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Union Carbide and Carbon Chemicals Corporation
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A LOW TEMPERATURE CALORIMETRIC CRYOSTAT

G. D. Oliver, J. W. Grisard, and V. E. Anderson

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A B S T R A C T

A low temperature adiabatic cryostat for determining precise calorimetric data has been described. The accuracy of the data produced by this apparatus has been established by measuring the thermal properties of n-hexane up to 300°K. These data agree with available precise data, in general, to within 0.2%. The precision of the heat capacity measurements is, for the most part, better than 0.1%.

A LOW TEMPERATURE CALORIMETRIC CRYOSTAT

In addition to their purely scientific interest, thermal data are useful and important in the design of processing equipment and in the solution of practical problems in chemistry. Because of the paucity of thermal data on fluorocarbons and because of their increasing industrial use, precise thermal data on these comparatively new compounds are needed.

This report constitutes a description of the apparatus constructed in the K-25 Laboratory for the purpose of determining precise thermal data on fluorocarbons. The cryostat, shown in figures 1 and 2, consists of chrome-plated copper refrigerant tanks, heat radiation shields, adiabatic shield and calorimeter. These are lowered into the large brass can that forms an overall vacuum jacket. The vacuum is essential in maintaining an adiabatic system. By using this system, heat exchange between the calorimeter and its environment is practically eliminated if their temperature difference approaches zero at all times. The usual principle of measuring heat capacity is used, i.e., the initial temperature is measured, energy in the form of electrical heat is added, then a final temperature is measured. This definite amount of energy and the temperature difference involved is used to calculate an instantaneous heat capacity value for the average temperature. Heat of fusion measurements are made in a similar manner.

EXPERIMENTAL

Apparatus

The apparatus is similar to that described by Ruehrwein and Huffman[1], who improved the design of Blue and Hicks[2], mainly, by the addition of the vacuum windlass and by the use of alternating current in the shield heater circuits.

Cryostat

The cryostat shown in figure 2 is essentially the same as described by Huffman; however, some modifications have been made in the calorimeter, heater and thermometer assembly. In this assembly, shown in detail in figure 3,[3] the heater is bifilarly wound on a copper sleeve separate from the platinum resistance thermometer, which permits the use of a thermometer made by the Leeds and Northrup Instrument Company. The copper sleeve, greased with Apiezon N fits tightly in a well in the calorimeter and in turn the thermometer fits tightly inside the heater.

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1. Ruehrwein, R. A., and H. M. Huffman, J. Am. Chem. Soc., 65, 1620 (1943).

2. Blue, R. W., and J. F. G. Hicks, J. Am. Chem. Soc., 59, 1962 (1937).

3. Detailed drawings of each part of the cryostat are available.

Shield Control Panel. Wiring diagrams of the two control panels are shown in figures 4 and 5. The adiabatic shield control panel, figure 4, is used by one operator to control the temperature of an adiabatic shield around the calorimeter. Non-inductive heaters wound separately on the top, bottom and tube of this shield, and on the floating ring are connected to a source of alternating current through appropriate series and parallel resistors and variacs on the panel. Four copper-constantan thermocouple junctions attached to the top, bottom and tube of the shield and to the calorimeter indicate the differences of temperature between the calorimeter and various parts of the shield. These differential couples are connected to a galvanometer and scale through a Leeds and Northrup ten point selector switch on the shield control panel. The present apparatus is different from Huffman's[1] in that there is a separate and extra differential couple between the shield and ring which indicates this temperature difference on a second galvanometer and scale.

Potentiometer Control Panel. The control panel, wiring diagram shown in figure 5, is used by the second operator in conjunction with a White double potentiometer and a high-sensitivity galvanometer, to measure the potential on the calorimeter heater and thermometer that is necessary to calculate the energy input to, and the temperature of the calorimeter and sample. The master, energy, and thermometer current switches on this panel are made of beryllium-copper knife-blade contacts with bakelite spacers, and patterned after the P-Q switch of the White double potentiometer. The master switch connects the desired thermometer or heater circuit to standard resistors and to the potentiometer as required in an established experimental procedure.

