STUDY OF SPECIFIC HEAT APPARATUS
AND
THE SPECIFIC HEAT OF MORPHOLINE

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By

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PREFACE

Modern chemical thermodynamics makes very extensive use of heat capacity data. The most obvious application is in calculating the change in heat content of a system when it is heated or cooled. The equations which set forth the functional relationships between heat of reaction and temperature and free energy of reaction and temperature are developed from heat capacity data for the substance involved. Such data may also be employed in calculating absolute entropies. The partial molal heat capacities of solutions are extensively used in dealing with many of their properties. In view of all this, the completing of the fragmentary information in this field is one of the urgent tasks of physical chemistry.

The heat capacities of volatile substances, of those which are corrosive and of those which readily suffer change on exposure to air have received less attention than those for other substances because of the obvious experimental difficulties. The study reported in this thesis had for its object the developing of apparatus and methods to be used with such substances.

INTRODUCTION

The direct methods which have been used in determining heat capacities of solids and liquids may be divided into two classes. The simpler consists in supplying to the body whose heat capacity is desired a known quantity of heat by electrical heating or otherwise, and measuring the rise in temperature which results. It is not applicable to volatile liquids or those which change on contact with air unless these be enclosed in sealed containers. This introduces considerable complexity of apparatus. For corrosive liquids glass or porcelain vessels are most feasible, though they may be constructed of gold, platinum, or tantalum.

A fairly simple apparatus may be employed if the second of the above methods, called the method of mixtures is used. In this method the sample is sealed hermetically in a glass tube or a tube made of an inert metal, which is brought to some constant temperature within the range to be covered and then dropped into a quantity of water in a calorimeter. From the change of temperature of the sample and the change in heat content of the calorimeter, the heat capacity of the substance may be calculated.

SAMPLE HEATERS

Sample heaters in calorimetric work are not discussed very fully in the literature. Apparently little importance is placed on the fact that a suitable heater is necessary for good results. The prime requisite of the heater is that it hold a constant temperature for a sufficient time to allow the sample to attain the temperature of the heater.

This temperature must be high if wide ranges of temperature are to be covered. Certain workers have gone to temperatures of 600° to 750° C. It is desirable to secure a constancy of ±0.05° C. if possible though this is difficult at high temperatures.

The oldest heater which fulfilled the above requirements is the Regnault vapor heater. Regnault's apparatus consisted of a boiler from which the vapor of a boiling liquid was passed to an annular space around the heater tube. This type heater maintains the temperature constant except when a change in barometric pressure causes a change in the boiling point of the liquid. The heater and boiler are rather bulky, and the temperatures at which the heater can be operated are limited to the number of neutral, nonflammable liquids which have the proper boiling temperatures.

Another type of heater is that manufactured by the Gaertner Scientific Corporation. It consists of a thin insulated wire wound heater tube in which the sample is placed. It is heated by a current from batteries controlled with the air aid of rheostats. Frederick and Hildebrand (1) employed a modification of this form consisting of a copper block with a hole bored lengthwise and wrapped with resistance wire. A small hole was bored in the block for a thermocouple. The resistance wire was electrically insulated by means of asbestos and a heavy lagging of the same material minimized the leak of heat from the heater block. The current for the heating was connected through a manually controlled resistance. A set of lead storage batteries would be the most convenient source of current. The chief difficulty with these heaters lies in the necessity of controlling the heating manually. This almost necessitates the employment of a second operator.

CALORIMETERS

The earliest work in calorimetry which can lay reasonable claims to accuracy is that of Regnault. His calorimeter was essentially an open can filled with water provided with a stirrer and a thermometer. Its primitive nature introduced important errors in his determinations.

The Bunsen ice calorimeter in spite of certain disadvantages is still in many respects unsurpassed for use in the method of mixtures. It is made by sealing a small glass tube within another in the manner of a Dewar flask. To the bottom of the outer tube is sealed a capillary tube which curves around the calorimeter to the top of the apparatus; then, in one form, extends horizontally along a scale. In another form, illustrated in Fig. I, the capillary tube is drawn down to a tip which dips into mercury in a small dish. The space between the cylinders contains air free water over mercury, which fills the bottom of the vessel and extends into the capillary tube. The body of the calorimeter is surrounded by an ice bath to keep the environing temperature of the calorimeter at zero degrees Centigrade.

In operation the water around the inner tube is frozen by introducing an ether-solid carbon dioxide mixture in a yet smaller tube into it. By controlling the freezing rate a suitable mantle of ice may be formed. During the freezing the mercury is partially expelled due to the formation of ice with its accompanying increase in volume. When a hot object is dropped into the inner tube, the mercury is drawn back along the capillary tube as the ice melts. The volume of mercury drawn back along the tube in the first form of the apparatus, or the weight of mercury drawn from the dish in the second is a measure of the quantity of the ice melted and so indicates the quantity of heat introduced. Bunsen used

