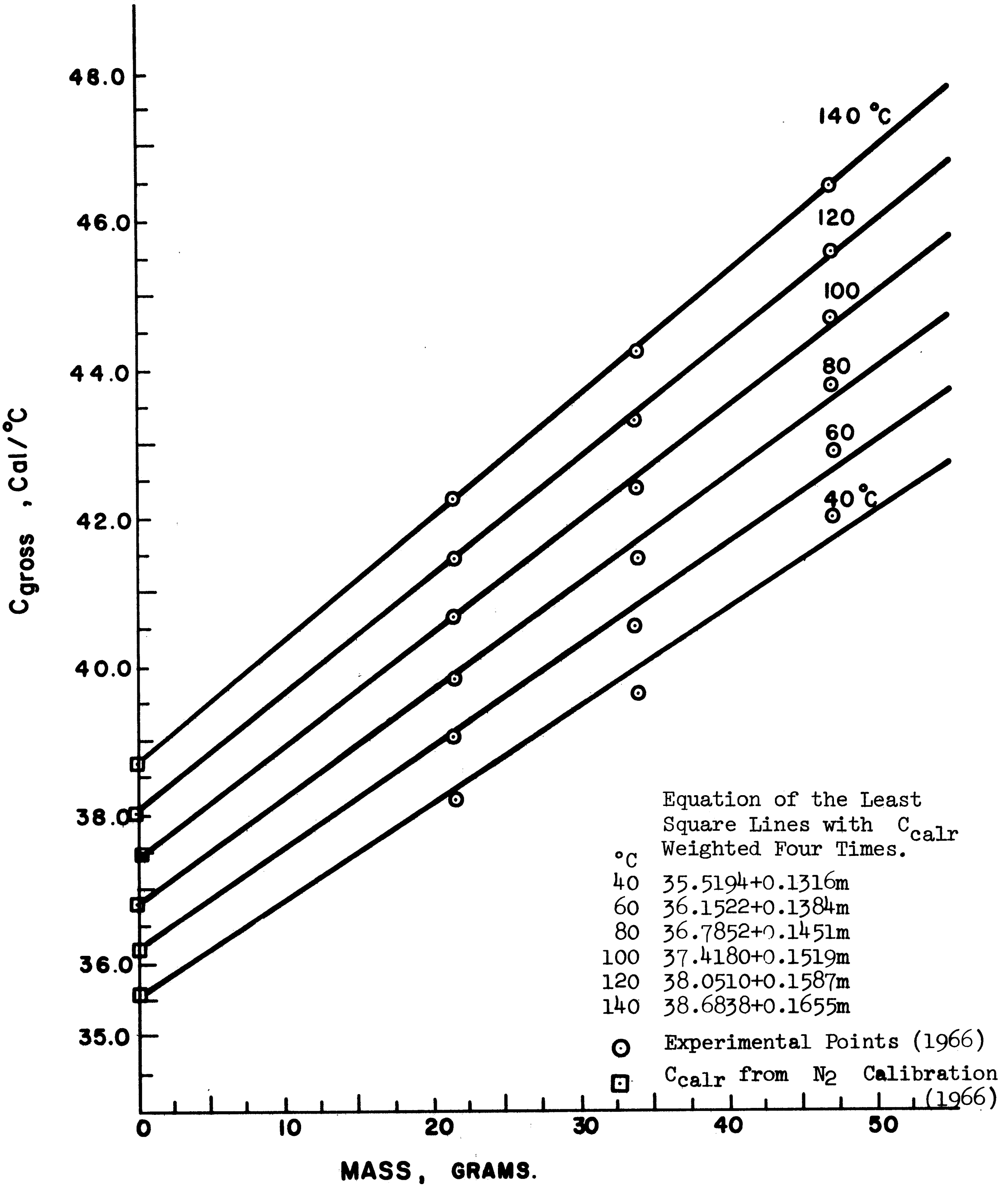

Figure 7-4. Gross Heat Capacities Versus Mass for Chlorodifluoromethane Using Calorimeter (1966).

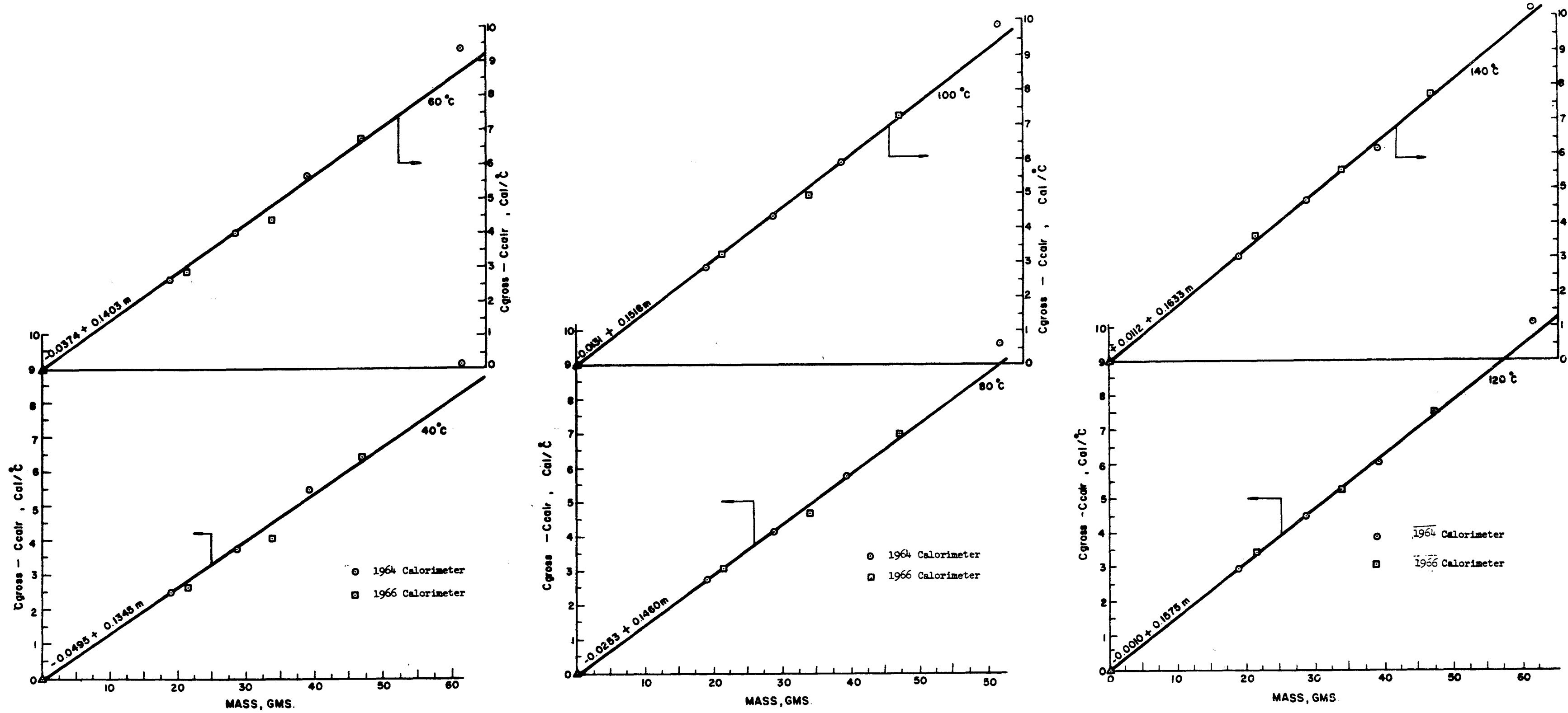

Figure 7-5. C_{gross}-C_{calr} Versus Mass for Chlorodifluoromethane. (Least Square Equation with Zero Mass Point Weighted Four Times and Neglecting 61.60 gm points)

TABLE 7-5

HEAT CAPACITY VALUES OF GASEOUS CHLORODIFLUOROMETHANE USING THE CALORIMETER (1964)

(From Runs F-22-B, F-22-C, and F-22-D and Neglecting F-22-A)

Temp. °C	C_v^* cal/gm°C
40	0.1374
60	0.1420
80	0.1466
100	0.1512
120	0.1558
140	0.1603

TABLE 7-6

HEAT CAPACITY VALUES OF GASEOUS CHLORODIFLUOROMETHANE USING THE CALORIMETER (1966)

(From Runs F-22-E, F-22-F, F-22-G)

Temp. °C	C_v^* Cal/gm°C
40	0.1316
60	0.1384
80	0.1451
100	0.1519
120	0.1587
140	0.1655

TABLE 7-7

(C_{gross}-C_{calr}) VALUES OF GASEOUS CHLORODIFLUOROMETHANE

		C_{gross}-C_{calr} Cal/°C					
Run No.	Mass	40°C	60°C	80°C	100°C	120°C	140°C
F-22-A	61.60	9.1305	9.3852	9.6399	9.8946	10.1492	10.4038
F-22-B	39.16	5.5127	5.6450	5.7773	5.9096	6.0418	6.1740
F-22-C	28.75	3.7900	3.9687	4.1474	4.3261	4.5047	4.6833
F-22-D	19.00	2.5084	2.6239	2.7394	2.8549	2.9703	3.0857
F-22-E	47.00	6.4535	6.7194	6.9852	7.2511	7.5169	7.7828
F-22-F	33.88	4.0618	4.3624	4.6629	4.9635	5.2640	5.5646
F-22-G	21.50	2.6695	2.8670	3.0643	3.2618	3.4592	3.6566

TABLE 7-8

HEAT CAPACITY VALUES OF GASEOUS CHLORODIFLUOROMETHANE USING COMBINED DATA TAKEN BY THE CALORIMETER (1964) AND THE CALORIMETER (1966)

Temp. °C	C_v^* Cal/gm°C
40	0.1345
60	0.1403
80	0.1460
100	0.1518
120	0.1575
140	0.1633

measurements in about the same temperature and density range. So the calorimeter was recalibrated as presented in Table 6-7. Gross heat capacity measurements were then taken for three more different masses, Table E-7, Figure E-10.

The gross heat capacity values for chlorodifluoromethane using the calorimeter with the 1964 calibration are presented in Figure 7-3 and Table 7-3. Those values with the 1966 calibration curve are presented in Figure 7-4, and Table 7-4. Smoothed gross heat capacity values were obtained by fitting the raw data with least square straight lines as given in Table 7-3 and Table 7-4. The smoothed values together with the corresponding calibration point were then cross plotted against mass as shown in Figure 7-3 and Figure 7-4. Putting four times more weight in the calibration point the smoothed gross heat capacity values were fitted with straight lines of the form $a+bm$ by the method of least squares. The slope of each isotherm is the desired heat capacity value for that temperature and is the best C_v^* value from this experiment. The C_v^* values are shown in Figure 7-6, and Tables 7-5 and 7-6.

To get more reliable C_V or C_v^* values, all the data were pooled together. From the smoothed gross heat capacity values for different masses at any temperature, the heat capacity value of the calorimeter was subtracted as shown in Table 7-7. Then $C_{gross}-C_{calr}$ values were plotted against the mass charged with temperature as parameter and fitted with least square straight lines weighing the zero mass point four times since the calorimeter calibration is believed to be known with four times more accuracy than any single smoothed gross heat capacity value. These are shown in Figure 7-5 and presented in Table 7-7. The slope of

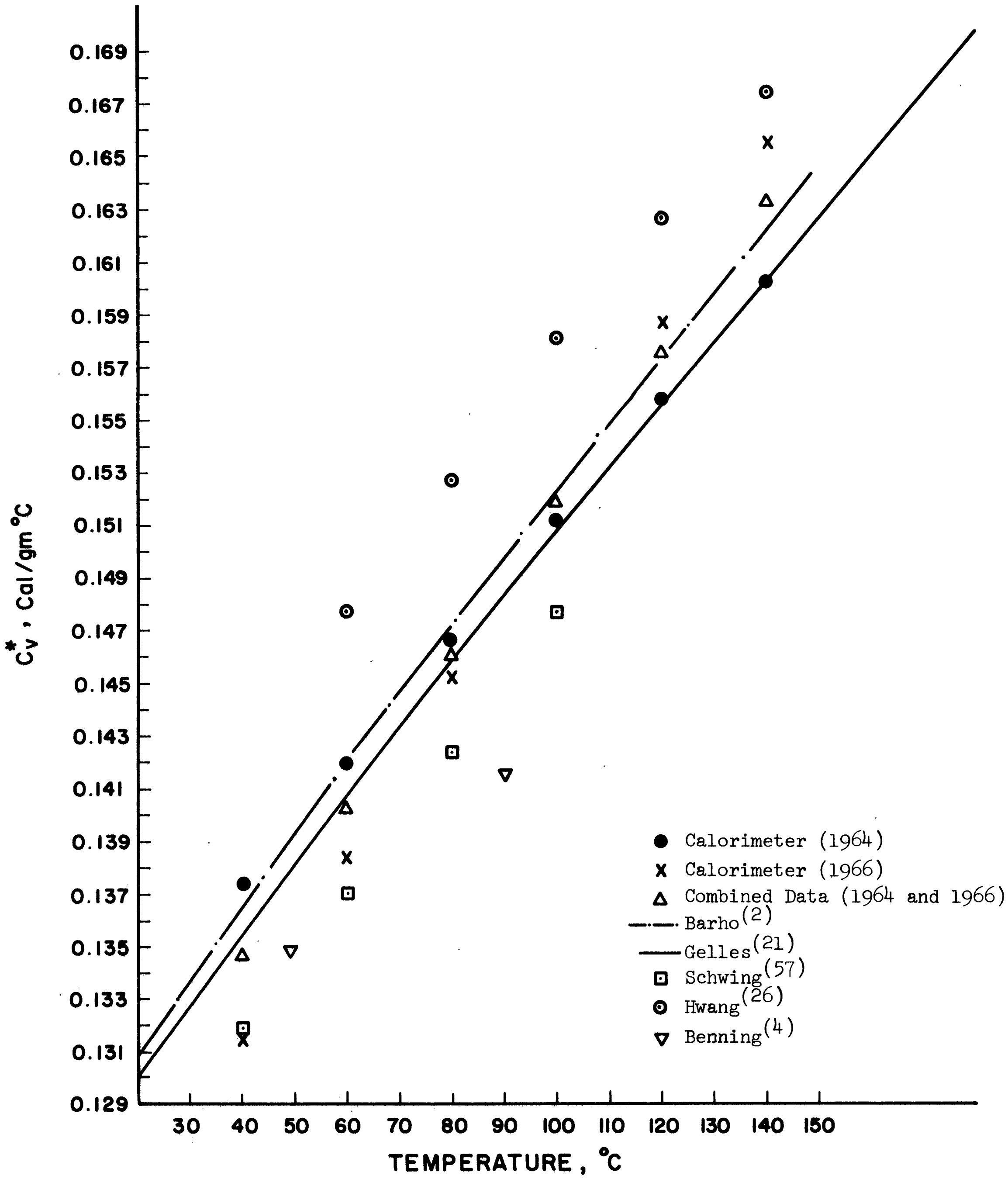

Figure 7-6. C_V^* Values of Chlorodifluoromethane Versus Temperature.

each isotherm which is the desired C_v or C_v^* value is presented in Table 7-8 and shown in Figure 7-6. In Figure 7-6, the solid curve represents C_v^* values by Weissman, Meister and Cleveland(65) which are in agreement with the values calculated by Gelles and Pitzer.(21) Experimental C_v^* values of Hwang,(26) Schwing,(58) and Benning, McHarness, Markwood and Smith(4) are also presented for comparison.

The first phase of the experiment judged alone, gives C_v^* values which are in excellent agreement with the spectroscopic values. The second phase of the experiment results in C_v^* values which are in agreement with the spectroscopic predictions with an average deviation of ± 2% . The combined data turn out C_v^* values which are in excellent agreement with the spectroscopic values with an average deviation of ± 1.5% .

Examining the $C_{gross}-C_{calr}$ versus mass plot, the internal consistency of the data can be checked. Generally the data appear to be consistent. For the mass charge of 61.60 gms, all data seem to be consistently high and the author believes that this particular run is in error and hence is ignored.

All data in each phase of the experiment indicate that the heat capacity of gaseous chlorodifluoromethane varies with density. From the Martin-Hou equation of state the values of $\left(\frac{\partial C_v}{\partial m}\right)_T$ at 40°C and 140°C are $(0.705)(10^{-4})$ Cal/gm^2)C and $(0.249)(10^{-4})$ cal/gm^2°C respectively. In order to evaluate these quantities with an accuracy of ± 100%, the experimental smoothed gross heat capacity data should be better than ± 0.07 cal/°C and 0.025 cal/°C at 40°C and 100°C respectively. Even the calibration point is not believed to be known with such precision. In the plot of C_{gross} versus mass in Figures 7-3, 7-4, fitting with a curved line is therefore not justified because the data points are not sufficient enough in number and also are not considered accurate enough to call for a second degree polynomial fit. When, however, all the data points are pooled together from each phase of the experiment, hardly any curvature is seen in the $C_{gross}-C_{calr}$ versus mass plot. Thus all data are fitted with straight lines and the slopes of such lines give the C_v or C_v^* values in this experiment.

VII-3 Constant Volume Heat Capacity of Dichlorofluoromethane

Three different masses were charged into the calorimeter (1964) for the measurement of gross heat capacities in the temperature range of 40°C to 140°C and density range of 0.0067 gm/c.c. to 0.0158 gm/c.c. The gross heat capacity values as shown in Figure E-11 and Table E-8, were smoothed with straight lines by the least square method. The smoothed values are presented in Table 7-9. For the determination of the heat capacity values at any temperature, the smoothed gross heat capacity values together with the calibration point are cross plotted against mass and fitted with a least square line with the calibration point weighted four times. The slope of such lines represents the heat capacity of the gas at that temperature for that density range. This is again the best C_v^* values that can be determined from the data. The smoothed gross heat capacity values are scattered enough and hence the variation of the heat capacity with density can hardly be ascertained with any confidence. The C_v^* values are presented in Table 7-10. The statistical predictions of C_v^* values by Gelles and Pitzer(22) and

TABLE 7-9

SMOOTHED GROSS HEAT CAPACITY VALUES OF GASEOUS DICHLOROFLUOROMETHANE
USING THE CALORIMETER (1964)

C_{gross} Cal/°C								
Run No.	Mass	40°	60°	80°	100°	120°	140°	Least Square Line
F-21-A	71.5			46.2526	46.9605	47.6684	48.3763	43.4210 + 0.035397T
F-21-B	40.0	40.5681	41.3312	42.0943	42.8574	43.6205	44.3836	39.0420 + 0.038153T
F-21-C	30.4	39.1683	39.8673	40.5663	41.2653	41.9643	42.6633	37.7703 + 0.034951T

TABLE 7-10

HEAT CAPACITY VALUES OF GASEOUS DICHLOROFLUOROMETHANE

Temp. °C	C_v^* Cal/gm°C
40	0.1328
60	0.1352
80	0.1381
100	0.1393
120	0.1404
140	0.1416

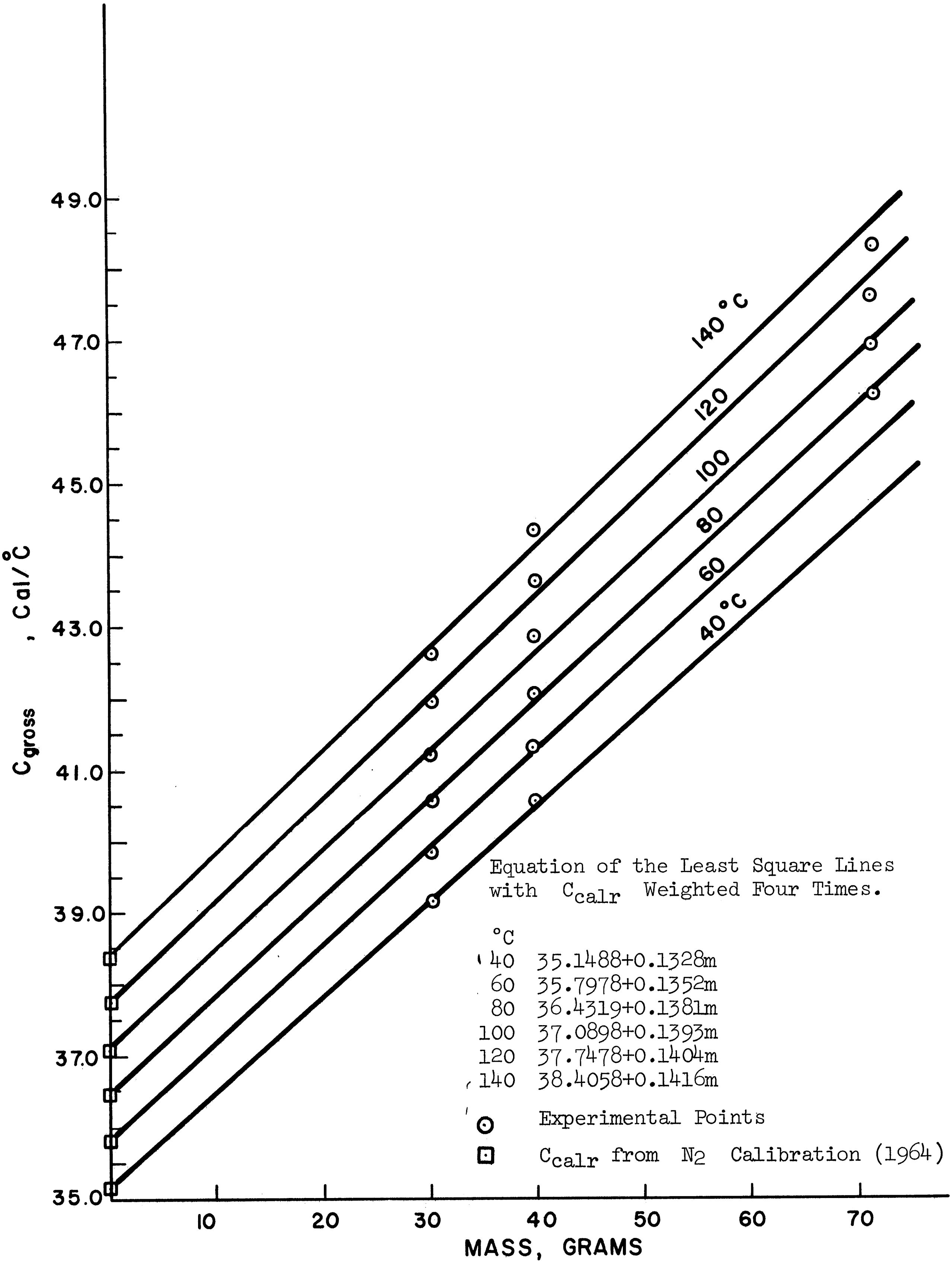

Figure 7-7. Gross Heat Capacities Versus Mass For Dichlorofluoromethane Using Calorimeter (1964).

