# NATIONAL BUREAU OF STANDARDS REPORT

9568

Progress Report

on

# APPARENT HEATS OF WETTING AND HEATS OF REACTION OF COMPONENTS OF TOOTH STRUCTURE

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NATIONAL BUREAU OF STANDARDS

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**NBS PROJECT** 311.05-11-3110561

June 30, 1967

**NBS REPORT** 9568

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## APPARENT HEATS OF WETTING AND HEATS OF REACTION OF COMPONENTS OF TOOTH STRUCTURE

By

Eugene F. Huget *
G. M. Brauer **
W. V. Loebenstein **

Data in this report were presented in a thesis by Eugene F. Huget in partial fulfillment of the requirements of the Graduate School of Georgetown University, Washington, D. C., for the degree of Master of Science.

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This investigation is part of the dental research program conducted by the National Bureau of Standards, in cooperation with the Council on Dental Research of the American Dental Association; the National Institute for Dental Research; the Army Dental Corps; the Aerospace Medical Division, USAF School of Aerospace Medicine; and the Veterans Administration.

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# Apparent Heats of Wetting and Heats of Reaction of Components of Tooth Structure

E. F. Huget, G. M. Brauer and W. V. Loebenstein

The apparent heats of wetting $\Delta H_W$ and heats of reaction $\Delta H_R$ of ground dentin, enamel, anorganic tooth and synthetic fluorapatite of known specific surface were determined calorimetrically. The values of $\Delta H_W$ in water are affected by the presence of collagenous matter. Dentin saturated with water vapor gave $\Delta H_W$ of 0.31 cal/gm compared to 12 cal/gm for powder dried at $10^{-3}$ mm Hg. Dry dentin reacts with 0.006-0.6 M aqueous $NH_4$ citrate, malonic, ascorbic, citric and methacrylic acid as evidenced by heats of reaction $\Delta H_R$ ranging from 29-56 cal/gm. These reactions at the surface are caused mainly by organic groups since the $\Delta H_R$ for anorganic tooth, enamel and fluorapatite are much smaller on exposure to these reagents. On the other hand, disodium EDTA and the phosphoric acid in cola beverages react primarily with the mineral components of tooth structure. Harkins method for surface area determination applied to water vapor saturated samples gave approximately the same specific surface values for dentin as those obtained by the BET method, but gave smaller values for anorganic whole tooth tissue. These results of the heats of reaction of odontic powders are useful for studying the modification of tooth surface and in determining those groups that will bond to tooth structure in an aqueous environment.

## 1. INTRODUCTION

### 1.1 Statement of the Problem

The development of an adhesive restorative material would contribute significantly to the enrichment of clinical operative dentistry. A truly adhesive material would be capable of adhering to a dentin or enamel surface through the production of a bond between the surface of the tooth and the proposed dental restorative material.

The properties of a proposed adhesive may be predicted to some extent on the basis of a fundamental knowledge of the chemical and physical nature of the material in question. However, true adhesion to tooth structure is complicated by the inherent nature of tooth structure itself as well as the mechanical, toxicological, bacteriological, and pathological conditions which may occur in the aqueous environment provided by the oral cavity.

In order to achieve maximum adhesion, wetting of the substrate by the adhesive agent must occur. It has been postulated that for good adhesion to develop, the placement of a small amount of adhesive on the appropriate substrate should produce a low or zero contact angle. The greatest adhesion should occur with complete wetting and the concurrent formation of chemical bonds.[1]

### 1.2. Theory of Heats of Wetting

The liberation of heat which occurs when a porous substance is immersed in a chemically inert liquid is a well-documented occurrence referred to as "heat of wetting" or "heat of immersion."[2] If, however, a chemical reaction takes place at the surface of a porous substance upon its immersion in a liquid medium, the "apparent heat of immersion" will be markedly changed. The difference in the "apparent heat of immersion" in aqueous solutions and the heat of wetting in pure water indicates that the added ionic species or functional groups present in the solution react with, dissolve, or modify the surface of the tooth structure.

The heat produced by a chemical reaction may be determined by allowing the reaction to take place in a suitable calorimeter. Most of the heat produced by the reaction which should occur at constant pressure and nearly constant temperature will be absorbed by the measured amount of water in the reaction chamber of the calorimeter. The heat of reaction can be calculated by multiplying the rise in temperature by the total heat capacity of the water, containers, and reaction products. If heat is absorbed by the reaction, the temperature of the measured amount of water within the calorimeter will decrease. However, the evolution of heat by a reaction produces an increase in the temperature of the water contained in the calorimeter. The measurement of the heat of reaction does not determine the heat content of any substance, but only the changes in heat content. By convention, the change in heat content $\Delta H$ is defined as the heat absorbed by the reaction at constant pressure. Therefore, from a thermodynamic standpoint, the evolution of heat by an exothermic reaction produces a negative $\Delta H$ value, whereas the absorption of heat by an endothermic reaction yields a positive $\Delta H$ value.[3]

The enthalpies of adhesion which give a direct measure of the forces of "wetting" can be determined by measuring the heats of immersion (wetting) of powders in liquids in a thermistor type calorimeter. The determined values of heats of immersion are usually small but highly significant exothermic quantities.[1]

## 1.3. Previous Work

A thermodynamic approach to the investigation of the problems of adhesion was utilized by Zettlemoyer[1] in which heats of immersion were determined to estimate the polarity of solid surfaces and the degree of wetting produced by surface active agents (surfactants). In this particular study, Zettlemoyer observed that the addition of small amounts of calcium ions profoundly affected the surface active properties of anionic surfactants in foaming, in detergency, and in the stability of emulsions. Zettlemoyer has suggested that the calcium in dentin might also strongly affect surfactant adsorption. Therefore, according to Zettlemoyer, the employment of a surfactant which could be bound to the calcium in dentin may possibly provide a new approach to the development of an adhesive restorative material.

A study of the reactivity of finely ground dentin in aqueous solutions through the measurement of heats of wetting was begun by Brauer and Wiedeman in 1962.[4] Brauer found the specific surface area of ground dentin as determined by the BET method[5] to be about 10 $m.^2/g.$, and the apparent heat of wetting of dentin to be 0.89 ± 0.04 $cal/m.^2$ (8.0 ± 0.4 cal/g.). From the comparison of the magnitudes of these heats of wetting values with the values of the heats of wetting of inert solids given in the literature ($7 \times 10^{-3}$ to 0.15 $cal./m.^2$),[6] Brauer concluded that there may be some chemical interaction between water and the surface of the powdered dentin.

## 1.4. Purpose of Current Research

The purpose of the determination of the apparent heats of wetting and heats of reaction of the components of tooth structure upon which the writing of the thesis is based was the expansion of the investigation begun by Brauer. The water content of selected sample powders was decreased to study the effects of residual water upon the apparent heats of wetting. Water vapor saturation of powdered tooth structure prior to its immersion was utilized to determine the surface areas of the components of tooth structure by the Harkins Absolute Method.[7] The apparent heats of wetting of the powdered components of tooth structure in various aqueous solutions were determined to quantitatively measure the reactivity of these powders with various ionic species and functional groups.

The measurement and the evaluation of the apparent heats of wetting and heats of reaction of powdered dentin, enamel, anorganic whole tooth tissue, and synthetic fluorapatite should facilitate both the study of any modification of tooth structure necessary to achieve a chemical bond, and the determination of those groups that will bond effectively to the components of tooth structure in an aqueous environment.

## 2. EXPERIMENTAL

### 2.1. Materials

### a. Preparation of Odontic Powders

Finely ground dentin and enamel powders utilized in this study were prepared in the same manner as the dentin powders used by Brauer.[4] In this procedure, freshly extracted teeth were cleaned by brushing and rinsing with water. The crown portions were removed with carborundum disks and the necrotic tissue from the pulp chambers and canals removed with round steel burs. No. 4 and No. 8 steel burs were then used to grind out the dentin which was subsequently sieved for 16 hours on a mechanical shaker using No. 100, No. 200, and No. 325 mesh sieves. The powder passing through the No. 325 sieve was placed on a No. 400 mesh sieve and shaken for 6 hours. The powder which passed the No. 400 sieve was stored in a deep freeze unit and later placed in a dessicator over anhydrous calcium sulfate for at least one week before use. Some samples were further dried under vacuum ($10^{-1}$ to $10^{-3}$ mm. Hg ). Other samples were saturated with water vapor prior to their use.

The enamel hulls which remained after the removal of the dentin were then ground to a fine powder with No. 558 carbide cross-cut fissure burs. The finely ground enamel thus produced was sieved and stored in the manner described for the sieving and storage of powdered dentin. Finely ground anorganic whole tooth tissue prepared by ethylene diamine extraction of the organic components of ground whole teeth was provided for use in this study by W. V. Loebenstein of this laboratory.

### b. Synthesis of Fluorapatite

Synthetic fluorapatite was prepared in a manner similar to that employed by Egan et al.[8] In this procedure, 8.850 grams (0.285 moles) of β tricalcium phosphate were thoroughly mixed with a stoichiometric amount of calcium fluoride (5.281 grams, 0.067 moles) in a platinum crucible. The mixture was heated in a globar furnace for 15 hours at 1300°C. and then for 2 hours at 1400°C. The platinum crucible was removed from the furnace, placed in a desiccator and cooled to room temperature. The resulting fusion product was ground with mortar and pestle into a fine powder. The powder was washed with 1 M ammonium citrate solution and then with distilled water to remove any α tricalcium phosphate that may have been produced during the fusion process. The washed powder was dried at 105°C. for 72 hours. Petrographic analysis of this material revealed that the fusion product was relatively free of extraneous phases. The refractive index ($n_o$ = 1.710 and $n_e$ = 1.707) was that of fluorapatite.[9] Fluorapatite served as a model inorganic compound, free of the many variables associated with organic substances.

## 2.2. Equipment

### a. Calorimeter

The measurement of the small amount of heat liberated by the immersion of a solid requires a highly sensitive and stable detector. A calorimeter utilizing a thermistor as a temperature sensitive device was found entirely satisfactory for the measurement of heats of immersion by Zettlemoyer, et al.[10]

The calorimeter assembly used for the determination of the apparent heats of wetting and heats of reaction of the components of tooth structure in this study was similar to the calorimeter described by Sunner and Wadso.[11] This assembly (Figure 1) consisted of a machined brass canister (A) with a screw-type lid. An "O" ring gasket placed between the lid and the canister provided a water tight seal. The can was immersed in an isothermal water bath, the temperature of which could be kept constant within 0.002°C. A 100 cm.$^3$ capacity glass vessel (B), which served as a reaction chamber, was suspended from the neck of the lid of the surrounding brass can. The glass calorimeter vessel contained wells for a 1,500 ohm thermistor (C), which served as one arm of a

