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PRECISION CLOSED BOMB CALORIMETER FOR
TESTING FLAME AND GAS PRODUCING
INITIATORS

D. Rae Carpenter, Jr., et al

VMI Research Laboratories

Prepared for:

Harry Diamond Laboratories
National Aeronautics and Space Administration

September 1972

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13. ABSTRACT

A calorimeter has been developed under this study to help meet the needs of accurate performance monitoring of electrically or mechanically actuated flame and gas producing devices, such as squib-type initiators. A ten cubic centimeter "closed bomb" (closed volume) calorimeter was designed to provide a standard pressure trace and to measure a nominal 50 calorie output, using the basic components of a Parr Model 1411 calorimeter.

Two prototype bombs were fabricated, pressure tested to 2600 psi, and extensively evaluated. The system water equivalent was measured as 284 cal/C°. Monitoring of temperatures to $\pm$ 0.001 C° was found to be feasible. Measurements of 50 calories to an accuracy of $\pm$ 1 calorie are easily obtainable. Greater accuracy is possible with appropriate attention to details of technique. A cycling time (or time ot complete the test of one initiator) or one hour was deemed feasible.

Calibration was accomplished using electrical heating of a resistor in the bomb by capacitor discharge and by constant current. Problems associated with measuring small quantities of heat are discussed including the effects of room temperature, stirring, bearing friction, stirrer belt tension, initial stabilization period and others. Actual initiators were not tested.

Calibration data subsequently obtained by the Harry Diamond Laboratories using this apparatus is included in an appendix.

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	ROLE	WT	ROLE	WT	ROLE	WT
Calorimeter	8	3				
Parr 1411 (calorimeter)	8	3				
Initiator	8	3				

SUMMARY

A calorimeter has been developed under this study to help meet the needs of accurate performance monitoring of electrically or mechanically actuated flame and gas producing devices, such as squib-type initiators. A ten cubic centimeter "closed bomb" (closed volume) calorimeter was designed to provide a standard pressure trace and to measure a nominal 50 calorie output, using the basic components of a Parr Model 1411 calorimeter.

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LIST OF FIGURES AND TABLES

1. INTRODUCTION

The need often arises for accurate measurements of the output performance of a variety of electrically or mechanically actuated flame and gas-producing devices, such as squib-type initiators. Examples of these needs are quality control during manufacture, lot acceptance testing, determining the effects of environments, and obtaining design information for use of the device in subsequent systems. The most commonly used performance monitoring standard relies solely on measuring the pressure produced in a ten cubic centimeter "closed bomb" (closed volume).[1] Some separate attempts have been made to measure the caloric output of these flame and gas-producing devices, but since their output is often in the order of 50 calories, accuracy has been lacking with existing apparatus. The purpose of this study was to develop a ten cubic centimeter closed bomb calorimeter, providing a precise heat energy measurement, as well as the standard pressure trace.

1.1 The Scope of Work (Quoted in part from the contract document.)

Make a theoretical analysis of the feasibility of using a modified No. 1411 heat powder calorimeter with the specifications outlined below for measuring the heat output of Apollo standard initiators. If the analysis shows that the No. 1411 calorimeter is not suitable, consider using a copper-block type calorimeter.

After the theoretical analysis is complete, design and build a calorimeter with the following specifications to measure the heat output of standard Apollo initiators:

(1) Precision within ±5 cal with a 50 cal. input.

(2) Withstand peak pressure of 650 psi generated as an impulse in about 1 ms or less (subsequently raised to 3000 psi static pressure by HDL).

---

[1] Bement, Laurence J.: "Monitoring of Explosive/Pyrotechnic Performance". Presented at the Seventh Symposium of Explosives and Pyrotechnics (Philadelphia, Penn.) September 8-9, 1972.

(3) Internal volume of calorimeter must be 10 cc
and shape must duplicate initiator tester
now used by NASA.

(4) Calorimeter must contain one and preferably
two pressure transducers with output cables.
(Transducers will be furnished by NASA and
no pressure measurements will be made by
contractor).

(5) Calorimeter must be reusable for at least
1000 tests.

(6) Recycle time must be less than 1 hour.

Calibrate calorimeter using a known electrical input and determine precision calculated for 95% of all values at a 90% confidence level. Summarize details of analyses, design, calibration, and evaluation of the calorimeter in a summary report.

1.2 Background Work

Bomb calorimetry is a well known field having techniques standardized over the years. Such techniques have been utilized to measure the heat output of heat powders by the Harry Diamond Laboratories (HDL).[2] Customarily several hundred to several thousand calories are generated so that calorimeters having water equivalents of several hundred cal/C° will experience temperature rises of about a degree or more. Mercury in glass thermometers provide a temperature measurement accuracy of about $\pm$ 0.01°C.

A frequently used calorimeter for heat powder measurements is the Parr Model 1411[3], which was suggested by HDL for this investigation. This apparatus was loaned to VMIRL for these studies. A bomb was designed to comply with the requirements of the Scope of Work, and also to be compatible with the vacuum flask which is a standard component of the Model 1411.

---

[2] Comyn, Raymond H.; and Marcus, Ira T.: Summary of Heat Powder Calorimetry. Diamond Ordnance Fuze Laboratories TR-862, August 1960.

[3] Parr Instrument Co., 211 Fifty-Third St., Moline, Illinois 61265

The chief problem was the measurement technique for detecting a temperature rise with an accuracy of a few thousandths of a degree. This was necessitated by the requirement to measure 50 calories using a metal bomb having a mass of several hundred grams (in order to meet the volume and pressure requirements) plus several hundred grams of water necessary to cover the bomb, stirrer and temperature detector.

Several problems were associated with the design of the bomb to meet the small volume requirement at a test pressure of 3000 psi and to maintain a particular design of the pressure port for the transducer.

2. FEASIBILITY ANALYSIS

The use of well designed, "off the shelf" components already tested in various uses is an obvious advantage. To assess the feasibility of using a Parr Model 1411 Calorimeter, a theoretical analysis was performed on the quantities of heat absorbed by each of the components to see if the required precision of measurement was possible.

Although this model is designed to be used with 450 gm of water, it was found possible to use 250 gm and still cover the proposed bomb for the initiator.

A summary of representative values will give the reader a better understanding of the precision of measurement needed.

Assume:

1. 200 gm of stainless steel bomb of specific heat 0.1 cal/gm $C°$.

2. 250 gm of water to cover the bomb with adequate depth for stirring.

3. 54 calories generated by the initiator.

Find: The temperature rise which results.

Solution: $Q = [(mc)_{bomb} + (mc)_{water}] \Delta T$

$54 = [(200 \times 0.1) + (250 \times 1)] \Delta T$

$\Delta T = \dfrac{54}{20+250} = \dfrac{54}{270} = 0.20 \ C°$

Precision Required: For the $\pm 10\%$ precision called for in the Scope of Work the value of ΔT must be $0.2 \ C° \pm 10\%$ or better. This is $0.20 \pm .02 \ C°$.

While the above precision is within the limits of a mercury in glass thermometer, it is clearly not as satisfactory as could be desired. The quartz crystal thermometer (such as the Hewlett Packard Model 2801 A) has an absolute accuracy of $\pm 0.002 °C$ when properly calibrated and corrected. For differential measurements, particularly where the differential is small, its accuracy in measuring ΔT is better, certainly $\pm 0.001 \ C°$. For a ΔT of $0.20 \ C°$ this is a precision of 1 in 200 or $1/2\%$.

Precision of Other Components

The mass of water used can certainly be measured by an analytical balance to less than 1 gm in 250 yielding a precision of less than 1/2%   In fact a volumetric pipette could suffice for this purpose. The precision of the water equivalent remains : be determined. however. repeated calibration run, should give its ..lue to a few percent or less.

On the basis of the above considerations, the Parr Model 1411 was deemed a· ·uate for the project and a specific bomb design was begun to fit the ·cuum flask which was a component of this model of calorimeter. The .·rror analysis in Appendix A gives specific sample values taken fro. ·ctual data and provides a more exact evaluation of the precision .·· each part of the measurement.

3. BOMB DESIGN

The following criteria were considered in the design:

1. An internal volume of 10.0 ± 0.5 cc
   including transducer port.

2. Withstand 3000 psi to account for any
   unanticipated transient pressures.

3. Ease of interchange between initiators
   and calibration devices with a minimum
   change of mass which would affect the
   water equivalent.

4. Ease of cleaning after each test.

5. Minimization of the water equivalent by
   minimizing the total mass and the height
   which must be covered by water.

6. Minimization of wall thickness to reduce
   thermal gradients.

7. Adequate space beside and/or above the
   bomb for hanger, stirrer, temperature
   detector(s) and electrical leads for the
   pressure transducer and for firing the
   initiator, or calibration.

8. Compatibility with the vacuum flask of the
   Parr Model 1411 Calorimeter.

Fig. 1 is a photograph of the bomb parts. An assembly drawing
and detail drawings of each part are shown in Appendix B. Two
prototypes were fabricated from these drawings and were designated
Model 1 and Model 2, with components stamped with a "1" or "2" to
facilitate identification. Masses in grams are as follows (nomen-
clature is that found on the detail drawing):
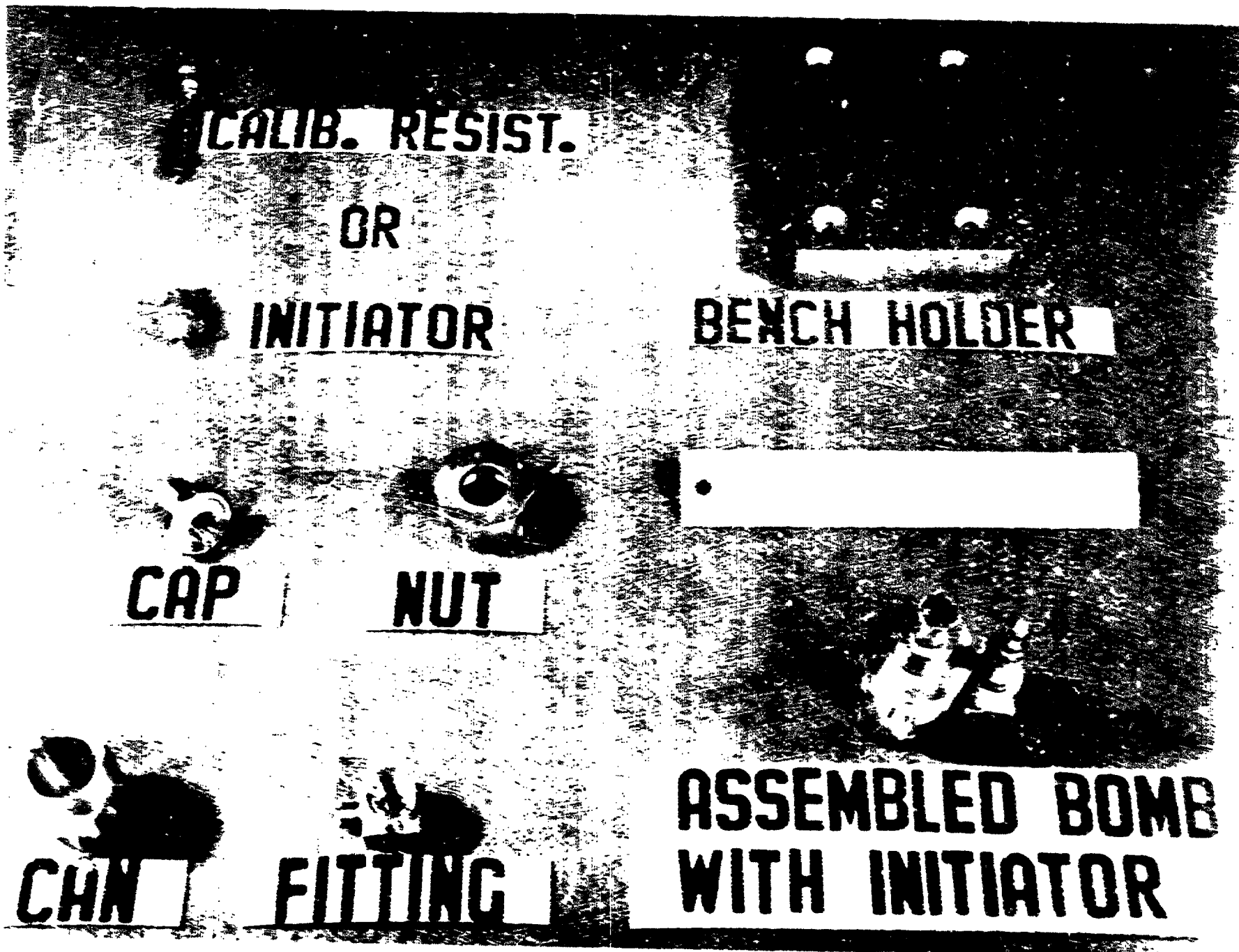
Fig. 1. Photograph of Bomb Parts

	Model 1	Model 2
Cup w/Pressure Fitting and Teflon Tape	105.0387 gms	105.0318 gms
Nut	50.3210	50.3012
Cap w/Teflon Gasket	24.6547	24.6668
Plug w/Calibration Resistor, Connector, and O-Ring	8.2028	8.2724
Complete Assembly Total	188.2172	188.2722
Transducer w/copper and brass washers		15.6092 gm
Initiator after firing (avg of 4)		12.2730

The two models differ in total mass by 0.03% for an average mass as follows:

Bomb w/calibration plug and resistor	188.2 gm
Bomb w/calibration, plug, resistor and pressure transducer	203.8
Bomb w/spent initiator and pressure transducer but w/o calibration plug and resistor	207.9

The initiator, calibration resistor plug and transducer each have mating electrical connectors which are partially or totally below the water. The masses of these are small and have not been included.

Slight modifications to the Parr Model 1411 Calorimeter were necessary. These included an extension of the stirrer shaft and bomb support, removal of the thermometer support rod and fabrication of a cover clamp for the electronic thermometer probes. These modifications are detailed in Appendix C.

4. CALIBRATION METHODS

It is desirable to provide more than one calibration method as a verification of the technique and measuring apparatus used. In this case the methods considered were heat powder and resistive heating from two sources, one from a capacitor discharing through a resistor and one from constant voltage.

4.1 Heat Powder

Heat powders are presently available from the National Bureau of Standards with certified values in the nominal region of 400 calories/gm. These require ignition by hot wire and are susceptible to incomplete combustion when used in small quantities unless the sample is well confined. For 50 calories the sample would be 1/8 gm and while larger quantities could be used, the calibration for very large quantities of heat could differ from the calibration for 50 calories.

In addition, there are problems of having the sample adequately dried, weighed, and ignited in an inert atmosphere. Results depend somewhat on the pressure of this atmosphere. Moderate safety precautions are necessary in handling and results may be somewhat variable in the hands of persons not familiar with heat powders.

4.2 Capacitance Discharge

To store 50 calories or 210 joules of energy in a capacitor requires either high capacitance values or large charging voltages. At about 100 volts a capacitance of about 42,000 microfarads is required. Such capacitances are avalable only in electrolytic type capacitors unless many individual units of another type are assembled in parallel.

Unfortunately electrolytic capacitors exhibit dielectric absorption, a phenomenon which is characterized by the recovery of a voltage across the plates following discharge. An alternative explanation is that the apparent capacitance is not constant with voltage during discharge as in an ideal capacitor but instead the capacitance increases and the plot of charge vs voltage is non-linear. Therefore the energy stored is not given by $CV^2/2$ as is true for an ideal capacitor.

This method was extensively investigated including the use of
larger capacitors than necessary so that they might be only partially
discharged. To minimize the dialectric absorption effects, two
capacitors in parallel of total value 0.084 farads were discharged
from 100 volts to 70 volts and, although the variation of capacitance
over this range was sufficiently small, the voltage recovery near 70
volts amounted to 1.5 to 2.2 volts. This made it difficult to com-
pute the energy actually supplied to the resistor as heat. The
resistor used was 300 ohms giving an electrical time constant, RC,
of 25 seconds. The peak current was then 1/3 ampere with a peak
power of 33 watts. Other considerations are included in Sec. 4.3.

This method was compared with that using a constant voltage
and the two energies so generated would agree quite well if the
final voltage, at the end of the discharge near 70 volts, was
taken 15 to 25 minutes following the discharge. That is, the final
voltage used in the energy calculation should be that taken some
time after the discharge has ceased and the capacitor has had a
chance to recover. This makes this method somewhat impractical and
uncertain but, with proper care on the part of the personnel using
it, it can be a secondary or backup calibration procedure. (See
Appendix D.)

4.3 Joule Heating (RI^2t)

A constant voltage applied for a known time to a resistor of
sufficient wattage rating to prevent excessive heating, results in
a conversion of electrical energy to heat which can be accurately
measured. A nominal 300 ohm, 5 watt resistor was selected for the
following reasons:

    a) Reasonable voltages could be applied to generate
        the needed heat in about one minute.

    b) Its pnysical size was the largest which would
        fit inside the bomb and pass through the 3/8"
        hole in the cap.

    c) Its resistance is high enough to make contact
        resistance negligible although a correction
        should be made for the small diameter connecting
        lead.

Immersion of the resistor in water inside the bomb appreciably
improves the heat transfer and assures that the temperature rise
at all times is too small to change the resistance as much as 0.05%.
The resistor must be sprayed with acrylic to prevent electrolytic
action between its leads and the water. Various alternatives are
available in calculating the energy; VIt, RI^2t or V^2t/R. In
addition to time, it is necessary to measure two of the three
quantities; resistance, voltage, and current. It was decided here
to measure the resistance with a Wheatstone bridge and to obtain
the current by reading the voltage across a high precision 10 ohm
resistor in series with the bomb calibrating resistor. The
decision to use I rather than V was based on the following:

a) If V were measured it must be taken to include the
   drop in the leads and then corrected whereas the
   current is the same at all points.

b) The Wheatstone bridge permits a measurement of the
   resistance of the 10 ohm precision resistor and the
   300 ohm bomb resistors before and after a run as a
   check. No measurements need be taken during the
   run except the voltage across the 10 ohm resistor.

c) The voltage across the 10 ohm resistor is nominally
   1 volt (I = 0.1 Amp = 30 volts/300 ohms). This is
   readily measured to four digits with a digital
   voltmeter to an accuracy of $\pm$ 1 mv or 0.1%.

A procedure for the calibration is given in Appendix E.
Included in Appendix B is a circuit which permits starting the
electrical timer simultaneously with the application of a constant
voltage to the bomb calibration resistor. The voltage across the
10 ohm resistor is conveniently read at terminals provided and a
dummy 300 ohm resistor is available for roughly adjusting the
current prior to the run.

5. PROBLEMS ASSOCIATED WITH MEASURING
MINUTE QUANTITIES OF HEAT

Calorimetry involving large quantities of heat minimizes the need for highly accurate allowances for stirring energy, transfer with the surroundings, stirrer bearing friction and the like. However, in a measurement of 50 calories, effects which might be ignored or grossly corrected for in the more common bomb calorimetry must be reduced and/or made to cancel out. Hopefully many of these can be evaluated. A chief concern in this study was the identification of all the sources of heat generation and transfer and the estimation or actual measurement of values for them.

5.1 The System - Its Parts and Its Surroundings

Fig. 2 is a schematic representation of the system. A photograph of its parts is shown in Fig. 3. Temeprature sensors are located at B and C.

