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*I hereby recommend that the thesis prepared under my supervision by* DONALD A PAYNTER

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# A STUDY OF THE TEMPERATURE COEFFICIENT OF THE HEAT OF IMMERSION

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# INTRODUCTION

Solid-liquid interfacial properties have received much attention from investigators largely because of the importance of these properties in lubrication, adhesion, flotation, and in other processes where interfacial phenomena play a part. Practical applications of interfacial properties have far out distanced the theoretical investigations. This can be attributed to the complexity of the solid surface and to the numerous experimental difficulties involved in the study of the solid-liquid interface.

The formation of a solid-liquid interface is usually accompanied by the liberation of a small quantity of heat. This property is utilized in heat of immersion, or as it is often called, heat of wetting experiments in which the finely divided solid is immersed in the liquid contained in a sensitive colorimeter. The heat evolved--of the order of a few calories per several square meters of surface -- is indicative of the energy changes which take place upon formation of the interface. Among the factors which influence the value obtained for the heat of immersion are: (1) magnitude and type of solid surface; (2) type of liquid; (3) impurities on the solid and in the liquid; and (4) temperature.

A considerable amount of work is reported in the literature on the variation of the heat of immersion with choice of solid and liquid,[1-7*] with preparation and activation of the solid surface,[8-15] and with respect to impurities either in the liquid,[16-17] or on the solid surface.[18-21] It should be noted that until recently investigators have generally adopted the easy course of measuring the heat evolved per unit weight of powder without attempting to measure the extent of the surface. These earlier results, therefore, cannot be related on a unit area basis. With the advent of the adsorbtion theory of Brunauer, Emmett, and Teller,[22] accurate surface area measurements of finely divided solids are now relatively easily obtained. The change in the heat of immersion with temperature has not been investigated extensively. The few experiments which have been performed indicate that the temperature coefficient is not large.[23,24] This fact has no doubt discouraged workers from initiating temperature studies, for the measurement of small changes of the heat of immersion -- itself a small quantity -- places extremely stringent requirements on the calorimetry involved. Nevertheless, a knowledge of the temperature coefficient is necessary if a complete picture of solid-liquid interfacial behaviour is to be had.

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*Heat of wetting data is referred to unit area in references 1 through 7.

This thesis is devoted to a study of the temperature dependence of the heat of immersion. The objectives of the investigation were to (1) determine the overall change in the heat evolved upon the immersion in water of a variety of solids over the range of temperatures from 0°C. to 25°C., and if experimentally feasible, to determine the detailed changes in this temperature range; (2) relate the temperature coefficient of the heat of immersion to the thermal properties of the solid-liquid system; and (3) evaluate the observed changes in terms of the results found in item (2).

The techniques of microcalorimetry were employed in the investigation. A twin differential microcalorimeter capable of measuring heat changes of about one calorie to within an accuracy of one percent was used in the immersion experiments. Selection of the materials used was governed by the necessity of minimizing the errors in the calorimetry and maintaining reproducibility for it was expected that the overall change due to temperature effects may be only a few percent of the total heat of immersion. This requirement indicated that solid-liquid combinations which yield as high an immersion heat as possible should be selected if useful results were to be obtained. Water was chosen as the wetting liquid because it furnishes a high heat of immersion with most substances; it is easily obtained and purified; and

data are available in the literature on its properties. The solids used were barium sulfate, silica gel and carbon black for they satisfy the above requirements and in addition can be obtained in a form having a high surface area per unit weight.

## HISTORICAL BACKGROUND

A comparitively large amount of work is reported in the literature pertaining to the heat of wetting, an effect first noted by Leslie[25] in 1802. Twenty years later Pouilett,[26] after whom the effect is sometimes called, observed the evolution of heat when finely powdered metals, oxides, silica, glass, sulfer, and porcelain were wet with ether, water, alcohol, and oil. The earlier work is marked by wide disagreement between the results of various workers for presumably similar systems.[27,28] However, the work indicated in a general way that the heat of wetting is dependent on the type of solid and liquid and is much higher for water and some alcohols on various solids than for saturated hydrocarbons and carbon tetrachloride.

Subsequent investigations have indicated possible reasons for the divergent results in the earlier work. It was found that the heat of wetting is quite sensitive to a number of factors, notably to the presence of impurities in the system and to the preparation of the solid surface. Since many of the immersion studies were conducted without extensive purification of the materials, it is not surprising that wide variations in the results exist. Harkins and Dahlstrom[17] determined the effect of adding traces of water to rigorously purified benzene

used in immersion experiments with titanium dioxide. The heat evolved with pure benzene is small; if traces of water are present, the heat of wetting is about doubled. Ewing[29] noted a substantial increase in the heat of immersion of zinc oxide when small amounts of zinc oleate were added to benzene acting as the wetting liquid. Significant changes in the heat of immersion of titanium dioxide in water were noted by Jura[30] when traces of water were present on the surface of the titanium dioxide used in the experiments. A similar effect has been noted in this laboratory[31] when aluminum oxide powders with preadsorbed films of stearic acid were immersed in water.

Experiments performed by Gregg and Sing[14] demonstrate the effect of activation on the heat evolved. Samples of alumina hydrate were activated at various temperatures for five hours, and the heat evolved upon immersion in the wetting liquid were measured. For activation temperatures below 300°C. and above 1100°C. small values were obtained for the heat of immersion. At some intermediate temperature a maximum occurs in the heat evolved with a magnitude several times the value measured at the lower or higher temperatures. Cannon, Griffith, and Hirst[15] conducted a similar investigation using methanol as the wetting liquid and coal activated at various temperatures for two hours. Two sharp maxima of the heats of immersion were obtained at activation temperatures of about 325° C.

and 500° C. These experiments emphasize the importance of careful control of the activation process if reproducible results are to be obtained in heat of wetting experiments.

Little work has been done either experimentally or theoretically on the temperature dependance of the heat of wetting. Harkins and Jura[30] determined the heat of immersion in water at 11.70° C. and 24.97°C. of titanium dioxide coated with aluminum oxide and obtained 1230 ergs per cm.$^2$ and 1130 ergs per cm.$^2$ respectively. Theoretical work was done by Jura[30] who investigated only the relationship of the free energy of immersion to the temperature coefficient of the heat of immersion.

# THEORY

## I. Intermolecular Forces

In order to appreciate the marked differences between the surface of a substance and the interior, it is well to briefly consider the intermolecular forces which hold the material together. The molecular interactions are usually classed as primary or secondary according to the magnitude of the binding energies. Primary interactions, which include ionic, homopolar, and metallic, are characterized by large dissociation energies ranging from 50 to 150 Kcal. per mole, whereas secondary interactions are associated with energies below 10 Kcal. per mole.

The forces which are important in interfacial phenomena arise from the secondary interactions. These include the van der Waals attractive forces. They are electrical in origin being due to the interactions of the charge distributions of adjacent molecules. Among the contributors to the van der Waals forces are the orientation,[32] induction,[33] and dispersion effects.[34,35] Since these forces arise from distributions of electrical charge, the van der Waals forces are always present. However, they may be obscured by interactions of the primary type.

## II. Surface Forces

Whatever the character of the intermolecular forces holding the substance together, each molecule can be thought of as being surrounded by a force field. In the interior of the substance any one molecule is completely enclosed by its neighbors, effecting a saturation of this field of force. However, an unbalance of the forces exists at the surface, and there results a net inward attraction on the surface molecules manifesting itself in the case of liquids as a spontaneous contraction of the surface to a minimum area. Furthermore, at the surface, the force fields surrounding the molecules cannot suddenly disappear, but will extend into the region beyond. Consequently, these fields of force can interact with the fields produced by other substances and lead to phenomena such as adsorption, adhesion, and heats of wetting to name a few.

It should be understood that the term "surface" as used here does not necessarily refer to a strictly geometric area enclosing the body but can include depth. The surface, as a region of discontinuity, is the locus of physical effects which are noticeably different from the properties of the bulk. A similar definition can be used for the term "interface", that is, a region of discontinuity between two substances in which the physical effects differ from the physical properties in the

interior of either substance. Thus the surface or interface as the case may be is an indefinite region which has a depth and extent dependent on the terms of the discussion.

Since the surface represents a sharp change in the molecular fields of force, it is reasonable to suspect that many of the properties of matter measured in the surface region will have values differing from the results of corresponding measurements made in the bulk. For example the specific heat is dependent on the vibrations and rotations of the various particles which make up the substance, and these motions are in turn dependent on the force fields present. Hence, in regions where the fields undergo a pronounced change such as in the surface, the specific heat would be expected to be different from that in the interior.

The presence of a second substance adjacent to the surface can influence the surface force field. The forces operative at the two surfaces interact when the two materials are placed in contact, and can cause marked changes in the properties of one or both substances in the vicinity of the interface. Thus for the case of a solid immersed in a liquid it is possible, for sufficiently strong interactions, that the liquid molecules at the interface can become relatively fixed in position and tend to a solid-like structure with consequent changes in physical properties. Irregularities of the surface

such as edges and corners also can effect the surface forces and cause a nonuniform surface energywise.

III. Heat of Immersion

When a finely divided solid is immersed in a liquid, a small amount of heat is usually liberated. The quantity of heat evolved is a measure of the energy changes which take place upon formation of the solid-liquid interface. If $\epsilon_s$ and $\epsilon_L$ are the energies per unit area peculiar to the solid and liquid surfaces respectively, then the energy associated with the surface of the solid and the liquid before immersion is

$$E_o = A\epsilon_s + A_L\epsilon_L \qquad (1)$$

where A is the surface area of the solid, and $A_L$ is the free surface of the liquid. Assuming that the interfacial area is equal to the area of the solid and that the area of the free surface of the liquid remains unchanged, the energy after immersion becomes

$$E_1 = A_L\epsilon_L + A\epsilon_{SL} \qquad (2)$$

where $\epsilon_{SL}$ is the energy associated with the interface. The interfacial energy term can be considered to be made up of the surface energy of the solid surface of area A , the surface energy of the liquid surface of area A , and two terms which take into account the changes in the solid

and the liquid surface energies resulting from the interactions which take place across the interface when the two surfaces are in contact. If $\Delta\epsilon_s$ and $\Delta\epsilon_L$ represent the solid and liquid surface energy changes which occur when the liquid is in contact with the solid, then equation (2) may be written as

$$E_1 = A_L\epsilon_L + A\left[\epsilon_L + \Delta\epsilon_L + \epsilon_s + \Delta\epsilon_s\right] \qquad (3)$$

Since the minute quantity of work done by the volume change accompanying immersion can be neglected,[1] the heat evolved during the process is equal to the energy change represented by the difference between the quantities (1) and (3). Thus,

$$\Delta H^I = \epsilon_L + \Delta\epsilon_L + \Delta\epsilon_s \qquad (4)$$

where $\Delta H^I$ is the heat of immersion per unit area of the solid $s$ in the liquid $L$.

