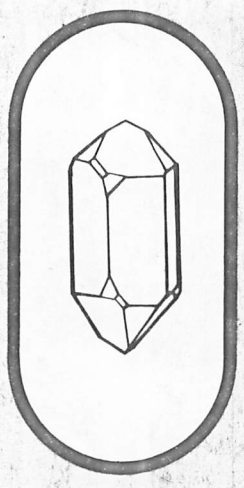
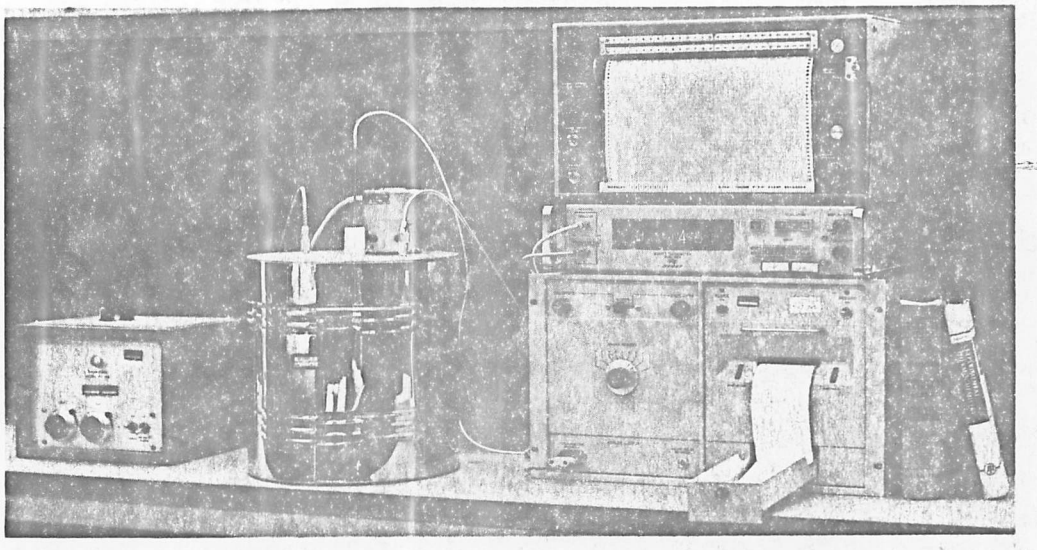
EWLETT CKARD hp DYMEC DIVISION

QUARTZ THERMOMETRY

APPLICATION NOTE 78-3 MARCH 1967





In typical experiment involving isothermally-jacketed calorimeter, HP-2801A Quartz Thermometer measures jacket temperature, vessel temperature, and temperature differential. Measurements are recorded digitally on printer, and also converted to analog form for strip-chart recording.

CALORIMETRY AND THE QUARTZ THERMOMETER

All chemical and physical processes involve energy changes, usually evidenced by the release or absorption of heat. Examples of chemical processes include heat of solution, heat of reaction, heat of combustion and heat of titration. Physical processes include the heat changes associated with changes in heat capacity (specific heat) and those accompanying changes of state.

The science of heat energy measurement is termed calorimetry, and the apparatus used is called a calorimeter. Normally the calorimeter is used to measure the change in heat energy produced by a change in state or condition of a sample. Absolute values are obtained by measuring (by conventional means) the amount of electrical energy necessary to duplicate (or nullify, in the case of an endothermic process) the thermal effect accompanying a chemical or physical process. To this end, the unit of heat energy, the calorie, has been redefined in electrical units; 1 calorie equals 4.1840 absolute joules.

The function of the calorimeter is therefore to provide a fixed environment in which a temperature change resulting from the energy change can be measured. For convenience, most measurements are made at or near standard pressure and temperature (i.e., typical room conditions).

While many different kinds of thermometers are employed to read the temperature changes occurring in calorimetric measurements, the Quartz Thermometer provides the high resolution and precision needed for accurate measurements, along with the convenience of digital temperature display and an output for digital printout and graphical recording. With a Quartz Thermometer, absolute temperatures and temperature differences can conveniently be measured at several points in a calorimeter. Furthermore, the instrument can be set to take a sequence of readings at repeatable time intervals, avoiding the need for separate time keeping. In short, a system consisting of a Quartz Thermometer and associated recording equipment provides the capabilities both necessary and desirable in calorimetric temperature measurement applications.

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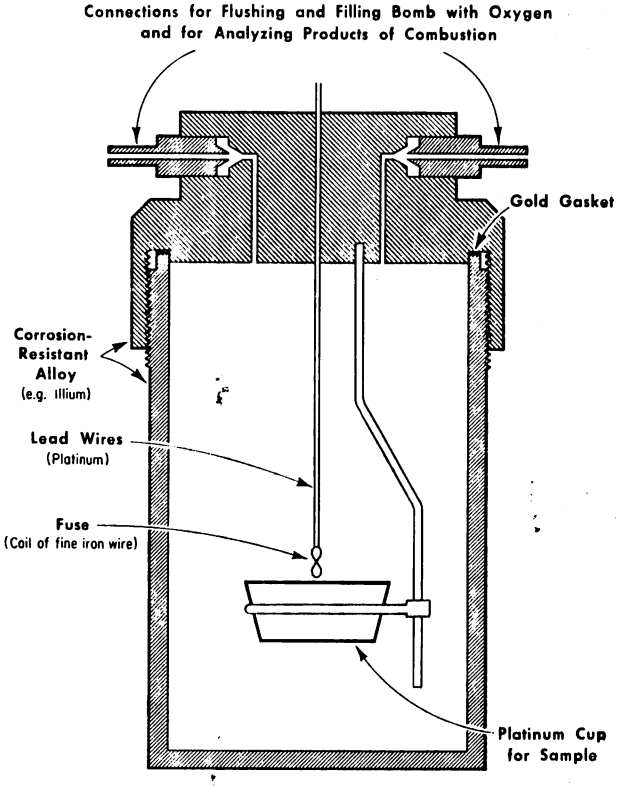
CALORIMETERS