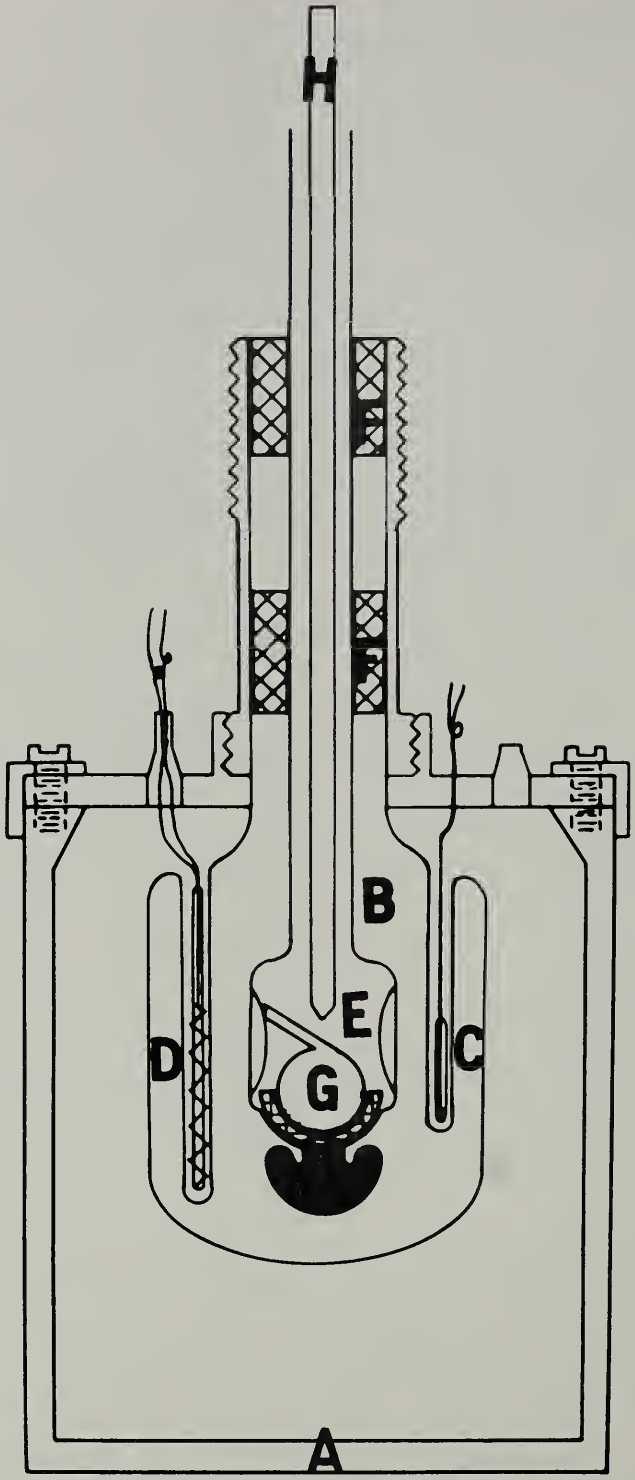

Figure 1. Calorimeter used for the determination of the apparent heats of wetting of odontic powders.

Wheatstone Bridge, and a manganin heating wire (D). A combination glass ampoule holder and stirrer (E) was attached to an 8 mm. diameter steel tube by means of a glass to Kovar seal. The steel tube, which served as a vertical extension of the stirrer shaft, was mounted in a Teflon bearing (F). The extended steel stirrer shaft was coupled by a belt and pulley to a synchronous motor rated at 300 r.p.m. The bulbous glass portion of the ampoule holder contained two openings through which a sealed bulb (G) containing the powdered sample could be inserted. The breaking of the glass bulb was accomplished by raising and then dropping the solid nickel center rod (H). This exposed the solid sample to the liquid in the calorimeter.

### b. Glass Sample Bulbs

The glass sample bulbs used in this study were fabricated from thin-walled glass tubing and had an outside diameter of approximately 1.3 cm., and a capacity of approximately 1.0 $cm.^3$ To obtain bulbs of uniform capacity and wall thickness, these bulbs should have been blown in a mold, as were the ampoules used by Sunner and Wadso.[11] However, since the purpose of this investigation was to determine relative rather than absolute values of heats of wetting and heats of reaction, small variations in the amount of heat evolved in the breaking of the bulbs were not considered significant. The measured amount of heat evolved in the breaking of a typical sealed, empty conventional sample bulb was 0.05 cal. (average of two trials), whereas the amount of heat liberated in the breaking of a bulb used for water vapor saturated samples was 0.2 cal. (average of two trials).

The wide funnel shaped stem of the conventional sample bulb (Figure 2), facilitated the filling of the bulb with finely ground odontic powders. The conventional bulbs were used in the determination of heats of wetting and heats of reaction of powdered samples conditioned over anhydrous $CaSO_4$ and of samples conditioned in a desiccator evacuated by a mechanical vacuum pump to $10^{-1}$ mm. Hg.

The bulb depicted in Figure 3 is a modified version of the conventional bulb. The thickened area of the neck portion of the filling tube made possible the sealing off of the filled sample bulbs under vacuum ($10^{-3}$ mm. Hg ) without the collapse of the bulb or the tube.

Saturation of finely ground powders with water vapor was accomplished through the use of bulbs of the type shown in Figure 4. After the filling of the bulb with powdered

Figure 2. Conventional sample bulb.

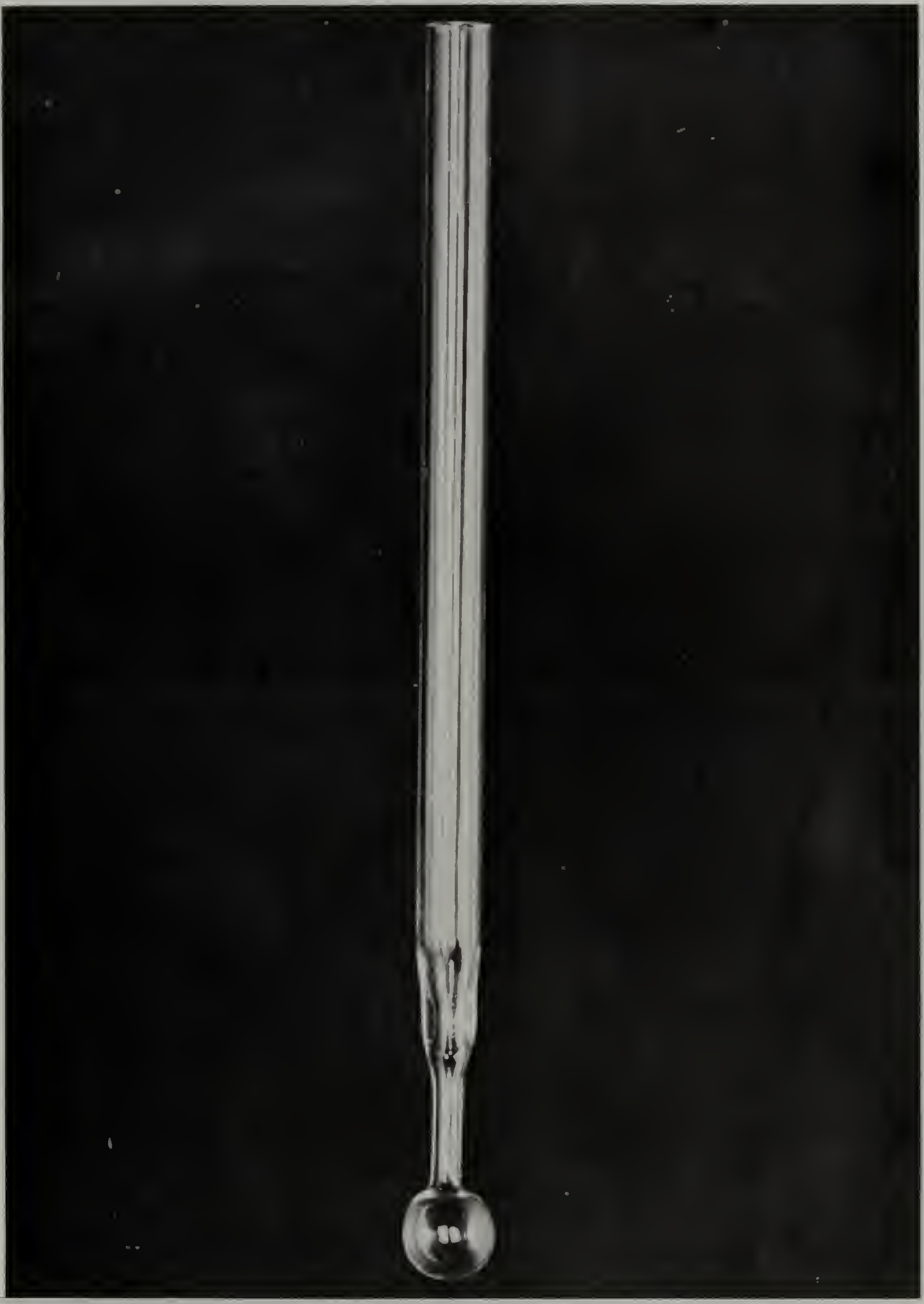

Figure 3. Bulb used for drying of sample powders at $10^{-3}$ mm. Hg.

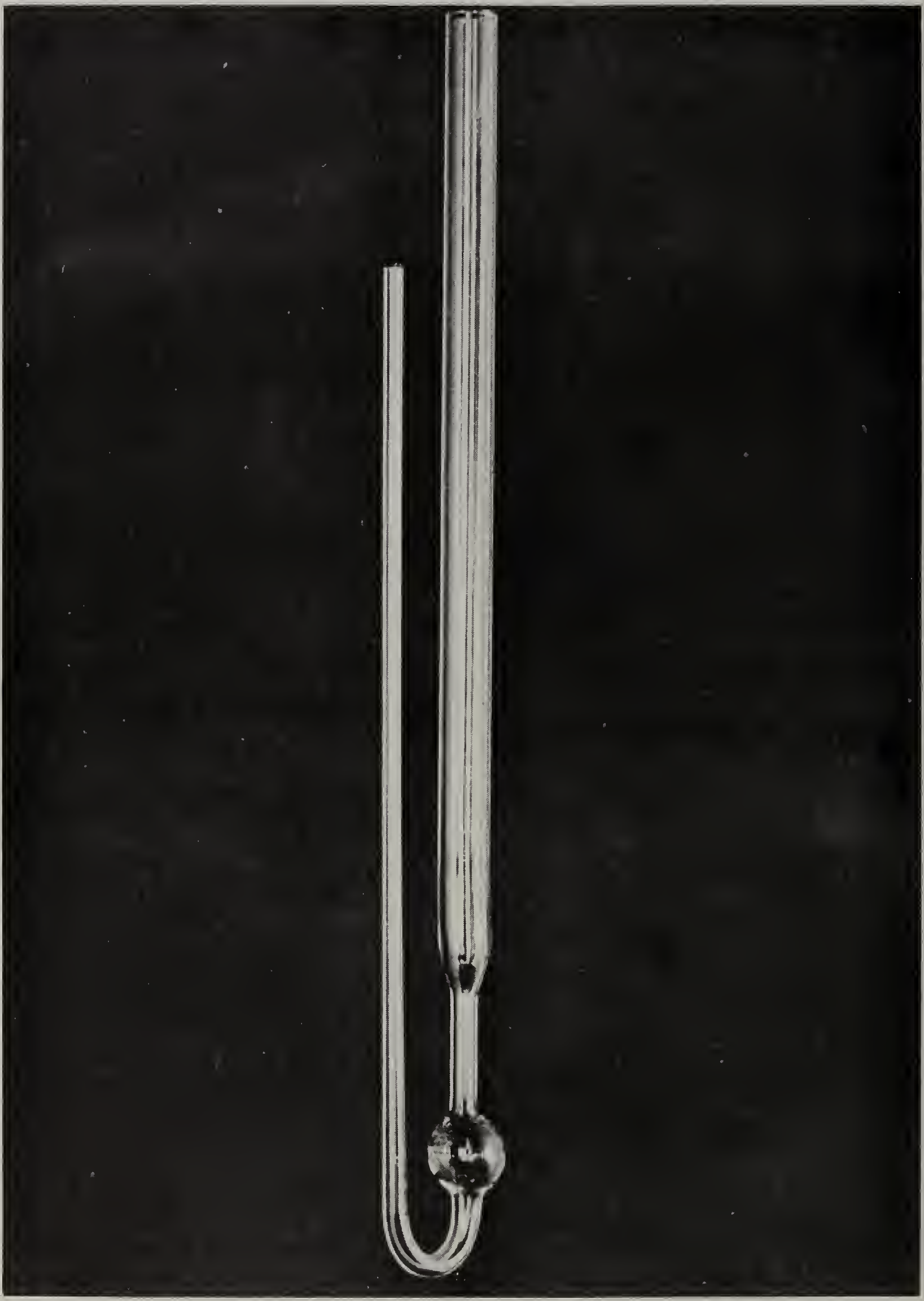

Figure 4. Bulb used for water vapor saturation of powdered samples.

specimen, the large filling tube was connected by rubber tubing to a gas washing bottle filled with water, through which argon was slowly passed. The small "U" shaped tube served as an exhaust. The gas washing bottle and the sample bulb were immersed in a constant temperature water bath. The sample bulb was removed from the water bath and weighed at intervals of one hour. This process was repeated until the powdered specimen and bulb reach constant weight. Upon the completion of the saturation, both the delivery and the exhaust tubes were heat-sealed prior to placement of the bulb in the bulb holder.