IV Temperature Dependence of the Heat of Immersion

The procedure involved in the measurement of the temperature dependence of the heat of immersion includes the immersion of the solid in the liquid at the temperatures $T$ and $T+\Delta T$. All other variables which occur in the immersion process are either held constant, eg., pressure, or produce negligible effects, eg., volume.[1] These restrictions make it possible to use total derivatives

in the development which follows. Suppose that the solid and the liquid, initially at the temperature $T$, are warmed by $\Delta T$ degrees and then the solid is immersed in the liquid; the energy changes accompanying the process are

$$\int_{T}^{T+\Delta T}\left[m c_s + n c_L + A C_s' + A_L C_L'\right] dT + A\,\Delta H^I(T+\Delta T) \qquad (5)$$

where $\Delta H^I(T+\Delta T)$ is the heat of immersion at the temperature $T+\Delta T$, $m$ and $n$ are the masses of the solid and liquid respectively, $c_s$ and $c_L$ are the specific heats of the bulk liquid and bulk solid respectively, and $C_s'$ and $C_L'$ are the surface specific heats of the solid and liquid respectively.

If the solid is immersed in the liquid at the temperature $T$ and the system warmed by $\Delta T$ degrees, then the heat changes which occur are

$$A\,\Delta H^I(T) + \int_{T}^{T+\Delta T}\left[m c_s + n c_L + A\left(C_s' + \Delta C_s' + C_L' + \Delta C_L'\right) + A_L C_L'\right] dT \qquad (6)$$

where $\Delta C_s'$ and $\Delta C_L'$ are the changes which occur in the surface specific heats when the solid is in contact with the liquid. Since the initial and final states are the same, the heat effects can be equated, so that

$$\Delta H^I(T+\Delta T) - \Delta H^I(T) = \int_{T}^{T+\Delta T}\left(C_L' + \Delta C_L' + \Delta C_s'\right) dT \qquad (7)$$

But

$$\int_{T}^{T+\Delta T}\left(C_L' + \Delta C_L' + \Delta C_s'\right) dT = \Delta T\left(C_L' + \Delta C_L' + \Delta C_s'\right)_{T=\xi} \qquad (8)$$

where

$$T \leq \xi \leq T+\Delta T$$

Thus,

$$\frac{\Delta H^I(T+\Delta T) - \Delta H^I(T)}{\Delta T} = (C_L' + \Delta C_L' + \Delta C_s')_{T=\xi} \qquad (9)$$

In the limit as $\Delta T \to 0$, $\xi \to T$ and the left side of equation (9) becomes $\frac{d(\Delta H^I)}{dT}$. Hence,

$$\frac{d(\Delta H^I)}{dT} = C_L' + \Delta C_L' + \Delta C_s'. \qquad (10)$$

The slope of the heat of immersion-temperature curve, therefore, is equal to the specific heat due to the liquid surface plus the changes in the surface specific heats of the solid and liquid arising from the interactions which may be present at the interface.

The surface energy of the liquid, $\epsilon_L$, and the surface energy changes, $\Delta\epsilon_s$ and $\Delta\epsilon_L$, can be related to the specific heats, $C_L'$, $\Delta C_L'$, and $\Delta C_s'$ in the following way. Differentiating equation (4) with respect to temperature under the conditions stated in section III, it is found that

$$\frac{d(\Delta H^I)}{dT} = \frac{d\epsilon_L}{dT} + \frac{d}{dT}(\Delta\epsilon_s + \Delta\epsilon_L). \qquad (11)$$

For a given solid and liquid, the right side of equations (10) and (11) may be equated yielding an equation which may be rearranged to the form.

$$\Delta C_s' + \Delta C_L' - \frac{d}{dT}(\Delta\epsilon_s + \Delta\epsilon_L) = \frac{d\epsilon_L}{dT} - C_L' \qquad (12)$$

The right hand side of equation (12), however, can be shown to be equal to zero.[54] Hence,

$$C_L' = \frac{d\epsilon_L}{dT} \tag{13}$$

$$\Delta C_S' + \Delta C_L' = \frac{d}{dT}(\Delta\epsilon_S + \Delta\epsilon_L) \tag{14}$$

Equations (13) and (14) state that the specific heat contributions by the surface and the interface are respectively equal to the rates of change with temperature of the surface energy and the interfacial energy changes.

With the aid of equation (10), it is possible to calculate the effect of the interface on the solid and liquid surface specific heats. The quantities which must be determined are $\frac{d(\Delta H^I)}{dT}$, which can be obtained from immersion experiments, and $C_L'$. The latter quantity can be calculated from equation (13) provided that $\epsilon_L$ is available as a function of temperature. A thermodynamic equation relating $\epsilon_L$ to the surface tension of the liquid is as follows:

$$\epsilon_L = \gamma_L - T\frac{d\gamma_L}{dT} \tag{15}$$

where $\gamma_L$ is the surface tension of the liquid at the temperature $T$. By means of equations (13) and (15), the surface specific heat of the liquid may be calculated once the surface tension has been measured as a

function of temperature, and the result may be used in equation (10) for the determination of the surface specific heat changes which occur at the interface.

# EXPERIMENTAL

## I. Calorimetry

Measurement of the small heat changes encountered in heat of immersion experiments necessitates the use of a calorimeter having a high temperature sensitivity. Such calorimeters have come to be called microcalorimeters not because of their physical size but because of their great sensitivity. Nernst and Orthman[37] began the development of this branch of calorimetry in 1926, and since then investigators have employed the techniques of microcalorimetry for the measurement of heats of immersion[1] dilution,[38] adsorption[39] and other chemical-physical reactions.[40]

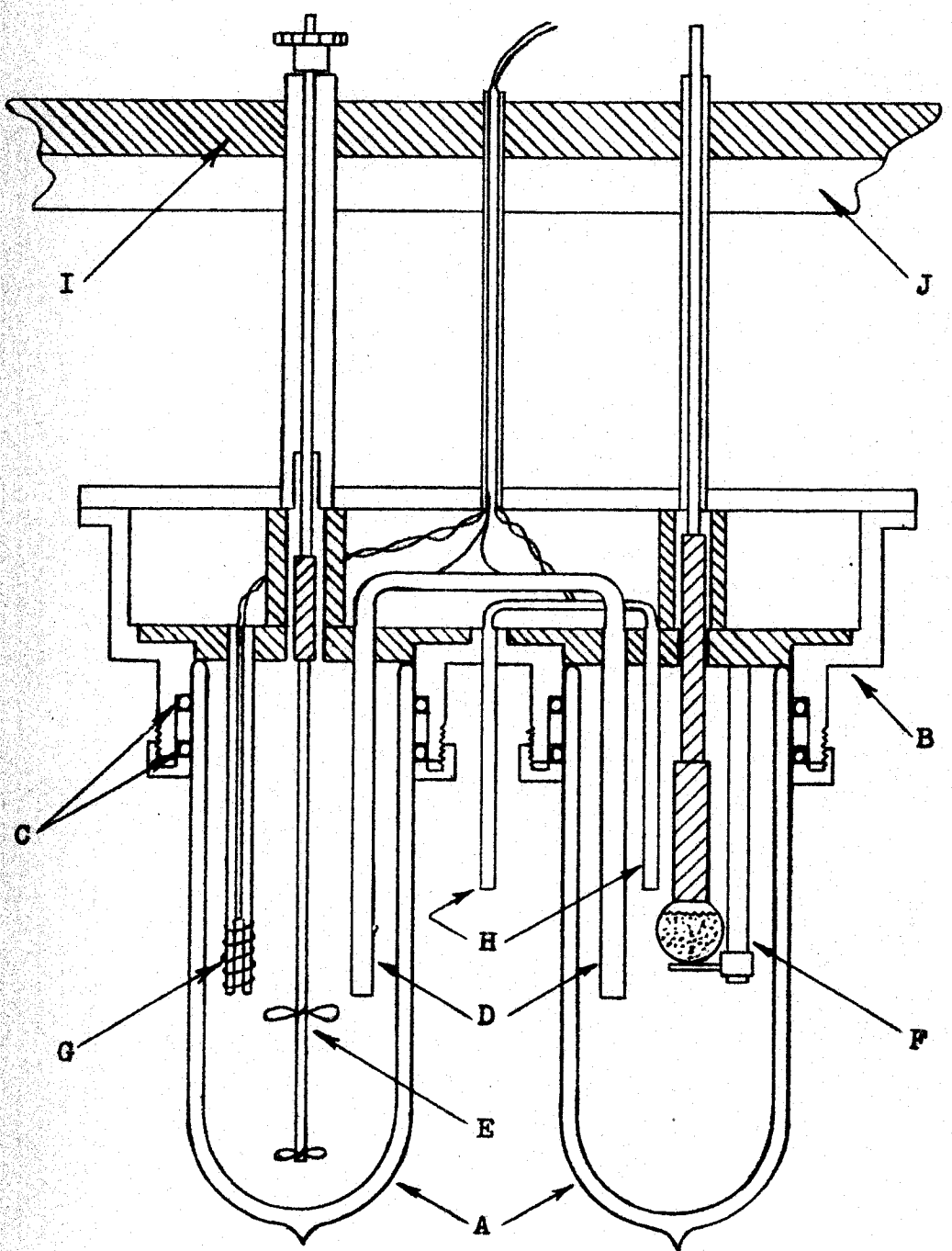
Twin differential microcalorimeters are especially useful for measurements of small heat changes. This type of calorimeter, first employed by Joule,[41] utilizes the comparative method of measurement. In this method two similar calorimeter units are used; one for the unknown heat change and the other for the introduction of known heats. Initially, the temperature difference between the two units is set to zero. After the unknown heat is liberated in one of the units, a temperature difference is then noted. Known quantities of heat are added to the second calorimeter unit until this temperature difference is reduced to zero. If the calorimeter units are identi-

cal, then the known heat added to the second unit is equal to the unknown heat change in the first. Additional heating operations can be performed to determine the corrections necessary if differences in the calorimeter units exist. It is unnecessary to measure the absolute temperature or heat capacities of the calorimeter units. High temperature sensitivity, reproducibility of measurements, ease of operation, and versatility are readily attained with this system.