Many techniques and types of calorimeters are used to measure heat energy. Calorimeters are classified in several ways, the first of which is by the kind of heat energy change to be measured, for instance:

a) Heat capacity change
b) Heat of solution
c) Heat of reaction
d) Heat of combustion
e) Heat of titration

The measurement of heat of combustion is a technique widely used to determine the heat of formation of chemical compounds, since it is not always convenient to measure heat of formation by direct synthesis from the elements of the compound. Instead, the usual procedure is to measure the heat released when the compound is decomposed into products of known heat content. In the combustion method the compound is "burned" in the presence of gaseous oxygen and the temperature rise of the calorimeter vessel noted. The apparatus used is popularly known as the "Bomb Calorimeter", and has been developed to a high degree of accuracy. (Figure 1.)

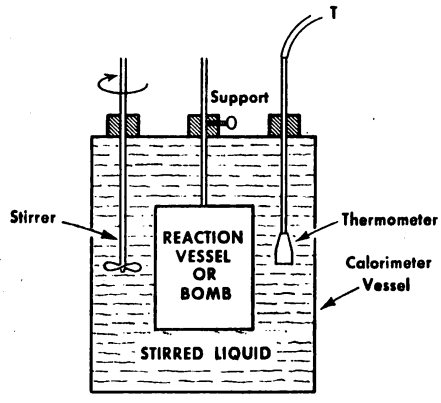


BOMB FOR COMBUSTION CALORIMETRY
FIGURE 1

The bomb calorimeter is also used as a standard test method for the heat of combustion of various fuels, such as coal, aviation gasoline, and oil.

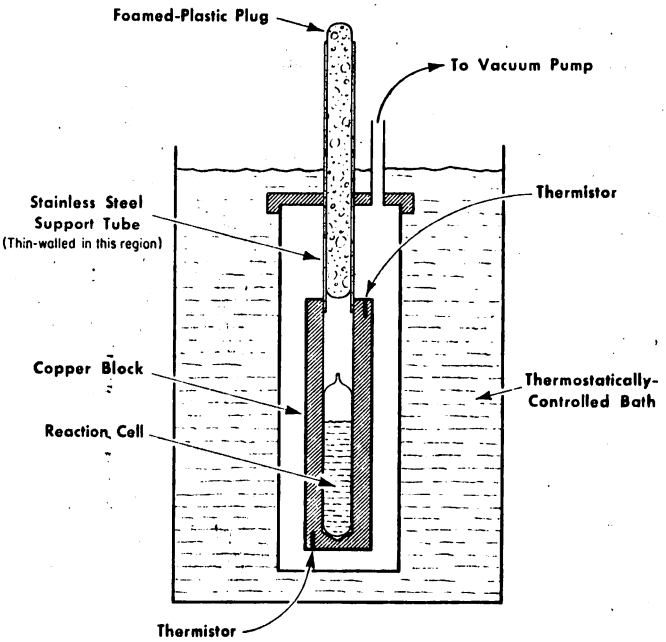
Liquid and Aneroid Calorimeters

The most common form of calorimeter is a metal shell filled with a stirred liquid. A "liquid calorimeter" is illustrated in Figure 2. This calorimeter basically consists of a reaction vessel, a calorimeter vessel containing the stirred liquid (usually water) and an insulated jacket. During the reaction the heat is absorbed by the mass in the calorimeter vessel, and the resulting temperature change is measured by a thermometer. The insulated jacket minimizes energy loss to the room environment.



BASIC LIQUID CALORIMETER
FIGURE 2

For some applications, particularly at very high and very low temperatures, an "aneroid calorimeter" is employed, in which a metal block (usually copper, because of its high thermal conductivity) replaces the liquid. (Figure 3.)



ANEROID CALORIMETER
FIGURE 3

An important design aim is to minimize the heat capacity of that portion of the calorimeter not involved directly in the process, in order to obtain a greater temperature change. Thus, in determining heat capacities by observing the temperature change produced by a known amount of electrical energy, the substance under investigation is used as the calorimeter filling. In a bomb calorimeter the amount of water surrounding the bomb should be no more than is needed for efficient stirring.

Non-Isothermal Calorimeters

Calorimeters can be further classified as non-isothermal and isothermal. In non-isothermal calorimeters, heat quantities are determined from the temperature changes they produce, whereas in isothermal calorimeters the heat quantity is determined by measuring a resultant process, such as a change of state, which takes place isothermally. There are four principal types of non-isothermal calorimeters:

a) Constant temperature environment
b) Adiabatic
c) Twin Calorimeters
d) Heat-leak calorimeters

Constant Temperature Environment: In this design the calorimeter is completely enclosed by a jacket of uniform temperature. The simplest form of this (known as a static jacket) may be only a polished metal container which creates a dead air space around the calorimeter vessel, or a silvered dewar flask which combines the vessel and jacket in one assembly. Since the temperature of the static jacket is influenced by both the vessel temperature and that of the surrounding environment, it is difficult to achieve a low and constant rate of heat leakage with this type of jacket, and it is employed only where large errors can be tolerated.

In a more sophisticated design, the constant temperature environment may be supplied by a jacket containing a stirred liquid, as illustrated in Figure 4, or by a relatively massive metal shield. The former type of jacket is employed in most work at ordinary temperatures, the latter type at low or high temperatures. In some designs a thermostatically-controlled heater is incorporated into the jacket, creating an isothermally-jacketed calorimeter.

