AN ISOPERIBOL, ANEROID, ROCKING-BOMB REACTION CALORIMETER

By

WALTER CLARENCE PARKS

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North Georgia College

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Thesis Approved:

Robert D. Freeman
Thesis Adviser

Clarence M. Cunningham

J. A. Bizzell
Dean of the Graduate School

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CHAPTER I

INTRODUCTION

Purpose

The purpose of this investigation was to design, construct, and test a calorimeter for the determination of heats of reactions in a liquid solvent. The calorimeter was to be highly versatile so that a variety of systems might be studied, and was to be a high-precision instrument with which heats of reaction might be determined with an accuracy limited only by the external measuring equipment.

Design Considerations

Although solution-reaction calorimeters have been in use since the nineteenth century, their development as high precision instruments has lagged behind that of the oxygen bomb calorimeter, primarily because strong emphasis has been placed on the oxygen bomb calorimeter, and on standardization of its equipment, for the study of the large number of similar combustion reactions possible with organic compounds. The solution-reaction calorimeter has not received similar emphasis, and due to the great variety of conditions and reactions studied, very little standardization has been possible.

The initial requirements for the design of the calorimeter were the following: minimal heat transfer to or from the reaction vessel by radiation, convection, and conduction; short equilibration time; and thermo-

dynamically-definable initial and final states for the reaction system.

The time for equilibration of a reaction vessel is directly related to the definiteness of the boundary of the reaction vessel. As shown by Sunner and Wadsö (27), any calorimeter which has an ill-defined boundary with respect to the surroundings has a long equilibration time. Their investigation emphasizes the advantages of a reaction vessel which is constructed of a metal with high thermal conductivity and which is suspended in vacuum; such a reaction vessel has a rather precisely defined boundary with respect to the surroundings. Reaction vessels constructed of metals with high thermal conductivity have been repeatedly described in the literature (24, 25); they range from micro-calorimeters (29) to high temperature calorimeters (16).

Thermal transfer can be minimized by suspending the calorimeter in vacuum and by using an adiabatic shield for the calorimeter. The reaction vessel changes temperature very rapidly during the reaction; the temperature of an adiabatic shield would lag behind that of the reaction vessel, thereby creating for the reaction vessel a constantly changing environment which is neither isothermal nor adiabatic. Therefore, the reaction vessel in the calorimeter constructed in this study is to be suspended in vacuum surrounded by a isothermal jacket.

If a reaction vessel is suspended in vacuum ("with no air"), the term "aneroid" is applied in calorimetry. The aneroid method was first employed by Eucken (9) in 1909 and later by Dickerson and Osborn (7, 20) in specific heat measurements. The first application of the aneroid principle to combustion bomb calorimetry was made in 1951 by Magnus and Becker (18). More recently Pilcher and Sutton, 1955 (22), Keith and Mackle, 1958 (15), and Meetham and Nicholls, 1960 (19) have described aneroid combustion bomb

calorimeters. Gunn (10) described an aneroid solution calorimeter in 1958.

The calorimeter described here is to be used for determining heats of reactions between a solid phase and a solution; therefore, it is essential that the reaction system be agitated. This agitation will insure more rapid reaction of the solid phase, a resulting homogenous solution, and a decrease in the equilibration time. Agitation in the vessel could be accomplished by a conventional stirrer as described by Sunner and Wadsö (27); however, the stirrer shaft would provide a path for thermal conduction and would extend and make ill-defined the boundary of the system. A method has been developed whereby the contents of the reaction vessel can be agitated by rocking but the vessel is left essentially isolated from the surroundings. The moving-bomb method was developed by Popov and Shirokich (23) in 1933. The method was modified by Sunner (26) and the United States Bureau of Mines (12). Sturtevant (28, 3) describes stirring of the contents of a micro-calorimeter by rocking, while Gunn (10) and Benson (1, 2) describe solution calorimeters which are stirred by a rocking motion. Keith and Mackle (15) describe an aneroid combustion bomb calorimeter which is stirred by rocking.

The use of an air bath, rather than a water bath, to establish isoperibol conditions has been described for high temperature calorimeters (17), micro-calorimeters (4), and combustion bomb calorimeters (15). Isoperibol is defined as constant surroundings and is applied to calorimeters that have constant temperature surroundings. We have designed and constructed an air bath by drawing from the descriptions contained in these publications.

The calorimeter described in this thesis has a reaction vessel which is made of copper, suspended in a vacuum, stirred by rocking, and surrounded by an isothermal air bath.

CHAPTER II

EQUIPMENT

General Description

The calorimeter system to be described consists of four main parts: the reaction vessel, the suspension and rocking mechanism, the constant-temperature bath, and the auxiliary measuring and calibrating equipment.

The reaction vessel (A) (Figure 1) is constructed of copper, plated inside with an inert material, and sealed by an O-ring. The sample is introduced into the solution from an ampoule (D) when the solenoid (C) is activated, which causes the plunger (E) to accelerate toward the center of the solenoid. The solenoid is de-energized before the plunger reaches the center; the plunger therefore passes through the solenoid and breaks the ampoule. The reaction vessel is calibrated electrically by passing a known current through a heater (B) for a known time.

The reaction vessel is suspended by eight nylon cords (F), which are connected to a cradle (G). The low thermal conductivity of the nylon cords effectively isolates the reaction vessel from the remainder of the system. The cradle is supported by a Plexiglas axle which fits into a Delrin AF socket (I). The socket is mounted on the end of an adjustable support (H) which is attached to the lid of a copper vacuum chamber (L).

The copper envelope (L) which supports the reaction vessel and suspension system is constructed of bright-nickel-plated copper. The exterior walls of the envelope are grooved for and wound with a resistance

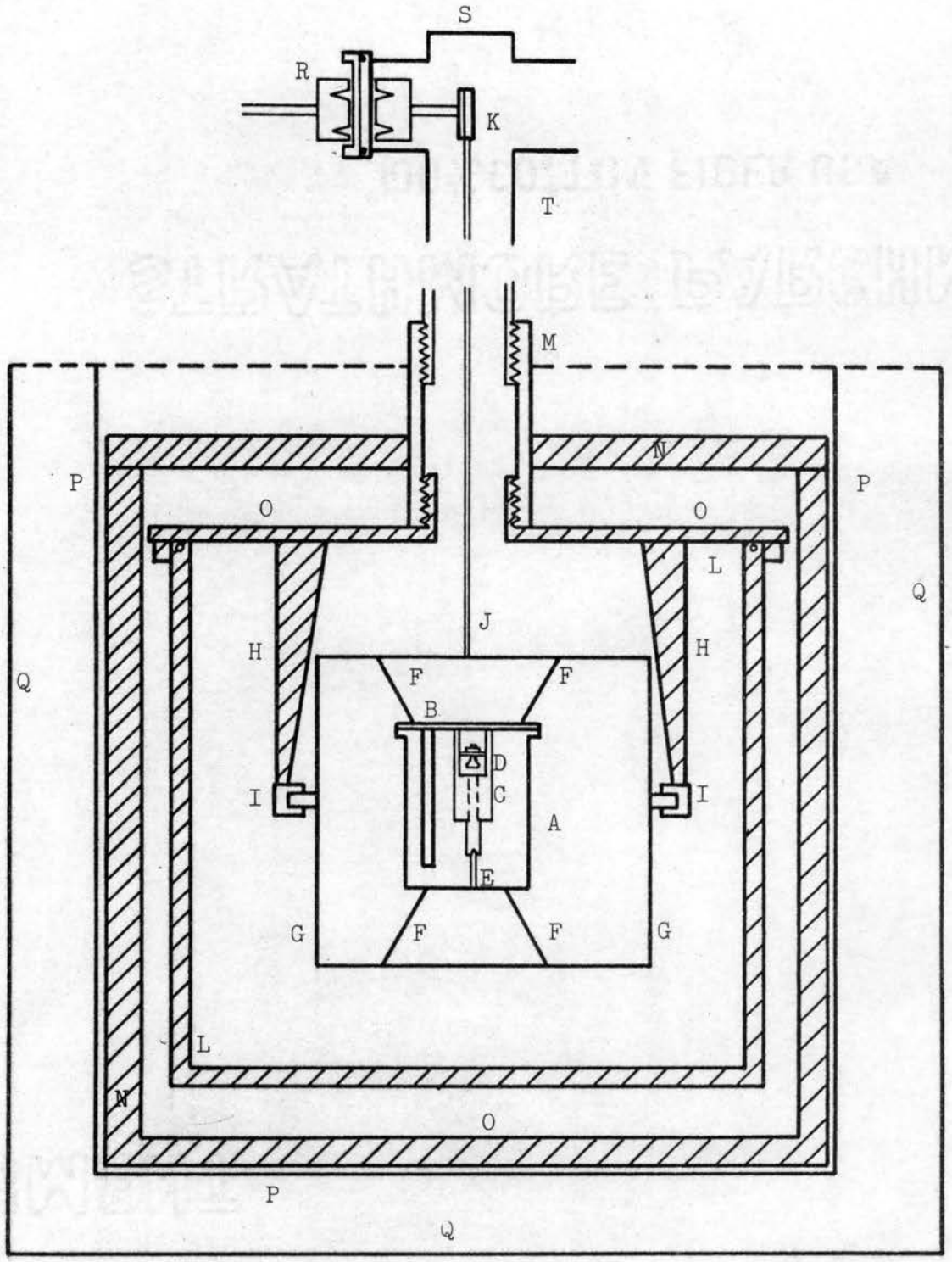

Figure 1. Assembled Calorimeter

thermometer which monitors the surface temperature. The air bath (O) is actually a rather small air gap between the copper envelope and an aluminum jacket. A heater and a resistance thermometer are wound non-inductively in grooves in the outer surface of the jacket and are connected to a commercial temperature controller. The aluminum jacket is insulated from the room by rock-wool insulation contained between two metal cans (P and Q).

The copper envelope (L) is evacuated through copper tubing (T) which is connected to the envelope by a short length of Plexiglas pipe (M). The low thermal conductivity of the pipe aids in the isolation of the envelope. The upper end of the copper tubing (T) is soldered into a "cross" copper fitting.

One of the horizontal arms of the "cross" supports a pulley system (K) which is used to rock the reaction vessel. The rocking motions are transmitted to the pulley (K) from an external oscillating fly wheel through a magnetic coupling system (R), and through nylon cords (J) to the cradle assembly (G). The longitudinal axis of the reaction vessel can be rotated approximately $\pm$ 90 degrees from the vertical.

The other horizontal arm of the "cross" is connected through copper tubing to a diffusion pump which is connected to a mechanical pump through flexible rubber tubing. Necessary vacuum gauges are connected to the copper tubing for monitoring the pressure. On the flange (S) at the top of the "cross" is mounted a large copper terminal block. All electrical leads (for temperature measurement, solenoid activation, and electrical calibration) to the reaction vessel pass through this terminal block.

Reaction Vessel

During the course of this investigation two reaction vessels have been

designed and constructed. The vessels are very similar; however, each has its interesting design characteristics, and each will be described separately.

Reaction Vessel I

Reaction vessel I (Figure 2) is constructed of metal with the exception of the ampoule, ampoule retaining sleeve, and Teflon insulation on the solenoid wire. Machining the cup of the reaction vessel (A) from solid copper rod eliminated two soldered joints (the bottom plate and the top flange) and insured uniformity of construction material throughout the cup. The outer surface of the cup is threaded, 28 grooves per inch; a nickel resistance thermometer is wound non-inductively in the grooves. This thermometer has a resistance of 44.8 ohms at 25° C. A copper shield (H) fits tightly over the grooved surface of the cup. The exterior of the copper cup and the shield are bright-nickel-plated.

The lid (B) of the cup is a copper disc with an O-ring groove (K) to mate with the flange of the cup. A re-entrant well (G) in the lid houses a heater for electrical calibration. The heater is manganin wire (AWG 32) wound non-inductively on a form (L) and is sealed in the well by an O-ring in the top of the form. The heater has a resistance of 56 ohms at 25° C. Several drops of Octoil diffusion pump oil are added to the well, before the heater assembly is installed, to achieve faster heat transfer from the heater to the calorimeter vessel. Suspended from the lid by two copper tubes, which also serve as conduits for its electrical leads, is a solenoid (C). The solenoid has 2000 turns of Teflon-insulated high-temperature magnet wire (AWG 32) wound on a brass spool which is 0.750 in. high and has a diameter of 0.750 in. The center of the spool is hollow to allow the plunger

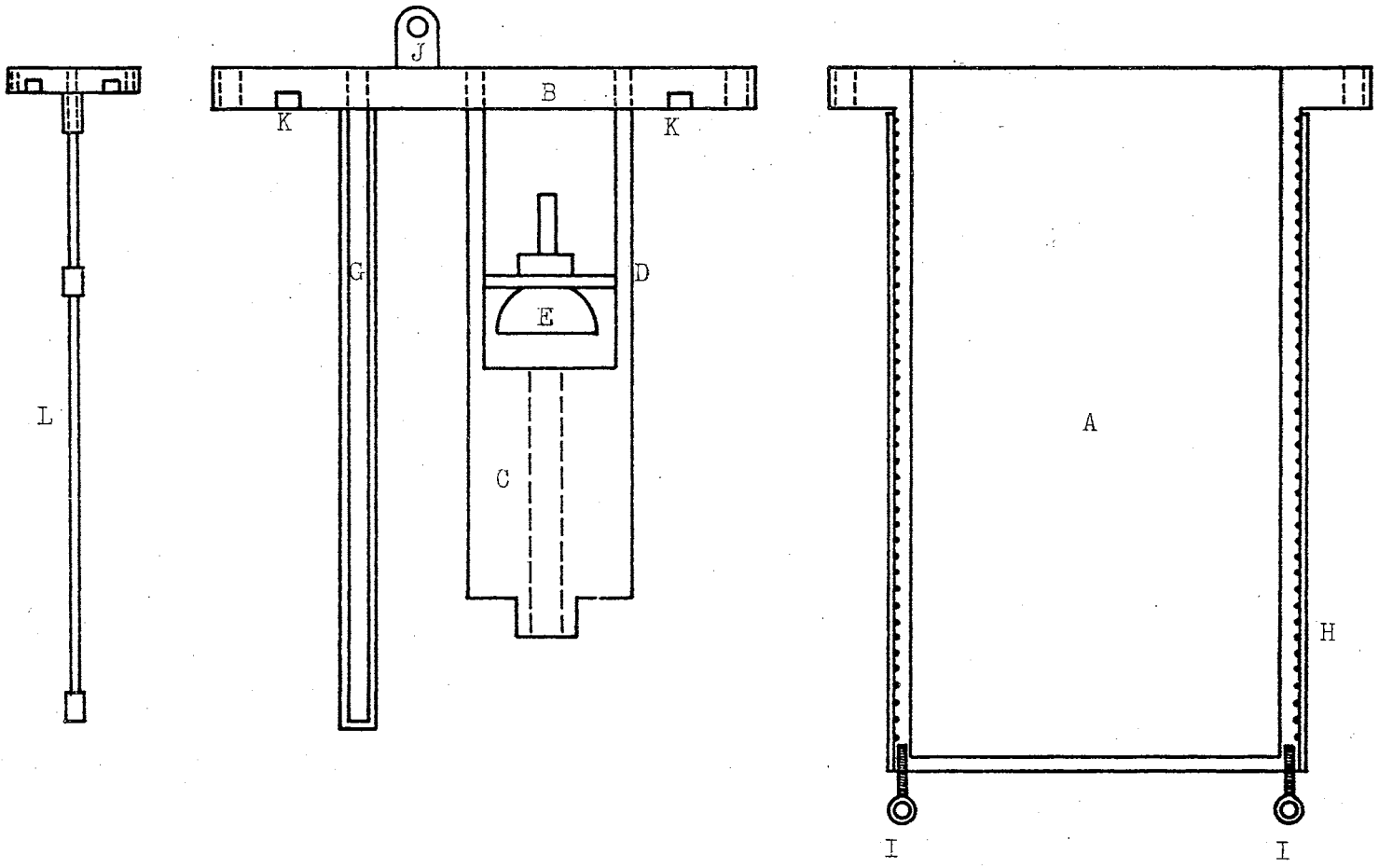

Figure 2. Reaction Vessel I

to pass through when the solenoid is activated. Enclosure of the solenoid is by a copper shield which is soldered to the spool with low-melting indium solder.