A twin differential microcalorimeter, which was designed and built at this laboratory by Berghausen, Fauser and Buelteman,[42,43,44] was employed in the investigation of the temperature dependence of the heat of immersion. Since the reproducibility required in this work was of a higher degree than that for which the instrument was designed, it was necessary to incorporate a number of electrical and mechanical refinements. A description of the microcalorimeter as modified by the author will now be given. References 42,43, and 44 give details of the original instrument.

(a) Mechanical Arrangement. The main components of the microcalorimeter are shown in Figure 1. Two 650 cc silvered Dewar flasks (A) are secured to a water-tight brass submarine jacket (B) by "O" ring seals (C). Each flask contains a branch of the main differential thermal (D), a stirrer (E), a sample bulb holder (F), a pair of electrical heaters (G), and a branch of the

FIGURE 1



bath to calorimeter thermal (H). The submarine jacket is attached to the top mounting plate(I) by means of four brass supports. Electrical leads, stirrer shafts, and bulb breaking rods are admitted through five brass tubes which terminate at the top of the submarine jacket. A 90 liter insulated water bath is positioned below the top plate in an angle iron frame. The bath is counter-balanced to facilitate raising and lowering. In the raised position the water contained in the bath completely surrounds the two flasks and the submarine jacket with its supports and tubes so that a uniform environment temmera-turewise is provided for the calorimeter working fluid. A 3/4 inch foam rubber gasket (J) glued to the underside of the mounting plate reduces heat leakage from the bath to the room. The laminated plastic mounting plate from which the submarine jacket is suspended supports the bath stirrers, bath heaters, and stirrer drive mechanism. Thermometer and thermocouple wells are also provided for bath temperature measurements.

The main thermal located in the submarine jacket is used together with associated electrical apparatus to detect differences in temperature between the Dewar flasks. It is composed of 125 series connected copper-constantan thermocouples and provides approximately 5000 $\mu$v. for each degree centigrade temperature difference between the Dewar flasks. Heat leakage from one flask to the other through the thermel was minimized and electrical conduct-

ance maximized by proper choice of wire size.[45] Temperature differences between the flasks and the bath were observed through the electrical output from two 10 couple thermels. Spurious electrical output from the main thermel due to water condensation was eliminated by filling the submarine jacket with petroleum jelly.

Stirring in the flasks was accomplished by monel propellors mounted on glass rods attached to the shafts located in the submarine jacket. The stirrers were driven by identical sprockets fed by a ladder chain from a synchronous motor thus assuring a constant stirring rate. The bath stirrers were driven in a similar fashion by the same motor.

Each calorimeter flask is provided with a bulb holder. Small thin-walled glass evacuated bulbs containing the sample are placed in the plastic extension of the bulb breaker rod shown in Figure I. At a fixed height above the uppermost end of the bulb breaker rod is located a weight which is suspended by a length of fuse wire stretched between two terminals. An immersion experiment is initiated by melting the fuse wire with a suitable electric current, thus releasing the weight which crushes the sample bulb. Once loading is accomplished and thermal equilibrium is attained it is not necessary to enter the temperature controlled room to break the bulb; hence, a determination free from external disturbances can be made.

The calorimeter flasks were each equipped with an electrical heater composed of a length of constantan wire wrapped on a plastic support. A pair of current leads and a pair of potential leads were provided for each heater to facilitate heater resistance measurements. The potential leads were connected at points in the heater circuit which include only the resistance capable of producing heat changes in the calorimeter fluids. In addition to the main heaters a set of trimmer heaters was installed to provide a means for balancing the effects of unequal rates of heat loss and differences in the rate of generation of heat due to stirring in the flasks.

(b) Electrical Control. In the course of the measurement process known quantities of heat are added to the calorimeter fluids. This is conveniently accomplished by electrical methods. The measured quantities are resistance, current, and time.

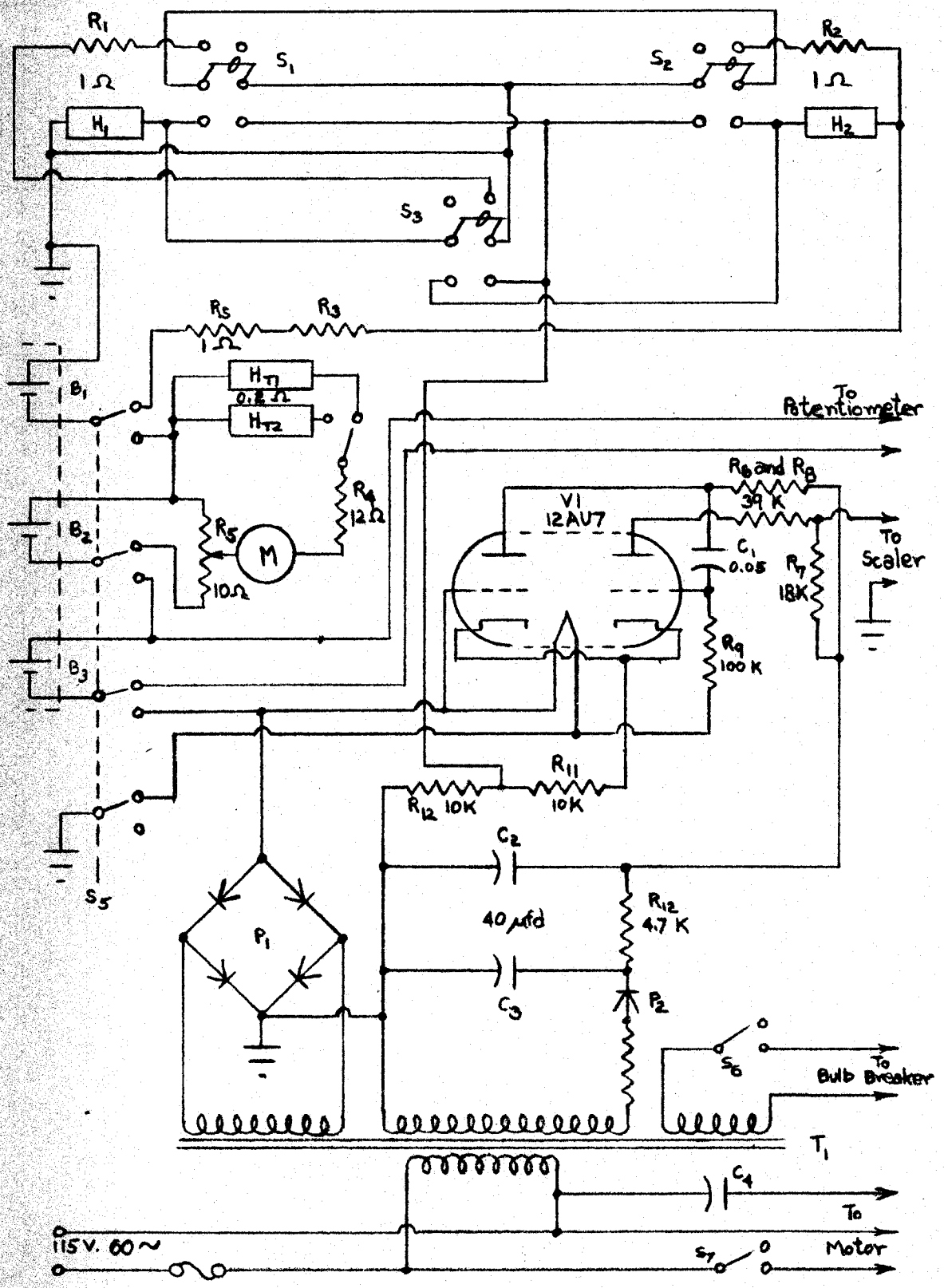
The electrical circuitry involved in the control and measurement of the known heats is shown in Figure 2. Toggle switches $S_1$, $S_2$, $S_3$; Resistors $R_1$, $R_2$, $R_3$, and $R_s$; heaters $H_1$ and $H_2$; and battery $B_1$ make up the main calorimeter heater circuit. Switches $S_1$, $S_2$ and $S_3$ when in the "off" position allow the battery current to pass through resistors $R_1$ and $R_2$ which are approximately equal in value to the resistances of the calorimeter heaters $H_1$ and $H_2$ respectively. If $S_1$ (or $S_2$)is placed in the "on" position,

the current flow is switched from $R_1$ (or $R_2$) to the calorimeter heater H1 (or H 2). Switch $S_3$ serves the same purpose with the exception that both resistors are simultaneously disconnected and replaced by the calorimeter heaters. It should be noted that the load on the battery is kept constant during operation of the three switches with the result that variations in heater current are minimized during a determination. The magnitude of the heater current can be set at various values through suitable choice of battery voltage and resistance of $R_3$. The one ohm standard resistor, $R_s$, furnishes a known value of resistance in the heater circuit to facilitate current measurements.