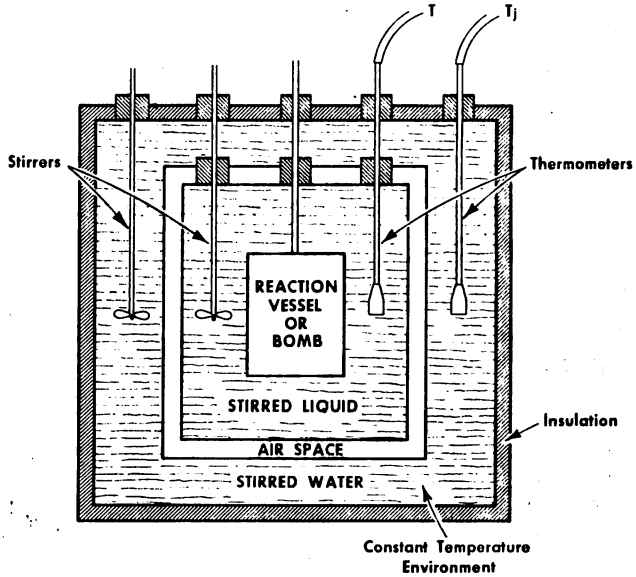
Heat loss from the calorimeter vessel to the jacket follows Newton's law of cooling for the small temperature difference usually permitted. If T is the calorimeter temperature at time t, and T_j is the jacket temperature,

$$dT/dt = K(T_j - T)$$

where K is the leakage modulus. Since K is fixed by the design, the rate of heat loss is thus determined by the "thermal head", $T_j - T$.

Adiabatic Method: Heat exchange between the calorimeter and its environment is eliminated if the thermal head, $T_j - T$, is zero at all times. Thus in the adiabatic method the observation of the calorimeter temperature-time curve, needed for the evaluation of the heat leakage correction in the previous method, is replaced by manual or automatic adjustment of the jacket temperature. However in practice, particularly in experiments of short duration such as with bomb calorimeters, the heat-loss correction can be calculated with greater accuracy than that of the control system to "eliminate" the heat loss. The adiabatic method therefore finds its greatest use in protracted experiments where the change of temperature of the calorimeter is slow enough that the jacket temperature can be held equal to it accurately.

Twin Calorimeters: This method is designed to take advantage of the higher accuracy obtainable through differential temperature measurements. The apparatus consists of two calorimeters constructed as closely identical as possible, supported in surroundings as similar as possible. The calorimeters can be calibrated by heaters of equal resistances, connected in series. If the designs are identical, the temperatures of the two calorimeters will change at very nearly the same rate, and the thermal leakages will be virtually equal. During experiments, the errors common to both the experimental and reference vessels are essentially balanced out.



ISOTHERMALLY-JACKETED CALORIMETER

FIGURE 4

Heat-Leak Calorimeters: In contrast to the adiabatic method (in which heat exchange between the calorimeter and its surroundings is avoided) the heat-leak calorimeter utilizes the calorimeter's loss of heat to its environment to evaluate heat energy. An example is the radiation calorimeter, where the calorimeter vessel is surrounded by a massive copper block whose temperature is

maintained at a value differing from that of the calorimeter by a constant amount. The rate of change of the calorimeter temperature is then inversely proportional to the heat capacity of the calorimeter and its contents. In another design, a constant thermal head is established between an electrically heated calorimeter and an isothermal jacket; the change in heater power needed to maintain this head gives a direct measure of the heat evolved or absorbed during a reaction.

Isothermal Calorimeters

Isothermal calorimeters, by definition, avoid a change in temperature in the calorimetric vessel or its surroundings; instead the heat energy produced is transferred to another medium where its effect is measured. There are two main types: the phase-change calorimeter in which the heat energy causes a change in state of the medium surrounding the calorimeter, and the liquid flow type wherein the heat energy is transferred to a liquid flowing at a controlled rate past the calorimeter.

Phase-Change Calorimeter: This type of calorimeter utilizes the heat of fusion of an ice-water mixture, or other liquid-solid transition (usually organic substances). Heat changes are measured by noting the change in volume of the medium surrounding the calorimeter vessel, as the ratio of liquid to solid alters during an energy transfer. Since only the latent heat of fusion is involved, the experiment occurs at constant temperature. (This type of calorimeter is therefore not a ready application for the Quartz Thermometer, but is described here for completeness.) The phase-change calorimeter is particularly suited to the measurement of small, very slow heat effects. Other versions utilizing the vaporization of a liquid or the condensation of a vapor are also in use.

Labyrinth Flow Calorimeter: In this design the calorimeter vessel is surrounded by a labyrinth of passageways through which water or some other liquid flows. The rate of flow is controlled so as to maintain essentially isothermal conditions in the calorimeter. The heat energy released in the calorimeter is derived from the flow rate, the specific heat of the liquid, and the temperature difference between the ingoing and outflowing liquid.

THERMOMETERS USED IN CALORIMETER SYSTEMS

Thermometers used to measure temperature changes in calorimeter systems fall into five classes:

1. Mercury-in-glass
2. Platinum resistance
3. Thermistor
4. Thermocouple
5. Integrating quartz

A brief review of the first four types is given below. The integrating quartz thermometer is discussed in more detail in the following section.

Mercury-in-Glass Thermometers

The majority of measurements have been done in the past with mercury-in-glass thermometers, and many measurements will undoubtedly continue to use this thermometer. A resolution of better than .001°C can be achieved with short-range mercury thermometers over the normal calorimeter range of 20° to 30°C. The maximum range is limited to -38°C to +360°C, although with high temperature glass and nitrogen filling, a range of 600°C can be obtained. The principal disadvantage of the mercury thermometer is that readings must be taken directly and visually. This limits the placement of the thermometer to where the bulb can be well immersed in the calorimeter vessel, with the stem still visible to the observer. The amount of emergent stem must be controlled as well, and a stem correction computed for the readings. A magnifying glass or telescope is usually employed and the data must be taken by hand.