Low discharge 2-volt wet cell batteries supply the potential for the thermometer, heater and potentiometer circuits.

Resistance Measurements. A 25.5 ohm platinum resistance thermometer, of the platinum capsule type, made by Leeds and Northrup, was used for measuring all temperatures. Resistance measurements on the thermometer were made by comparing the potential drop across the thermometer with that across a Leeds and Northrup certified resistor: 25 ohms for temperatures below 35°K. and 100 ohms above 35°K. A current of 4 ma. was used across the 25 ohm and 1 ma. across the 100 ohm resistor. An Eppley standard cell served as a standard for all potentials.

Energy Measurements. Current used by the calorimeter heater is obtained by measuring the potential drop across an 0.8 ohm N.B.S. type resistor in series with it. The voltage is obtained by measuring the potential drop across a similar 500 ohm resistor in parallel to the heater and in series with a shunting resistor of 100,000 ohm. The shunting circuit in parallel to the heater is connected to the heater inside the cryostat; consequently, two small lead wires are connected to each heater lead at the heater. One set of these leads carry current to the heater. By using this arrangement all the resistors may be placed in a thermostated box

separate from the panel[4]. The heat energy used in each run was calculated in the usual manner from these current, voltage and necessary time measurements.

Time Measurements. These were made by a precision timer attached to the calorimeter heater switch so that the timer and current to the heater are turned on simultaneously.

All lead wires inside the cryostat are either size No. 30 or 32 enameled silk covered copper. All difference and absolute thermocouples are made of N.B.S. 1938 calibrated constantan wire size No. 30, and size No. 32 copper wire.

Procedure. Liquid samples were distilled into a calorimeter under their own vapor pressure in the following manner. Samples were placed in a glass bulb of a vacuum system to which the calorimeter was attached by a kovar-glass connection soldered to a small monel tube that in turn was soldered to the filling tube of the calorimeter. After the sample was degassed by repeatedly freezing and evacuating, it was allowed to distill into the calorimeter. Then the small monel connecting tube was pinched off and sealed by soft soldering. The calorimeter and sample were placed in the cryostat after obtaining a constant weight by intermittent weighing and evacuation. Considerable care should be taken in soldering lead wires to the thermometer and heater leads, and in connecting the difference thermocouple junction to the calorimeter. A vacuum of 10^{-5} mm. was obtained in the outer brass can before refrigerants were applied.

The cooling operations were similar to those previously described[1]; however, a temperature of 48°K., instead of 52°, was obtained by maintaining a partial vacuum in the lower tank previously filled with liquid nitrogen. A Welch Duo-Seal vacuum pump was used for the evacuation. Liquid helium, furnished by Oak Ridge National Laboratory, was used to obtain temperatures below 50°K. Since five liters of liquid helium cooled the sample to only 18°K., this part of the cooling operations was considered unsatisfactory.

Heat capacity measurements were carried out in a series of experimental "runs". One operator maintained the temperature difference between the adiabatic shield and calorimeter to a minimum; while the other operator successively read a temperature, applied a measured amount of electrical heat and measured another temperature. The final temperature of the first run was the initial temperature of the second run, etc. Below 40°K., the Δt for each run was corrected for heat gain or loss by obtaining a rate on the initial and final temperature.

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4. See notations on bottom of figure 5.

Using the applied heat energy, the temperature difference, and a correction for the calorimeter heat capacity and heat of vaporization correction in the region necessary, the mole heat capacity was calculated from experimental data. No correction for heat loss or gain was made except below about 40°K. Heat of fusion and transition measurements were made in a similar manner. The determination of the purity and triple point of the compound has been adequately described[5]. Entropy calculations were made in the usual manner of graphical integration of a heat capacity -lnT curve from the lowest point of measurement to 298.16°K. Entropy from 0°K. to the lowest point of measurement was obtained by using Debye's T^3 law extrapolation. Energy measurements made in terms of the joule were converted to calories by multiplying by 0.239046.