The heat necessary to equalize the net rate of gain or loss of heat in the flasks for a given equilibrium condition is supplied by the trimmer heat circuit composed of resistor $R_4$, potentiometer $R_5$, trimmer heaters $H_{T1}$ and $H_{T2}$ located in the calorimeter flasks, battery $B_2$, and a milliameter. Current through one heater or the other, as determined by the position of the switch $S_4$, can be adjusted by means of the potentiometer $R_5$.

The control circuitry also includes timing, bulb breaking and stirring motor circuits. Resistors $R_6$ through $R_{11}$, condenser $C_1$, vacuum tube $V_1$, and rectifier $P_1$ comprise the timing circuit. Upon closing any one of the three main heater switches, timing pulses, which are generated from the 60 cycle power lines at the rate of

FIGURE 2

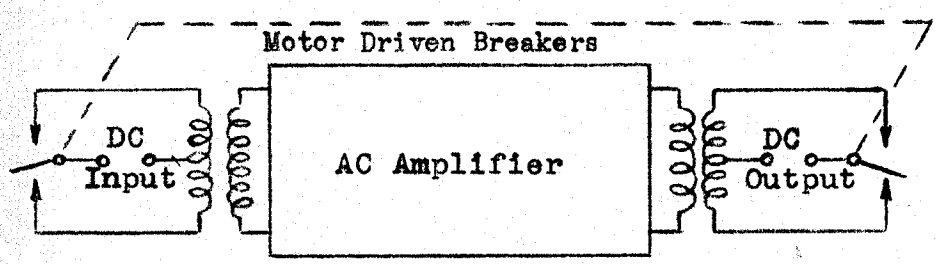


120 pulses per second, appear in the output circuit of $V_1$. Switch $S_6$ connects the bulb-breaking circuit to the power source. Condenser $C_4$ and switch $S_7$ are used in the operation of the synchronous stirring motor. The remaining circuit elements shown in Figure 2 are used in the power supply for the microcalorimeter. Three lead storage cells provide a steady current for the operation of the main heater, trimmer heater and potentiometer circuits.

(c) Resistance, Current, and Time Measurements. Heater resistance was determined by taking the ratio of the potential measured by a Leeds and Northrup type K potentiometer connected across the heater to the potential measured with the potentiometer connected across the one ohm standard resistor, $R_s$. Since the standard resistor has a value of one ohm, the potential measured across this resistor gives the value of the heater current directly.

Measurement of the duration of the heater current was accomplished by means of a scale of 256 counter connected to the output of $V_1$, the timing pulse generator. For each second that a main heater switch is closed 120 pulses are supplied to the counter. Hence, the total count indicated by the scaler divided by 120 gives the elapsed time in seconds.

(d) Temperature Difference Indicator. Temperature differences between the calorimeter flasks were detected by means of the 125 couple main thermel, a DC amplifier, and a recording voltmeter. A Liston-Folb, model 10, DC Breaker Amplifier, which is designed to operate in the fractional microvolt region, amplifies the output of the main thermel. The signal from the main thermel is converted to an 8 cps alternating current by motor driven contacts at the input of the amplifier. A 3-tube resistance-capacitance coupled amplifier followed by a set of contacts driven in synchronism with the input breaker amplifies and then rectifies the 8 cps AC signal. The output of the overall amplifier is a direct current with a polarity which corresponds to that of the original signal from the main thermel. A maximum gain of about 5 million can be realized when the




amplifier feeds a 1000 ohm load. Thus, a temperature difference of 1 microdegree, which corresponds to 0.005 microvolts, is amplified to 0.025 volts.

A Micromax recorder connected to the DC Amplifier output terminals records the amplified replica of the main thermel signal; hence, the Micromax graph gives a

curve of the calorimeter temperature difference versus time. Temperature changes of one microdegree can be detected on the Micromax chart.

In order to realize a one microdegree temperature sensitivity it was necessary to construct the main thermel and amplifier input circuitry with great care. Careful shielding and grounding of all input elements was necessary to eliminate induced AC voltages. Extraneous DC voltages due to thermoelectric emfs was reduced by employing an input cable composed of copper matching that used in the construction of the amplifier input. A special solder which exhibits a low thermoelectric emf with copper was utilized in making the input connections. Since variations in room temperature caused spurious thermal emfs to be generated by the DC amplifier input connector, it was necessary to solder the input cable directly to the amplifier input.

(e) Bath Temperature Control. The adiabatic system was selected for the heat of immersion determinations. In this method the temperature of the bath is varied so that the difference between the bath temperature and the mean of the temperatures of the calorimeter flasks is zero during a heat determination. A number of advantages are derived through the use of the adiabatic method. Thermal "noise" (non-periodic variations in the main thermel output due to changing rates of heat flow from the flasks) was reduced from a 6 microdegree peak

to peak variation in the case of the isothermal bath system to about 1 microdegree variation with the adiabatic method. Because heat leakage from the calorimeter flasks is greatly reduced in the adiabatic case, immersion experiments in which the heat is evolved over a relatively long period of time can be successfully performed.

An examination of the equation for the slope of the time-temperature difference curve depicted on the Micromax recorder chart disclose another advantage of the adiabatic system. The slope of the time-temperature difference curve is given by

$$\frac{d}{dt}(T_1-T_2) = A + BT_B + \frac{K_2}{C_2}T_2 - \frac{K_1}{C_1}T_1 \qquad (16)$$

where

$$A = \frac{W_1}{C_1} - \frac{W_2}{C_2}, \qquad B = \frac{K_1}{C_1} - \frac{K_2}{C_2},$$

$W_1$ and $W_2$ are the respective heats of stirring per unit time in the calorimeter flasks 1 and 2,

$K_1$ and $K_2$ are the respective heat leakage rates per degree,

$C_1$ and $C_2$ are the respective heat capacities,

$T_1$ and $T_2$ are the temperatures in flasks 1 and 2,

$T_B$ is the calorimeter bath temperature.

In the adiabatic system

$$T_B = \frac{T_1+T_2}{2} \qquad (17)$$

so that equation (16) becomes

$$\frac{d}{dt}(T_1-T_2) = A + \frac{1}{2}\left(\frac{K_1}{C_1} + \frac{K_2}{C_2}\right)(T_2-T_1). \qquad (18)$$

Initially, $t = o$ , $T_2(o) = T_1(o)$ and A is adjusted so that

$$\frac{d}{dt}\left[T_1(o) - T_2(o)\right] = o$$

Thus

$$\frac{d}{dt}(T_1 - T_2) = \frac{1}{2}\left(\frac{K_1}{C_1} + \frac{K_2}{C_2}\right)(T_2 - T_1) \qquad (19)$$

Using the same assumptions with the exception that the bath temperature is held constant for the isothermel condition, it is found that

$$\frac{d}{dt}(T_1 - T_2) = \frac{K_2}{C_2}\left[T_2(t) - T_2(0)\right] - \frac{K_1}{C_1}\left[T_1(t) - T_1(0)\right] \qquad (20)$$

The procedure for measuring the heat of immersion includes immersion of the sample in flask number 1 and simultaneous electrical heating in flask number 2, until $T_2(t)$ equals $T_1(t)$. Inspection of equation (19) and (20) reveals that under the conditions stated, the slope of the time-temperature difference curve does not change after the heating period in the adiabatic case, whereas in the isothermal method, a definite change can occur if the calorimeter constants $\frac{K_1}{C_1}$ and $\frac{K_2}{C_2}$ are not equal. Furthermore in the isothermal case the larger the temperature difference between the flasks and the bath, the greater the change in the slope. As time passes heat leakage from the flasks reduces the temperature difference between the bath and the flasks, and the slope eventually returns to the initial value. This condition causes difficulty

when the deflections of the Micromax recorder are determined.

The adiabatic condition is attained by appropriate heating of the bath. A null type control based on the electrical output from the bath-to-calorimeter thermel was devised to maintain the bath temperature to within $\pm 0.001^{\circ}$ C. of the mean temperature of the calorimeter flasks. The output from the bath thermel was connected to a galvanometer. A light beam reflected off the galvanometer mirror falls on a phototube connected in a vacuum tube relay circuit. Deflections of the galvanometer mirror from the zero position actuate the phototube-relay circuit which in turn energizes the bath heaters. When sufficient heat is added to the bath to reduce the bath-to-calorimeter temperature difference to zero, the galvanometer mirror returns to its initial position, and the photocell circuit interrupts the bath heater current.

(f) Calorimeter Preparation and Measurement Procedure. After the value of the temperature for the immersion experiment was selected, the room temperature control was set. The optimum room temperature was found to be about $0.4^{\circ}$ C. below the selected temperature. Bath temperature was adjusted to the agreed value either by electrical heating or by cooling with ice as the situation required.

All parts of the calorimeter which come in

contact with the calorimeter fluid were carefully cleaned with C.P. grade carbon tetrachloride followed by thorough rinsing with double distilled water. Glass articles -- Dewar flasks, sample bulbs, graduates, beakers etc. -- which are exposed to the calorimeter liquid were cleaned with chromic acid cleaning solution and rinsed in double distilled water. In order to facilitate a rapid approach to thermal equilibrium the double distilled water for the experiments and all glassware used in its handling were kept in the temperature controlled room. Hence, the calorimeter water after loading is slightly below the bath temperature. This is a desirable condition for it is a simple matter to carefully heat the calorimeter water until its temperature equals that of the bath.

After the sample bulb is cleaned and placed in the bulb holder, the calorimeter flasks are each filled with 450 cc. of double distilled water. This quantity of water is sufficient to cover all active parts of the calorimeter and at the same time allow a suitable insulating air space over the liquid level. The flasks are then tightened into place on the submarine jacket, and the bath is raised into position. The stirrers, bath control, DC amplifier, and heater circuits are turned on, and the flask temperatures are equalized by careful electrical heating. If necessary, trimmer heat is added to balance the net rate of heat gain of the calorimeter flasks.

The condition of balance is indicated by zero output from the DC amplifier and a zero slope of the temperature difference-time curve which appears on the Micromax recorder chart. Since the sample powder ordinarily has poor heat transfer characteristics, a waiting period of several hours is necessary to assure that thermal equilibrium is attained before the heat determination is performed. Neglect of this requirement can lead to serious error in the experiment.