Platinum Resistance Thermometer

The platinum resistance thermometer provides one of the most accurate means of measuring temperature. Like most pure metals, its resistance changes approximately 0.4% per degree. Since platinum is obtainable in a highly purified form, has a moderately high resistivity and is little affected by gases or fumes, it is preferred over other metals, such as copper or nickel. The resistance thermometer is usually wound from annealed wire, on mica supports so as to be free from thermal or mechanical strain. It is normally sealed in a glass or metal tube for protection. The precision units used in calorimetry have a resistance of 25.5 ohms at 0°C so that the resistance change will be about 0.1 ohm per degree.

A special form of resistance bridge, called the Mueller bridge, is usually employed to read the thermometer resistance changes. Since the current through the thermometer must be limited to prevent excessive heat transfer to the calorimeter, a very sensitive galvanometer must be employed. The bridge has several knobs to be adjusted in obtaining a balance, and therefore the calorimeter temperature trend should be predicted in advance in order to get uniformly spaced readings. The usual procedure is to position the bridge dials to the anticipated temperature and then note the time at which the galvanometer passes through the null position; this is repeated for the entire calorimeter run.

Thermistor

The thermistor is a semi-conducting mixture of metal oxides which is frequently employed as a

thermometer in calorimetry. It has a negative temperature coefficient, exponential in form, and at ordinary temperatures can be 10 times as sensitive as a metal resistance thermometer. Thermistors are available in a variety of forms such as beads, rods, or discs. They provide moderately good stability when protected by a sheath or glass coating. The thermistor is also used in a Wheatstone bridge circuit, but with a less sensitive galvanometer. The poor linearity of the thermistor is its principal disadvantage. This makes it necessary to use a resistance-temperature conversion table. Some thermistor thermometers now use fixed-bridge elements and a calibrated galvanometer to eliminate the need for bridge balancing, at some sacrifice in accuracy.

Thermocouple

Thermocouples provide the simplest and most flexible means of temperature measurement. A couple consists of two junctions between dissimilar metals. When the junctions are connected in series and placed at different temperatures, a voltage is generated between the leads. This may be as high as 50 microvolts per degree Celsius. Metal-pairs commonly used are: iron-constantan, copper-constantan, and chromel-alumel. Noble metal thermocouples provide the best means for measuring temperatures above 500°C. The International Practical Temperature Scale (IPTS) is defined from 500°C to 1000°C by the use of a platinum to platinum-rhodium thermocouple.

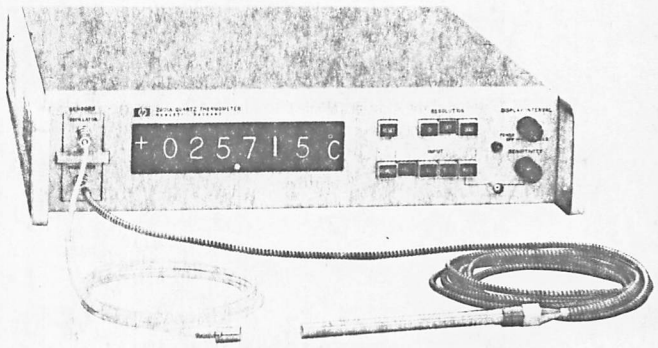
Thermocouples are easily constructed by soldering or welding the junctions and shaping the wires to fit the vessel being monitored. The wire gauge and length can be selected to minimize response time and thermal leakage. Thermocouple junctions may be used in series to form thermopiles (or thermels) in order to increase sensitivity or to provide a means for averaging temperature over a large area. The junctions must alternate, however, between the measurand and reference, e.g., between the calorimeter vessel and the jacket or ice-bath reference.

Thermocouple sensitivity varies considerably with temperature and metals involved. The stability is also influenced by strain, and thermocouples should only be calibrated after they are placed in position. When used in calorimeters, an absolute calibration is seldom required, since the system is calibrated by electrical energy or standard chemical samples. The sensitivity must be well defined, however, to correct for the difference between a calibration reading and an actual experiment.

Sensitive galvanometers are commonly used for reading thermocouple voltages, but the modern integrating digital voltmeter (such as the HP-2401C or 3460A) is superior in sensitivity and in freedom from such common mode voltages as electrical leakage from the calibration circuit. The digital voltmeter also will take readings at self-initiated, precise time intervals, which eliminates the need for time-keeping during a calorimetric measurement.

INTEGRATING QUARTZ THERMOMETER

The Quartz Thermometer (Model HP-2801A) eliminates many of the tedious chores usually associated with precision thermometry, particularly those involved in calorimetric experiments. It displays the temperature in degrees directly and automatically in six figures, to a resolution of 1/10 millidegree. It supplies a digital output which can drive simultaneously a printer and strip-chart recorder, to provide both a numerical tabulation and means for graphical evaluation. The Quartz Thermometer displays the average temperature value at the end of a fixed integration period, which is selectable (by pushbutton) in decade values from 0.1 second (0.01°C resolution) to 10 seconds (0.0001° resolution). An integration period of 100 seconds is optionally available (Option M40).



HP-2801A Quartz Thermometer, shown with two probes from HP-2850 series. Thermometer can measure absolute temperature of either probe or temperature difference between them, by pushbutton selection.