Calibration and Accuracy

The platinum resistance thermometer was calibrated by the National Bureau of Standards. From 10°K. to 90°K. it was compared to a group of thermometers set up as a standard and above 90°K. it was calibrated at the usual points represented by the modified Callendar equation.

In order to establish an overall accuracy for the apparatus, the thermal data of n-hexane were determined over the temperature range 50° to 300°K. A precision of 0.1% was obtained in both the heat capacity and heat of fusion measurements. It is evident from a comparison of these data with those of Douslin and Huffman[6] on n-hexane that the agreement is better than .2% except at lower temperatures. These two sets of data are in much better agreement than those of Douslin and Huffman and Pitzer and Kilpatrick[6] especially at low temperatures.

DATA AND RESULTS

Accurate thermal data is essential for the calculation of reliable entropy values at the usual temperature of 298.16°K. After constructing a low temperature cryostat designed to measure thermal properties with an accuracy of 0.2%, it was desirable to test the apparatus by measuring these properties of a compound, in this case n-hexane, that have been more or less established by reliable workers[6], who claim an accuracy uncertainty of 0.2%.

---

5. Oliver, G. D., M. Eaton, and H. M. Huffman, J. Am. Chem. Soc., 70, 1502 (1948).

6. Douslin, D. R. and H. M. Huffman, J. Am. Chem. Soc., 68, 1704 1502 (1948).

The heat capacity of n-hexane was measured over the temperature range of 50° to 300°K. These data were plotted as mole heat capacity against T °K., and values selected from a smooth curve drawn through these points are listed in table I. In column three of table I is listed the percentage difference between the smoothed data of Douslin and Huffman[6] and this research.

An average of three heat of fusion measurements gave a value of 3127 ± 2 cal./mole as compared to Douslin's value of 3126 cal./mole. Even though the impurity of the samples differed by approximately 0.4 mole %, the triple point of 177.844°K. determined by this research checked Douslin's value of 177.84 ± .05°K.

SUMMARY

A low temperature calorimetric cryostat has been constructed for the purpose of determining thermal data with an accuracy uncertainty of not more than 0.2%.

The thermal data obtained on n-hexane by this apparatus has been compared with available precise data to show a general agreement of less than 0.2%. The precision of the measurements was in general, better than 0.1%.

NOTEBOOK REFERENCES

Notebook Number 1081 G. D. Oliver 9/28/48

ACKNOWLEDGEMENT

We gratefully acknowledge the splendid cooperation and assistance given by the laboratory machine shop in the construction of this apparatus.