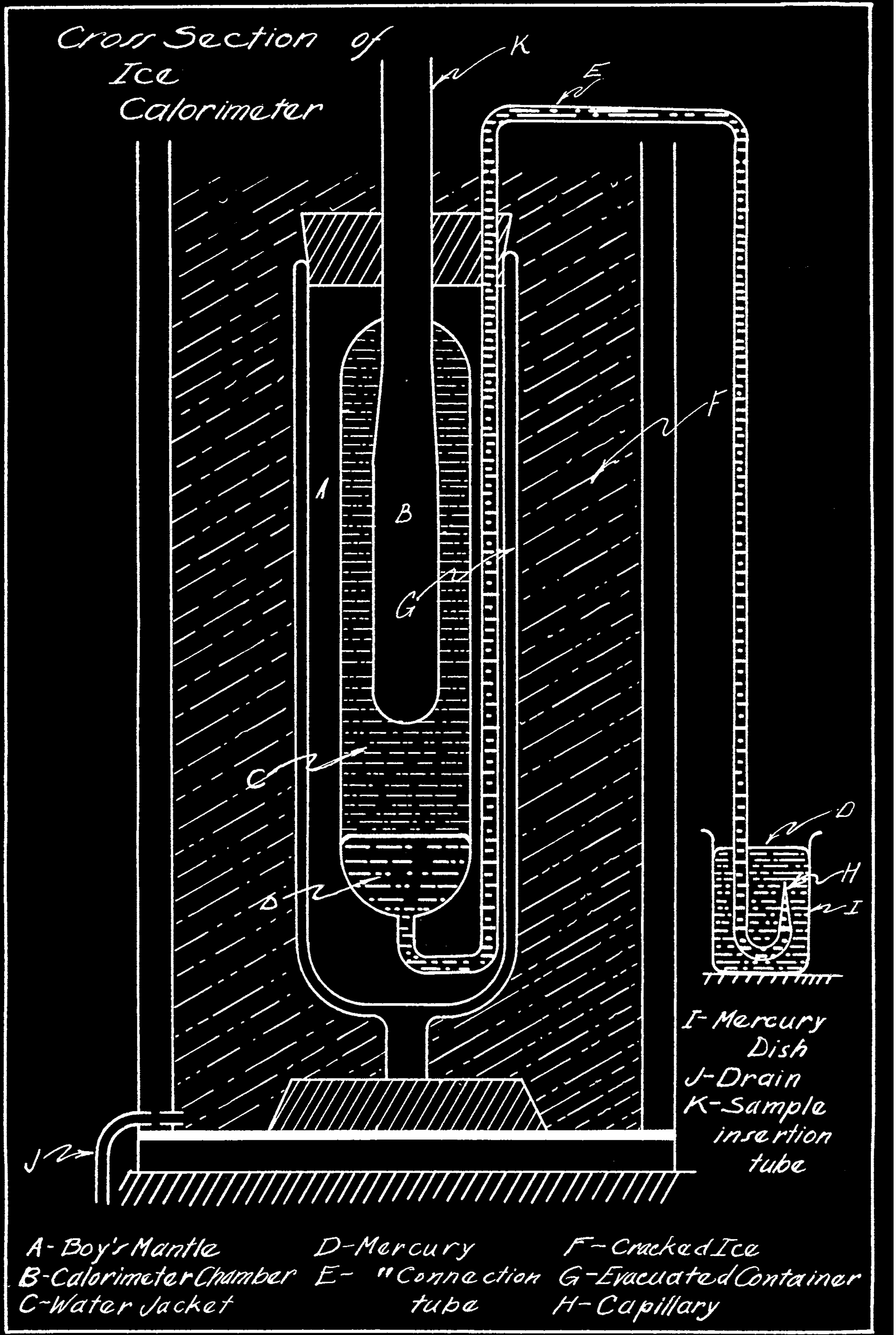

Cross Section of Ice Calorimeter
K
E
F
A
B
G
C
D
D
H
I
J
I- Mercury Dish
J-Drain
K-Sample insertion tube
A-Boy's Mantle
B-Calorimeter Chamber
C-Water Jacket
D-Mercury
E- " Connection tube
F-Cracked Ice
G-Evacuated Container
H-Capillary

FIGURE I

the calorimeter to determine the heat capacities of several of the lesser known elements and their oxides. The proof of the instrument's versatility is shown by the fact that it has been used to determine such quantities as heats of adsorption of hydrogen on platinum black (2) and the adsorption of oxygen on charcoal. (3)

In the words of White (4)

> "The Bunsen ice calorimeter is the best device for eliminating thermal leakage introduced so far".

This statement is rather remarkable since the ice calorimeter was first built in 1870, and White published his monograph "The Modern Calorimeter" in 1928.

There are some disadvantages in the case of the ice calorimeter which should be mentioned. The error most frequently discussed in the literature is the error caused by the variation of the density of ice. (5) Experiments show that ice does not form with uniform density. Several investigators have studied this variation in density. They report results which do not agree. Nichols (6) gives for the density 0.91616 ±0.00009. Vincent (7) gives 0.9160 and Leduc (8) reports 0.9176. More recent work by Griffiths (5) states that the density of ice is 0.9161 with an error of two parts in ten thousand. Griffiths also states that the discrepancy in the results of the several investigators is due to traces of air dissolved in the water.

The literature already referred to mentions other errors but proper construction and modification eliminates them. There is a depression of the freezing point of water by the pressure of the mercury in the capillary column which amounts to .005 degree if the capillary height is 50 centimeters, but in later apparatus an equalizing column of mercury compensates for this error.

Two disadvantages, not errors are also encountered in work with the ice calorimeter. The apparatus is constructed entirely of glass and is therefore necessarily fragile. The other difficulty is that the calorimeter can be operated only at zero Centigrade. Because of the difficulties involved, we decided against its use.

The conventional calorimeter without control of the temperature of the environment involves too many sources of error to be acceptable in accurate work when the quantity of water used is small, as it must be in these experiments.

Another type calorimeter which may be employed is the adiabatic calorimeter. It consists of a calorimeter cup supported within a convection shield and mounted in a specially designed outer jacket filled with liquid which can be circulated. A liquid tight lid fits over the cup and shield with appropriate holes for stirrer shaft, temperature measuring instrument and tube for the introduction of the sample. The difference between the adiabatic calorimeter and the ordinary type calorimeter lies in the fact that the temperature of the jacket is so altered as to follow the temperature of the water in the calorimeter cup.

This procedure maintains zero thermal head between the cup and jacket and eliminates thermal losses. The adiabatic calorimeter was designed by Richards (9) and his students. It is suited to the measurements of slow and small temperature changes. With the ordinary type calorimeter slow or small temperature changes can not be measured with accuracy since the radiation losses from the calorimeter are large. In Richards' original calorimeter the jacket temperature is raised by mixing solutions of acid and base in the jacket, the heat of neutralization furnishing the heat. Later work with the adiabatic calorimeter employed other means of controlling the jacket temperature. Cohen and Moesveld (10) used an electrically heated coil; Swientoslawski (11) employed injections of hot or cold water as the occasion demanded and could follow changes in the calorimeter as great as 0.3 degrees per minute. In still later work Williams and Daniels (12) filled the jacket with glycerol containing ferric chloride to make the solution conducting and passed alternating current through the solution for the desired heating effect.

The adiabatic calorimeter is cumbersome, and control of the jacket temperature is difficult experimentally. We decided therefore not to employ it.

Modifications of the submerged type calorimeter are used to a greater extent than the other forms mentioned. The construction of the apparatus is similar to that of the adiabatic calorimeter. A calorimeter cup is supported in one or more convection shields. The cup and shield are placed in a can with a liquid tight cover. The cover is provided with tubes leading into the calorimeter chamber for a thermometer, stirrer, and means of introducing the sample into the cup. The whole of the calorimeter is submerged in a thermostated liquid bath. With this arrangement the environing temperature of the calorimeter is held constant. The use of the convection shields minimizes the radiation losses so that reliable corrections for thermal leakage can be made.

Since this type calorimeter is the type used in the present work, the errors will be discussed rather fully. Most of the discussion is from White "The Modern Calorimeter".

Thermal leakage is the most important source of error. As soon as the calorimeter temperature changes heat will flow from or to the calorimeter according to Newton's law of cooling. By use of equations for thermal head losses in the monograph referred to above the thermal leakage constant can be calculated. Direct evaluation of this differential equation however is not usually satisfactory.

A second error is introduced by the heat given to the calorimeter by the stirrer. For this correction White suggests the use of an equation derived from hydraulics. The heat transferred to the water in the calorimeter cup can be found with this equation after empirical constants in the equation have been evaluated. The evaluation of these constants is sometimes difficult.

The third is introduced by the variable evaporation of the water from the calorimeter. This error is the most difficult of the three to evaluate, due to its variability. It might seem that with the calorimeter in the thermostat, external conditions would not alter conditions in the calorimeter.