Although only relative values of heats of wetting and heats of reaction were to be determined, thin-walled bulbs were used in all determinations to facilitate the breaking, and to minimize any possible heat effects. The use of a large rigid bulb results in the evolution of a higher heat of rupture. Theoretically, heat could be produced through the wetting of the inner surface of the glass bulb. However, this quantity is usually negligible and of significance only in the microcalorimetric measurements of heats of adsorption.[11]

### c. Constant Temperature Water Bath

A constant temperature environment was maintained for the calorimetric determinations made in this study through the employment of a "Fisher Isotemp Bath."

### d. Electrical Components

The electrical components used for the detection of small changes in heat content included a 1,500 ohm thermistor, a Wheatstone Bridge, a light beam galvanometer, an attenuator, and a 6-volt dry cell battery.

The thermistor which serves as one arm of a Wheatstone Bridge is a 1,500 ohm resistor with a high negative temperature coefficient of resistance. This detector is a hard, ceramic-like semi-conductor with electrical resistance that varies extensively with changes in temperature. The thermistor was placed in the well of the glass calorimeter vessel (Figure 1). The well of the vessel was filled with mineral oil prior to the insertion of the thermistor. The mineral oil insulated the temperature sensitive portion of the thermistor from air, and also prevented the contact of the thermistor with moisture that may have possibly formed on the sides of the well through condensation.

In contrast to the behavior of the conventional resistor, the resistance of the thermistor decreases with a rise in temperature, and increases as the temperature falls. Therefore, small variations in temperature which occur upon the immersion of the powdered specimen due to heat of immersion and/or heat of reaction bring about a change in the resistance value of the thermistor and a concurrent disruption of the electrical balance of the Wheatstone Bridge.

The state of imbalance of the bridge caused by the changing of the resistance value of the thermistor in response to small temperature changes resulted in the deflection of the light beam of the galvanometer from its equilibrium position. An attenuator was used to manually control the sensitivity of the galvanometer. The D. C. power supply for the electrical circuitry was provided by a 6-volt dry cell battery.

## 2.3. Procedure

### a. Calibration of the Calorimeter

Calibration was necessary to equate a measured resistance change to the value of a known thermal equivalent. Calibration can be accomplished electrically, or with a standard such as determining the endothermic heat of solution of KCl.

The calorimeter was initially calibrated electrically by Brauer.[4] The electrical system employed in calibrating the calorimeter is illustrated in Figure 5. A ballast resistor of approximately the same resistance as the calorimeter heater was used for at least one hour or more before an experiment until the batteries reached a constant voltage. The energy dissipated = $VV_{st}/4.184R_s$. Where:

$R_s$ Resistance of standard resistor;

$V_s$ Potential drop across standard resistor;

$V$ Potential drop across heater;

$T$ Time in seconds.

In all runs the voltage across the heater and across the standard resistor were kept within a narrow range so that the total energy dissipated varied between 3 and 4 cal. (1 cal. = 4.1840 joules = $4.1840 \times 10^7$ ergs). The time in

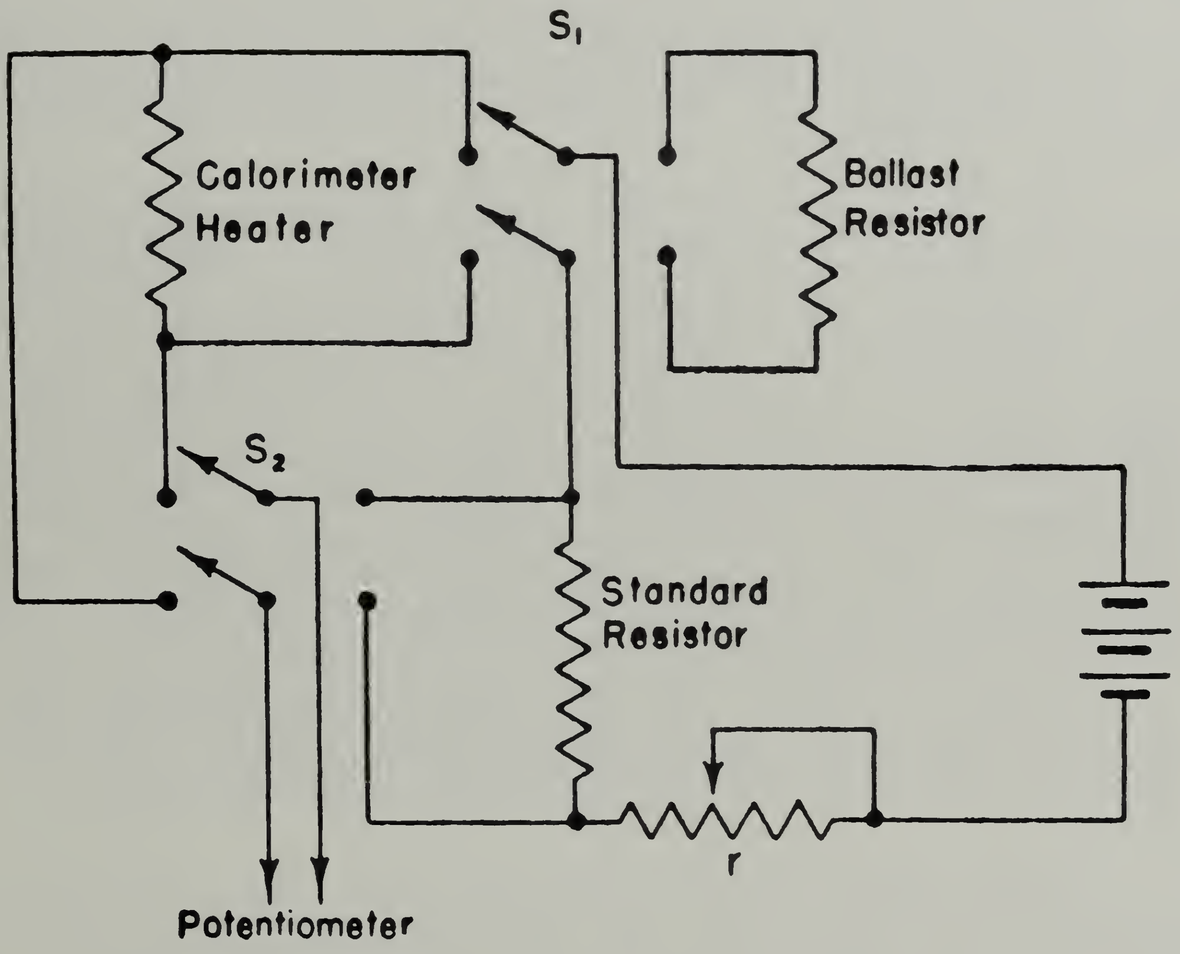

Figure 5. Electrical system employed in calibrating the calorimeter.

seconds and the resistance of the standard resistor were accurately known. The observed temperature rise (as measured by the change in resistance of the thermistor) corresponding to the electrical input yielded an energy equivalent of 1.875 cal./ohm with a calculated standard error of the mean of 0.016 cal./ohm (with a 95 percent confidence interval of 0.041 cal./ohm for 6 runs) for this calorimeter. Since 0.05 ohms could be estimated, it was possible to detect $10^{-4\circ}$ C. or 0.01 cal. if the volume of the water in the calorimeter was 100 ml.

This calorimeter was also calibrated by Brauer through the determination of the endothermic heat of solution of 0.1 g. samples of KCl. The results of these measurements are given in Table I.

The "best" value for the heat of dilution at infinite dilution at 25.0°C. is 4155 ± 10 cal./mole.[12] Correcting for the average KCl concentration employed ($1.41 \times 10^{-2}$M) by using Table XV of reference 12 gives a value of 4160 cal./mole. Since $\Delta H_{30\,^\circ C.} = \Delta H_{25.0\,^\circ C.} + dT[c_{P(Solution)} - c_{P(Solid)}]$ where T is the temperature and $c_P$ are the apparent molal heat capacities of the solute (-26.7 cal./deg./mole) and the crystalline solid (12.3 cal./deg./mole) a "best" value for $\Delta H_{30.2}$ of 53.1 cal./g. is obtained. The 1.5 percent difference between the accepted and the observed value (53.9 ± 0.3 cal./g.) was satisfactory considering that the results were obtained using much lower concentrations of KCl which will decrease the accuracy of the measurement.

Since calibration with KCl requires considerably less equipment and can be accomplished by one person, the calibrations required for this study were conducted by this method.

Finely ground KCl was dried at 105°C. for two hours, and stored in vacuum ($10^{-1}$mm. Hg ) over anhydrous $CaSO_4$. A clean and dry sample bulb was weighed. A Petri dish with dried KCl was removed from the desiccator and placed in the balance housing. A dish containing anhydrous $CaSO_4$ was also placed in the balance to minimize the picking up of water from the air by the powder. While holding the neck of the weighed bulb with tweezers, the bulb was filled with sample powder, and weighed. The original (empty) bulb weight was subtracted from the weight of the bulb plus the sample. The weight difference represented the weight of the sample.

## TABLE I

### Heat of Solution of KCl

T = 30.2 ± 0.1°C

| Weight of Sample | Resistance Change | | Heat of Solution |
|---|---|---|---|
| g. | ohms | ohms/g. | cal./g. |
| 0.1002 | 2.895 | 28.89 | 54.17 |
| .1040 | 3.017 | 29.01 | 54.39 |
| .1054 | 3.016 | 28.61 | 53.64 |
| .1156 | 3.318 | 28.70 | 53.81 |
| .1016 | 2.923 | 28.77 | 53.94 |
| .1044 | 2.980 | 28.54 | 53.51 |

Average value: 53.91 cal./g.

95 percent confidence limit = 0.35 cal./g;
standard error = 0.14 cal./g.

The sample bulb was heat-sealed immediately after the final weighing. The bulb was then placed in the glass bulb holder and set aside until needed.

The thermistor well of a clean and dry glass calorimeter vessel was filled with mineral oil and the thermistor inserted. The neck of the vessel was slipped through the neck assembly of the lid of the brass canister. Tightening of the knurl lock nut stabilized the position of the vessel within the canister. The lid was then attached to the canister with four Allen screws.

A 100 ml. volume of water was added by pipette to the calorimeter vessel. The hollow shaft of the combination stirrer and bulb holder was inserted through the center hole of a Teflon bearing which was seated in the neck of the vessel. The bulb holder was then lowered into the chamber of the vessel.

The entire calorimeter assembly was clamped to the constant temperature water bath and the stirrer shaft coupled to a 300 r.p.m. synchronous motor by a belt. This reduced the amount of heat transferred from the motor to the shaft of the stirrer. The nickel center rod was inserted through the drive unit and stirrer shaft until it rested upon the sample bulb.

The thermistor leads were connected to the Wheatstone Bridge, the attenuator set at the position producing the least amount of galvanometer sensitivity, the light beam of the galvanometer activated, and a balancing load (1,500 ohms to 1,800 ohms) set up in the variable arm of the bridge.

Equilibrium between the temperature of the liquid in the calorimeter and the temperature of the water bath was generally reached in six to eight hours. At equilibrium the rate of deflection of the galvanometer light beam was no greater than 0.2 cm./30 sec. at maximum sensitivity.