The sample is contained in a thin-walled glass ampoule (E) which is located above the solenoid. The ampoules are made from Pyrex tubing and are blown to uniform size in a graphite mold.

The ampoule is positioned above the solenoid by a brass plate (D) which is soldered to the solenoid support tubing. The bottom of the brass plate has a spherical recess with the same curvature as that of the ampoule; hence, when an ampoule is in position, approximately one-third of the outside surface area of the ampould is in good physical contact with the plate. A slot cut from the outer edge of the plate to the center of the spherical recess accepts the thin neck of the ampoule and permits the ampoule to be seated in the recess. The ampoule is held in place by a Teflon sleeve which fits the neck of the ampoule securely and rests on top of the plate.

The sample is introduced into the solution by energizing the solenoid for approximately 10 milliseconds with 1 ampere. A gold-plated iron plunger, which is located in a guide shaft below the solenoid, is accelerated toward the center of the resulting magnetic field. Before the plunger gets to the center of the field, the solenoid is de-energized; the plunger then passes through the solenoid, impinges on the glass ampoule, and breaks it.

All parts of the reaction vessel which contact the solution have been gold-plated, 0.005 to 0.008 in. thick, and all exterior parts have been bright-nickel-plated. The reaction vessel is supported in the cradle (Figure 1) by eight suspension eyelets, four on the lid (J) and four on the cup (I). The reaction vessel has an internal volume of approximately one

hundred cubic centimeters and a heat capacity of approximately seventy-five calories per degree.

Reaction Vessel II

The second reaction vessel is constructed in three main parts from a 3.500-in.-diameter billet of beryllium copper purchased from Brush Beryllium Company. Beryllium copper alloy A 10 was chosen for its high thermal conductivity and its strength when anealed. Each of the three main parts of the vessel (Figure 3), the base with solenoid well (A), the central cylinder (B), and the lid with re-entrant wells (C), was machined from a solid bar and has no soldered joints or welds. The exterior surfaces of the vessel are bright-nickel-plated to minimize radiative thermal transfer to and from the vessel. The interior surfaces are plated (0.008 in. thick) with tantalum which is extremely inert to all solvents and solutions of current interest with the exception of fluorides.

The lid has a diameter of 3.625 in. and a flange thickness of 0.200 in. Eight bolt holes spaced at 45 degree intervals were drilled to mate the lid and the central cylinder. The two re-entrant wells (D) was for a heater and one for a thermometer, are 1.500 in. long, 0.250 in. in outside diameter and 1.350 in. from center to center. The inner diameter of these wells is 0.173 in. and the thickness of the bottom is 0.075 in.

The central cylinder has an inner diameter of 2.100 in., an outer diameter of 2.500 in., and a total height of 3.000 in. The upper and lower flanges are 0.290-in. thick and 3.625 in. in diameter. Eight threaded holes, 45 degrees apart, accept screws to connect the lid and base to the cylinder. About two-thirds of the original flanges have been removed to eliminate unwanted mass and heat capacity. O-ring grooves

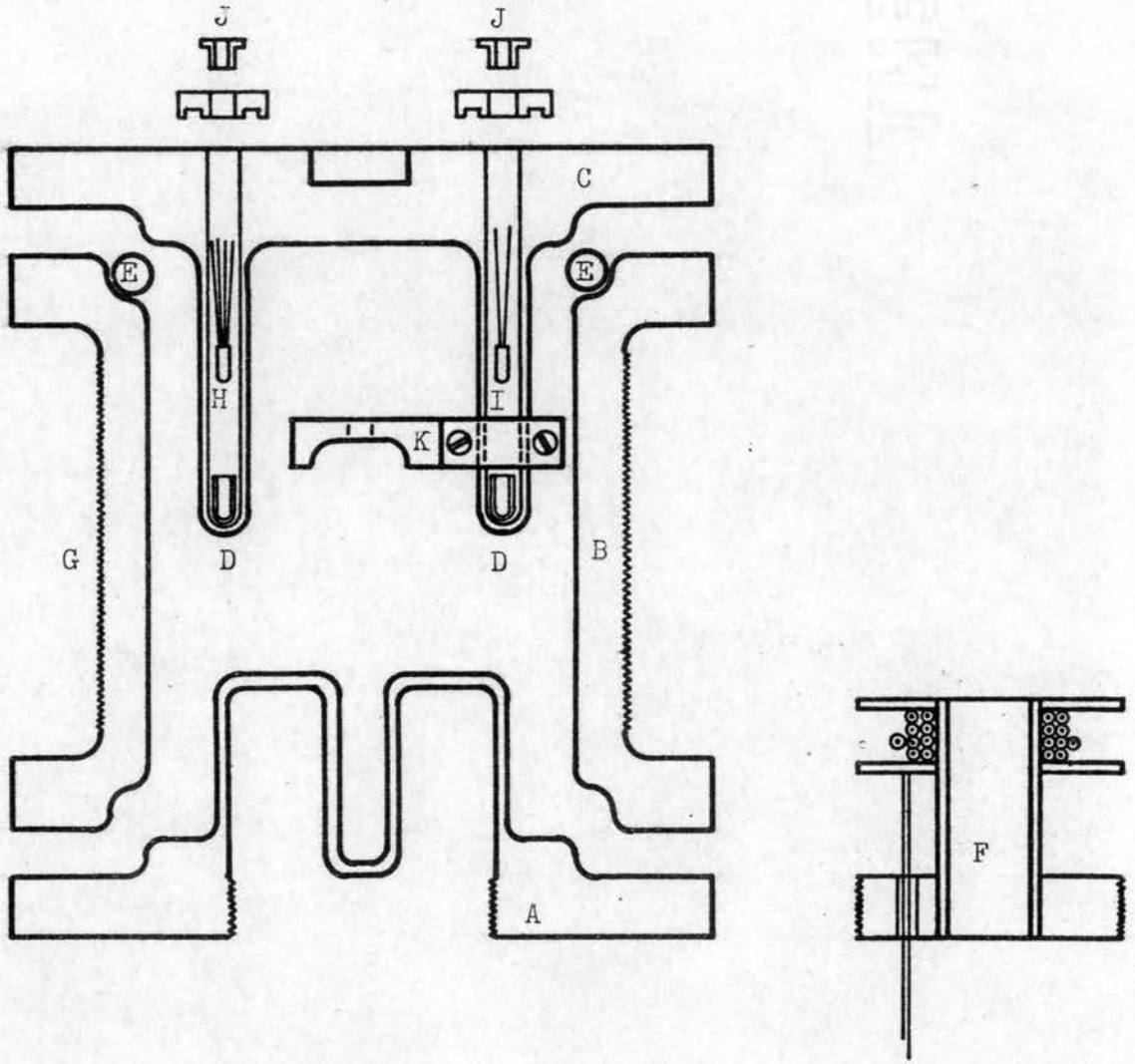

Figure 3. Reaction Vessel II

(0.210 in. wide, with a radius of 0.125 in.) in the wall of the cylinder accept a Viton O-ring (Parker number 2-330) (E).

The base has a diameter of 3.625 in. and a flange thickness of 0.200 in. The base has eight bolt holes which mate with the flange on the center cylinder. The solenoid housing unit is cylindrical, rises 0.932 in. above the base plate, and has a wall thickness of 0.062 in. A cylindrical well, with a 0.250-in. inner diameter, is located in the center of the housing. The outer diameter of the plunger well is 0.375 in. and the well has a total length of 1.000 in. The inner diameter of the solenoid housing is 1.375 in; the lower portion is threaded (thirty two threads per inch) to accept the solenoid and its support.

The solenoid (F) has 1023 turns of Formvar-coated, copper magnet wire, (AWG 30) and has a resistance of 26 ohms. It is wound on the upper portion of the solenoid spool which is 1.373 in. in diameter and 0.375 in. between plates. A tube, machined for very close fit with the plunger well connects the solenoid spool to a threaded plug which screws into the threaded opening to the solenoid housing. Good thermal contact is maintained between the reaction vessel and the solenoid by close machining tolerances and a few drops of silicone oil. The leads from the solenoid pass through holes drilled in the base.

The outer wall (G) of the central cylinder is threaded and is wound non-inductively with a nickel resistance thermometer. Because of its location, the thermometer will give a surface temperature which is effectively an average over any "hot" or "cold" spots in the reaction vessel (11).

The interior thermometer (H) and the heater (I) are miniature four-lead platinum resistance thermometers developed by Minco Products, they are 0.393

in. long and 0.125 in. in diameter. Each has a nominal resistance at 25°C of 100 ohms. The heater and the resistance thermometer are mounted in copper blocks which are in good thermal contact with the interior walls of the respective wells; a few drops of silicone oil insure this good contact. The leads which pass through a Plexiglas vacuum seal (J) in the top of the lid are insulated with Teflon "spaghetti".

The ampoule used in vessel II is the same type and is constructed in the same manner as those previously described. The ampoule is supported above the plunger well by a tantalum bar (K). The support bar is clamped to the heater well with two tantalum screws. The bottom of the support is machined with the same curvature as the ampoule; secure seating is thereby provided for the ampoule. The ampoule is held in place by a Teflon sleeve. When assembled, the reaction vessel has an internal volume of approximately 130 cubic centimeters, a mass of approximately 1200 grams, and a heat capacity of approximately 220 cal. per degree.

The Suspension System

The reaction vessel is suspended from a cradle by eight nylon cords, four on the top and four on the bottom. The cradle assembly (Figures 4 and 5) is in the general shape of two parallel "X's" with tubes connecting the corresponding ends of the "X's". The "X's" (A) were machined from a 0.250-in. thick copper plate and are 4.250 in. high. Each of the connecting tubes (B) is a 0.250-in. copper tube and is 4.250 in. long. The cradle pulley (D) was constructed from 0.125-in. copper plate, has an inside diameter of 5.875 in. and an outside diameter of 6.875 in. The outside diameter of the pulley is grooved to accept a nylon cord; the ends of which are connected to an eyelet on a retaining screw (F). Each of these retain-

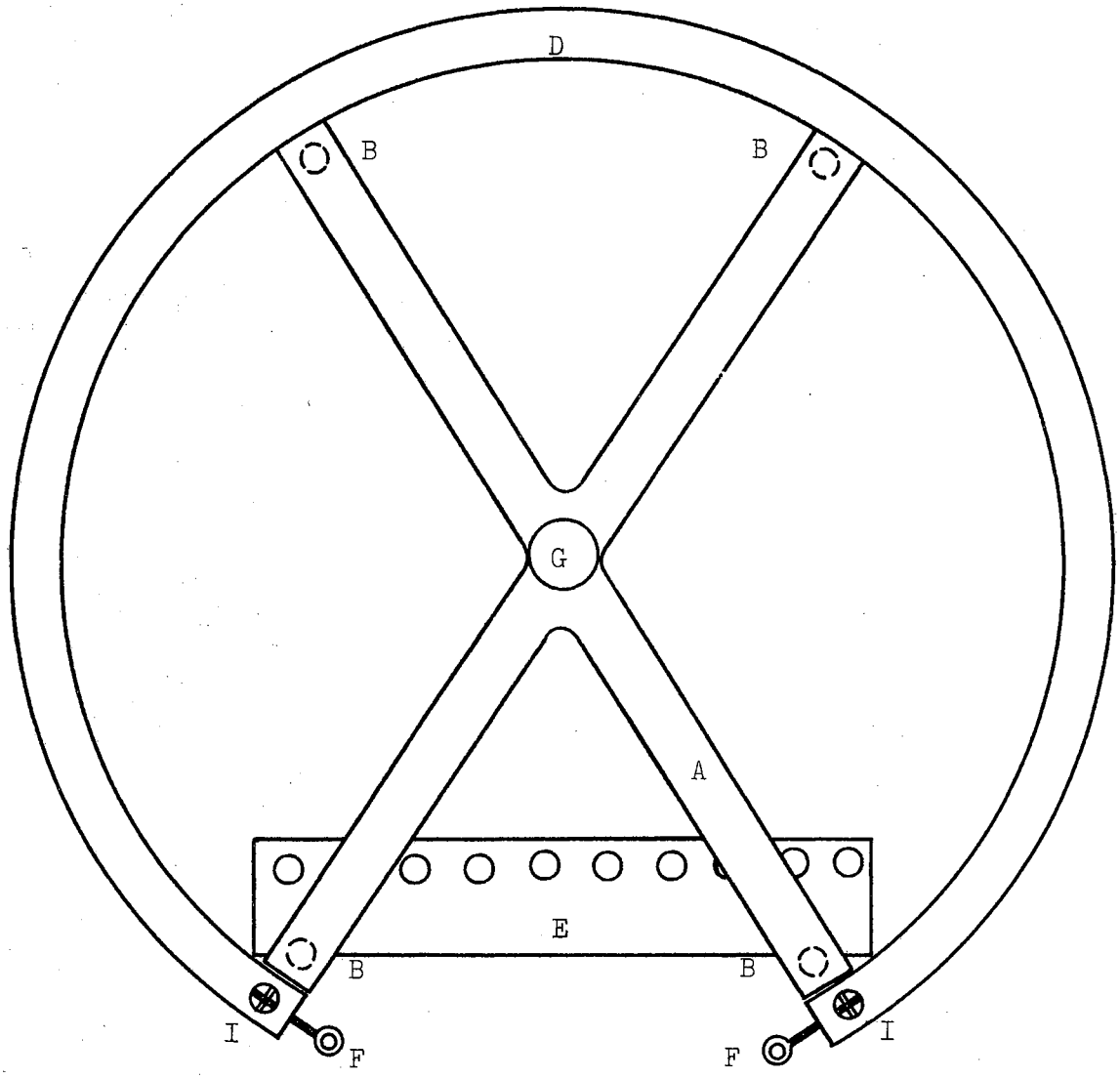

Figure 4. Cradle Assembly (End View)