TEMPERATURE MEASUREMENTS IN CALORIMETRY

The accuracy of temperature determinations will affect the quality of the calorimetric data. The original work in calorimetry employed mercury in glass thermometers. Later these instruments were calibrated and various corrections made such as corrections in capillary diameter and correction for exposed stem of the thermometer. Another difficulty lay in the fact that wide range and accuracy could not be incorporated in one instrument. The one type of mercury thermometer which is still used to some extent is the Beckmann thermometer. Barry (13) has made an extensive study of its use for this purpose and states that the accuracy is limited to about .0005 degrees. He also states that for satisfactory performance the thread must not stick or change on tapping. There is commonly a lag of about thirty seconds with a Beckmann. Work in calorimetry has turned of late from mercury thermometers. Thermocouples and resistance thermometers have replaced them when possible. The thermocouples are either single or multiple junction according to the accuracy desired. Resistance thermometers give satisfactory results, especially in conjunction with a Mueller bridge. The fact remains, however, that no other thermometric device approaches the Beckmann thermometer in convenience. It was used in this investigation.

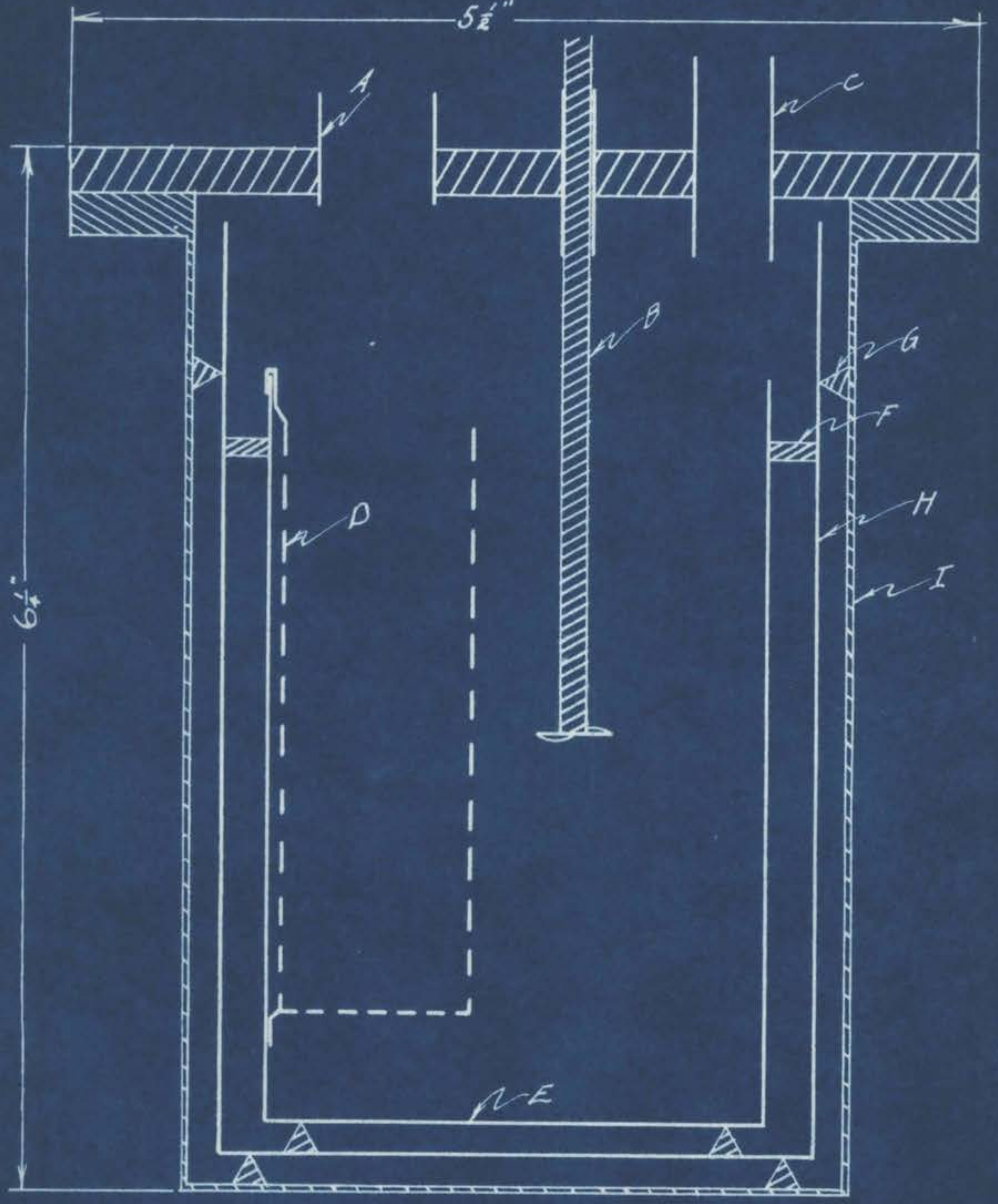
EXPERIMENTAL

DESCRIPTION OF CALORIMETER

Earl L. Richardson (14) has employed the Bunsen ice calorimeter in some preliminary work on determinations of specific heat. He found that it is slow in operation. It was also found to be subject to obscure changes such that results could not be checked. This was finally traced to a slight crack from which water progressively leaked out. Because of its fragility it seemed better to turn to a calorimeter of another type.

The calorimeter used in this work is of the submerged type discussed in the foregoing introduction. It was chosen over the other types because of its simplicity and ease of manipulation. It is true that some of the errors are eliminated by the use of some of the other types but in our estimation this type calorimeter was the most suitable for the work.

A sketch of the calorimeter is shown in Fig. II. The calorimeter cup is of nickel plated copper. A convection shield is placed around the cup to minimize and standardize heat leak. The shield and cup are supported in a copper can with a water tight lid. The lid is fitted with tubes which hold, respectively, bearings for the stirrer shaft, a Beckmann thermometer, and a tube for the introduction of a sample. The calorimeter cup is provided with a lid to which a perforated basket to receive the sample as it drops from the heater is attached. For the runs the calorimeter is mounted in a twenty-five liter water bath which is maintained at 25°C.



Cross Section of Calorimeter

A Sample insertion tube
B Stirrer
C Thermometer tube
D Sample receptacle
E Calorimeter cup
F Bakelite spacer
G Wood spacers
H Convection Shield
I Calorimeter container

FIGURE II

DESCRIPTION OF HEATERS

For this work two types of heaters were employed, a modification of the Regnault vapor heater and a combination of electrical heater and thermo-regulator. The vapor heater shown in Fig. III consisted of a copper boiler of about a liter capacity with a copper tube connecting the top of the heater and the annular space around the heater tube. A return tube from the bottom of the annular space was used to lead the condensed liquid back to the heater for recycling. In addition to the return tube a second tube open to the air was connected to the return tube to insure boiling of the liquid at atmospheric pressure. Both tubes were fitted with copper cooling coils to prevent loss of uncondensed vapor.