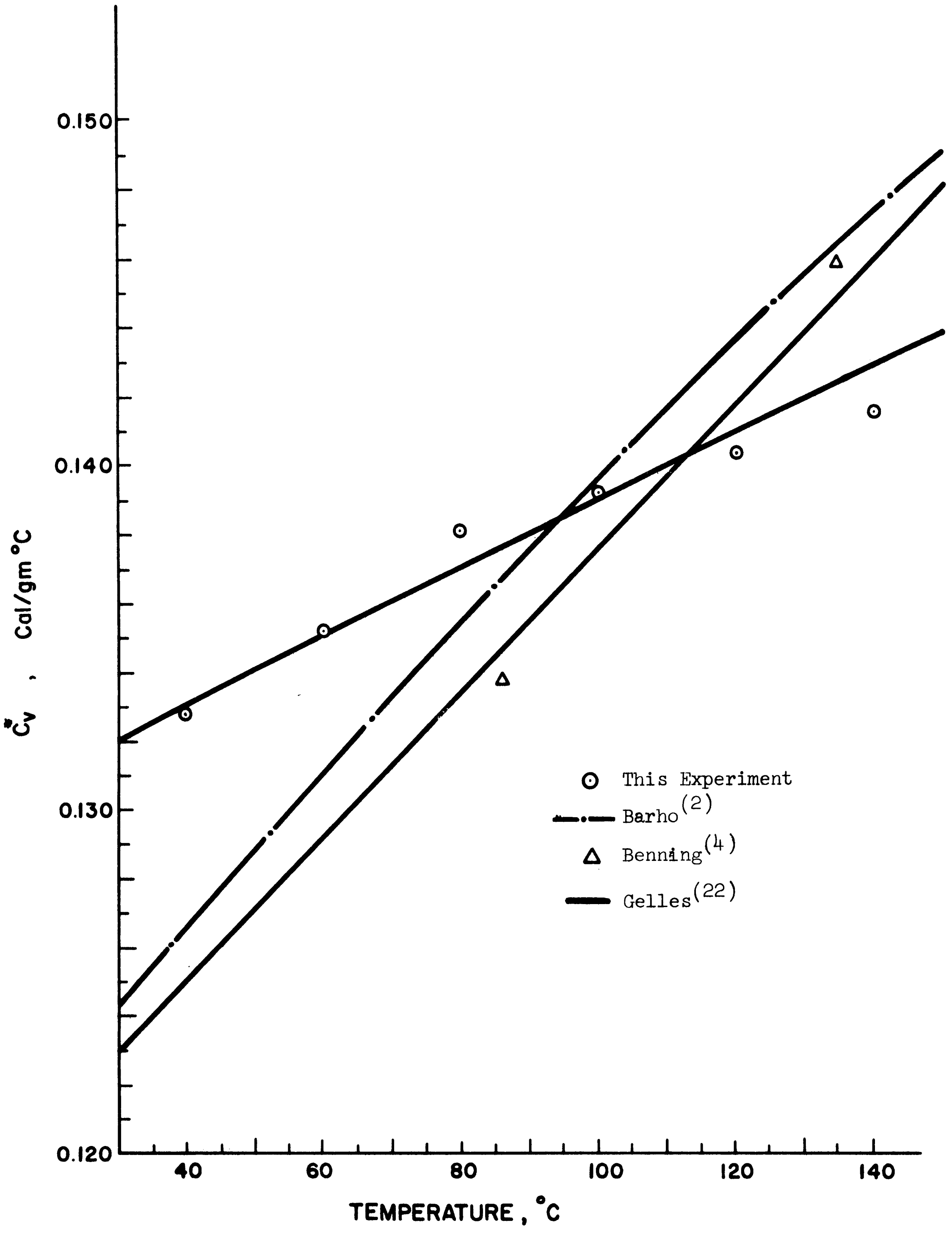

Figure 7-8. C_V^* Values of Dichlorofluoromethane Versus Temperature.

Weissman, Meister and Cleveland(65) are plotted in Figure 7-8 for comparison. The statistical predictions agree with this experiment within ± 3% . Experimental measurements by Benning, McHarness, Markwood and Smith(4) are shown in the same figure.

VIII. DISCUSSION OF EXPERIMENTAL RESULTS

VIII-1 General:

Since the accuracy of the experiment depends upon the relative heat capacity of the mass of gas and the calorimeter, the experimental errors in this work are estimated as ± 2% and ± 3% at densities of 0.01 gm/c.c. and 0.006 gm/c.c. respectively for trifluoromethane, chlorodifluoromethane and dichlorofluoromethane. Because of the low density, the measured heat capacity is that of the ideal gas, C_V^*, and can be compared with the heat capacity calculated from statistical mechanics using fundamental vibrational frequencies obtained from measurements of infra-red and Raman spectra. Within the precision of this experiment, the results verify the accepted fundamental frequency assignments for these compounds. However, they fail to explain the difference in the effect of temperature on the ideal-gas heat capacity.

VIII-2 Comparison with Theoretical Predictions and Experimental Results:

Pitzer(22) reported that the error in theoretical C_V^* values is ± 0.1 cal/°C mole or approximately ± 1%. The error could be larger since in his calculations no anharmonicity correction was made. Martin(40) corrected for anharmonicity and estimated C_V^* values for trifluoromethane. At 40°C, Martin's C_V^* value is + 0.7% higher than Pitzer's for trifluoromethane. Barho(2) calculated C_p^* values with anharmonicity correction and claimed an accuracy of his results within ± 0.3%. For trifluoromethane, C_V^* values calculated from C_p^* values of Barho, are in agreement with Martin's values. Vander Kooi and De Vries(63) experimentally determined C_V^* value for trifluoromethane at 26.8°C. They claimed an accuracy of ± 1.3% in their result which is identical with the predictions of Pitzer and Cleveland. Schwing(57) experimentally determined C_V values for trifluoromethane in the density region of 0.01 gm/c.c. and temperature range of 20°C to 100°C. He reported C_V* values by extrapolation of his C_V values. His C_V* values are 3.5% lower at 20°C and 1.5% lower at 100°C than the values reported by Pitzer and Cleveland. The experimental C_V* values of trifluoromethane obtained in this research are 3% higher and 2% lower than the predictions of Martin and Barho at 40°C and 140°C respectively. At 100°C, however, the experimental C_V* value of this work is in complete agreement with all theoretical predictions to within ± 0.5%.

The compound chlorodifluoromethane has been studied extensively by various authors. Pitzer and Cleveland(13) are identical in their predictions of C_V* values. Barho(2) calculated C_p* values for chlorodifluoromethane correcting for anharmonicity. C_V* values calculated from his C_p* values are generally + 1.0% higher than the values of Pitzer. Hwang(26) reported C_V* values for chlorodifluoromethane by extrapolating his C_V values taken at very high density range of 0.04 gm/c.c. to 0.10 gm/c.c. and temperature range of 50°C to 200°C. Hwang's C_V* values are generally 5% higher than the values of Pitzer. Schwing(57) measured C_V values for chlorodifluoromethane in the density region of 0.01 gm/c.c. and his extrapolated C_V* values are 2.4% lower than the values of Pitzer. Benning et. al.(4) reported C_V* values of chlorodifluoromethane which are in agreement with Schwing's values. The experimental C_V* values obtained in this research are in agreement with the spectroscopic values in the literature. The average deviation is +1.5% from the spectroscopic predictions in the temperature range of 40°C to

140°C. The density region in which these data have been taken is such that C_V values are not significantly different from C_V* values. Even at the lowest temperature and highest density point of this experiment, where the curvature of C_V isotherm is expected to be maximum, the C_V values differ from C_V* values only by 2.5% on the basis of Martin's(39) equation of state. Therefore, it is concluded that since C_V-C_V* is small in the density region of this experiment, the data being not precise enough cannot be used as a test of the equation of state and simultaneously determine accurate C_V* values. It is, however, believed that the data are consistent enough to result in accurate C_V* values if fitted with a curvature which is known accurately for a particular isotherm. It is also believed that these data can be used to simultaneously determine accurate C_V* and C_V-C_V* values, if they are coupled with the data of Hwang taken at fairly high density range.

For dichlorofluoromethane, the spectroscopic predictions of Pitzer(22) and Cleveland et. al. are identical. Benning et. al. agree with spectroscopic predictions within ± 0.5%. The experimental C_V* value obtained in this research at 100°C is almost identical with the C_V* value predicted by Barho. At 40°C, the experimental C_V* value is about 4% higher while at 140°C it is 3% lower than the calculated C_V* values of Barho.

With the calorimeter (1964), C_V* values at 40°C are always a few percent higher than the values theoretically calculated for gaseous trifluoromethane, chlorodifluoromethane and dichlorofluoromethane. With the same calorimeter, experiemental C_V* values at 140°C are generally lower than the theoretical values for trifluoromethane and dichlorofluoromethane. Also in the plot of C_V* versus temperature, the experimental slope, dC_V*/dT , is always less than the theoretical slope for all the compounds. If one, however, chooses to use the dichlorodifluoromethane calibration of the calorimeter (1964), it is observed that the agreement between the experimental and theoretical C_V* values is improved in the entire temperature range of 40 to 140°C. The experimental slope, dC_V*/dT , also agrees better with the theoretical slope. It may also be argued that for the calculation of C_V* values dichlorodifluoromethane calibration should be used instead of nitrogen calibration since freon compounds may have similar heat transfer characteristics. Despite these reasonings, nitrogen calibration was chosen to calculate C_V* values because it is believed to be more accurate, nitrogen gas being more well known than dichlorodifluoromethane.

Finally, one might be quite skeptical of the final C_V* results from this experiment because of the discrepancy existing between the several calibration curves of the calorimeter, Figure 6-3. The calorimeter (1964) calibration by nitrogen agrees well with the calibration by dichlorodifluoromethane. At 40°C, C_{calr} (1964) by nitrogen is about 0.1 cal/°C lower than that by dichlorodifluoromethane and at 140°C, it is about 0.03 cal/°C higher. Thus at 40 and 140°C, the experimental C_V* values could differ as much as 3% and 1% respectively depending on the calibration curve chosen. The author, however, does not claim that at 40°C, the precision of this experiment is any better than 3%.

Chlorodifluoromethane was studied in this research in two phases using the calorimeter (1964) and the calorimeter (1966). The calorimeter (1966) calibration was generally higher than the calorimeter (1964) calibration by about 0.35 cal/°C or approximately 1%. This discrepancy in the calibration of the calorimeter may raise doubts about the reliability of the experimental data. It was observed, however, that although the calibration curves were different, $C_{gross}-C_{calr}$ values were reproducible. Thus the final results i.e. C_v* values remained unaffected despite the fact that the calibration curves of the calorimeter were different.

Although no quantitative explanations are known at this time, the following facts may, however, account for the observed difference between the 1964 and 1966 calibrations of the calorimeter. Before the 1966 calibration runs were started, a few thermocouple tips were resoldered and some of the thermocouple wires leading to the calorimeter and the shield were allowed to run a more substantial length inside the shield as compared to the 1964 experimental set-up; the lead wires from the calorimeter were also kept in closer contact with the inner surface of the lower radiation shield before reaching the vacuum container. Also, the calorimeter (1964) was calibrated under a vacuum of 1μ while a vacuum of 5μ was maintained during the calibration of the calorimeter (1966). The main purpose of vacuum insulation in such an experiment was to eliminate completely heat losses by gaseous conduction and convection. In the pressure range of 1 to 5μ, there are, however, heat losses, though considerably minimized, through the residual gas. In fact, at such low pressures, the molecules of a gas have long mean free path and they collide with the surrounding walls much more frequently than with each other. Thus each molecule is a potential carrier of energy from the warm to the cold surface. It is, therefore, believed that because of the change in the set-up of wires and, more particularly, the change in vacuum from 1 to 5μ in 1966, the heat transfer characteristics between the calorimeter and the surroundings had been different from those in 1964. This experiment being highly sensitive to such heat transfer characteristics between the calorimeter, the radiation shield and the surroundings, it is conjectured that the changes in the physical surroundings of the calorimeter as mentioned above resulted in different calibrations of the calorimeter as observed.

IX. CONCLUSIONS AND RECOMMENDATIONS

IX-1 Conclusions

1. A light-weight thin-walled stainless steel spherical calorimeter, surrounded by a radiation shield within an evacuated chamber, can be used to determine the constant-volume heat capacities of gases. The accuracy of the experiment depends upon the relative heat capacity of the charge of gas and the calorimeter.
2. A calorimeter of 0.0085 inch wall thickness and having a volume of 4530 c.c. has been designed. The heat capacity of the calorimeter is approximately 35 calories/°C at room temperature. This calorimeter has the lowest heat capacity of all previous calorimeters having approximately the same volume.
3. A uniform heating system inside the calorimeter eliminates extreme temperature gradients due to convection currents. With this type of uniform heating system, it is not necessary to install a stirring mechanism which increases the heat capacity of the calorimeter.
4. The electrical circuitry of the heaters has been so designed that all the heaters act as a platinum resistance thermometer. Thus an integrated temperature of the calorimeter and its contents can be recorded which has been reliably used as the true average temperature. Such a design also allows the approximate estimation of the temperature of the calorimeter and its contents during the heating period.
5. With a uniformly heating radiation shield, the temperature difference between the calorimeter and the radiation shield can be maintained within ± 0.2°C and a stable control can be achieved.

6. Constant-volume heat capacities of gaseous trifluoromethane, chlorodifluoromethane and dichlorofluoromethane were determined in the density region of 0.01 gm/c.c. and a temperature range of 40 to 140°C. The heat capacity values are believed to be accurate within ± 2% and ± 3% at densities of 0.01 gm/c.c. and 0.006 gm/c.c. respectively.
7. Because of low density, the measured heat capacity is that of the ideal gas, C_V*, and can be compared with the heat capacity predicted by statistical mechanics using the fundamental vibrational frequencies from molecular spectroscopy.
8. For trifluoromethane and dichlorofluoromethane, the measured and predicted values of C_V* are almost identical at 100°C. However, the measured values are about 3% higher than the predicted at 40°C while at 140°C they are 3% lower.
9. For chlorodifluoromethane, the agreement between the measured and predicted values is nearly perfect at 100°C. The measured values are 1.5% lower than the predicted at 40°C and 1.5% higher than the predicted values at 140°C.
10. The fundamental frequency assignments of trifluoromethane, chlorodifluoromethane and dichlorofluoromethane are thus verified within the precision of this experimental study.

IX-2 Recommendations

1. It is recommended that each shield be segmented and heated with two separate heaters. Thus for two shields four heaters are recommended, each to be controlled separately. This will insure a better temperature difference control between the calorimeter and the shield.

2. It is recommended that a thermocouple be installed in the outer body of the calorimeter. After the heating period, a record of the temperature of the calorimeter shell could answer the questions of attainment of equilibrium and proper estimation of drift rate.
3. It is also recommended that the temperature of the vacuum container be measured by a thermocouple before and after the heating period.
4. It is recommended that automatic control be installed on the radiation shield in place of manual control.
5. For the attainment of better adiabaticity, the vacuum system should be maintained below 1 micron pressure and hence it is recommended that special high vacuum valves and fittings be used wherever necessary.
6. In order to improve the adiabaticity of the system, two concentric heat shields should be used.
7. It is recommended that a transistorized voltage-regulated Kepco power supply be installed in place of an auto battery. The stability of such a powersupply is ± 0.01 per cent for eight hours or more.

APPENDICES

APPENDIX A

CALIBRATION OF RESISTANCE THERMOMETER

The built-in platinum resistance thermometer of the calorimeter was calibrated by immersing it in an insulated constant temperature agitated oil bath whose temperature was measured by the Leeds and Northrup resistance thermometer for which a calibration report from the National Bureau of Standards was available. The temperature fluctuations at certain points of the bath fluctuated within ± .05°C at the lowest temperature and at higher temperatures the fluctuations were limited to ± .01°C .

The ice point was determined in an ice bath of ice and water slurry and is considered very reliable. The resistance for the ice bath is 14.1980 and this has been taken as Ro . Other resistances were then fitted by least square with $R_t = Ro(1 + A + BT^2)$ and the values of A and B were found as $A = 3.934564\ (10^{-3})$ and $B = -4.757502\ (10^{-7})$. The average deviation is ± .018°C and the maximum deviation is ± .045°C . The following data were used to evaluate the constants A and B for the platinum resistance thermometer of the calorimeter:

Resistance of the NBS Resistance Thermometer ohms.	Temperature °C	Resistance of the Calorimeter Thermometer ohms.
30.6353	50.856122	8.5094
32.6435	70.974634	9.0654
34.3717	88.385822	9.5414
37.7617	122.807772	10.4785
41.2431	158.537962	11.4421

APPENDIX B

SAMPLE CALCULATIONS

Run Number F-22-G-2 is given here as an example to illustrate the method for calculation of the gross heat capacity. The primary data are presented in Tables E-1 and E-2.

Definitions:

N: Normal reading of the resistance thermometer by Mueller Bridge before bridge correction.

R: Reverse reading of the resistance thermometer before bridge correction.

$2R_1$: Sum of the normal and reverse readings i.e. N+R before the heating period after bridge correction of -0.0060 ohms.

R_2 (Equil): Sum of the normal and reverse readings at the end of the heating period after bridge correction.

$2R_2$: Total resistance (after bridge correction) that would have been at the end of the heating period had there been no heat loss. $2R_2$ is reported as $2R_2$(corr) here.

Drift: Change in $2R_1$ and $2R_2$ per five minutes due to heat loss.

Differential Thermocouples:

3- Side of the upper shield versus side of the lower shield.

4- Side of the calorimeter versus top of the calorimeter.

5- Top of the calorimeter versus side of the calorimeter.

6- Bottom of the calorimeter versus side of the calorimeter.

7- Side of the upper shield versus side of the calorimeter.

8- Top of the upper shield versus top of the calorimeter.

9- Side of the lower shield versus side of the calorimeter.

10-Bottom of the lower shield versus bottom of the calorimeter.

Heaters:

Bottom: The variac reading of the lower shield heater.

Top: The variac reading of the upper shield heater.

Control: Sum of the differential thermocouple readings from control points 7, 8, 9, and 10 as observed in the deflection of the light beam from zero position during five minute period.

Several resistance readings were taken at intervals of five minutes before the start of the heating period. The change in resistance was plotted against the average control for that period, Figure E-4. The initial drift rate was graphically determined to be -0.0010 ohm/5 min for zero control. The slope of the line was used to estimate the effect of the shield control.. The last resistance reading was 16.7089 at 1:59.

The power was turned on at 1:59 1/2. The power to the calorimeter was estimated by measuring the voltage and current three times during the heating period. The calorimeter was heated for 30.0005 mins. and the power was turned off at 2:29 1/2. After allowing the whole system to equilibrate for ten minutes, resistance readings were again taken every five minutes from 2:39 1/2. The final drift rate after the heating period was graphically determined in identically the same way as the initial drift rate was estimated. The final drift rate was found to be -0.0020 ohm/5 min. The slope of the line in Figure E-4 determined the effect of the shield control on the final drift rate. Using the final drift rate and correcting for the effect of the shield control during the equilibrium period, the resistance at 2:39 1/2 was extrapolated back to 2:29 1/2: R' = 17.4016 + (.0020)(2) - (.0005)(2) = 17.4046 ohms where drift correction is 0.0005 ohms per five minutes due to shield control. After bridge correction, R_2 (Equil): 17.4046 - 0.0060 = 17.3986 . The average drift rate is calculated as

$$\frac{0.0010 + 0.0020}{2} = 0.0015 \text{ ohm/5 min}$$

Accounting for the shield control during the heating period, the corrected drift rate was found to be from Figure E-4,

$$\frac{\text{(Corrected Drift Rate)}}{\text{(5 min)}} = 0.0015 + 0.0001 = 0.0016 \text{ ohm/5 min}$$

Using this corrected drift rate, the resistance change that would have occurred if there were no heat loss during the heating period is calculated.

$$\therefore \; \Delta R = \frac{\text{(Corrected Drift Rate)(Time)}}{\text{(5 min)}} = \frac{(0.0016)(30.0005)}{(6)} = 0.0096 \text{ ohms}$$

Therefore, the total resistance after bridge correction that would have been at the end of the heating period (assuming no heat loss) is: $2R_2 = R_2\,(\text{Equil}) + \Delta R = 17.4046 + .0096 - .0060 = 17.4082$ ohms . For the calculation of $(C_{gross})_{mean}$, a computer program in MAD language, Appendix C, was written. The following informations were fed in as data:

$2R_1 = 16.7027$ $I_1 = 0.3693$ $V_1 = 3.0910$

$2R_2 = 17.4082$ $I_2 = 0.3681$ $V_2 = 3.1250$

R_2 (Equil) = 17,3986 $I_3 = 0.3887$ $V_3 = 2.1550$

Time = 30.0005

The computer program calculates and prints out the following results:

(a) Using the values of $2R_1$, $2R_2$, and $2R_2$(Equil), T_1, T_2, T_2(Equil) are calculated from the formula, $R = 14.1920\ (1 + 3.934564 \times 10^{-3}\ T - 4.75702 \times 10^{-7}\ T^2)$ as:

$T_1 = 45.0823$, $T_2 = 57.8705$, T_2(Equil) $= 57.6963$. T_2 is reported as T_2(corr) in Appenidx E. (b) The heat input is calculated from the formula,

$$\text{Power} = (1.010) * \frac{14.3403\ \text{Cal}}{\text{Watt min.}} * \text{Time} * \text{Watts}$$

$$\text{where Watts} = \frac{(V_1 * I_1 + V_2 * I_2 + V_3 * I_3 - \frac{3 * V_2 * V_2}{2018})}{3}$$

The quantity $\frac{3 * V_2 * V_2}{2018}$ is the amount of heat lost in the voltage measuring circuit. The factor 1.010 comes from the consideration of the voltage dividing circuit.