After thermal equilibrium is attained, three distinct operations are necessary for the determination of the heat of immersion; they are:

(a) break the glass bulb containing the sample in flask number 1 and simultaneously introduce electrical heat in number 2,

(b) add heat electrically to both calorimeter flasks,

(c) electrically heat flask number 1.

When the equations which relate the Micromax recorder deflections to the heats introduced during operations (a), (b), and (c) are combined, the following equation is derived:[43]

$$\Delta H = R_1 I_a^2 t_a \left[ 1 + \left(\frac{I_c}{I_a}\right)^2 \frac{t_c}{t_a} \frac{d_a}{d_c} - \left(\frac{I_c}{I_b}\right)^2 \frac{t_c}{t_b} \frac{d_b}{d_c} \right] \qquad (21)$$

In which

$\Delta H$ is the unknown heat evolved in flask number 1 during operation (a),

$R_1$ is the resistance of heater number 1,

$I$ is the heater current,

$t$ is the elapsed time,

$d$ is the recorder deflection corresponding to the change in temperature occuring during the operation.

Numerical subscripts refer to the calorimeter flask, whereas letter subscripts refer to the particular operation. Since the system is symmetrical, it is possible to perform the measurement with the bulb in flask number 2; $R_2$ replaces $R_1$ in equation(21).

II Sample Preparation.

(a) Materials. Barium sulfate, carbon black, and silica gel were used in the determinations for the temperature coefficient of the heat of immersion in this research. Silica gel and carbon black can be obtained in a form having a very large surface area per unit weight, and barium sulfate exhibits a high heat of immersion per unit area coupled with a moderately high surface area per unit weight; hence, the overall heat of wetting for a given weight of these solids is large. Because relatively large heats are evolved; calorimetry errors are reduced. It was found that the reproducibility of the immersion experiments with these materials was satisfactory, the deviation being less than 1 percent of the total heat in the case of silica gel, 1.5 percent for barium sulfate, and 2.5 percent in the case of carbon black.

Commercial samples of silica gel were used in the investigation. The gel was of uniform conformation, was not discolored, and was found to be free of water soluble impurities. The B.E.T. area of the dry gel was found to be 701 $m^2$ per gram assuming 16.2 $Å^2$ as the nitrogen molecule area.[46]

Carbon black, Graphon number (L-2808), was obtained from the Godfrey L. Cabot Company. This powder had been subjected to a special heat treatment during its preparation with the result that a graphite structure was induced in its surface. Since the powder as received contained water soluble materials, additional purification was necessary. The removal of the soluble materials was accomplished by thorough washing in a Soxhlet extractor. The rinsing was continued until the wash water exhibited a conductivity of that of pure water. The area as measured by the B.E.T. $N_2$ adsorption method had been found to be 95 $m^2$ per gram.[47] An ash content of 0.23 percent was specified by the Cabot Company.

Samples of C.P. grade barium sulfate were obtained from the Baker Chemical Company. The B.E.T. surface area was found to be 4.68 $m^2$ per gram.[46] Aside from a thorough extraction in double distilled water, the powder was used without further purification.

(b) Glass Bulbs. Since the presence of gases on the surface of the solid can alter the heat of immersion,[21]

it is necessary to keep the sample under vacuum until the liquid is admitted during the immersion process. Glass bulbs are convenient containers for the powder for they are easily connected to a vacuum system and sealed off after evacuation. In addition immersion of the sample is accomplished by merely shattering the glass; the resulting implosion aids in dispersing the powder in the liquid. It should be noted, however, that the energy required to break the bulb plus the energy of the implosion must be allowed for in the heat determination. In order that this correction term in the heat of immersion be constant, bulbs of uniform size and wall thickness should be selected.

The glass bulbs used in the experiments were made to specification by the Corning Glass Company. The bulbs were blown from 8 mm. O.D. Pyrex brand tubing, and had a diameter of 2.22 cm. ± 0.8 mm. with a wall thickness of 0.25 mm. ± 0.12 mm. Visual inspection showed that the bulbs were of uniform shape and were free of bubbles and other imperfections.

(c) Evacuation Procedure. Sample powder was weighed into the bulbs in an amount sufficient to fill them to a set level in each bulb. After the bulbs were filled, they were connected to a vacuum system and evacuated to a pressure of less than 1 micron of mercury. The temperature and duration of evacuation of all samples were 250° C. and

6 hours respectively. The evacuation period was of sufficient length to insure the removal of all gaseous material from the samples under the pressure and temperature conditions used.

## RESULTS AND DISCUSSION

Immersion experiments with water and the three solids, carbon black, silica gel, and barium sulfate, were performed at various temperatures in the range from 0° C. to 25° C. The objective was to determine the variations with respect to temperature of the heat of immersion in the range cited for different types of solid surfaces in water, and from these results to ascertain the effect produced by the formation of an interface on the surface specific heats of the solid and the liquid. The overall change in the heat of immersion of a particular solid was established by performing two or more measurements at each limit of the temperature range. These measurements also served as an indication of the reproducibility that could be expected for the substance. In order that sharp changes in the heat of immersion-temperature relation not be overlooked, individual measurements were performed at intermediate temperatures usually at 5° intervals.

The three solids chosen for this research present widely different surface properties. Silica gel is a highly porous substance with a structure composed of many fine capillaries, cracks, and fissures. Hence, the surface is for the most part "internal" as opposed to the "external" surface exhibited by the barium sulfate samples. The latter were shown to be largely non-porous by gas flow measurements.[48,49]

Both silica gel and barium sulfate are polar solids; the carbon black samples on the other hand present a non-polar graphite surface.

I Heat of Immersion Data

Heat of immersion determinations with silica gel were performed at 5° intervals over the specified range of temperatures. The results are shown in Figure 3 in which the heat of immersion per unit area of solid is plotted against temperature. It is seen that the overall change in the heat of immersion is practically zero in comparison to the magnitude of the total heat evolved. Furthermore, no "peaks" or "valleys" are in evidence in the plot. A least squares fit of the data to a straight line leads to a slope of 0.03 ± 0.01 ergs/cm$^2$ per degree and a 0° C. temperature intercept of 170.0 ± 0.2 ergs/cm$^2$ This value of the slope corresponds to a percentage change of less than 1 percent in the heat of immersion for a 25° temperature interval.

The heats evolved in the carbon black determinations are plotted in Figure 4. A change of about 4 percent is noted in the heat of immersion for a 25° change in temperature. The decrease in the heat of immersion with increase of temperature is apparently uniform, although the spread of points, arising from reproducibility considerations, may obscure any small "dips" or "rises" which may exist. Aside from these possibilities the slope of the heat of