The second type heater mentioned above is a new device as far as we can ascertain. It is shown in Fig. IV. It consists of the conventional heater tube surrounded by an annular space filled with mercury and connected to the usual thermo-regulator head, so combining the two devices in one. It is wrapped externally with asbestos for insulation on which is wound a heating coil of resistance wire. The wire in turn is covered with asbestos for further insulation and to minimize heat leak. The making and breaking of the mercury contact in the regulator operates a relay which in turn opens and closes the heating circuit. The heater can be operated at any temperature above room temperature up to the boiling point of mercury as a limit by adjusting the regulator screw to give contact between the mercury and needle at different temperatures.

A test run was made with the heater to check its constancy. For the test a single junction copper-costantan thermocouple in conjunction

Cross Section of Vapor Heater

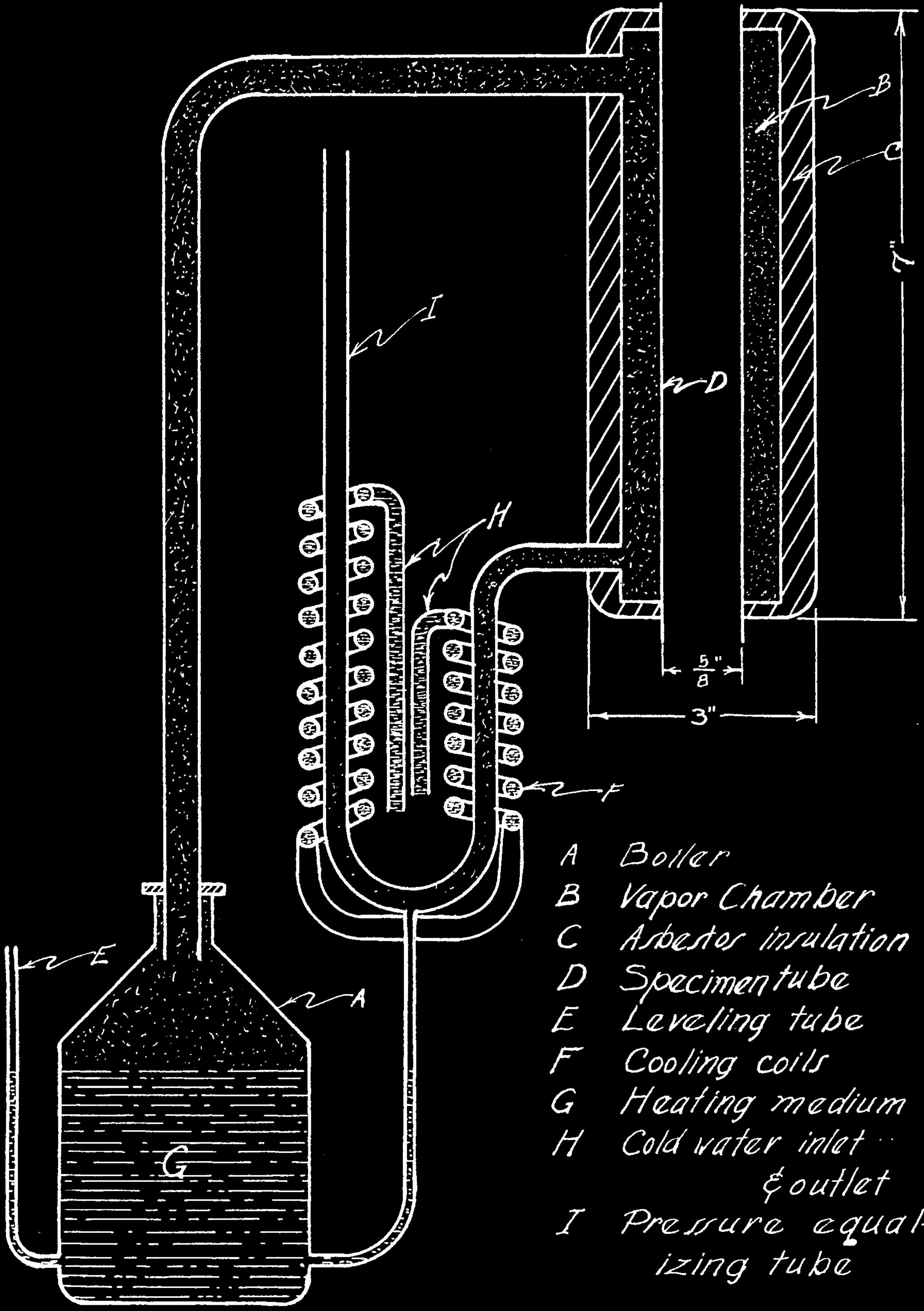
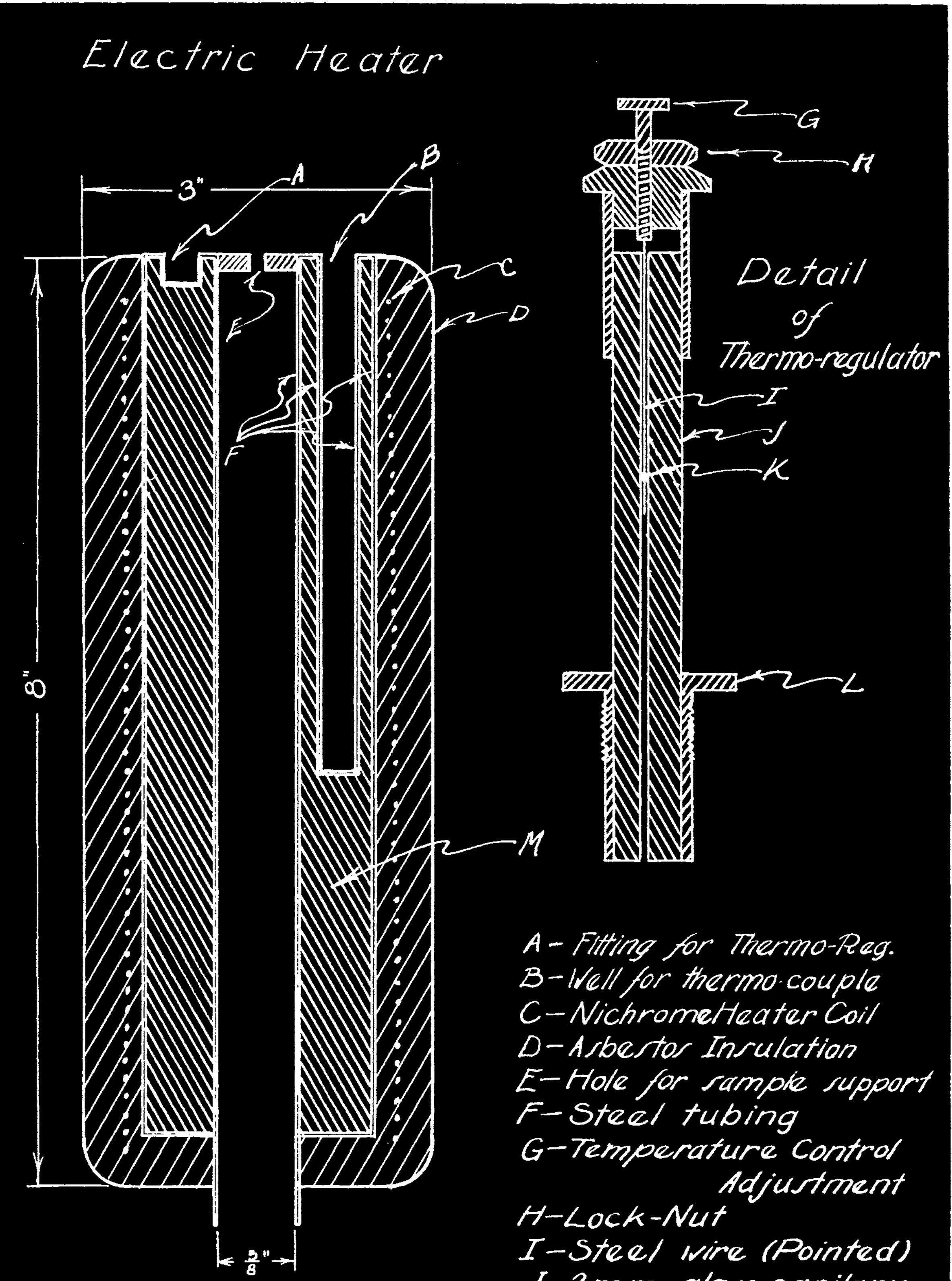