Table I

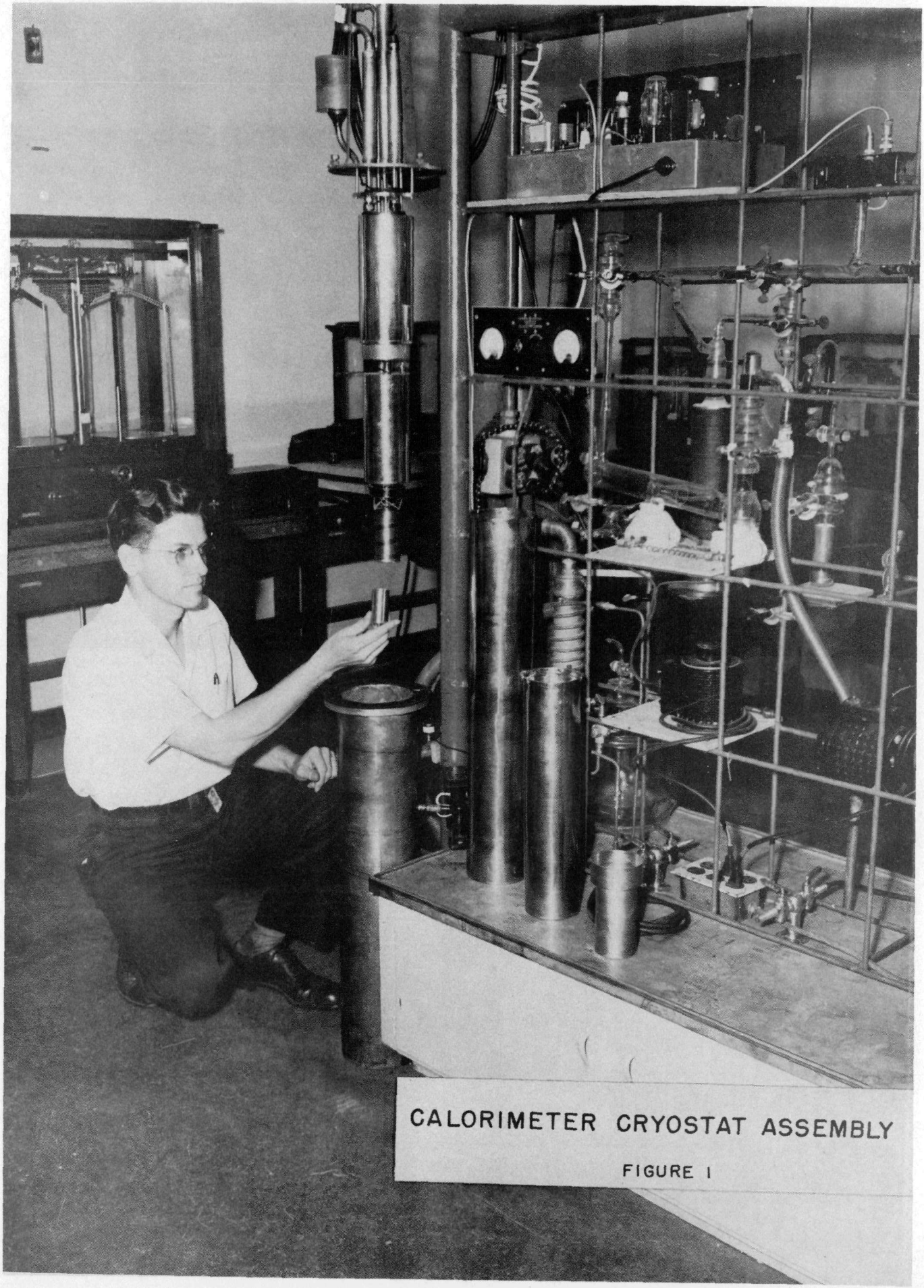
Smoothed Molal Heat Capacity of n-Hexane

0°C. = 273.16°K., Mol. Wt. = 86.172

T °K.	C sat.	Dev., %[b]
50	10.85	
55	11.98	+ .33
60	13.06	+ .23
65	14.06	+ .28
70	14.99	+ .13
75	15.88	0
80	16.74	- .07
85	17.57	- .06
90	18.37	- .05
95	19.09	0
100	19.77	- .05
110	21.09	- .05
120	22.36	0
130	23.60	- .04
140	24.83	+ .04
150	26.05[a]	0
160	27.27[a]	0
170	28.48[a]	0
180	40.57	- .17
190	40.73	- .10
200	40.94	- .10
210	41.25	- .02
220	41.64	
230	42.09	- .02
240	42.62	- .09
250	43.22	- .12
260	43.87	- .09
270	44.56	- .07
280	45.28	- .09
290	46.04	- .07
300	46.84	- .02