$\therefore$ Power = 482.1769 calories

(c) The gross heat capacity is then calculated as

$$C_{gross} = \frac{\text{Power}}{T_2(\text{corr}) - T_1} = \frac{q}{\Delta T - \Delta T_{corr}} = \frac{482.1769}{12.6463} = 38.1279\ \text{Cal/°C}$$

APPENDIX C

COMPUTER PROGRAM FOR CALCULATION OF GROSS HEAT CAPACITY

```
$COMPILE MAD,EXECUTE,PRINT OBJECT,PUNCH OBJECT,DUMP
START      READ FORMAT DATA,R1,R2,REQ,I1,I2,I3,V1,V2,V3,TIME
           VECTOR VALUES DATA=$10F7.4*$
           A=4.757502E-07
           B=3.934564E-03
           C1=(R1/14.1980)-1.0
           T1=(B-SQRT.(B*B-4.*A*C1))/(2.*A)
           C2=(R2/14.1980     )-1.0
           T2=(B-SQRT.(B*B-4.*A*C2))/(2.*A)
           C3=(REQ/14.1980)-1.0
           TEQ=(B-SQRT.(B*B-4.*A*C3))/(2.*A)
           TDRIFT=T2-T1
           TAVE=(T2+T1)/2.0
           WATTS=(V1*I1+V2*I2+V3*I3-3.0*V2*V2/2018)/3.0
           POWER=1.010*14.3403*TIME*WATTS
           CGROSS=POWER/TDRIFT
           PRINT FORMAT ANSWER,R1,R2,REQ,T1,T2,TEQ,TDRIFT,POWER,CGROSS,
          1TAVE
           VECTOR VALUES ANSWER=$1H0,10F10.4*$
           TRANSFER TO START
           END OF PROGRAM
$DATA
```

APPENDIX D

GENERALIZED PLOT OF $C_V-C_V^*$ AS FUNCTION OF REDUCED DENSITY WITH REDUCED TEMPERATURE AS PARAMETER

If the law of corresponding states holds good for several gases, then at the same reduced temperature and density those gases have the same $C_V-C_V^*$ in a molar basis. From the law of corresponding states, the compressibility factor $Z = \frac{PV}{RT}$ can be expressed as a function of reduced temperature and density.

From the equation $Z = \frac{p}{RT\rho}$, we get

$$\left(\frac{dp}{dT}\right)_\rho = R\rho\left[T\,\frac{dZ}{dT} + Z\right] \qquad (D\text{-}1)$$

and

$$\left(\frac{d^2p}{dT^2}\right)_\rho = R\rho\left[T\left(\frac{d^2Z}{dT^2}\right)_\rho + \frac{2}{\rho}\left(\frac{dZ}{dT}\right)_\rho\right] \qquad (D\text{-}2)$$

combining equations (D-1) and (D-2), we have

$$C_V-C_V^* = -RT\int_0^\rho\left[\frac{T}{\rho}\left(\frac{d^2Z}{dT^2}\right)_\rho + \frac{2}{\rho}\left(\frac{dZ}{dT}\right)_\rho\right] \qquad (D\text{-}3)$$

Substituting $T = T_r\,T_c$ and $\rho = \rho_r\,\rho_c$, it follows

$$C_V-C_V^* = -\,RT_r\int_0^{\rho_r}\left(\frac{T_r}{\rho_r}\right)\left(\frac{d^2Z}{dT_r^2}\right)_\rho + \left(\frac{2}{\rho_r}\right)\left(\frac{dZ}{dT_r}\right)_\rho\ d\rho r \qquad (D\text{-}4)$$

Hwang(26) plotted experimental $C_V-C_V^*$ values on the reduced basis for chlorodifluoromethane, dichlorotetrafluoroethane, chloropentafluoroethane and propylene. The worst scatter is about 30 per cent and on the average the data agree within 10 per cent. However, De Never's perfluorocyclobutane data did not agree with the generalized values and it can be explained by the fact that it has a cyclic configuration instead of chain structure. The generalized plot is shown in Figure D-1.

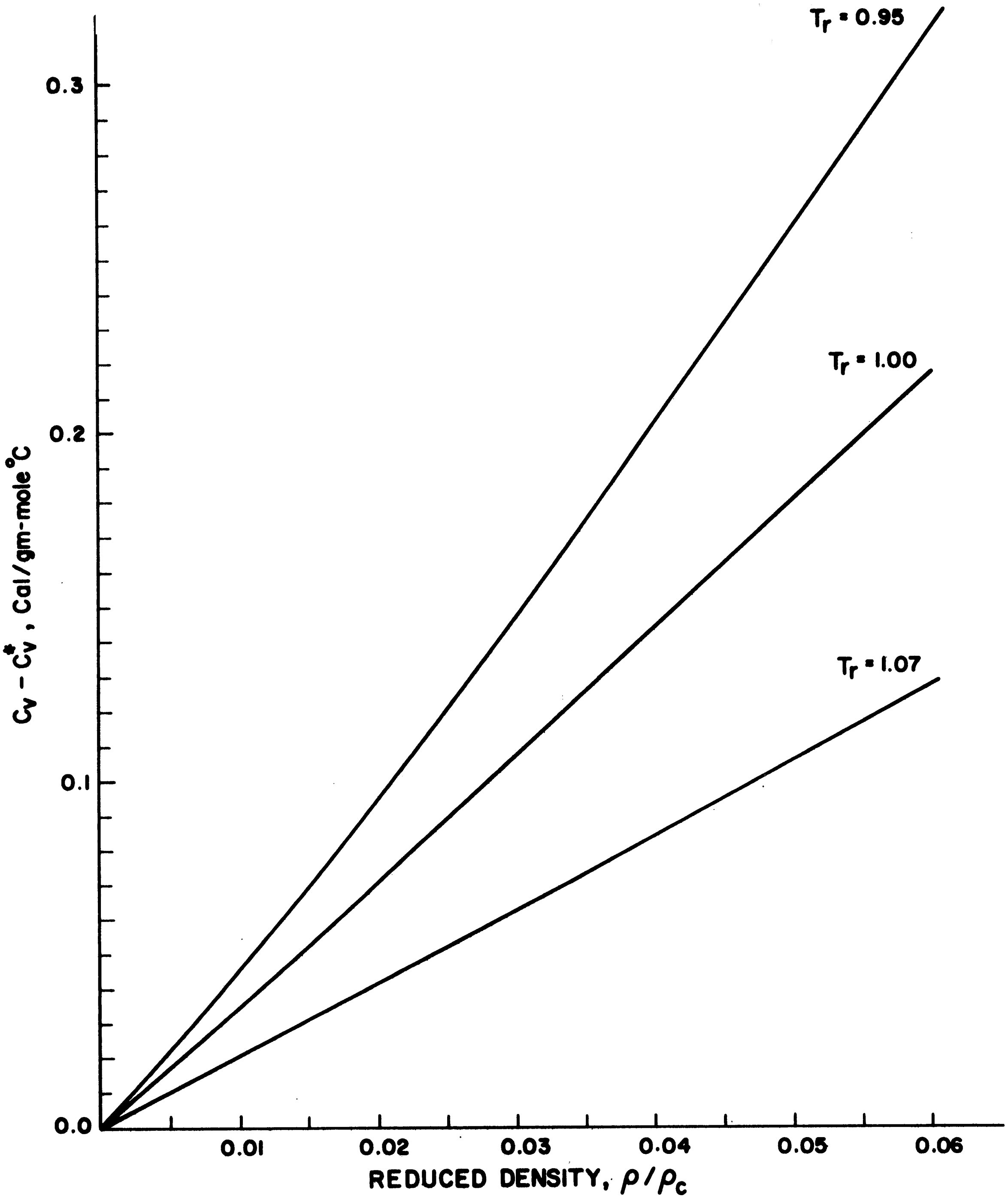

Figure D-1. Generalized Plot of $C_V - C_V^*$ Versus Reduced Density for Chlorodifluoromethane by Hwang.(26)

APPENDIX E

PRIMARY DATA AND TABULATED GROSS HEAT CAPACITY DATA

TABLE E-1

PRIMARY DATA
(Before Heating)

DATE: March 23, 1966 Run No. 2 CHARGE: F-22-G-2

Time	N	R	Total	Drift (5 min)	Control	Heaters Bottom	Top
1:24	8.3440	8.3716	16.7156	-.0004	13/10 min	14	13
1:34	8.3436	8.3712	16.7148	-.0004	-5		
1:39	8.3430	8.3710	16.7140	-.0008	4		
1:44	8.3428	8.3704	16.7132	-.0003	3		
1:49	8.3425	8.3704	16.7129	-.0014	3		
1:54	8.3420	8.3695	16.7115	-.0026	-8		
1:59	8.3405	8.3684	16.7089				

TABLE E-2

PRIMARY DATA
(During and After Heating)

DATE: March 23, 1966 Run No. 2-A CHARGE: F-22-G-2

Time	N	R	Total	Drift (5 min)	Control	Heaters Bottom	Top
2:39½	8.6808	8.7208	17.4016	-.0024	-9	16	15
2:44½	8.6796	8.7196	17.3992	-.0015	12		
2:49½	8.6971	8.7186	17.3977	-.0012	4		
2:54½	8.6784	8.7181	17.3965	-.0023	-7		
2:59½	8.6774	8.7168	17.3942	-.0026	1		
3:04½	8.6760	8.7156	17.3916	-.0024	-2		
3:09½	8.6750	8.7142	17.3892	-.0022	2		
3:14½	8.6738	8.7132	17.3870				

Differential Thermocouple Readings

3					18				12																										
4					14				15						17															3					
5																														1					
6					-20				-20						-22															0					
7	1	4	6	10	12	13	11	10	8	8	8	8	8	8	+11	12	10	8	5	2	0	-1	1	2	2	1	0	-1	0	1	1	1	1	1	1
8	0	-2	-5	-7	-6	-7	-8	-8	-10	-11	-11	-11	-12	-12	-10	-10	-7	-4	-2	-2	-3	-3	-2	0	1	0	0	-1	-1	-1	0	0	0	0	0
9	-2	-3	-6	-6	-4	-3	-3	-2	-3	-3	-5	-5	-8	-7	-6	-6	-4	0	1	1	0	0	1	3	4	3	1	0	0	1	1	0	0	1	1
10	-2	-2	-1	-1	4	7	8	7	7	6	5	4	3	3	4	3	4	3	2	1	-1	-2	-2	0	0	0	-1	-2	-2	-1	-1	-2	-2	-1	-1

Heating Period Control

Equilibrium Period

Control

HEATER:

On	1:59½
Off	2:29½
Time	30.0005
$2R_1$	16.7027
$2R_2$	17.4082
Drift	-.0020Ω (5 min)

Current (amp)	.3694	.3682	.3667
Voltage (volt)	3.0910	3.1250	3.1550
Current	.3692	.3680	.3667

Temperature Control	O.K.
Temperature Drift	O.K.
Current Stability	O.K.
Voltage Stability	O.K.
Drift Reasonable	O.K.
Vacuum	5μ

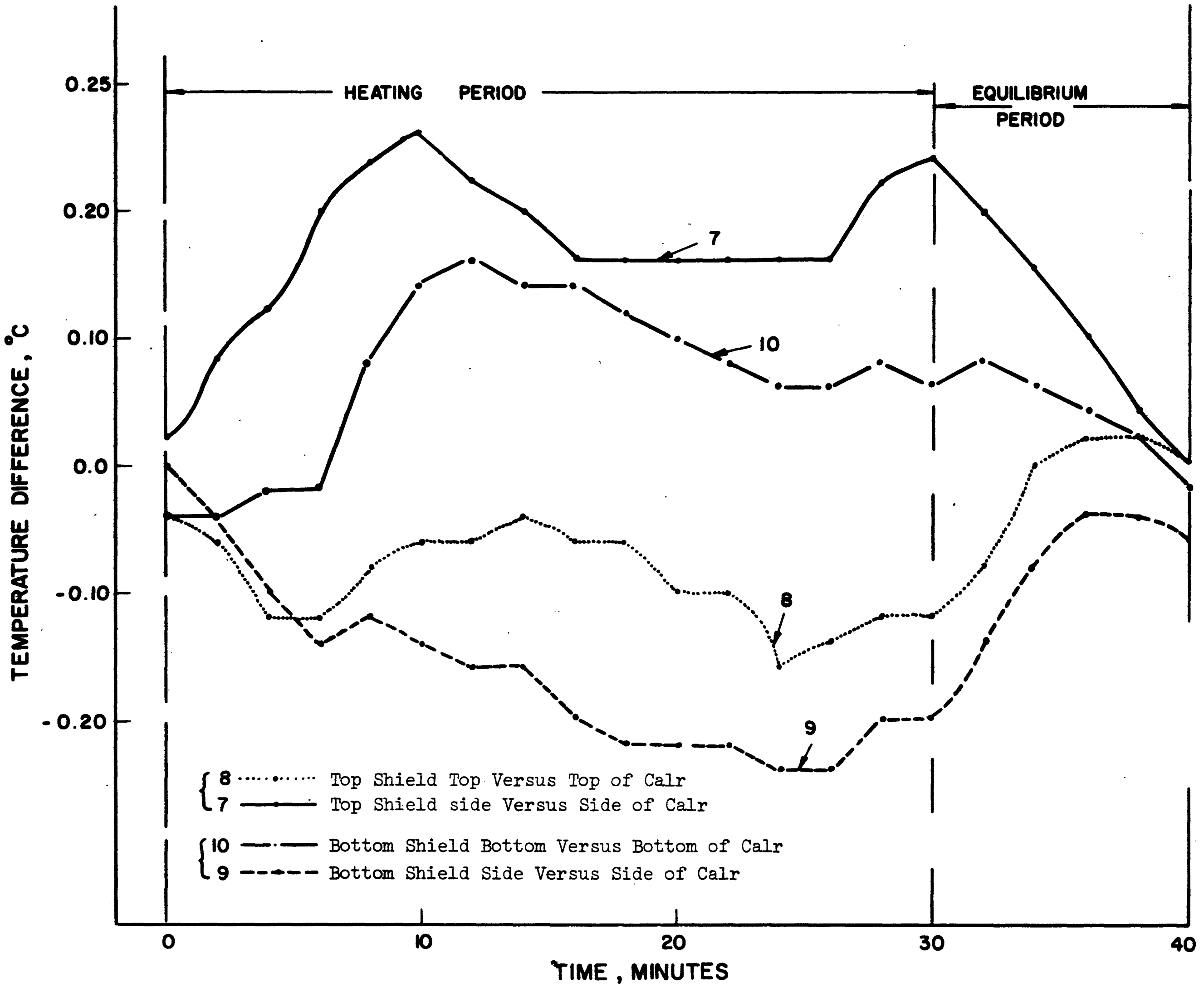

Figure E-1. Shield Control Versus Time in Minutes.
(Run No. F-22-G-2)

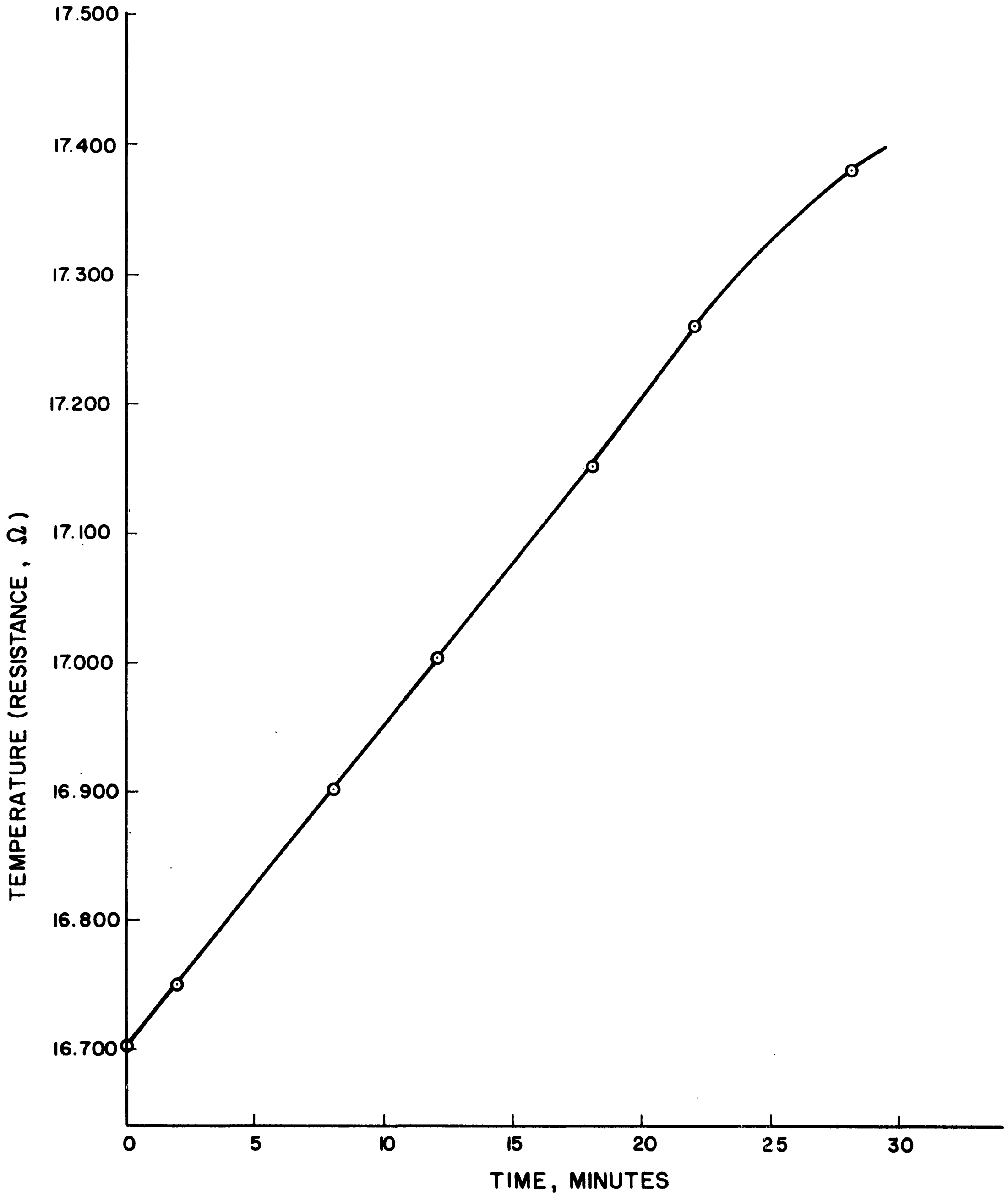

Figure E-2. Temperature (Resistance) Versus Time During Heating.
(Run No. F-22-G-2)

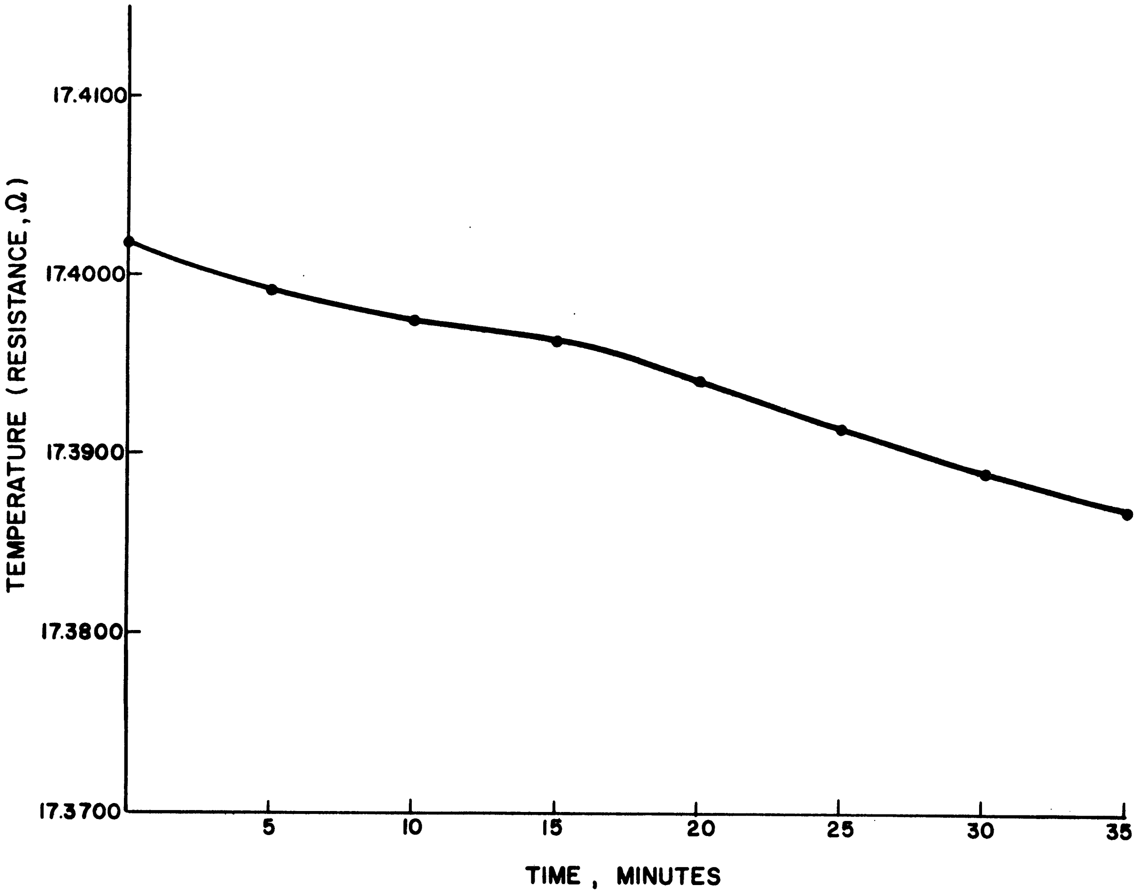

Figure E-3. Temperature (Resistance) Versus Time After Equilibrium.