FIGURE III



A - Fitting for Thermo-Reg.
B - Well for thermo-couple
C - Nichrome Heater Coil
D - Asbestos Insulation
E - Hole for sample support
F - Steel tubing
G - Temperature Control Adjustment
H - Lock-Nut
I - Steel wire (Pointed)
J - 2 m.m. glass capilary
K - Glass bead (Centers steel contact wire)
L - Fitting to match (A)
M - Hg in all-steel well

FIGURE IV

with a type K_2 potentiometer was used to measure the temperature of the heater. The data in Table I were taken for a three and one-half hour run.

TABLE I

Time in Minutes	Potentiometer reading in Millivolts
0	4.2503
15	4.2503
30	4.2503
45	4.2503
60	4.2503
75	4.2503
90	4.2503
105	4.2503
120	4.2503
135	4.2503
150	4.2503

For this temperature 0.04 millivolts as registered by the thermocouple is equal to $1^{\circ}C.$ so the heater maintained a constancy of better than $0.01^{\circ}C.$

CALORIMETER CALIBRATION

The calorimeter cup held 400 grams of water. This water was brought to 25°C. so that no time would be lost in waiting for it to take the temperature of the bath. The calorimeter was assembled, placed in the water bath and the stirrer set in motion about fifteen minutes before a run was started.

The samples used in the calibration were doubly distilled water sealed hermetically in pyrex capsules. Two samples were used in the calibration. The weights of water and pyrex in each are given in Table II.

TABLE II

Sample No.	Weight H_2O	Weight Pyrex
1.	10.1987	12.7056
2.	8.6019	11.7073

There follows the procedure, data, and calculations involved in a typical run. All runs for calibration and the runs on the morpholine were made in this manner.

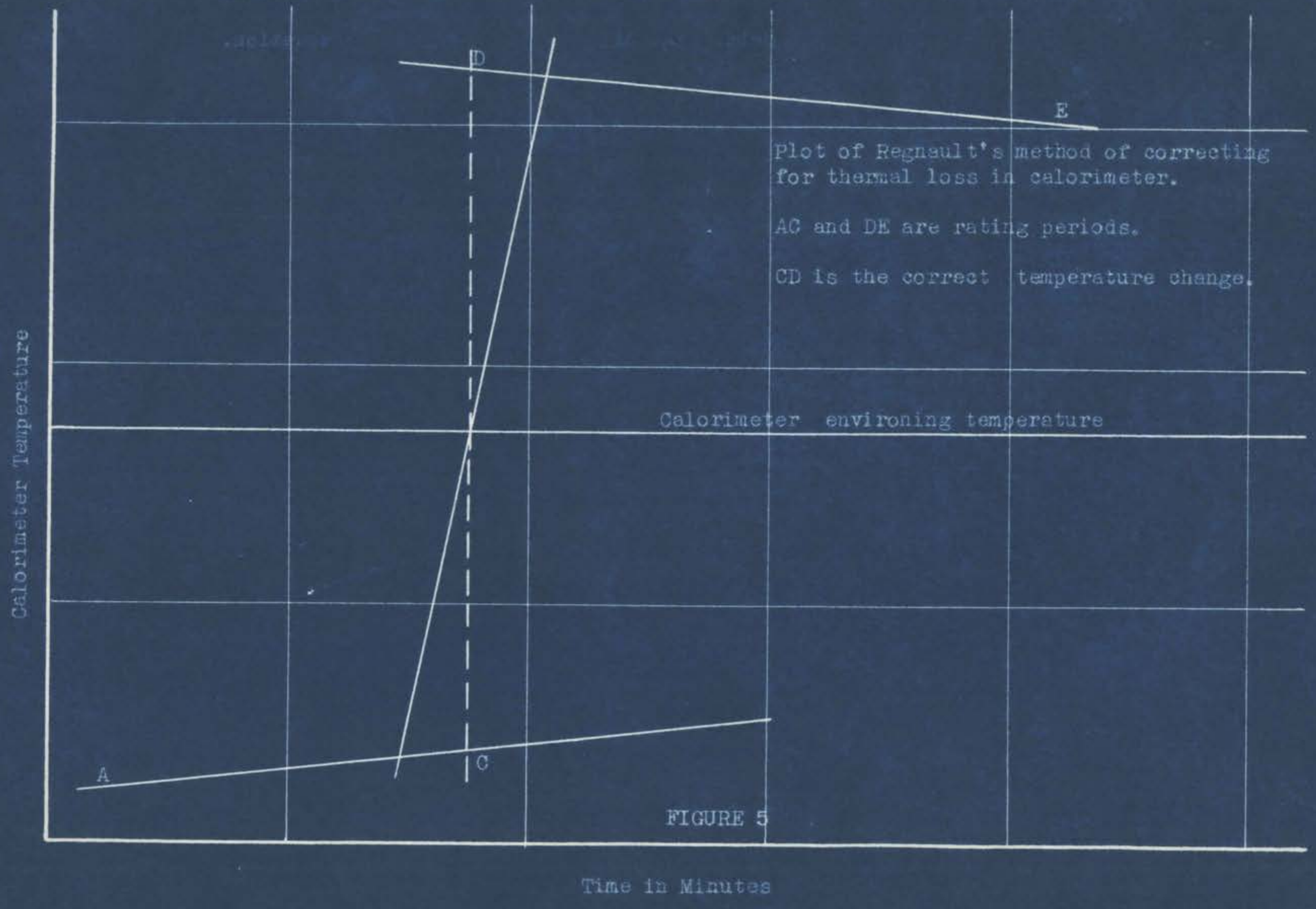
The water sample was placed in the heater which was then stoppered and allowed to heat for an hour and a half to bring the charge to temperature. The temperature of the heater was taken as the temperature of the sample. Fifteen minutes before the sample was dropped the calorimeter was assembled and the stirrer set in motion. After eight or nine minutes readings of the Beckmann thermometer were taken and recorded. These readings were not used in the calculations but they showed in each case that the temperature remained constant. The sample was dropped at this time and the changes of temperature in the calorimeter were followed by reading the temperature every minute. After the maximum reading had been taken readings were continued for five or six minutes to evaluate the heat leak from the calorimeter. The readings of a typical run are given in Table III.