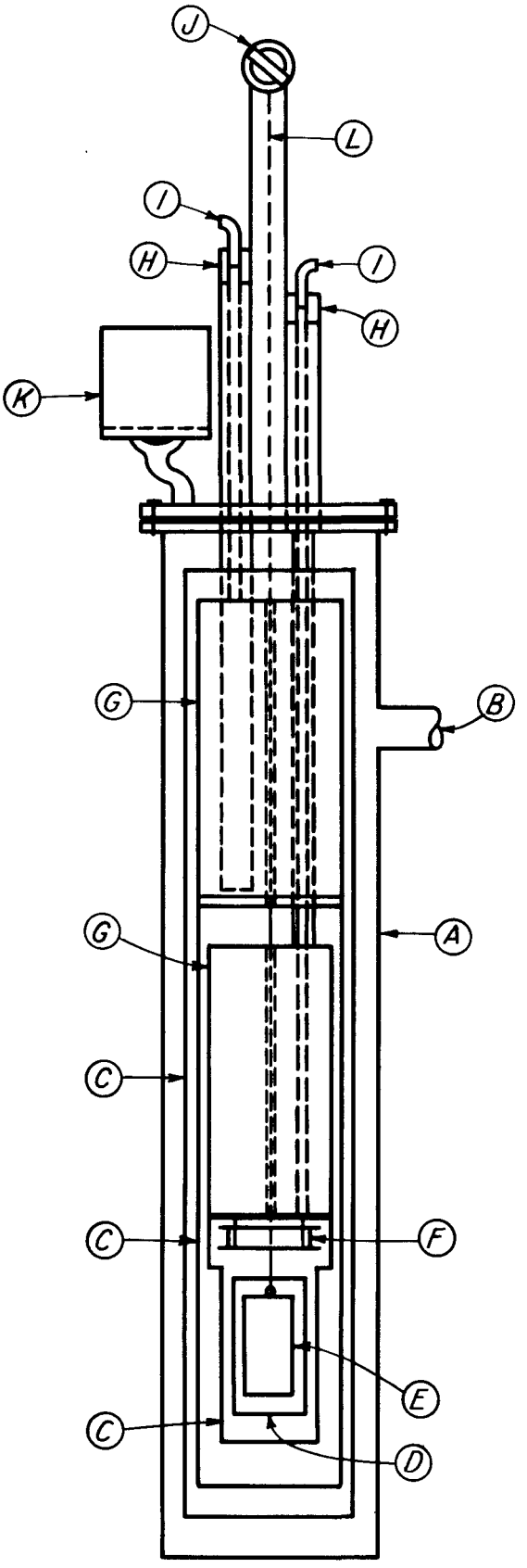
[a]Corrected for premelting

[b]This column gives the % deviation of the smoothed data from that of Douslin and Huffman.



CALORIMETER CRYOSTAT ASSEMBLY

FIGURE 1



LEGEND:

A____Cryostat outer jacket (brass).
B____Connection to evacuation system.
C____Radiation shields 1,2,3.
D____Adiabatic shield.
E____Calorimeter assembly.
F____Rings.
G____Refrigerant tanks.
H____Refrigerant filling tubes.
I____Vents and nipples for attachment to evacuation system.
J____Stopcock and vacuum windlass (brass).
K____Wax sealed leadwire distributor head.
L____String from J to E.

Scale: 5 0 5 10 15 20 cm.

FIGURE 2

CHEMISTRY DEPARTMENT LABORATORY DIVISION	
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DRWN Hammer	APPV'D J.D. Oliver
DATE: OCT. 26, 1946	DWG NO: LD-A960