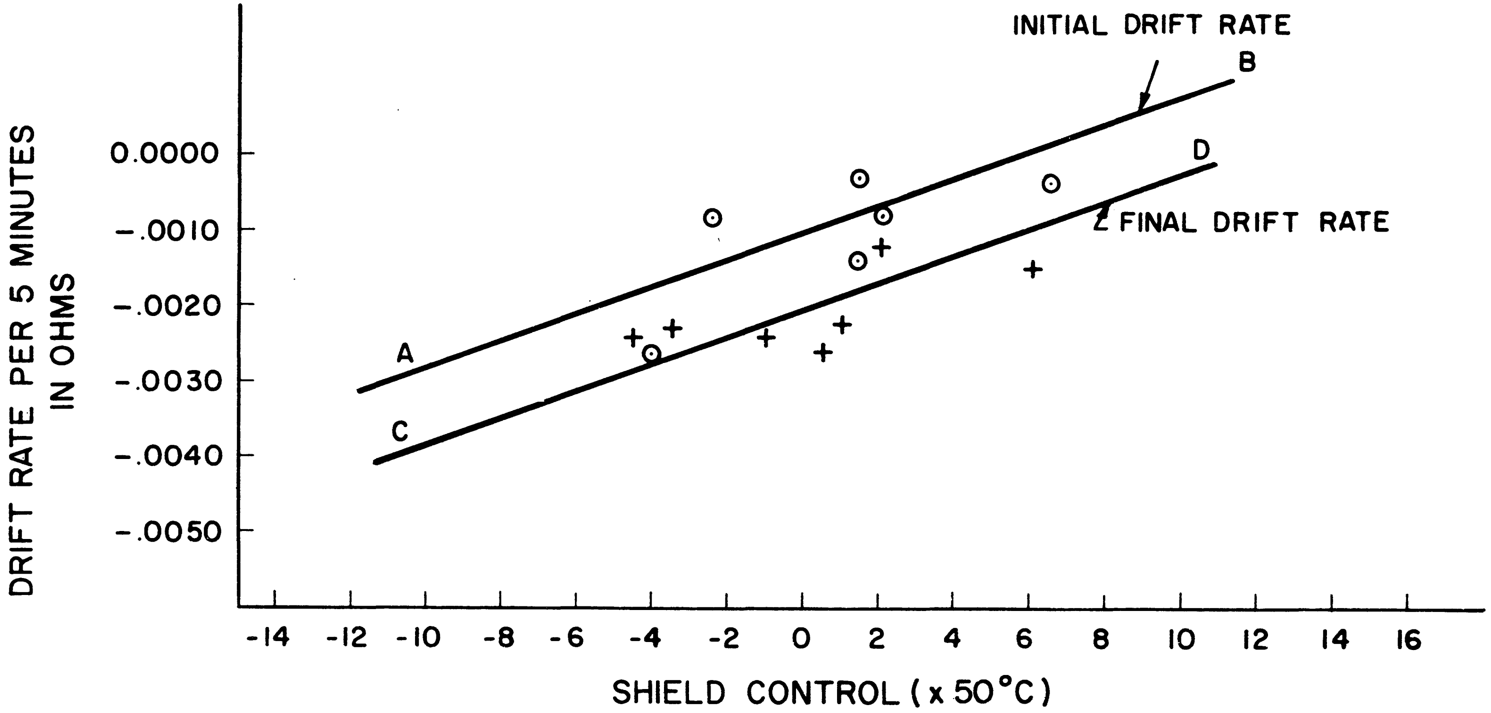

Figure E-4. Estimation of Drift Rate.
(Run No. F-22-G-2)

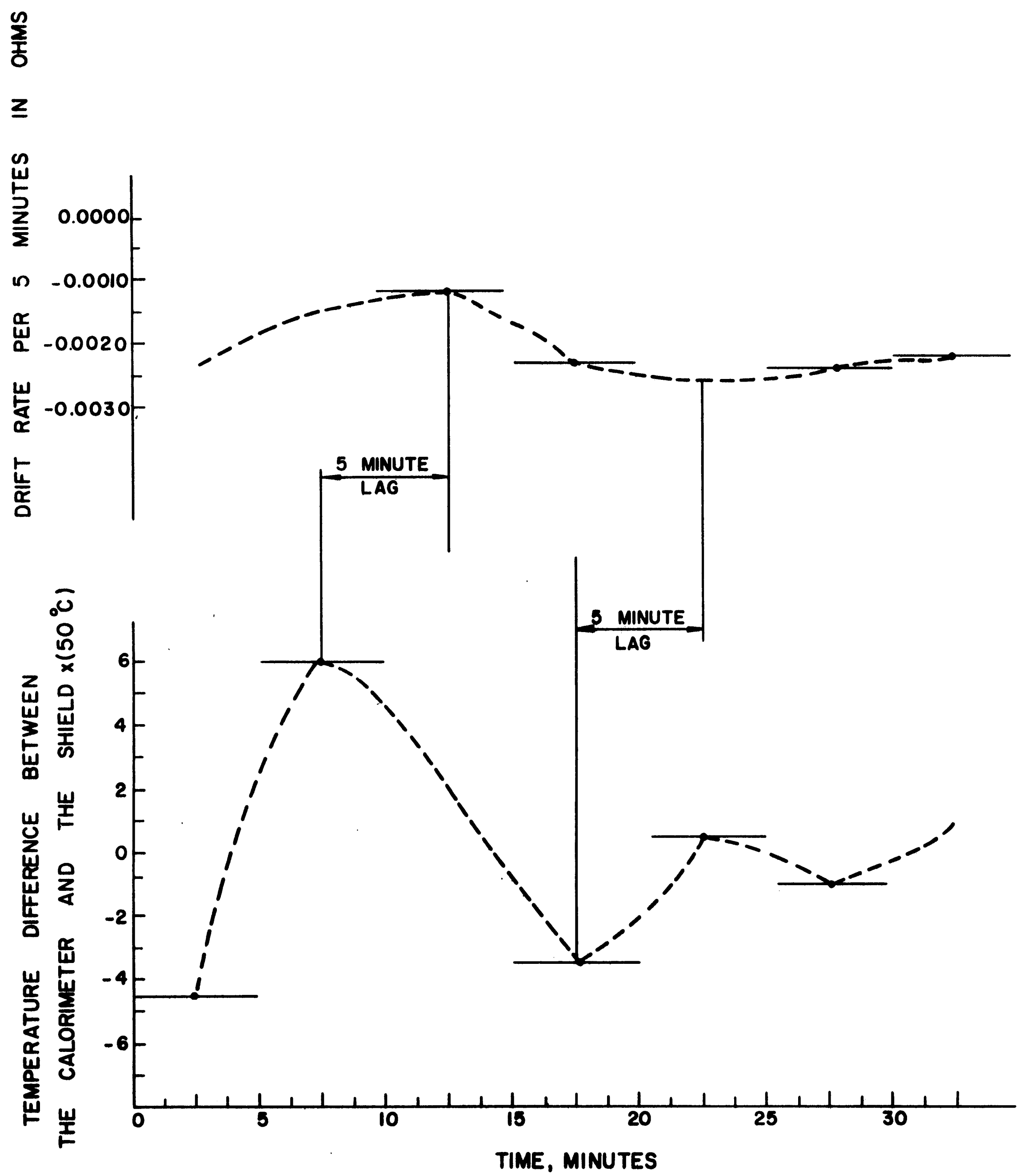

Figure E-5. Effect of Shield Control on Drift Rate after Equilibration. (Run No. F-22-G-2)

TABLE E-3

TABULATED DATA FOR GASEOUS NITROGEN (N_2)

Run No.	$2R_1$ ohms	$2R_2$(Corr.) ohms	$2R_2$(Equil.) ohms	T_1 °C	min.	Initial Drift Rate ohms/5 min.	Final Drift Rate ohms/5 min.	T_2(Corr.) °C	T_2(Equil.) °C	ΔT-$\Delta T_{corr.}$ °C	Energy Input Calories	C_{gross} Cal/°C	T_{mean} °C
N_2-A-1	16.0842	16.6838	16.6838	33.9038	30.0000	+0.0002	-0.0004	44.7403	44.7403	10.8365	422.7967	39.0161	39.3220
2	16.6778	17.2910	17.2874	44.6317	29.9990	-0.0004	-0.0013	55.7434	55.6781	11.1118	435.1919	39.1650	50.1876
3	17.2676	17.9117	17.9021	55.3188	29.9975	-0.0013	-0.0017	67.0219	66.8473	11.7031	464.1022	39.6564	61.1704
4	17.8453	18.6431	18.6281	65.8139	30.0000	-0.0017	-0.0033	80.3523	80.9784	14.5383	581.9233	40.0268	73.0831
5	18.5532	19.3445	19.3229	78.7114	30.0040	-0.0033	-0.0038	93.1771	92.7815	14.4657	584.3381	40.3948	85.9442
6	19.2364	20.0356	20.0110	91.1979	30.0020	-0.0033	-0.0048	105.8535	105.4016	14.6556	596.3316	40.6896	98.5257
7	19.8921	20.6844	20.6478	103.2181	30.0000	-0.0048	-0.0068	117.7904	117.1161	14.5723	602.5581	41.3494	110.5043
8	20.5521	21.3666	21.3204	115.3534	30.0000	-0.0068	-0.0081	130.3803	129.5264	15.0268	621.7302	41.3747	122.8669
9	22.0272	22.8118	22.7458	142.6093	30.0002	-0.0092	-0.0115	157.1827	155.9547	14.5734	617.4606	42.3691	149.8960
N_2-B-1	16.0285	16.8310	16.8310	32.8986	30.0020	+0.0000	-0.0009	47.4050	47.4050	14.5064	562.5752	38.7813	40.1518
2	16.8168	17.6270	17.6144	47.1478	30.0000	-0.0009	-0.0020	61.8449	61.6159	14.6970	574.1182	39.0635	54.4964
3	15.9822	16.6539	16.6521	32.0632	29.9990	+0.0001	-0.0006	44.1992	44.1667	12.1360	467.2566	38.5018	38.1312
4	16.7620	17.7029	17.6987	46.1557	30.0000	+0.0000	-0.0008	63.2244	63.1481	17.0688	661.2134	38.7382	54.6901
5	17.9623	18.7368	18.7272	67.9428	30.0000	-0.0011	-0.0018	82.0632	81.8879	14.1204	557.7172	39.4972	75.0030
6	18.6924	19.4874	19.4730	81.2524	30.0000	-0.0018	-0.0024	95.7950	95.5311	14.5426	583.0215	40.0907	88.5237
7	19.4347	20.2380	20.2176	94.8293	30.1000	-0.0021	-0.0035	109.5736	109.1985	14.7443	597.9170	40.5525	102.2014
8	21.6458	22.4812	22.4460	135.5443	30.0000	-0.0046	-0.0058	151.0355	150.3816	15.4913	642.5965	41.4812	143.2899
9	16.1285	17.0420	17.0336	34.7034	29.9980	-0.0004	-0.0014	51.2277	41.0754	16.5242	635.1648	38.4384	42.9656
10	17.0160	17.9313	17.9175	50.7564	29.9990	-0.0014	-0.0026	67.3786	67.1275	16.6222	649.9440	39.1010	59.0675
11	18.5225	19.4313	19.4097	78.1512	30.0000	-0.0026	-0.0038	94.7670	94.3713	16.6158	661.5201	39.8127	86.4591
12	19.5568	20.5559	20.4265	97.6669	30.0010	-0.0038	-0.0049	113.5824	113.0412	16.5154	666.9135	40.3812	105.3247
13	20.3674	21.5630	21.5126	111.9537	40.0000	-0.0049	-0.0065	134.0121	133.0798	22.0584	907.6113	41.1458	122.9829
14	21.4668	22.6347	22.5629	132.2328	40.0000	-0.0065	-0.0083	153.8885	152.5537	21.6557	918.8437	42.4296	143.0606
N_2-C-1	16.1816	17.1214	17.1082	35.6622	29.9700	-0.0007	-0.0016	52.6671	52.4277	17.0049	629.7091	37.0310	44.1646
2	17.0920	18.0233	18.0107	52.1340	30.0010	-0.0016	-0.0025	69.0531	68.8238	16.9191	641.4756	37.9142	60.5936
3	17.9853	18.9059	18.8867	68.3614	30.0000	-0.0025	-0.0033	85.1527	84.8018	16.7913	648.9518	38.6481	76.7570
4	18.8624	19.7785	19.7521	84.3577	30.0000	-0.0033	-0.0044	101.1330	100.6486	16.7753	654.8821	39.0385	92.7454
5	19.7895	20.7045	20.6771	101.3349	30.0200	-0.0036	-0.0054	118.1608	117.6560	16.8259	659.6261	39.2030	109.7478
6	20.6212	21.5298	21.4872	116.6261	30.0000	-0.0054	-0.0068	113.3980	132.6100	16.7719	666.8723	39.7613	125.0120
N_2-D-1	19.3089	20.2242	20.1804	92.5252	30.0000	-0.0069	-0.0082	109.3198	108.5145	16.7946	640.0189	38.1085	100.9225
2	18.6301	19.5478	19.5166	80.1149	30.0010	-0.0041	-0.0065	96.9020	96.3301	16.7870	627.2210	37.3634	88.5085
3	19.4433	20.3539	20.3089	94.9869	30.0000	-0.0065	-0.0081	111.7053	110.8775	16.7185	637.7543	38.1467	103.3461
4	15.9516	16.7190	16.7130	31.5112	30.0000	-0.0005	-0.0015	45.3773	45.2687	13.8661	498.7318	35.9677	38.4443
5	16.7028	17.4715	17.4571	45.0841	30.1000	-0.0015	-0.0025	59.0200	58.7585	13.9359	508.6856	36.5019	52.0521
6	17.3487	18.1150	18.0964	56.7906	30.0000	-0.0022	-0.0042	70.7229	70.3841	13.9323	513.2577	36.8394	63.7567
7	18.1246	18.8883	18.8631	70.8977	29.9960	-0.0030	-0.0048	84.8310	84.3705	13.9333	525.9800	37.7497	77.8644
8	18.8223	19.5727	19.5391	83.6250	30.0020	-0.0048	-0.0059	97.3584	96.7425	13.7334	521.9021	37.9434	90.4917
9	20.3957	21.3994	21.3478	112.4744	30.0000	-0.0067	-0.0089	130.9866	130.0328	18.5122	736.5653	39.7882	121.7305
10	21.2374	22.2619	22.1941	127.9929	30.1000	-0.0089	-0.0116	146.9631	145.7049	18.9402	751.9584	39.5914	137.4780
11	16.4637	17.4182	17.4146	40.7591	30.0000	0.0000	-0.0012	58.0522	57.9868	17.2931	626.9316	36.2533	49.4057
12	17.4013	18.3476	18.3356	57.7454	29.9990	-0.0012	-0.0027	74.9613	74.7425	17.2159	635.5648	36.9173	66.3533
13	18.3090	19.2351	19.2153	74.2576	30.0000	-0.0077	-0.0037	91.1740	90.8117	16.9164	632.6550	37.3988	82.7158
14	19.1451	20.0609	20.0333	89.5270	30.0000	-0.0037	-0.0048	106.3183	105.8113	16.7913	639.0969	38.0611	97.9277
15	20.1315	21.0404	21.0038	107.6157	30.0000	-0.0048	-0.0063	124.3554	123.6800	16.7397	646.3965	38.6145	115.9855
16	20.9333	21.8411	21.7901	122.3792	30.0000	-0.0063	-0.0077	139.1604	138.2158	16.7812	653.8653	38.9642	130.7698
17	21.7248	22.6259	22.5701	137.0066	30.0000	-0.0077	-0.0089	153.7249	152.6876	16.7183	661.2802	39.5543	145.3658

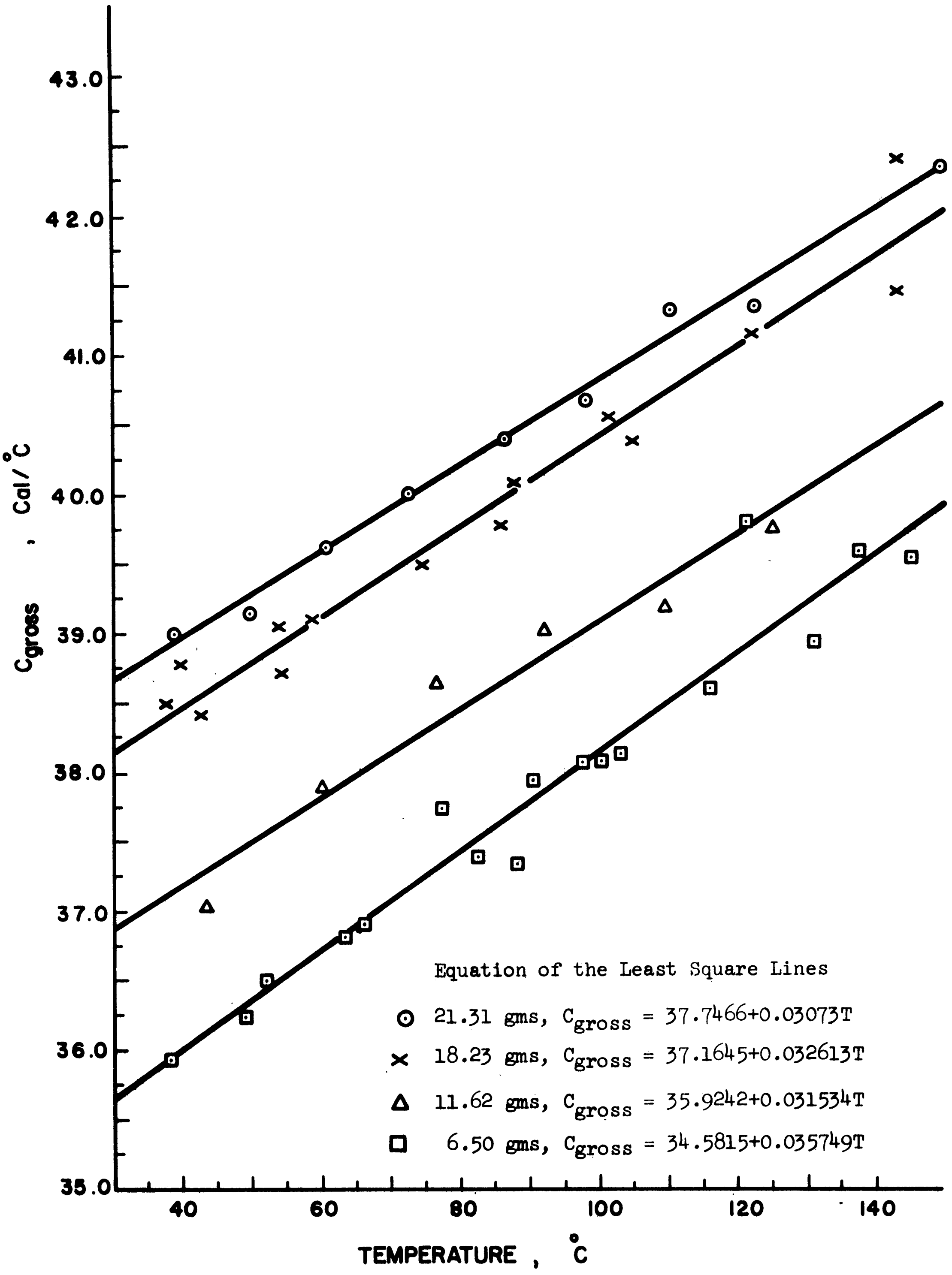

Figure E-6. Gross Heat Capacities with Nitrogen for Calibration of the Calorimeter (1964).