TABLE III

Time in Minutes	Beckmann Rdg.	Temp. loss °C/minute
0	2.962	
1	2.962	
2	2.962	
3	2.962	
4	2.962	
5	4.550	
6	4.760	
7	4.780	
8	4.773	
9	4.760	0.013
10	4.749	0.011
11	4.735	0.014
12	4.722	0.013
13	4.710	0.012
	Average:	0.012

Calculations:

Corrections for the loss of heat in calorimeters of this type are most conveniently made by a graphical method. Readings are made, as in our experiments, and the temperatures as read are plotted against time. This gives such a curve as shown in Fig. V. The straight lines found



Plot of Regnault's method of correcting for thermal loss in calorimeter.

AC and DE are rating periods.

CD is the correct temperature change.

FIGURE 5

by connecting the readings of the initial and final rating periods are extended until they meet the ordinate corresponding to the temperature of the surroundings, and the corrected rise is the intercept of the lines on this ordinate. In our experiments the first rating period serves to establish the fact that the calorimeter is at the temperature of the surroundings. The only correction comes from the second rating period. We have preferred to make this correction analytically. For this purpose the average rate of fall in temperature during this period is taken and multiplied by the time elapsing between the dropping of the sample and the time when the maximum temperature is reached. This is added as a correction to the difference between these two temperatures. The method employed in making our calculations is illustrated in detail in the following:

Experiment with Sample 2:

A. Observed temperature change in the calorimeter:

$4.780 - 2.962 = 1.818^\circ C$ (corrected)

B. Correction for thermal loss:

Time for sample to lose heat to calorimeter = 3 minutes.

Temperature fall in calorimeter = $0.012^\circ C$/minutes.

Temperature loss = $3 \times 0.012 = 0.036$.

C. Corrected temperature change in calorimeter:

$1.818 + 0.036 = 1.854^\circ C$.

D. Heat transferred to the calorimeter by the water in the sample: The values of the heat capacity of water as taken from Lange's handbook were plotted versus temperature and the plot integrated graphically. It was found however that the recent values for specific heat given by the equations of Roth (15) checked the graphical integration almost exactly so these equations were used for convenience. These equations when integrated within the proper limits give the heat change involved when a gram of water is cooled between two temperatures.

For the interval 0°- 40°C. we have

$$1. \quad Cp = 1.0066 - 0.0005696t + 0.000008742t^2$$

and for the interval 40°- 100°C.

$$2. \quad Cp = 0.9989 - 0.000111t + 0.00000189t^2$$

Integrating between limits with respect to temperature we have

$$1a. \quad \Delta H = 1.0066t - 0.0002848t^2 + 0.000002914t^3$$

$$2a. \quad \Delta H = 0.9989t - 0.0000555t^2 + 0.00000063t^3$$

The equations are employed as follows:

Temperature of the heater = 99.44°C.

Temperature of the calorimeter = 27.69°C.

Substitution in 1a between 27.69 and 40°C.

$$\Delta H = 12.258 \text{ cal/gram } H_2O$$

Substitution in 2a between 40° and 99.44°C.

$$\Delta H = 59.507 \text{ cal/gram } H_2O$$

The total heat change is the sum of the above H values which is equal to 71.765 cal/gram H_2O.

ΔHeat lost by the water in Sample 2

71.765 x 8.6019 = 617.32 calories

E. The heat lost by the pyrex in the capsules was calculated by the heat capacity equation given by Frederick and Hildebrand (16):

$$Cp = 0.186 + 5.5 \times 10^{-5} \; (t-25) + 1.15 \times 10^{-6} \; (t-25)^2$$

The corresponding ΔH equation is

$$\Delta H = 0.186t + 2.75 \times 10^{-5} \; (t-25)^2 + 0.383 \times 10^{-6} \; (t-25)^3$$

Between the above limits, namely 27.69°C and 99.44°C, we have

ΔH = 13.653 calories/gram pyrex.

Heat lost by pyrex in the capsule = 13.653 x 11.7073 = 159.84

Total heat given to the calorimeter = 159.84 + 617.32 = 777.16 calories.

Temperature change in the calorimeter = 1.854°C.

Heat equivalent of calorimeter = 777.16/1.854 = 419.3 calories/degrees.

Table IV gives the heat equivalents of the calorimeter on four runs which were averaged to give the heat equivalent used in the calculations on morpholine.

TABLE IV

Sample No.		Heat Equivalent
1		418.8
2		421.7
1		418.4
2		418.2
	Aver.	419.3 ± 1.7 cal/deg.C.

As a theoretical check on the value of the heat equivalent given above, the calorimeter and basket weighed 230 grams. Taking the specific heat of copper as 0.1 at this temperature the calculated heat equivalent would be (230 x 0.1) + 400 or 423 calories. The results obtained in the actual calibration are considered in good agreement with this value.

In runs made with the Regnault vapor heater its temperature was measured by means of a calibrated mercury thermometer reading to the nearest 0.2°C. in the heater. The calorimeter temperatures were followed with a Beckmann thermometer calibrated by the Bureau of Standards for both the vapor heater and the new heater. With the new heater a single junction copper-constentan thermocouple was used, the potential of the couple being measured with a type K_2 potentiometer. All temperatures as read were standardized by comparison with a special mercury thermometer reading from 0° to 206°C. calibrated by the Bureau of Standards. The heater temperature measured to the nearest tenth of a degree was sufficiently accurate for the calculations.

HEAT CAPACITY OF MORPHOLINE

Morpholine is a cyclic compound with the formula $HN(CH_2CH_2)_2O$. It combines the properties of a cyclic ether and a secondary amine being miscible with water in all proportions, and also soluble in many organic solvents. Morpholine forms an addition compound with carbon dioxide and is hygroscopic. For these reasons, the determination of its physical constants must be made with air excluded. The morpholine used in this work was obtained from the Union Carbide and Carbon Corporation. It was refluxed over sodium to purify it and distilled. The samples were sealed in pyrex capsules similar to the capsules used in the calorimeter calibration. The weights of the two samples used in the runs are given in Table V.