Cover

Multi-layer Jacket

Vacuum Flask

Bomb

Water

D

A - Bomb Interior
B - Calorimeter Water
C - Ambient Air
D - Bearing

A B

C
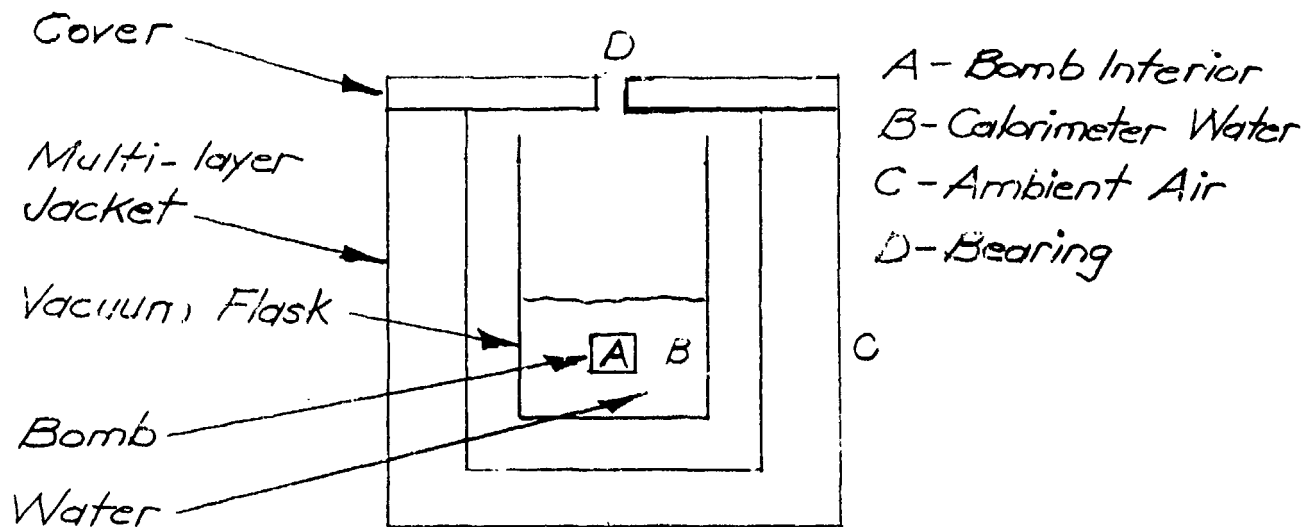
Fig. 2 - Heat Transfer System Schematic
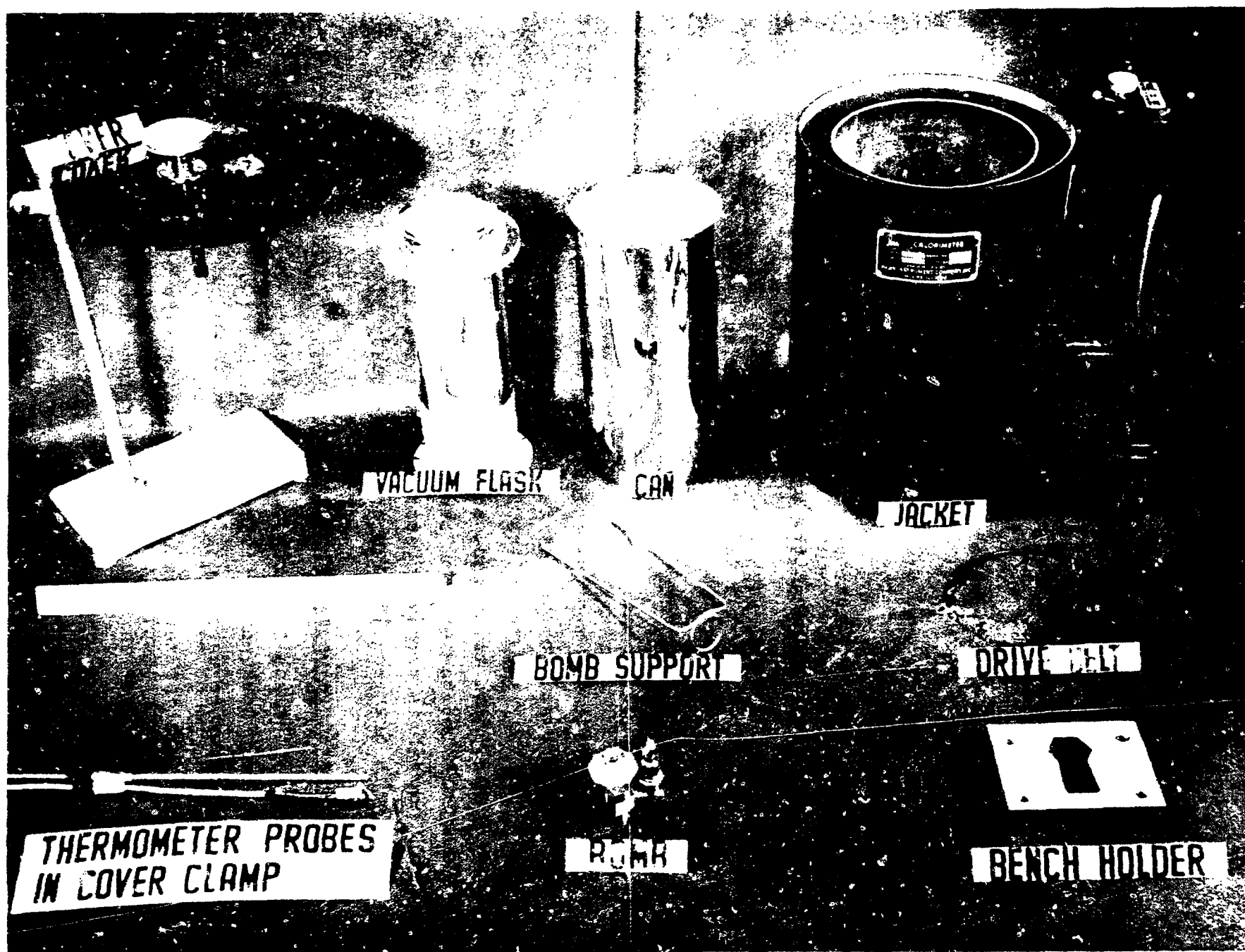
Fig. 3. Photograph of Calorimeter Components

Heat is generated within the system by conversion from:

a) mechanical energy at D due to bearing and belt friction, both functions of belt tension

b) mechanical energy at B due to viscous friction of the stirrer in the calorimeter water

c) electrical energy at B from the power to operate the pressure transducer which contains an integrated circuit

d) electrical energy at A during calibration due to resistive heating

e) chemical energy at A during initiator tests due to ignition of the initiator

Exchanges with the surrounding room occur through

f) radiation through the various jacket layers

g) conduction through the jacket, along the stirrer shaft, along the temperature sensing probes or connecting cables

h) convection effects beneath the cover and outside the jacket.

Thermal gradients must be established throughout all parts of the system whenever a change of temperature occurs, i.e., continuously but very slowly in the uses described here. Whenever such gradients cease to change, equilibrium has been established. In this system the temperature sensors are of such high resolution that equilibrium is rarely effectively established and one must be satisfied with near equilibrium or quasi-steady state conditions.

5.2 Non-Temperature Dependent Transfers

Items (a) through (e) in Sec. 5.1 constitute transfers which are temperature independent. Item (a), the bearing friction, is slightly temperature dependent in that

(1) the bearing temperature increases during operation thereby producing increased radiation, convection and conduction which are temperature dependent

(2) the bearing friction increases with decreasing
ambients due to increased viscosity of the
bearing lubricant.

These effects were believed to be second order effects and were
neglected.

For this general class of transfers, the rate of heat flow,
dQ/dt, will be designated as dQ/dt = N. A theoretical treatment
of this transfer will be found in Appendix F.

Fig. 4 shows the effect of two of these non-temperature
dependent transfers, a changing belt tension and the transducer
power.

5.3 Temperature Dependent Transfers

Items f, g, and h in Sec. 5.1 constitute transfers which may
be considered proportional to the temperature difference between
the calorimeter water at B and the ambient air surrounding the
jacket at C. Conduction, convection and radiation may all be
represented by a product of a constant and the temperature
difference if that difference is not too large.

For this general class of transfers, the rate of heat flow,
dQ/dt, will be represented by $U (T_R-T)$. A theoretical treatment
of this transfer will be found in Appendix F.

If the temperature dependent transfers are made to constitute
losses from the system by making the water temperature, T, larger
than the room temperature, T_R, and if such losses can be made to
balance the gains from the non-temperature dependent transfers,
then the net transfer rate, dQ/dt, will be zero and the system will
remain at constant temperature. In practice this is rarely
obtainable, but at least the rate of change of temperature can be
made small.

5.4 Initial Temperature Variations Following Assembly

Whenever the system is assembled, there follows a period in
which the interior temperature is changing in an attempt to reach
an equilibrium condition. The transient is affected by the stirrer

Fig. 4
EFFECTS OF CHANGING
BELT TENSION & TRANSDUCER POWER
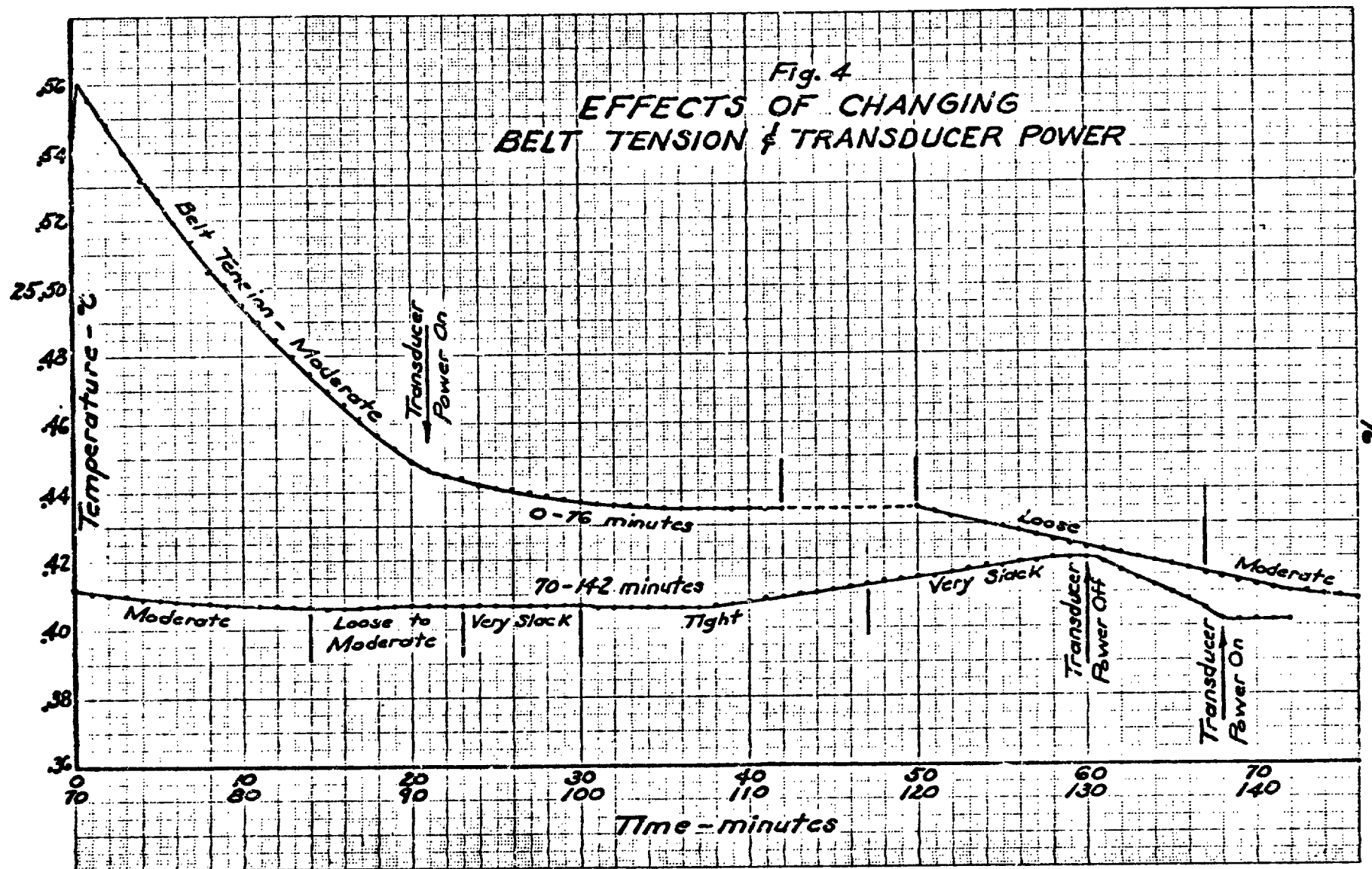
action, transducer power, and the initially different temperatures of water, flask, jacket, bomb, etc.

Fig. 5 shows the temperature variation for a 93 minute period following assembly. The shape of this curve depends on the initial temperature difference between the water and the surrounding air. In this case that difference was 1.2 to 1.5 C°. A constant slope is not reached, in theory, for a very long time. In practice, the subjective judgement that the slope has become constant depends on the precision of the temperature measurement and the time interval of observation. In the figure, constant slope appears to have been attained after about 75 minutes, the value being 3.3 millidegrees per minute. The temperature difference between inside and outside the calorimeter is continually changing since most laboratory areas are not temperature controlled better than perhaps ± 0.5 C° over a 15 minute period.

Such small changes would not affect systems used to measure large quantities of heat. In the case of small quantities, attention must be paid to whether or not the slope of the T vs t curve is changing rapidly enough to produce a measurable effect on the results of an eighteen minute initiator test. This is specifically accounted for in the Operating Procedure in Appendix C.

It was found that if the calorimeter water were 2 to 3 C° above the surroundings, the slope was close enough to zero that it changed very slowly. The waiting period prior to a test could then be as short as fifteen minutes, just enough time for the stirring and transducer energies to establish initial heat flow paths to the room and to accomplish a nearly uniform temperature between the water, vacuum flask wall, and bomb. Variations in belt tension will also affect the required temperature difference. The chief criteria are that the rate of change of temperature be small and relatively constant over the nominal eighteen minute initiator test period and that at least fifteen minutes has elapsed since the stirring began.

5.5 Thermal Time Constants

Application of a heat energy pulse to a thermal system or a

Fig. 5
TEMPERATURE VARIATION
FOLLOWING ASSEMBLY

75-93 minutes

50-75 minutes

25-50 minutes

0-25 minutes

Temperature - °C

Time-minutes   five minutes
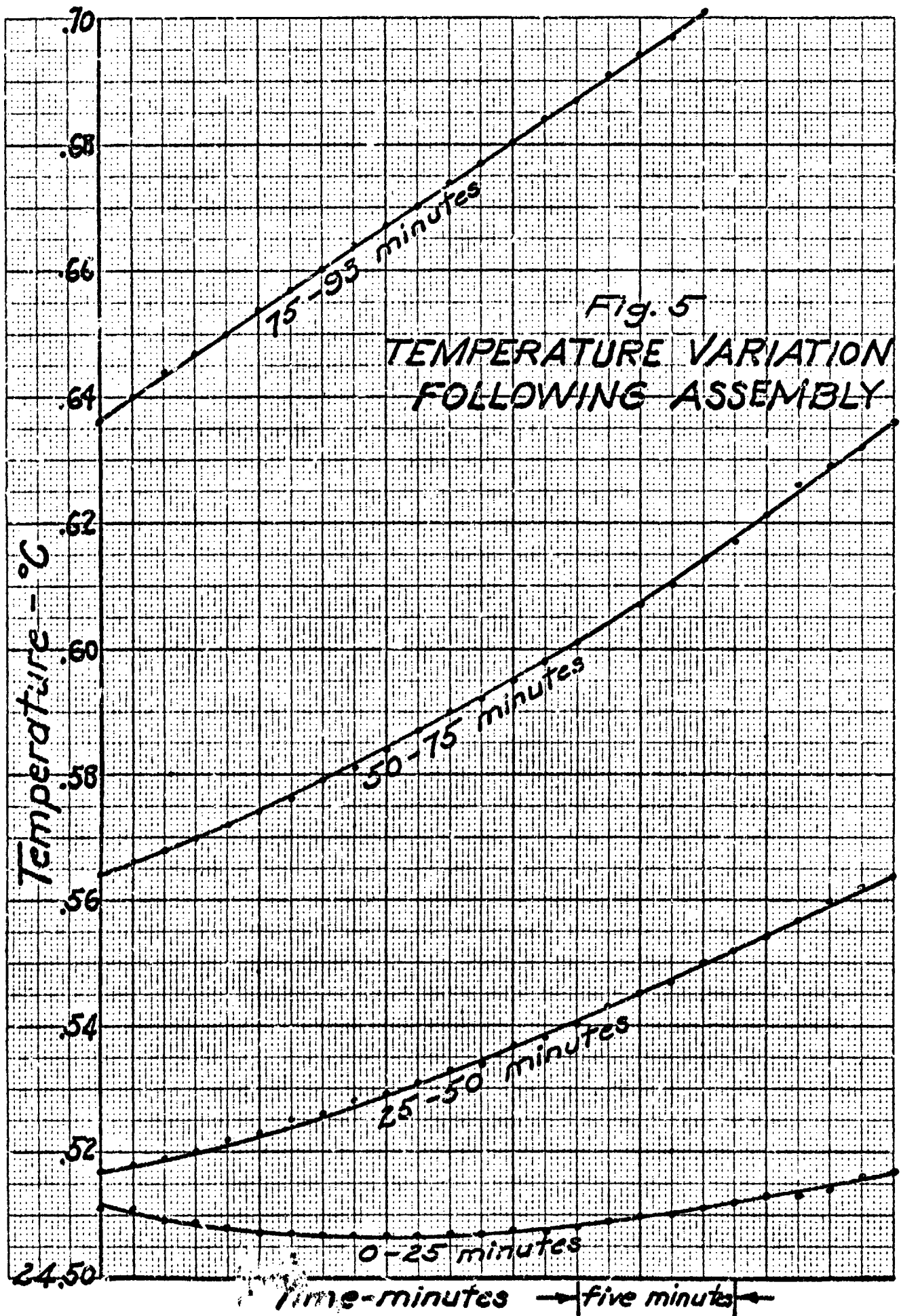
sudden temperature change between the interior and exterior of a system produces a thermal pulse, the effect of which decays slowly with time. Two specific applications are of interest here:

(a) A change of ambient air surrounding the system induces a change of thermal gradients affecting the water temperature.

(b) A heat pulse is supplied to the interior of the bomb by an initiator or during calibration. This pulse is subsequently detected as an increase of water temperature.

Time Constant for Transfer From Water to Surroundings

The entire calorimeter assembly was placed in a freezer at -17°C to -20°C. The calorimeter water temperature was monitored over a five hour period during which it reduced from 24°C to 7°C. A plot of the logarithm of $\Delta T/\Delta T_{max}$ vs time is shown in Fig. 15 in Appendix F. This semi-log plot yielded a time constant of 8.5 hours.

A value of 9.0 hours for this constant was obtained from Fig. 14 in Appendix F. The theory relating to these values also is discussed in this appendix.

The approximate 6% difference between the values is not important but rather the fact that the time constant is quite long. A nine hour time constant means that it will take nine hours for 63% of an imposed change in ΔT between the room and the water to be observed as a change of water temperature. It takes five time constants or 45 hours for 99% of the change to be accomplished. It would therefore appear that the system is well insulated.

This is misleading in that the water temperature sensor detects changes of 1 millidegree. It is appropriate here to calculate how long it should take the water inside the calorimeter to change 1 millidegree following a change in ΔT across the calorimeter insulation of 0.1 C° (about the limit of stabilization for a well controlled laboratory).

$$\Delta T = \Delta T_{max} \left(1 - e^{-t/\tau}\right)$$

$$0.001 = 0.1 \left(1 - e^{-t/\tau}\right)$$

$$e^{-t/\tau} = 1 - \frac{0.001}{0.1} = 0.99$$

$$t/\tau = .01$$

$$t = .01 \times 540 \text{ minutes}$$

$$= 5.4 \text{ minutes}$$

In general, for room temperature variations 100 times the temperature sensor resolution, the sensor will detect the change after 1% of a time constant.

It is concluded that because this 5.4 minutes is less than the 18 minute test interval, changes in room temperature should be minimized. Fig. 11 in Sec. 6.2 shows the effect of turning the air conditioner on and off.

Time Constant for Energy Pulses

During an initiator test, it is recommended in Appendix C that a time of six (or perhaps twelve) minutes be allowed for the energy pulse to be completely detected by the rise of water temperature. The initiator energy is released chemically in a fraction of a second but the heat from this flash of flame (and possibly molten ash) must be transferred through the bomb wall to the calorimeter water to be detected. An estimate of the time constant for this transfer was desirable since VMIRL was not going to perform any tests using actual initiators.

Fig. 10 in Sec. 6.2 shows a typical pulse produced by electrical heating. This pulse appears to produce an exponential temperature rise. A plot of the logarithm of ΔT vs time measured from the actual curve to a corresponding point on the dotted line above it (which corrects for the rise due to room temperature) was linear, except for a small initial time period. Fig. 6 shows the results of six such plots, three using the capacitance discharge method and three using the RI^2t method. In the RI^2t method the energy for the pulse

Fig. 6
TIME CONSTANT
FOR ENERGY PULSES
Resistor Immersed in Air

Capacitor Method
RI^2t Method
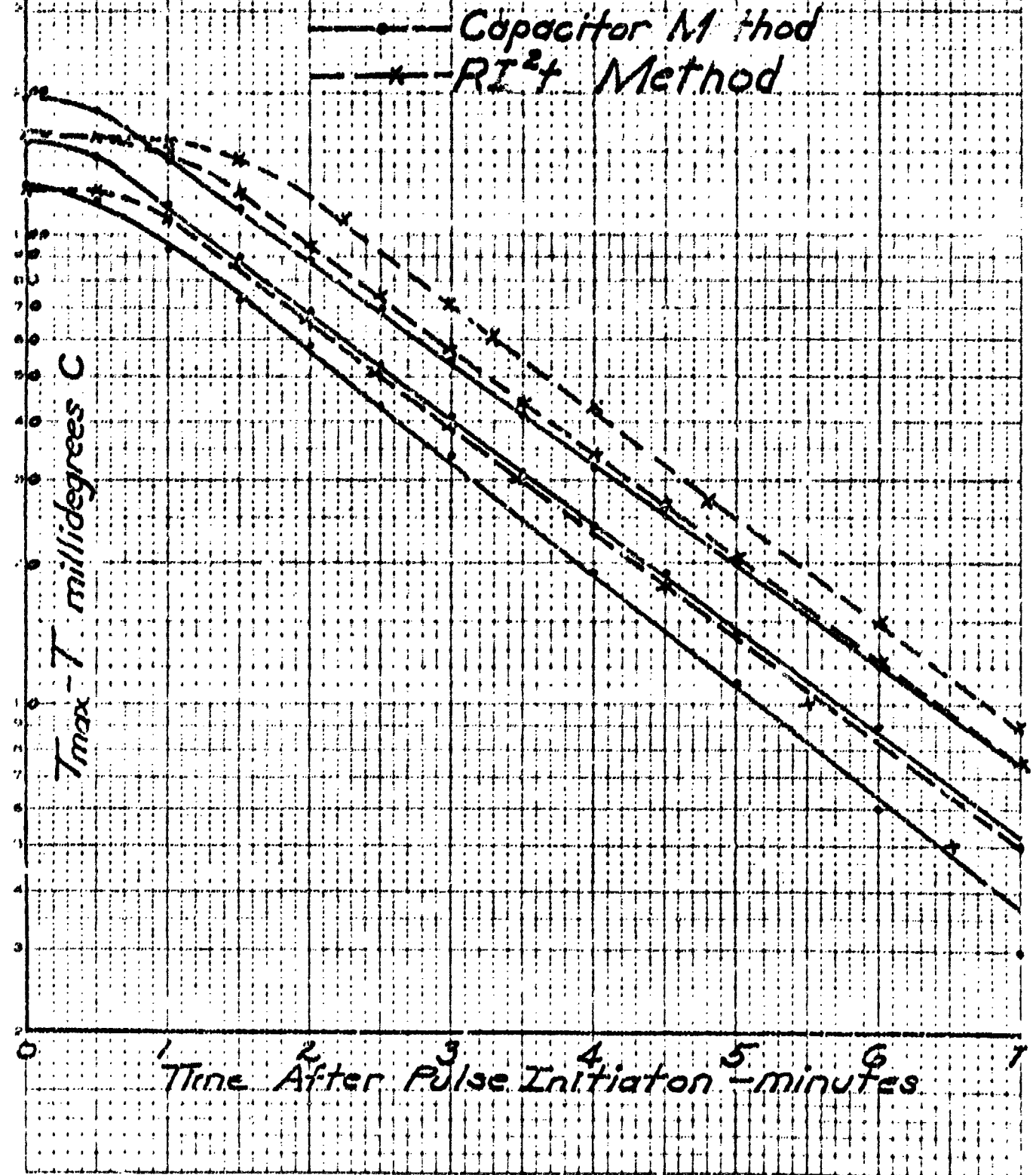
was supplied over a 70 second interval at a constant rate. Using
the capacitor, the energy was supplied at an exponentially decreasing
rate with an electrical time constant, RC, of 25 seconds. The
resistor inside the bomb was transferring its heat through air to
the interior bomb wall. The slopes of these curves are essentially
equal, yielding a time constant of 117 seconds.