FIGURE 3

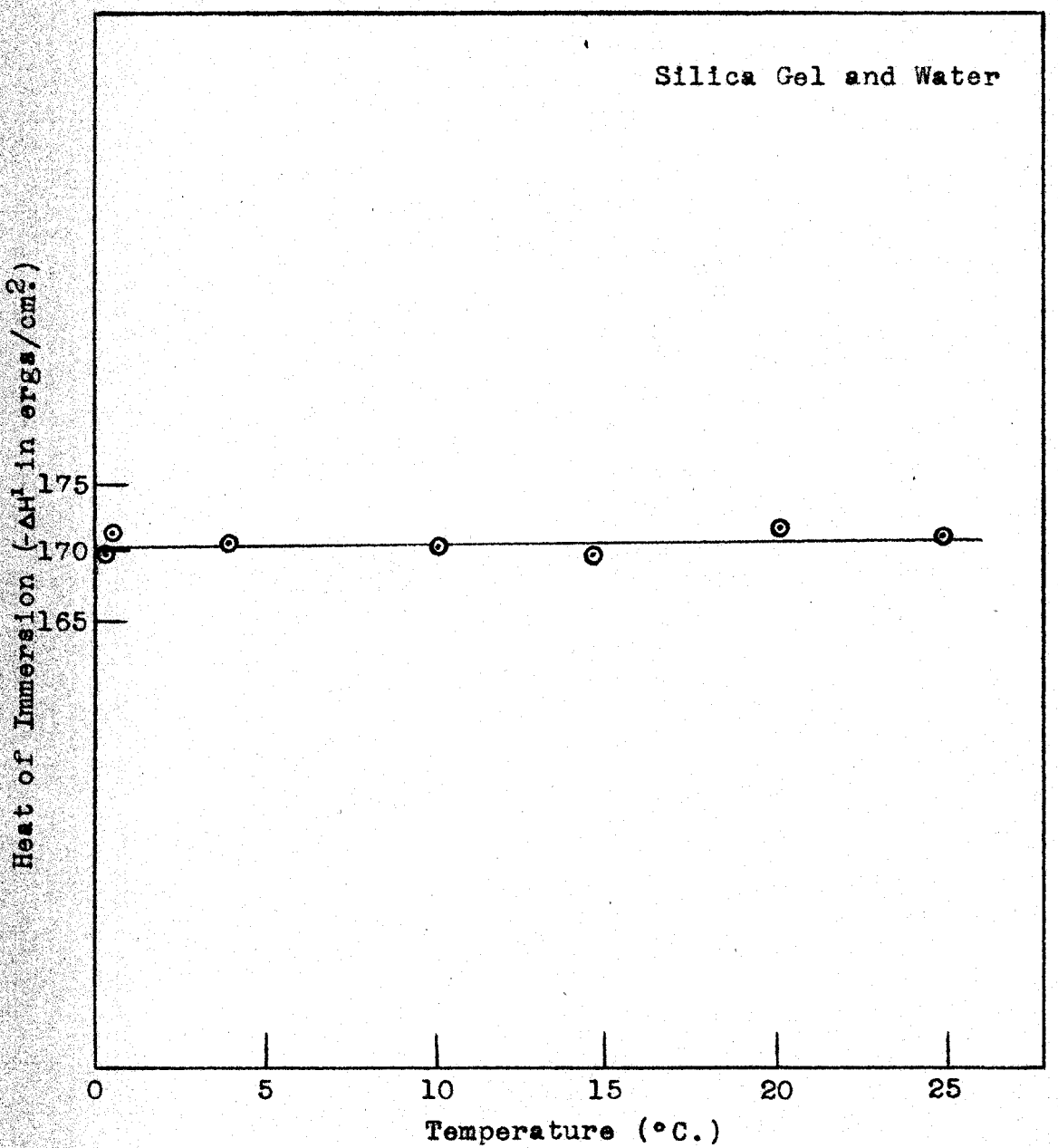


FIGURE 4

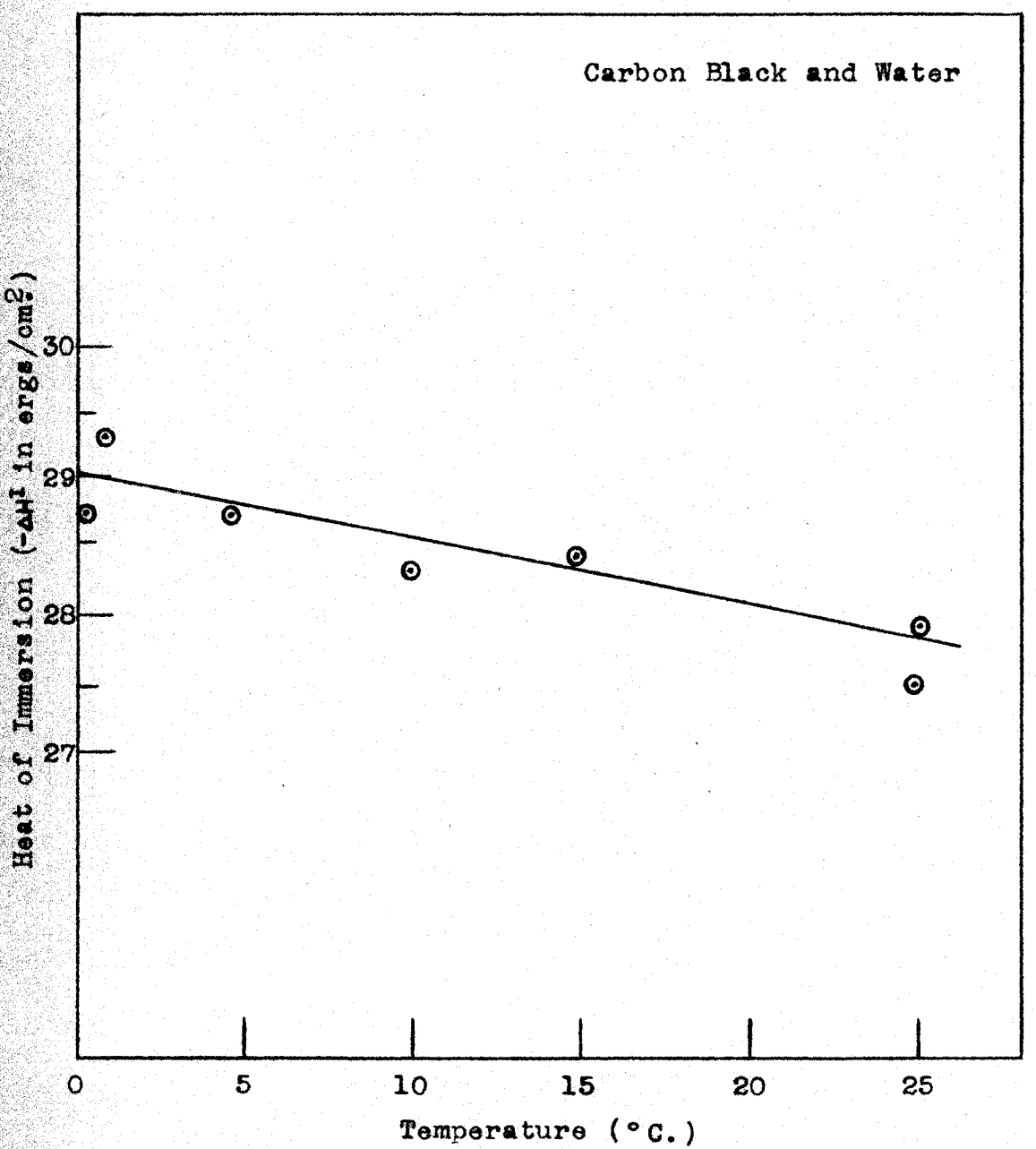
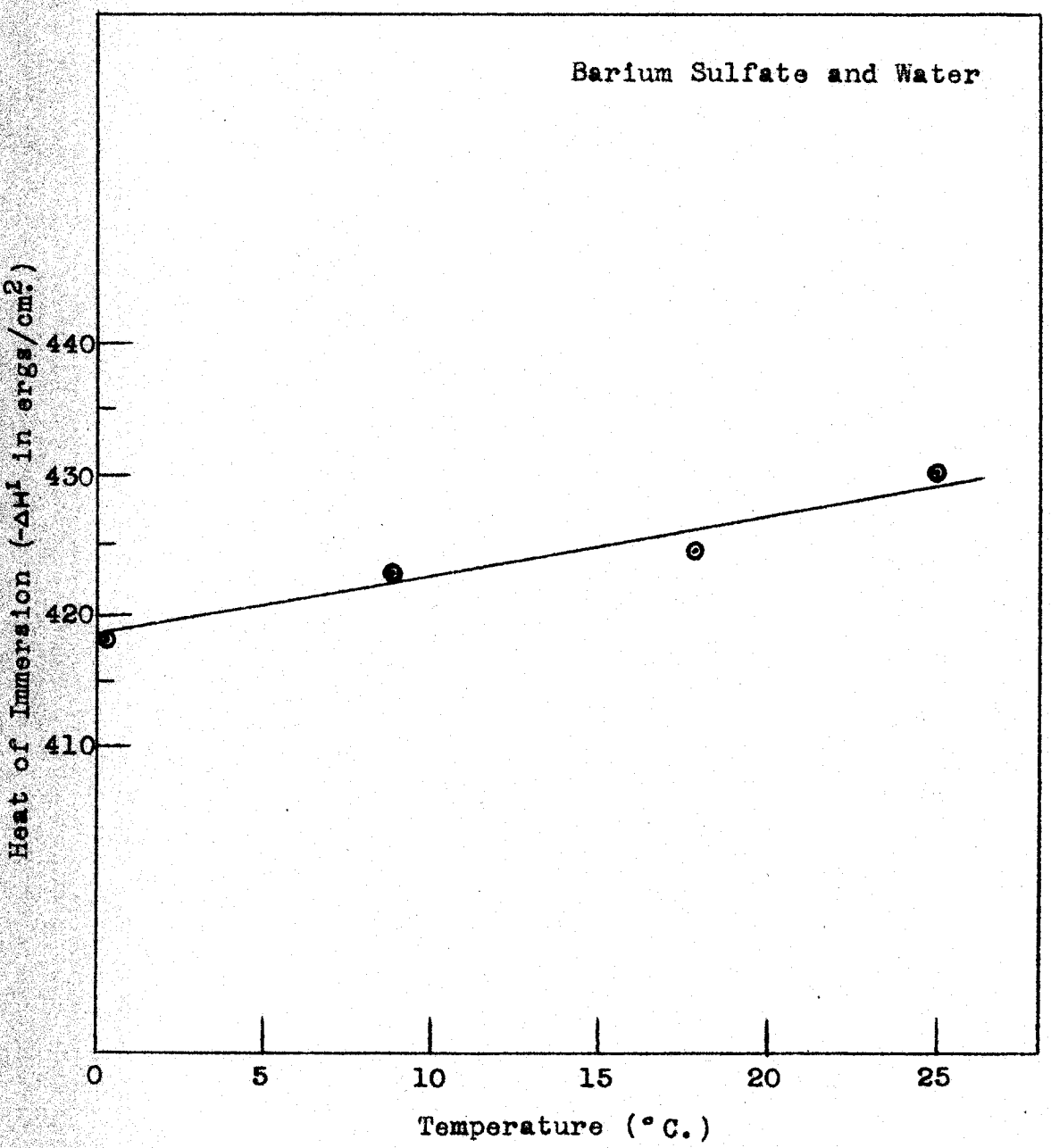


FIGURE 5



immersion versus temperature relation appears to be constant. A value of 0.05 ± 0.01 ergs/cm$^2$ decrease in heat evolved per degree increase in temperature is obtained for the slope of a least squares line determined from the data. The intercept of the line at 0° C. is 29.0 ± 0.1 ergs/cm$^2$.

A plot of the results of the barium sulfate experiments is given in Figure 5. The overall change of the heats of immersion amounts to less than 3 percent. As in the silica gel and carbon black experiments, no sharp changes in the curve are in evidence. The slope of the least squares line is 0.45 ± 0.05 ergs/cm$^2$ per degree, and the intercept value is 418 ± 2 ergs/cm$^2$.

The heats of immersion at 0°C. and the temperature coefficients of the heat of immersion for the three solids are listed in Table I together with the probable errors as determined from a least squares calculation of the data.