The Quartz Thermometer will automatically take successive readings; the interval between readings can be varied from 0.2 second to 5 seconds by a front panel control, or can be controlled externally. Repeatability of the internally-controlled reading rate is sufficiently precise over short periods (in the order of one hour) to avoid the need for a separate time-of-reading record. The repeatability is best at the minimum interval setting (0.2 second) and typically varies less than 0.5 milliseconds per degree Celsius change in ambient temperature. Since normal room temperature variations seldom exceed ±5°C, a stability of ±2 to 3 milliseconds can be expected. With the 10-second integration period usually used in calorimetric experiments, the repeatability of the sample "clock rate" will therefore be better than 0.03%.

Since two or more thermometer probes can be used with the same instrument system by push-button selection, it is convenient to read and record several temperatures during an experiment. For example, the jacket temperature T_j can be recorded at the beginning and end of an experiment, while the value of $T_j - T$ can be recorded during the rest of the run.

Principle of Operation

The operation of the Quartz Thermometer is based on the temperature sensitivity of quartz piezoelectric resonators. The resonator is a precisely ground disc of quartz crystal approximately 0.18 mm thick by 6.3 mm diameter. Gold electrodes are vacuum deposited on either side and brazed to platinum ribbons which serve as supports and electrical connections. The resonator is sealed into a cold-welded copper case containing helium at standard temperature and pressure. The sealed resonator assembly is normally enclosed in type 304 stainless steel to protect the copper case and leads from corrosion.

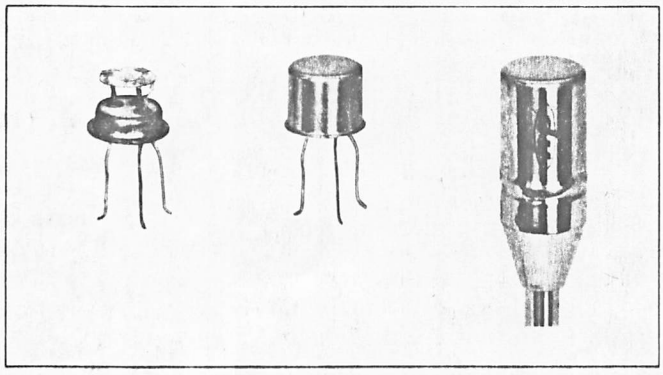
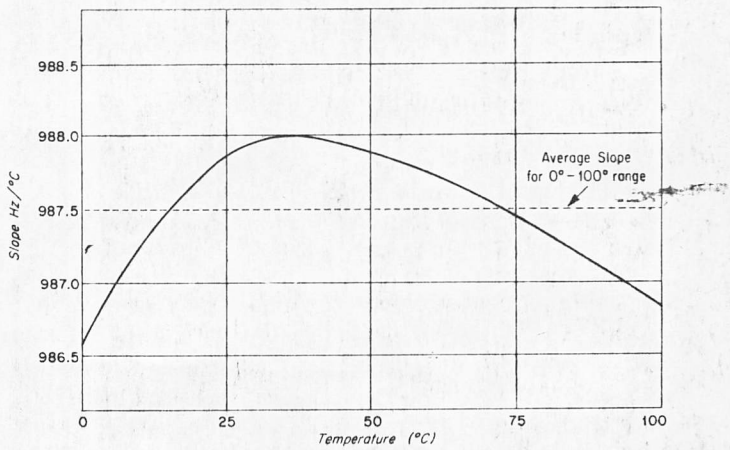
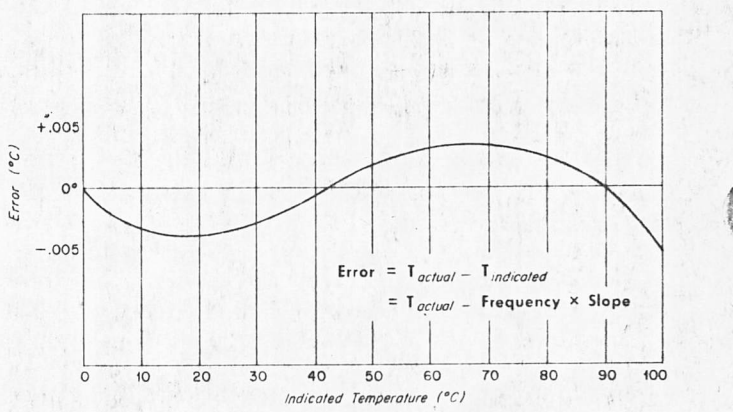


Photo shows, left to right: sensor crystal and its mounting; crystal hermetically sealed within copper case; sensor assembly enclosed in stainless steel body, in this case an HP-2850D probe.

A small diameter, Teflon-insulated, coaxial cable is used to connect the sensor to an electronic solid-state oscillator. The oscillator supplies a small amount of power to the resonator which acts as a highly selective filter that holds the frequency of oscillation very close to the natural frequency of the resonator. A special LC (linear coefficient) cut is used in the Quartz Thermometer sensor crystal that exhibits a very linear, yet sensitive, correspondence between resonant frequency and temperature. The resonator frequency is 28,208 kHz at 0 °C, and varies by 1000 Hz (nominal) per °C. Figure 5a shows the typical variation in slope of LC-cut crystals over the temperature range 0 to 100 °C, while Figure 5b illustrates the typical consequent linearity error over the same temperature range. (Actual operating range of the Quartz Thermometer is -80 to +250 °C, but the 0 to 100 °C span is of interest in calorimetric measurements.) Linearity of the Quartz Thermometer is specified to be within .05 °C over the 0 to 100 °C span; individual calibration charts are supplied with each probe. The power dissipation is typically less than 100 μw, about the same level normally supplied to a standard grade platinum resistance thermometer.



5a. Typical Slope Characteristic of LC Crystal Sensor



5b. Typical Error Curve for LC Crystal Sensor

(Linearity specification of ±.05°C over this span includes calibration error.)