It should be noted that the initial periods of non-linearity
on the plot are longer for the RI^2t method than for the capacitor
method but that this does not affect the final slope value and
time constant.

To improve this transfer, about 8 gm of the 250 gm of calori-
meter water was placed inside the bomb. Fig. 7 is a semi-log plot
of ΔT vs time, again using both the capacitor and the RI^2t cali-
bration methods. The results are similar to those discussed above
except for a time constant which is 35 seconds.

It is concluded that the time constant for heat transfer from
the initiator to the calorimeter water will have an upper limit of
about 117 seconds and a lower limit of about 35 seconds. It could
be closer to this latter value if an appreciable amount of molten
ash is projected against the bomb wall since this should speed the
transfer. The very short time required for the chemical energy to
produce heat energy is an insignificant factor compared to the time
constant for transfer.

The six minutes allowed in the calibration procedure of
Appendix C was clearly verified by the fourteen pulses plotted in
Fig. 11 of Sec. 6.2 in which the 8 gm of water was used inside the
bomb. Six minutes is 8.5 time constants which theoretically includes
99.98% of the complete energy pulse. Since a typical temperature
rise is 180 millidegrees with a reading accuracy of 1 millidegree
or 0.55%, the time allowed to essentially complete the pulse should
be that for 99.45% of the pulse or 5.4 time constants. If 5.4 time
constants are necessary for an initiator test which allows 6 minutes,
then the time constant for an initiator pulse transfer should be
5.4/6 or 0.9 minutes which might be possible since it was shown above
that the resistor in air gave a 2 minute thermal time constant.

Fig. 7
TIME CONSTANT
FOR ENERGY PULSES
Resistor Immersed in Water
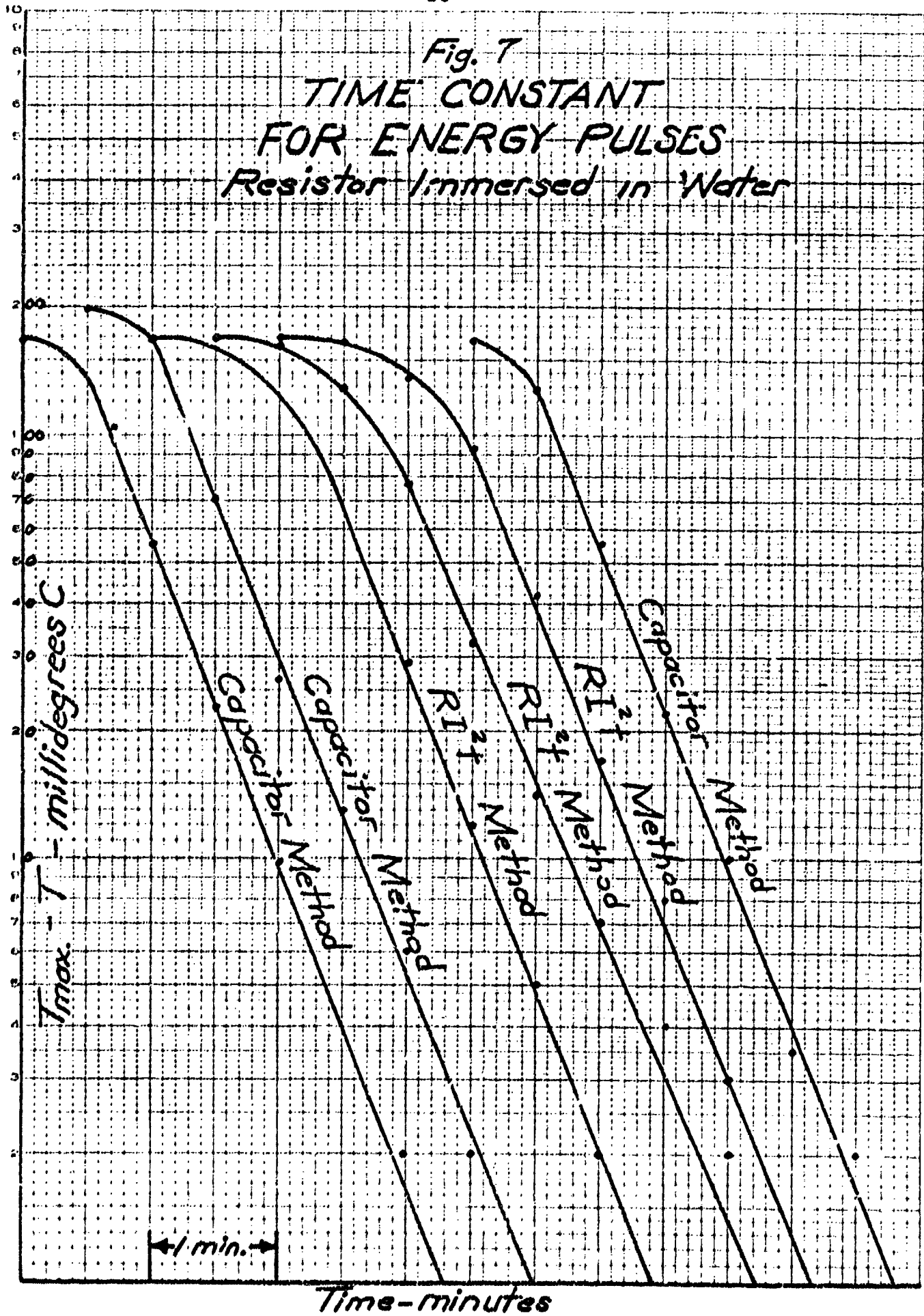
Should subsequent tests on the actual initiator by others indicate a longer time is needed, the operating procedure of Appendix C should be modified to increase the middle time interval (for pulse temperature rise) to 9 or even 12 minutes rather than the 6 minutes presently specified.

6. EVALUATION OF VMIRL DESIGNED BOMB

The components of the VMIRL bomb are shown in Fig. 1 of Sec. 3. Detail drawings of each part are shown in Appendix B. The parts of the Parr model 1411 Calorimeter into which the bomb fits, are shown in Fig. 3 in Sec. 5.1. Fig. 8 is a photograph of the entire apparatus used in determining the water equivalent.

6.1 Water Equivalent - Approximate Calculation

Theoretically the water equivalent of a system can be obtained by summing the products of the mass and specific heat of the individual components. In practice this is not completely successful but a lower limit can be obtained using those components, the temperature of which must vary by the temperature variation of the water with which they are in contact. In this design, those components include:

(a) 250 gm of water in the vacuum flask

(b) approximately 200 gms of bomb made of Type 17-4 PH stainless steel

(c) 16 gm of pressure transducer

(d) 12 gm of stirrer

(e) 18 gm of bomb support (wire)

(f) metal temperature probe(s)

(g) some allowance for the inner glass wall of the vacuum flask.

Approximate values for items (b) through (g) might total 270 gms. Assume all these components have a specific heat of 0.10 cal/gm C° yielding a water equivalent of

$$(250 \times 1) + (270 \times 0.1) = 277 \text{ cal/C°}$$

6.2 Water Equivalent - Actual Measurement

In theory, the water equivalent, h, is obtained by dividing the quantity of heat energy added, Q, by the temperature rise, ΔT, which it produces or $h = Q/\Delta T$.

ROOM TEMPERATURE PROBE

PRESSURE TRANSDUCER
POWER SUPPLY
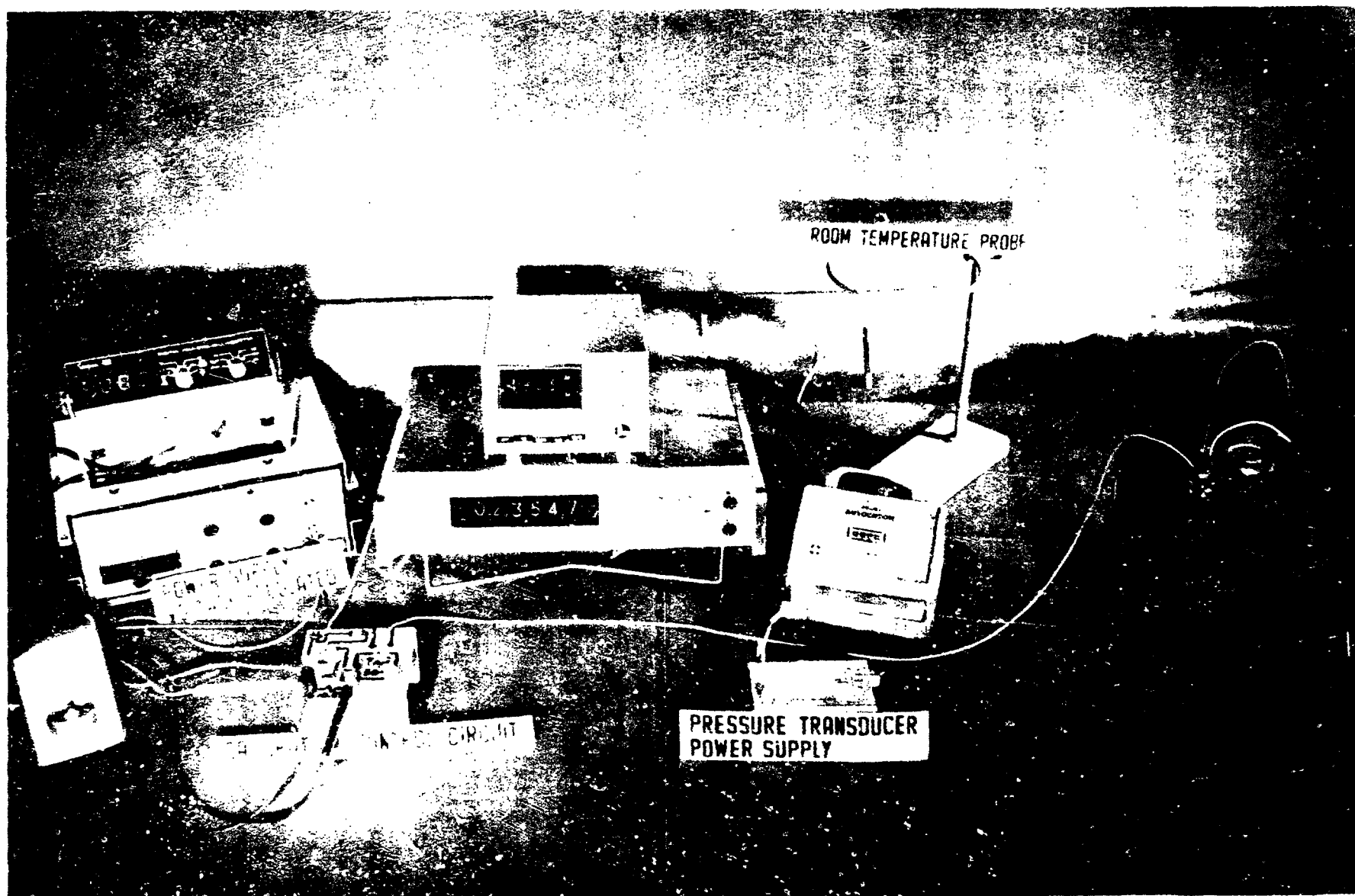
Fig. 8. Photograph of Complete Instrumentation

In practice, the bomb placed under water in the calorimeter reaches a temperature equilibrium rather quickly with the well-stirred water but rather slowly with the remainder of the calorimeter which must have established within it some temperature gradient through its layers of air, metal, glass and bakelite. In Sec. 5.3 it was shown that the thermal time constant for the entire calorimeter system was about 9 hours. In Sec. 5.4 the stablization period was discussed.

It is well known that bomb calorimetry techniques include an allowance for the rising or falling of the water temperature at a slow rate dependent upon whether the interior is gaining or losing heat due to its surroundings. A typical curve from which the value of ΔT due to an energy pulse must be extracted might be one of the following:
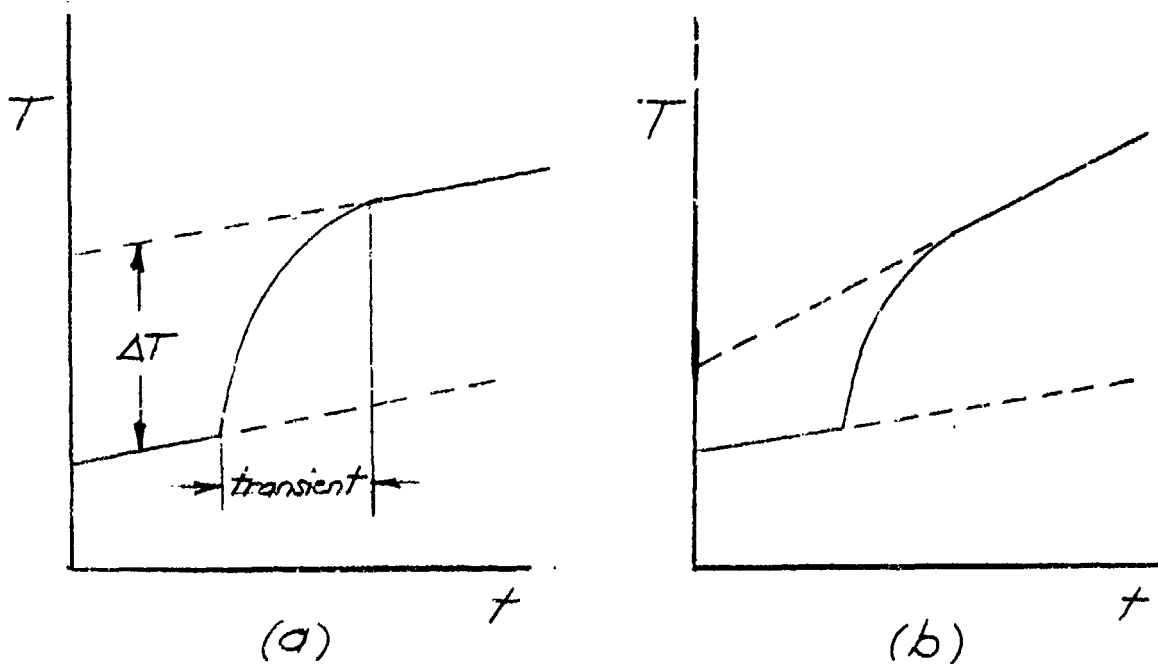
Fig. 9 — Energy Pulses with Different Slopes

In (a) the original and final slopes are so nearly identical that the rise, ΔT, may be measured at any point between the parallel lines. In (b) this is not so and ΔT must be read at some point within the transient period, that point being selected based on some fraction of the transient period to compensate for the different slopes.

In this report, considerable care is taken to assure that these slopes are so nearly equal that it is possible to measure this ΔT conveniently, at the start of the energy pulse (initiator or calibration), without substantial error. The actual procedure for taking readings is outlined in Appendix C (initiator tests) and Appendix E (calibration tests).

Fig. 10 is a plot of a typical curve obtained when an energy pulse of about 50 calories was supplied to the bomb via electrical heating of the calibration resistor. The plot uses a scale in which each small division represents 1 millidegree centigrade. On such a scale the slope of the temperature-time plot is very evident. In this study, data was taken over periods of typically several hours with 50 calorie energy pulses supplied to the bomb about every 15 to 25 minutes. In this way a reliable slope could be determined prior to, and following, each pulse.

The rise, ΔT, was obtained by extending the slope following the pulse backward to the start of the pulse and measuring the rise there, 179 millidegrees on the sample shown.

The energy supplied is calculated from $RI^2 t$ using for R the corrected resistance obtained by subtracting the lead resistance from that for lead plus resistor. The current is read from the voltage across a 10.00 ohm precision resistor and the time from an electrical timer readable to $\pm$ 0.1 seconds for which an estimate to 0.03 seconds is possible. Precisions are as follows:

In R, 303.1 $\pm$ 0.05 ohms from a Wheatstone bridge whose accuracy was verified with Leeds and Northrup standard resistors of accuracy $\pm$ 0.01%. The overall precision of R is judged not to exceed 0.05% including connector resistance.

Fig. 10
TYPICAL ENERGY
PULSE
$\Delta T = 25.995 - 25.816$
$= 0.179 \, C°$
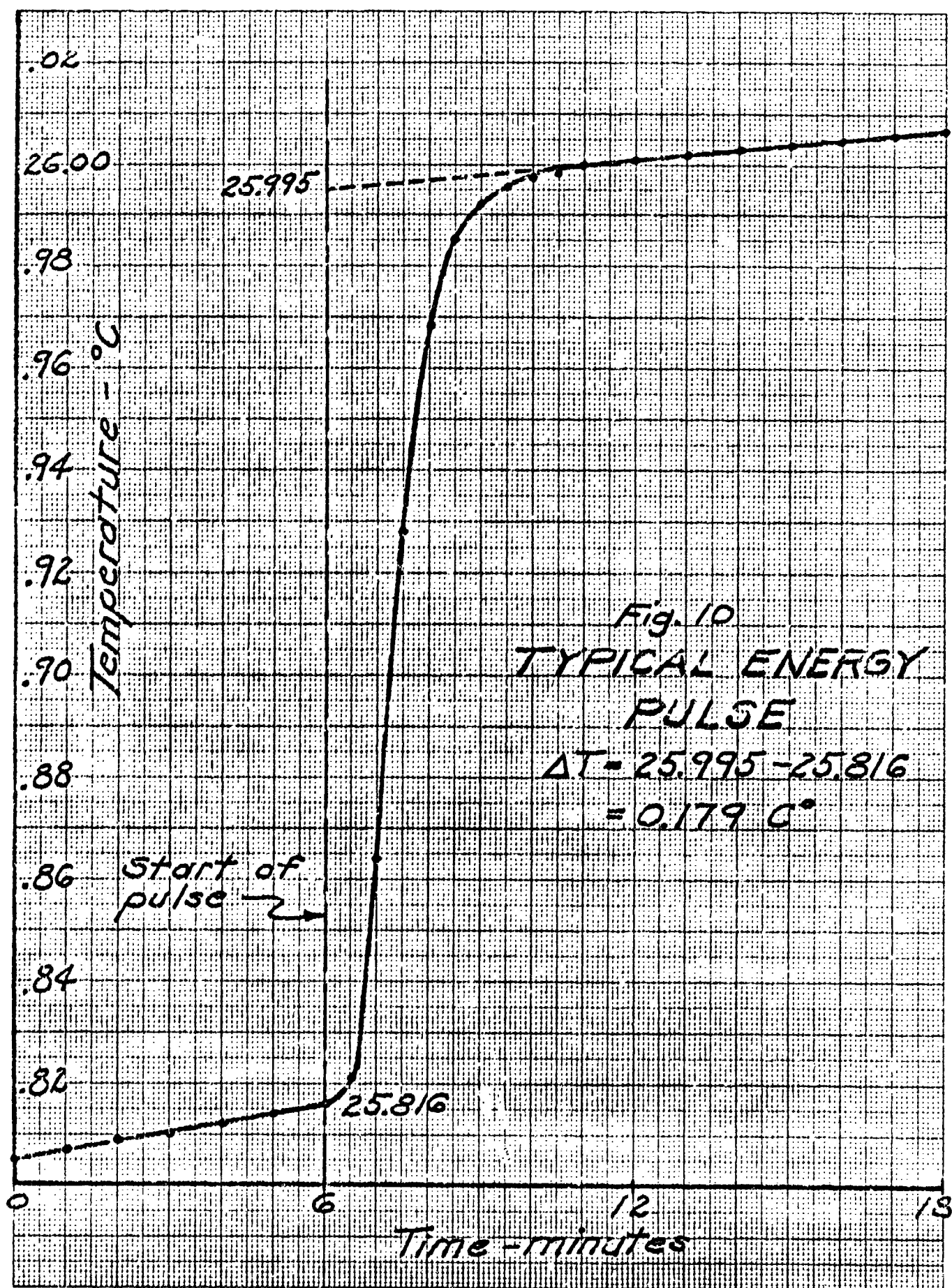
In t, simultaneous application of the energy to the bomb and starting of the timer is assured by using a common switch in the circuit shown in Appendix B. The precision of t is 70.0 $\pm$ 0.07 sec or $\pm$ 0.10%. This makes some allowance for the inertia of starting and stopping the timer which allowances tend to partially cancel.

In I, the digital voltmeter reading the voltage across the 10.00 ohm resistor has a resolution of $\pm$ 1 digit in four or 1.001 $\pm$ 0.001 volts. This meter accuracy was verified using a potentiometer readable to 1 digit in 5, the standard voltage cell of which had been recently checked. The precision of I is thus estimated to be 0.2%, that of I^2 is then 0.4%.

Combining these percent precisions by taking the square root of the sum of their squares, one obtains $\sqrt{.1^2 + .05^2 + .4^2} = \sqrt{.1725} = 0.41\%$ as the precision of the energy calculation.

Typical measurements of ΔT from the graphs or from the data taken at specific six minute intervals (as in the procedure of Appendix E for calibration) indicate precisions of 180 $\pm$ 2 milli-degrees or about 1%.

Values of the water equivalent, h, then have percent precisions due to Q/ΔT of $\sqrt{0.41^2 + 1^2} = \sqrt{1.173} = 1.08\%$. That is, the precision of h is essentially that due to the ΔT measurement. It should also be remembered that of the total water equivalent of 284 cal/C°, 250 is due to actual water inside the vacuum flask and the bomb. A possible precision of $\pm$ 0.2 cm^3 in a volumetric pipette and some allowance for improper drying could introduce an additional inaccuracy in h of 0.5 in 250 or 0.2%. It seems safe to conclude that h can then be relied upon to less than $\pm$ 2% conservatively. See Error Analysis - Appendix A.

Fig. 11 is a plot of a series of 14 energy pulses applied to the bomb without a change of water in the surrounding calorimeter between pulses. The scale is broken to show all 14 pulses. The values obtained for each of these trials are listed in Table 1.