TABLE I

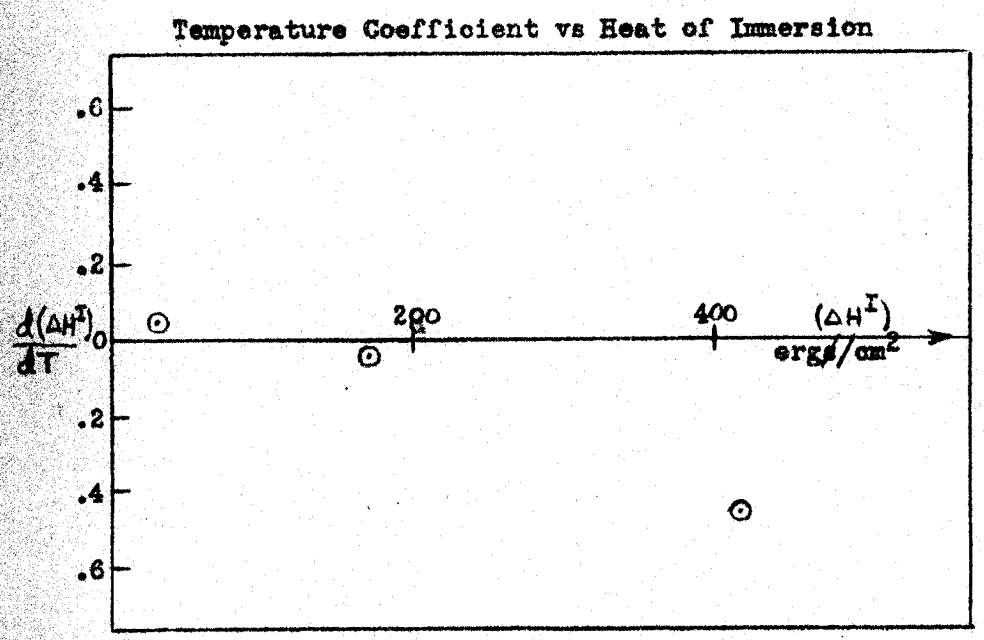
Heat of Immersion and Temperature Coefficient Results

| Substance | $(\Delta H^I)$ ergs/cm$^2$ | $\frac{d(\Delta H^I)}{dT}$ ergs/cm$^2$° |
|---|---|---|
| Barium Sulfate | -418 ± 2 | - 0.45 ± 0.05 |
| Silica gel | -170.0 ± 0.2 | - 0.03 ± 0.01 |
| Carbon Black | - 29.0 ± 0.1 | 0.05 ± 0.01 |

The temperature coefficients are seen to be negative for the polar solids, barium sulfate and silica gel, and positive for the non-polar carbon black. It is interesting to note

that the larger heats of immersion are accompanied by increasingly negative temperature coefficients. This observation is illustrated in Figure 6 in which the temperature coefficients are plotted against the heat of immersion.

FIGURE 6




The results of the experiments indicate that the temperature sensitivity of the heat of immersion in water of the three solids is small. In no case, despite the differences among the surfaces employed, did the heat of immersion change by more than 4 to 5 percent for a 25° change in temperature. In addition the plots of the data exhibit no large peaks which might occur if a phenomena similar to melting occurred in the interfacial region.

II Surface Specific Heat Considerations.

It is of interest to calculate the surface specific heat changes which occur when the liquid comes in contact with the solid. From equation (10) it is found that

$$\Delta C'_s + \Delta C'_L = \frac{d}{dT}(\Delta H^I) - C'_L \qquad (22)$$

The surface specific heat of the liquid, in this case water, is obtained from surface tension data through the use of equations (13) and (15). An equation which very accurately relates the surface tension of water to temperature as expressed by Young, Gross, and Harkins[50] is

$$\gamma = 75.796 - 0.145\,\theta - 0.000\,24\,\theta^2 \qquad (23)$$

where $\theta$ is the centigrade temperature. By means of equations (13), (15), and (23) a value of 0.14 ergs/cm$^2$ per degree is obtained for the surface specific heat of water at 20° C. Taking the slope of the barium sulfate curve as -0.45 ergs/cm$^2$ per degree, the sum of the surface specific heat changes of the barium sulfate and water amounts to -0.59 ergs/cm$^2$ per degree as calculated from equation (22). Similar calculations for silica gel and carbon black lead to values of -0.17 ergs/cm$^2$ per degree and -0.09 ergs/cm$^2$ per degree respectively for the sum of the surface specific heat changes.

The surface specific heat results are compiled in Table II together with values of the interaction energies, $\Delta\epsilon_s + \Delta\epsilon_L$, calculated from equations (4) and (15). It is apparent that the changes in the surface energies and

TABLE II

Interaction Energy and Surface Specific Heat Results

| Substance | Type of Surface | | $\Delta\epsilon_s + \Delta\epsilon_l$ ergs/cm$^2$ | $\Delta C_s' + \Delta C_l'$ ergs/cm$^2$ |
|---|---|---|---|---|
| Barium Sulfate | Polar | Non-porous | 547 | -0.59 |
| Silica Gel | Polar | Porous | 290 | -0.17 |
| Carbon Black | Non-polar | Non-porous | 148 | -0.09 |

surface specific heats induced by the interactions at the interface are small for non-polar carbon black as compared to the polar substances, silica gel and barium sulfate. Furthermore, the substances which yield greater interaction energies with water also exhibit larger surface specific heat changes when the surfaces are placed in contact. It should be noted that in each of the three cases the specific heat changes are negative; consequently, the specific heat of the system is reduced when the solid surface is placed in contact with the water surface, other things being equal.

These results are consistent with the view[51,52] that the liquid molecules in the interfacial region can take on solid-like properties. One characteristic of the solid state is its lower specific heat in comparison with the same matter in liquid form. Since the three solids used in this research each cause a decrease in the specific heat, it is quite possible that a certain degree of "solidification" of the water occurs at the interface. In addition the solids which yield the larger interaction energies,

and hence the ones more apt to produce this effect, also produce a greater change in the specific heat, e.g., the polar compounds barium sulfate and silica gel. Non-polar carbon black on the other hand has a small interaction energy with water and a correspondingly small reduction of the surface contribution to the specific heat.

III. Reproducibility Considerations.

Electrical calibrations of the calorimeter indicated that heat changes of about 6.5 joules -- the minimum quantity involved in the immersion experiments -- could be measured to within 0.3 percent. It should be noted, however, that the unknown heat evolved in a wetting experiment includes the heat due to immersion of the powder plus a small quantity of heat arising from the fracturing of the evacuated glass bulb. The latter heat must be subtracted from the total heat as measured in the calorimeter in order to obtain the heat of immersion. The overall reproducibility of the heat of immersion, therefore, is dependent not only on the calorimetry but also on the bulb-breaking heat.

An investigation was undertaken to determine the magnitude and reproducibility of the heat of bulb-breaking. Boyd and Harkins[1] observed a small heat effect due to bulb-breaking; however, numerical values were not reported. No detectable energy change due to bulb breaking was found by Westrum and Eyring[53] in their heats of dilution experiments

or by La Porte[18] in his heat of immersion experiments. Bartell and Suggitt[7] report a series of bulb-breaking experiments in which the heat of vaporization of the liquid was considered as part of the heat change which occurs during breaking. Their work indicated that the reproducibility of the heat of breaking is not good, and that when reasonably volatile liquids were used, the heat of vaporization nearly cancelled the heat of bulb breaking. They also proposed two sources of the heat of bulb breaking: (1) the mechanical energy needed to break the bulb, and (2) the strain energy built up in the walls of the bulb to resist the pressure differential between the inside and the outside of the bulb.

A third and by far the most important contributor to the bulb-breaking heat, namely the implosion energy, was overlooked or misinterpreted by previous investigators. The inplosion energy may be derived by considering the energy changes which accompany the following cycle of events:

(1) evacuation of the bulb,

(2) placement of the bulb in the calorimeter fluid at a specified depth,

(3) filling the bulb with fluid (corresponds to the implosion of a real bulb),

(4) replacement of the fluid by air,

(5) removal of the bulb from the calorimeter fluid.

Since the initial and final states are the same, the

energy changes accompanying the five steps add to zero. Calculations and experiment show that the energy changes accompanying steps 2, 4, and 5 are small in comparison with those of steps 1 and 3, so that the implosion energy, $Q$, is given by

$$Q \cong P_o V \qquad (24)$$

where $P_o$ is the atmospheric pressure and V is the bulb volume. Assuming that the energy change resulting from filling the bulb appears as heat, equation (24) indicates that the heat evolved in filling an evacuated bulb is equal to the pressure-volume work done in evacuating the bulb, to the extent that the assumptions are correct. The total heat of breaking will also include the energy of fracturing, heat of vaporization, and energy due to the release of strains in the glass.

Experiments were conducted to test the validity of equation (24). In order to eliminate as many of the variables as possible ( e.g., energy of fracturing, strain energy of the glass, etc.) and to improve the reproducibility of the heat determinations, a cylindrical brass chamber was constructed and used to simulate bulbs of various volumes in bulb-breaking experiments. Evacuation of the chamber was made possible through the use of a glass tube sealed into a hole drilled in one of the end walls. After the chamber was evacuated and sealed off, the assembly was weighed and

then mounted in a fixture attached to one of the calorimeter bulb holders. Initiation of the heat determination was accomplished by puncturing a thin brass diaphram soldered over a small hole drilled in the brass chamber. After the determination was completed, the water-filled chamber was again weighed, and the volume of the chamber was computed from the difference between the initial and final weights.

The results of the brass chamber experiments are plotted in Figure 7. It is seen that the experimental points agree quite satisfactorily with the curve given by equation (24). The points lie slightly above the line indicating that there is a small quantity of heat arising from other causes such as the energy of puncturing the diaghram and the energy due to the hydrostatic pressure of the water.

A series of experiments was performed using glass bulbs of the type used in the immersion study in place of the brass chamber. Bulb volume was varied by filling the bulbs to different levels with glass beads, prior to evacuation. The same procedure for breaking the bulbs was utilized in the heat determinations as was used in actual heat of wetting experiments. A plot of the results of these experiments is given in Figure 8. Despite the poor reproducibility the linear relationship with volume as predicted by equation (24) is followed. The heat of fracturing of the glass varies from almost zero to 0.4 joules as estimated from Figure 8.