TABLE E-4

TABULATED DATA FOR GASEOUS NITROGEN (N_2)

Run No.	$2R_1$ ohms	$2R_2$(Corr.) ohms	$2R_2$(Equil) ohms	T_1 °C	min.	Initial Drift Rate ohms/5 min.	Final Drift Rate ohms/5min.	T_2(Corr) °C	T_2(Equil) °C	ΔT-ΔT_{corr} °C	Input Calories	C_{gross} Cal/°C	T_{mean} °C
N_2-E-1	15.9592	16.6103	16.6001	31.6483	30.0000	-0.0012	-0.0022	43.4104	43.2259	11.7620	453.7152	38.5745	37.5293
2	16.5831	17.2283	17.2061	42.9183	30.0010	-0.0023	-0.0031	54.6059	54.2032	11.6875	456.9348	39.0959	48.7621
3	17.9632	18.6126	18.5826	67.9591	29.9990	-0.0026	-0.0040	79.7955	79.2480	11.8364	466.5975	39.4207	73.8773
4	18.5260	19.1908	19.1626	78.2151	30.8000	-0.0040	-0.0048	90.3632	89.8472	12.1481	485.9015	39.9980	84.2892
5	19.1173	19.7643	19.7351	89.0184	30.0001	-0.0048	-0.0065	100.8725	100.3367	11.8541	480.7475	40.5555	94.9454
6	19.6796	20.3292	20.2854	99.3187	30.0000	-0.0065	-0.0075	111.2509	110.4453	11.9323	484.5902	40.6118	105.2848
N_2-F-1	15.6737	16.3562	16.3538	26.5014	30.0010	+0.0005	-0.0005	38.8161	38.7727	12.3147	474.9278	38.4929	32.6587
2	16.3776	17.0534	17.0468	39.2028	30.0010	-0.0008	-0.0016	51.4343	51.3147	12.2315	473.0714	38.6765	45.3185
3	15.7968	16.4498	16.4468	28.7198	30.0005	+0.0002	-0.0010	40.5078	40.4536	11.7880	448.6201	38.0574	34.6138
4	16.4422	17.1097	17.1001	40.3704	30.0000	-0.0010	-0.0018	52.4549	52.2809	12.0845	468.0937	38.7351	46.4127
5	17.0802	17.7474	17.7306	51.9201	30.0005	-0.0018	-0.0030	64.0335	63.7280	12.1133	472.5639	39.0119	57.9768
6	17.7037	18.3759	18.3567	63.2390	30.0005	-0.0030	-0.0040	75.4773	75.1272	12.2383	478.9023	39.1315	69.3581
7	19.0030	19.6675	19.6435	86.9278	30.0000	-0.0032	-0.0047	99.0967	98.6566	12.1689	489.8740	40.2562	93.0123
8*	19.6073	20.2705	20.2393	97.9928	30.0010	-0.0047	-0.0057	110.1712	109.5975	12.1785	496.6468	40.7808	104.0820
9*	20.1730	20.8370	20.7986	108.3785	30.0015	-0.0057	-0.0069	120.6032	119.8952	12.2247	502.2640	41.0860	114.4909
10*	15.6504	16.2218	16.2188	26.0817	30.0000	+0.0003	-0.0001	36.3881	36.3339	10.3064	387.7158	37.6189	31.2349
11	16.0674	16.4923	16.4940	33.6006	29.9990	+0.0003	+0.0001	41.2762	41.3069	7.6756	292.2842	38.0798	37.4384
12	16.5490	17.1147	17.1057	42.3016	30.0010	-0.0004	-0.0015	52.5456	52.3824	10.2441	398.4382	38.8946	47.4236
13	17.4544	18.0851	18.0683	58.7095	30.0000	-0.0026	-0.0026	30.1784	69.8724	11.4689	449.9782	39.2347	64.4439
14	18.2717	18.9008	18.8714	73.5778	30.0200	-0.0028	-0.0038	85.0595	84.5222	11.4817	453.2373	39.4746	79.3186
15	18.6986	19.3216	19.2982	81.3656	29.9995	-0.0030	-0.0047	92.7577	92.3293	11.3921	454.4259	39.8894	87.0617
16	19.2547	19.8852	19.8516	91.5328	30.0010	-0.0047	-0.0061	103.0914	102.4746	11.5586	461.9990	39.9701	97.3121
17	19.8005	20.4286	20.3926	101.5367	30.0000	-0.0061	-0.0069	113.0799	12.4174	11.5432	469.6845	40.6894	107.3083
N_2-G-1	16.3570	17.0276	17.0183	38.8305	30.0010	-0.0007	-0.0018	50.9667	60.7981	12.1362	456.3621	37.6035	44.8986
2	17.0044	17.6936	17.6785	50.5462	30.0005	-0.0018	-0.0028	63.9554	62.7827	12.5092	474.3102	37.9170	56.8008
3	18.1727	18.8582	18.8324	71.7738	29.9998	-0.0026	-0.0042	84.2810	83.8095	12.5071	482.1120	38.5470	78.0274
4	19.5483	20.2327	20.2021	96.9111	29.9998	-0.0043	-0.0058	109.4761	108.9135	12.5650	494.4811	39.3539	103.1936
5	18.9224	19.6061	19.5881	85.4543	30.0000	-0.0035	-0.0043	97.9708	97.6408	12.5165	488.7374	39.0474	91.7125
6	17.6522	18.3348	18.3078	62.3029	30.0020	-0.0028	-0.0040	74.7280	74.2357	12.4251	471.0935	37.9147	68.5154

* Data points are neglected

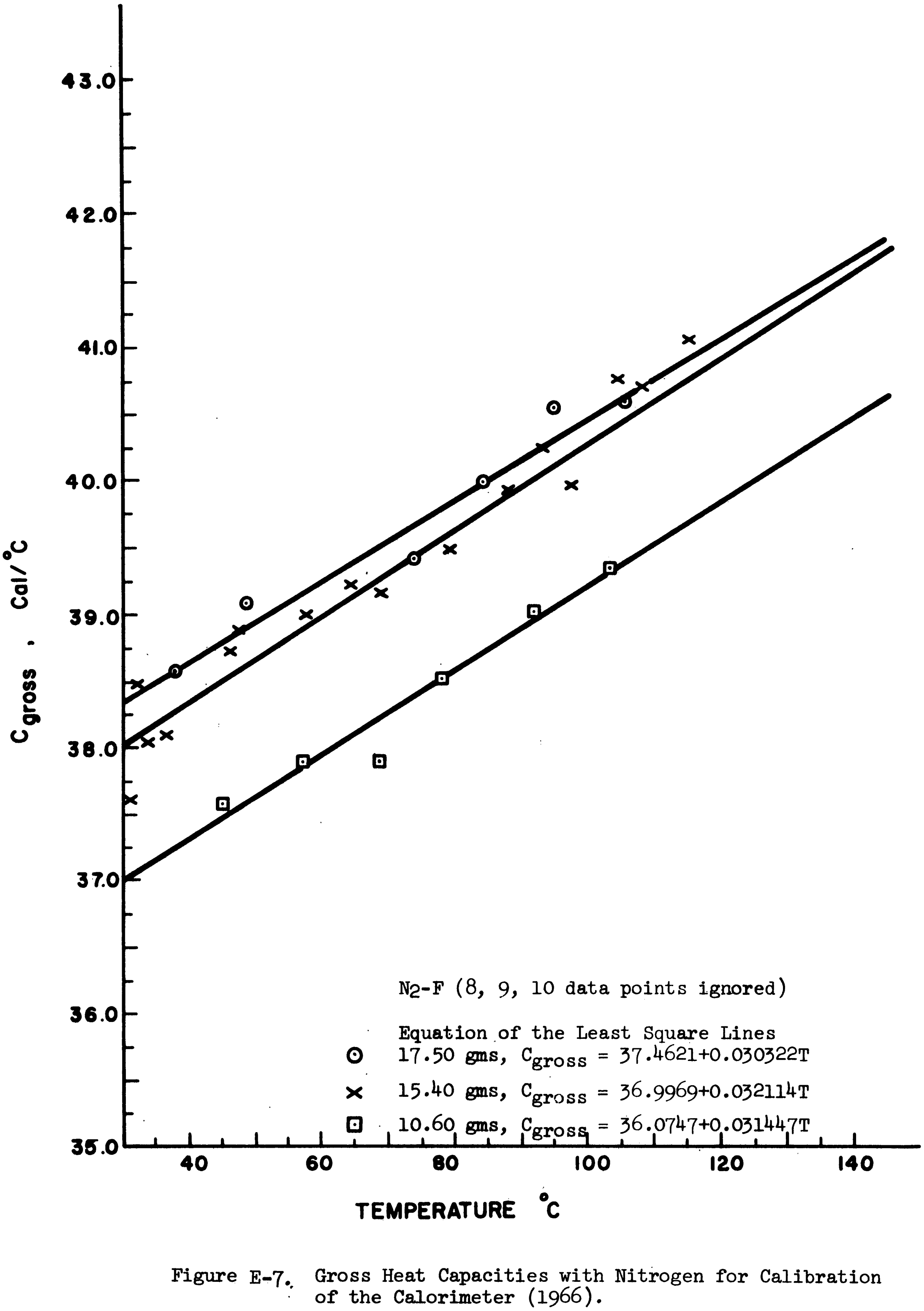

Figure E-7. Gross Heat Capacities with Nitrogen for Calibration of the Calorimeter (1966).

TABLE E-5

TABULATED DATA FOR GASEOUS TRIFLUOROMETHANE (CHF_3)

Run No.	$2R_1$ ohms	$2R_2$(Corr) ohms	$2R_2$(Equil) ohms	T_1 °C	min.	Initial Drift Rate ohms/5 min.	Final Drift Rate ohms/5 min.	T_2(Corr) °C	T_2(Equil) °C	ΔT-ΔT_{corr} °C	Input Calories	C_{gross} Cal/C	T_{mean} °C
F-23-A-1	16.0958	16.6707	16.6695	34.1132	30.0000	-0.0000	+0.0000	44.5032	44.4815	10.3900	446.8356	43.0062	39.3082
2	16.8122	17.3957	17.3883	47.0646	29.9999	-0.0006	-0.0012	57.6437	57.5094	10.5791	458.5518	43.3449	52.3541
3	17.3803	17.9615	17.9501	57.3642	30.0000	-0.0012	-0.0018	67.9282	67.7207	10.5641	464.8305	44.0011	62.6462
4	17.9311	18.5206	18.5068	67.3750	30.0010	-0.0018	-0.0026	78.1166	77.8648	10.7416	475.0897	44.2290	72.7458
5	18.4821	19.0749	19.0503	77.4141	30.0000	-0.0026	-0.0039	88.2427	87.7928	10.8286	480.1593	44.3417	82.8284
6	19.1294	19.7154	19.6938	89.2397	29.9990	-0.0027	-0.0037	99.9753	99.5791	10.7356	484.2838	45.1101	94.6075
7	19.6574	20.2471	20.2213	98.9115	30.0000	-0.0038	-0.0048	109.7409	109.2665	10.8294	489.5696	45.2073	104.3262
8	20.0212	20.6896	20.6566	105.5890	30.0000	-0.0044	-0.0058	117.8862	117.2782	12.2973	566.8109	46.0925	111.7376
9	20.4596	21.1436	21.1058	113.6505	30.0000	-0.0054	-0.0061	126.2605	125.5626	12.6101	580.2229	46.0126	119.9555
10	21.0488	21.9281	21.8795	124.5104	30.0000	-0.0061	-0.0082	140.7724	139.8718	16.2619	754.9760	46.4260	132.6414
11	21.8120	22.7016	22.6428	138.6214	30.0000	-0.0082	-0.0093	155.1326	154.0391	16.5112	782.7309	47.4061	146.8770
F-23-B-1	16.2035	16.8260	16.8190	36.0576	30.0010	-0.0012	-0.0012	47.3144	47.1877	11.2568	462.3787	41.0754	41.6860
2	16.8110	17.4361	17.4251	47.0428	30.0000	-0.0012	-0.0016	58.3772	58.1774	11.3344	469.3935	41.4133	52.7100
3	17.4150	18.0429	18.0309	57.9941	30.0000	-0.0016	-0.0025	69.4100	69.1915	11.4159	478.5442	41.9193	63.7020
4	17.9765	18.6085	18.5941	68.2012	30.0000	-0.0018	-0.0027	79.7207	79.4579	11.5194	488.9561	42.4462	73.9610
5	18.5677	19.1988	19.1796	78.9760	30.0015	-0.0027	-0.0035	90.5097	90.1583	11.5336	497.4279	43.1284	84.7428
6	19.7899	20.4064	20.3866	101.3239	30.0000	-0.0033	-0.0040	112.6713	112.3070	11.3475	502.4134	44.2754	106.9976
7	20.2965	21.0033	20.9733	110.6494	29.9990	-0.0040	-0.0054	123.6707	123.1172	13.0213	585.5060	44.9652	117.1601
8	20.9179	21.6229	21.5881	122.0952	30.0000	-0.0054	-0.0066	135.1204	134.4765	13.0253	589.4849	45.2570	128.6078
9	21.5494	22.5464	22.4948	133.7605	30.0010	-0.0065	-0.0090	152.2471	151.2882	18.4866	850.5391	46.0085	143.0038
F-23-C-1	16.2195	17.2654	17.2540	36.3466	30.0000	-0.0008	-0.0020	55.2789	55.0721	18.9324	763.3245	40.3185	45.8127
2	17.1700	17.7184	17.7052	53.5484	30.0000	-0.0020	-0.0026	63.5062	63.2663	9.9578	405.7182	40.7437	58.5273
3	17.6875	18.3411	18.3201	62.9455	29.9995	-0.0026	-0.0039	74.8428	74.4600	11.8983	490.1160	41.1922	68.8936
4	18.2919	18.9628	18.9352	73.9459	30.0000	-0.0039	-0.0050	86.1928	85.6882	12.2469	508.6455	41.5327	80.0694
5	19.1682	19.9002	19.8720	89.9497	30.0000	-0.0040	-0.0053	103.3668	102.8491	13.4171	566.5248	42.2240	96.6583
6	19.8245	20.5628	20.5244	101.9772	30.0000	-0.0053	-0.0066	115.5505	114.8434	13.5733	578.2114	42.5992	108.7639
7	20.4272	21.1635	22.1155	113.0541	29.9990	-0.0066	-0.0078	126.6280	144.2468	13.5738	582.0979	42.8838	119.8410
8	21.0674	21.7893	21.7383	124.8538	30.0010	-0.0078	-0.0093	138.2011	137.2566	13.3472	582.3645	43.6319	131.5274
9	21.6912	22.5040	22.4428	136.3846	30.0000	-0.0093	-0.0109	151.4592	150.3221	15.0746	653.9952	44.0474	143.9219
10	15.8254	16.4482	16.4363	29.2355	30.0020	-0.0006	-0.0016	40.3722	40.2638	11.1368	446.1306	40.0592	34.8039
11	16.3701	16.9913	16.9769	39.0672	30.0000	-0.0016	-0.0030	50.3088	50.0479	11.2416	453.2979	40.3234	44.6880
12	16.9554	17.5826	17.5634	49.6583	29.9990	-0.0030	-0.0037	61.0381	60.6893	11.3798	462.5597	40.6475	55.3482
13	17.5405	18.1546	18.1282	60.2733	30.0010	-0.0037	-0.0048	71.4442	70.9633	11.1709	468.1153	41.9048	65.8587
14	16.0057	16.6176	16.6098	32.4872	30.0000	-0.0007	-0.0013	43.5425	43.4013	11.0552	448.1063	40.5334	38.0148
15	16.0000	16.6239	16.6131	32.3844	29.9990	-0.0003	-0.0016	43.6564	43.4610	11.2720	452.3848	40.1334	38.0204
16	16.2003	16.8765	16.8697	35.9998	29.9990	-0.0005	-0.0021	48.2290	48.1058	12.2292	487.4770	39.8617	42.1144
17	16.8467	17.5347	17.5173	47.6893	30.0000	-0.0021	-0.0027	60.1679	59.8518	12.4786	500.4977	40.0764	53.9286
18	17.4843	18.1669	18.1411	59.2525	30.0000	-0.0037	-0.0049	71.6682	71.1982	12.4157	507.5252	40.8776	65.4603
19	18.0360	18.7182	18.6822	69.2843	29.9990	-0.0049	-0.0063	81.7235	81.0661	12.4392	515.5160	41.4429	75.5039
20	18.6527	19.3272	19.2858	80.5275	30.0000	-0.0063	-0.0071	92.8603	92.1022	12.3327	517.5471	41.9653	86.6939
21	19.4895	20.0576	20.0156	95.8334	30.0000	-0.0060	-0.0079	106.2577	105.4861	10.4243	446.6757	42.8496	101.0456
22	19.9683	20.7788	20.1218	104.6173	30.0010	-0.0079	-0.0099	119.5302	107.4374	14.9129	646.7473	43.3683	112.0738
23	20.6409	21.4678	21.3982	116.9890	30.0010	-0.0099	-0.0121	132.2513	130.9644	15.2623	664.2911	43.5251	124.6201
24	21.5360	22.5318	22.4538	133.5127	30.0000	-0.0090	-0.0148	151.9757	150.5265	18.4631	822.4496	44.5456	142.7442

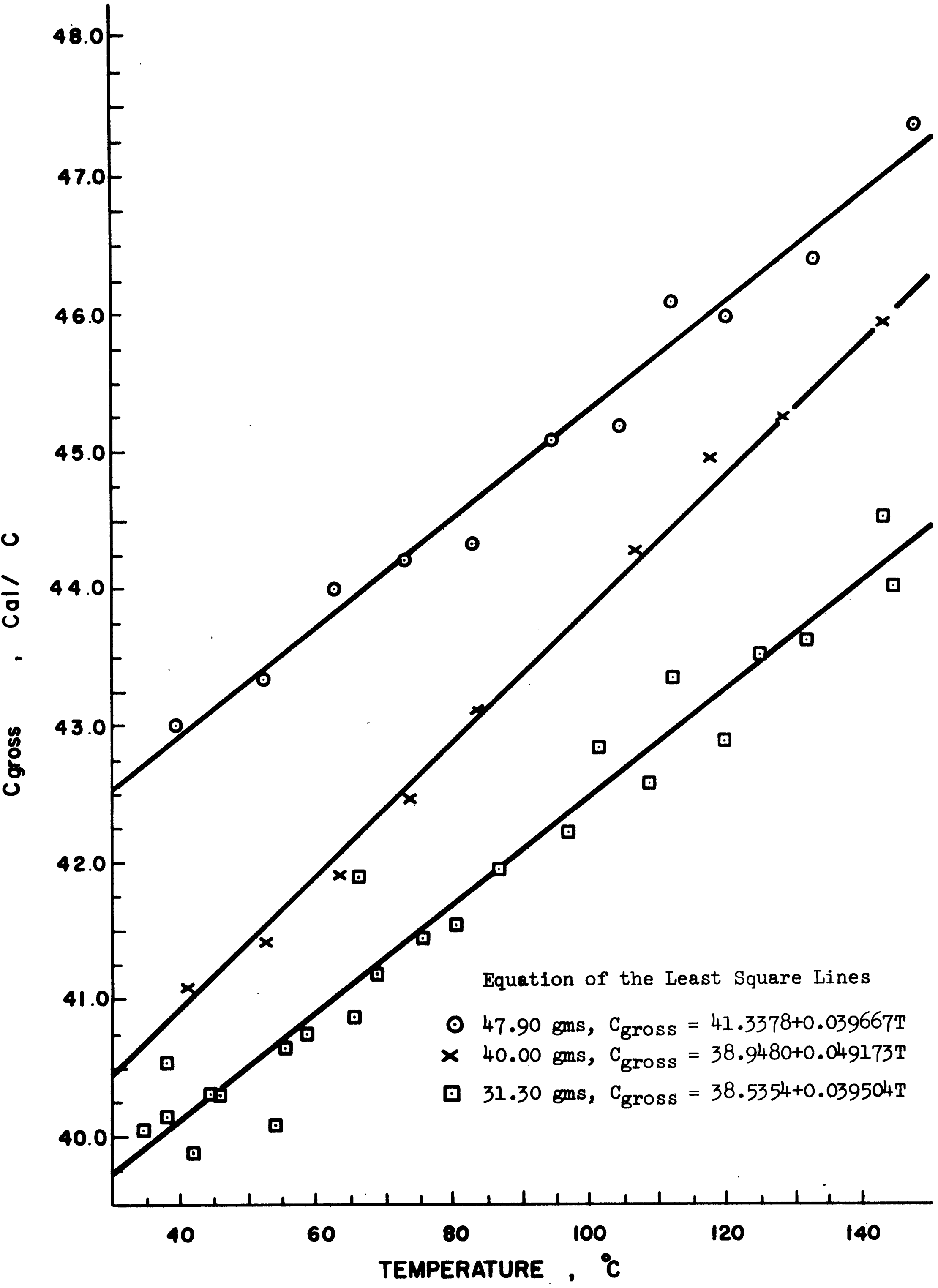

Figure E-8. Gross Heat Capacities for Trifluoromethane Using the Calorimeter (1964).

TABLE E-6

TABULATED DATA FOR GASEOUS CHLORODIFLUOROMETHANE ($CHClF_2$)

Run No.	$2R_1$ ohms	$2R_2$(Corr) ohms	$2R_2$(Equil) ohms	T_1 °C	min.	Initial Drift Rate ohms/5 min.	Final Drift Rate ohms/5 min.	T_2(Corr) °C	T_2(Equil) °C	ΔT-ΔT_{corr} °C	Energy Input Calories	C_{gross} Cal/°C	T_{mean} °C
*F-22-A-1	16.1313	16.7235	16.7200	34.7540	29.9980	-0.0005	-0.0011	45.4588	45.3954	10.7048	473.3933	44.2226	40.1064
2	16.7038	17.2905	17.2863	45.1022	30.0010	-0.0011	-0.0015	55.7343	55.6581	10.6321	475.3298	44.7070	50.4183
3	17.8500	18.4492	18.4354	65.8994	30.0010	-0.0020	-0.0027	76.8140	76.5623	10.9146	498.3403	45.6582	71.3567
4	19.0354	19.6795	19.6679	87.5203	30.0000	-0.0032	-0.0036	99.3168	99.1041	11.7965	552.0239	46.7956	93.4186
5	19.6139	20.2600	20.2378	98.1138	30.0015	-0.0036	-0.0043	109.9781	109.5699	11.8643	559.4324	47.1525	104.0459
6	20.1914	20.8318	20.8024	108.7168	29.9980	-0.0043	-0.0051	120.5073	119.9653	11.7906	561.8363	47.6513	114.6120
7	21.3067	22.0131	21.9753	129.2732	30.0000	-0.0057	-0.0062	142.3479	141.6472	13.0747	635.8915	48.6353	135.8106
8	21.9050	22.6102	22.5688	140.3443	30.0000	-0.0066	-0.0073	153.4330	152.6634	13.0887	641.1951	48.9884	146.8887
F-22-B-1	15.9893	16.8089	16.8023	32.1913	30.0010	-0.0005	-0.0011	47.0048	46.8853	14.8135	596.2672	40.2516	39.5981
2	17.3416	17.9812	17.9680	56.6617	29.9950	-0.0018	-0.0023	68.2868	68.0465	11.6251	485.1976	41.7372	62.4742
3	17.9433	18.6126	18.5958	67.5970	31.0000	-0.0023	-0.0028	79.7955	79.4889	12.1985	514.5396	42.1805	73.6962
4	18.5640	19.2138	19.1928	78.9085	30.0000	-0.0028	-0.0035	90.7842	90.3999	11.8757	503.9409	42.4345	84.8463
5	19.7610	20.4105	20.3871	100.8119	30.0010	-0.0035	-0.0041	112.7468	112.3162	11.9349	516.9027	43.3103	106.7794
6	20.3544	20.9972	20.9708	111.7145	30.0000	-0.0037	-0.0047	123.5582	123.0711	11.8436	518.0181	43.7381	117.6363
7	20.9226	21.5651	21.5333	122.1819	30.0005	-0.0047	-0.0056	134.0510	133.4627	11.8691	522.8693	44.0531	128.1164
8	21.4767	22.1178	22.0806	132.4159	30.0020	-0.0056	-0.0062	144.2894	143.5995	11.8736	526.6781	44.3571	138.3527
9	22.0300	22.6665	22.6299	142.6612	30.0000	-0.0062	-0.0067	154.4798	153.7993	11.8186	529.6912	44.8184	148.5705
F-22-C-1	15.9682	16.5311	16.5263	31.8107	30.0010	-0.0002	-0.0015	41.9778	41.8910	10.1672	395.1594	38.8663	36.8943
2	16.5153	17.0844	17.0766	41.6921	30.0005	-0.0015	-0.0021	51.9962	51.8548	10.3042	400.8590	38.9026	46.8442
3	17.2573	17.8452	17.8296	55.1320	30.0000	-0.0021	-0.0030	65.8121	65.5283	10.6801	426.8263	39.9645	60.4720
4	17.7880	18.3950	18.3726	64.7718	30.0000	-0.0030	-0.0038	75.8256	75.4171	11.0538	444.8527	40.2443	70.2987
5	19.1588	19.7288	19.7024	89.7777	30.0010	-0.0038	-0.0050	100.2211	99.7368	10.4435	428.4844	41.0290	94.9994
6	19.6606	20.2522	20.2198	98.9702	29.9990	-0.0050	-0.0055	109.8347	109.2389	10.8645	453.6727	41.7574	104.4024
7	20.6564	21.2248	21.1780	117.2746	30.0000	-0.0075	-0.0081	127.7601	126.8958	10.4856	444.8526	42.4252	122.5173
8	21.0970	21.6610	21.6070	135.4002	30.0100	-0.0081	-0.0090	135.8256	134.8262	10.4254	443.3897	42.5297	130.6129
F-22-D-1	15.9681	16.6938	16.6908	31.8089	29.9980	+0.0002	-0.0012	44.9212	44.8670	13.1124	493.0463	37.6016	38.3651
2	16.6814	17.2948	17.2870	44.6969	30.0015	-0.0012	-0.0018	55.8124	55.6708	11.1155	423.1761	38.0707	50.2546
3	17.2727	17.8400	17.8256	55.4114	30.0000	-0.0018	-0.0026	65.7175	65.4556	10.3061	394.9355	38.3204	60.5644
4	17.8011	18.3801	18.3627	65.0100	29.9990	-0.0026	-0.0035	75.5538	75.2336	10.5439	408.9261	38.7833	70.2819
5	18.3337	18.9096	18.8862	74.7079	30.0005	-0.0035	-0.0043	85.2203	84.7927	10.5125	413.0735	39.2937	79.9641
6	18.8483	19.4247	19.4001	84.1001	30.0000	-0.0043	-0.0047	94.6461	94.1955	10.5460	416.2716	39.4718	89.3731
7	19.3550	19.9358	19.9070	93.3694	30.0000	-0.0047	-0.0054	104.0205	103.4916	10.6511	422.4022	39.6579	98.6949
8	20.6930	21.2748	21.2400	117.9489	30.0000	-0.0060	-0.0067	128.6838	128.0409	10.7349	439.8627	40.9748	123.3164
9	21.1464	21.8730	21.8274	126.3122	30.0010	-0.0067	-0.0078	139.7514	138.9066	13.4392	557.8718	41.5108	133.0318
10	21.7488	22.5648	22.5060	137.4510	30.0000	-0.0078	-0.0095	152.5891	151.4963	15.1381	626.3680	41.3770	145.0200

* Believed to be a bad run.