Fig. 11

DETERMINATION OF WATER EQUIVALENT
Model 1, 250 gm. H₂0
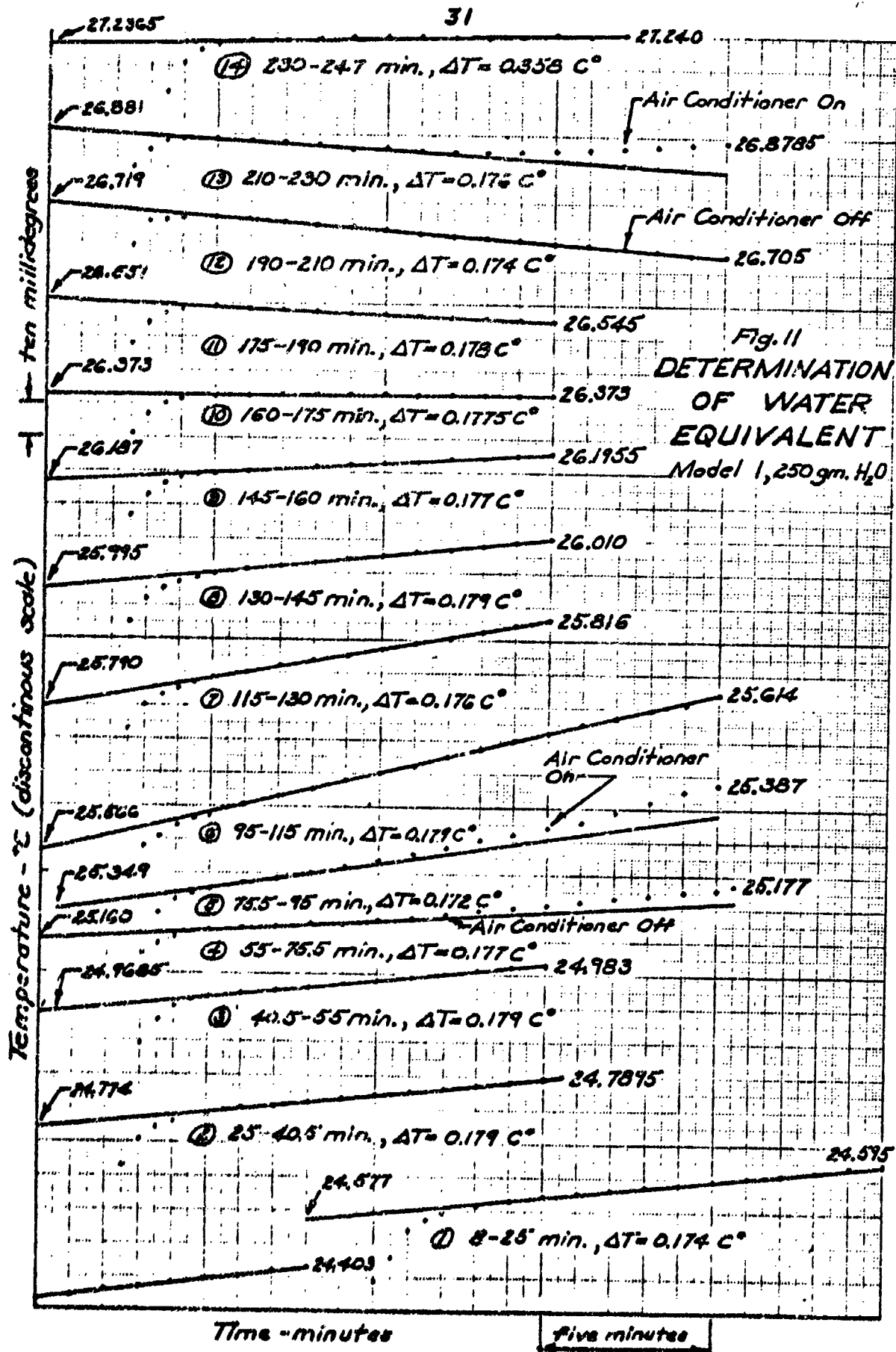
These were determined from plots like that of Fig. 10. The method
of Appendix C using data at specific times was applied to this same
data and the resulting values of ΔT agreed with the graphical
method exactly or differed by no more than 1 millidegree as shown
in the last column of Table 1. The water equivalent was determined
to be 283.8 cal/C° with a standard deviation, σ, of 1.37 cal/C° or
0.5%. This value was obtained from 12 trials summarized in Table
1. It should be emphasized again that this standard deviation is
low because these pulses were applied without a change of water
(250 cal/C°). If a possible deviation of 0.5 gm in the water used
is added to the above, the standard deviation could be 3.3 cal/C° or
1.2% (see example in Appendix A) which remains well within
acceptable limits. This value should apply to Model 1 or Model 2
since their masses are identical within 0.03%. It should apply
equally well when the initiator replaces the calibration resistor
plug since this results in an increase of mass of 4 gm or about
0.4 cal/C°, 0.15% of h.

TABLE 1

SUMMARY OF WATER EQUIVALENT CALCULATIONS

250 gm of Water (includes 8 gm inside bomb)

RI^2t Method   R = 303.1 excluding leads   t = 69 sec.(approx)

Trial	Energy Pulse Calories	Temp. Rise by graph C°	Calc. Water Equivalent Cal/C°	Temp. Rise by formula C°
1	49.38	0.174	283.8	0.174
2	51.05	.179	285.2	.179
3	51.31	.179	286.6	.178
4	50.36	.177	284.5	.177
5 *	49.50	.172	287.8	.171
6	50.59	.179	282.6	.178
7	49.71	.176	282.4	.176
8	50.49	.179	282.1	.179
9	50.09	.177	283.0	.176
10	50.30	.1775	283.4	.176
11	50.23	.178	282.2	.177
12	49.70	.174	285.6	.175
13 *	50.79	.176	288.6	.176
14	101.80	.358	284.4	.359

Average of 12 trials 283.8

Standard Deviation σ ~ 1.37 or 0.5%

2σ ~ 2.74 or 281.1 to 286.5

*This trial was discarded before averaging. It was affected by turning off the room air conditioner just prior to the trial. See Fig. 11. Turning on the air conditioner does not alter the room temperature as suddenly.

Table 1 indicates two standard deviations, 2σ, is 2.74 yielding a range of 281.1 to 286.5 cal/gm. 2σ in a Gaussian distribution should contain 95.4% of the values. In Table 1, 11 of the 12 (92%) are within this range. Had there been many more than 12 trials the standard deviation of the mean would be expected to be $1.37/\sqrt{12} = 0.4$ cal/C° or 0.14%.

Two trials, numbers 5 and 13 in Fig. 11, were omitted from the average in Table 1. As explained in Sec. 5.5, a sudden and sizeable change in room temperature will affect a test. Trials 5 and 13 were performed immediately after the room air conditioner was turned off. The room temperature was rising sharply during the next 20-25 minutes (a total rise of about 2 C° in each case). This had a marked effect on the slope during the latter part of that period. The effect of turning on the air conditioner was far less pronounced because the room temperature changed more slowly when decreasing on a hot day than when increasing.

Data to determine the bomb water equivalent was taken with the same apparatus following the VMIRL tests by Mr. Frank Krieger of the Harry Diamond Laboratories. Details are listed in Appendix G. Table 1 in Appendix G lists 12 usable values obtained without changing water. These yield an average of 284.3 cal/C° with a standard deviation of 2.3 or 0.8%. When this average is combined with three other runs in which the water was changed, the average water equivalent is 284.8 cal/C° with a standard deviation of 2.1 or 0.7%. This is in good agreement with VMIRL values and confirms the accuracy of less than 1% in the bomb constant.

6.3 Pressure Testing

An early bomb design utilized an unsupported neoprene gasket between the bomb cup and cap. This gasket design was improved as suggested by the Parr Instrument Co. to include a teflon gasket with a machined seat in the cap. It was believed that this alteration would improve the ability of the gasket to withstand the design pressure of 3000 psi. Details of the gasket, gasket seat, etc., are shown in the drawings in Appendix B.

Both the neoprene and teflon gasket designs were pressure tested in the Physics Department of the University of Virginia using a dead weight tester having a useful range to 2400 psi. The unsupported neoprene gasket held at 1600 psi for about five minutes. Failure after that was due to the gasket being extruded into the threaded portion of the nut along the outer and unsupported edge.

The model with the supported teflon gasket set in a grooved seat as shown in Appendix B held at 2400 psi with no leaks under a water immersion test. A 2600 psi pressure was applied and there was no leaking visible but accurate and prolonged testing was not possible because this value exceeded the upper limit of the test facility.

During this testing the pressure transducer developed a leak at 1000 psi which increased markedly at 1600 psi so that extra tightening of transducer components was necessary. Leaking also appeared at the tapered screw threads between the pressure transducer fitting and the cup body. This was eliminated by using two layers of teflon tape and by tightening the thread by one or two complete turns (this necessitated subsequent machining of the end of the fitting which had then protruded into the cup by a thread or two).

6.4 Volume

The Scope of Work in Sec. 1.1 called for an internal volume of 10 ml. Each of the models was checked for conformity to this specification by weighing the bomb with transducer and then filling with water to a point in the threads of the cap which was estimated to be the bottom of the spent initiator. Reweighing and subtraction yields the water mass added in grams which is equivalent to the volume in ml. Care was exercised to remove trapped air bubbles.

MODEL 1 - 9.85 + 0.05 ml.   MODEL 2 - 9.60 + 0.05 ml.

The inaccuracy in the measurement is due to an inability to exactly duplicate the level of filling.

6.5 Cycling Time

The Scope of Work in Sec. 1.1 called for a recycle time of less than 1 hour. This time depends on the speed with which an individual technician can disassemble, clean and reassemble the calorimeter in addition to the stabilization time and time for the test run.

These latter two times are fixed at 15 min and 18 min, respectively, for a total of 33 min. If 20 min is allowed for disassembly, cleaning and reassembly, the total time is 53 min which is within the requirement. The 20 min period would seem reasonable for an experienced technician after several trials.

It should be noted that the test runs conducted by VMIRL were all calibration runs, none being with actual initiators. It was shown in Sec. 5.5 that the thermal time constant for the initiator tests could be longer than for a calibration test because of poorer transfer. Should this prove to be the case the time for the transient due to the energy pulse might have to be increased from 6 min to 9 or 12 min but this should still not exceed the one hour total for recycle time.

6.6 Thermometer Comparison

A Hewlett Packard Model 2801 A Quartz Thermometer was the primary instrument used. The sensor is a quartz crystal having a frequency of oscillation which is temperature dependent. It is enclosed in a 3/8" diameter by 11/16" long stainless probe connected by a miniature coaxial cable. The electrical circuitry includes a frequency counter with digital readout directly in °C. Two probes are available for readout using push buttons. Readings may be taken to a resolution of 0.01, 0.001, or 0.0001 °C, the sampling time being 0.1, 1, and 10 seconds, respectively. Calibration, linearity, and stability errors are in the order of a few hundredths of a degree. Calibration and linearity errors are insignificant for temperature difference measurements. Short term stability is ± 0.0001 C°. This instrument with probes is valued at over $3500.

A less expensive instrument would be desirable if it were equally suited to this application. The Parr Instrument Company provided on loan their Model 1666 Calorimetric thermometer manu-

factured by the Yellow Springs Instrument Co., Yellow Springs, Ohio.
(YSI Model CT 11) This instrument, valued at about $2000, has a
thermistor as a sensor enclosed in a 0.150" diam. by 10" long probe
(only about the last 3/4" need be immersed). Its range is limited
to 20 to 30°C with a resolution of 0.001 C° and a sampling rate
estimated to be well under one second. Provision is made for
zeroing the instrument and for an internal calibration check by
push buttons on the front panel. Temperature rise measurements over
a 3 C° span are claimed by the distributor to be repeatable to
± 0.002 C°.

These two instruments were used simultaneously on several test
runs and the less expensive thermistor thermometer appears equally
suitable for the application described here. A Model 1656 Digital
Printer is available for a permanent tape record. A Model 1654
Automatic Programmer is also available for actuating the printer
reading mechanism on a preset schedule of readouts. Neither of these
latter items was tested.

7. CONCLUSIONS AND RECOMMENDATIONS

A bomb useable in a commercially obtainable calorimeter was designed and two models were fabricated and tested with the following specifications (Refer to Scope of Work Sec. 1.1 for design goals):

(1) Predicted precision for measuring a 50 cal pulse from an initiator of $\pm$ 1 cal.

(2) Static pressure tested to 2600 psi.

(3) Internal volume of 9.6 cc and 9.85 cc $\pm$ 0.5% for two models fabricated.

(4) Fitted for use with one pressure transducer.

(5) Made of Type 17-4PH Stainless Steel which should be suitable for at least 1000 cycles. Easily accessible for cleaning.

(6) Recycle time of one hour was based on calibration tests and estimated to be that for initiator tests.

(7) Water equivalent measured as 283.8 cal/C° with a standard deviation of 1.37 cal/C° in repeatability tests. Predicted standard deviation including error of various operators in weighing water is 3.3 cal/C° or 1.2%.

(8) Operating procedure and calibration procedure provided separately in an appendix.

No actual tests of initiators were performed. It is recommended that, following subsequent completion of these by NASA, the operating procedure be reviewed for possible changes in the time interval $(T_{12} - T_6)$ allowed for equilibrium to be attained. The standard deviations the water equivalent calibrations and initiator tests of subsequent operators would be of interest in a continuing evaluation of performance at least for some initial test period.

APPENDICES

APPENDIX A - ERROR ANALYSIS

Introduction

To assess the precision of the various quantities calculated from experimentally measured values requires a knowledge of the precision of the experimental quantities and the application of appropriate statistical data treatment of these precisions depending on whether they enter the calculations in a sum, difference, product, quotient or raised to a power.

It would also be helpful to identify the relative effect of the precision of each experimental quantity the precision of the final result - the calculated quantity of heat from an experimental test on a given initiator.

Distinction Between Absolute Precision and Percent Precision

As an example, suppose an experimentally determined average value of a quantity is 81.2 and its standard deviation from a number of determinations is ± 0.4. Its absolute precision is ± 0.4. Its percent precision is 0.4/81.2 or ± 0.49%.

Rules for Precision of Calculated Quantities

The following are generally accepted methods for obtaining the precision of a quantity calculated from an equation involving the addition, subtraction, multiplication, etc., of a group of quantities.

(a) Multiplication and Division - The percent precision of a product or quotient (or of a combination of these) is the square root of the sum of the squares of the percent precision of the individual terms in the product or quotient.

(b) Addition and Subtraction - The absolute precision of a sum or difference (or of a combination of these) is the square root of the sum of the squares of the absolute precision of the individual terms in the sum or difference. If the experimental quantity is multiplied by a constant before addition or subtraction, the rule for handling percent precision in multiplication must first be applied.

(c) Quantities Raised to a Power - The _percent_ pre-
     cision of R^n is n times the _percent_ precision of R.

Inspection of the above rules indicates that the precision
calculation for a quantity involving the mixture of sums, products,
powers, etc., will require the computation of both absolute and
percent precisions and a conversion from one to the other for
different parts of the calculation.

Quantities and Approximate Values

Table 2 includes quantities that must be determined by experi-
mental measurement and ones calculated from these measurements.
Experimental quantities have precisions that depend on the quality
of the measuring instrument and on the individual making the
measurement or operating the instrument. In those cases in which
a repeat measurement (or trial) is possible, a standard deviation
for a group of trials can be obtained. In other cases such as for
a voltmeter reading, the precision must be estimated from (1) the
least reading on the scale of the instrument and (2) the inherent
accuracy of the instrument as determined by calibration or comparison
with a documentable standard. In this table a combination of the
above precisions has been made and the values shown are those
typical of this study.

TABLE 2

PRECISIONS OF EXPERIMENTAL AND CALCULATED QUANTITIES

Approx. Percent Precision	Expt. or Calc.	Quantity	Nominal Value	Appropriate Equation for Calc. Quan.
1%	E	Temperature Rise	$\Delta T = 0.178C°$	
0.2%	E	Water Heat Capacity	$h_W = 250$ cal/C°	
1%	E	Capacitance	$C = 0.084$ F	
	E	Voltage on Capacitor		
0.2%		- Initial	$V_o = 100$ V	
2% *		- Final	$V_F = 70$ V	
0.05%	E	Resistance	$R = 300$ ohm	
0.2%	E	Current	$I = 0.1$ A	
0.1%	E	Time	$t = 70$ sec	
$\sqrt{.05^2+.4^2+.1^2}$ = 0.41%	C	Calib. Energy Pulse	$G = 210$ J	$G = RI^2t$
4.1% (see example)	C	Calib. Energy Pulse (alternate method)	$G = 210$ J	$G = 1/2\ CV^2$
1.1% or 4.2%**	C	Water Equivalent (total)	$h = 282$ cal/C°	$h = \dfrac{0.239\ G}{\Delta T}$
10% or 37%**	C	Water Equivalent (excluding water)	$h' = 32$ cal/C°	$h' = h-250$
1.6% or 4.3%**	C	Initiator Energy Pulse	$Q = 50$ cal	$Q = h\Delta T$

*   Includes allowance for dielectric absorption error.

** Second value is for calibration by capacitor discharge method.

Explanation and Examples

If each initiator test were preceded by a calibration without
a change of calorimeter water and if it could be assumed that no
water were lost in the operation of replacing the calibrating
resistor with the initiator, a water equivalent, h (nominally 284
cal/C°) and the initiator energy, Q, would not depend on the pre-
cision of the water measurement. For a series of calibration runs
the water need not be disturbed at all, in which case a calculated
precision predicts a repeatability which includes the precision of
the temperature and energy pulse measurements.

Another calculation of precision is needed to predict the
repeatability of the calibration among groups of such runs using
water reweighed between each group. Reweighing between each
initiator test is recommended and this possible source of uncertainty
must be evaluated in this error analysis.

To accomplish this it is necessary to separate the water
equivalent, h, into two parts:

1. h_w = mc due to the water - 250 cal/C°

2. h' due to the bomb, stirrer, walls, etc. - about
   32 cal/C°

It will be noted in the treatment which follows that this results
in a large uncertainty in h' but this uncertainty does not reappear
in Q because it is diluted by the precision of h_w. The treatment
also makes it clear how uncertainties might be evaluated in the case
of a careful technician who performed the calibration followed by
a careless operator who performed the initiator tests. If the
reader wishes to do such an evaluation, he may use a low uncertainty
for the 250 used in h' and a high uncertainty in the 250 used in Q
in the following examples.

Example for Calibration Data:

$$h' = \frac{G}{\Delta T} - h_w = \frac{.239\ (210 \pm .4\%)}{(.178 \pm 1\%)} - 250 \pm .2\%$$

$$= (282 \pm 1.1\%) - (250 \pm 0.2\%)$$

$$= (282 \pm 3.1) - (250 \pm .5)$$

$$= 32 \pm 3.2 = 32 \pm 10\%\ Cal/C°$$

Example for Initiator Test:

$$Q = h\Delta T = (h' + h_w)\ \Delta T$$

$$= [(32 \pm 3.2) + (250 \pm .5)]\ [.178 \pm 1\%)$$

$$= (282 \pm 3.3)\ (.178 \pm 1\%)$$

$$= (282 \pm 1.2\%)\ (.178 \pm 1\%) = 50.2 \pm 1.6\%$$

Note in the calculation for Q that h = 282 ± 3.3 has a slightly increased uncertainty over the value in the h' calculation because <u>another</u> water sample is involved, not a reuse of the same water but the 10% uncertainty in h' is diluted to 1.2% in the new h because of the large mass of water compared to the non-water items.

Example for Alternate Calibration by Capacitor:

$$G = \frac{1}{2}\ C\ (V_0^2 - V_F^2)$$

$$= \frac{1}{2}\ (.084 \pm 1\%)\ [(100 \pm .2\%)^2 - (70 \pm 2\%)^2]$$

$$= (.043 \pm 1\%)\ [(10000 \pm .4\%) - (4900 \pm 4\%)]$$

$$= (.043 \pm 1\%)\ [(10000 \pm 40) - (4900 \pm 196)]$$

$$= (.043 \pm 1\%)\ (5100 \pm 204)$$

$$= (.043 \pm 1\%)\ (5100 \pm 4\%) = 214 \pm 4.1\%\ joules$$

A precision of 0.2% is used for the 100 volt reading which is dependent only on meter accuracy while 2% is used for the 70 volt reading since the dielectric absorption produces an above normal reading unless adequate time is allowed for voltage recovery of an electrolytic capacitor before taking the final reading. A careful technician with practice could reduce this uncertainty considerably, possibly to 0.4%.

Conclusions

The largest contribution to the uncertainty in the measurement of the water equivalent, h, is caused by the uncertainty of the temperature rise, ΔT (somewhat less than 1%).

A measurement of the water equivalent, h, should be repeatable to 1.1% for a group of runs without changing the water. Several such groups should be repeatable to 1.2%. The measured heat generated by a given initiator should be accurate to 1.6%.

The preferred calibration method using RI^2t for an energy pulse should be accurate to 0.4%. The alternate method using a capacitor discharge can be relied upon to 4% or less depending on the amount of dielectric absorption exhibited by the electrolytic capacitors used and the technician's care in correcting for it.