SENSITIVITY AND LINEARITY OF LC QUARTZ CRYSTAL SENSORS

FIGURE 5

The quartz crystal sensor, unlike other thermometers, indicates temperature by a proportional change in frequency rather than a change in resistance, dimensions, or voltage generation. Two basic advantages are obtained by this method of sensing: (1) the temperature indication is almost completely immune to changes in connecting wire resistance, eliminating the need for 4-wire lead systems, and (2) the digital method of reading frequency eliminates the problems of calibration usually associated with analog instruments such as dc amplifiers and voltmeters.

The response time of the quartz sensor is less than two seconds, when measured to 63.2% of the change induced by inserting the probe into water at a dissimilar temperature, flowing at 2 feet per second. This fast response is made possible by the flat disc shape of the sensor crystal, which permits close coupling between it and the flat end

of the probe. Since this sensitive region is concentrated in the first 7 mm of the probe, stem conduction errors are minimized and a shorter insertion length can be tolerated.

The resolution of the quartz thermometer is primarily a function of the selected integration period. The one-second period provides a least significant digit of 1×10^{-3} °C, the 10-second period 1×10^{-4} °C, and the optional 100-second period 1×10^{-5} °C. After being stabilized at a constant temperature, such as that encountered in a calorimeter, short-term variations (standard deviation) are less than 5×10^{-5} °C. Long-term drift is usually negative in sign and does not exceed 1×10^{-5} °C per hour, when averaged over a month.

RECORDING QUARTZ THERMOMETER READINGS

As a standard feature, the Quartz Thermometer provides a digital output for each reading which can be printed by an HP-562A Digital Recorder. Figure 7 shows an example of such a printout. In this recording the thermometer was set to its .0001° resolution mode; the temperature read was in the order of 1°C, displayed and recorded as 010000. The decimal point position, available as the negative decimal exponent, was not recorded in the example, but could have been.

The Quartz Thermometer readings can also be recorded graphically on a strip-chart recorder by first converting the digital output to analog form. This can be accomplished either with a plug-in digital-analog converter for the HP-562A printer, or with an HP-580A or 581A Digital-Analog Converter. The 580A and 581A differ only in physical configuration: the 580A is a half-rack module (requiring 7 inches of vertical panel space when rack mounted) while the 581A is a rack mount unit (3-1/2 inches vertical panel space).

With all these converters, any three consecutive digits, or the two least significant digits, of the Quartz Thermometer display may be chosen (by front panel switch) for analog output. By choosing the two or three least significant digits, high-resolution strip-chart recordings are possible. Full scale deflections from 1000°C down to .01°C are obtainable with this feature. (Or down to .001°C with the optional 100-second sample period.)

In Figure 7 the initial period was graphically recorded at a full-scale sensitivity of .01°C, by selecting the two least significant displayed digits for digital-analog conversion (00.0100). Note that the recorder retraces when full scale is exceeded, as the reading reduces from approximately 1.02° to 1.00°C. During the reaction period the temperature change is much greater; the full scale sensitivity was reduced to 1°C simply by selecting more significant digits for conversion (01.0000).

Of the various strip-chart recorders available from hp, models 680 and 7101A are best suited to this type of application. Model 680 is a half-rack module which may be rack-mounted together with the 580A converter; it provides a writing width of 5 inches. Model 7101A has twice the writing width (10 inches) and is recommended because of the increased resolution this offers. (Model 7101AR is a rack-mount version, requiring 8-3/4 inches of vertical rack space.) For metric applications, models 680M and 7101AM are available; these provide, respectively, writing widths of 12 and 25 centimeters. (The chart in Figure 7 was made on a model 7101AM recorder.)

DETERMINATION OF CALORIMETER TEMPERATURE CHANGE

Measurement of the temperature rise occurring in a bomb calorimeter is used as an example in the following discussion; the general technique may, however be applied to most calorimetric experiments. There are usually three phases to a calorimetric experiment: the initial period during which the temperature change is principally due to heat of stirring; the reaction period during which the temperature rise is principally from the reaction being measured, or to the introduction of electrical or chemical calibration energy; and the final period in which the changes are again due only to heat leakage and stirring energy.

Figure 6 represents the time-temperature curve for such a process, which is usually fairly rapid – less than one hour overall. The initial and final periods are usually monitored for intervals of 15 to 20 minutes. The reaction period depends upon the lag of the bomb itself. The initial temperature rise during this period is quite rapid; it approximates an exponential change such that 63% of the final temperature is usually achieved in the first 10% of the reaction period.

In an ideal calorimeter, the thermal leakage and therefore the initial and final slopes would be zero and no correction to the value of $T_c - T_b$ would be required. In practice, however, the slopes are finite, typically in the order of 1 to 5×10^{-3}°C/min. As indicated earlier, this temperature change is caused by two effects: the leakage modulus and the heat of stirring. The first closely follows Newton's law of cooling and is expressed as

$$(1) \quad \frac{dT}{dt} = K\ (T_j - T)$$

Although this represents an exponential approach to the jacket temperature T_j, the small value of K usually encountered permits a linear approximation to be used. The heat of stirring can be represented as a constant rate u, so that the total rate of change is then given by

$$(2) \quad \frac{dT}{dt} = u + K\ (T_j - T)$$

The bomb calorimeter is usually operated so that the initial temperature is about 2° to 3° below T_j and the final temperature very close to the jacket temperature. When this situation exists, the rate of the initial period is largely a function of K due to the large value of $(T_j - T)$, while the final rate is primarily determined by u, since $T_j - T \cong 0$.