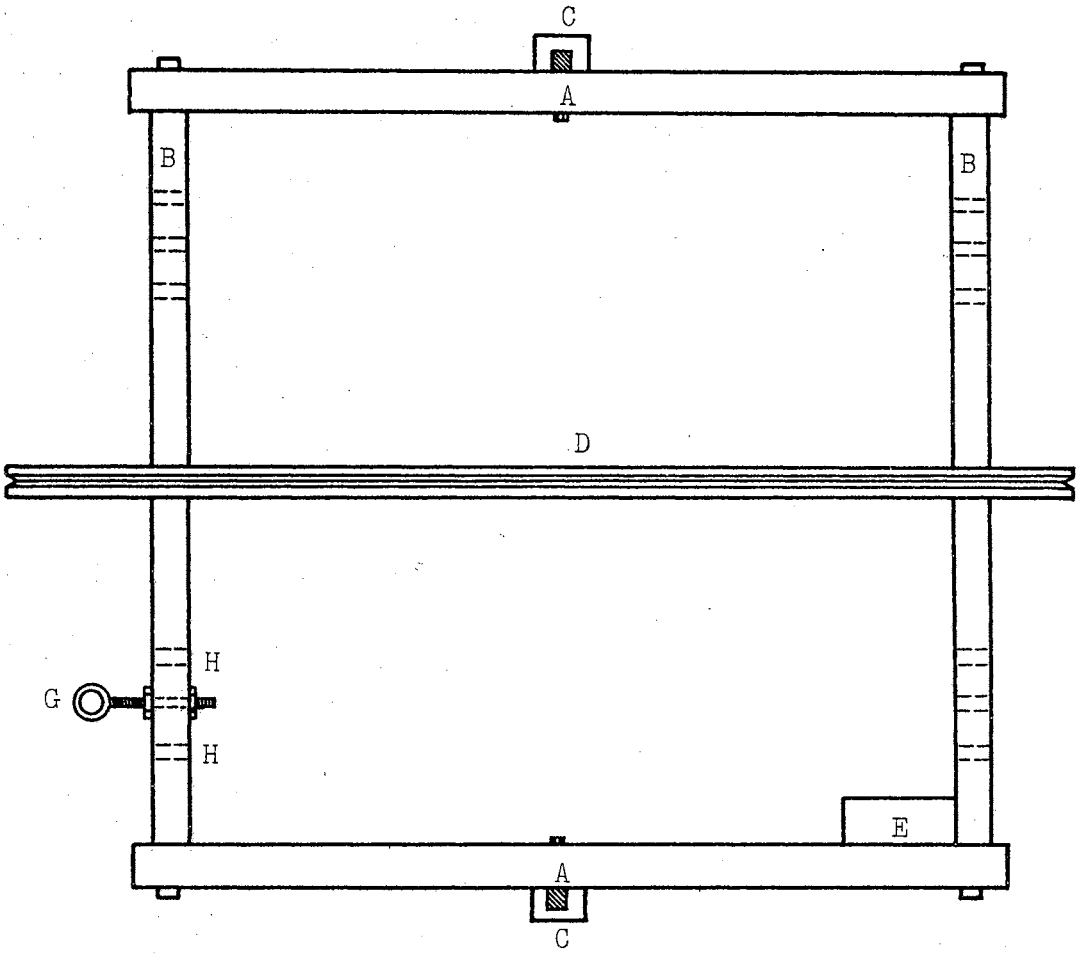

Figure 5. Cradle Assembly (Top View)

ing screws is adjustable in length, by means of a retaining nut and finger hole (I), over a distance of approximately 0.500 in. Each of the four connecting rods (B) has two sets of three 0.063-in.-diameter holes (H) the axes of which are at an angle from the vertical of 45 degrees. The first hole is 0.500 in. from the "X" support; succeeding holes are 0.250 in. apart. An adjustable eyelet (G) may be placed in any of the holes; the nylon cords from the reaction vessel are secured to eight of these eyelets.

An electrical barrier strip (E) is connected to the bottom of one "X" support. Leads to external equipment are soldered to the strip while the leads to the reaction vessel are connected by the conventional screw. Location of the barrier strip on the cradle insures that no physical strains will be placed on the electrical connections to the reaction vessel as the vessel rotates; the barrier strip rotates with the reaction vessel.

At the center of the "X's" are Plexiglas shafts (I) which have a diameter of 0.375 in. and are 0.250 in. long. A brass insert (G) in the center of the Plexiglas shaft provides added strength and a convenient means for attaching the shaft to the cradle.

The entire cradle assembly is supported by two nickel-plated copper arms (Figure 6). The Plexiglas shaft (I) fits into a Delrin AF socket (B) which is 0.625 in. in diameter, 0.250 in. long, and is machined to accept the Plexiglas shaft with a minimum of play. Delrin AF, which is acetal resin polymer reinforced with Fluorocarbon resin, was used for the bearing material because it has a very low coefficient of friction. The socket is threaded to accept a screw for mounting on the adjustable socket block (C) which is 1.625 in. long, 0.500 in wide, and has a one-inch slot

to allow adjustment along the vertical axis. The adjusting screw also serves as the mounting screw which holds the socket block to the support bar (D). The support bar has a hole (H) through the top to allow it to slide on a 0.200-in.-diameter rod (E) which is flattened on the bottom and side to allow the support bar to be secured by set screws. The rod is 2 in. long and provides one inch of adjustment along the horizontal axis. The rod is secured to two brackets (F) which are screwed to the lid of the copper envelope.

The Vacuum Envelope

The vacuum envelope is constructed from a 9.500-in. length of copper pipe which has an inner diameter of 9.000 in. and an outer diameter of 10.125 in. A 0.250-in. thick copper plate is silver-soldered to the bottom to form a can. The envelope is bright-nickel-plated. The envelope has in its outer cylindrical surface shallow grooves (4 threads per inch) into which is wound (non-inductively) a nickel thermometer the resistance of which is approximately 93 ohms at 25°C. A small terminal block which is near the top of the envelope provides a place for external connections to the nickel thermometer. The terminal block is mounted on a copper block which is 0.750 in. wide, 0.750 in. long, and 0.188 in. thick; the copper block has the same curvature and is in good thermal contact with the envelope.

A 0.188-in. square groove in the top edge of the envelope retains a 0.188-in.-diameter O-ring which seals the envelope. Six lugs, 0.500 in. by 0.375 in. by 1 in., are silver-soldered to the top edge at 60-degree intervals and are drilled and tapped to mate with bolt holes in the lid of the copper envelope which was machined from a copper plate 0.375 in.

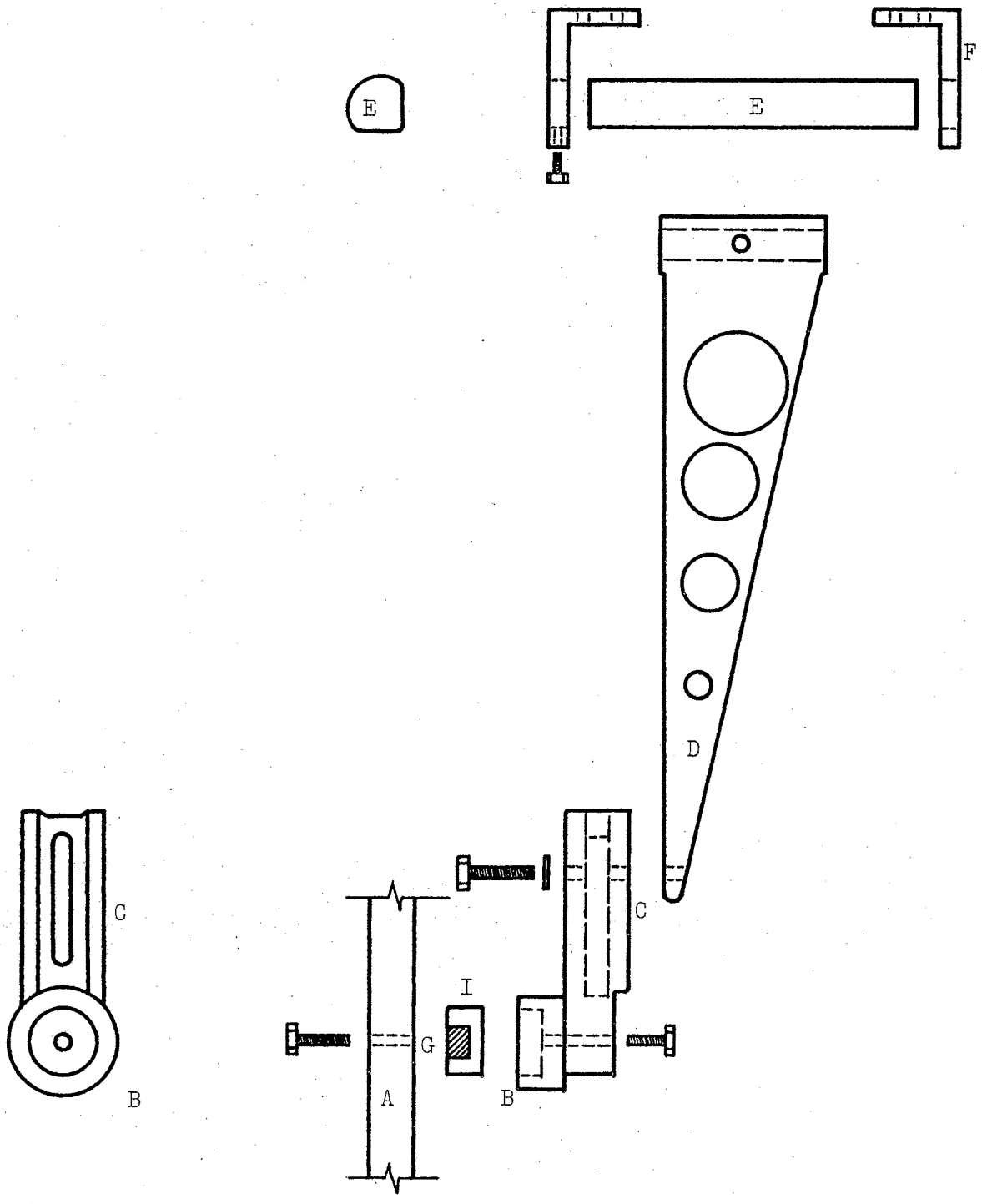

Figure 6. Cradle Support Arm

thick. The edges of the lid are notched so that a platinum resistance thermometer can be inserted into the air gap between the copper envelope and the aluminum jacket. A one-in. length of 1.500-in.-diameter copper tube is silver-soldered into a 1.500-in.-hole in the center of the lid.

The Isothermal Jacket

The isothermal jacket is constructed from a cast cylinder of aluminum. The top is constructed from a 0.250-in. plate of aluminum. The outer diameter of the jacket is twelve in. and the inner diameter is eleven in. The sides are grooved (Figure 7) such that a heating element of Evanohm wire and a 100-ohm nickel thermometer may be wound non-inductively on it. The side view (A) shows that the heating element was wound on the extreme exterior of the vessel and the resistance thermometer was in deeper grooves. This arrangement allows the heat from the heater to be dissipated to the entire vessel before reaching the thermometer. The heating element was also wound non-inductively on the bottom of the vessel and the lid as indicated in figure 7 (B). The heater and the nickel thermometer were connected to a Hallikainen Thermotrol temperature regulator.