APPENDIX B - DETAIL DRAWINGS

Fitting

Teflon Gasket
.865 OD .745 ID
.025 thick

.50

Teflon Tape

Can   Nut   Cap
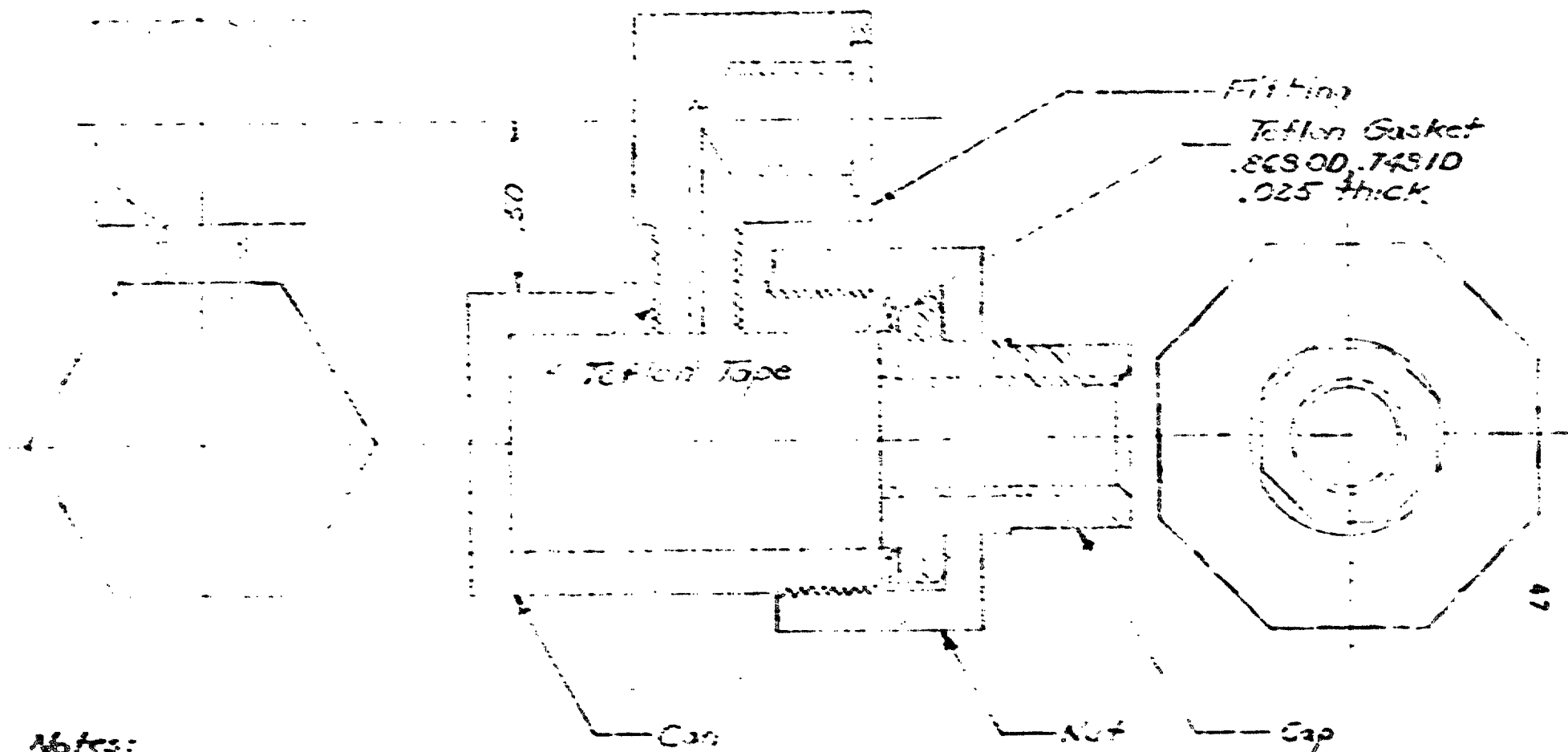
BOMB ASSEMBLY

Notes:
1. All parts except gasket
   to be of 17-4 PH Stainless Steel.
2. Fillet radii to be 1/16".
3. Finish all interior and mating
   surfaces.
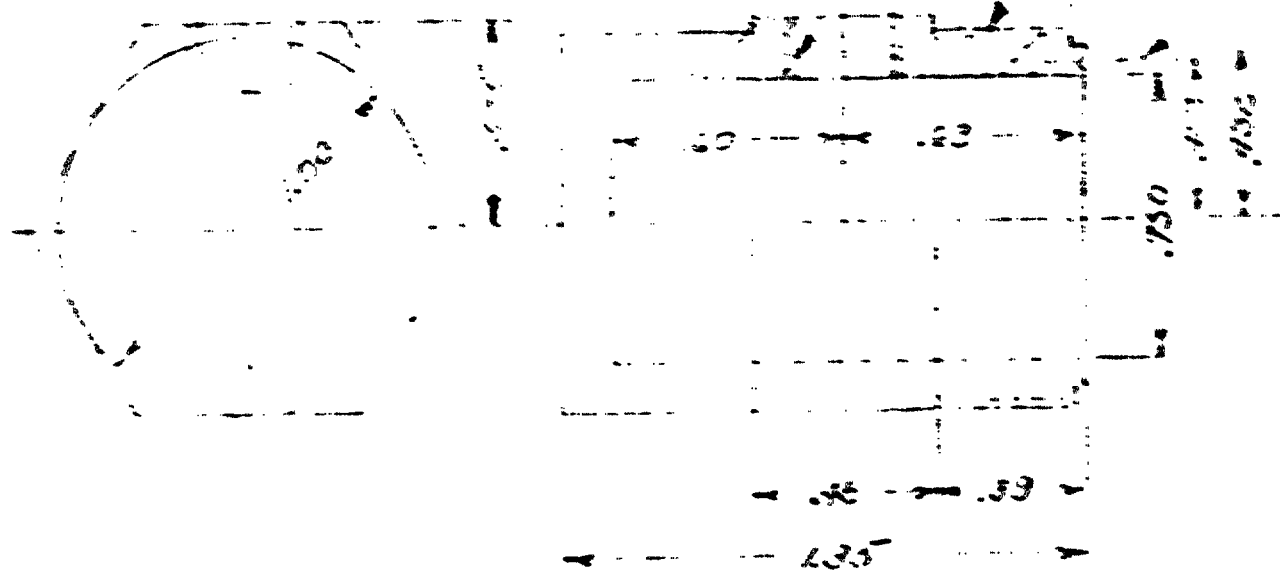
½-NEF

1-20.NEF

.020

.750

.23

.59

.135

CAN

6/72

CAP

ZONEF

HUT

60

$\frac{3}{8}-24NF$

$\frac{1}{2}-NCT$

10-32 NF

3-56 NF

Counter bore:
.30 O by .08 deep

.30
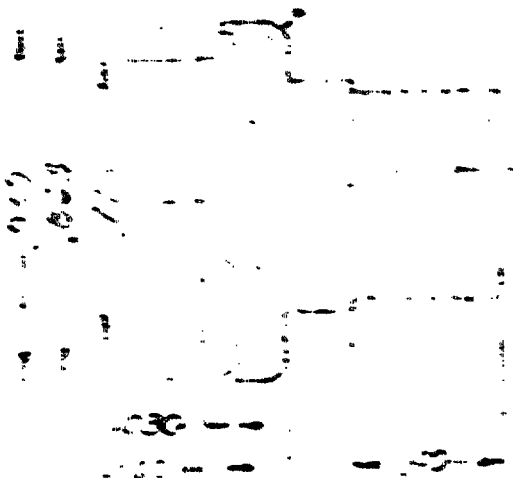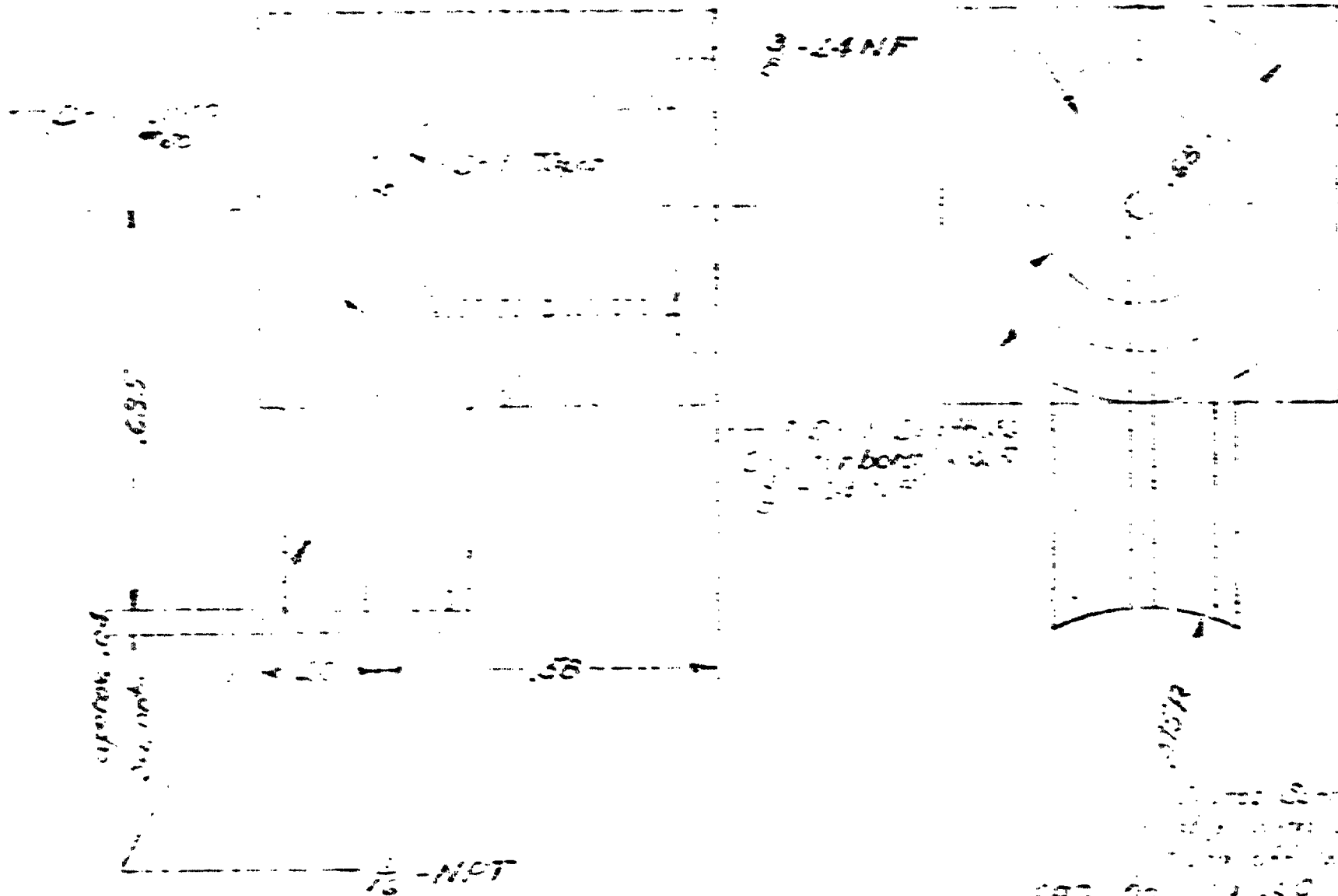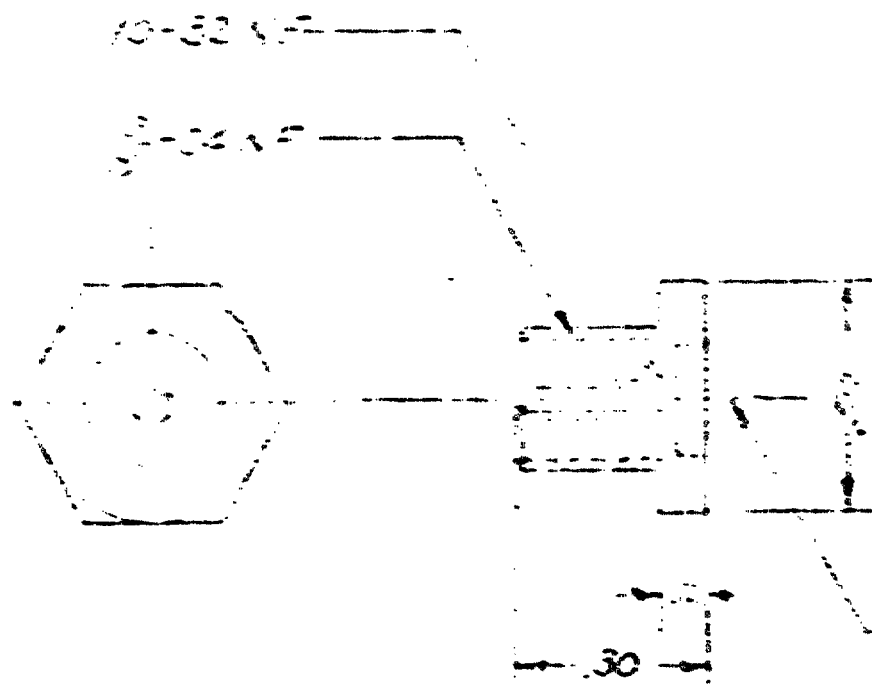
CALIBRATION PLUG
Material: 17-4 PH Stainless Steel

WHIRL
Scale: 2=1

62

.75

1.50

3.00

.50

4.00

1.00

BENCH HOLDER FOR BOMB

Material: Stainless steel

AARL
Sketch 1-1

54

.01 (Machine .005
from both faces)

.10 D

.20

.16

.16 D (.15 for Farr
Thermometer Probe
plus .05 thick plastic
sleeve)

.20   .35 R

.15

No. 43 Drill
+ 40 NC
two places

4°

COVER CLAMP

Scale: 5"=1"

55
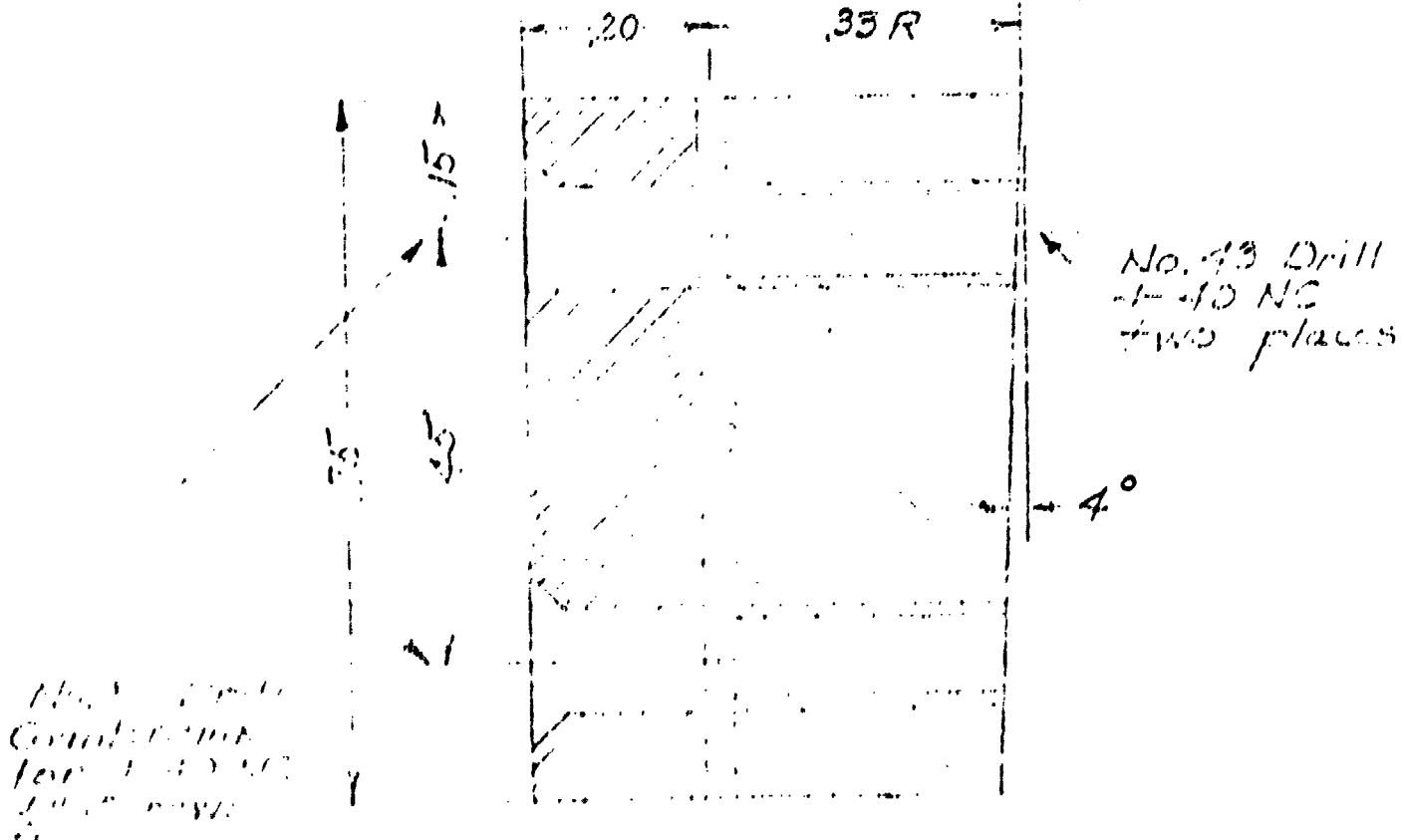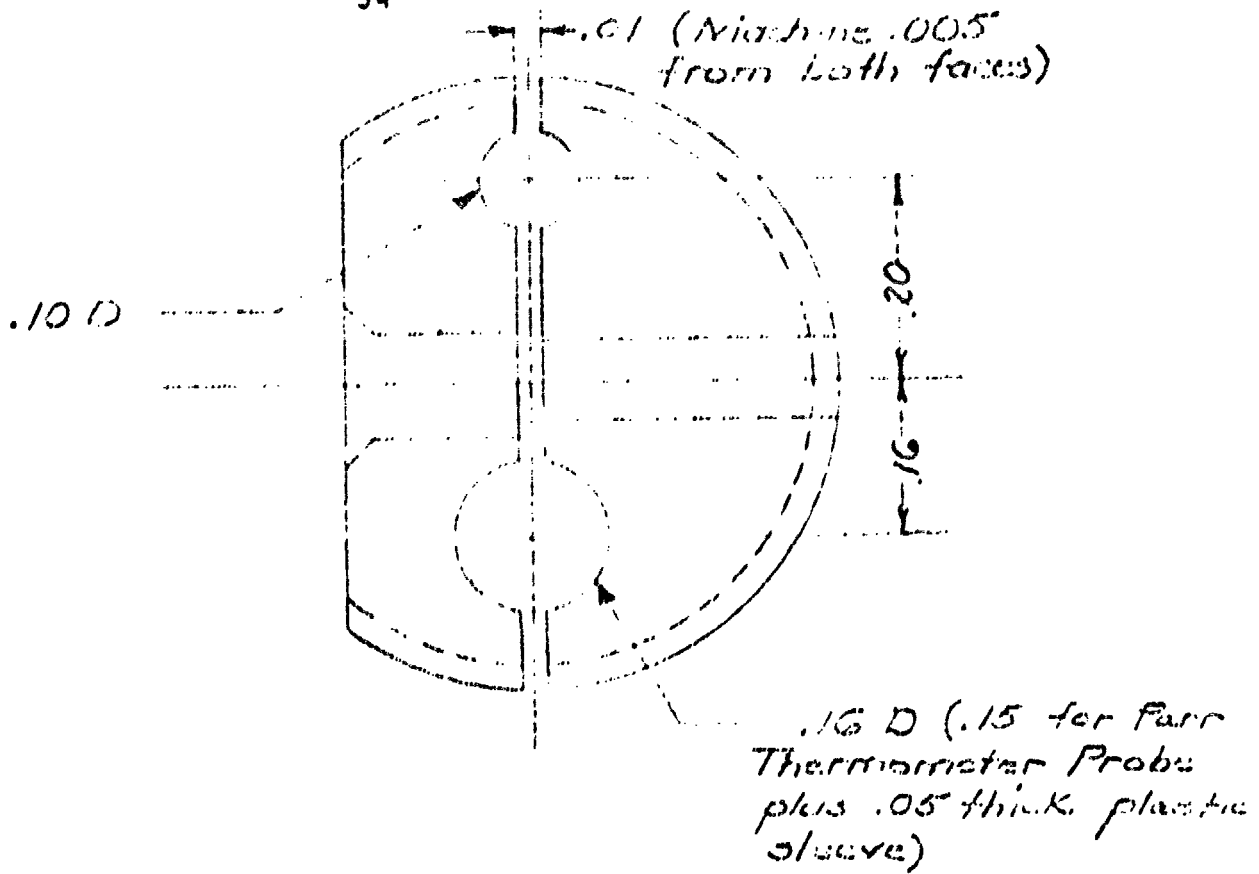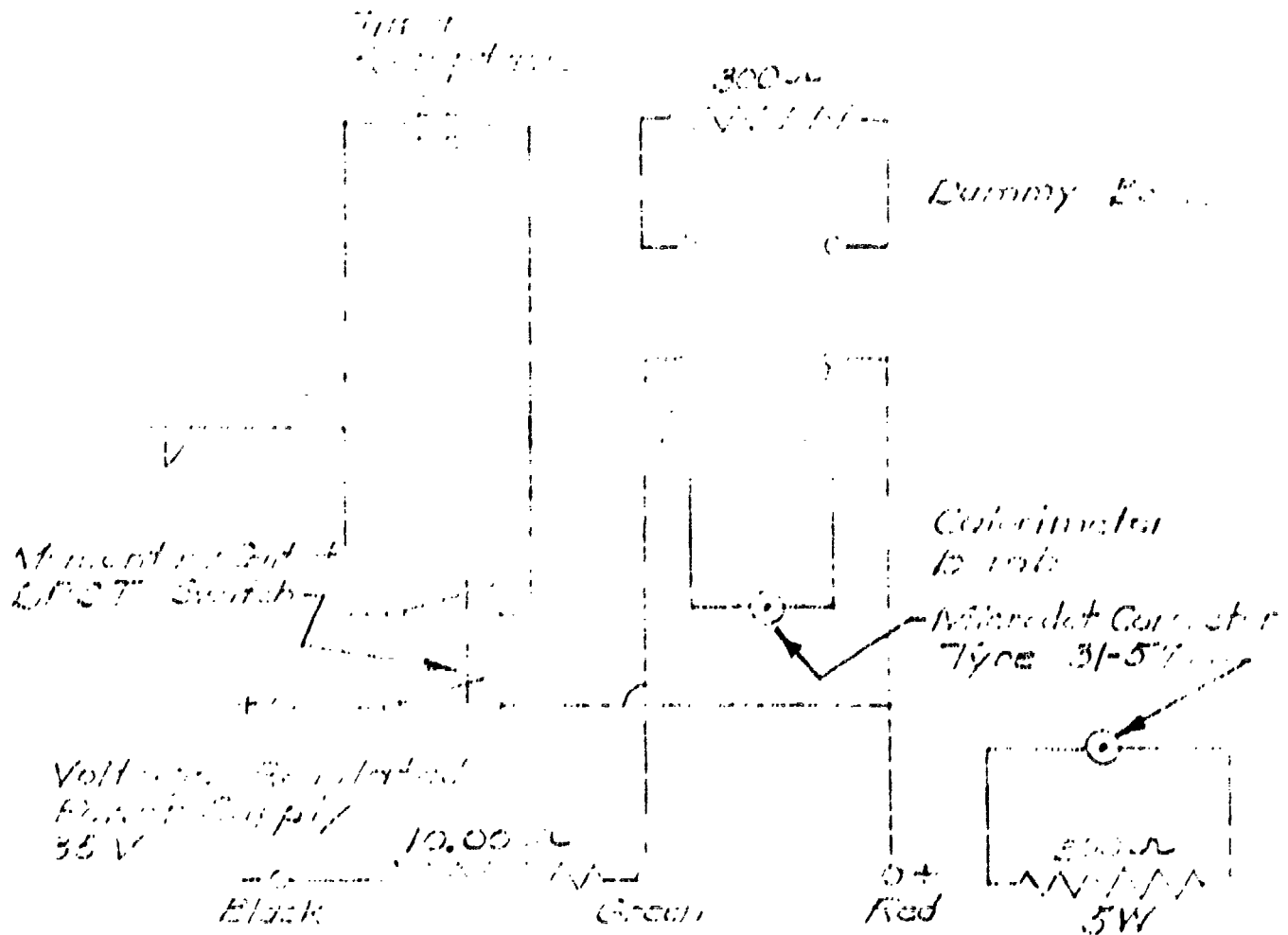
1. To *read trash voltage*, connect digital voltmeter to green & red *terminals* — nominal 30V

2. To *read leak current*, connect digital voltmeter to black & green *terminals* — nominal IV, I = V/10.00

3. Turn *recorder timer* on and plug into receptacle shown. *Timer will start recording whenever bomb energy* *exceeds* ...