Before the actual start of a determination, the peg in the 0.0 to 0.9 ohm range of the variable arm of the bridge was moved forward 1 unit and backward 1 unit from its position of electrical balance. The amount of deflection of the galvanometer light beam was recorded. This step of the procedure was repeated at the end of the determination. The average of these deflections was equal to the deflection of the beam caused by a change in resistance of 0.1 ohm.

With the attenuator positioned to provide maximum galvanometer sensitivity, deflection readings were recorded every 30 seconds for at least 7 minutes. At the end of this period, the nickel center rod was raised and dropped causing the breaking of the sample bulb and the subsequent exposure of the powdered sample to the liquid. Deflection readings were recorded every 30 seconds for 20 to 30 minutes, and the pegs of the bridge moved to compensate for the changing resistance of the thermistor.

The following data were obtained for a typical calibration run using KCl.

Sample weight 0.1325 g. KCl.

0.1 ohm, equivalent to 0.6 cm. deflection (start of run).

0.1 ohm, equivalent to 0.6 cm. deflection (end of run).

TABLE II

Resistance Changes Due to the Endothermic Heat of Solution of KCl

| Interval of Time | Resistance of Bridge | Light Beam Deflection | Corrected Resistance |
|---|---|---|---|
| 30 sec. | ohms | cm. | ohms |
| 0 | 1759.700 | +4.10 | 1760.383 |
| - | 1759.700 | +4.00 | 1760.366 |
| 1 | 1759.700 | +3.90 | 1760.350 |
| - | 1759.700 | +3.80 | 1760.333 |
| 2 | 1750.700 | +3.70 | 1760.316 |
| - | 1759.700 | +3.60 | 1760.300 |
| 3 | 1759.700 | +3.50 | 1760.283 |
| - | 1759.700 | +3.45 | 1760.275 |
| 4 | 1759.700 | +3.35 | 1760.258 |
| - | 1759.700 | +3.30 | 1760.250 |
| 5 | 1759.700 | +3.20 | 1760.233 |
| - | 1759.700 | +3.10 | 1760.215 |
| 6 | 1759.700 | +3.00 | 1760.200 |
| - | 1759.700 | +2.90 | 1760.183 |
| 7 | 1759.700 | +2.80 | 1760.166 |
| - | 1759.700 | +2.70 | 1760.150 |

TABLE II (Cont.)

| Interval of Time | Resistance of Bridge | Light Beam Deflection | Corrected Resistance |
|---|---|---|---|
| 8 | 1759.700 | +2.60 | 1760.133 |
| - | 1759.700 | +2.45 | 1760.108 |
| 9 | 1759.700 | +2.35 | 1760.089 |
| - | 1759.700 | +2.20 | 1760.066 |
| 10 | 1759.700 | +2.10 | 1760.050 |
| - | 1759.700 | +2.00 | 1760.033 |
| 11 | 1759.700 | +1.85 | 1760.008 |
| - | 1759.700 | +1.70 | 1759.983 |
| 12 | 1759.700 | +1.60 | 1759.966 |
| - | 1759.700 | +1.45 | 1759.941 |
| 13 | 1759.700 | +1.30 | 1759.916 |
| - | 1759.700 | +1.20 | 1759.900 |
| 14 | 1759.700 | +1.10 | 1759.883 |
| - | 1759.700 | +1.00 | 1759.866 |
| 15 | 1759.700 | +0.90 | 1759.850 |
| - | Break | ----- | -------- |
| 16 | ----- | ----- | -------- |
| - | 1762.900 | +4.90 | 1763.716 |
| 17 | 1762.900 | +4.50 | 1763.650 |
| - | 1762.900 | +4.10 | 1763.583 |
| 18 | 1762.900 | +3.70 | 1763.516 |
| - | 1762.900 | +3.25 | 1763.411 |
| 19 | 1762.900 | +2.85 | 1763.375 |
| - | 1762.900 | +2.25 | 1763.275 |
| 20 | 1762.900 | +1.80 | 1763.200 |
| - | 1762.900 | +1.20 | 1763.100 |
| 21 | 1762.900 | +0.70 | 1763.016 |
| - | 1762.900 | +0.15 | 1762.925 |
| 22 | 1762.900 | -0.40 | 1762.834 |
| - | 1762.900 | -0.90 | 1762.750 |
| 23 | 1762.900 | -1.40 | 1762.667 |
| - | 1762.900 | -1.90 | 1762.585 |
| 24 | 1762.900 | -2.40 | 1762.500 |
| - | 1762.900 | -2.90 | 1762.417 |
| 25 | 1762.900 | -3.40 | 1762.334 |

The heat equivalent of KCl per unit resistance (ohm) was determined by the following procedure.

1. The change in resistance of the system was plotted as a function of time (Figure 6). Line (ab) was drawn parallel to the ordinate and positioned with respect to the abscissas so that the shaded area (ace) would be equal to

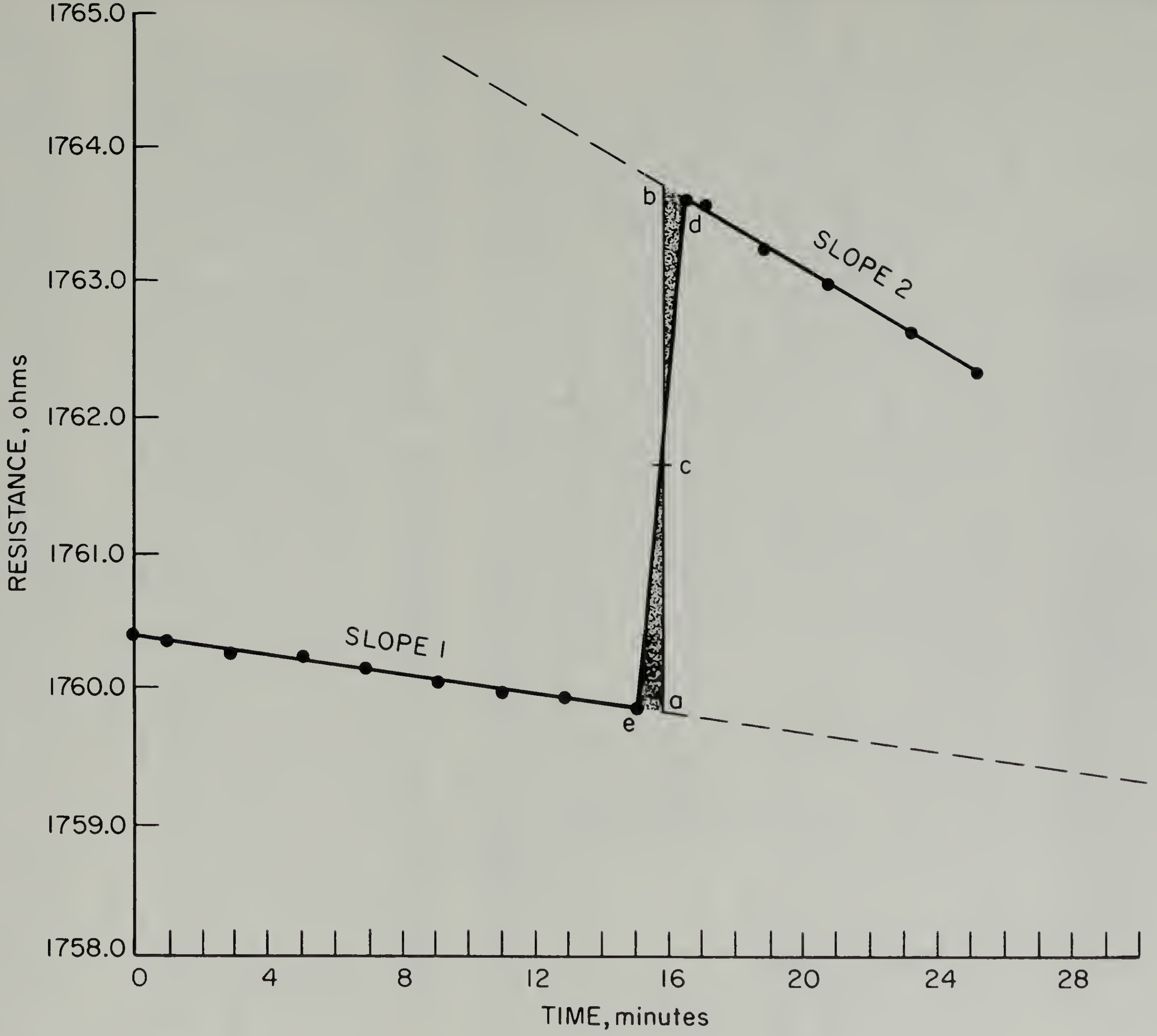

Figure 6. Typical run for the determination of the heat of solution of KCl.

shaded area (bcd).[13] The numerical difference between the intercepts of slope 1 (rate of change of resistance prior to breaking of bulb) and slope 2 (rate of change of resistance after breaking of bulb) was determined.

| | |
|---|---|
| (point **b** of slope 2) | 1763.980 ohms |
| (point **a** of slope 1) | 1759.850 ohms |
| Difference | +4.130 ohms |

2. The change in resistance caused by the breaking of a sealed empty conventional sample bulb (-0.04 ohms) was subtracted from the resistance change observed when a similar sealed bulb containing a known amount of KCl was broken. The difference (+4.170 ohms) represents the increase in resistance caused by the loss of heat which accompanied the solution of 0.1325 g. KCl in 100 ml. of water. A larger "breaking error" (-0.134 ohms) was subtracted from the change in resistance when water vapor saturation bulbs were used.

3. The resistance change per gram KCl was determined.
   4.170 ohms = resistance/0.1325 g. KCl
   Therefore, 4.170/0.1325 = 31.471 ohms/g.

4. The conversion factor was determined.

$$\frac{\text{Heat of solution of KCl(cal/g.)}}{\text{ohms/g.}} = \frac{53.1}{31.471} = 1.687 \text{ cal./ohm}$$

Tables III and IV summarize the results of three calibration runs with KCl.

The average value of the ratio of the known heat of solution (KCl) to the change in resistance per gram (KCl) was 1.687. Therefore, the change in resistance per gram of sample multiplied by the conversion factor (1.687) gave the amount of heat absorbed or consumed. For example, if the change in resistance caused by the wetting of 1 gram of dentin were 6.19 ohms, the heat of wetting would be equal to (6.19 x 1.687) or 10.44 cal./g.

The geometry of the calorimeter vessel and individual differences peculiar to all thermistors profoundly affected the calibration. Therefore, recalibration was required when either the vessel or the thermistor was changed. However, substitution of one combination bulb holder and stirrer for another did not significantly affect the calibration.

### b. Determination of Heats of Wetting and Heats of Reaction of Odontic Powders

The same procedure was used for the determination of

## TABLE III

KCl Calibration

(T = 30.0 ± 0.1°C.)

Conventional Sample Bulb*

| Sample Weight | Resistance Change | | Factor |
|---|---|---|---|
| g. | ohms | ohms/g. | cal./ohm |
| 0.1172 | +3.650-(-0.040) | 31.484 | 1.686 |
| 0.1325 | +4.130-(-0.040) | 31.471 | 1.687 |
| 0.1540 | +4.800-(-0.040) | 31.428 | 1.689 |
| | | Avg. | 1.687 |

*Breaking error for conventional sample bulb was -0.040 ohms.

## TABLE IV

### KCl Calibration

(T = 30.0 ± 0.1°C.)