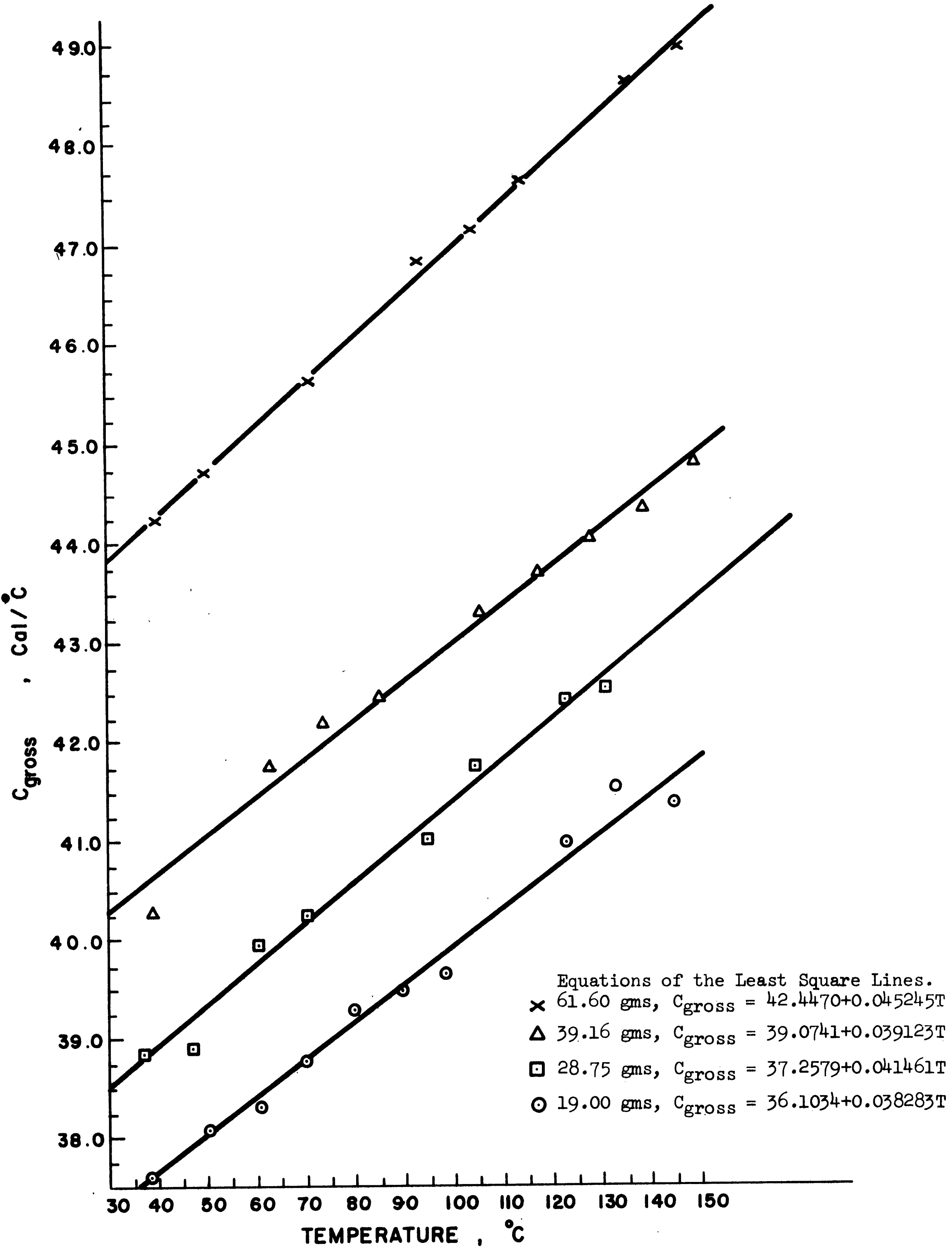

Figure E-9.. Gross Heat Capacities for Chlorodifluoromethane Using the Calorimeter (1964).

TABLE E-7

TABULATED DATA FOR GASEOUS CHLORODIFLUOROMETHANE ($CHClF_2$)

Run No.	$2R_1$ ohms	$2R_2$(Corr) ohms	$2R_2$(Equil) ohms	T_1 °C	min.	Initial Drift Rate ohms/5min.	Final Drift Rate ohms/5min.	T_2(Corr) °C	T_2(Equil) °C	ΔT-ΔT_{corr} °C	Input Calories	C_{gross} Cal/°C	T_{mean} °C
F-22-E-1	15.8900	16.4914	16.4910	30.4002	30.0010	-0.0001	-0.0007	41.2599	41.2527	10.8597	454.3486	41.8379	35.8301
2	16.4847	17.0911	17.0851	41.1388	29.9980	-0.0007	-0.0017	52.1177	52.0090	10.9789	464.1632	42.2776	46.6283
3	17.0661	17.6725	17.6557	51.6645	30.0002	-0.0017	-0.0027	62.6719	62.3665	11.0073	470.3931	42.7345	57.1682
4	17.6332	18.2433	18.2253	61.9576	30.0005	-0.0027	-0.0033	73.0602	72.7322	11.1026	478.7291	43.1186	67.5089
5	19.5430	20.1388	20.1112	96.8140	29.9999	-0.0044	-0.0044	107.7499	107.2426	10.9359	494.1819	45.1890	102.2819
6	20.2777	20.8703	20.8385	110.3037	30.0000	-0.0043	-0.0059	121.2173	120.6309	10.9136	497.1736	45.5554	115.7605
7	20.5984	21.2944	21.2554	116.2061	30.0010	-0.0050	-0.0068	129.0460	128.3254	12.8398	583.0821	45.4119	122.6261
8	21.1892	21.8841	21.8403	127.1026	30.0010	-0.0068	-0.0078	139.9571	139.1456	12.8545	591.8884	46.0453	133.5298
F-22-F-1	15.7473	16.4679	16.4661	27.8276	30.0010	-0.0000	-0.0008	40.8351	40.8025	13.0075	511.9620	39.3591	34.3313
2	16.4565	17.1792	17.1654	40.6290	29.9980	-0.0008	-0.0020	53.7153	53.4650	13.0863	525.0208	40.1198	47.1721
3	17.1469	17.8791	17.8635	53.1295	30.0005	-0.0020	-0.0032	66.4288	66.1450	13.2994	536.2010	40.3178	59.7792
4	17.8381	18.5852	18.5654	65.6830	29.9980	-0.0032	-0.0033	79.2954	78.9340	13.6124	560.8404	41.2006	72.4892
5	19.2129	19.9361	19.9109	90.7677	29.9995	-0.0023	-0.0047	104.0260	103.5633	13.2583	561.5187	42.3524	97.3969
6	19.8723	20.5886	20.5568	102.8546	30.0005	-0.0047	-0.0060	116.0256	115.4400	13.1710	565.2661	42.9174	109.4401
7	20.4967	21.2065	21.1651	114.3334	30.0010	-0.0060	-0.0069	127.4221	126.6576	13.0887	569.8669	43.5388	120.8778
8	20.8720	21.5792	21.5418	121.2486	29.9990	-0.0058	-0.0076	134.3119	133.6199	13.0633	574.7251	43.9956	127.7802
9	21.6176	22.3230	22.2756	135.0224	30.0000	-0.0062	-0.0083	148.0973	147.2174	13.0749	574.7620	43.9592	141.5598
F-22-G-1	16.0469	16.7466	16.7394	33.2306	30.0005	-0.0006	-0.0010	45.8769	45.7466	12.6463	482.1769	38.1279	39.5538
2	16.7027	17.4082	17.3986	45.0823	30.0005	-0.0010	-0.0020	57.8706	57.6963	12.7883	497.4133	38.8959	51.4765
3	17.3808	18.0900	18.0690	57.3732	30.1990	-0.0020	-0.0035	70.2676	69.8852	12.8944	505.5477	39.2069	63.8204
4	18.0397	18.7565	18.7337	69.3517	29.9950	-0.0035	-0.0042	82.4230	82.0065	13.0713	517.6555	39.6025	75.8873
5	18.7707	19.4779	19.4519	82.6823	30.0005	-0.0039	-0.0051	95.6209	95.1444	12.9385	521.6213	40.3154	89.1516
6	19.6823	20.3854	20.3494	99.3681	30.0002	-0.0046	-0.0062	112.3849	111.6225	12.9167	526.7627	40.7814	105.8265
7	20.1510	20.8427	20.6467	107.9741	30.0008	-0.0060	-0.0070	120.7083	117.0958	12.7342	525.0486	41.2313	114.3412
8	20.7210	21.4106	21.3644	118.4649	30.0005	-0.0070	-0.0083	131.1936	130.3396	12.7288	531.1201	41.7260	124.8293
9	21.4790	22.1610	22.1134	132.4584	30.0000	-0.0073	-0.0083	145.0908	144.2078	12.6324	535.3818	42.3816	138.7746

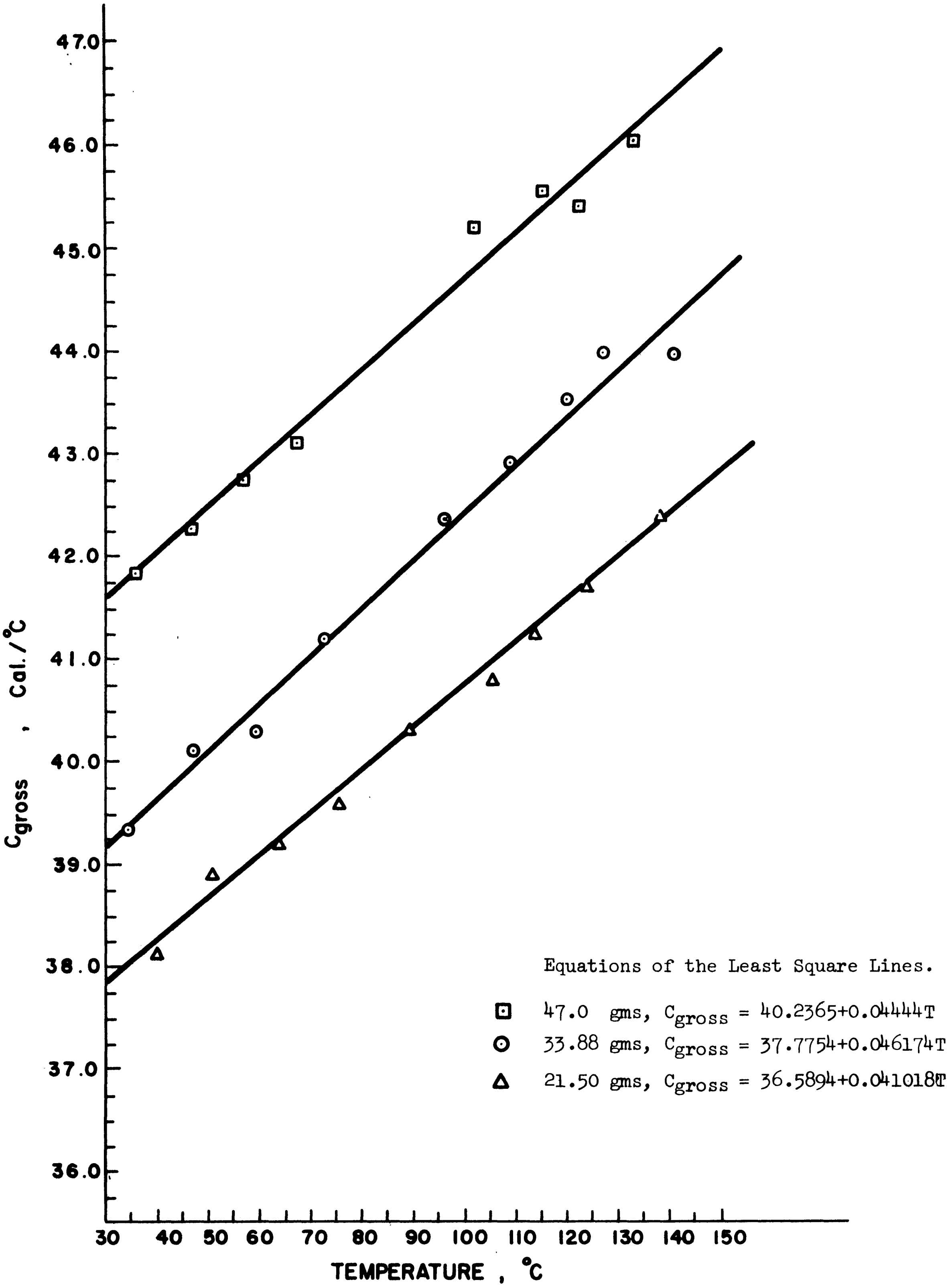

Figure E-10. Gross Heat Capacities for Chlorofluoromethane Using the Calorimeter (1966).

TABLE E-8

TABULATED DATA FOR GASEOUS DICHLOROFLUOROMETHANE ($CHCl_2F$)

Run No.	$2R_1$ ohms	$2R_2$(Corr) ohms	$2R_2$(Equil) ohms	T_1 °C	min.	Initial Drift Rate ohms/5min.	Final Drift Rate ohms/5 min.	T_2(Corr) °C	T_2(Equil) °C	ΔT-ΔT_{corr} °C	Energy Input Calories	C_{gross} Cal/°C	T_{mean} °C
F-21-A-1	17.7271	18.3717	18.3603	63.6644	30.0010	-0.0010	-0.0020	75.4007	75.1928	11.7363	537.3660	45.7867	69.5325
2	18.3476	19.0125	18.9958	74.9613	30.1000	-0.0020	-0.0024	87.1015	86.7962	12.1403	564.2836	46.4804	81.0314
3	18.9676	19.6297	19.6117	86.2806	30.0013	-0.0024	-0.0035	98.4035	98.0734	12.1229	567.4953	46.8117	92.3420
4	19.5742	20.2418	20.2172	97.3859	30.0000	-0.0035	-0.0043	109.6434	109.1911	12.2575	576.3708	47.0218	103.5147
5	20.1815	20.8511	20.8240	108.5348	29.9990	-0.0043	-0.0051	120.8614	120.3635	12.3266	582.6715	47.2695	114.6981
6	20.7765	21.4434	21.4134	119.4878	30.0000	-0.0051	-0.0056	131.8001	131.2454	12.3122	587.0519	47.6803	125.6440
7	21.3692	22.0315	21.9973	130.4283	30.0010	-0.0056	-0.0062	142.6890	142.0550	12.2607	593.6110	48.4157	136.5587
8	21.9180	22.5819	22.5345	140.5852	30.0000	-0.0062	-0.0068	152.9069	152.0259	12.3217	600.0573	48.6992	146.7461
F-21-B-1	17.1861	17.8110	17.8014	53.8404	30.0000	-0.0010	-0.0019	65.1900	65.0155	11.3497	473.1063	41.6846	59.5152
2	17.7844	18.4230	18.4080	64.7063	30.0000	-0.0019	-0.0027	76.3362	76.0626	11.6299	489.0568	42.0518	70.5212
3	18.3791	19.0148	18.9968	75.5356	30.0000	-0.0022	-0.0038	87.1436	86.8145	11.6079	491.7199	42.3606	81.3396
4	18.9622	19.6092	19.5816	86.1819	30.0000	-0.0038	-0.0048	98.4276	97.5216	11.8458	502.5820	42.4272	92.1047
5	20.0318	20.6699	20.6429	105.7837	30.0000	-0.0034	-0.0055	117.5233	117.0259	11.7396	505.4813	43.0579	111.6535
6	20.5985	21.2350	21.1960	116.2080	30.0999	-0.0055	-0.0070	127.9486	127.2282	11.7406	517.6527	44.0908	122.0783
7	31.1135	21.7453	21.6991	125.7048	30.0000	-0.0070	-0.0082	137.3862	136.5309	11.6814	512.6495	43.8858	131.5455
8	21.6267	22.4966	22.4408	135.1908	30.0000	-0.0082	-0.0094	151.3217	150.2850	16.1309	721.2221	44.7106	143.2562
9	16.8328	17.5454	17.5364	47.4276	30.0000	-0.0019	-0.0027	60.3623	60.1988	12.9247	530.7143	41.0620	53.8999
10	17.5231	18.1392	18.1260	59.9572	30.0000	-0.0026	-0.0040	71.1637	70.9232	11.2065	462.8773	41.3045	65.5604
11	18.1050	18.7325	18.7157	70.5407	30.0000	-0.0040	-0.0045	81.9846	81.6779	11.4439	478.0886	41.7723	76.2627
12	18.6873	19.3100	19.2896	81.1593	30.0000	-0.0045	-0.0058	92.5453	92.1718	11.3861	479.1994	42.0865	86.8523
13	19.2342	19.8538	19.8292	91.1576	30.0000	-0.0058	-0.0063	102.5150	102.0635	11.3574	482.7727	42.5073	96.8363
F-21-C-1	16.4008	17.0446	17.0398	39.6221	30.0000	-0.0005	-0.0014	51.3748	51.1878	11.6527	459.4863	39.4317	45.4484
2	17.0280	17.6755	17.6635	50.9739	30.0000	-0.0014	-0.0020	62.7264	62.5082	11.7524	468.7010	39.8812	56.8501
3	17.6492	18.2992	18.2818	62.2483	30.0010	-0.0020	-0.0030	74.0790	73.7618	11.8306	475.0280	40.1523	68.1637
4	18.2563	18.9071	18.8855	73.2971	29.9995	-0.0030	-0.0041	85.1746	84.7799	11.8775	480.4781	40.4527	79.2359
5	18.8494	19.4962	19.4674	84.1202	30.0000	-0.0041	-0.0049	95.9562	95.4284	11.8360	482.2732	40.7462	90.0382
6	20.0867	20.7398	20.7104	106.7924	29.9995	-0.0043	-0.0056	118.8114	118.2695	12.0189	500.4001	41.6343	112.8019
7	20.6607	21.3196	21.2830	117.3538	30.0010	-0.0056	-0.0066	129.5117	128.8353	12.1579	510.3136	41.9737	123.4327
8	21.2290	21.8821	21.8431	127.8377	30.0000	-0.0066	-0.0074	139.9200	139.1975	12.0823	514.8713	42.6137	133.8788
9	21.7846	22.4364	22.3840	138.1139	30.0005	-0.0074	-0.0088	150.2033	149.2300	12.0893	518.5772	42.8955	144.1586

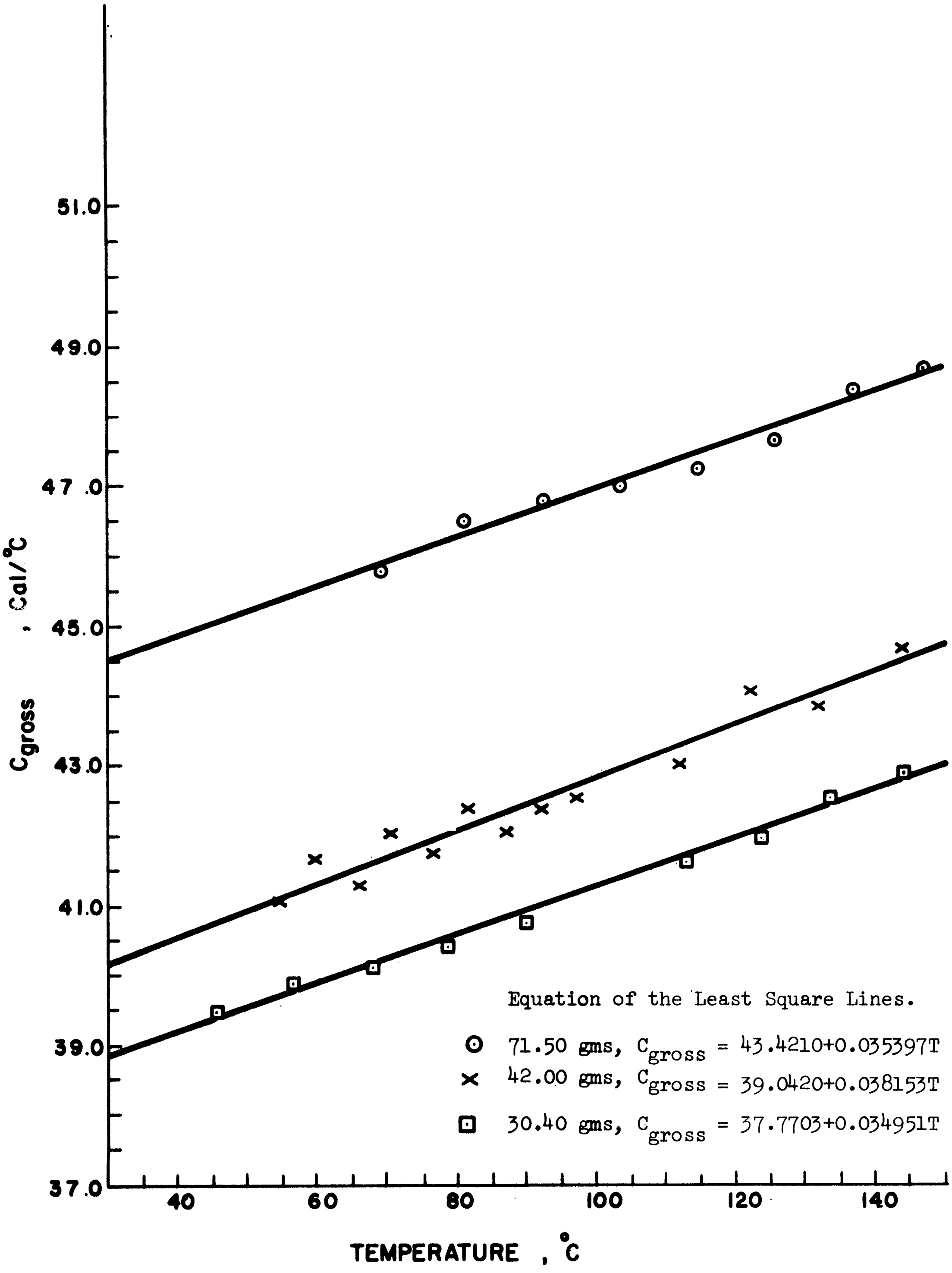

Figure E-11. Gross Heat Capacities for Dichlorofluoromethane Using the Calorimeter (1964).