4. To *reset timer after electrical reset*, throw the double pole *d.p.* *throw switch* to the dummy resistor position.

CIRCUIT DIAGRAM - BOMB
ENERGY *PULSES*
RLC Method

VA 11402
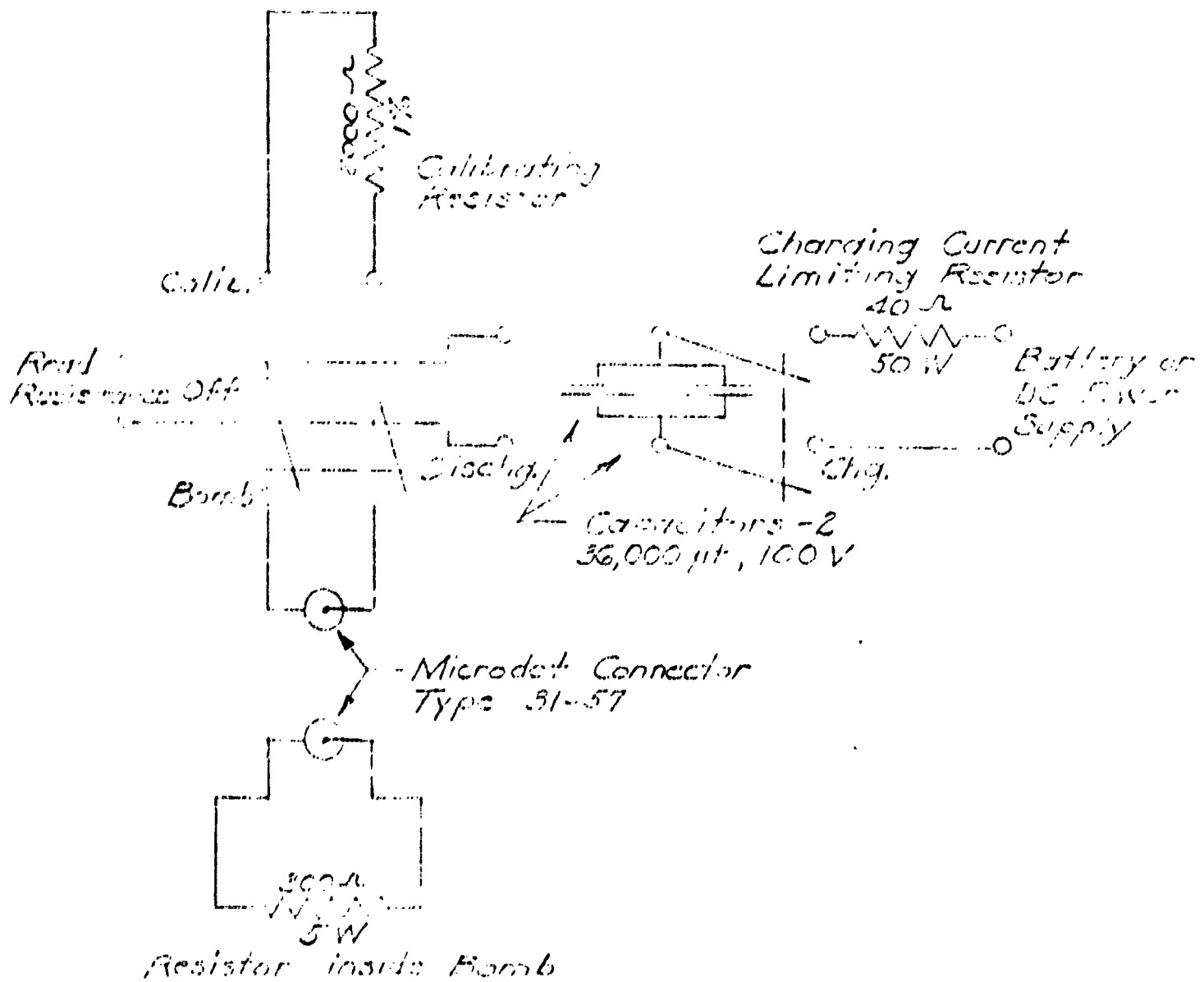
CIRCUIT DIAGRAM - BOMB
ENERGY PULSES
Capacitor Method

VMIRL
6/72

APPENDIX C

OPERATING PROCEDURE

This procedure utilizes the Parr Instrument Company Model 1411 Combustion Calorimeter with slight modifications to accommodate the VMIRL bomb design. It is specifically intended for the measurement of small quantities of heat, typically 50 calories.

The inclusion of the names of specific equipment manufacturers is intended to convey the type of instrumentation needed and that used by VMIRL in preparing this report. It does not imply that equivalent equipment by other manufacturers could not be used.

It is recommended that the user familiarize himself with the "Instructions for the No. 1411 Combustion Calorimeter"; Parr Manual No. 128, for the general operating procedures for this type calorimeter. Items used by VMIRL have been designated using the letter designation found in the above manual.

Equipment List

The following items from the Model 1411 Parr Combustion Calorimeter were used without modification, not used, or modified as indicated below:

Item	Description	
A	Calorimeter Jacket	Not Modified
B	Calorimeter Cover	Modified
C	Cover Support Stand	Not Modified
F	Calorimeter Can	Not Modified
G	Vacuum Flask	Not Modified
H	Bomb Support Assembly	Modified
J thru N and D, E, and P		Not Used
O	Stirrer Drive Belt	Not Modified

Modifications

Item A - Calorimeter Jacket. This part was not modified, however, the terminals and cable for the ignition circuit were not used.

Item B - Calorimeter Cover. The thermometer support rod was not used. The stirrer drive shaft was extended 4.7 cm by addition of a bakelite shaft extension. This was necessary to place the stirrer in the reduced volume of water and also serves to reduce the heat losses from inside the calorimeter.

Item H - Bomb Support Assembly. This wire support was not long enough to support the new bomb in the reduced volume of water. A new longer bomb support was constructed so that the bottom of the VMIRL bomb would be approximately 1 cm from the bottom of the flask.

Additions

The following items were added by VMIRL specifically for this application:

Item Q - Bomb Assembly. This item, made of stainless steel (type 17-4), consists of four parts: can, cap with Teflon gasket, nut, and transducer fitting. See the first sheet of Appendix B for the assembly of these parts. The 3/8" threaded hole in the cap accepts the initiators or the calibration plug. The transducer fitting also has a 3/8" threaded hole for the pressure transducer.

Item R - Model 2801A, Hewlett-Packard Quartz Thermometer. This equipment is accurate, for temperature differences, to 0.001 C°. It has a digital display with two probes and two channels. If a unit with only one channel is to be used, an additional thermometer, reading to 0.1 C° will be needed to read the room temperature and to aid in adjusting the temperature of the calorimeter water initially.

Item S - Model 587 MIII Kistler Pressure Transducer Assembly. This item consists of transducer, cable, and power supply for monitoring the pressure simultaneously with the heat measurement.

Item T - 2-012, N219-7 Parker O-Rings (two required). These O-rings are used for pressure seals for the initiator in the bomb cap and for the pressure transducer in the bomb fitting.

Item U - Electric Timer. A digital seconds timer is preferable, but a clock with a sweep second can be used so that readings can be taken at prescribed intervals to the nearest 1/2 second.

Item V - Bench Holder for Bomb. See the drawing of this item in Appendix B.

Item W - 500 ml Beaker. This item is used to adjust the initial temperature of the calorimeter water.

Item X - 250 ml Volumetric Pipette. This item is used to measure the calorimeter water. Other size pipettes may be used providing that the water can be measured correct to 250 ± 0.1 ml.

Item Y - Cover Clamp This clamp supports the thermometer probe at the correct position in the vacuum flask and allows for passage of cables to the pressure transducer and the initiator (or calibrating resistor). See drawing in Appendix B.

Item AA - Adjustable Wrenches (3/4" and 1-1/4" capacity). These are used to tighten and loosen the bomb nut, the initiators, and the pressure transducer.

Item BB - Teflon Tape. This is used as a pressure seal for the transducer fitting in the side of the bomb can.

Additions for Calibration Only

The following items are used in the calibration of the calorimeter. For convenience, several of these items may be mounted on a board with the bench holder, pressure transducer power supply, and a chassis with the necessary electrical circuitry.

Item CC - Calibration Plug. This item, shown in Appendix B, screws into the top of the bomb cap and has attached to it a 300 ohm, 5 watt, 5% resistor. A Microdot Type 31-57 subminiature female fitting is screwed into the top of the calibration plug for the electrical connection.

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Item DD - Calibration Circuit. Wired per diagram in Appendix B, this item consists of a double pole, momentary contact switch to simultaneously energize the calibrating resistor and the timer for the RI^2t method. It also contains a precision 10 ohm resistor adjusted to less than 0.1% and a double pole double throw switch and dummy bomb resistor.

Item EE - Electric Timer. (In addition to Item u) A digital timer having a resolution of 0.1 sec which can be estimated to 0.03 sec.

Item FF - Digital Voltmeter. Simpson Model 460 or equivalent, accuracy of 0.1% with four digit display.

Note: Accuracy of 0.1% is desirable for the voltage reading across the 10.00 ohm resistor calorimeter. No particular accuracy is required for the voltmeter used in calibrating the capacitor (if this method is used) so long as it is linear.

Item GG - Wheatstone Bridge. Leeds and Northrup Cat. No. 4760 or equivalent - 0.01% accuracy, readable to four significant figures for measuring the resistance of the calibration plug resistor in the bomb, the leads to this resistor and the resistor used to calibrate the capacitors (if this method is used).

Item HH - Power Supply. A variable 40 volt well regulated supply is needed for the calibration circuit, Item DD. Ability to maintain a constant current of about 100 ma to within 0.1% through 300 ohms for 70 sec is required.

The following items are needed, in addition to some of the previous items, if the alternate calibration method by capacitor discharge is used.

Item JJ - Capacitors. Two Sprague Model 36D "Powerlytic" capacitors - 36,000 microfarad at 100 VDC - or equivalent. These are used to store the electrical energy used for calibration. (See circuit diagram in Appendix B.)

Item KK - Calibration Circuit Board. Wired per diagram in Appendix B, this item consists of two nominally 36,000 microfarad, 100 VDC capacitors (Item JJ) wired in parallel, a nominal 2,000 ohm, 1% precision resistor with associated switches and terminals.

Item LL - Power Supply or Battery. A 100 volt source capable of supplying 2.5A is needed for the calibration circuit, Item KK. The 2.5A rating may be reduced if the 40 ohm resistor in the capacitor charging circuit is increased proportionately.

Preparing the Bomb

Step 1. Be certain that the interior surfaces of the bomb are cleaned of any material remaining from previous runs. Also be certain that the #60 drill hole in the pressure transducer fitting is open. If necessary, remove the fitting, clean and retighten with two layers of teflon tape. The 3/8" opening in this fitting must be up and aligned with the axis of the can as shown in the bomb assembly drawing in Appendix B. The end of the pipe threads should be flush with the inside of the can.

Step 2. Place the can in the bench holder.

Step 3. Place the cap with the teflon gasket on the can, place the nut over the cap, and tighten with a wrench.

Step 4. Screw the pressure transducer into the fitting using one of the O-rings as a seal. Tighten with a wrench.

Step 5. Screw an initiator into the cap using an O-ring as a seal. Tighten with a wrench.

Preparing the Calorimeter Water

Step 1. Turn the electronic thermometer on and allow it to warm up. Fill a 500 ml beaker more than half way with distilled water or tap water. Adjust the temperature of the water to 2.8 ± 0.2 C° greater than room temperature. To do this, use the two probes of the Hewlett-Packard thermometer with one in the room and the other stirring the water. If an electronic thermometer with only one probe used, then a mercury in glass thermometer, correct to 0.1 C°, will be needed to measure the room temperature.

Step 2. Of the water adjusted in Step 1, measure 250 ± 0.1 ml with a calibrated volumetric pipette.

Step 3. Be certain that the vacuum flask is clean and dry from previous use.

Step 4. Pour the measured water into the vacuum flask, being careful not to spill or splash on the sides of the flask.

Assembling the Calorimeter

Step 1. Place the vacuum flask, with water inside, into the calorimeter can.

Step 2. Place the calorimeter can into the calorimeter jacket

Step 3. Connect the appropriate cables to the transducer and the initiator which are mounted on the bomb. Be certain that the cables pass through the hole in the calorimeter cover. Turn the transducer power on

Step 4. Place the bomb assembly on the modified wire bomb support assembly and lower into the vacuum flask. The bomb assembly should be on the side of the vacuum flask away from the calorimeter cover pin hole. (This maximizes the distance between the stirrer and the suspended components.) Be certain that the water covers the metal parts of the bomb and connectors.

Step 5. Place the probe of the thermometer through the hole in the calorimeter cover and adjust so that the end of the probe is 17 to 17.5 cm below the bottom of the cover. This is done with the cover clamp that fits in the hole and supports the thermometer probe.

Step 6. Carefully put the calorimeter cover in place. It is necessary to see that the probe is free in the water, that the slack is taken out of the transducer and initiator cables, and that the stirrer does not touch the cables or bomb assembly. Turn the stirrer by hand to be certain it is not touching

Step 7. Place the stirrer drive belt in place and start the motor. Adjust the belt tension sufficiently to reduce belt vibration (overtightening will produce unwanted heating from the stirrer bearing).

The Test Run (See Note below for those following this procedure for the first time)

It will be necessary to take six temperature readings to 0.001 C° at the times (in minutes) indicated by the subscripts below:

$$T_0, \; T_3, \; T_6, \; T_{12}, \; T_{15}, \; T_{18}$$

Step 1. Start the stirrer running and allow it to run for at least 10 and preferably 15 minutes before starting the test. This establishes the temperature gradients within the calorimeter and improves the correction to the apparent temperature rise.

Step 2. Start the timer and read the temperature. This is T_0. Read the temperature again three minutes later. This is T_3. Note the difference, $T_3 - T_0$.

Step 3. When the timer indicates six minutes, read T_6 and note the difference, $T_6 - T_3$. If $T_6 - T_3$ differs from $T_3 - T_0$ by 0.001 C° or less, fire the initiator within 10 seconds of T_6. If this difference is more than 0.001, reset the timer and start temperature readings over.

Step 4. Continue to read temperatures at 12, 15 and 18 minutes. These are T_{12}, T_{15} and T_{18}. The largest part of the total temperature rise should be over by 12 minutes.

(This step and the associated calculations may have to be modified following subsequent tests by NASA on actual initiators.)

Note: To familiarize the operator on the first use of the instrument, the temperature of the water and atmosphere should be taken at three minute intervals for a two hour period, varying the room temperature, the stirrer belt tension and turning on and off the transducer power. Appendix G contains a sample of data taken by the Harry Diamond Laboratories.

The Calculations

Step 1. The apparent temperature rise is $T_{12}-T_6$. Compute this.

Step 2. Check on the temperature gradients within the calorimeter or the linearity of the heat losses or gains as follows:

(a) T_3-T_0 should be within 0.001 C° of T_6-T_3.

(b) $T_{18}-T_{15}$ should be within 0.001 C° of $T_{15}-T_{12}$.
In some cases this may be as much as 0.002 C°.

Step 3. Check to see that the heat losses or gains are nearly equal before and after the firing by computing $T_{18}-T_{12}$ and T_6-T_0. These should be nearly equal but in no case differ by more than 0.004 C°.

Step 4. The true temperature rise is the apparent rise minus $T_{18}-T_{12}$. Note this correction can be positive or negative.

Step 5. The total heat released by the initiator is equal to the water equivalent of the calorimeter times the true temperature rise.

TABLE 3
DATA SHEET FOR OPERATING PROCEDURE

__Measurements__

T_0 _____

T_3 _____

T_6 _____

__Calculations__

T_3-T_0 = _____

T_6-T_3 = _____

At time T_6, it is necessary to see if T_6-T_3 is within 0.001 C° of T_3-T_0. If it is, fire within 10 seconds of T_6. If it is not, reset timer and start over.

T_{12} _____

T_{15} _____

T_{18} _____

$T_{15}-T_{12}$ = _____

$T_{18}-T_{15}$ = _____

$T_{15}-T_{12}$ should be within 0.001 C° of $T_{18}-T_{12}$ (never more than 0.002).

T_6-T_0 = _____

$T_{18}-T_{12}$ = _____

$T_{18}-T_{12}$ must be within 0.004 C° of T_6-T_0

Apparent Temperature Rise = $T_{12}-T_6$ = _____

Subtract Correction = $T_{18}-T_{12}$ = - _____

True Temperature Rise = ΔT = _____

Heat Released = True Temperature Rise x Water Equivalent

= _____ C° x _____ cal/C° = _____ cal

APPENDIX D - CAPACITOR MEASUREMENT

When a charged capacitor discharges through a resistive circuit the voltage across the capacitor versus time is given by:

$$V = V_0 e^{-t/RC}$$

The derivation of this expression can be found in most elementary physics texts. The time constant, τ, is RC and is the reciprocal of the slope of the straight line which results when ln V is plotted versus t

To measure a capacitance requires a charging circuit and a resistor of known value through which the capacitor may be discharged.
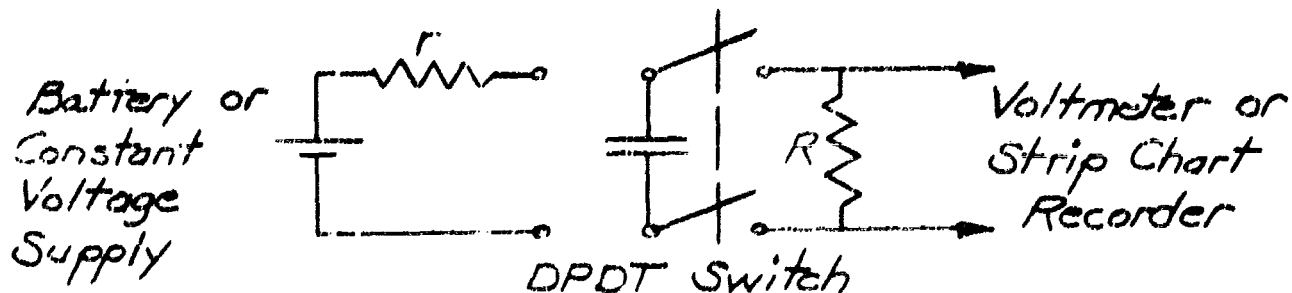
A small resistance r is used in the charging circuit to prevent a severe transient from being imposed on the power supply or battery when the charging begins. It should be remembered that the charging process is also exponential having time constant $(r+r_b)C$ where the battery resistance, r_b, has been included. After five time constants, the charging or discharging is 99.3% complete. This is a convenient number of time constants to keep in mind.

To obtain 200 joules of stored energy requires the use of large capacitances or high voltages. To utilize voltages less than 100 volts requires somewhat less than 10^5 microfarads. Such capacitances are only available in electrolytics which exhibit dielectric absorption effects. These effects produce a curve of ln V vs t

which is somewhat non-linear for large values of t. The slope, which is inversely proportional to the capacitance, decreases steadily as shown in Fig. 12. This was obtained using 2000 ohms and the discharge was monitored for about an hour. The capacitance computed from the slope varies from an initial value of about 0.09F to a final value of 1.1F.

The above effect makes it infeasible to utilize energy over the entire discharge. The effect is small and negligible at the higher voltages. Hence a discharge in the region from 100 V to 75 V will be quite linear and the energy can be computed by $c(V_2^2 - V_1^2)/2$ although this is more inconvenient since the initial and final voltages must be measured.

A plot of the discharge over the limited region is shown in Fig. 13. Calculation of the time constants is shown on the graph in addition to the value of C calculated from them.

The precision of C depends on three factors.

    (1)   Accuracy of the time measurement.

    (2)   Precision with which resistance, R, is known (and the fact that it is not sufficiently heated in the discharge to alter its value).

    (3)   Precision with which the technician draws the "best fitting" curve to the points.

The "time constant" for the discharge is RC which is typically 175 sec., a sufficiently long interval that an electric timer of the 60 hz synchronous motor type can be used with a digital voltmeter to record voltage readings every 15 or 20 sec. Nationwide, the accuracy of the 60 hz frequency is about 0.03% barring easily detectable transients from lightning, surges, etc. Accuracy in timing is thus limited only by the operator's accuracy in reading the voltmeter at the proper time intervals.