The constants K and u can be calculated from data taken during the initial and final periods. The average temperatures T_i and T_f can be obtained by

$$(3) \quad T_i = \frac{T_b + T_a}{2} \text{ and}$$

$$(4) \quad T_f = \frac{T_d + T_c}{2}$$

while the initial and final rates are

$$(5) \quad \frac{dT_i}{dt} = \frac{T_b - T_a}{t_b - t_a} \text{ and}$$

$$(6) \quad \frac{dT_f}{dt} = \frac{T_d - T_c}{t_d - t_c}$$

The two equations can be written by substituting the proper values into (2), thus:

$$(7) \quad \frac{dT_i}{dt} = u + K(T_j - T_i)$$

$$(8) \quad \frac{dT_f}{dt} = u + K(T_j - T_f)$$

and solved simultaneously for u and K.

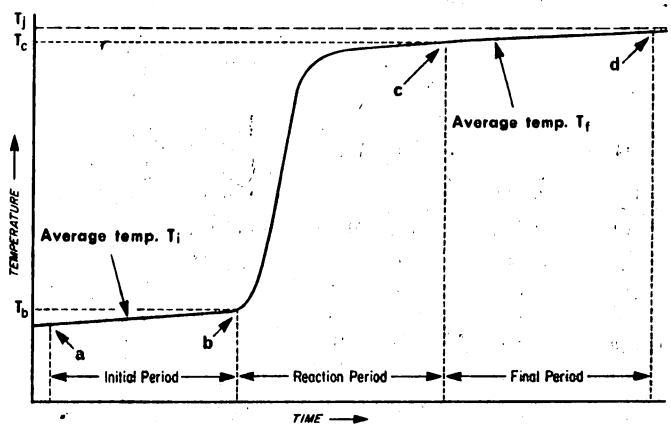
Since the reaction period takes a finite time $t_c - t_b$, the true temperature change during the reaction period is given by:

$$(9) \quad \Delta T_{corr} = T_c - T_b + \Delta T \text{ where}$$

$$(10) \quad \Delta T = u(t_c - t_b) + K \int_{t_b}^{t_c} (T_j - T)dt.$$

The Quartz Thermometer in combination with the printer and strip-chart recorder provide an excellent data acquisition system that simplifies the task of solving these equations. The following procedure is suggested.

The .0001° Quartz Thermometer mode provides readings at equal intervals of slightly more than 10 seconds and can be used throughout the experiment. One probe, T_1, should be positioned in the jacket water to read T_j, and probe T_2 placed in the calorimeter vessel. When the calorimeter has been stabilized and has entered the initial period (corresponding to point a in Figure 6) the printer and recorder should be turned on. The recorder should be set by digit selection to provide a full scale span of .01°C. A constant chart speed of 1 inch per minute is suggested. At the selected time a, the absolute jacket and calorimeter temperatures should be read and printed by pressing the T_1 and T_2 buttons in sequence. The $T_1 - T_2$ button is then pressed so that the recorders will provide $T_j - T$ data for rating the initial period. Figure 7 shows a typical recording of $T_j - T$ for the initial, reaction, and final periods of a calorimetric experiment.