TABLE E-9

TABULATED DATA FOR GASEOUS DICHLORODIFLUOROMETHANE (CCl_2F_2)

Run No.	$2R_1$ ohms	$2R_2$(Corr) ohms	$2R_2$(Equil) ohms	T_1 °C	min.	Initial Drift Rate ohms/5 min.	Final Drift Rate ohms/5min.	T_2(Corr) °C	T_2(Equil) °C	$\Delta T-\Delta T_{corr}$ °C	Input Calories	C_{gross} Cal/°C	T_{mean} °C
F-12-A-1	15.9982	16.6912	16.6870	32.3519	30.0000	+0.0000	-0.0009	44.8742	44.7982	12.5223	566.5946	45.2468	38.6130
2	17.4241	18.1136	18.1058	58.1593	30.0000	-0.0009	-0.0015	70.6974	70.5553	12.5381	583.3200	46.5239	64.4283
3	18.0812	18.7650	18.7560	70.1074	30.0001	-0.0014	-0.0020	82.5782	82.4138	12.4709	585.6293	46.9598	76.3428
4	18.5960	19.2820	19.2658	79.4925	30.0150	-0.0020	-0.0024	92.0362	91.7361	12.5401	591.5350	47.1714	85.7626
5	19.2256	19.9126	19.8964	91.0002	30.0980	-0.0024	-0.0034	103.2971	103.2971	12.5943	598.6575	47.5340	97.2973
6	19.8422	20.5229	20.5013	102.3021	29.9970	-0.0034	-0.0034	114.8158	114.4181	12.5137	605.0726	48.3528	108.5589
7	20.4566	21.1353	21.1125	113.5952	30.0000	-0.0034	-0.0040	126.1073	125.6863	12.5120	611.4970	48.8728	119.8513
8	21.4370	22.1014	22.0714	131.6817	29.9990	-0.0045	-0.0048	143.9853	143.4289	12.3035	606.3429	49.2820	137.8335
9	22.0288	22.7054	22.6700	142.6390	29.0000	-0.0048	-0.0060	155.2032	154.5449	12.5643	662.7805	49.5675	148.9211
F-12-B-1	15.5508	16.2554	16.2554	24.2878	29.9990	-0.0000	-0.0000	36.9950	36.9950	12.7071	563.0093	44.3066	30.6414
2	16.2475	16.9646	16.9604	36.8523	30.0010	-0.0000	-0.0010	49.8250	49.7489	12.9727	579.0717	44.6375	43.3386
3	16.9452	17.6543	17.6459	49.4735	30.0000	-0.0010	-0.0012	62.3410	62.1884	12.8675	588.7135	45.7519	55.9073
4	18.6764	19.3840	19.3726	80.9602	29.9990	-0.0012	-0.0021	93.9006	93.6917	12.9404	609.1137	47.0709	87.4304
5	19.3315	20.0428	20.0266	92.9390	30.0001	-0.0021	-0.0035	105.9858	105.6882	13.0467	616.3316	47.2403	99.4624
6	20.7052	21.4728	21.4776	118.1737	29.9990	-0.0032	-0.0047	132.3437	132.4325	14.1700	687.6885	48.5314	125.2587
7	21.4037	22.1657	22.1221	131.0661	30.0000	-0.0043	-0.0051	145.1780	144.5547	14.1119	691.5456	48.9335	138.1220
8	15.7182	16.5160	16.5130	27.3032	30.0000	-0.0002	-0.0008	41.7047	41.6505	14.4015	638.3576	44.3256	34.5040
9	16.6346	17.2465	17.2429	43.8500	30.0010	-0.0002	-0.0012	54.9360	54.8707	11.0860	502.7959	45.3541	49.3930
10	17.2296	17.9012	17.8898	54.6294	30.0000	-0.0012	-0.0022	66.8309	66.6235	12.2015	559.0105	45.8151	60.7302
11	18.6563	19.3176	19.3008	80.5932	30.0000	-0.0025	-0.0025	92.6845	92.3768	12.0913	566.1793	46.8255	86.6389
12	19.2743	19.9326	19.9158	91.8917	29.9990	-0.0025	-0.0031	103.9617	103.6532	12.0701	577.2655	47.8263	97.9267
13	19.8828	20.5418	20.5190	103.0474	29.9990	-0.0031	-0.0039	115.1638	114.7440	12.1164	582.8332	48.1029	109.1956
14	21.1744	21.8291	21.8021	126.8293	30.0000	-0.0039	-0.0049	138.9382	138.4380	12.1089	590.6990	48.7822	132.8837
F-12-C-1	16.7964	17.5572	17.5488	46.7785	30.1000	-0.0004	-0.0019	60.5766	60.4241	13.7981	578.2436	41.9073	53.6775
2	17.5282	18.2935	18.2815	60.0498	30.3000	-0.0019	-0.0021	73.9751	73.7564	13.9253	591.9008	42.5055	67.0125
3	18.2623	19.0142	18.9986	73.4064	30.0000	-0.0018	-0.0028	87.1326	86.8474	13.7262	594.2746	43.2949	80.2695
4	18.9600	19.7132	19.6934	86.1416	30.0010	-0.0028	-0.0038	99.9350	99.5718	13.7933	602.9132	43.7104	93.0383
5	19.7646	20.5122	20.4846	100.8780	30.0000	-0.0036	-0.0047	114.6188	114.1106	13.7408	606.5399	44.1415	107.7484
6	20.4208	21.1638	21.1338	112.9363	30.0000	-0.0047	-0.0058	126.6355	126.0796	13.6972	610.9087	44.6011	119.7849
7	21.0633	21.8056	21.7684	124.7781	30.0010	-0.0058	-0.0068	138.5029	137.8139	13.7248	619.5386	45.1400	131.6405
8	21.6952	22.4208	22.3734	136.4586	30.0010	-0.0068	-0.0078	149.9135	149.0331	13.4548	614.7819	45.6923	143.1861
9	16.1711	16.9942	16.9846	35.4726	30.0000	-0.0002	-0.0016	50.3614	50.1874	14.8888	613.5063	41.2059	42.9170
10	17.3708	18.1610	18.1502	57.1917	30.0000	-0.0008	-0.0018	71.5607	71.3640	14.3690	613.4111	42.6898	64.3762
11	18.1232	18.9174	18.9008	70.8722	30.0010	-0.0018	-0.0028	85.3629	85.0595	14.4907	624.5568	43.1005	78.1176
12	18.8730	19.6601	19.6391	84.5514	30.0001	-0.0028	-0.0038	98.9610	98.5759	14.4096	630.7826	43.7753	91.7562
13	19.8500	20.6301	20.6085	102.4453	30.0000	-0.0030	-0.0040	116.7901	116.3922	14.3448	635.8505	44.3262	109.6177
14	20.7158	21.4924	21.4642	118.3691	30.0000	-0.0040	-0.0050	132.7062	132.1847	14.3371	638.0698	44.5047	125.5376
15	21.1923	21.9670	21.9388	127.1599	30.1000	-0.0041	-0.0056	141.4933	140.9707	14.3335	649.9583	45.3455	134.3266

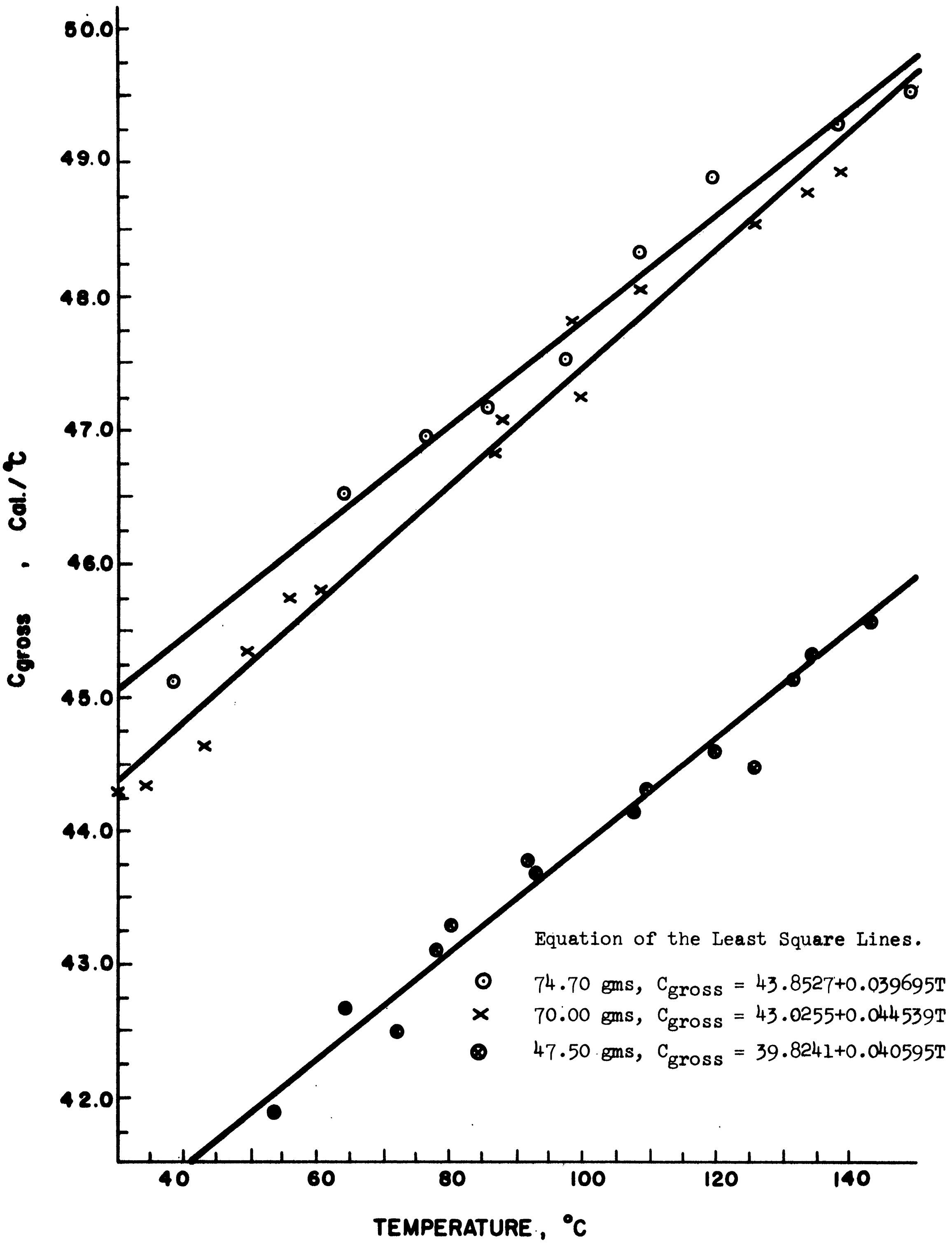

Figure E-12. Gross Heat Capacities with Dichlorodifluoromethane for Checking the Calibration of the Calorimeter (1964).

TABLE E-10

TABULATED DATA FOR EVACUATED CALORIMETER

Run No.	$2R_1$ ohms	$2R_2$(Corr) ohms	$2R_2$(Equil) ohms	T_1 °C	min.	Initial Drift Rate ohms/5 min.	Final Drift Rate ohms/5 min.	T_2(Corr) °C	T_2(Equil) °C	ΔT-ΔT_{corr} °C	Energy Input Calories	C_{gross} Cal/°C	T_{mean} °C
A-1	16.2481	17.3014	17.3042	36.8631	30.0000	+0.0004	-0.0005	55.9320	55.9830	19.0690	667.4358	35.0010	46.3976
2	17.3584	18.4010	18.3938	56.9666	30.0980	-0.0003	-0.0021	75.9350	75.8037	18.9683	674.5623	35.5625	66.4508
3	18.3633	19.3917	19.3728	75.2475	30.0010	-0.0021	-0.0041	94.0416	93.6954	18.7941	674.9777	35.9144	84.6446
4	20.1140	21.1247	21.0845	107.2941	30.3020	-0.0049	-0.0073	125.9115	125.1694	18.6175	692.4519	37.1937	116.6028
5	21.1371	22.1240	22.0724	126.1405	30.0000	-0.0068	-0.0095	144.4044	143.4474	18.2639	689.9154	37.7748	135.2725
6	16.0524	17.0238	17.0226	33.3299	30.0000	+0.0008	-0.0013	50.8978	50.8760	17.5679	608.3876	34.6306	42.1139
7	17.0131	18.0852	18.0732	50.7039	29.9990	-0.0013	-0.0025	70.1801	69.9617	19.4763	695.0923	35.6892	60.4420
8	18.2084	19.2651	19.2429	72.4243	30.0001	-0.0024	-0.0047	91.7232	91.3168	19.2990	700.3451	36.2893	82.0738
9	19.4010	20.4363	20.4069	94.2119	30.0485	-0.0036	-0.0060	113.2216	112.6805	19.0096	703.9242	37.0299	103.7168
10	20.3347	21.3567	21.3123	111.3521	30.0000	-0.0060	-0.0082	130.1973	129.3767	18.8452	706.8685	37.5093	120.7747

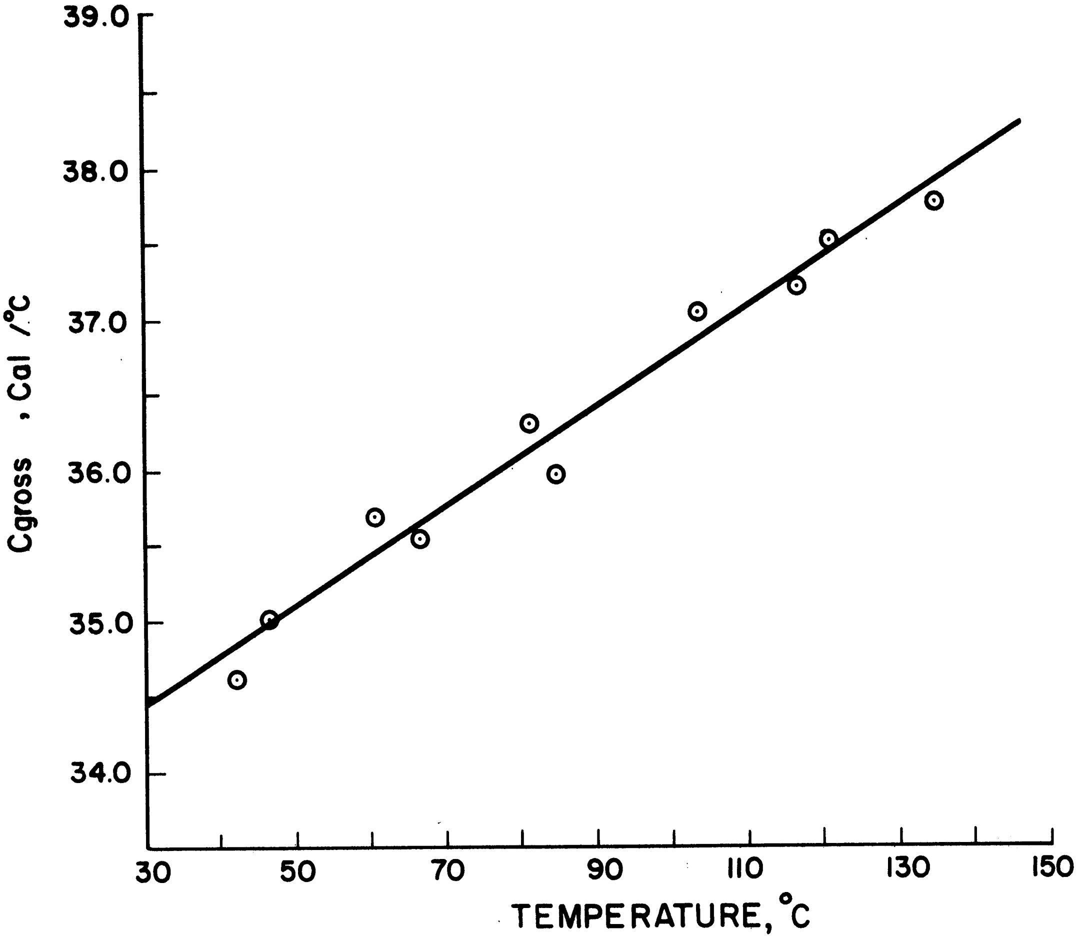

Figure E-13. Gross Heat Capacities with the Evacuated Calorimeter.

APPENDIX F

CALCULATION OF THE VOLUME EXPANSION OF THE CALORIMETER

During this experiment, the calorimeter was heated to a temperature as high as 150°C. Thus it is expected that there would be a change in volume due to thermal and elastic expansion. This change can be calculated from the following equation:

$$\frac{dV}{V} = \left(\frac{dV}{VdT}\right)_p dT + \left(\frac{dV}{Vdp}\right)_T dp \qquad \text{(F-1)}$$

where $\frac{dV}{VdT}$ is the volumetric co-efficient of thermal expansion and approximately three times the co-efficient of thermal expansion (9.4×10^{-6}).

$$\therefore \quad \left(\frac{dV}{VdT}\right)_p \cong (3)(9.4)(10^{-6}) = (28.2)(10^{-6}) \text{ per°C}$$

Also,

$$\left(\frac{dV}{Vdp}\right)_T = \left(\frac{d\ell nV}{dp}\right)_T = 3\left(\frac{d\ell nr}{dp}\right)_T \qquad \text{(F-2)}$$

Again $p = \frac{(t)(4E)}{D}$, where p is the pressure of the gas inside the calorimeter, t is the thickness of the wall, E is the Young's modulus, and D is the diameter. From Equation (F-2), it can be shown

$$\frac{d\ell nr}{dp} = - \frac{r}{(2E)(t)} \qquad \text{(F-3)}$$

Inserting eight inches for the diameter, .008 inch for the thickness and (28×10^{-6}) p.s.i.$^{-1}$ for Young's modulus,

$$\left(\frac{d\ell nV}{dp}\right)_T = 3\left(\frac{d\ell nr}{dp}\right)_T$$

$$= \frac{(3)(4)}{(2)(28 \times 10^{-6})(0.008)}$$

$$= (2.68)(10^{-5}) \text{ p.s.i.}^{-1}$$

Therefore

$$\frac{dV}{V} = (2.82)(10^{-5})dT + (2.68)(10^{-5})dp \qquad \text{(F-4)}$$

For an average temperature of 100°C and 100 p.s.i. during a run,

$$\frac{dV}{V} = (2.82)(10^{-5})(100-30) + (2.68)(10^{-5})(100-20)$$

$$= .0041$$

The volume of the calorimeter is 4530 c.c. Therefore average volume expansion is (4530)(.004) = 18.12 c.c. Thus an expansion of 0.4% can occur at the average temperature and pressure.

APPENDIX G

BASIC THEORY OF CALCULATION OF C_v^* IN MOLECULAR SPECTROSCOPY

From the definition, $C_V = \left(\frac{\partial U}{\partial T}\right)_V$, it follows that all temperature dependent components of the internal energy contribute to heat capacity. From classical statistical mechanics, the equipartition of energy tells us each translational degree of freedom contributes $\frac{R}{2}T$ to the internal energy U of the medium (R = universal gas constant). The three translational degrees of freedom, therefore, contribute $\frac{3}{2}R$ to the molar heat capacity. The rotational molar heat capacity of polyatomic molecules is determined by their rotation about the three space-co-ordinates. At not too high a temperature, the three rotational degrees of freedom give rise to $\frac{3}{2}RT$ for the internal energy. A measure for the temperature so that one can calculate the rotational heat capacity with constant contribution of $\frac{R}{2}$ is given by the condition, $\Theta_r << T$, where

$$\Theta_r = \frac{h^2}{8\pi^2 IK} \qquad \text{(G-1)}$$

and I = moment of inertia

h = Planck constant

K = Boltzmann constant

Θ_r is known as the characteristic rotation temperature. In contrast to the fluoro-chloro derivatives, the characteristic rotation temperature for methane, which has low moment of inertia $(I = (5.47)(10^{-40})\text{gm cm}^2)$, is only 7.5°K .