Vacuum Manifold

One end of a one-inch length of 1.500-in. diameter copper tubing is silver-soldered into a hole in the lid of the copper envelope. The other end is threaded and mated with a threaded 6.000-in. length of Plexiglas tubing. Before the two were connected, a thin coating of Epoxy resin was applied to the threads to add strength and insure impermeability. The Plexiglas tube has an inner diameter of 1.500 in. and an outer diameter of 2.500 in. A 7.000-in. length of 1.500-in. diameter copper tube is sealed to the top of the Plexiglas in the same manner. The Plexiglas

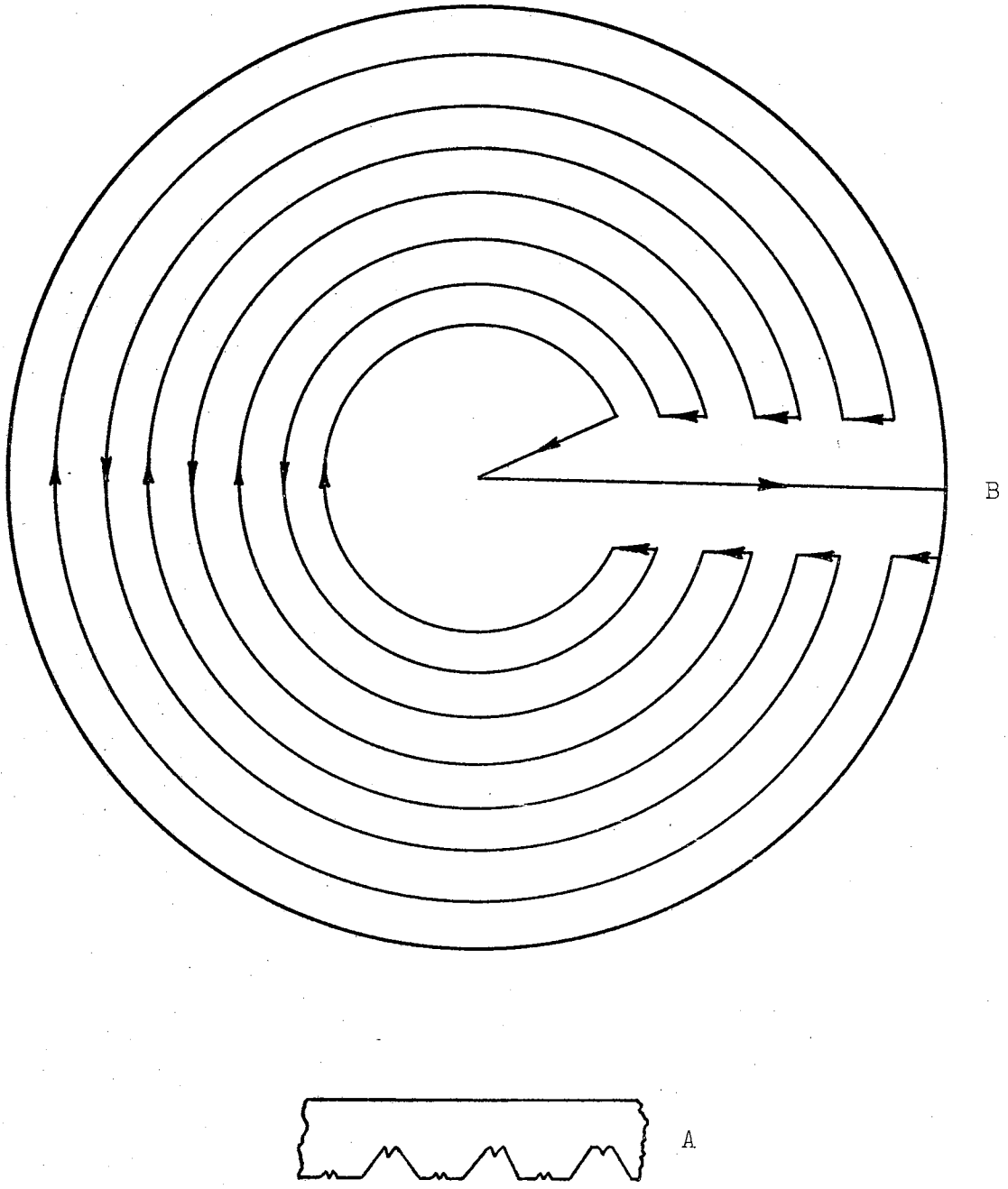

Figure 7. Aluminum Jacket Heater Winding (Top And Side View)

connector was installed to reduce thermal transfer between the copper envelope and the surrounding. The 7-in. length of copper tube is silver-soldered into the bottom arm of a standard 1.500-in. copper "cross". The remaining three arms of the "cross" are fitted with flanges which have O-rings.

One of the horizontal arms of the "cross" is connected to a CVC type VMF-20W diffusion pump by an 8-in. horizontal section, a horizontal-to-vertical "elbow" and a 37-in. vertical section of 1.5-in. copper tubing. The diffusion pump is silver soldered to the copper tube through a 1.500-in.-to 2-in. adapter. The diffusion pump is connected by a two-foot length of rubber hose to a Welch Duo-Seal mechanical pump. The pressure is monitored at the "cross" by a Hastings DV-6M thermocouple gauge and a cold cathode ionization gauge. The pressure is read on a Miller-Oklahoma State University vacuum gauge.

The Rocking Mechanism

The rocking of the reaction vessel is accomplished with a system of pulleys connected with nylon cord. One end of the cord is connected to the adjustable eyelet (F, Figure 4) on the cradle pulley. The cord follows the groove around the pulley, over a guide, up the Plexiglas tubing to the "cross," around an upper pulley which is in the copper "cross," and back down to the other eyelet on the cradle pulley.

The upper pulley has a diameter of 1.250 in., is 0.500 in. thick, and is threaded with 24 threads per inch. It is connected to a six-pole magnet by a 0.250-in. diameter stainless steel shaft. The shaft is supported in one of the horizontal arms of the copper cross by two sets of ball bearings which are mounted in two circular brass plates connected by a brass tube;

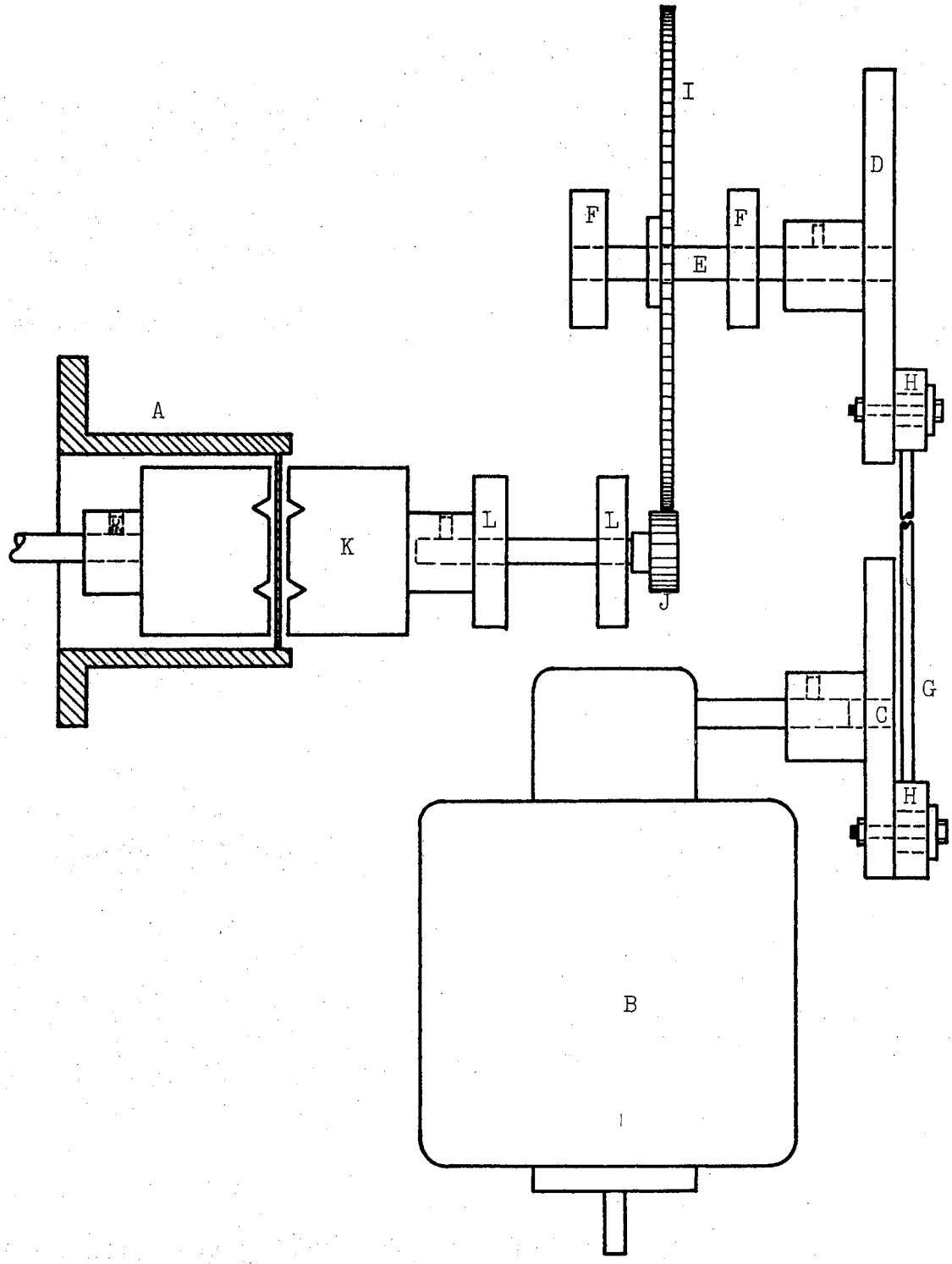

Figure 8. Rocking Mechanism

correct alignment of the pulley shaft is thereby insured.

The upper pulley is rotated by a coupled magnetic drive similar to the ones described by Coenraad and Lavelle (5) and Edwards (8). The two six-pole magnets (Figure 8) are separated by a brass cup (A) which is mounted on the flange of one horizontal arm of the "cross". The driving magnet is rotated, through a fly-wheel-gear train mechanism, by an adjustable speed motor (B) controlled by an electronic controller.

A 2.500-in. diameter brass fly-wheel (C) is mounted on a flattened portion of the motor's shaft by a set screw. A larger brass fly-wheel (D) (3.0 in. in diameter) is mounted on a 0.250-in. shaft (E) supported by ball bearings in two mounting blocks (F). The two fly-wheels are connected by a rod (G) with similar cylindrical bearings (H) on each end. The two fly-wheels are separated by 4.500 in., center to center, and the connecting rod is 4.375 in. from center to center of the cylindrical bearings. Mounted to the same shaft as the larger fly-wheel (D) is a 2.125-in.-radius aluminum gear (I) with 128 teeth, and the aluminum gear mates with a 0.312-in.-radius brass gear (J) which has 15 teeth; the increase in speed of rotation from aluminum gear to brass gear is therefore 8.5 to 1. The brass gear is mounted on a 0.250-in.-diameter shaft which passes through a ball bearing and thrust bearing set mounted on two mounting blocks (L and M); the 6-pole magnet (K) is mounted on the other end of the shaft.

The rocking motion (figure 9) is achieved by requiring the smaller fly-wheel (C) to rotate continuously while the larger fly-wheel (D) oscillates through an arc of 165 degrees. This is achieved by properly positioning the two fly-wheels and the connecting rod (G). Figure 9 shows that when the connecting rod (G) and bearing on the smaller fly-

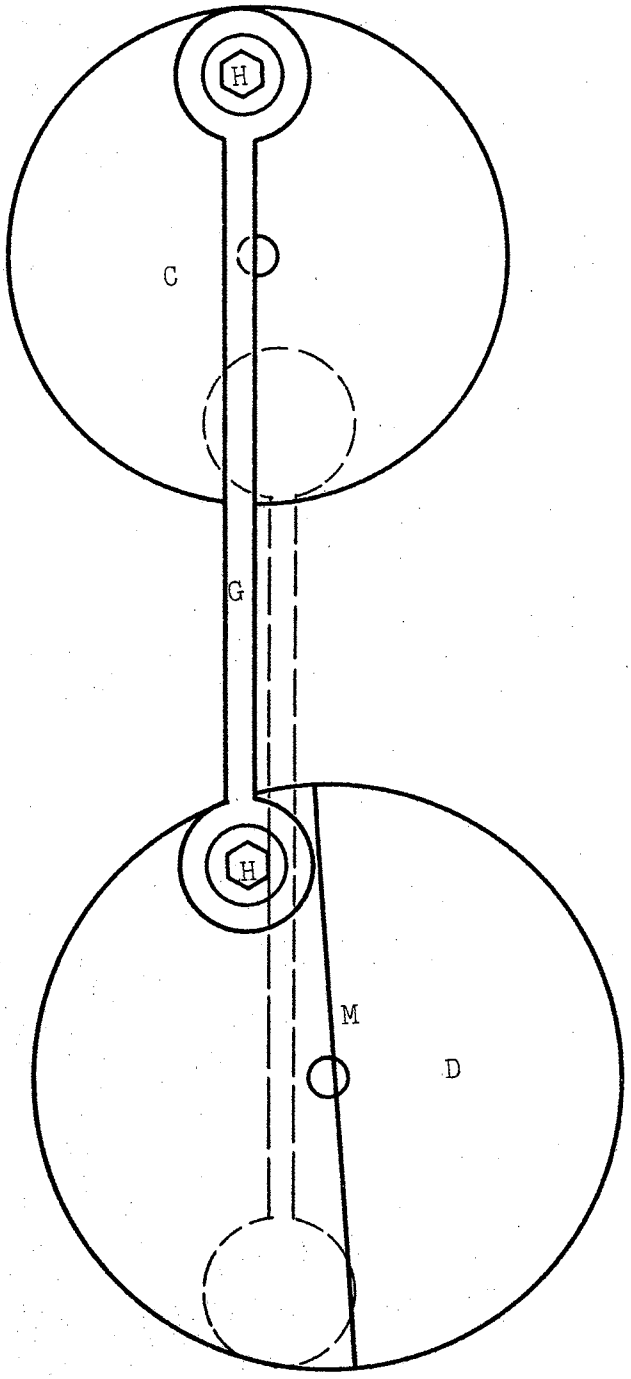

Figure 9. Conversion of rotary motion to oscillatory motion

wheel is maximum distance from the larger fly-wheel, the bearing of the smaller fly-wheel has not arrived at the center horizontal line (M). Similarly, the dotted lines show the bearing of the smaller fly-wheel being at the nearest approach to the large fly-wheel; the bearing on the larger is still below the center horizontal line.

In the power train for rocking, the smaller fly-wheel has direct coupling with the shaft of the motor which causes it to rotate in a clockwise direction. This motion is transmitted to the larger fly-wheel through a connecting rod causing this wheel to oscillate. The oscillations are transmitted through direct coupling to the large gear. The oscillations are converted by the mated smaller gear to several rotations which are transmitted to the upper pulley by direct coupling of the six-pole magnet. The diameters of the upper pulley and cradle pulley are such that the several rotations of the upper pulley produce an oscillation through 140 degrees of the cradle.

Terminal Block

A large copper-enclosed terminal block (Figure 10) was designed, built, and mounted on the top arm of the "cross" to serve a dual purpose. First this is a convenient place to make the electrical connections; second, the mass of the copper enclosure and the isolation of the terminals from the surrounding minimize the possiblity of thermal electromotive forces at the connection points.