Voltmeter accuracy of $\pm$ 1 digit in a three or four digit figure is attainable. Absolute accuracy is not necessary here since only relative voltage readings are required for the graph. A precision of less than one percent is attainable. For the four plots in Fig. 13 the average is 0.0842 F with a standard deviation of 0.00067 or 0.7%.

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Fig. 12
LONG TIME VARIATIONS
OF CAPACITOR VOLTAGE

Fig. 13
SHORT TIME VARIATIONS
OF CAPACITOR VOLTAGE
Resistance = 1998.5 Ohms
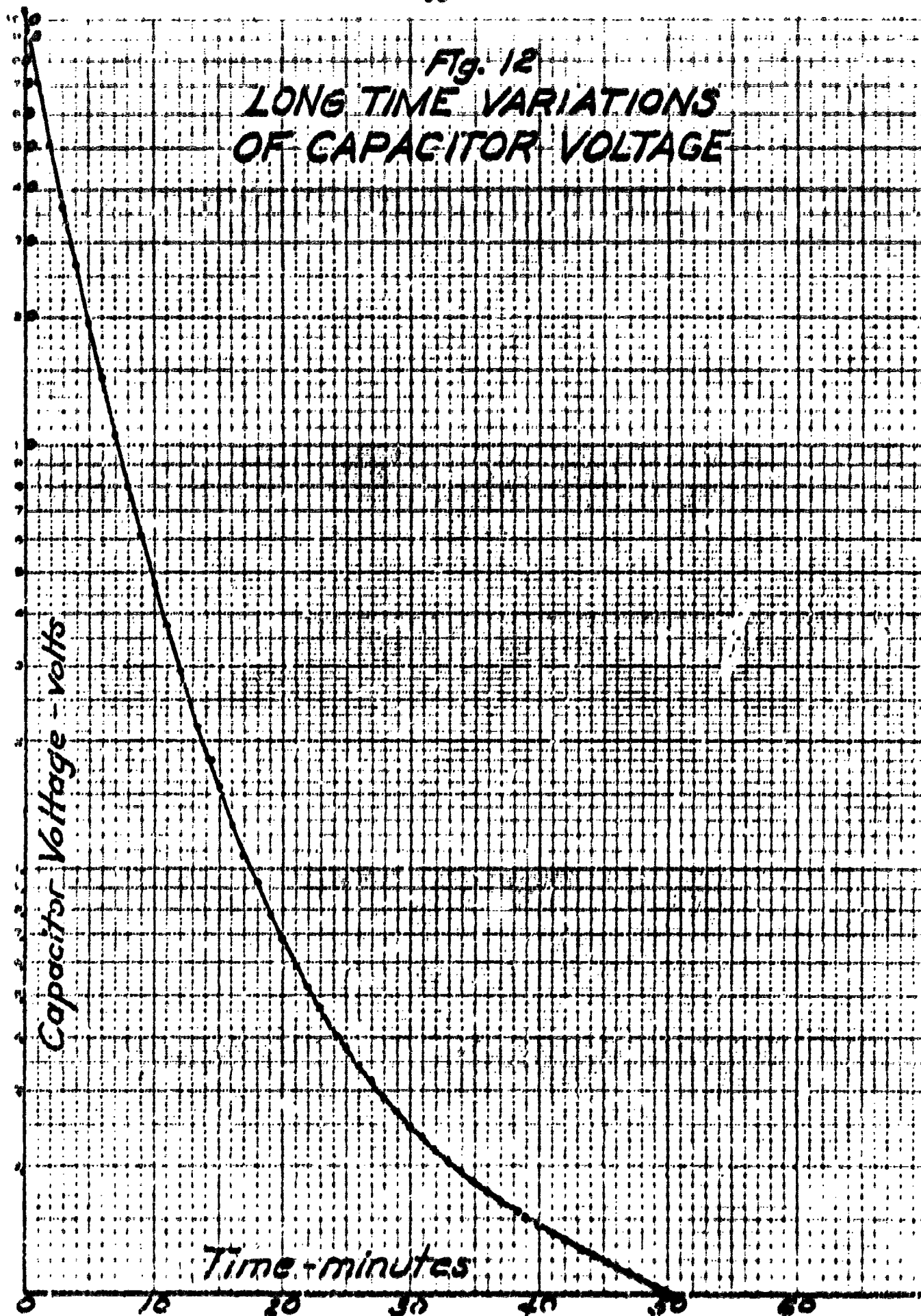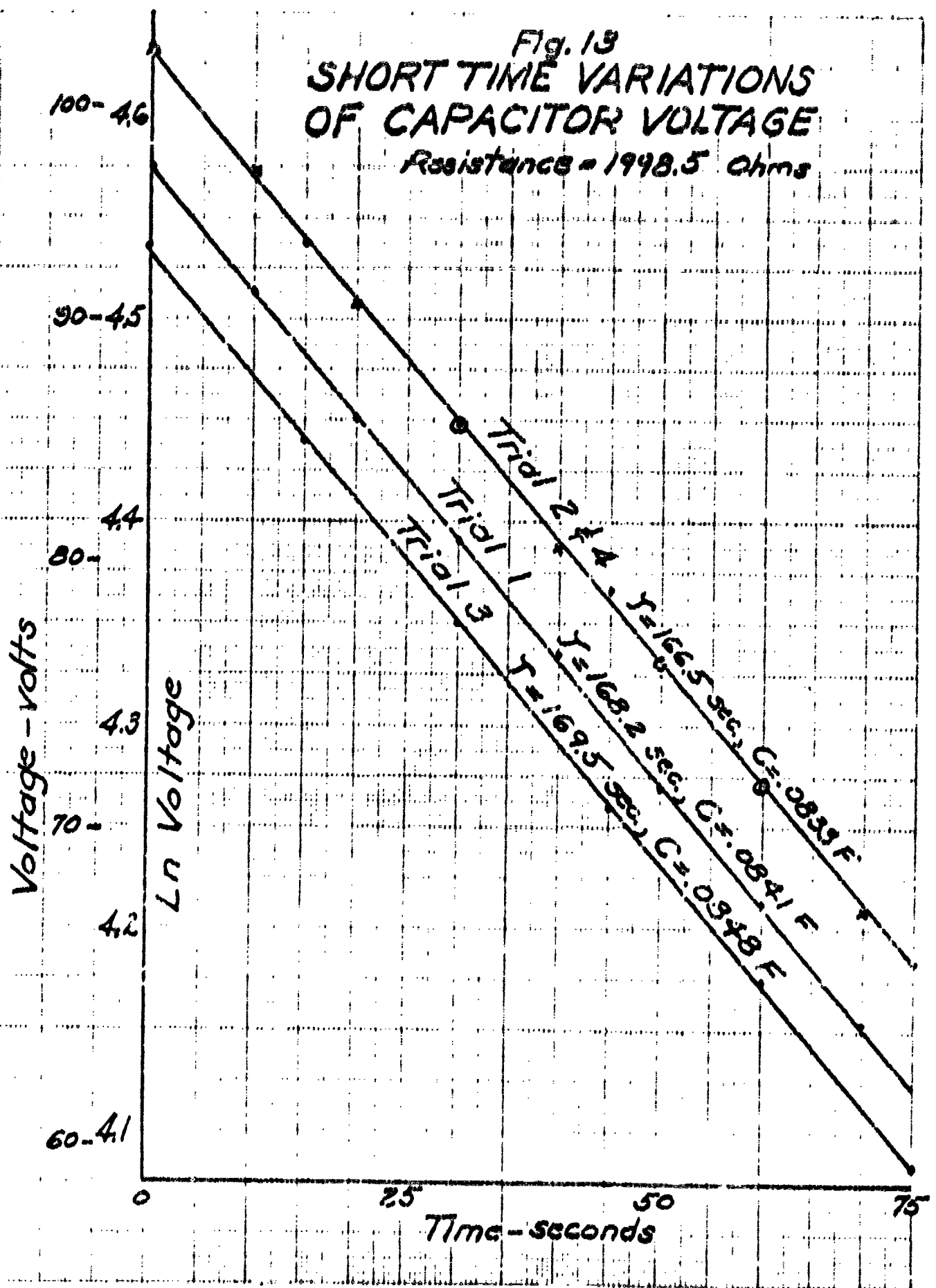
R can be measured using a Wheatstone bridge, the accuracy of which has been verified using appropriate standard resistors. These usually have an accuracy of 0.1% or better. A box bridge typically has four resistance dials and the galvanometer used with it should be of sufficient sensitivity that a change of one digit in the fourth significant figure is detectable.

In drawing the best fitting curve it is most important that all the points have been plotted correctly and that they span a total length on the graph paper of 5 to 10 inches. If the plot significantly departs from a straight line by exhibiting definite curvature as opposed to scatter, the data should be discarded and a new trial taken. For a single calibration a quick and suitable test of the probable precision is to draw three straight lines and measure the slope of each. The middle one of these lines is the "best fit" by the technician's judgement. The other two lines would lie one on either side of the "best fit" and would represent the fit selected by a "reasonably careless" person. The percent precision of the slope thus obtained would be the percent precision of C assuming the resistance and the time had percent precisions which were quite small (less than 1/2% for these purposes).

For convenience, the charge/discharge circuit for capacitor calibration is included with that for the bomb constant. The circuit is shown in Appendix B.

APPENDIX E

CALIBRATION PROCEDURE - WATER EQUIVALENT

Two alternative electrical calibration methods for determining the water equivalent have been tested. Each utilizes energy generated by electrically heating a 300 ohm - 5 watt resistor immersed in water inside the bomb.

In one method, heating is accomplished by the current from a voltage regulated power supply for a measured time. The energy generated is the product of the resistance, R, the current squared, I^2, and the time, t. It will be referred to as the RI^2t method.

The other method utilizes the discharge of a capacitor through the resistor. The energy generated is $CV^2/2$ where C is the capacitance and V is the voltage to which the capacitor was initially charged. A procedure for measuring C is given in Appendix D.

Circuit diagrams for the components used in each method are given in Appendix B.

The following procedure is for determining the water equivalent. A complete calibration requires about 2 1/2 hours.

Preparing the Calorimeter Water

Step 1. Turn on the electronic thermometer and allow it to warm up, about 15 to 30 minutes. Fill a 500 ml beaker more than half way with distilled water or tap water. Adjust the temperature of the water to 1.8 ± 0.2 C° greater than room temperature. (See footnote below) To do this, use the two probes of the Hewlett-Packard Thermometer with one in the room and the other stirring the water. If an electronic thermometer with only one probe is used, then a

Note: For a test run as described in the Operating Procedure 2.8 ± 0.2 C° is used. For the Calibration Procedure this is reduced by 1 C° to allow for a number of repeated runs with the same water without attaining calorimeter temperatures much in excess of room temperature.

mercury in glass thermometer, correct to 0.1 C°, will be needed to measure the room temperature.

Preparing the Bomb

Step 1. Inspect the resistor for any obvious defects in the acrylic coating used to insulate its leads, particularly the lead to the center of the plug (the ungrounded lead). If a defect is observed, repair the coating by respraying.

Step 2. Be certain that the interior surfaces of the bomb are cleaned of any material remaining from previous runs. Also be certain that the #60 drill hole in the pressure transducer fitting is open. If necessary, remove the fitting, clean and retighten with two layers of teflon tape. The 3/8" opening in this fitting must be up and aligned with the axis of the can as shown in the bomb assembly drawing in Appendix B. The end of the pipe threads should be flush with the inside of the can.

Step 3. Be certain that the vacuum flask is clean and dry from previous use.

Step 4. Connect the calibration plug to the small lead wire and measure the resistance of the combination on a Wheatstone bridge whose accuracy has been verified to better than 0.1%, preferably 0.01%. Record the value obtained.

Step 5. Disconnect the calibration plug and replace with a Microdot 31-57 female plug, the terminals of which have been shorted together. With the Wheatstone bridge measure the lead resistance alone and record the value obtained. Subtract this from the value in Step 4 to obtain the corrected resistance for use in the RI^2t calculation.

Step 6. Place the can in the bench holder.

Step 7. From the water adjusted in Step 1 of the previous section, measure 250 ml $\pm$ 0.1 ml with a calibrated volumetric pipette.

Step 8. Pour about 8 ml of water from the pipette into the bomb can. Be certain that some water enters the transducer fitting.

Step 9. Pour the remainder of the 260 ml of prepared water into the vacuum flask being careful not to spill or splash on the sides of the flask.

Step 10. Screw the transducer into position finger tight using one of the O-rings a a seal.

Step 11. Place the cap with the teflon gasket on the can, place the nut over the cap, and tighten with a wrench.

Step 12. Place the calibration plug in the cap and screw firmly but finger tight (leakage of water from the flask into the bomb will not matter).

Assembling the Calorimeter

Step 1. Place the vacuum flask, with water inside, into the calorimeter can.

Step 2. Place the calorimeter can into the calorimeter jacket.

Step 3. Connect the appropriate cables to the transducer and the calibration plug which are mounted on the bomb. Be certain that the cables pass through the hole in the calorimeter cover.

Step 4. Place the bomb assembly in the modified wire bomb support assembly and lower into the vacuum flask. The bomb assembly should be on the side of the vacuum flask away from the calorimeter cover pin hole. (This maximizes the distance between the stirrer and the suspended components.) Be certain that the water covers the metal parts of the bomb and connectors.

Step 5. Place the probe of the thermometer through the hole in the calorimeter cover and adjust so that the end of the probe is 17 to 17.5 cm below the bottom of the cover. This is done with the cover clamp that fits in the hole and supports the thermometer probe.

Step 6. Carefully put the calorimeter cover in place. It is necessary to see that the probe is free in the water, that the slack is taken out of the transducer and resistor cables, and that the stirrer does not touch the cables or bomb assembly. Turn the stirrer by hand to be certain it is not touching.

Preparing the Circuitry

Step 1. Lead connections and electronic supplies.

(a) Connect the transducer lead (miniature coaxial cable with threaded connector) to its power supply and turn the power ON.

(b) Connect the calibration resistor lead (miniature coaxial cable with push connector) into its female receptacle on the side of the breadboard chassis. (Circuit diagram in Appendix B.)

(c) Plug the tenth second digital timer into its receptacle on the calibrating circuit chassis and turn the timer switch ON (the one on the timer itself).

(d) Connect the constant voltage supply to the calibration chassis, turn the supply ON and set the voltage at about 35 V.

(e) Connect the digital voltmeter to the black/green terminals on the calibration chassis. Set the voltmeter to read a nominal 1 V and turn the power ON.

Step 2. On the calibration chassis, set the double pole double throw switch to the dummy resistor position and close the momentary contact switch. Verify that the seconds timer cuts on and off properly when the momentary contact switch is depressed. With this switch ON, adjust the power supply voltage so the voltmeter reads very close to 1 V (this makes the dummy resistor current 0.1 A).

Step 3. Reset the timer to zero and switch the double pole double throw switch to the bomb resistor position.

The Calibration Run

Unlike the initiator tests, it is not necessary to change the calorimeter water between runs. Therefore one run may be begun immediately following the preceding one. A waiting period of about 15 minutes after beginning the stirring is required to stabilize the temperature conditions. After that, the initial run requires 18 minutes as follows: 6 min constant temperature rise, 6 min energy pulse detection, and 6 min new constant temperature rise.

Subsequent runs after the first may be done every 12 min since the last 6 min period of the preceding run can be used as the first 6 min period of the next run.

It will be necessary to take temperature readings to 0.001 °C at the times (in minutes) indicated by the subscripts below:

T_0, T_3, T_6, T_{12}, T_{15}, T_{18}, T_{24}, T_{27}, T_{30}, T_{36}, etc.

Step 1. The stirrer, which was started earlier, should be allowed to run at least 10 minutes following the time the transducer power was turned ON. This establishes reasonably uniform conditions.

Step 2. Start the timer and read the temperature. This is T_0. Read the temperature again three minutes later. This is T_3. Note the difference, $T_3 - T_0$.

Step 3. When the timer indicates six minutes, read T_6 and note the difference $T_6 - T_3$. If $T_6 - T_3$ differs from $T_3 - T_0$ by 0.001 C° or less, depress the momentary contact switch on the calibration chassis to begin the heating pulse to the bomb within 10 seconds of T_6. If the difference is more than 0.001 C°, reset the timer and start temperature readings over.

Step 4. Read and record the digital voltmeter reading as often as convenient but at least once every 15 or 20 seconds, more frequently if it changes more than 0.001 V.

Step 5. After 67 to 70 seconds energy pulse duration, release the momentary contact switch and record the indicated time to the nearest 0.03 sec. RESET the timer to zero. To reset timers using electrical reset, throw the double pole double throw switch to the dummy resistor position.

Step 6. Continue to read temperatures at 12, 15, and 18 minutes. These are T_{12}, T_{15}, and T_{18}. The largest part of the total temperature rise should be over by 12 minutes.

WITH SOME EXPERIENCE, THE NEXT STEP IS NOT NECESSARY AND THE
PROCEDURE CONTINUES AS IF IT WERE OMITTED.

This is Run #1 and it is now complete. The next run may be
started immediately but certain checks on the previous data are
advisable to verify that the temperature rise is remaining constant
as follows:

$T_{18}-T_{15}$ should be within 0.001 C° of $T_{15}-T_{12}$. In
some cases this may be as much as 0.002 C°. Check
to see that the heat losses or gains are nearly
equal before and after firing by computing $T_{18}-T_{12}$
and T_6-T_0. These should be nearly equal but in no
case differ by more than 0.004 C°.

Step 7. At 18 minutes, depress the momentary contact switch
to begin a second heat pulse to the bomb.

Step 8. Record the digital voltmeter reading at least every
15 to 20 seconds.

Step 9. After 67 to 70 seconds, release the momentary contact
switch and record the time to the nearest 0.03 sec. RESET the
timer to zero.

Step 10. Continue to read temperatures at 24, 27, and 30
minutes. These are T_{24}, T_{27}, and T_{30}. The largest part of the
total temperature rise should be over by 12 minutes.

Step 11. Continue sequence for successive runs until 12 runs
have been completed.

Step 12. Use the Wheatstone bridge to remeasure the resistance.
If it has changed as much as 2 ohms from its earlier value, the
acrylic coating has probably deteriorated and the data should be
discarded.

The Calculations

Step 1. The apparent temperature rise is $T_{12}-T_6$ for the first run. For the second run it is $T_{24}-T_{18}$, then $T_{36}-T_{30}$, etc. Compute this rise for each run.

Step 2. Check on the temperature gradients within the calorimeter or the linearity of the heat losses or gains as follows:

T_3-T_0 should be within 0.001 C° of T_6-T_3. Also $T_{18}-T_{15}$ should be within 0.001 C° of $T_{15}-T_{12}$. The same comparison should be made between $T_{30}-T_{27}$ and $T_{27}-T_{24}$, etc. Some of these differences may be as much as 0.002 C°, but if any are more than this, the preceding run must be discarded from further calculations.

Step 3. Check to see that the heat losses or gains are nearly equal before and after a run. Compare $T_{18}-T_{12}$ with T_6-T_0 and $T_{30}-T_{24}$ with $T_{18}-T_{12}$, etc. These should be nearly equal but in no case differ by more than 0.004 C°. If the difference is more than 0.004 C°, discard the run in question.

Step 4. The true temperature rise is the apparent rise minus the correction. For the first run the correction is $T_{18}-T_{12}$, for the second run the correction is $T_{30}-T_{24}$, for the third it is $T_{42}-T_{36}$, etc. Compute all of the true temperature rises for runs that passed the earlier tests.

Step 5. Average the digital voltmeter readings for each run. Divide the average voltage in volts by 10.00 to obtain the average current in amperes. Note that these values should not differ greatly if the power supply was functioning properly.

Step 6. Compute the heat released in calories for each pulse by the formula $0.239\,RI^2t$. R is the resistance in ohms of the calibrating resistor, corrected for the resistance of the leads; I is the average current in amperes from Step 5; and t is the time of the pulse in seconds measured to ± 0.03 seconds. The factor 0.239 cal/J is a factor to change joules to calories.

Step 7. Compute the water equivalent, h, in calories per C° for each run by dividing the heat released for each pulse in calories by the true temperature rise in C°.

Statistical Treatment of Data

Step 1. Average the above 12 values of h and determine the deviation, d_i, of each individual reading from the average.

Step 2. Square each deviation and average the squares. This number is σ^2 and is called the variance.

Step 3. Take the square root of the variance to obtain σ, the standard deviation.

Step 4. If σ is greater than 1% of the mean value of h the data shows excessive scatter and the calibration should probably be repeated.

Step 5. Had a very large number (several hundred) runs been made the expected standard deviation of the mean, σ_m, for this large group is given by $\sigma_m = \sigma / \sqrt{N}$ where N is the number of runs in the group.

Note: Because the above runs were all done without a change of calorimeter water, the above σ does not contain an allowance for inaccuracies in measuring the water. When groups of runs are done using a change of water, the standard deviations for each group may be averaged to obtain a σ which does allow for this latter inaccuracy.

References:

Young, Hugh D.: Statistical Treatment of Experimental Data. McGraw-Hill Book Co., Inc., 1962.

Bevington, Philip R.: Data Reduction and Error Analysis for the Physical Science. McGraw-Hill Book Co., Inc., 1969.

CHANGES IN PROCEDURE FOR ALTERNATE CALIBRATION METHOD - CAPACITOR DISCHARGE

The following procedure is based on that for the RJ^2t method. Only the altered steps in that method are detailed below. A different calibrating circuit chassis is used. See circuit diagram in Appendix B.

Preparing the Circuitry

Step 1.

    (c)   Omit

    'd)   Connect the constant voltage supply (or battery capable of supplying 100 volts at about 2 A) to the calibration chassis and set the voltage at about 100 V.

    e)   Connect the digital voltmeter to the "Read Resistance" terminals. Set the voltmeter to read a nominal 100 V and turn the power ON.

Step 2. On the calibration chassis, set one of the DPDT switches to "Off" and the other to "Chg".

Step 3. Omit

The Calibration Run

Step 3. No change except replace *depress the momentary contact switch* by *throw the DPDT switch from 'Chg' to 'Dischg', read the voltmeter, and record as V. Throw the other DPDT switch from 'OFF' to 'Bomb' on the calibration ....*

Step 4. Omit

Step 5. When the voltmeter reads about 70 V, throw the DPDT switch from "Bomb" to "OFF", Note and record the voltmeter reading as a tentative value, V_F'.