File 7-50A

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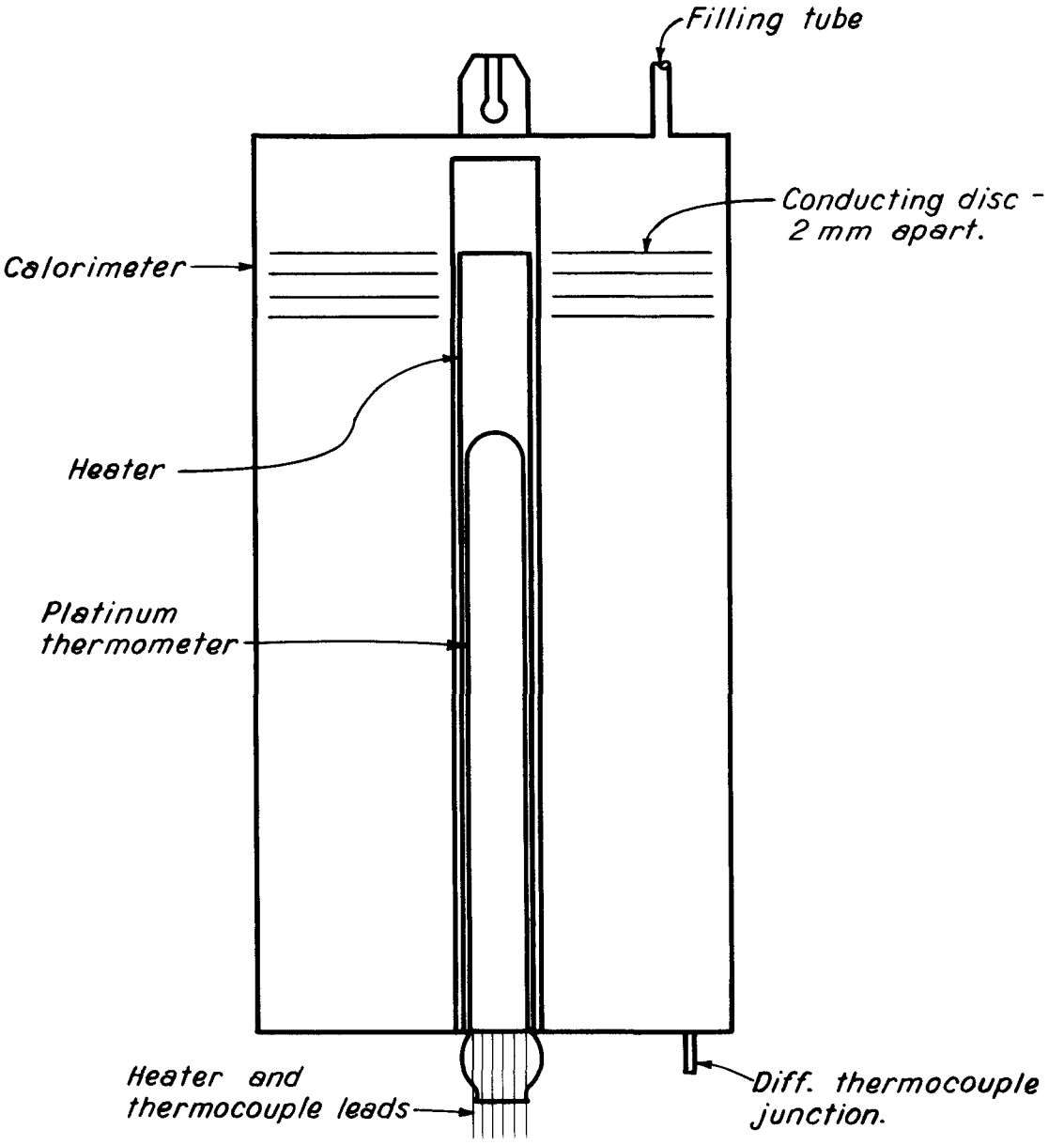

FIGURE 3

CHEMISTRY DEPARTMENT LABORATORY DIVISION	
CALORIMETER ASSEMBLY	
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File 7-50B