The electrical leads from the reaction vessel exit from the upper arm of the "cross" and the vacuum system through a Kovar glass-to-metal seal (A) which is soldered into the mating flange (B) of the upper arm of the "cross"; the Kovar seal has fifteen tubular feed-throughs which

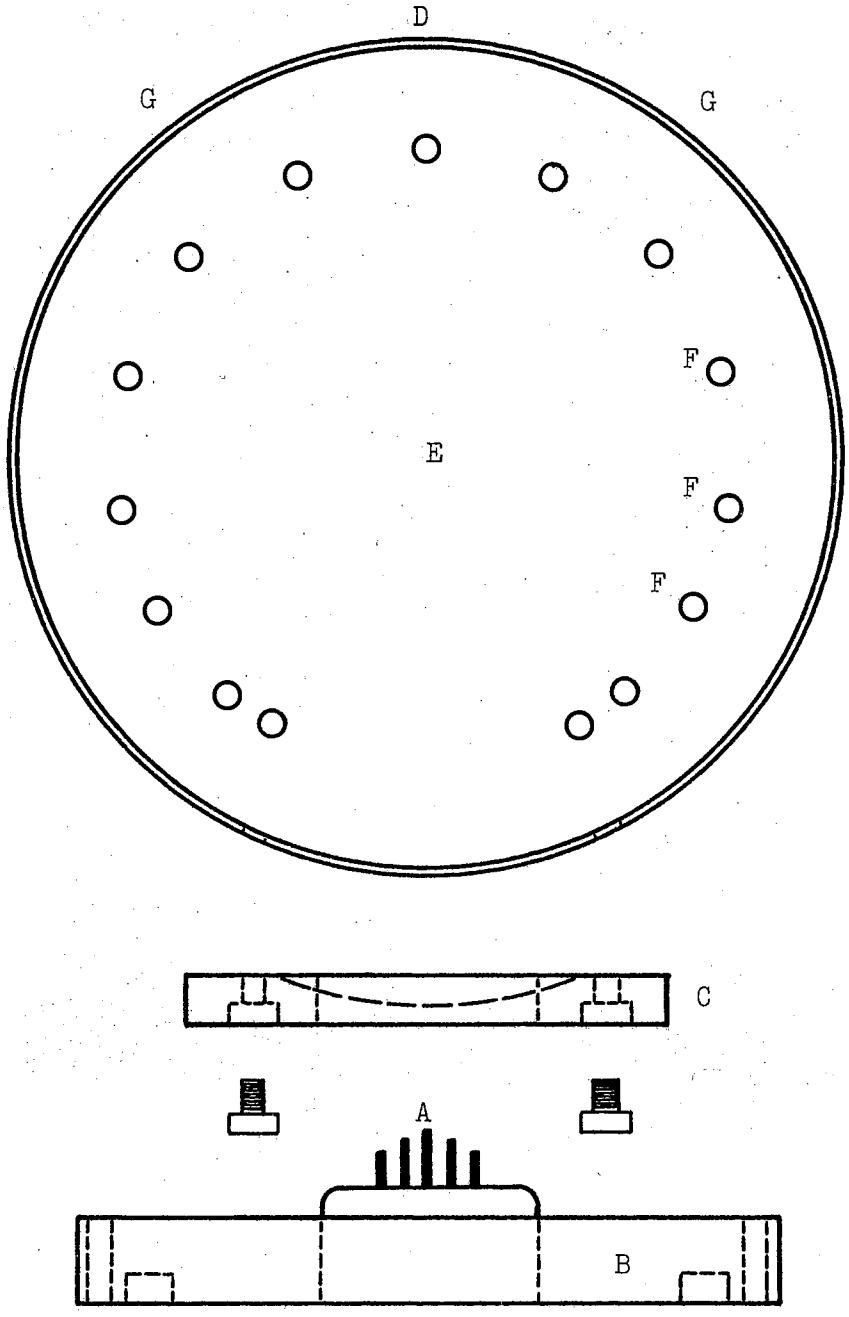

Figure 10. Terminal Block

permit unbroken passage of the electrical leads. The terminal block is mounted to a 1.75-in. brass ring (C) which is held in place by two retaining screws. The terminal block consists of a large copper ring (D) 4.125-in. outer diameter, 3.875-in. inner diameter, and 1.250-in. wide. A 0.188-in. thick circle of Plexiglas (E) is mounted in the center of the copper ring by two set screws through the copper ring. Fourteen 0.500-in. lengths of copper wire (AWG 16) (F) are mounted in the Plexiglas on a 2.875-in. diameter circle concentric with the ring. Electrical connections are made to the two ends of the wire.

The copper ring is recessed to accept two 0.0625-in. copper lids which protect the connections from the surroundings. The ring has four 0.250-in. access holes (G) across the top, one inch apart. A 0.750-in. bottom hole is provided for leads from the Kovar seal.

CHAPTER III

ELECTRICAL EQUIPMENT

The electrical components will be discussed in the specific circuits where they are used. These circuits, grouped according to their function, are the temperature measuring circuit, the solenoid control circuit and the electrical calibration circuit. Commercial components in the circuits will not be discussed in detail and the reader is referred to the indicated references or the manufacturer for additional information.

Temperature Measuring Circuit

The temperature measuring circuit (Figure 11) is designed to measure independently the resistance of three resistance thermometers: $\underline{R}_e$ is a nickel thermometer which is located on the copper envelope and monitors the surface temperature of the envelope; $\underline{R}_1$ is a nickel thermometer which is wound on the surface of the reaction vessel; $\underline{R}_2$ is a miniature platinium thermometer which is in a re-entrant well of the reaction vessel and monitors the interior temperature of the vessel. The two nickel thermometers were locally fabricated from AWG 35 Ballast nickel wire.

The miniature platinium thermometer is a special modification of a commercial item; it has a nominal resistance at 25°C of 100 ohms and four leads rather than the three of the commercial item.

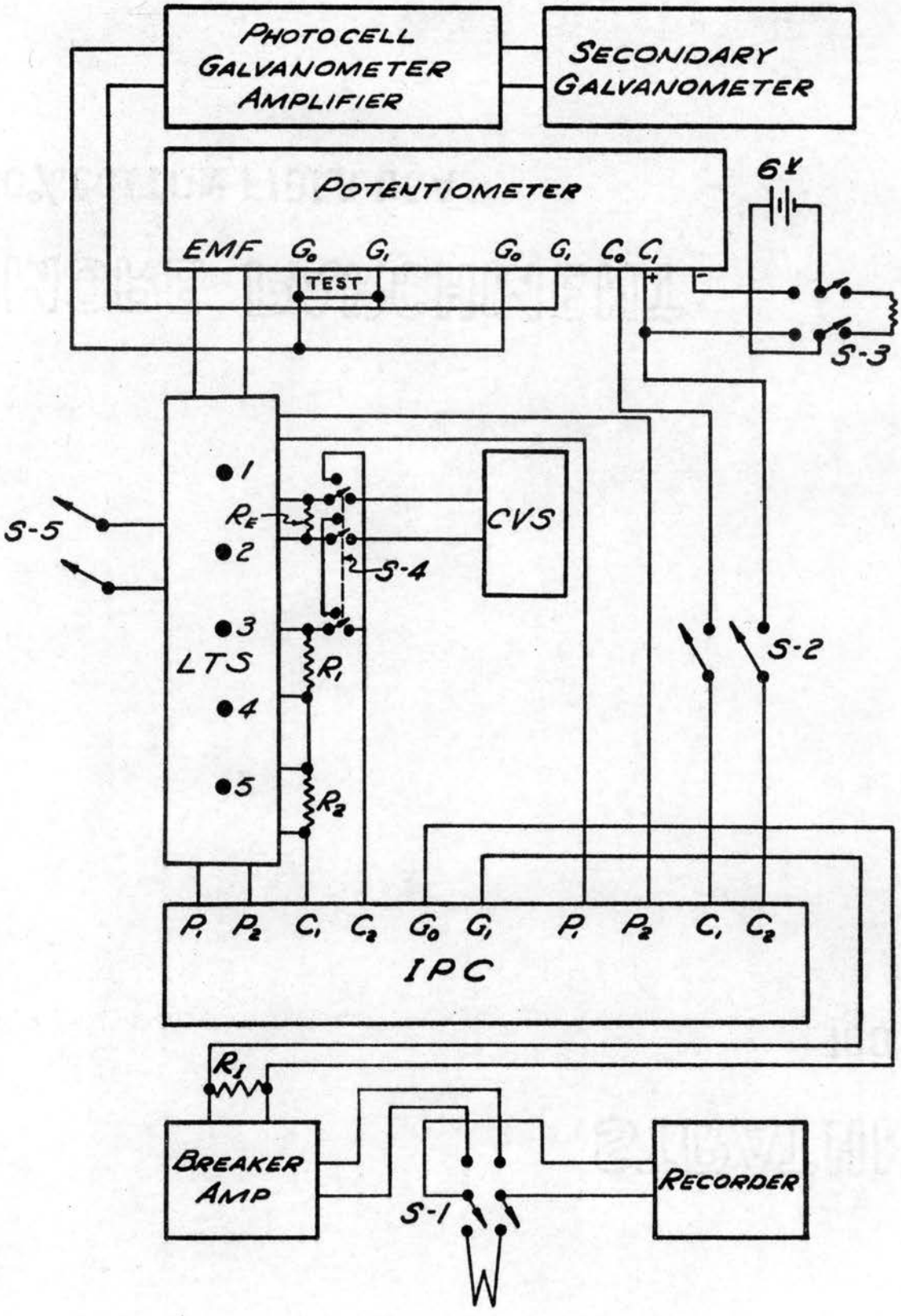

Figure 11. Temperature Measuring Circuit

The resistance is measured by comparing the potential drop across the resistor with the potential drop across a variable four-terminal standard resistor. The resistors are wired in series; therefore, any change in the current will cause a proportional change in the voltage across both resistors and will not effect the comparison. The comparator is a Commander type 9800 isolating potential comparator and the variable four-terminal standard resistor is a Commander type 9144-L Dauphinee potentiometer.

As described by Dauphinee (6), the comparator isolates the compared potentials with a low-noise chopper. The voltages are compared by impressing each in turn across a capacitor. When the voltages are unequal, a current flows and is detected at the galvanometer terminals. A Beckman breaker amplifier is connected across these terminals in parallel with an impedance-matching resistor $\underline{R}_i$. The output of the amplifier is connected to a Sargent MR recorder which provides a continuous record of the resistance.

Since it is desirable to measure any of the resistances at any time, the resistors are connected in series to the current terminals of the comparator. The connection between $\underline{R}_1$ and $\underline{R}_2$ is made on the barrier strip inside the copper envelope; $\underline{R}_e$ is connected to a low-thermal-EMF selector switch (Figure 12). The potential from each resistor is applied to the potential terminals of the comparator by "making" the appropriate connecting switch which is a break-before-make type.

When the potentiometer is used as a standard four-terminal variable resistor, it cannot simultaneously be used to measure potentials; there-

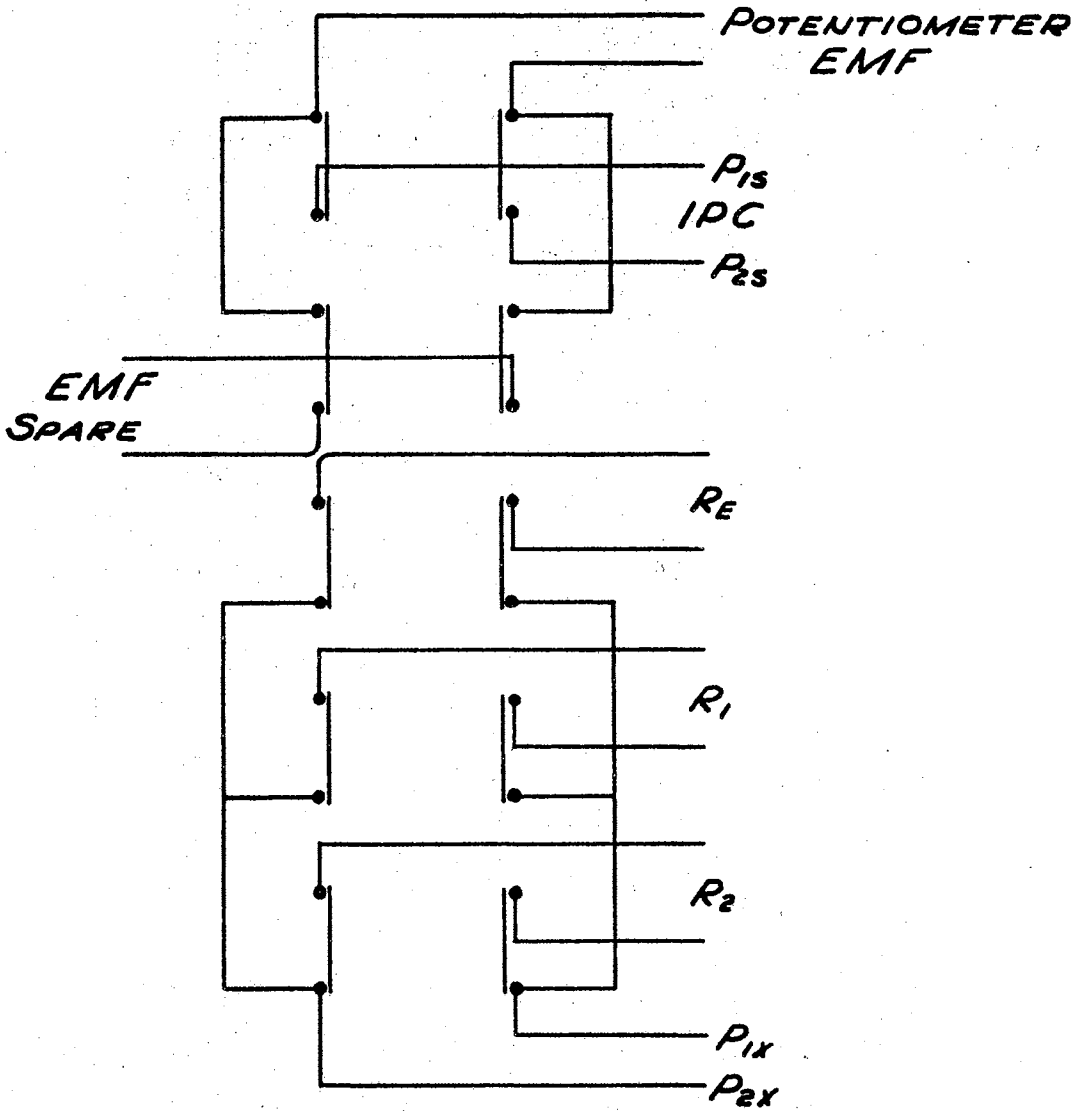

Figure 12. Wiring Diagram for Low Thermal Switch

fore, the six-volt battery is disconnected by operating S-3. A 300-ohm resistor is connected to the other side of the switch to keep a constant load across the battery.