Correction for Use of Water Vapor Saturation Bulbs*

| Sample Weight | Resistance Change | | Factor |
|---|---|---|---|
| g. | ohms | ohms/g. | cal./ohm |
| 0.1172 | +3.650-(-0.134) | 32.287 | 1.644 |
| 0.1325 | +4.130-(-0.134) | 32.181 | 1.650 |
| 0.1540 | +4.800-(-0.134) | 32.038 | 1.657 |
| | | Avg. | 1.650 |

*Breaking error for water vapor saturation bulb was -0.134 ohms.

heats of wetting and heats of reaction of finely ground odontic powders and synthetic fluorapatite as was used for calibration of the calorimeter with KCl.

Figure 7 illustrates a typical apparent heat of wetting curve for dry 400 mesh (less than 0.032 mm. particle size) dentin. The resistance of the thermistor decreases with an increase in temperature. Therefore, at the time of wetting the resistance shows a sharp decrease. To obtain the corrected total change in resistance the shaded area above the curve should be equal to the area below theccurve.[13]

### c. Determination of Specific Surfaces of Odontic Powders and Synthetic Fluorapatite by the BET Method

The specific surfaces of dentin, enamel, anorganic whole tooth tissue, and synthetic fluorapatite were determined by the Brunauer-Emmett-Teller method.[5] In this technique, the number of nitrogen molecules which form a monolayer were calculated. The sample of dry powder was degassed at 40°C. for at least 18 hours. In the determination of the area, the temperature was kept constant at 77.3°K. (b.p. of liquid nitrogen) and the amount of gas adsorbed was measured as the pressure was altered.

In the development of the BET equation:

$$\frac{P}{V(P_o-P)} = \frac{1}{V_m c} + \frac{c-1}{V_m c} = P/P_o$$

where

$V$ Volume of gas at 273°K., 760 mm.;

$P_o$ Vapor pressure of gas at the temperature of adsorbent;

$P$ Pressure;

$c$ Constant related to the heat of adsorption;

$V_m$ Volume of gas adsorbed in a monolayer;

it was assumed that the adsorbed molecules did not interact with each other, that the net energies of adsorption of the second and subsequent layers were equal to the heat of liquefaction and that there was no limit to the number of layers that could be adsorbed on the surface.

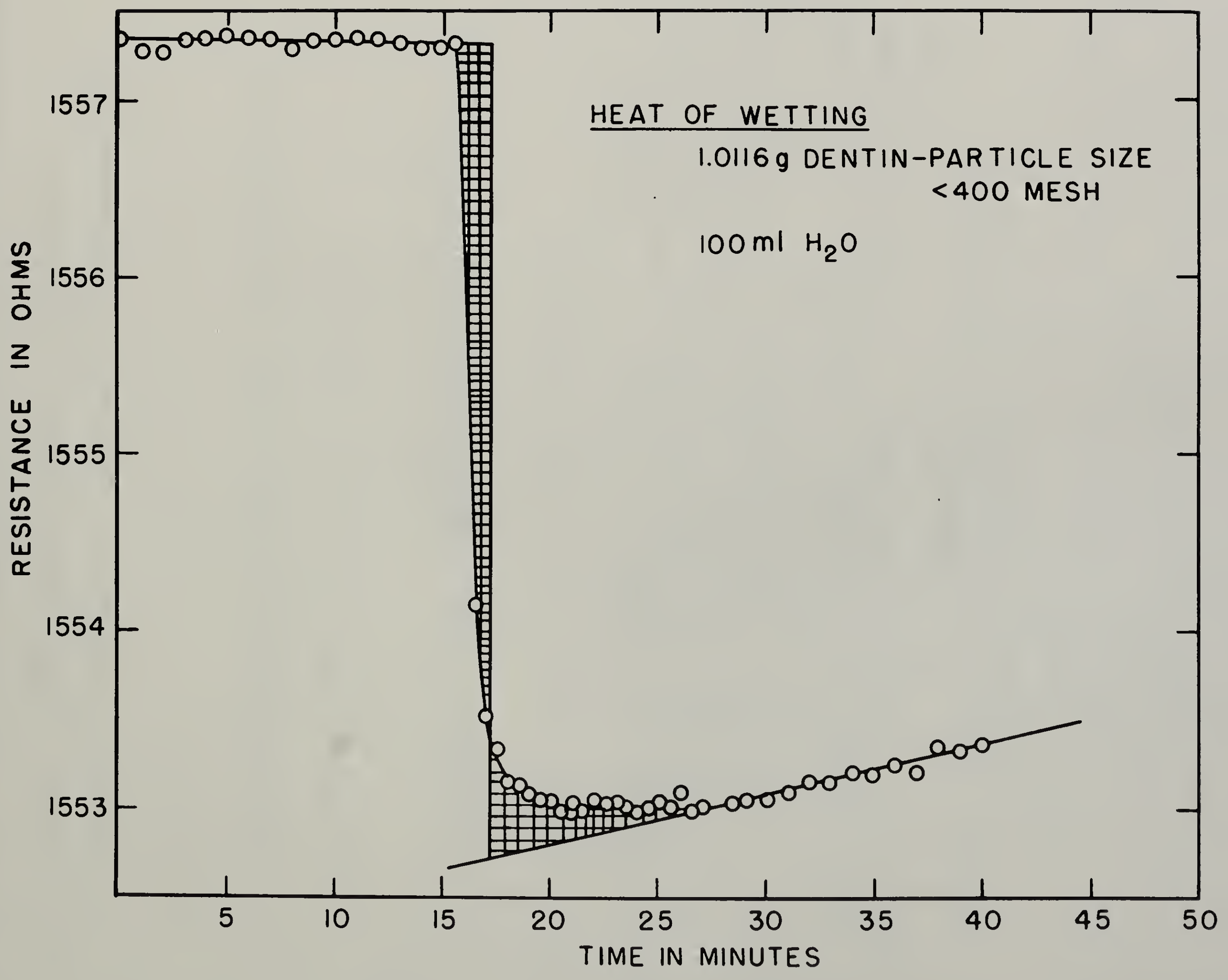

Figure 7. Typical run for the determination of heat of wetting.

In Figure 8, $P/P_o n(1-P/P/_o) \cdot 10^5$ versus $P/P_o$ where n = number of micromoles per g. of sample (273°K. + 760 mm.) is plotted. It is seen that for dentin the BET equation holds over the relative pressure range from 0.05 to 0.25. The specific surface of the particles can then be obtained from the equation:

$$\text{Specific surface } 0.0982 \left(\frac{1}{\text{Slope + Intercept}}\right) \text{m}^2/\text{g.}$$

Results of the area measurements of dentin powders made by Brauer are given in Table V.[4]

Variations between different runs of dentin of the same particle size were not significant since the values of the specific surface measured by the BET method were considered accurate only within 10 percent. For the two larger particle sizes the specific surface was practically the same but unexpectedly the smallest particle size dentin had a somewhat smaller specific surface. The small change of surface area with particle size was an indication of the porous nature of dentin powders.

The results of the specific surface measurements of enamel, anorganic whole tooth tissue, anorganic dentin, and synthetic fluorapatite powders are given in Table VI.

### d. Determination of the Specific Surfaces of Odontic Powders and Synthetic Fluorapatite by the Harkins Absolute Method

Harkins and Jura determined the surface area of titanium dioxide, a nonporous solid, through the measurement of heat of immersion.[7] Powdered titanium dioxide equilibrated with saturated water vapor was immersed in bulk water and the heat of immersion measured. Dividing the value of the observed heat of immersion (0.409 cal./g.) of the film covered powder by the surface energy of water (118.5 erg/cm.$^2$ or 2.83 X $10^{-6}$ cal./cm.$^2$) gave a surface area of 14.4 m.$^2$/g. This value was in reasonable agreement with the value (13.8 m.$^2$/g.) obtained from the adsorption isotherm.

**The** Harkins Absolute Method for the determination of specific surface was applied to water vapor saturated samples of dentin and anorganic whole tooth tissue.

### e. Extraction and Recovery of Collagenous Material

The procedure for the extraction of collagen from dentin

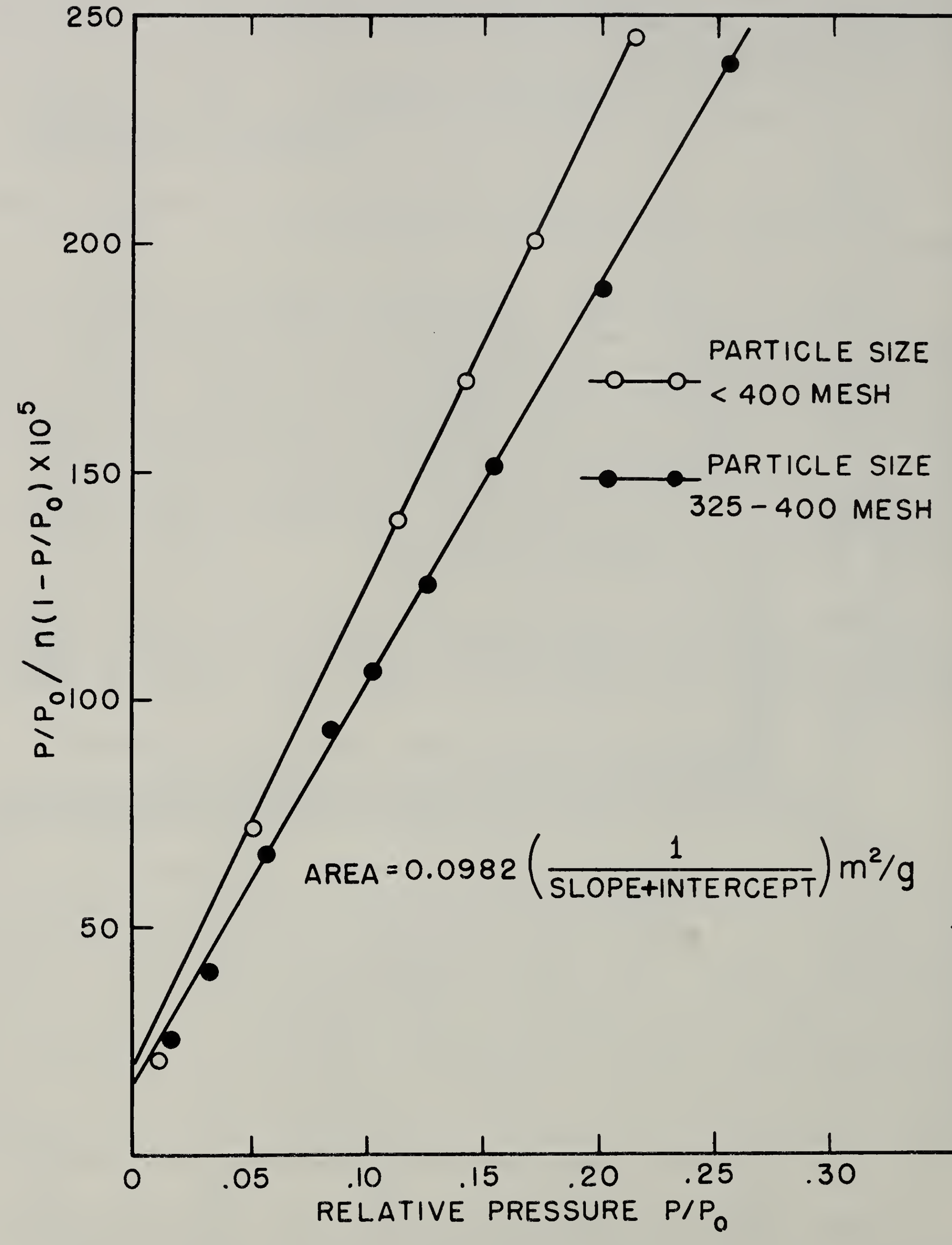

Figure 8. BET free surface plots for dentin.