Step 5A (new). About 10 or 15 minutes later again record the voltmeter reading as the final value, V_F. This will be a volt or two higher than V_F' above due to the dielectric absorption effect.

The Calculations

Step 6.   Replace the $0.239 \; RI^2 t$ by $0.239 \; \dfrac{C}{2} \; (V^2 - V_F^2)$

Note: The time delay in Step 5A makes this calibration method longer since the capacitor must be allowed to recharge following the wait and reading of Step 5A.

APPENDIX F

HEAT TRANSFERS - Temperature
Dependent and Non-Temperature Dependent

Theory

In Sec. 5 it was indicated that small quantities of heat could produce noticeable effects in the measurement of the nominal 50 calories from the initiator. Such small transfers were attributed to two broad classes; temperature dependent and non-temperature dependent.

Temperature Dependent   Let $\frac{dQ}{dt} = D\ (T_R-T)$

Non-Temperature Dependent   Let $\frac{dQ}{dt} = N$

Transfer to Water and Bomb $\frac{dQ}{dt} = h\ \frac{dT}{dt}$

where dQ/dt = Time rate of heat transfer into the calorimeter system

dT/dt = Time rate of increase of calorimeter water temperature

D = The constant related to all temperature dependent terms

N = The constant related to all non-temperature dependent terms

h = Water equivalent of bomb, water, and calorimeter

T_R = Ambient temperature (Room) of calorimeter surroundings

T = Calorimeter water temperature

T_o = Initial calorimeter water temperature

Combining terms,

$$h\ \frac{dT}{dt} = \frac{dQ}{dt} = D\ (T_R-T) + N \qquad (1)$$

The temperature dependent term, θ (T_R-T), represents a "lumping" of terms due to conduction, convection and radiation, all of which may be represented by a constant times a temperature difference between the system and its surroundings.

The non-temperature dependent term, H, represents a "lumping" of terms due to viscous friction from stirring the water, bearing friction (which changes with belt tension and increases at lower temperatures due to stiffening of the lubricant), and transducer power. All of these represent heat "generated" from electrical or mechanical energy at a rate not depending on the temperature (except for the effect due to cold lubricant).

Evaluation of Heat Transfer Terms

Eq. (1) is based on an assumption that the heat transfer paths and thermal gradients have been established for a sufficient time that a negligible amount of the dQ/dt term is being utilized to produce the gradient or to heat the insulating portions of the calorimeter. This near equilibrium condition is called quasi-equilibrium or quasi-steady state. For this system experimental evidence indicates this condition obtains after 15 to 25 minutes while true equilibrium is not reached for 15 to 25 hours.

Data was obtained during quasi-steady state conditions for temperature vs time over a wide range of temperature differences, T_R-T. If the slope, dT/dt, was constant for about five minutes or more and if the water had been well stirred for 15 to 25 minutes, it was evident that quasi-steady conditions existed. See typical curves in Fig. 11 of Sec. 6.2 for these constant slope regions.

A plot of dT/dt vs T_R-T was needed to experimentally verify Eq. (1). Data was not taken specifically for this plot shown in Fig. 14. Instead, data from numerous other tests was used, much of it being for preliminary calibration runs and therefore clustered near room temperature. Well over one hundred data points are shown covering circumstances such as:

(a) Transducer power ON and OFF

(b) Belt tension low, moderate and high

Fig. 14
CALORIMETER HEAT
TRANSFER CHARACTERISTICS

Ambient minus Calorimeter Temperature $(T_r - T)$, C°

Rate of Temperature Change, $\frac{dT}{dt}$, millidegrees per minute

$$\frac{dT}{dt} = 1.86(T_r - T) + 4.4$$
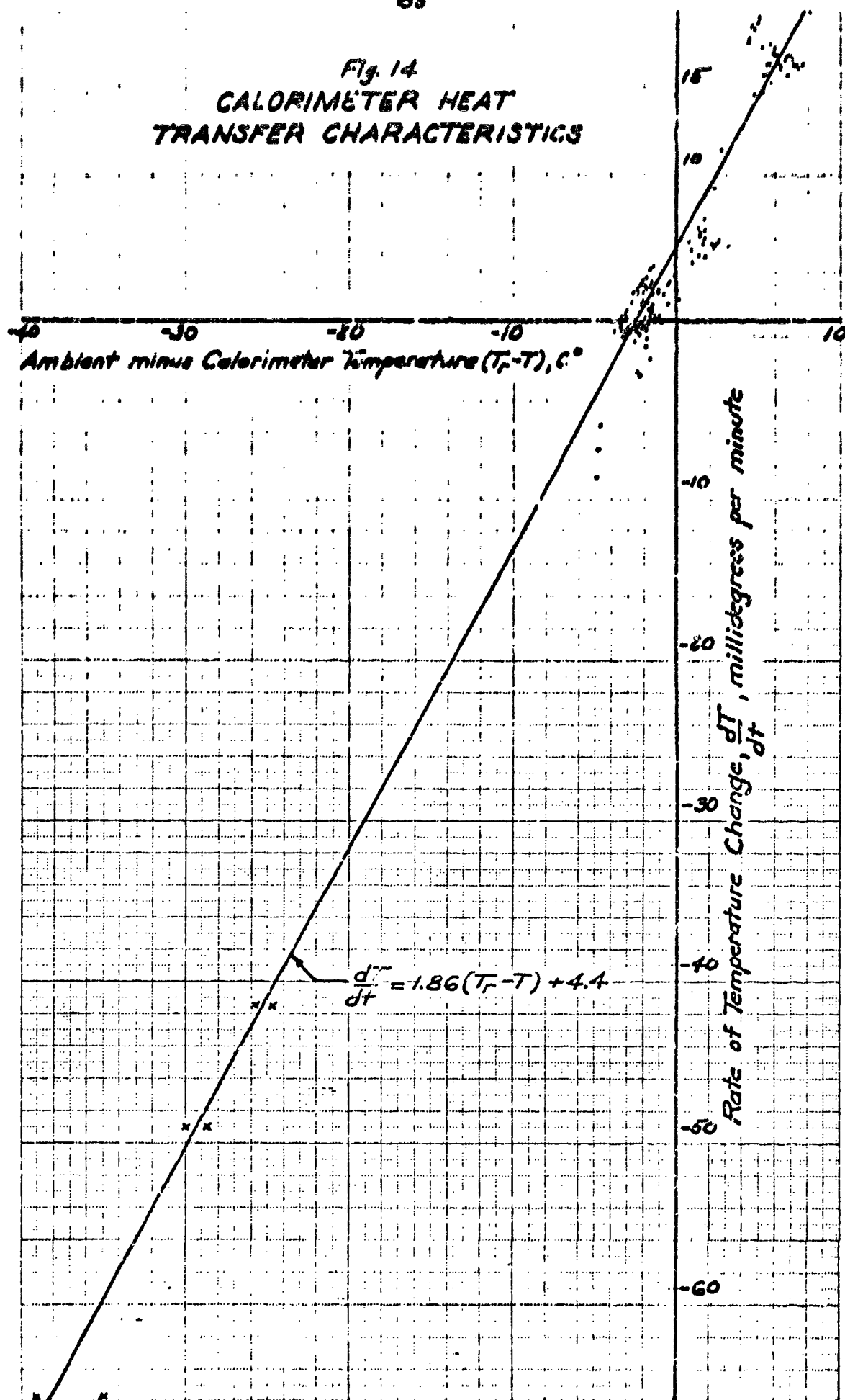
(c) Ambient temperatures form -20°C to +30°C

(d) Rapid changes of room (ambient) temperature due to heaters, radiators and air conditioners

(e) Addition of direct conducting paths such as thermometer probes, stirrer shaft, and cables

Fig. 14 should be straight line if Eq. (1) is true. The slope of this line is D, the temperature dependent constant, and the "y intercept" is N, the non-temperature dependent constant.

D should depend primarily on the calorimeter construction and should be almost constant for all tests shown. On the other hand, N should vary primarily according to belt tension although some tests were done without the transducer, which also has an effect. Changes of D will be seen as a change of slope while an increase of N will move the curve of Fig. 14 to the left but remaining parallel to the line shown.

All the data was shown even though there were differing conditions in some tests in order to show the general agreement with Eq. (1). The line selected was a best estimate for moderate belt tension with transducer power on.

The points on Fig. 14 denoted by an X were obtained from a test in a freezer with large temperature differences. To secure values of dT/dt, a plot of T vs t was drawn and the slopes from this plot were measured. The pairs of data points are due to the slope remaining constant for periods of 20 to 60 minutes while the temperature difference was two substantially different values at the ends of the interval.

The equation of the experimentally obtained line in Fig. 14 is:

$$\frac{dT}{dt} = 1.86\ (T_R-T) + 4.4 \text{ using units of Fig. 14}$$

$$= 0.00186\ (T_R-T) + 0.0044 \text{ deg/min}$$

$$\frac{dT}{dt} = \frac{D}{h}\ (T_R-T) + \frac{N}{h} \qquad \text{Eq. (1)}$$

Solving for D and N using h = 284 cal/C°

$$D = 284 \times 0.00186 = 0.53 \; \frac{cal}{C° \; min}$$

$$N = 284 \times 0.0044 = 1.25 \; cal/min$$

These values are probably accurate to $\pm$ 20% depending on the judgment used in selecting the best fitting line in Fig. 14.

Equilibrium Temperature

It is desirable that determinations of these small quantities of heat be done near dT/dt = 0 to balance, as nearly as possible, the heat gains and losses. Eq. (1) predicts the equilibrium temperature difference as

$$0 = D \; (T_R - T) + N$$

$$T_R - T = - N/D$$

$$T - T_R = N/D = 0.0044/0.00186 = 2.4 \; C°$$

This is also indicated graphically in Fig. 14 by the X-axis intercept.

Transducer Power

A communication from the transducer manufacturer indicates the rate of energy generation is

$$P = VI = 11 \times 0.004 = 0.044 \; j/sec$$

$$= 0.0105 \; cal/sec = 0.631 \; cal/min$$

Stirrer and Bearing Friction Power

Subtracting P above from N above gives:

$$N - P = 1.25 - 0.63 = 0.62 \; cal/min$$

It would therefore appear that about equal amounts of electrical power (from the transducer) and mechanical power (from frictional and viscous effects) are converted to heat.

Calorimeter Thermal Time Constant

Integration of Eq. (1) yields:

$$\int_{T_0}^{T} \frac{dT}{D(T_R-T)+N} = \int_{0}^{t} \frac{dt}{h}$$

$$\ln\left[\frac{D(T_R-T) + N}{D(T_R-T_0) + N}\right] = -\frac{Dt}{h}$$

$$D(T_R-T) + N = [D(T_R-T_0) + N]\, e^{-Dt/h} \tag{2}$$

This is an exponential as is common for many systems approaching equilibrium. If $N/D << (T_R-T)$ then Eq. (2) reduces to

$$T_R-T = (T_R-T_0)\, e^{-Dt/h}$$

or $\qquad \Delta T = \Delta T_{max}\, e^{-Dt/h}$

indicating that a temperature difference plotted on a logarithmic scale versus time should be linear, having a time constant $T = h/D$.

N/D = Equilibrium Temperature = 2.4 C°

$h/D = 1/0.00186 = 538$ min = 9.0 hr

The above calculations are verified by Fig. 15 which is a plot of the logarithm of $(T_R-T)/(T_R-T_0)$ vs time. The data was taken by placing the calorimeter inside a freezer maintained near -17°C. The calorimeter water was initially at 24°C so the condition $n/D << T_R-T$ is reasonably fulfilled (2.4 << 41). Initially, points did not fall on the line until quasi-steady state was reached. As the calorimeter temperature dropped, the final points did not fall on the line probably because at these temperatures (7°C) the approximation was poorer (2.4 << 24). The break in the

Fig. 15
THERMAL TIME
CONSTANT

$$\frac{T_r - T}{T_r - T_0} = e^{-\frac{t}{310}}$$

$Ln\ (T_r - T)/(T_r - T_0)$

Time – minutes
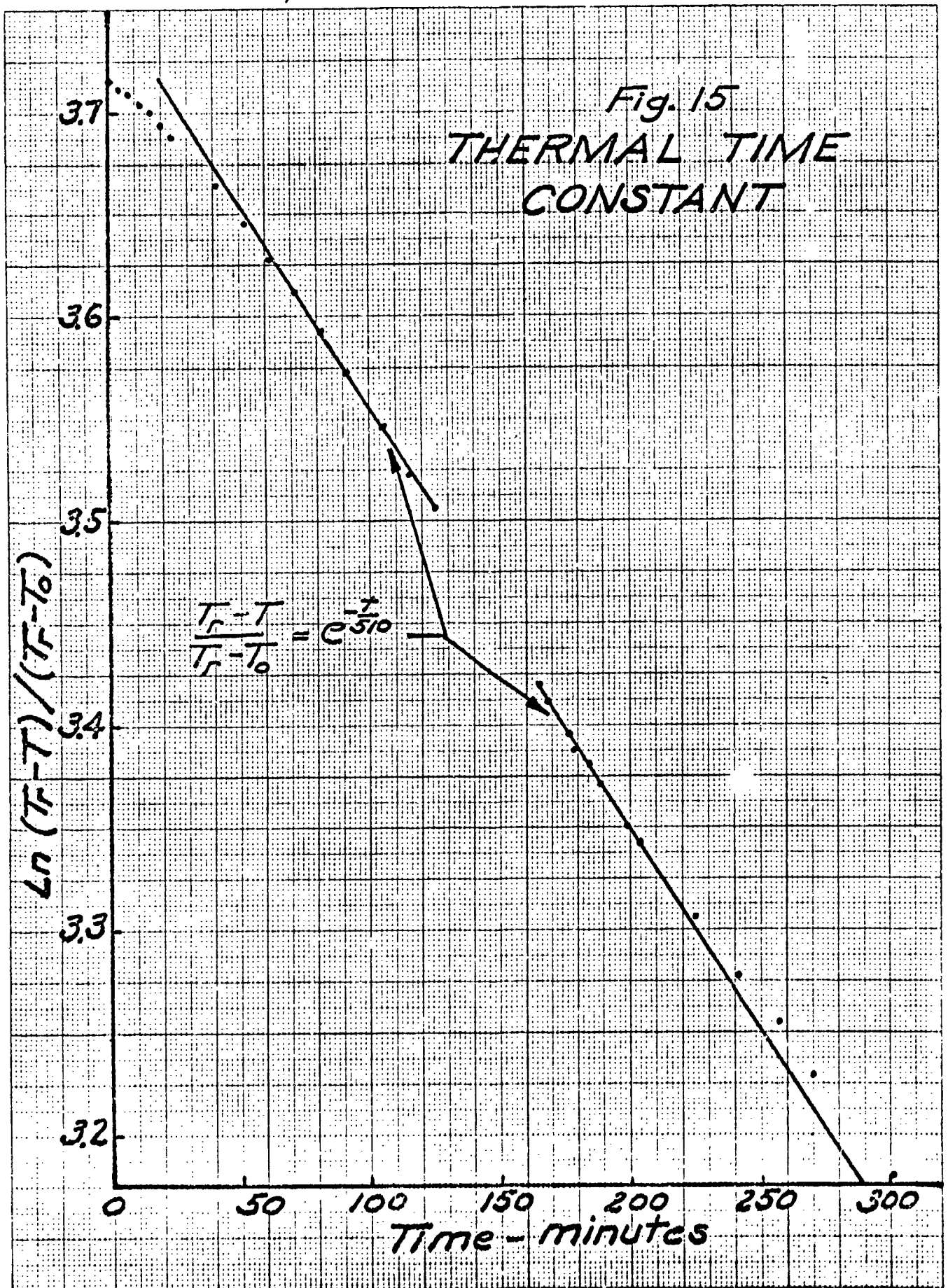
intermediate points was caused by a temporary failure of the freezer thermostat resulting in a change of ambient from -17°C to -20°C over a 40 minute period after which the -17°C ambient was restored.

The slopes on either side of this break are equal and have a value of 0.00196 min^{-1} yielding a time constant of 510 min or 8.5 hrs which agrees well with the previous value of h/D of 9.0 hrs.

Appendix G

Calibration of Bomb Calorimeter at Harry Diamond Laboratories

Data taken during calibration of the bomb calorimeter at the H- ry Diamond Laboratories is shown below. Table 1 shows data for 14 runs without changing water. Table 2 shows data for 3 runs in which the water was changed each time.

During each run, the room temperature varied by about 0.2 to 0.5°C. The maximum measured room temperature was 24.333°C, and the minimum was 23.747°C during the 14 run sequence. The water temperature was therefore 4° to 6°C above room temperature instead of the 1.8°C value recommended by VMIRL, but this did not appear to affect the accuracy of the experiment, although the higher temperature did cause large negative slopes in the time-temperature curves. For the three runs in which the water was changed, the water temperature was about 2°C above room temperature, as shown in Table 2.

The 14 run sequence had 12 usable calibrations which produced a water equivalent of 284.3 cal/C° with a σ of 2.275 cal/C° or 0.80%. When this value is used with the data for the 3 runs in which the water was changed, a total of 4 runs were made with different water samples, and the water equivalent for the four runs is 284.75 cal/C° with a σ of 2.05 or 0.72%. The data obtained was therefore in good agreement with the capabilities of the calorimeter as reported by VMIRL.

Table 1
Water Equivalent of Precision Calorimeter Measured
Without Removing Water

Run No.	Time (Min)	Bomb Temp. (°C)	Pulse Duration (Sec)	Average V Across 10.00 ohm Resistor (V)	Total Heat Supplied by Pulse (Cal)	Apparent Temp. Rise (°C)	Correction for Heat Losses or Gains from Surroundings (°C)	True Temp. Rise (°C)	Water Equivalent (Cal/C°)	Deviation of Water Equivalent from Average Value (Cal/C°)
	0	28.544								
	3	28.537								
	6	28.530								
	12	28.693								
	15	28.685								
1	18	28.676	69.62	1.005	50.97	.163	.017	.180	283.2	-1.1
	0	28.672								
	6	28.833								
	9	28.824								
2	12	28.816	69.62	1.0045	50.92	.161	.017	.178	286.1	+1.8
	0	28.796								
	6	28.958								
	9	28.951								
3	12	28.943	69.95	1.0045	51.16	.162	.015*	.177		
	0	28.943								
	6	29.101								
	9	29.089								
4	12	29.078	69.78	1.005	51.09	.158	.023	.181		
	0	29.078								
	6	29.231								
	9	29.219								
5	12	29.206	69.13	1.005	50.61	.153	.025	.178	284.3	0.0
	0	29.206								
	6	29.361								
	9	29.348								
6	12	29.334	69.60	1.005	50.96	.155	.027	.182	280.0	-4.3
	0	29.334								
	6	29.486								
	9	29.471								
7	12	29.457	69.78	1.005	51.09	.152	.029	.181	282.3	-2.0

90

Table 1 (Cont)
Water Equivalent of Precision Calorimeter Measured Without Removing Water

Run No.	Time (Min)	Bomb Temp. (°C)	Pulse Duration (Sec)	Average V Across 10.00 ohm Resistor (V)	Total Heat Supplied by Pulse (Cal)	Apparent Temp. Rise (°C)	Correction for Heat Losses or Gains from Surroundings (°C)	True Temp. Rise (°C)	Water Equivalent (Cal/C°)	Deviation of Water Equivalent from Average Value (Cal/C°)
	0	29.457								
	6	29.606								
	9	29.591								
8	12	29.577	69.50	1.0045	50.83	.149	.029	.178	285.6	+1.3
	0	29.577								
	6	29.723								
	9	29.708								
9	12	29.692	69.30	1.005	50.74	.146	.031	.177	286.7	+2.4
	0	29.692								
	6	29.838								
	9	29.821								
10	12	29.804	69.62	1.005	50.97	.146	.034	.180	283.2	-1.1
	0	29.804								
	6	29.948								
	9	29.930								
11	12	29.912	69.60	1.005	50.96	.144	.036	.180	283.1	-1.2
	0	29.912								
	6	30.054								
	9	30.035								
12	12	30.016	69.60	1.0045	50.91	.142	.038	.180	282.8	-1.5
	0	30.016								
	6	30.155								
	9	30.135								
13	12	30.116	69.60	1.003	50.76	.139	.039	.178	285.2	+0.9
	0	30.116								
	6	30.253								
	9	30.233								
14	12	30.214	69.60	1.004	50.86	.137	.039	.176	289.0	+4.7

Table 1 (Cont)

Bomb resistor 303.3 ohms excluding leads before and after calibration runs.

Average value of water equivalent (excluding runs 3 and 4) 284.3 Cal/C°
  σ (excluding runs 3 and 4) 2.275 Cal/C°.

Room temperature 23.747°C to 24.333°C minimum and maximum during 14 runs.

*This correction is in error because of a mistake in measurement of time at
the end of the run. Runs 3 and 4 were therefore omitted from the calculations.

Table 2

Water Equivalent of Precision Calorimeter Measured with Separate Water Fillings

Run No.	Time (Min)	Bomb Temp. (°C)	Pulse Duration (Sec)	Average V Across 10.00 ohm Resistor (V)	Total Heat Supplied by Pulse (Cal)	Apparent Temp. Rise (°C)	Correction for Heat Losses or Gains from Surroundings (°C)	True Temp. Rise (°C)	Water Equivalent (Cal/C°)	Deviation of Water Equivalent from Average Value (Cal/C°)
1	0	26.452								
	3	26.455								
	6	26.457								
	1	26.639								
	15	26.641								
	18	26.643	69.59	1.0035	50.60	.182	-.004	.178	285.4	+0.65
2	0	26.200								
	3	26.207								
	6	26.215								
	12	26.408								
	15	26.416								
	18	26.424	69.64	1.004	50.89	.193	-.016	.177	287.5	+2.75
3	0	26.695								
	3	26.698								
	6	26.701								
	12	26.887								
	15	26.890								
	18	26.894	69.80	.9985	50.45	.186	-.007	.179	281.8	-2.95

Bomb resistor 303.3 ohms excluding leads before and after calibration.
Average value of water equivalent for 4 runs with different water 1/4(284.3 + 285.4 + 287.5 + 281.8) = 284.75 Cal/C°.
Room temperature 23.348°C to 24.337°C minimum and maximum during 3 runs.