TABLE V

Sample No.	Weight Morpholine	Weight Pyrex
1	11.7693	13.0201
2	11.4162	13.6187

The problem of determining the specific heat of a substance involves finding an equation which will give the change in heat content between certain temperatures. The heat capacity equation is not obtained directly.

The ΔH equation takes the form:

$$\Delta H = At + Bt^2 + Ct^3$$

and the Cp equation:

$$Cp = A + B/2t + C/3t^2$$

In this work the changes in heat content of morpholine over the temperature range 0°C to 100°C were determined. Four sets of runs for ΔH were made with the vapor heater. Water was used in the boiler for the interval (100°- 25°), Benzene for the interval (80°- 25°), Chloroform for the interval (60°- 25°), and an ice bath for the interval (0°- 25°).

SAMPLE RUN WITH MORPHOLINE

The calorimeter was prepared for these runs just as in the calibration runs. The description of the mechanical details will be omitted, and only the data of a run and accompanying calculations will be given. Table VI gives the data for a run with the heater at 99.63°C.

TABLE VI

Time in Minutes	Beckmann Reading	Temp. lost/Minute
0	2.260	
1	2.260	
2	2.260	
3	2.260	
4	2.260	
5	3.150	
6	3.460	
7	3.600	
8	3.630	
9	3.640	
10	3.645	
11	3.645	
12	3.643	
13	3.638	0.005
14	3.630	0.008
15	3.622	0.008
16	3.615	0.008
17	3.608	0.007
		Av. 0.007

Calculations: data for sample 1

1. Observed temperature change in calorimeter: 3.645 - 2.261 = 1.384.
2. Correction for thermal loss 0.007 x 3 = 0.021.
3. Corrected temperature change 1.384 + 0.021 = 1.405.
4. Heat lost by pyrex in capsule = 181.1.
5. Heat given to the calorimeter = 419.3 x 1.405 = 589.1 calories.
6. Heat lost to the calorimeter by morpholine:

   589.1 - 181.1 = 407 calories.

7. Heat lost by one gram morpholine = 407/11.7693 = 34.58 cal/gram.

The last calculation shows the heat lost by one gram of morpholine and was obtained by dividing the heat from the morpholine in the sample by the weight of morpholine in the sample. To make a series of runs from 100°C. to 25°C. exactly is almost impossible. Therefore to have all runs on the same basis for comparison, the values obtained as above were converted to these temperatures by proportion in the following manner:

$$34.58 \times 100/99.63 \times 26.53/25 = 36.83 \text{ calories/gram.}$$

The assumption made in this calculation is that the ΔH curve is a straight line, and that the above corrections are valid for the small intervals not covered.

The values in Table VII give the heats lost by one gram of morpholine when it is cooled through the ranges given in column one. The averages were used in the calculations of the ΔH equation, and the subsequent heat capacity equation.

TABLE VII

Temp. interval	ΔH change	Average
100° - 25°	36.83	
	36.45	
	36.60	
	36.64	36.63
80° - 25°	26.98	
	26.36	
	26.21	
	26.02	26.39
60° - 25°	16.55	
	16.55	
	16.45	
	15.92	16.37
25°-0°	10.42	
	10.43	
	10.49	
	10.48	10.46

For the derivation of the ΔH equation we employ the summations of heat effects from 0°C to the several temperatures as given in Table VIII.

TABLE VIII

Temp. interval	ΔH changes in calories
25° - 0°	10.46
60° - 0°	26.83
80° - 0°	36.85
100° - 0°	47.09

The data from Table VIII has been plotted in Figure 6. ΔH is plotted versus temperature Centigrade. It will be noted that the curve is not a straight line. It is slightly concave upward. Using these data we set up four equations for ΔH in the form of series expressions with the power terms as temperatures Centigrade, and solved them to secure the desired empirical constants A, B and C. This gives:

$$\Delta H = 0.3864t + 1.697 \times 10^{-3} t^{2} - 4.537 \times 10^{-6} t^{3}$$

On calculating H at ten degree intervals from this equation, we find the values represented by circles in Fig. 6.

The heat capacity equation obtained by differentiation of the above H equation is:

$$Cp = 0.3864 + 2.596 \times 10^{-3} t - 1.361 \times 10^{-5} t^{2}$$

Fig. 7 is a plot of the specific heat of morpholine obtained by substitution in the equation. In the plot the specific heat is plotted against temperature Centigrade. The data for the ΔH curve and the heat capacity curve were given in Table IX.

TABLE IX

Temp. °C.	ΔH	Cp
0	00.00	0.3864
10	3.99	0.4110
20	8.21	0.4329
30	12.64	0.4521
40	17.25	0.4684
50	21.99	0.4822
60	26.87	0.4932
70	31.85	0.5014
80	36.89	0.5070
90	41.98	0.5098
100	47.07	0.5099