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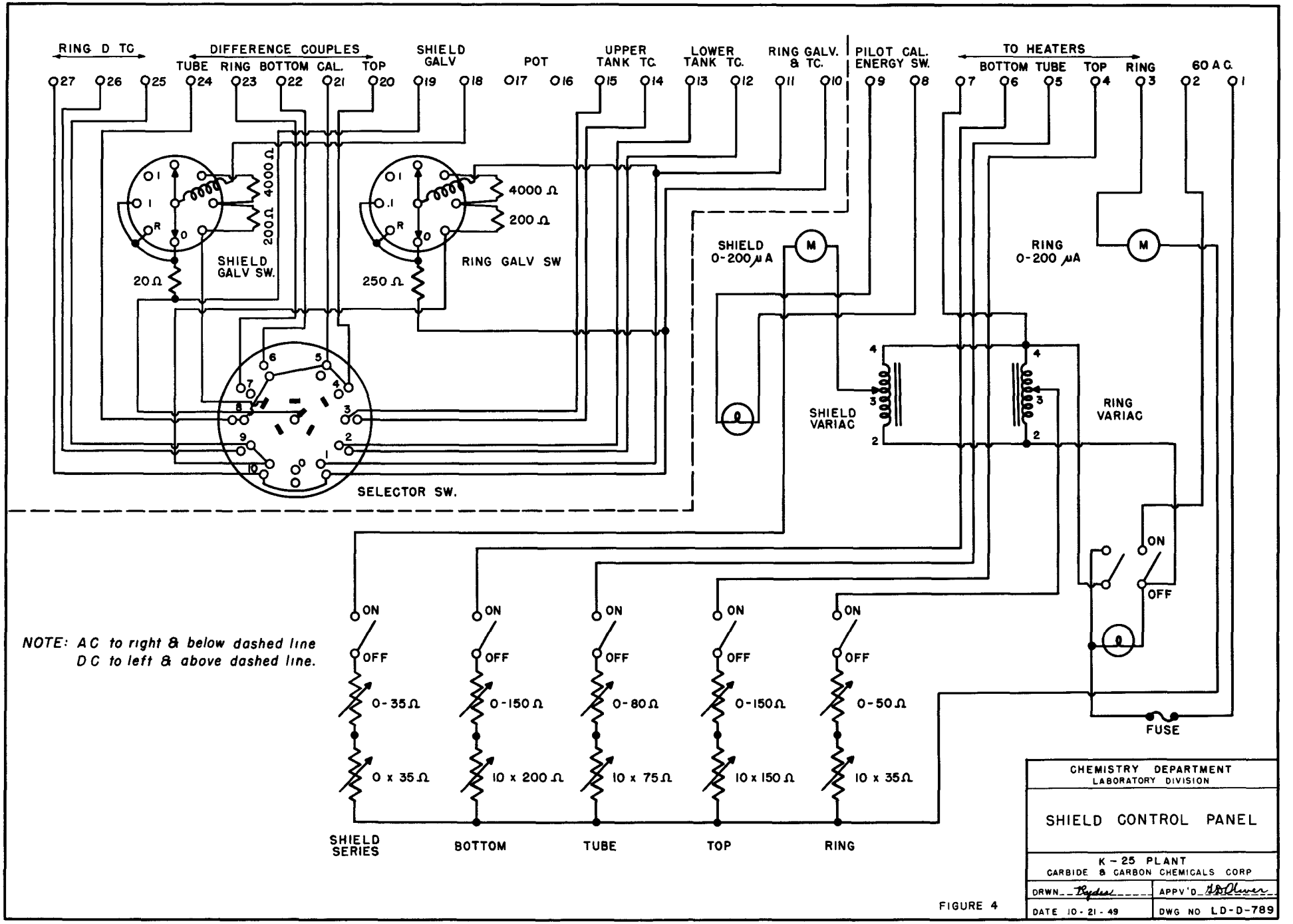

NOTE: AC to right & below dashed line
DC to left & above dashed line.