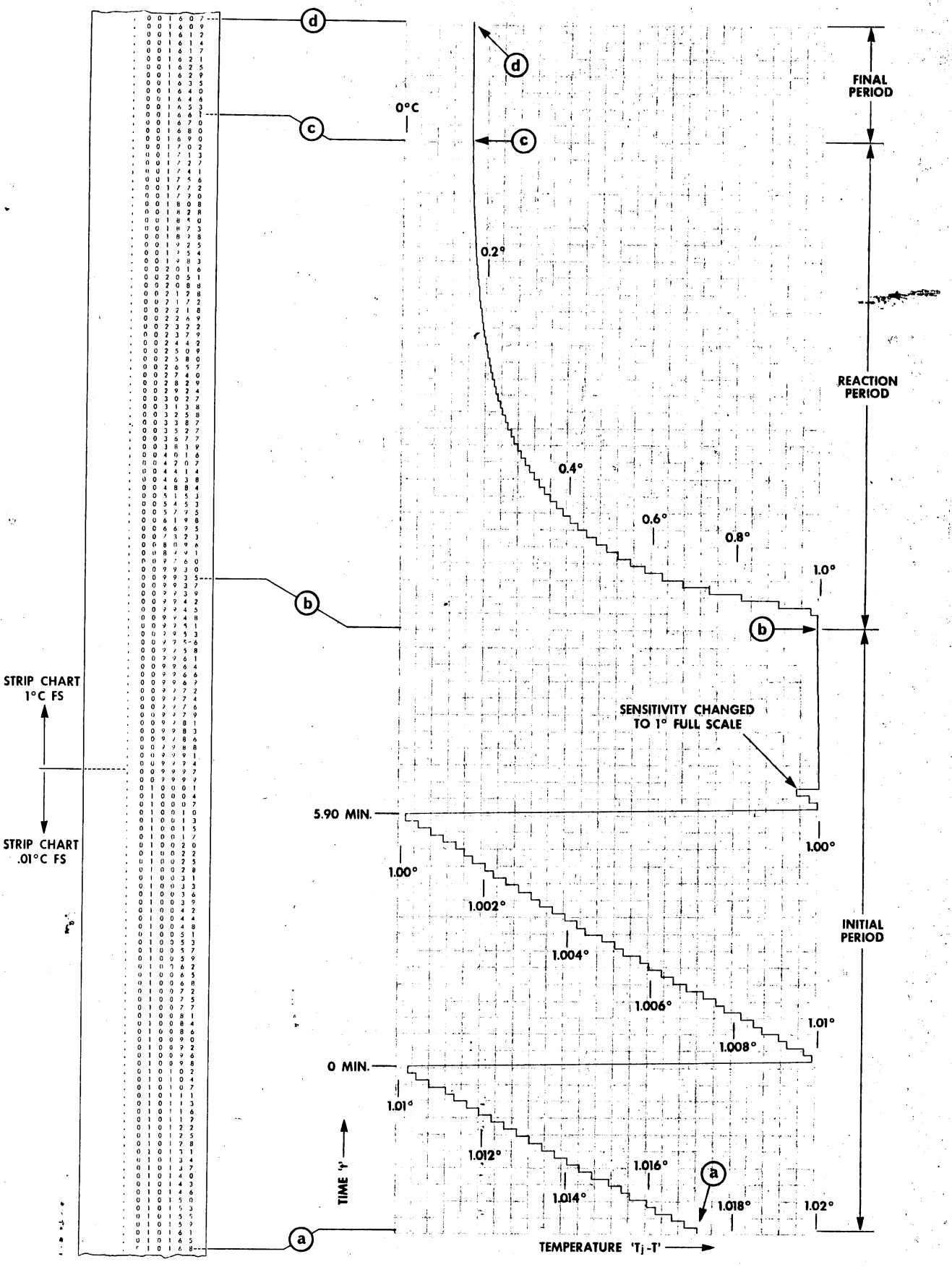
TYPICAL TIME-TEMPERATURE CURVE FOR CALORIMETER EXPERIMENT

FIGURE 6

The average rate of change of temperature between points a and b can then be determined by fitting a straight line to the graphic plot. The mean temperature T_i can also be read as the average value at the midpoint of the a-b interval, or by summing the printed readings from a to b and dividing by the number of readings in the summation. At time t_b, the reaction or bomb firing is initiated and the recorders will acquire the reaction period data. Since the temperature rise during this period is usually 2-3°C, the digital selection of strip-chart span can be expanded to either 1° or 10° full scale. (1° was chosen in the experiment of Figure 7.) The graphic record provides a clear indication of the reaction's trend, and enables the operator to select point c, the end of the period.

The printer, in providing precisely-spaced temperature readings to ±.0001°, permits an accurate determination of the integral in equation (10) which is equal to the arithmetic sum of the printed values of the period b-c, times the length of each interval (10 seconds in this example).

Because of the precise clock rate at which the temperature readings are printed, the number of readings involved in each of the periods can be used in the calculations instead of the actual time in seconds.



ACTUAL RECORDING OF CALORIMETRIC EXPERIMENT

FIGURE 7

The final rating period from c to d is treated exactly as the initial period was. The straight line fit can be extrapolated from d toward c in order to determine the best selection of point c. This point, which marks the end of the reaction period and the return to equilibrium, can be selected as the point where a noticeable departure from linearity occurs.

If a digital computer is available, the printed data can be entered into an established program to rate the initial and final periods and determine the critical values of $T_j - T$. Alternatively, the Quartz Thermometer readings can be recorded on punched tape or cards, or magnetic tape, for subsequent computer entry. (Recording systems for these media are available from Hewlett-Packard.)

Acknowledgement

We are indebted to Dr. Frederick D. Rossini for his contributions to this Application Note, both directly and from his treatment of Chemical Thermodynamics, published in reference 2, below.

References

1. Experimental Thermochemistry. Frederick D. Rossini, Editor. Interscience Publishers, New York (1956).

2. Chemical Thermodynamics. Frederick D. Rossini, Wiley and Sons, New York (1950).

3. Technique of Organic Chemistry Vol. 1, Part 1: Physical Methods of Organic Chemistry. Arnold Weissburger, Editor. Interscience Publishers, New York (third edition, 1959).

4. Standard Method of Test for Heat of Combustion of Hydrocarbon Fuels by Bomb Calorimeter (High-Precision Method). ASTM Designation D2382-65. (Adopted 1965.)

APPENDIX 1 SPECIAL PROBE CONFIGURATIONS

While six different standard probe configurations (models HP-2850A through 2850F) are available for the Quartz Thermometer, situations do arise where none of these is quite satisfactory for a particular application. Some general guidelines to the types of variations available on special order are given below. (Price quotations on request.)

Probe Sheath Material

Standard probes are sheated in type 304 stainless steel. Probes can be supplied sheathed in other materials, such as type 316 stainless steel and nickel.

Probe Dimensions

The technical data sheet for the HP-2801A Quartz Thermometer gives outline drawings for the HP-2850A-F probes. The diameter of the sensing element of the probe (the tip) cannot be reduced from 3/8 inch, since it is governed by the design parameters of the basic quartz crystal sensor. However, probe lengths and neck diameters other than those shown can be furnished.

For calorimetric applications involving very small samples, special probes have been furnished which serve as both the sample container and the temperature sensor. In these probes, a flat-bottomed, gold-plated copper cup, about 8 mm internal diameter and 5 mm long, is attached to the probe tip.

Probe Cable

The standard coaxial cable used for the probes is type RG-187A/U, with an external diameter of 0.110 inch. A thinner cable, type RG-196A/U, with a diameter of only 0.080 inch can be furnished instead. (Both types of cable employ TFE Teflon for both dielectric and jacket material.)

Intermediate plugs and hermetically-sealed coaxial bulkhead connectors, that permit routing the sensor cable through vacuum seals or various other calorimeter enclosures, are available for the type RG-196A/U cable.

The length of the sensor cable (nominally 12 feet) should not be changed by more than 1/2 inch, nor should open wires or two-pin connector lengths of more than 1/2 inch be spliced into this cable if it must be cut for routing through the wall or lid of a calorimeter vessel. Alterations within these limits may shift the calibration slightly, but will not affect the sensitivity or linearity. It will only be necessary to adjust the zero set controls to restore the calibration.