The potentiometer EMF terminals are connected to the post 1 of the low-thermal-EMF switch by AWG 24 copper thermocouple-extension wire. Two short copper extensions are connected between post 2 and post 1 thereby providing dual access to the EMF terminals of the potentiometer. Post 1 leads to the potential terminals of the comparator and post 2 to an exterior heavy-duty double-pole double-throw all copper switch S-5. If post 2 is locked down, two external EMFs can be measured depending on the position of the switch S-5.

To make an EMF measurement with the potentiometer the following procedure must be observed. Switch S-2 is opened to disconnect the current leads of the comparator from the potentiometer. The shorting strip is removed from the measuring galvanometer terminals G_o and G_1. Switch S-3 is thrown from the dummy load to the potentiometer battery terminals. Post 2 of the low-thermal-EMF switch is locked in position and switch S-5 is moved to the desired position. As soon as the potentiometer current is adjusted and is checked for stability, potentiometric determinations can be made. The reverse procedure is used to connect the potentiometer to the comparator for resistance determinations.

The procedure for measuring resistances is as follows. With the system assembled as shown in figure 11, the comparator is turned on and allowed to warm-up for several minutes. While the comparator is warming-up, the null point of the recorder is displaced to a reading of 100 chart units. The current through the resistors is adjusted by controls on the

comparator to 2 milliamperes.

Since the resistance thermometers all have resistances below 100 ohms, the maximum power dissipated in any one is less than 4 microwatts. The calorimeter has two of these resistors and the power dissipated in the vessel is approximately 8 microwatts, or for a run of 2000 seconds the energy input remains constant and can be corrected for in the drift rate.

Post 3, 4, or 5 of the low-thermal-EMF switch is depressed to select the resistance to be measured. The lead-balance switch is moved from the "OFF" position to "L-B" and the lead balance is adjusted to give zero deflection on the Lindeck current meter on the front panel of the comparator. A more precise adjustment of lead balance was found to be necessary and the photocell galvanometer amplifier and secondary galvanometer were used. The connection between the comparator and galvanometer was made by phone jack in the rear of the comparator. After balance is accomplished, the lead-balance switch is turned to the "OFF" position.

The high-sensitivity galvanometer key on the potentiometer, "TEST 4", is depressed and an approximate balance is obtained. The lead-balance is readjusted and turned to the "OFF" position. Final adjustment of the potentiometer dials to return the recorder pen to "100" on the strip chart gives true balance point. The true resistance is determined from the potentiometer dial reading and the setting of the range selector switch.

The maximum resistance which the potentiometer can read on the highest (XI) range is 105.0000 ohms and on the lowest range (X 0.01), 1.050000 ohms. The range selector switch on the potentiometer has two other positions, (X 0.1) and (X10 ohms), for which the maximum resist-

ance is 10.5000 and 21.0000 ohms, respectively.

Since the heat capacity of the copper envelope is much greater than that of the aluminum jacket and heat is transferred to the copper envelope by conduction of the air in the gap, the time required for the copper envelope to equilibrate is normally long. If the nickel thermometer on the copper envelope is used as a heater, the equilibration time may be reduced by a factor of almost ten. In order to determine approximate equilibration, a copper-constantan differential thermocouple is connected between the copper envelope and the aluminum jacket. The EMF from the thermocouple can be read directly on the recorder or on the potentiometer if the temperature of the reaction vessel is not desired during this period, or the thermocouple may be connected to the photocell galvanometer amplifier and secondary galvanometer is simultaneous monitoring of the calorimeter temperature is desired. When $\underline{R}_e$ is used as a heater and the temperature of the calorimeter is monitored simultaneously, switch S-4 provides the appropriate connections.

Electrical Calibration Circuit

A reaction calorimeter is essentially a comparison device. The resistance change of the resistance thermometer caused by a given reaction is compared to the same resistance change caused by a known amount of electrical energy supplied to the calorimeter. If the electrical energy is supplied over the same resistance and for the same length of time, then a direct correlation can be made between the two.

The electrical calibration circuit (Figure 13) consist of a power supply, a resistance heater, and a read-out unit. These components will

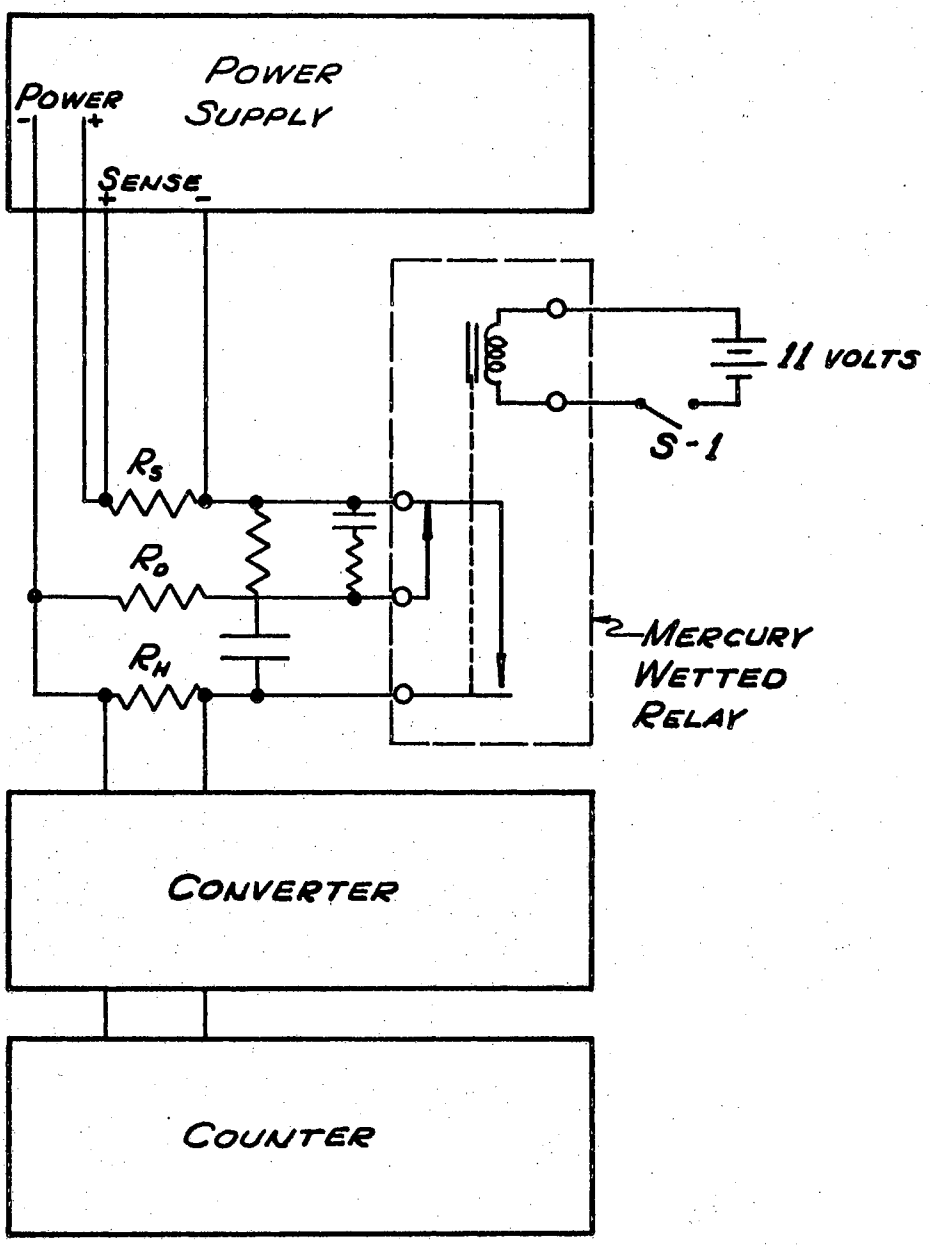

Figure 13. Electrical Calibration Circuit

be discussed separately.

The power supply is a PAR constant-voltage-constant-current reference source model TC-100-2AR. The power supply has the built-in feature of controlling the potential at some point exterior to the output terminals. In order to maintain a constant current through the heater even if the resistance of the heater changes, the potential is controlled across a standard resistor $\underline{R}_s$ which is wired in series with the heater $\underline{R}_h$ and the dummy heater $\underline{R}_d$.

The heater and dummy heater are wired in parallel through a mercury-wetted relay. The relay is a make-before-break type with an operation time of 1.4 milliseconds and a bridging time of 0.5 milliseconds. The relay is powered by 11 volts dc from a rectified laboratory power supply. The relay contacts are protected by a 750 ohm resistor in series with a 0.005 microfarad 600 v dc capacitor between each contact lead and the common lead.

The potential leads are connected from the heater to the input terminals of the voltage-to-frequency converter. The converter gives an output of 10,000 pulses per second for each volt of input signal. The output from the converter is connected to the input of a totalizing counter. The counter gives a direct readout of the integrated value of the voltage-time curve of the complete heating period.

The accuracies given by the manufacturers of the commercial components are as follows: PAR power supply, 0.01% when used in the constant voltage mode; the counter absolute; and the voltage-to-frequenty converter, 0.02% of full scale. The expected accuracy of an electrical calibration is 0.02%.

Solenoid Activation Circuit

The movement of the plunger of reaction vessel II (Figure 3) is much more restricted than that of reaction vessel I (Figure 2). The plunger in both vessels has to pass through a liquid to reach the ampoule, but vessel II has a plunger well to pass through. Also the solenoid of reaction vessel II needs to be much shorter if it is to be located above the plunger. Therefore; a current pulse through the solenoid of reaction vessel I which would be sufficient to break the ampoule may not be sufficient to break the ampoule in reaction vessel II when passed through the solenoid of reaction vessel II.

The circuit which we have used is simple, effecient, and keep power disipation in the solenoid to a minimum. The circuit (Figure 14) has a 235 volt dc power supply which charges a 51.2 microfarad electrolytic capacitor. A 4700-ohm resistor is placed in series to increase the charging time to a few seconds. The final potential developed across the capacitor is monitored by a volt meter. When the solenoid is to be activated, switch S-1 is closed and the capacitor discharges through the solenoid. The time constant for the capacitor-solenoid system is 1.33 milliseconds; therefore, the surge of current through the solenoid is great. Since the solenoid is also a current storage element, the current oscillates, but in a highly damped manner, and is rapidly dissipated as heat in the solenoid.

It is assumed that the total energy of the capacitor is discharged as heat in the calorimeter vessel. Since the energy required to break the ampoule has been shown to be negligible (1) and that which is lost by the

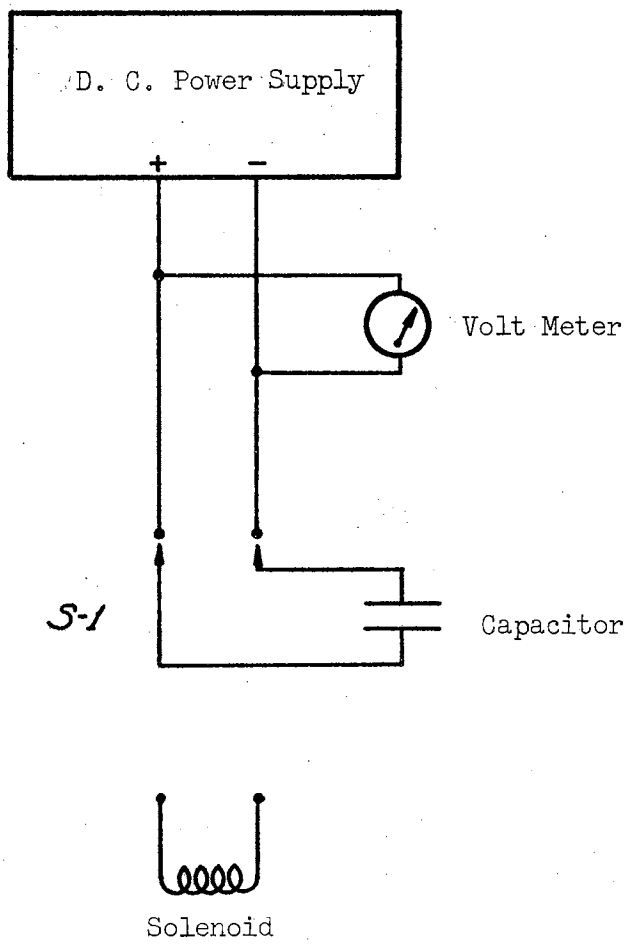

Figure 14. Solenoid Activation Circuit

collapse of the magnetic field of the solenoid is small, and since the resistance of the lead wire is small compared to that of the solenoid, this assumption seems justified. The total energy stored in the capacitor is given by $W=\frac{(V^2)\ C}{2}$ and is 1.600 joules when the voltage is 250 volts and the capacitance is 51.2 microfarads.