## TABLE V

### Specific Surfaces of Dentin Powders

| Particle Diameter Range | Specific Surface ($m^2/g.$) | | | |
|---|---|---|---|---|
| | Run 1 | Run 2 | Run 3 | Average |
| mm. | | | | |
| 0.044 - .074 | 10.5 | 10.4 | 10.7 | 10.6 |
| .037 - .044 | 11.1 | 9.8 | -- | 10.5 |
| $<$ 0.37 | 8.67 | 9.25 | 8.67 | 8.9 |

## TABLE VI

### Specific Surfaces of Odontic Powders*

| Powder | Specific Surface (m.$^2$/g.) |
|---|---|
| Anorganic Whole Tooth Tissue (120 mesh) | 75 |
| Dentin (400 mesh) | 10.5 |
| Enamel (400 mesh) | 3.9 |
| Synthetic Fluorapatite (400 mesh) | $<$0.1 |

*Measurements of specific surfaces made by W. V. Loebenstein.

recommended by Randall, et al. was employed.[14] A 1.0 gram sample of dentin was placed in 100 ml. of 0.1 M ammonium citrate solution and stirred for 15 minutes (the average length of time of exposure of the powdered sample to the aqueous solution during a heat of wetting determination). The reaction mixture was filtered under suction and the clear filtrate poured into a dialysis bag. The contents of the bag were dialyzed against tap water. The product which had been extracted by the citrate solution began to precipitate within one hour. Dialysis appeared to be complete after 48 hours. The same procedure was repeated for 1.0 gram samples of powdered dentin exposed to water and other samples exposed to dilute methacrylic acid. The product extracted from dentin by distilled water and methacrylic acid was also recovered in the form of a precipitate through dialysis against tap water.

## 3. RESULTS AND DISCUSSION

The results of the determinations of the apparent heats of wetting and apparent heats of reaction of synthetic fluorapatite and the powdered components of tooth structure are presented in Tables VII through XX.

### 3.1. Heats of Wetting of Dry Powders

The observed heat of wetting of dentin powders appeared to be independent of particle size. Residual water content, however, did have an affect upon the apparent heat of wetting. Drying of dentin powders under vacuum ($10^{-1}$ mm. Hg) increased the value of the observed heat of wetting from 8 to 10 cal./g. Values ranging from 11 to 13 cal./g. were obtained on drying at $10^{-3}$ mm. Hg. No increase in the apparent heat of wetting values was noted, however, for finely ground enamel, anorganic whole tooth tissue, and synthetic fluorapatite with vacuum drying. Therefore, it appears that the collagenous and other organic constituents of dentin bind water through hydrophilic groups, and further dissolve, absorb, or react upon contact with water in the calorimeter vessel.

Stack has shown that the slight amount of heating that occurs during the mechanical preparation of dentin powder does not result in any significant destruction of collagen.[15] Stack further observed that after grinding, a considerable portion of the collagen in dentin becomes readily soluble. This increased solubility may be caused in part by the increase in surface area of the small particles which results in the exposure of an increased amount of collagen, i.e., more collagen is made readily available to dissolve or react.

The comparison of the apparent heats of wetting values of dry powders illustrates the reactive nature of the organic constituents of powdered tooth substance. Although the measured specific surface of dry anorganic whole tooth tissue is approximately 7.2 times that of dry dentin, the observed heat of wetting value for dentin (10.29 cal./g.) is greater than that of anorganic whole tooth tissue (2.06 cal./g.) by a factor of 4.9. On a unit area basis, the observed heat of wetting of dry dentin (0.980 cal./m.$^2$) is greater than the observed heat of wetting of anorganic whole tooth tissue, (0.028 cal./m.$^2$) by a factor of 35. The observed heat of wetting of dentin is therefore dependent upon factors other than available surface area. The observed heat of wetting of anorganic whole tooth tissue is within the range of the heats of wetting values for inert solids ($7 \times 10^{-3}$ to 0.15 cal./m.$^2$) given in the literature.[6] The magnitude of the value obtained for the observed heat of wetting of powdered dentin suggests that more than simple wetting occurs when this substance is immersed in water.

Although the immersion of dry dentin and dry anorganic whole tooth tissue resulted in the evolution of heat, fluorapatite and enamel powders appeared to absorb heat upon immersion. The relatively non-porous nature of the surfaces of these substances greatly lowers the magnitudes of their surface areas (Table VI). The small amounts of heat evolved upon the immersion of such powders are not within the range of sensitivity of this thermistor calorimeter. Since a measurable amount of heat is evolved in breaking an empty sample bulb, the net endothermic effect observed when enamel and fluorapatite powders were exposed to water through the breaking of a filled bulb could possibly be regarded as an artifact. These endothermic values, however, not only increased as the available surface area decreased (0.6 cal./g. for enamel with a surface area of 3.9 m.$^2$/g. versus 1.5 cal./g. for fluorapatite with a surface area of less than 0.1 m.$^2$/g.), but the values obtained were also reproducible (Tables VIII and X). Because of the reproducibility of the apparent endothermic values obtained for enamel and fluorapatite upon immersion in water, these values were considered valid, and were used in the computation of the apparent heats of reaction of these powdered substances in aqueous solutions.

### 3.2. Heats of Reaction of Dry Powders

The observed heat of wetting of dry dentin was markedly increased in dilute aqueous solutions of ammonium citrate, disodium EDTA, malonic, ascorbic, citric, and methacrylic acid. The apparent heats of reaction of dentin with these reagents was determined by subtracting the value obtained for the observed heat of wetting in water from the value of the observed heat of wetting in the appropriate aqueous solution. Powdered anorganic whole tooth tissue and powdered enamel were also exposed to dilute aqueous solutions of ammonium citrate, disodium EDTA, and methacrylic acid. The higher values observed for the heats of reaction of dentin in dilute ammonium citrate (Tables XI, XIII, XIV, XV, and XVII) and methacrylic acid (Tables XII, XIV, and XVI) indicate that these reactions are caused mainly by organic groups.

To demonstrate the existence of a reaction which frees collagen from the powdered tooth surface by the reagents which produced higher heats of wetting values for dentin than for anorganic whole tooth tissue and enamel, the clear filtrates of the reaction mixtures of dentin with water, 0.1 M ammonium citrate, and dilute methacrylic acid were dialyzed against tap water for 48 hours. During this time period, the formation of a white, apparently crystalline precipitate within the dialysis bags suggested the presence of collagenous matter. Further tests to characterize definitively the chemical nature of this precipitate should be conducted.

Anorganic whole tooth tissue and enamel on exposure to disodium EDTA gave higher apparent heats of reaction values (18.4 cal./g. and 18.3 cal./g.) respectively than dentin (15.6 cal./g.). These data suggest that the observed heats of reaction of these powders with ammonium citrate and methacrylic acid are more dependent upon the relative amounts of calcium available for chelation than upon the presence of organic matter. Examination of the apparent heats of reaction values on a unit area basis (0.25 cal./m.$^2$ for anorganic whole tooth tissue, 4.7 cal./m.$^2$ for enamel, and 1.5 cal./m.$^2$ for dentin) reveals that the reactions of disodium EDTA with odontic powders are dependent upon factors other than available surface area.

A popular cola beverage produced higher observed heats of reaction values for anorganic whole tooth tissue (17.4 cal./g.), and enamel (17.2 cal./g.) than with dentin (7.7 cal./g.), on a weight basis. However, on the basis of unit area, the observed heats of reaction were 0.23 cal./m.$^2$ for anorganic whole tooth tissue, 4.4 cal./m.$^2$ for enamel, and 0.73 cal./m.$^2$ for dentin. These results indicate that the phosphoric acid of the beverage reacts principally with the mineral rather than the organic components of tooth tissue, and that the reactions are dependent upon factors other than available surface area.

In vitro studies have shown a decrease in the acid solubility of tooth structure after treatment with dilute fluoride solutions.[16] If an enamel or dentin surface can be modified in such a way that it will resist acid attack, it seems reasonable to conclude that the substance producing the modification must first react with the surface of the tooth.

An aqueous solution of stannous fluoride (8%) has been recommended for clinical use as a caries preventive agent.[17] Clinical studies have shown a decrease in the incidence of dental caries resulting from the topical application of dilute stannous fluoride solutions.[18,19,20]

The reactivities of finely ground dentin, enamel, and anorganic whole tooth tissue in 8% aqueous stannous fluoride were investigated in this study. "Stannous fluoride occurs as an odorless, white crystalline solid, which is very soluble in water and only slightly soluble in alcohol. Aqueous solutions are relatively acid, and deteriorate within several hours, with formation of a white precipitate. Because of this instability in water, which is probably due to hydrolysis, solutions should be freshly prepared and used promptly."[17] However, "pure" stannous fluoride crystals marketed for clinical use as a caries preventive agent and obtained for use in this study were only slightly soluble in distilled water. An 8% aqueous solution was eventually made by passing a suspension of stannous fluoride in distilled water through a suction filter. Stannous fluoride apparently will not dissolve in the presence of air. Therefore, the preparation of an 8% aqueous solution in a dental office is highly unlikely unless the solution is made in an air free environment.

The observed values for the heats of reaction with stannous fluoride of dentin (13.1 cal./g. or 1.2 cal./m.$^2$), enamel (3.7 cal./g. or 0.94 cal./m.$^2$) and anorganic whole tooth tissue (0.0 cal./g. or 0.0 cal./m.$^2$) indicate that this reagent reacts entirely with the organic matter of powdered samples of these tissues.

The effects of fluorides upon vital organic tissue have been the subject of numerous investigations dealing with the etiology and manifestation of mottled enamel.[21] Although the mode of action of the fluoride ion is not entirely clear, the site of action is the ameloblast.[22] Fluoride ions prevent normal enzyme activity and inhibit cellular metabolism resulting in the production of dystrophied enamel characterized by poorly calcified rods and little or no interprismatic substance.

Dilute aqueous solutions of sodium fluoride (2%) had no effect upon the heat of wetting of dentin powder (Table XXI); that is, approximately the same value was obtained for heat of wetting in sodium fluoride solution as in water. Therefore, it appears that the increase in the heat of wetting value obtained when dentin was immersed in stannous fluoride solution was dependent upon factors other than the reactivity of the fluoride ions with the non-vital organic constituents.

An approximately 1% solution of methyl methacrylate had no effect upon the apparent heats of wetting of dentin, enamel, and anorganic whole tooth tissue. These observations indicate that the formation of a true bond between tooth structure and methyl methacrylate cannot be achieved without the modification of the surface of the tooth or the addition of reactive groups to the polymer chains that would react with the components of tooth structure.

Synthetic fluorapatite was prepared to make available a substance for study that would be free of the variables associated with the organic constituents of natural tooth structure. Synthetic fluorapatite did not react with any of the aqueous solutions used in this investigation (Tables XVIII and XIX).

### 3.3. Heats of Wetting of Water Vapor Saturated Samples

If a solid is equilibrated with saturated vapor and then immersed in a pure liquid adsorbate, the film-vapor interface will be destroyed and the heat liberated per unit area should correspond to the surface energy of the pure liquid. Heats of immersion provide a measure of specific surfaces of solids. The comparison of the experimental heat of immersion with the expected value per unit area has been made by numerous authors.[23,24,25]

Finely ground odontic powders equilibrated with water vapor prior to immersion were used to determine the applicability of the Harkins Absolute Method of surface area measurement in the investigation of the surface properties of the components of tooth structure.[7] To liberate an amount of heat sufficient to allow measurement by means of a thermistor calorimeter, the surface area of the sample must exceed 10-20 m.$^2$/g.[3] Therefore, in practice, measurements of heats of wetting are restricted to porous or finely divided solids.

The immersion of water vapor saturated samples of enamel and fluorapatite in water yielded endothermic rather than exothermic values. The destruction of the film-vapor interface of the water vapor saturated samples on immersion appeared to result in the evolution of small amounts of heat as noted by the decrease in the apparent endothermic values obtained on the immersion of dry samples. Inspection of Tables VIII and X reveals that the observed endothermic value obtained for enamel dried at $10^{-1}$ mm. Hg decreased from 0.6 to 0.07 cal./g., while fluorapatite dried at $10^{-1}$ mm. Hg decreased from 1.5 to 0.09 cal./g. The low specific surfaces of enamel and synthetic fluorapatite, as evidenced by the failure of water vapor saturated samples to evolve measurable amounts of heat, prohibited the application of the Harkins method.