Since the atoms in a molecule are not rigidly connected, vibrations can occur around equilibrium positions of the atoms. The amplitudes of such vibrations depend upon the temperature. A polyatomic molecule of n atoms can have 3n-6 degrees of vibration. Corresponding vibrational modes of freedom can be evaluated if one assumes that the total vibrational energy of the system is comprised of potential and kinetic energy which are quadratic functions. From classical quantum statistics, the internal energy of vibration of a molecule is given in terms of the vibrational frequency ν_i as

$$U_i^{vib} = R \frac{h\nu_i}{K} \frac{1}{e^{h\nu_i/KT}-1} \qquad \text{(G-2)}$$

From Equation (G-2) with the substitution of $\frac{h\nu_i}{K} = \Theta_i$, one obtains

$$C_i^{vib} = R\left(\frac{\Theta_i}{T}\right)^2 \frac{e^{\Theta_i/T}}{(e^{\Theta_i/T}-1)^2} = P\left(\frac{\Theta_i}{T}\right) \qquad \text{(G-3)}$$

where $\Theta_i = \frac{h\nu_i}{K}$. Θ_i is designated as characteristic vibrational temperature. The function $P(\Theta/T)$ is called the Planck-Einstein function. This function approaches the classical value R at higher temperature as indicated in the following figure:

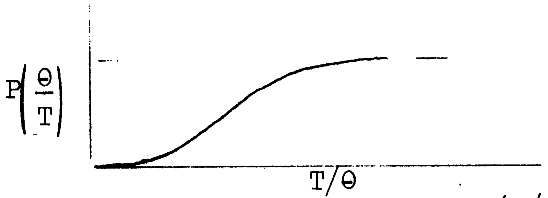

Figure G-1. Plot of $P(\Theta/T)$ Versus (T/Θ).

With

$$C^{trans} = \frac{3}{2} R,$$

$$C^{rot} = \frac{3}{2} R, \quad \text{and} \quad C^{vib} = \sum_{i=1}^{3n-6} P\left(\frac{\Theta_i}{T}\right)$$

it follows:

$$C_v^* = 3R + \sum_{i=1}^{3n-6} P(\Theta_i/T) \qquad \text{(G-4)}$$

and

$$C_p^* = 4R + \sum_{i=1}^{3n-6} P(\Theta_i/T) \qquad \text{(G-5)}$$

Therefore for a complete calculation of the molal heat capacity one needs to know the 3n-6 fundamental vibrational frequencies.

Instead of frequency ν, ($\nu = \frac{c}{\lambda}$, where C is the velocity of light and λ, wave length of vibration), in spectroscopic work, wave number is used where $\bar{\nu} = \frac{1}{\lambda}$.

The Planck-Einstein function gives the vibrational component of molal heat capacity under the assumption of harmonic oscillations of a molecule. This is because the basic assumption is that the potential energy is a quadratic function. On the basis of such assumption, if one observes the spectroscopic energy level patterns, one would expect that the separation between energy levels should be constant. But for real molecules this is not always so. Schafer(56) gives the following expression for the vibrational heat capacity due to anharmonicity of vibration of the molecule,

$$\Delta C_{anh} = R - x_e\left(\frac{\Theta}{T}\right)^2 \cdot \frac{\cosh(\Theta/2T)}{\sinh^3(\Theta/2T)} + \frac{x_e}{4}\left(\frac{\Theta}{T}\right)^3 \cdot \frac{1+2\cosh^2(\Theta/2T)}{\sinh^4(\Theta/2T)}$$

$$+ \frac{x_e^2}{16}\left(\frac{\Theta}{T}\right)^2 \cdot \frac{4+16\cosh^2(\Theta/2T)}{\sinh^4(\Theta/2T)} - \frac{x_e^2(\Theta/2T)^3\{\cosh(\Theta/2T)\ 3+2\cosh^2(\Theta/2T)\}}{\sinh^5(\Theta/2T)}$$

$$+ \frac{x_e^2}{8}\left(\frac{\Theta}{T}\right)^4 \cdot \frac{3+18\cosh^2(\Theta/2T)+4\cosh(\Theta/2T)}{\sinh^6(\Theta/2T)} \qquad \text{(G-6)}$$

In Equation (G-6), a new parameter x_e , anharmonicity constant,is introduced. It can be spectroscopically determined if one observes some of the overtone bands and one assumes no deviations of the overtones from the fundamental.

The molal heat capacity in the ideal state of polyatomic non-linear gases is therefore given by

$$C_v^* = 3R + \sum_{i=1}^{3n-6} R\left(\frac{\Theta_i}{T}\right)^2 \frac{e^{\Theta_i/T}}{(e^{\Theta_i/T}-1)^2} + \Delta C_{anh,i} \qquad (G-7)$$

where $\Delta C_{anh,i}$ is given by Equation (G-6).

The characteristic vibrational temperature Θ_i as also the wave number $\bar{\nu}_i$ can be obtained from infrared and Raman spectroscopic measurements. They can also be calculated from the known structure of the molecule by Wilson's F-G matrix method(66).

Bernstein and Pullin(7) have shown empirically that the zero-point energy in substituted methanes may be treated as a constitutive property when the interaction between nonbonded atoms is taken into account. Thus the sum of the vibration frequencies $(\Sigma\nu)$ of the halogenated methanes is found to have the predicted quadratic dependence on the number of substituents. This reduces to a linear dependence in the case of isotopically substituted homologs, compared to the linear dependence for $\Sigma\nu^2$ found theoretically by Recius, Wilson and Sverdlov.

Barho calculates C_p^* for methane and its fluochloro-derivatives with Equation (G-7) in the temperature range 175°K to 1000°K. For the temperature range 200°K to 1000°K, the results of such calculations and shown in Table I-2 at temperature intervals of 50°. The results are claimed to be accurate within ± .3% .

APPENDIX H

THEORY OF CALCULATION OF VIBRATIONAL FREQUENCIES AND NORMAL CO-ORDINATES OF POLYATOMIC MOLECULES

In a many-particle system natural or normal modes of vibration are characterized by vibrational energy level patterns and absorption bands will be observed due to interaction of the oscillating dipole moment of the system with electromagnetic radiation. In a polyatomic molecule there are $3n-6$ degrees of freedom for vibration and hence in absorption bands $3n-6$ transitions would be observed. These fundamental transitions are related to the force constants and the atomic masses of the molecule. Therefore it is interesting to determine what is the nature of the molecular vibrations and what is the form of the normal co-ordinate in these normal vibrations.

The molecular motions constrained by a particular potential energy function can be located adequately from the principles of classical mechanics. If a co-ordinate q_i is chosen, Lagrange's equation can be used to describe the motion of the system with respect to that co-ordinate as follows:

$$\frac{d}{dt}\left(\frac{dT}{d\dot{q}_i}\right) + \frac{\partial U}{\partial q_i} = 0 \qquad \text{(H-1)}$$

where T is the kinetic energy and U is the potential energy and $\dot{q}_i$ is the time derivative. For a polyatomic molecule there will be $3n-6$ such equations which can be solved for $3n-6$ vibrational frequencies.

To apply the above equation to a system, both T and U expressions must involve the same set of co-ordinates. T can be conveniently set up in Cartesian co-ordinates and U in terms of internal co-ordinates which describe the displacement of the atoms from their equilibrium internuclear distances. Thus, if $R_1, R_2, \ldots, R_{3n-6}$ represent the internal displacement co-ordinates and $x_1, x_2, \ldots, x_{3n}$ represent the Cartesian displacement co-ordinates, kinetic and potential energy functions can be expressed as

$$T = \frac{1}{2} \sum_{j=1}^{3n-6} m_j x_j^2 \qquad \text{(H-2)}$$

$$U = \frac{1}{2} \sum_{i,j=1}^{3n-6} K_{ij} R_i R_j \qquad \text{(H-3)}$$

where m_j is the mass of the j-th particle and K_{ij} is the force constant of the spring interacting between i-th and j-th particle. The complexity of the problem lies in the transformation of x co-ordinates in terms of R co-ordinates. Once this is done the problem is solved. Wilson(66) by matrix transformation method elegantly solves this problem and this procedure is the basis for many of the calculations of molecular vibrations now being done.

In this method kinetic and potential energies are expressed in terms of internal co-ordinates R. The Equation (H-3) above, since it is quadratic in form, can be written in matrix notation as $2U = R'FR$ where R' is the transpose of R and the F matrix involves the spring constants. To set up the kinetic energy in terms of R co-ordinates Wilson goes through an elaborate matrix manipulation and assuming six conditions of zero translational and angular momentum shows that kinetic energy can be expressed as

$$2T = \dot{R}' G^{-1} \dot{R} \qquad \text{(H-4)}$$

where R^{-1} is the transpose of R and G^{-1} is the inverse of G matrix. The elements of the G-matrix can be expressed as

$$G_{K\ell} = \sum_{i=1}^{3n} \frac{B_{Ki}B'_{\ell i}}{m_i} \qquad \text{(H-5)}$$

where $K = 1,2,\ldots,3n-6$ and $\ell = 1,2,\ldots,3n-6$. Incidentally, B matrix is the transformation matrix between the internal co-ordinates and Cartesian co-ordinates. When Lagrange's equation is applied to each of the R_k co-ordinates and solutions of the type $Rk, = A_k \cos 2\pi\nu t$ is desired, the secular determinant formed by the co-efficients of A_k's has the form

$$\begin{bmatrix} F_{11}-(G^{-1})_{11}\lambda & F_{12}-(G^{-1})_{12}\lambda & \cdots \\ F_{21}-(G^{-1})_{21}\lambda & F_{22}-(G^{-1})_{22}\lambda & \cdots \\ \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots \end{bmatrix} = 0 \qquad \text{(H-6)}$$

where $\lambda = 4\pi^2\nu^2$. Equation (H-6) can be represented in terms of a diagonal matrix Λ with λ's on the diagonals in the following way

$$|F - G^{-1}\Lambda| = 0 \quad \text{or} \quad |GF - \Lambda| = 0 \qquad \text{(H-7)}$$

From the molecular structure certain symmetry operations are carried out on the normal co-ordinates to evaluate F and G matrix elements. Once F and G matrix elements have been calculated, the secular determinant given by the Equation (H-6), is solved for values of Λ and hence ν values are obtained.

APPENDIX I

FUNDAMENTAL FREQUENCIES AND CALCULATED C_p^* VALUES FOR METHANE AND ITS FLUORO-CHLORO DERIVATIVES

For methane and all its fluoro-chloroderivatives, the fundamental frequencies as obtained from infrared and Raman Spectra or from Wilson's(66) FG-matrix method are reported in the literature. Table I-1 represents all such values used by Barho(2) in the calculation of C_p^* values presented in Table I-2.

TABLE I-1

FUNDAMENTAL FREQUENCIES OF METHANE AND ITS FLUORO-CHLORO DERIVATIVES IN Cm^{-1}

Compound	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ν_7	ν_8	ν_9
CH_4	3020	3020	3020	2914	1499	1499	1306	1306	1306
CH_3Cl	3041.8	3041.8	2937	1454.6	1454.6	1354.9	1015	1015	732.1
CH_2Cl_2	3049	2985	1419	1255	1149	898	735	700	234
$CHCl_3$	3034.4	1218.9	1218.9	771	771	681	366.4	261.1	261.1
CCl_4	794	794	794	458	310	310	310	218	218
CH_3F	3009	2009	2863	1469.7	1469.7	1467.9	1200	1200	1049.5
CH_2F_2	3029.8	2963.4	1508	1435	1261.7	1167.1	1089.7	1078.6	532.4
CHF_3	3031	1372	1372	1152	1152	1140	700	507	507
CF_4	1277	1277	1277	908.2	630	630	630	434.5	434.5
CF_3Cl	1212	1212	1105	781.7	560	560	475.8	350	350
CF_2Cl_2	1162	1099	922	667.2	457.5	446	435	322	261.5
$CFCl_3$	1085	847	847	535.2	398	398	349.5	241	241
$CHFCl_2$	3028	1312	1241	1082	804	743	457	367	277
CHF_2Cl	3025	1345	1312	1178	1116	808	536	421	369
CH_2FCl	3049	2993	1470	1351	1236	1068	1004	760	385

TABLE I-2

THE MOLAL HEAT CAPACITY C_p^* FOR METHANE AND ITS FLUORO-CHLORO DERIVATIVES AS A FUNCTION OF TEMPERATURE

T°K	CH_4	CH_3Cl	CH_2Cl_2	$CHCl_3$	CCl_4	CH_3F	CH_2F_2	CHF_3 (F 23)	CF_4 (F14)	CF_3Cl (F 13)	CF_2Cl_2 (F 12)	$CFCl_3$ (F 11)	$CHFCl_2$ (F 21)	CHF_2Cl (F 22)	CH_2FCl
200	33.49	35.22	42.74	54.58	70.41	33.82	36.77	41.41	47.68	53.35	58.96	64.84	50.32	45.71	39.69
250	34.29	37.76	47.15	60.63	78.04	35.23	39.67	46.39	55.03	60.96	66.70	72.59	56.14	51.12	43.33
300	35.87	41.05	51.77	66.06	84.01	37.62	43.32	51.55	61.78	67.[illegible]9	73.16	78.84	61.52	56.36	47.44
350	38.13	44.71	56.27	70.80	88.67	40.72	47.40	56.63	67.79	73.30	78.56	83.88	66.39	61.31	51.73
400	40.85	48.44	60.46	74.90	92.31	44.22	51.59	61.44	73.03	78.17	83.04	87.94	70.72	65.85	55.93
450	43.80	52.08	64.25	78.40	95.18	47.84	55.68	65.84	77.57	82.30	86.76	91.23	74.51	69.94	59.88
500	46.83	55.51	67.64	81.39	97.45	51.41	59.54	69.80	81.45	85.78	89.85	93.90	77.81	73.57	63.50
550	49.85	58.73	70.67	83.96	99.29	54.84	63.10	73.33	84.77	88.73	92.42	96.08	80.68	76.78	66.81
600	52.80	61.73	73.39	86.18	100.79	58.10	66.37	76.45	87.60	91.22	94.58	97.90	83.18	79.60	69.81
650	55.66	64.52	75.85	88.09	102.03	61.17	69.36	79.22	90.03	93.33	96.39	99.41	85.37	92.09	72.53
700	58.42	67.13	78.07	89.83	103.08	64.05	72.09	81.68	92.12	95.14	97.93	100.68	87.31	84.31	75.00
750	61.06	69.56	80.10	91.35	103.96	66.74	74.59	83.86	93.92	96.68	99.25	101.77	89.04	86.27	77.27
800	63.59	71.84	81.95	92.72	104.73	69.26	76.88	85.82	95.47	98.02	100.38	102.70	90.59	88.03	79.34
850	66.00	74.97	83.67	93.95	105.39	71.62	78.97	87.47	96.83	99.19	101.37	103.52	91.98	89.62	81.24
900	68.29	75.96	85.25	95.07	105.98	73.81	80.90	89.16	98.02	100.20	102.23	104.23	93.24	91.05	83.00
950	70.43	77.83	86.71	96.09	106.50	75.86	62.67	90.58	99.06	101.09	102.98	104.85	94.38	92.34	86.61
1000	72.50	79.58	88.07	97.03	106.97	77.77	84.31	91.88	100.00	101.89	103.66	105.42	95.43	93.52	86.11

APPENDIX J

ELECTRICAL CIRCUIT FOR CONSTANT POWER INPUT

Hoge(25) has suggested the use of a balancing resistor in the power circuit for the generation of constant power input. If there is a battery source of constant voltage E and zero internal resistance, a balancing resistor of resistance U and a heater of variable resistance, R , the power generated by the heater is given by,

$$q_h = IE_h = \frac{E}{(U+R)}\frac{RE}{(U+R)} = \frac{RE^2}{(U+R)^2} \qquad \text{(J-1)}$$

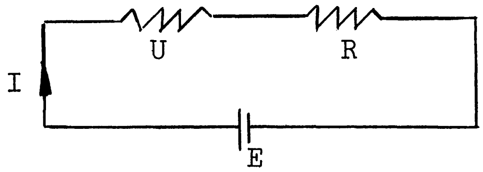

Figure J-1. Power Circuit.

where q_h is the power dissipated by the heater, I is the current in the circuit and E_h is the voltage drop across the circuit.

$$\therefore \frac{dq_h}{dR_h} = \frac{(U+R)^2E^2-(R)(E^2)(2)(U+R)}{(U+R)^4}$$

$$= \frac{E^2(U-R)}{(U+R)^3} \qquad \text{(J-2)}$$

When R is equal to U , q_h is maximum and is given by

$$q_{hmax} = \frac{E^2}{4U}$$

$$\therefore \quad \frac{q_h}{q_{hmax}} = \left[\frac{RE^2}{(U+R)^2}\right]\left[\frac{4U}{E}\right] = \frac{4UR}{(U+R)^2}$$

$$= \frac{4}{2+\frac{R}{U}+\frac{U}{R}} \tag{J-3}$$

that $\frac{q_h}{q_{hmax}}$ is rather insensitive to changes in $\frac{R}{U}$. In the actual experiment, the power fluctuations were on the average within ± 1/2 per cent.

APPENDIX K

CONSTANTS AND CONVERSION FACTORS

The constants and conversion factors used in this research are summarized here:

1 calorie = 1 thermo-chemical calorie = 4.1840 abs. joules

= 0.0412917 lit-atm.

1 Btu. = 1055.18 abs. joules = 5.4046 p.s.i.-cu. ft.

1 abs. watt-minute = 14.3403 calories.

T°K = t°c plus 273.16°C

T°R = T°K multiplied by 1.8 = °F + 459.69

1 atmosphere = 14.696 p.s.i.

R(the universal gas constant) = 1.985 Btu/lb-mole - °R

= 1.98719 Cal/gm-mole - °K

= 0.0820544 lit.-atm./gm-mole - °K

= 10.7315 p.s.i.a.-Cuft/lb-mole - °R

$h = 6.62377 \times 10^{-27}$ erg-sec/(mole)

$c = 2.997902 \times 10^{10}$ Cm/sec

$R = 1.380257 \times 10^{-16}$ erg/(mole) - °K

$\frac{hc}{R} = 1.43868$

Molecular weight of dichlorodifluoromethane = 120.924

Molecular weight of trifluoromethane = 70.01

Molecular weight of chlorodifluoromethane = 86.476

Molecular weight of dichlorofluoromethane = 102.93

Molecular weight of nitrogen = 28.02

For the calculation of $C_v - C_v^*$ values, Martin's Equation in the present form has been used. The constants in the equation are as follows:

1. For chlorodifluoromethane(39): p in p.s.i, T in °R, V in cuft/lb, T_c = 664.5 deg. R., p_c = 32.76 lb/ft^3, p_c = 721.906 p.s.i.a

Equation of State:

$$p = \frac{RT}{v-b} + \frac{A_2+B_2T+C_2e^{KT/T_c}}{(v-b)^2} + \frac{A_3+B_3T+C_3e^{KT/T_c}}{(v-b)^3}$$

$$+ \frac{A_4+B_4T}{(v-b)^4} + \frac{A_5+B_5T+C_5e^{KT/T_c}}{(v-b)^5} + \frac{A_6+B_6T}{e^{548.2V}}$$

$R = 0.124098$
$b = 0.002$
$A_2 = 4.353547$
$B_2 = 0.002407252$
$C_2 = -44.066868$
$A_3 = -0.017464$
$B_3 = 7.62789 \times 10^{-5}$
$C_3 = 1.483763$

$A_4 = 0.002310142$
$B_4 = -3.605723 \times 10^{-6}$
$A_5 = -3.724044 \times 10^{-5}$
$B_5 = 5.355465 \times 10^{-8}$
$C_5 = 5.355465 \times 10^{-8}$
$A_6 = 1.363387 \times 10^{-8}$
$B_6 = -1.672612 \times 10^{5}$
$K = -4.2$

2. For trifluoromethane(37): Units are the same as above. T_c = 538.33 R, V_c = 0.030510 CH/15, p_c = 701.42 p.s.i.a

Equation of State:

$$p = \frac{RT}{v-b} + \frac{A_2+B_2T+C_2e^{KT/T_c}}{(v-b)^2} + \frac{A_3+B_3T+C_3e^{KT/T_c}}{(v-b)^3} + \frac{A_4+B_4T}{(v-b)^4}$$

$$+ \frac{A_5+B_5T+C_5e^{KT/T_c}}{(v-b)^5} + \frac{A_6+B_6T}{e^{520V}}$$

$R = 0.153270$

$b = 0.00125$

$A_2 = -4.679499$

$B_2 = 3.472778$

$C_2 = -159.775232$

$A_3 = -0.012475$

$B_3 = 7.733388 \times 10^{-5}$

$C_3 = 5.941212$

$A_4 = 2.068042 \times 10^{-8}$

$B_4 = -3.684238 \times 10^{-6}$

$A_5 = -3.868546 \times 10^{-5}$

$B_5 = 6.455643 \times 10^{-8}$

$C_5 = -7.394214 \times 10^{-4}$

$A_6 = 7.502357 \times 10^{-7}$

$B_6 = -1.114202 \times 10^{5}$

$K = -5.50$

3. For dichlorodifluoromethane(45): units are the same as above.

$T_c = 699.3$ R, $p_c = 596.9$ p.s.i.a, $\rho_c = 34.84$ lb/cuft.

Equation of State:

$$p = \frac{RT}{v-b} + \frac{A_2+B_2T+C_2e^{KT/T_c}}{(v-b)^2} + \frac{A_3+B_3T+C_3e^{KT/T_c}}{(v-b)^3} + \frac{A_4+B_4T}{(v-b)^4} + \frac{A_5+B_5T+C_5e^{KT/T_c}}{(v-b)^5}$$

$A_2 = -3.409727134$

$A_3 = 0.06023944654$

$A_4 = -5.4873007 \times 10^{-4}$

$A_5 = 0$

$C_1 = 0$

$C_2 = -56.7627671$

$C_3 = 1.311399084$

$C_4 = 0$

$B_1 = 0.088734$

$B_2 = 1.59434848 \times 10^{-3}$

$B_3 = -1.879618431 \times 10^{-5}$

$B_4 = 0$

$B_5 = 3.46883400 \times 10^{-9}$

$C_5 = -2.54390678 \times 10^{-5}$

$b = 0.0065093886$

$K = -5.475$

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