TABLE I

MAJOR COMMERCIAL COMPONENTS IN AND PROCESSES RELATED TO, THE CALORIMETER SYSTEM

Item and Description	Source	Identifying Number
Amplifier, Breaker D.C.	Beckman Instruments, Inc. Scientific and Process Instruments Division Fullerton, California	Model 14 S.N. 249858
Amplifier, Photocell Galvanometer	Guildline Instruments Ltd. Smiths Falls, Ont., Canada	Type 9460 S.N. 174705
Battery, Storage, Low Discharge Type, Willard, 2 Volts	E. H. Sargent & Co. Chicago 30, Illinois	Catalog No. S-30905
Battery, Storage, Low Discharge Type, Willard, 6 Volts	E. H. Sargent & Co. Chicago 30, Illinois	Catalog No. S-30915
Bridge, Mueller	Leeds & Northrup Co. 4901 Stenton Avenue Philadelphia 44, Pa.	
Commutator, Mercury	Leeds & Northrup Co. 4901 Stenton Avenue Philadelphia 44, Pa.	
Comparator, Isolating Potential	Guildline Instruments Ltd. Smiths Falls, Ont., Canada	Type 9800 S.N. 24366
Controller, Motor	Gerald K. Heller Co. 2673 S. Western Street Las Vegas, Nevada	Type GT21
Converter, Voltage to Frequency	Hewlett-Packard Co. Dallas, Texas	Dymec Model 2211AR S.N. 323-00712
Counter, Totalizing	Computer Measurements Co. San Fernando, Calif.	Model 316A S.N. 18218
Gage, Vacuum, Thermocouple	Hasting-Raydist, Inc. Hampton, Virginia	Model DV-6

TABLE I (Continued)

Gage Tubes, Thermocouple	Hasting-Raydist, Inc. Hampton, Virginia	Type DV-6M
Gage Tubes, Vacuum, Cold-Cathode	Miller Laboratories P. O. Box 97 Brea, California	Type T-100
Galvanometer	Leeds & Northrup Co. 4901 Stenton Avenue Philadelphia 44, Pa.	Model 2430A
Galvanometer, Secondary	Guildline Instruments, Ltd. Smiths Falls, Ont., Canada	Type SR 21 S.N. 24119
Magnet, Vacuum Gage	Miller Laboratories P. O. Box 97 Brea, California	Type N-100
Magnets, 6 Pole	General Electric Permanent Magnet Sales 4435 W. 12th Street Houston 24, Texas	5X12 B
Meter, Volt	Simpson Electronic Co. 5128 W. Kinzie Street Chicago 44, Illinois	Model 260 Series I
Motor, Reversible	Gerald K. Heller Company 2673 S. Western Street Las Vegas, Nevada	Type GT21
O-Rings, Various Size	Industrial Gasket and Packing Co. 801 S. Walker Street Oklahoma City, Oklahoma	
Plating, Gold	Sel-Rex Corporation 75 River Road Nutley 10, N. J.	
Plating, Nickel	Jones Plating Co. Oklahoma City, Oklahoma	
Plating, Tantalum	Union Carbide Corporation Development Dept. Cleveland 1, Ohio	
Potentiometer, Dauphinee	Guildline Instruments, Ltd. Smiths Falls, Ont., Canada	Type 9144-L S.N. 24157

TABLE I (Continued)

Power Supply, Constant Voltage/Current	Princeton Applied Research Corp. Highstown Road Princeton Junction, N.J.	Model TC-100-2AR S.N. 105
Pump, Metal, Oil Diffusion	Consolidated Vacuum Corp. 7900 Carpenter Freeway Dallas 35, Texas	Type VMF-20W
Recorder, Strip Chart	E. H. Sargent & Co. 5919 Peeler Street Dallas, Texas	Model MR S.N. 718022
Relay, Mercury Wetted Dummy Heater	C. P. Clare & Co. West Concord, Mass.	Type 1432 S.N. 34051
Resistor, Standard, 10 ohms	Electro Scientific Ind. Portland, Oregon	S.N. 33817
Resistor, Standard, 100 ohms	Electro Scientific Ind. Portland, Oregon	S.N. 33886
Resistor, Standard, 100 ohms	Leeds and Northrup Co. 4901 Stenton Avenue Philadelphia 44, Pa.	S.N. 1614577
Switch, Low Thermal	Guildline Instruments, Ltd. Smiths Falls, Ont., Canada	Type 9145A S.N. 24073
Switch, Pinch-type	Leads & Northrup Co. 4901 Stenton Avenue Philadelphia 44, Pa.	
Thermometer, Precision Platinum Resistance	Minco Products, Inc. Minneapolis, Minn.	Model S1061 S.N. 3, 4, 5, & 6
Thermometer, Standard Platinum Resistance	Leeds & Northrup Co. 4901 Stenton Avenue Philadelphia 44, Pa.	Catalog No. 8164 S.N. 1605882
Temperature Controller	HallikainenInstruments Inc. 1341 Seventh Street Berkely 10, California	Thermotrol Model 1053 S.N. 8921
Timer	Precision Scientific Co. Chicago, Illinois	Type "Time-It"
Wire, Ballast Nickel	Wilbur B. Driver Co. Newark, N. J.	AWG 35

Wire, Constantan thermocouple	Leeds & Northrup Co. 4901 Stenton Avenue Philadelphia 44, Pa.	AWG 30
Wire, Copper Thermocouple	Leeds & Northrup Co. 4901 Stenton Avenue Philadelphia 44, Pa.	AWG 30
Wire, Evanohm	Wilber B. Driver Co. Newark, N. J.	AWG 26
Wire, Thermocouple Extension	Thermo Electric Co. Saddle Brook, N. J.	AWG 24

CHAPTER IV

EXPERIMENTAL RESULTS

The calorimeter system has been assembled and the following studies made: a method of operation was developed for the system which would optimize the use of the auxillary equipment, minimize the time required for operation, and be easily controlled by one operator; the stability of the air bath was checked; the response of the reaction vessel during a given reaction was determined; and the reproducibility of the electrical calibration was determined. The reaction of tris(hydroxymethyl) animomethane (THAM) with 0.1 N hydrochloric acid (14) was chosen as the test reaction.

Method of Operation

A typical run will be discussed to explain the method of operation developed for this system. For this run the THAM sample was obtained from Fisher Scientific Company and was designated as "Fisher Primary Standard" with a purity listed as 100.1%. The hydrochloric acid solution was obtained from Anderson Laboratories and was listed as "Banco Standardized" 0.1 N hydrochloric acid. The THAM was prepared as described by Irving and Wadsö (14) and was stored in a desiccator over silica gel.

Ampoules which had been previously visually examined for flaws, wall thickness, and correct stem length were stored in the desiccator. One of

the ampoules was removed, weighed, and the weight recorded. The operator wore dry rubber gloves during all handling of the ampoule. The ampoule was then filled with the THAM sample, the ampoule and rubber gloves were brushed with a camel's hair brush to remove any particles of THAM from the outer surface of the ampoule, and the ampoule-plus-sample weighed. The ampoule was then sealed by a thin flame from an oxygen-gas torch; after the sealed ampoule had cooled to room temperature, the ampoule was re-weighed to determine any weight change during handling and sealing.

The reaction vessel was washed with distilled water and allowed to dry in air. A gold-plated plunger was added to the solenoid well and 90 ml. of hydrochloric acid was added to the vessel. The ampoule was firmly installed on the retaining plate with the Teflon sleeve.

The lid was attached to the body of the vessel and the vessel was suspended in the cradle with nylon cords. The leads from the various electrical components were connected as shown in figure 15: the solenoid leads are connected to terminals 1 and 2 of the barrier strip located on the cradle; the heater current leads go to terminals 3 and 4; terminals 5 (positive) and 6 (negative) are potential connects from thermometer 1 and terminals 7 (positive) and 8 (negative) are potential connections from thermometer 2; one current lead from the thermometer 1 goes to terminal 11; the second current lead from thermometer 1 and one of the current leads from thermometer 2 are connected on terminal 13; the second current lead from thermometer 2 is secured at terminal 12; potential leads for the heater are connected to terminals 9 and 10.

The reaction vessel is sprayed with reagent grade acetone to cool the vessel below room temperature. The vacuum envelope is assembled and the

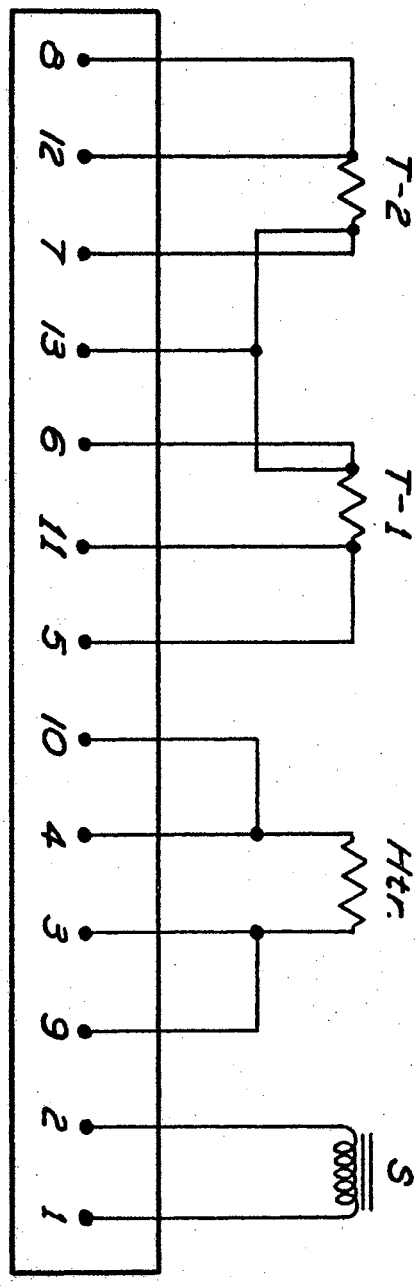

Figure 15. Wiring Diagram for Barrier Strip

leads of the thermometer on the vacuum envelope are connected. One junction of the thermocouple is connected firmly to the lid of the jacket. The nickel thermometer and the heater on the aluminum jacket are connected to the control unit. The system is evacuated and the jacket temperature control unit is turned on.

The equilibration of the air bath with the copper envelope is expedited if the nickel thermometer on the copper envelope is used as a heater. As shown in figure 11, switch S-4 is thrown to connect the thermometer to the power supply. The power supply is activated and operated at maximum power until the EMF from the differential thermocouple approaches zero. The power is then reduced and heating is continued until the EMF from the thermocouple is zero. Switch S-4 is reversed and the temperature of the envelope is monitored with the nickel thermometer until equilibrium is established. The rocking mechanism is started and adjusted to the desired rate. As the reaction vessel rocks, the temperature of the reaction vessel appears to have an oscillation with the same frequency as the rocking. These oscillations result from the cutting of the earth's magnetic field by the leads from the reaction vessel. The oscillations are of the order of 0.001 degree centigrade but can be reduced if pairs of twisted leads (e.g. the potential leads) are used.

The reaction vessel is then heated until the temperature approaches the desired temperature for initiating the reaction. The power supply for the solenoid is turned on and allowed to warm-up. After warm-up, switch S-1 (Figure-14) is thrown, the capacitor is charged, and the voltage across the capacitor is read.

Approximately ten minutes before the initiating temperature is reached,

the drift rate of the reaction vessel is determined. The temperature is determined by adjusting the dial setting of the potentiometer until the pen position on the recorder chart is below the predetermined null point. The recorder's pen passes over null point when the thermometer resistance is equal to the value set on the potentiometer dials. A higher value is then set on the potentiometer dials, resulting in another displacement of the recorder pen below null, and the process is continued.

When the initiating temperature is reached, the voltage across the capacitor is rechecked and the solenoid switch S-1 is thrown. Temperature readings during the main period are continued at approximately 15 second intervals. After the reaction is complete, the drift rate is again determined.

During the determination of the drift rate of the vessel, the rate and direction of drift of the voltage-to-frequency converter is determined. This drift is probably due to thermal EMF's and is approximately 0.100 volt-seconds per 200 seconds. After a steady drift rate is established for the reaction vessel, the heater is activated and a timer is started. The temperature is monitored, although not as often as during a chemical reaction since the power input is constant. When the required temperature rise is accomplished, the heater is deactivated and the timer is stopped. Again, a steady drift rate is determined for the reaction vessel. The time during which the heater was energized is recorded and the value of the integrated potential-time curve is recorded from the totalizing counter. The drift rate of the converter is again determined.

The calorimeter is then cooled by the evaporation of acetone which is injected on the top of the reaction vessel. Three additional calibra-

tions are determined by the above procedure: one is over the temperature range of the reaction; the second is at a lower temperature; and the last is at a higher temperature.

The Reaction of THAM and HCl (aq)

Results for the heat of reaction of THAM and 0.1 N hydrochloric acid are included not for the purpose of determining this heat effect since it has been determined elsewhere (14) but to give some indication of the precision which can be expected form the calorimeter system.

The reaction of THAM with 0.1 N hydrochloric acid was considered as a standard by the 1963 Calorimetry Conference. This reaction was tested in conjunction with other laboratories to determine the merits and reproducibility of the proposed reaction.

Five runs are reported not because of the agreement from run to run but to aid in the continuing development of the system by indicating errors and possible errors in the determinations.

All measurements reported here were made with reaction vessel II. The air bath was operated between 26.5-27.0° C and the pressure in the vacuum envelope was 2-7X 10^{-4} torr.

Sample 14 and 15 were Fisher samples from the same master batch. Sample 16 was an Eastman sample pretreated in the same manner as the Fisher sample. The results in Tables II, III, and IV give some indication of the reproducibility obtained between several electrical calibrations for a given sample and run. No explanation is given for the differences in the determined heats for runs 14, 15, and 16. However, during run 18 the temperature-measuring equipment was found to be

defective; this could explain both the low values of 14 and 15 when compared with the values determined by Irving and Wadsö, and the discrepancy of runs 14 and 15 when compared with run 16.

If an operational error such as incorrectly recording the integrated value of the voltage-time curve from the totalizing counter is assumed in calibration 2 of run 15, then the average value is 6782± 1 calories per mole. The average value for run 14 is 6782± 5 calories per mole. These determinations indicate that very high reproducibility between different samples can be accomplished.

DEFINITIONS OF SYMBOLS USED IN TABLES II-VI

Mole Factor	The quantity by which the corrected enthalpy change must be multiplied to convert to enthalpy change per mole.
Solenoid Correction	Energy introduced into the reaction vessel by the discharge of the capacitor through the solenoid (joules).
Number	The number of the calibration run.
T_o	The initiating temperature for the electrical calibration (°C).
$\triangle R$	The change in resistance of the thermometer corrected for the drift during the reaction or calibration period (ohms).
I_h	The current through the heater during the calibration (Amperes).
$\int Edt$	The integrated value of the voltage-time curve obtained from the converter-counter combination (volt-seconds).
D_c	The drift rate of the converter-counter combination (volt-seconds per second).
$\triangle H$	Enthalpy change (heat of reaction) per mole (calories per mole)

TABLE II

THAM-HYDROCHLORIC ACID RUN 14

Chemical Reaction Data

Mass of Sample	0.4214	grams
Moles of Sample	0.003479	moles
Mole Factor	287.47	$moles^{-1}$
Corrected $\triangle R$	0.05170	ohms
Capacitor Voltage	237.0	volts
Capacitor Voltage	1.234	joules
Capacitor Correction		

Calibration Data

Number	T_o	$\triangle R$	I_h
2	24.82	0.02610	0.05000
3	24.99	0.02480	0.05000
4	25.08	0.03555	0.05000
	$\int Edt$	D_c	$\triangle H$
2	1010.151	6.67×10^{-4}	6790.
3	957.271	6.58×10^{-4}	6778.
4	1373.616	6.75×10^{-4}	6777.