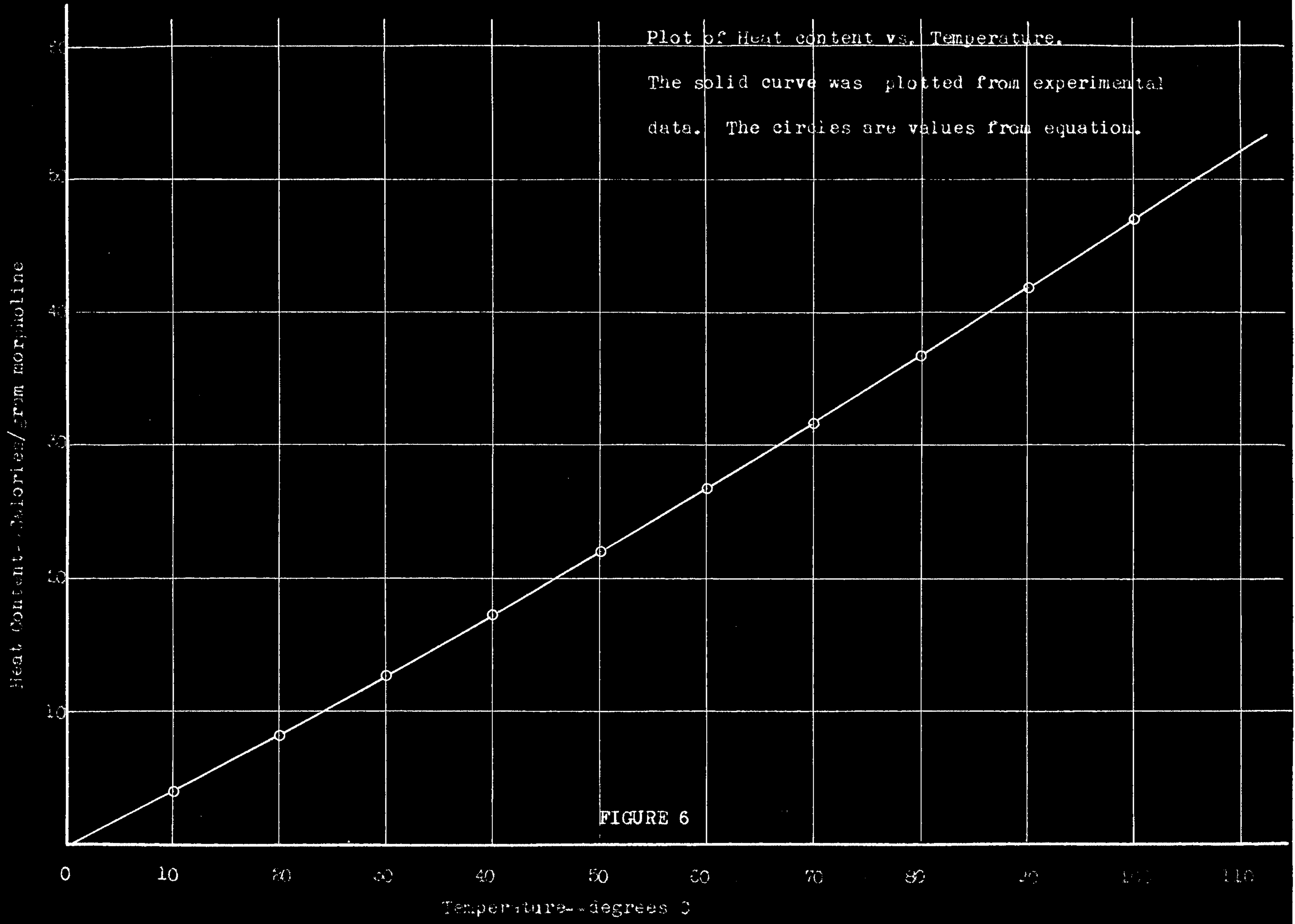


FIGURE 6

Plot of Heat content vs. Temperature.

The solid curve was plotted from experimental data. The circles are values from equation.

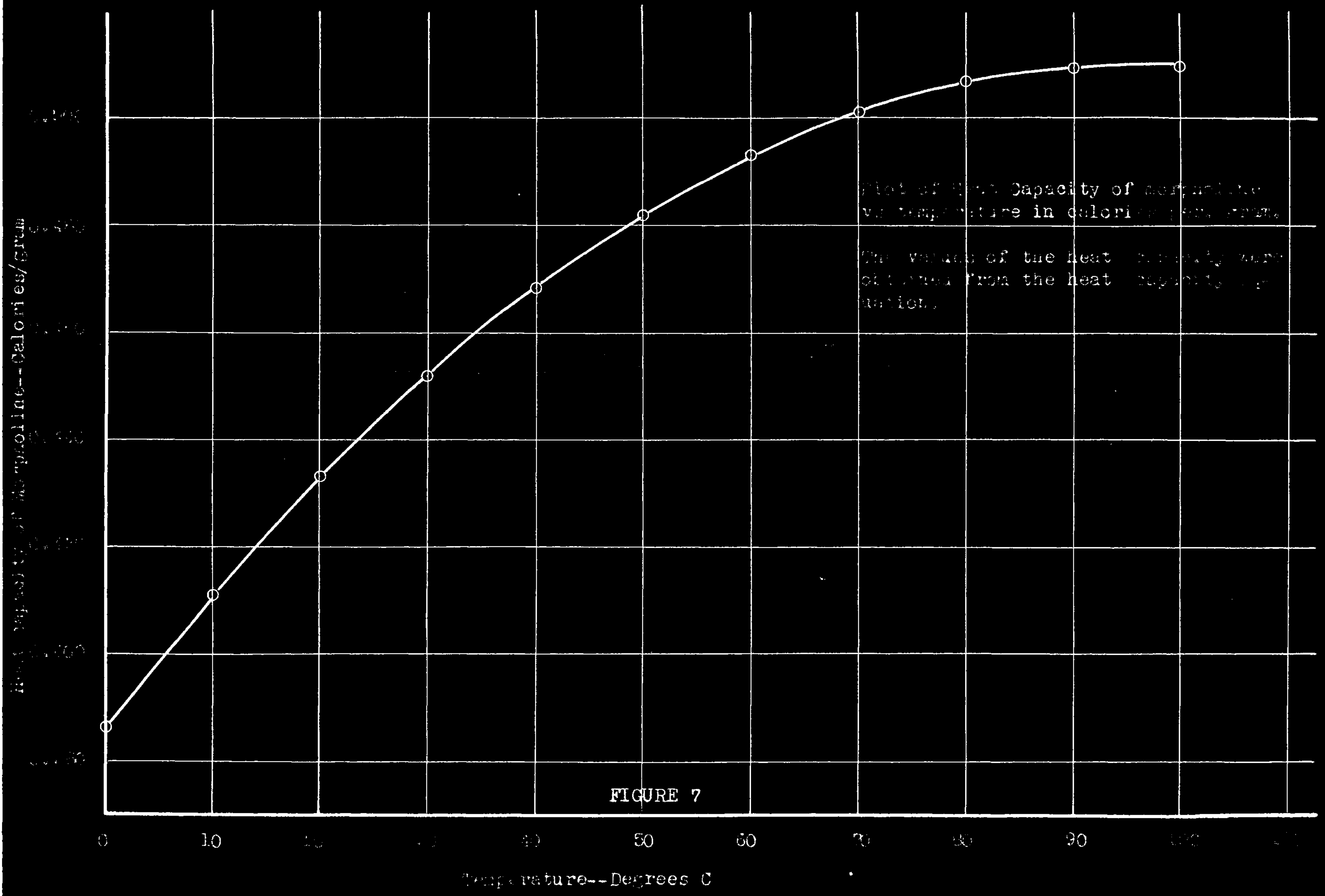


FIGURE 7

Plot of Heat Capacity of morpholine vs temperature in calories per gram.

The values of the heat capacity were obtained from the heat capacity equation.

SUMMARY

A study has been made of the apparatus which may be employed in determining the heat capacities of substances and solutions which are volatile or which may not be exposed to the atmosphere. A new form of heater suitable for this work has been developed. A direct study of the technique of these determinations has been made by assembling the apparatus and determining the heat capacity of morpholine. The data are presented in the form of tables and curves. The heat capacity of morpholine in the range 0°C to 100°C is given by the equation:

$$Cp = 0.3846 + 2.596 \times 10^{-3} t - 1.361 \times 10^{-5} t^2$$

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AUTOBIOGRAPHY

I, Charles J. Engle, was born in Fairview, West Virginia, October 26, 1916. My elementary and high school education were received in the public schools of Oklahoma.

Two years of my undergraduate college work were completed at the University Preparatory School and Junior College at Tonkawa, Oklahoma during the years 1935-1936. The following year I entered Oklahoma Agricultural and Mechanical College, and received the degree of Bachelor of Science in Chemical Engineering in July 1938. I have spent the past two years, while employed by the Department of Chemistry as a graduate assistant, pursuing courses leading toward the degree of Master of Science in Chemistry.