Powdered dentin and anorganic whole tooth tissue, however, presented areas of sufficient magnitude to yield a measurable evolution of heat. On dividing the average observed values of heats of immersion of water vapor saturated samples of dentin (0.306 cal./g.) and anorganic whole tooth tissue (0.660 cal./g.) by the surface energy of water ($2.83 \times 10^{-8}$ cal./cm.$^2$),[26] surface area values of 10.9 m.$^2$/g. for dentin and 23.3 m.$^2$/g. for anorganic whole tooth tissue were obtained. The values for the specific surfaces of dentin and anorganic whole tooth tissue by the BET method were 10.5 m.$^2$/g. and 75.0 m.$^2$/g. respectively.

Although extremely close agreement exists between the values for the specific surface of dentin by the two methods of determination, the value obtained for anorganic whole tooth tissue by the BET procedure exceeds the value obtained by the Harkins Method by a factor greater than 3. The low value obtained by the Harkins Method reflects the highly porous nature of the anorganic tissue. Molecules of water vapor are excluded from the smaller pores which allow the entrance and diffusion of the smaller molecules of nitrogen used in the BET procedure. Measurement of the specific surface of finely ground anorganic whole tooth tissue by the BET method includes the contributions of the smaller pores to the total surface area, thereby yielding a higher value.

### 3.4. Heats of Reaction of Water Vapor Saturated Powders

The comparison of the heats of reaction on contact with dilute aqueous solutions of disodium EDTA obtained for water vapor saturated samples of anorganic whole tooth tissue (15.0 cal./g. or 0.20 cal./m.$^2$), enamel (9.0 cal./g. or 2.3 cal./m.$^2$) and dentin (7.5 cal./g. or 0.7 cal./m.$^2$), with the values obtained for dry powders shows an approximately 50% reduction in magnitude of the values for dry dentin and enamel. However, the value obtained for dry anorganic whole tooth tissue is reduced only about 8%. These results suggest that the changes in the organic constituents of dentin and enamel that occur with water vapor saturation reduce the number of reactive sites at which chelation of calcium by EDTA may take place. This effect is not as profound in the case of a water vapor saturated pure mineral substance.

Since water vapor saturated samples of dentin powders more closely approximate the native or physiologic state of intact dentin, the continued investigation of the heats of reaction of water vapor saturated samples would be appropriate from a clinical point of view. To obtain adhesion to dentin, water adsorbed at the surface must be removed. Zisman [27] has suggested the use of various compounds such as butanol to remove water and organic liquid contaminants from the tooth surface by chemical displacement prior to the application of an adhesive. Changes in the apparent heats of wetting and heats of reaction of water vapor saturated samples of dentin powders and subsequent exposure to water displacement chemicals would provide a means of evaluation of the effectiveness of these reagents.

## 3.5. Conclusions

1. The magnitude of the value obtained for the observed heat of wetting of powdered dentin suggests that more than simple wetting occurs when this substance is immersed in water.

2. The surface area of finely ground dentin as determined by the Harkins absolute method was in close agreement with the value obtained by the BET procedure. The Harkins method was not applicable to anorganic whole tooth tissue because of its extremely porous nature, nor could it be applied to enamel or synthetic fluorapatite because of the failure of these substances to evolve significant measurable amounts of heat upon immersion.

3. Heats of reaction of odontic powders are caused by one or more reactions between the mineral component, the organic component, or both, with the functional groups or ionic species supplied by the aqueous solution. The most profound changes in magnitude of the apparent heat of wetting values occurred when the organic matter in the powdered tooth tissue reacted with the added groups.

The results obtained to date clearly demonstrate that the apparent heats of wetting of dentin and anorganic whole tooth tissue in water and in aqueous solutions can be measured with a high degree of reproducibility by means of the calorimetric technique used in this study. Although the apparent heat of wetting of enamel could not be determined in water, the apparent heats of wetting and apparent heats of reaction of this substance were obtainable in aqueous solutions if the amounts of heat evolved through a reaction or reactions at the surface of the powdered specimen were large enough to compensate for the small surface area.

### 3.6. Suggested Future Studies

Many substances not readily soluble in water may be capable of modifying the surface of tooth structure. The technique presently employed could be modified to determine the relative reactivities of odontic powders with these substances. In future studies, solvents showing a minimum degree of interaction with the tooth surface may be substituted for water. Initially, the apparent heats of wetting of the components of tooth tissue will be determined in a 1:1 ethanol-water mixture. This medium will be employed to prepare solutions of reactive groups which are not water soluble, and the heats of wetting and heats of reaction of odontic powders will be measured by the technique previously described.

## TABLE VII

### The Apparent Heats of Wetting of Powdered Dentin

| Powder | Conditioning Procedure | Apparent Heats of Wetting Individual Runs (cal./g.) | Apparent Heats of Wetting Average (cal./g.) | Apparent Heats of Wetting Average (cal./m.$^2$) |
|---|---|---|---|---|
| Dentin (400 mesh) | Anhydrous $CaSO_4$ | 7.78<br>7.64 | 7.71 | 0.734 |
| Dentin (400 mesh) | $10^{-1}$ mm. Hg | 10.35<br>10.55<br>9.99 | 10.29 | 0.980 |
| Dentin (200 mesh) | $10^{-1}$ mm. Hg | 9.95<br>10.05 | 10.00 | 0.952 |
| Dentin (400 mesh) | $10^{-3}$ mm. Hg | 11.68<br>12.86<br>11.80 | 12.11 | 1.15 |
| Dentin (400 mesh) | Saturation with $H_2O$ Vapor | 0.30<br>0.40<br>0.22 | 0.31 | 0.029 |
| Anorganic Dentin (400 mesh) | Saturation with $H_2O$ | 0.99<br>1.00 | 0.995 | 0.009 |

## TABLE VIII

The Apparent Heats of Wetting of Powdered Enamel

| Powder | Conditioning Procedure | Apparent Heats of Wetting | | |
|---|---|---|---|---|
| | | Individual Runs (cal./g.) | Average (cal./g.) | Average (cal./m.$^2$) |
| Enamel (400 mesh) | $10^{-1}$ mm. Hg | +0.61<br>+0.54<br>+0.58 | +0.58 | +0.148 |
| Enamel (400 mesh) | $10^{-3}$ mm. Hg | +0.63<br>+0.64 | +0.64 | +0.164 |
| Enamel (400 Mesh) | Saturated with $H_2O$ Vapor | +0.11<br>+0.02 | +0.07 | +0.02 |

## TABLE IX

The Apparent Heats of Wetting of Anorganic Whole Tooth Tissue

| Powder | Conditioning Procedure | Apparent Heat of Wetting Individual Runs (cal./g.) | Apparent Heat of Wetting Average (cal./g.) | Apparent Heat of Wetting Average (cal./m.$^2$) |
|---|---|---|---|---|
| Anorganic Whole Tooth (120 mesh) | $10^{-1}$ mm. Hg | 2.18<br>2.02<br>1.98 | 2.06 | 0.028 |
| Anorganic Whole Tooth (120 mesh) | $10^{-3}$ mm. Hg | 1.84<br>1.86 | 1.85 | 0.024 |
| Anorganic Whole Tooth (120 mesh) | Saturation with $H_2O$ Vapor | 0.658<br>0.477<br>0.845 | 0.660 | 0.009 |

## TABLE X
## The Apparent Heats of Wetting of Fluorapatite (Synthetic)

| Powder | Conditioning Procedure | Apparent Heats of Wetting<br>Individual Runs (cal./g.) | <br>Average (cal./g.) | <br>Average (cal./m.$^2$) |
|---|---|---|---|---|
| Fluorapatite (400 mesh) | Anhydrous $CaSO_4$ | +1.36<br>+1.23<br>+1.19 | +1.26 | --- |
| Fluorapatite (400 mesh) | $10^{-1}$ mm. Hg | +1.40<br>+1.49 | +1.45 | --- |
| Fluorapatite (400 mesh) | $10^{-3}$ mm. Hg | +1.35<br>+1.38 | +1.37 | --- |
| Fluorapatite (400 mesh) | Saturation with $H_2O$ Vapor | +0.06<br>+0.12 | +0.09 | --- |

TABLE XI

The Apparent Heats of Wetting And Heats of Reaction of Dentin (400 mesh) in Aqueous Solution. Sample Powders Stored ($10^{-1}$ mm. Hg )

| Solution | Apparent Heat of Wetting | | | Apparent Heat of Reaction | |
|---|---|---|---|---|---|
| | Individual Runs (cal./g.) | Average (cal./g.) | Average (cal./m.$^2$) | Average (cal./g.) | Average (cal./m.$^2$) |
| Ammonium Citrate (0.044 M) | 45.52<br>46.15<br>45.27 | 45.65 | 4.43 | 35.35 | 3.37 |
| Disodium EDTA (0.0067 M) | 25.99<br>25.86 | 25.92 | 2.46 | 15.64 | 1.49 |
| Malonic Acid (0.02 M) | 56.54<br>55.48 | 56.01 | 5.33 | 45.72 | 4.35 |
| Ascorbic Acid (0.56 M) | 39.37<br>39.60 | 39.48 | 3.76 | 29.20 | 2.78 |
| Citric Acid (0.047 M) | 42.40<br>42.75 | 42.58 | 4.05 | 32.29 | 3.07 |

TABLE XII

The Apparent Heats of Wetting and Apparent Heats of Reaction of Dentin (400 mesh) in Aqueous Solution. Sample Powders Stored ($10^{-1}$ mm. Hg )

| Solution | Apparent Heat of Wetting | | | Apparent Heat of Reaction | |
|---|---|---|---|---|---|
| | Individual Runs (cal./g.) | Average (cal./g.) | Average (cal./m.$^2$) | Average (cal./g.) | Average (cal./m.$^2$) |
| Glacial Methacrylic Acid (10 ml./100 ml.) | 66.29<br>66.06 | 66.18 | 6.30 | 55.89 | 5.32 |
| Methyl Methacrylate (1%) | 9.87<br>9.78 | 9.82 | 0.945 | None | None |
| Cola Beverage (25 ml./100 ml.) | 17.91<br>18.00 | 17.96 | 1.70 | 7.66 | 0.729 |

## TABLE XIII

The Apparent Heats of Wetting and Apparent Heats of Reaction of Dentin (400 mesh) in Aqueous Solution. Sample Powders Saturated with Water Vapor,

| Solution | Apparent Heat of Wetting | | | Apparent Heat of Reaction | |
|---|---|---|---|---|---|
| | Individual Runs (cal./g.) | Average (cal./g) | Average (cal./m.$^2$) | Average (cal./g.) | Average (cal./m.$^2$) |
| Ammonium Citrate (0.044 M) | 16.25<br>15.83 | 16.04 | 1.52 | 15.73 | 1.49 |
| Disodium EDTA (0.0067 M) | 8.01<br>7.62 | 7.82 | 0.743 | 7.50 | 0.714 |

### TABLE XIV

The Apparent Heats of Wetting and Apparent Heats of Reaction of Enamel (400 mesh) in Aqueous Solution. Sample Powders Stored ($10^{-1}$ mm. Hg)

| Solution | Apparent Heat of Wetting | | | Apparent Heat of Reaction | |
|---|---|---|---|---|---|
| | Individual Runs (cal./g.) | Average (cal./g.) | Average (cal./m$^2$) | Average (cal./g.) | Average (cal./m.$^2$) |
| Ammonium Citrate (0.044 M) | 10.51<br>10.47 | 10.49 | 2.68 | 11.07 | 2.83 |
| Disodium EDTA (0.0067 M) | 17.52<br>17.95 | 17.74 | 4.54 | 18.32 | 4.69 |
| Glacial Methacrylic Acid (25 ml./100ml.) | 19.63<br>19.10 | 19.36 | 4.96 | 19.95 | 5.11 |
| Methyl Methacrylate (1 ml./100ml.) | +0.86<br>+0.56 | +0.71 | +0.18 | None | None |
| Cola Beverage (25 ml./100 ml.) | 16.78<br>16.45 | 16.62 | 4.26 | 17.20 | 4.41 |