FIGURE 4

CHEMISTRY DEPARTMENT
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SHIELD CONTROL PANEL

K-25 PLANT
CARBIDE & CARBON CHEMICALS CORP

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File 7-50D

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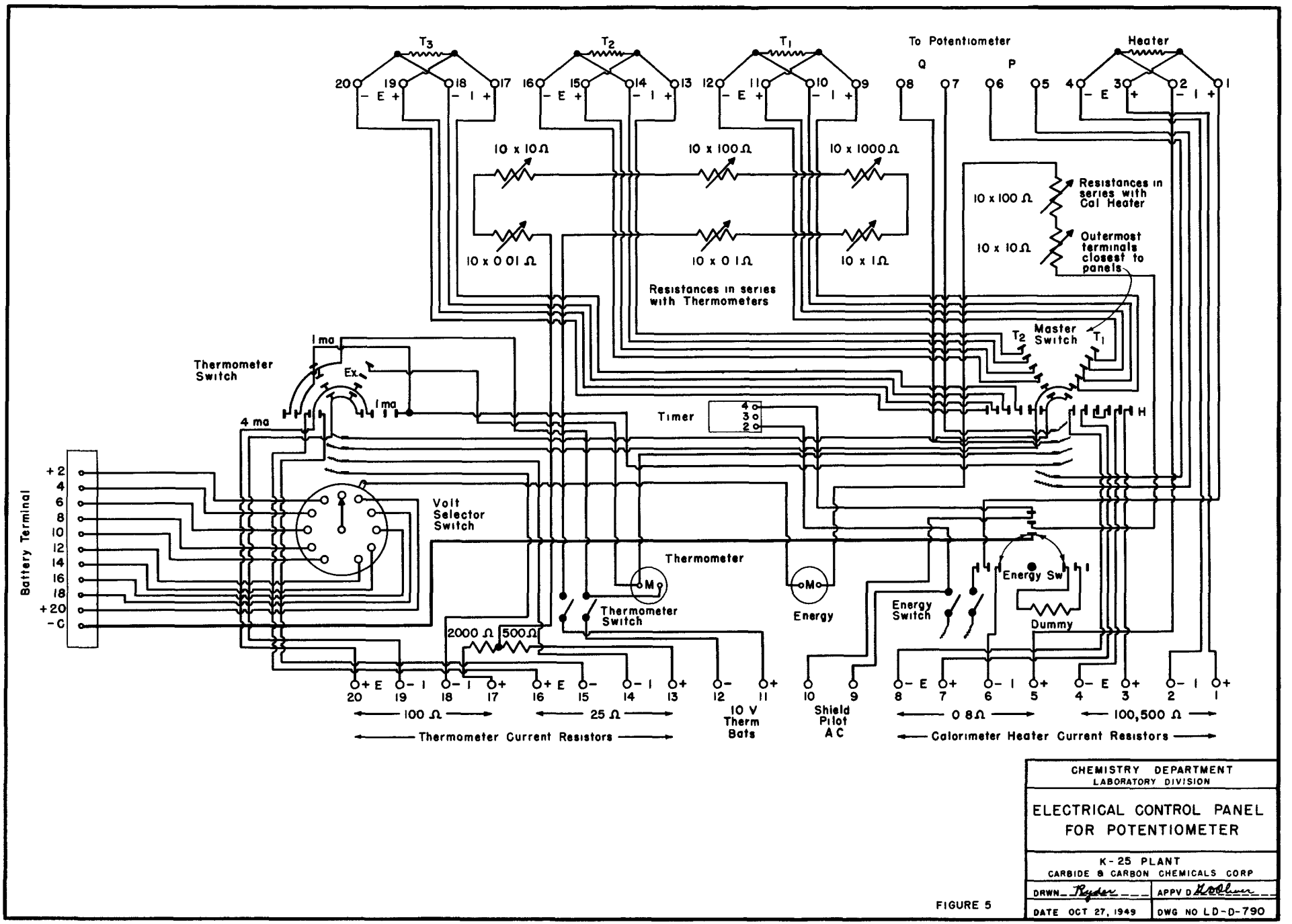

FIGURE 5

CHEMISTRY DEPARTMENT
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ELECTRICAL CONTROL PANEL FOR POTENTIOMETER

K-25 PLANT
CARBIDE & CARBON CHEMICALS CORP

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