These experiments indicate that at least two

FIGURE 7

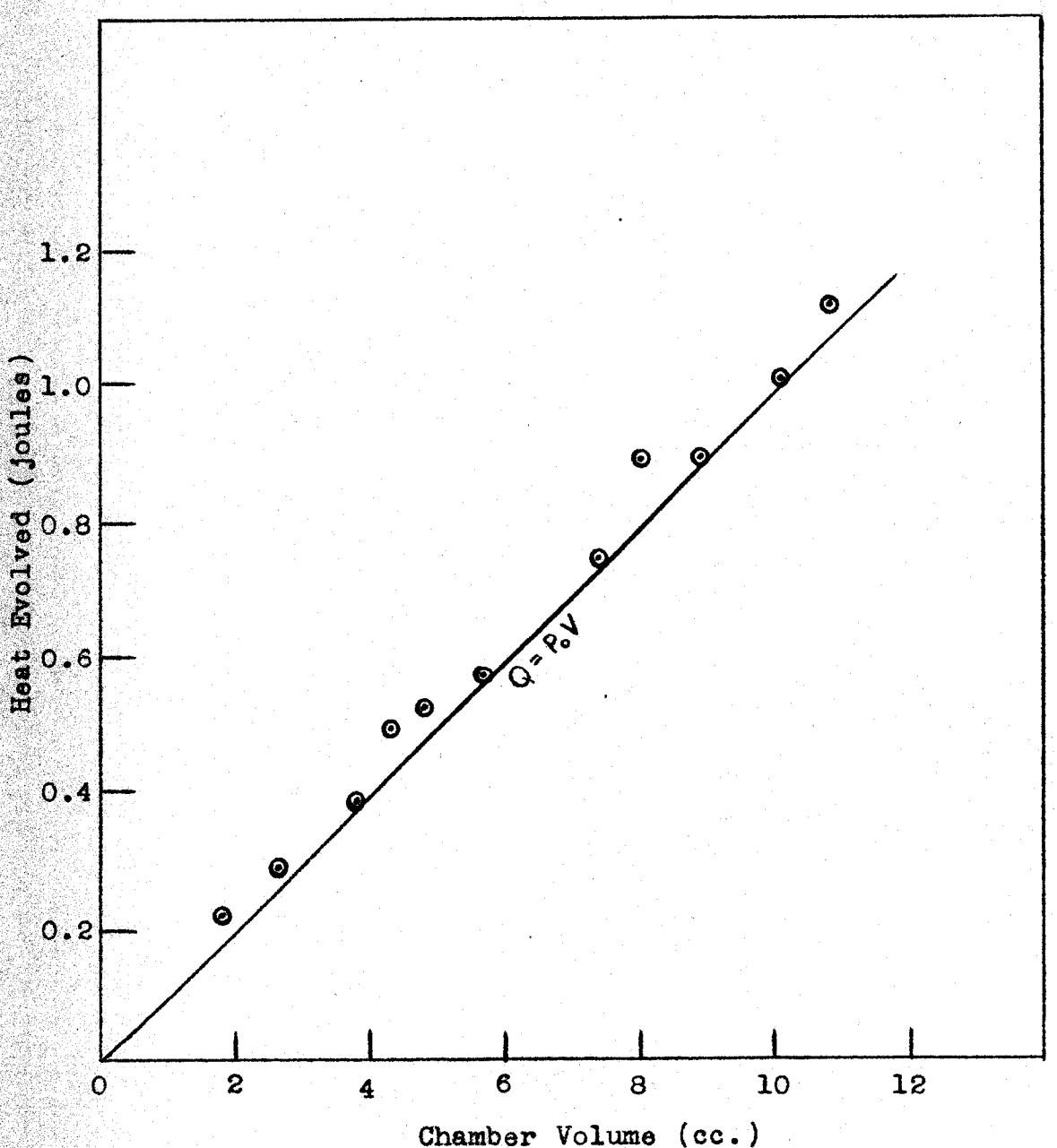
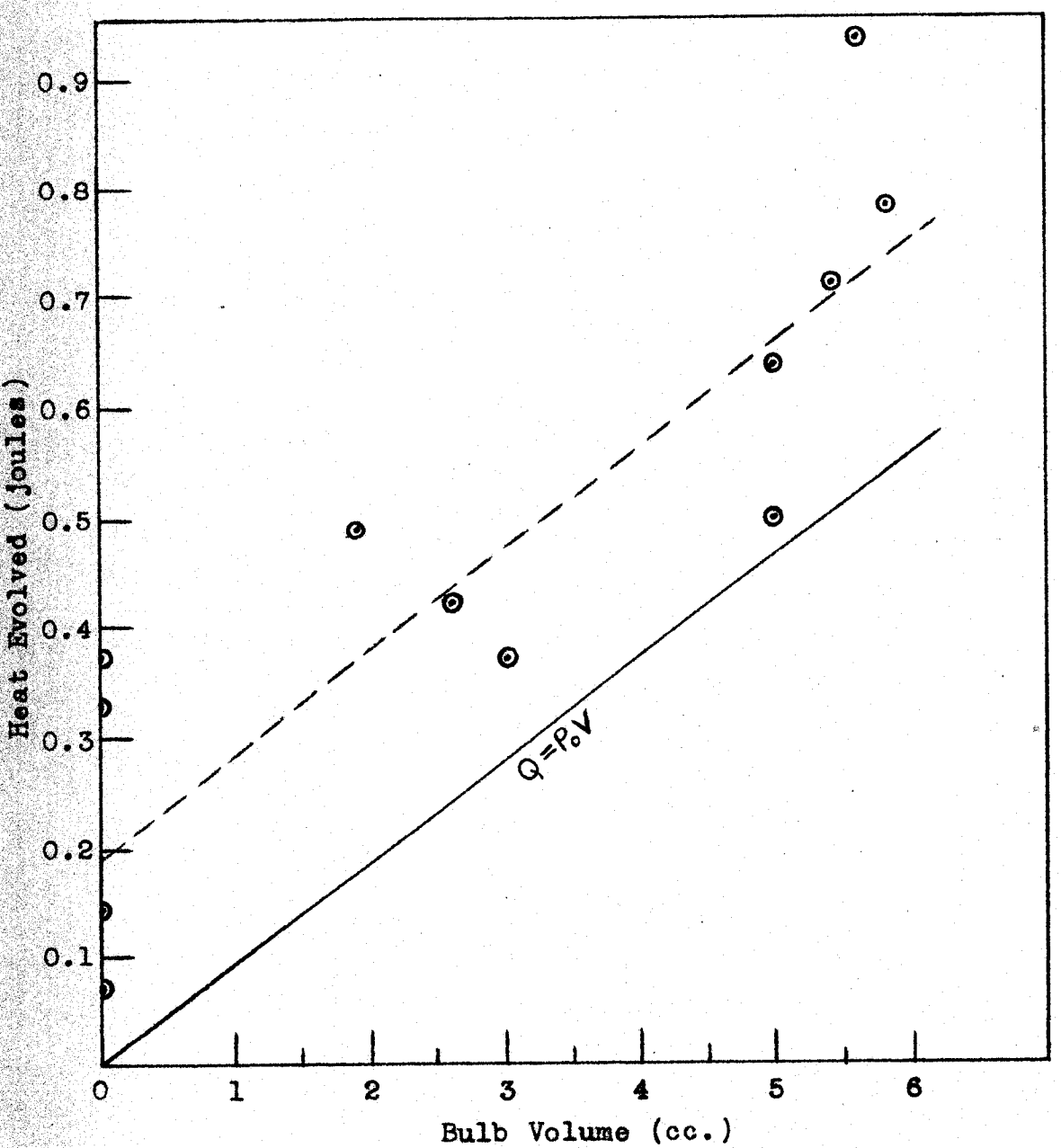


FIGURE 8



correction terms are necessary to account for the bulb-breaking heat in the calculation of the heat of immersion of the powder; they are: (1) a term which is proportional to the bulb volume, and (2) a term which is equal to the mechanical heat of fracturing.

It is apparent from Figure 8 that the mechanical heat of fracturing varies from bulb to bulb. The mean value of the fracture heat was found to be 0.19 joules with an average deviation from the mean of 0.10 joules. This deviation places a definite limitation on the reproducibility of the immersion determinations; for in order to maintain the reproducibility to within 2 percent, it is necessary that at least 5.5 joules total heat be evolved in the experiment. This situation definitely narrowed the field of materials from which selections could be made for the immersion determinations in this research. The solids which were found suitable for this work produced at least 6.5 joules per bulb. The overall measure of reproducibility, however, must include the errors in weighing, variations in evacuation, etc. Experiment indicated that the silica gel determinations were reproducible to within 0.8 percent, the barium sulfate to within 1.5 percent and the carbon black to within 2.5 percent.

In this work the value of the heat of bulb-breaking was determined by calculating the pressure-volume work according to equation (24) and then adding to this result

the heat of fracturing, in this case 0.19 joules. It should be noted that the volume used in equation (24) is the volume of the glass bulb less the volume of the powder. The bulb breaking correction term in most cases amounted to about 0.35 joules.

## SUMMARY

The contributions made by this research may be set forth as follows:

(1) An equation relating the temperature coefficient of the heat of immersion to the surface contributions of the specific heats of the solid and the liquid was derived.

(2) Determinations of the unit area heats of immersion in water of the three solids, silica gel, barium sulfate, and carbon black, were performed at various temperatures in the range from 0° C. to 25° C. with a twin differential microcalorimeter. These measurements indicate a 3 percent change in the heat of immersion of barium sulfate for a 25° change in temperature, a 4.5 percent change for carbon black, and a change of less than 1 percent for silica gel.

(3) The change in the surface contribution of the specific heat accompanying the formation of a solid-liquid interface was calculated on the basis of the heat of immersion data and the equation cited in item (1). It was found that the surface contribution of the specific heat is reduced in each of the three cases studied. The polar solids, barium sulfate and silica gel, cause a larger reduction than non-polar carbon black.

(4) The solid-liquid interaction energies were calculated for the three solids and water, and the results were compared with the surface specific heat changes accompanying the formation of the solid-liquid interface. It was

found that the substances which exhibit the greater interaction energies with water also cause a larger change in the surface specific heat contributions.

(5) The experimental procedures involved in the heat determinations were set forth, and the correction term arising from the breaking of evacuated glass sample bulbs during the immersion experiments was studied. The main contribution to this correction term, which was either overlooked or misinterpreted by other workers, was found to be due to the implosion energy. A cyclic process was considered, and the implosion energy was found to be approximately equal to the pressure-volume work done in evacuating the sample bulb.

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