TABLE XV

The Apparent Heats of Wetting and Apparent Heats of Reaction of Enamel (400 mesh) in Aqueous Solution. Sample Powders Saturated with Water Vapor.

| Solution | Apparent Heat of Wetting | | | Apparent Heat of Reaction | |
|---|---|---|---|---|---|
| | Individual Runs (cal./g.) | Average (cal./g.) | Average (cal./m$^2$) | Average (cal./g.) | Average (cal./m.$^2$) |
| Ammonium Citrate (0.044 M) | 2.49<br>2.29 | 2.39 | 0.61 | 2.46 | 0.63 |
| Disodium EDTA (0.0067 M) | 8.91<br>8.90 | 8.90 | 2.28 | 8.98 | 2.30 |

### TABLE XVI

The Apparent Heats of Wetting and Apparent Heats of Reaction of Anorganic Whole Tooth Tissue (120 mesh) in Aqueous Solution. Sample Powders Stored ($10^{-1}$mm. Hg)

| Solution | Apparent Heat of Wetting | | | Apparent Heat of Reaction | |
|---|---|---|---|---|---|
| | Individual Runs (cal./g.) | Average (cal./g.) | Average (cal./m.$^2$) | Average (cal./g.) | Average (cal./m$^2$) |
| Ammonium Citrate (0.044 M) | 10.04<br>10.11 | 10.08 | 0.134 | 8.02 | 0.106 |
| Disodium EDTA (0.0067 M) | 20.51<br>20.48 | 20.50 | 0.273 | 18.44 | 0.245 |
| Glacial Methacrylic Acid (10 ml./100ml.) | 22.79<br>22.63 | 22.71 | 0.302 | 20.65 | 0.275 |
| Cola Beverage (25 ml./100 ml.) | 19.57<br>19.40 | 19.48 | 0.259 | 17.43 | 0.232 |

## TABLE XVII

The Apparent Heats of Wetting and Apparent Heats of Reaction of Anorganic Whole Tooth Tissue (120 mesh) in Aqueous Solution. Sample Powders Saturated with Water Vapor.

| Solution | Apparent Heat of Wetting | | | Apparent Heat of Reaction | |
|---|---|---|---|---|---|
| | Individual Runs (cal./g.) | Average (cal./g.) | Average (cal./m.$^2$) | Average (cal./g.) | Average (cal./m.$^2$) |
| Ammonium Citrate (0.044 M) | 4.52<br>5.03 | 4.76 | 0.063 | 2.70 | 0.036 |
| Disodium EDTA (0.0067 M) | 16.88<br>17.20 | 17.04 | 0.227 | 14.98 | 0.199 |

## TABLE XVIII

The Apparent Heats of Wetting and Heats of Reaction of Synthetic Fluorapatite (400 mesh). Sample Powders Stored ($10^{-1}$ mm. Hg )

| Solution | Apparent Heat of Wetting | | | Apparent Heat of Reaction | |
|---|---|---|---|---|---|
| | Individual Runs (cal./g.) | Average (cal./g.) | Average (cal./m.$^2$) | Average (cal./g.) | Average (cal./m.$^2$) |
| Ammonium Citrate (0.044 M) | +0.63<br>+0.61 | +0.62 | --- | +0.8 | --- |
| Disodium EDTA (0.0067 M) | +0.47<br>+0.58 | +0.52 | --- | +0.9 | --- |
| Glacial Methacrylic Acid (10 ml./100 ml.) | +1.24<br>+1.25 | +1.24 | --- | +0.3 | --- |
| Cola Beverage (25 ml./100 ml.) | +1.26<br>+1.26 | +1.26 | --- | +0.2 | --- |

TABLE XIX

The Apparent Heats of Wetting and Apparent Heats of Reaction of Synthetic Fluorapatite (400 mesh) in Aqueous Solution. Sample Powders Saturated with Water Vapor

| Solution | Apparent Heat of Wetting | | | Apparent Heat of Reaction | |
|---|---|---|---|---|---|
| | Individual Runs (cal./g.) | Average (cal./g.) | Average (cal./m.$^2$) | Average (cal./g.) | Average (cal./m$^2$) |
| Ammonium Citrate (0.044 M) | +0.03<br>+0.04 | +0.04 | --- | None | --- |
| Disodium EDTA (0.0067 M) | +0.02<br>+0.02 | +0.02 | --- | None | --- |

## TABLE XX

The Apparent Heats of Reaction of Odontic Powders in 8% Stannous Fluoride Solution. Sample Powders Stored ($10^{-1}$mm.Hg)

| Sample Powder | Apparent Heat of Wetting | | | Apparent Heat of Reactions | |
|---|---|---|---|---|---|
| | Individual Runs (cal./g.) | Average (cal./g.) | Average (cal./m.$^2$) | Average (cal./g.) | Average (cal./m.$^2$) |
| Dentin (400 mesh) | 23.45<br>23.28 | 23.36 | 2.22 | 13.08 | 1.24 |
| Enamel (400 mesh) | 2.99<br>3.10 | 3.04 | 0.76 | 3.68 | 0.94 |
| Anorganic Whole Tooth Tissue (120 mesh) | 1.98<br>1.97 | 1.98 | 0.03 | None | None |

# SUMMARY

The liberation of heat which accompanies the immersion of a porous substance in a chemically inert liquid is a well documented occurrence referred to as heat of wetting or heat of immersion. Heat of wetting is a surface phenomenon, the magnitude of the observed value being proportional to the surface area of the sample.

The apparent heat of immersion will be changed profoundly if chemical reactions take place at the surface. The numerical difference between apparent heat of wetting in aqueous solution and heat of wetting in water indicates that the added ionic species or functional groups present in the solution react with, dissolve, or modify the surface of the immersed substance.

The apparent heats of wetting and heats of reaction of powdered dentin, enamel, anorganic whole tooth tissue, and synthetic fluorapatite were determined calorimetrically. The reproducibility of the results indicated that the experimental procedure was adequate for the determination of the heats of wetting and heats of reaction of odontic powders in water and in aqueous solutions of water soluble functional groups. Thus, the method is suitable to study the modification of tooth surface by ions or functional groups.

Since heat of wetting is a function of surface area, the specific surfaces of the powdered components of tooth structure were determined by the conventional gas adsorption method of Brunauer-Emmett-Teller, so that the observed heats of wetting values could be expressed in terms of unit area. Ground whole tooth tissue rendered anorganic by extraction with ethylene diamine, presented the largest surface area, which was approximately seven times the area of dentin. The surface area of enamel was approximately one-third that of dentin, while the specific surface of synthetic fluorapatite was so small that it could only be estimated by the BET procedure.

The observed heats of wetting of dentin powders appeared to be independent of particle size. Residual water content, however, did have an effect upon the apparent heats of wetting as evidenced by an increase in the observed heats of wetting values from 0.31 cal./g. (0.03 cal./m.$^2$) for water vapor saturated samples to 12.11 cal./g. (1.15 cal./m.$^2$) for carefully dried samples. No increase in the apparent heats of wetting values was noted, however, for finely ground enamel, anorganic whole tooth tissue, and synthetic fluorapatite on vacuum drying. Therefore, it appears that the collagenous and other organic constituents of dentin bind water through hydrophilic groups, and further dissolve, absorb, or react upon contact with water in the calorimeter.

The immersion of dry dentin and dry anorganic whole tooth tissue resulted in the evolution of heat. Dry fluorapatite and enamel powders, however, absorbed heat upon immersion. The observed heat of wetting of dry anorganic whole tooth tissue (2.06 cal./g. or 0.028 cal./m.$^2$) was within the range of the heats of wetting values for inert solids. The observed heat of wetting of dry dentin (10.20 cal./g. or 0.98 cal./m.$^2$) however, exceeded this range.

Although many factors contribute to the net value of the observed heat of wetting, the most profound changes in the magnitude of this value occurred when the organic constituents of powdered tooth tissue reacted with the functional groups and/or ionic species supplied by the solution in which the sample powders were immersed. Dry dentin reacted with 0.006 to 0.6 M aqueous ammonium citrate, malonic, ascorbic, citric, and methacrylic acid as evidenced by the heats of wetting values ranging from 25.9 to 66.1 cal./g. (2.5 to 6.3 cal./m.$^2$). These reactions were caused mainly by organic groups since the heats of wetting values for anorganic whole tooth tissue, enamel, and fluorapatite were much smaller on exposure to these reagents. The recovery of a collagen-like substance in the form of a white crystalline precipitate upon the dialysis of the reaction mixtures of dentin with water, 0.1 M ammonium citrate, and dilute methacrylic acid, proves that these substances are capable of liberating the collagenous matter of finely ground dentin.

Anorganic whole tooth tissue and enamel gave heats of reaction values on the order of 18 cal./g. (0.25 cal./m.$^2$) and 18 cal./g. (4.5 cal./m.$^2$) respectively when exposed to dilute solutions of disodium EDTA and phosphoric acid (cola beverage). Dentin on the other hand, yielded heats of reaction values of 15.6 cal./g. (1.5 cal./m.$^2$) when immersed in dilute aqueous disodium EDTA, and 8 cal./g. (0.73 cal./m.$^2$) when immersed in dilute cola solutions. The magnitudes of these values are dependent upon the relative amounts of calcium available for chelation, but not upon the surface areas of the powdered tissues.

Dry dentin and enamel reacted with aqueous stannous fluoride to produce heats of reaction values of 13 cal./g. (1.2 cal./m.$^2$) and 3.7 cal./g. (0.94 cal./m.$^2$) respectively. A heat of wetting value of 1.98 cal./g. (0.03 cal./m.$^2$) was obtained for anorganic whole tooth tissue upon its exposure to stannous fluoride Since this value was also obtained for heat of wetting in water, reaction between anorganic whole tooth tissue and stannous fluoride did not take place. Stannous fluoride appeared to react entirely with the organic constituents of powdered tooth tissue.

Synthetic fluorapatite was prepared to make available a substance for study that would be free of the variables associated with the organic constituents of natural tooth structure. Synthetic fluorapatite did not react with any of the aqueous solutions used in this investigation.

The Harkins Absolute Method for the determination of specific surface was applied to finely ground odontic powders saturated with water vapor prior to immersion. The specific surface of dentin by the Harkins Method was determined to be 10.9 m.$^2$/g. as compared to 10.5 $m.^2/g.$ by the BET procedure. The apparent heat of immersion of water vapor saturated samples of anorganic whole tooth tissue, a highly porous material, gave a surface area of 23.3 $m.^2/g.$ by the Harkins Absolute Method. Surface area measurements of this powder by the BET method yielded a value of 75 $m.^2/g.$ Measurement of the specific surface of finely ground anorganic whole tooth tissue by the BET method included the contributions of the smaller pores which were inaccessible to the larger molecules of water, to the total surface area, thereby yielding a higher value.

The specific surfaces of enamel and synthetic fluorapatite were much too small to yield a measurable evolution of heat upon immersion. The Harkins Absolute Method for the determination of specific surface was, therefore, not applicable to these powders.

The measurement and the evaluation of the heats of wetting and heats of reaction of finely ground odontic powders should facilitate both the study of any modification of tooth structure necessary to achieve a chemical bond, and the determination of those groups that will bond effectively to the components of tooth structure in an aqueous environment.

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