TABLE III

THAM-HYDROCHLORIC ACID RUN 15

Chemical Reaction Data

Mass of Sample	0.4630	grams
Moles of Sample	0.003822	moles
Mole Factor	261.64	$moles^{-1}$
Corrected $\triangle R$	0.0569	ohms
Capacitor Voltage	236.0	volts
Capacitor Correction	1.234	joules

Calibration Data

Number	T_o	$\triangle R$	I_h
1	25.18	0.03270	0.0500
2	24.78	0.03233	0.0500
3	25.00	0.03265	0.0500
	$\int Edt$	D_c	$\triangle H$
1	1217.777	6.00×10^{-4}	6782.
2	1187.484	6.75×10^{-4}	6688.
3	1216.324	7.00×10^{-4}	6782.

TABLE IV

THAM-HYDROCHLORIC ACID RUN 16

Chemical Reaction Data

Mass of Sample	0.34055	grams
Moles of Sample	.002811	moles
Mole Factor	355.72	$moles^{-1}$
Corrected $\triangle R$	0.03575	ohms
Capacitor Voltage	237.5	volts
Capacitor Correction	1.234	joules

Calibration Data

Number	T_o	$\triangle R$	I_h
1	25.08	0.04535	0.05000
2	25.00	0.03225	0.05000
3	25.14	0.03420	0.05000
	$\int Edt$	D_c	$\triangle H$
1	1692.495	8.17×10^{-4}	6186.
2	1198.205	3.94×10^{-4}	6173.
3	1271.140	0	6176.

TABLE V

THAM-HYDROCHLORIC ACID RUN 18

Chemical Reaction Data

Mass of Sample	0.34525	grams
Moles of Sample	0.002853	moles
Mole Factor	350.57	$moles^{-1}$
Corrected $\triangle R$	0.02340	ohms
Capacitor Voltage	237 x 2	volts
Capacitor Correction	2.73279	joules

Calibration Data

Number	T_o	$\triangle R$	I_h
1	25.33	0.03073	0.05
	$\int Edt$	D_c	$\triangle H$
1	2154.341	5.00×10^{-4}	6655.

TABLE VI

THAM-HYDROCHLORIC ACID RUN 22

Chemical Reaction Data

Mass of Sample	0.48450	grams
Moles of Sample	.004000	moles
Mole Factor	250.03	$moles^{-1}$
Corrected ΔR	0.06015	ohms
Capacitor Voltage	236 x 2	volts
Capacitor Correction	2.852	joules

Calibration Data

Number	T_o	ΔR	I_h
1	25.54	0.03651	.10000
2	24.70	0.04597	.10000
3	25.14	0.05710	.10000
4	25.00	0.04771	.10000

	$\int Edt$	D_c	ΔH
1	687.026	6.17×10^{-4}	6724.
2	850.951	6.16×10^{-4}	6563.
3	1029.246	6.13×10^{-4}	6307.
4	881.202	5.44×10^{-4}	6468.

Only one calibration was made for run 18 because the heater relay on the Thermotrol unit was accidently activated and the air bath was continuously heated for 18 hours; the excessively high temperature which resulted caused serious damage to the calorimeter heater. A new heater was constructed of manganin wire (AWG 32) and runs were continued. Since the temperature measuring equipment was found to be defective during run 18, a G-1 Mueller bridge was used to monitor the temperature in subsequent runs.

Run 22 is a typical example of these. After run 22 the calorimeter was disassembled and the heater examined. It was discovered that the silicone oil which is used as a heat transfer medium in the heat re-entrant well had evaporated from the well. It therefore seems reasonable that the differences in the enthalpies of reaction are due to poor thermal contact between the heater and the calorimeter and to variable and excessive heat loss from the heater leads.

Summary

It has been shown that the isoperibol, aneroid, rocking-bomb reaction calorimeter which was designed and constructed during this research is capable of giving highly reproducible results. The air bath described provides isothermal surroundings (for isoperibol operation) which are stable within 0.001 degree centigrade. Various minor modifications to the original design have been described and probable sources of various errors have been identified. Failure to obtain accurate data for the THAM-HCl reaction resulted from defects in new commercial temperature-measuring equipment.

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APPENDIX

A METHOD FOR DETERMINING THE CORRECTED TEMPERATURE CHANGE FOR THE REACTION VESSEL

If during the course of a reaction the drift rate of the temperature of the reaction vessel remains constant, the temperature change due to the reaction would be $\theta_e - \theta_b \pm \Delta\theta_c$, where θ_e is the temperature of the reaction vessel at the end of the reaction, θ_b is the temperature of the reaction vessel at the beginning of the reaction and $\Delta\theta_c$ is the correction due to the temperature drift of the calorimeter during the reaction period. $\Delta\theta_c$ can be determined by $\Delta\theta_c = (d\theta/dt)(t_e - t_b)$ where $d\theta/dt$ is the slope of the drift of the reaction vessel $(t_e - t_b)$ is the time of the reaction. Since the temperature of the reaction vessel is converging to the jocket temperature, the correction due to a changing drift rate is more involved; however, the corrected temperature rise can still be express as

$$\Delta\theta corr = \theta_e - \theta_b \pm \Delta\theta \qquad (1)$$

It is assumed that Newton's law of cooling applies for all heat transfer to the reaction vessel other than the energy introduced internally by chemical reaction or by the electrical heater. Newton's law can be expressed as

$$d\theta/dt = u + k(\theta j - \theta) \qquad (2)$$

where $d\theta/dt$=change in temperature of the reaction vessel with time,

u=the heat of stirring,

k=cooling constant of the calorimeter,

θj=temperature of the jacket, and

θ=temperature of the reaction vessel at time t.

A more useful expression for $d\theta/dt$ can be obtained by defining a quantity θ_∞ as the temperature the calorimeter would reach at infinite time. At θ_∞, $d\theta/dt$ would be equal to zero: if these substitutions are inserted into equation (2), the results are

$$u=-k(\theta j-\theta_\infty). \tag{3}$$

Substitution of equation (3) into (2) produces

$$d\theta/dt=k(\theta_\infty-\theta). \tag{4}$$

The following symbols are now defined:

$g_b=(d\theta/dt)_b$ at the mean temperature θ_b, and

$g_e=(d\theta/dt)_e$ at the mean temperature θ_e.

By substituting the symbols in expressions (2) and (4), one obtains expressions for k and u in terms of the experimentally measured quantities, g_b and g_e. Two expressions for θ_∞ are obtained when the slopes, g_b and g_e, are substituted in expression (4):

$$\theta_\infty=g_b/k+\theta_b \tag{5}$$

$$\theta_\infty=g_e/k=\theta_e. \tag{6}$$

When expression (4) is integrated over the reaction time, t_b to t_e, one obtains

$$d\theta=k\int_{t_b}^{t_e}(\theta_\infty-\theta)dt$$

$$\Delta\theta=k(\theta_\infty-\theta_m)(t_e-t_b). \tag{7}$$

If (t_e-t_b) is split up to (t_e-t_x) and (t_x-t_b), where t_x is some time between t_e and t_b, and (5) and (6) are substituted in expression (7) and the results are rearranged, one obtains

$$\Delta\theta=g_e(t_e-t_x)+g_b(t_x-t_b)+k(\theta_e-\theta_m)(t_e-t_x)+k(\theta_b-\theta_m)(t_x-t_b) \quad (8)$$

Where θ_m is defined as the mean value of θ_i during this period. Since t_x can vary over the entire time interval t_e-t_b, there exist some value of t_x such that

$$k(\theta_e-\theta_m)(t_e-t_x)+k(\theta_b-\theta_m)(t_x-t_b)=0. \quad (9)$$

When expression (9) is solved for $\underline{t}_x$, one obtains

$$t_x=(\theta_e-\theta_m)t_e-(\theta_m-\theta_b)t_b/(\theta_b-\theta_e). \quad (10)$$

Since $\int_{t_b}^{t_e} f(\theta)dt=\theta_m(t_e-t_b)$ and $\int_{\theta_b}^{\theta_e} f(t)d\theta=t_m(\theta_e-\theta_b)$, it can be seen from figure 16 that

$$(\theta_m-\theta_b)(t_m-t_b)=(\theta_e-\theta_m)(t_e-t_m). \quad (11)$$

When expression (11) is solved for $\underline{t}_m$, the solution is identical with the expression for $\underline{t}_x$; therefore, $\underline{t}_x$ is equal to $\underline{t}_m$ when expression (9) is zero. When $\underline{t}_m$ is substituted in expression (8), one obtains

$$\Delta\theta=g_e(t_e-t_m)+g_b(t_m-t_b). \quad (12)$$

If expression (12) is used to find $\Delta\theta$ graphically (Figure 16), the time required to determine $\Delta\theta$corr is reduced; of course, the accuracy is directly dependent upon the plotting. The following procedure has been used to determine the corrected temperature rise.

The data points are plotted on a graph to give the required sensitivity and are connected by a contenuous line. The time at the beginning and end of the reaction is determined by observing the first deviation from the constant drift. The value of $\underline{\theta}_m$ is determined by preforming a numerical integration from the beginning time to the ending time of the reaction. This integration is done by the Regnault-Pfaundler method (21): n temperatures are measured (or obtained by interpolation) at equal time intervals of not more than 15 seconds in very rapid reactions (e.g., combustion bomb

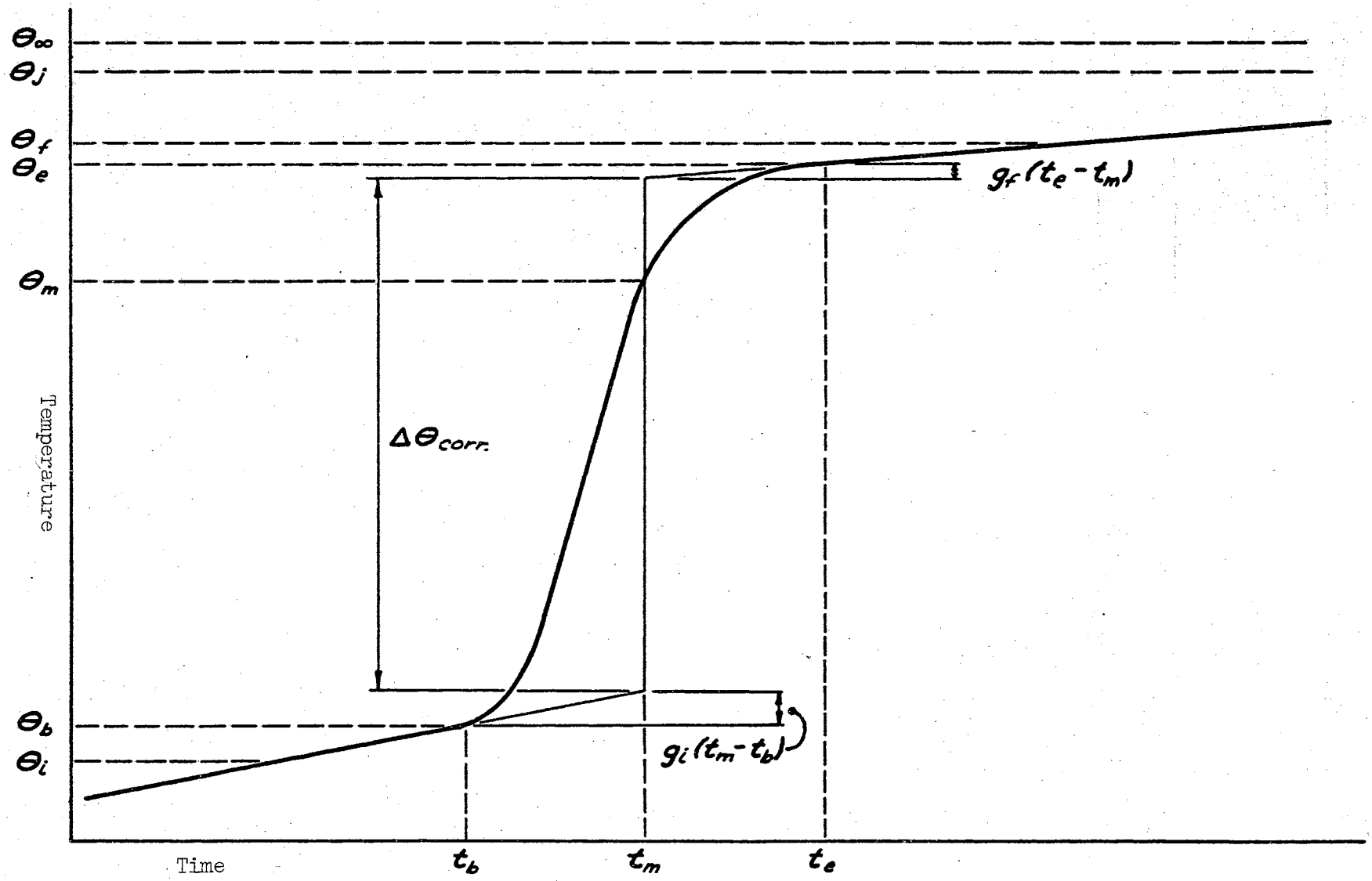

Figure 16. Graphical Determination Of θ_{corr}

type); somewhat larger time intervals are permissible for slower reactions. The average surface temperature is then given by

$$\theta_m = \left[\sum_{r=2}^{r=a-1} \theta_r + \frac{\theta_b + \theta_e}{2} \right] \frac{\Delta t}{t_e - t_b} . \qquad (13)$$

When the slopes of the initial period and the final period are extrapolated to the time t_m at which θ_m occurs, the corrected temperature change θcorr is given by

$$\Delta\theta_{corr} = \theta_{em} - \theta_{bm} \qquad (14)$$

where θ_{em} is the temperature obtained by extrapolating the final period to the time t_m, and θ_{bm} is the temperature obtained by extrapolating the initial period to time t_m. This is essentially a graphical execution of expression (12).

VITA

Walter Clarence Parks

Candidate for the Degree of

Master of Science

Thesis: AN ISOBERIBOL, ANEROID, ROCKING-BOMB REACTION CALORIMETER

Major Field: Chemistry

Biographical:

Personal Data: Borm at Dalton, Georgia, December 29, 1937, the son of W. C. And Leila Parks.

Education: Attended the public schools of Dalton, Georgia and graduated from Dalton High School in May, 1956; received the Bachelor of Science degree in June, 1960 from North Georgia College, Dahlonaga, Georgia, with a major in chemistry and minor in physics and mathematics; completed the Officers Basic Course, Honest John Rocket Nuclear Warhead School, and Chemical Warfare course while on active duty in the Army; completes the requirements for the Master of Science degree in May, 1965.