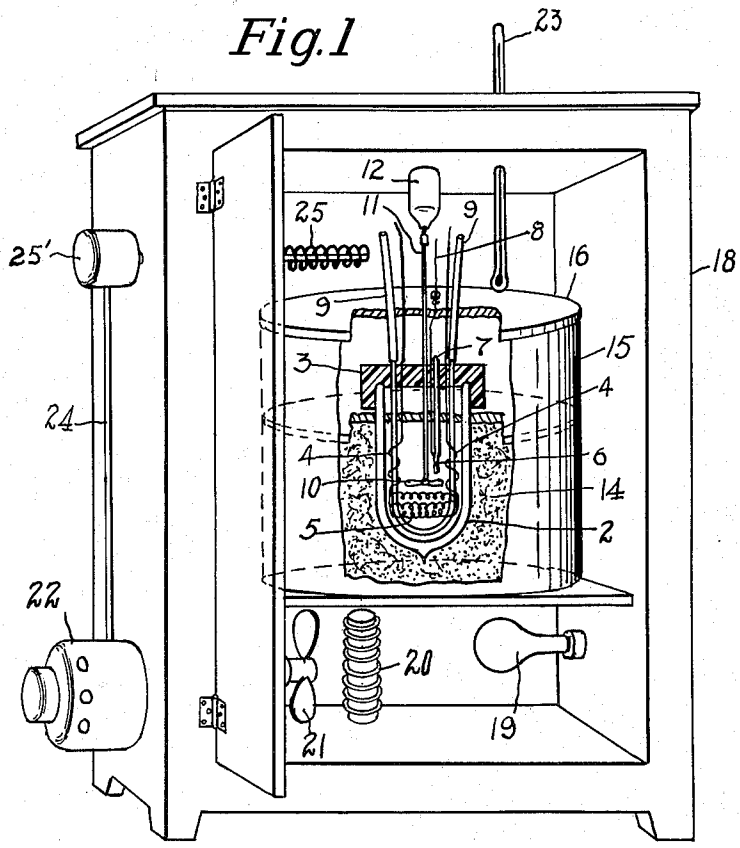
Feb. 7, 1956 W. JACKSON, JR., ET AL 2,733,602

ISOTHERMAL CALORIMETER

Filed Jan. 19, 1953

Fig.1



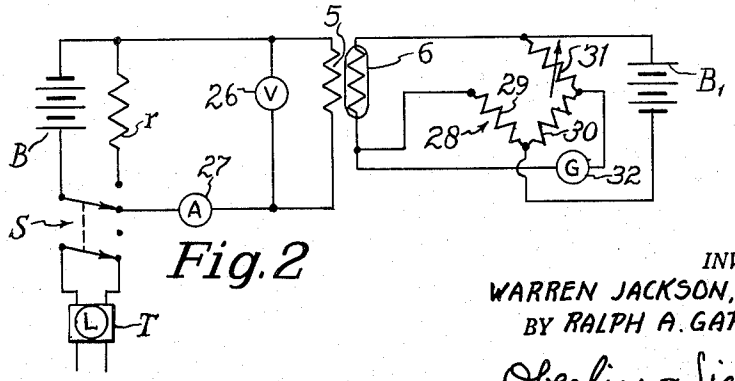


Fig.2

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ISOTHERMAL CALORIMETER

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Application January 19, 1953, Serial No. 331,982

6 Claims. (Cl. 73—190)

Calorimeters as heretofore known have been complex and costly instruments, and capable in general of operating on only relatively large samples of material. A calorimeter having sufficient sensitivity to produce analytical data from quite small volumes of material has long been desired. Many factors contribute against attainment of desirable accuracy for small sample determinations. Forms of the device as heretofore known have themselves had too large a heat capacity, and have not been adequately temperature-sensitive for minute variations. And, in general inadequate provisions have been made against errors from heat leakage and from irregular heat transfer through the body of the sample being tested. Overall it has not been possible to obtain close duplicate determinations on a given sample. By the present invention, a construction is had which is capable of yielding extremely accurate results, in using small samples. And withal, the apparatus is relatively simple and of reasonable cost. Other objects and advantages will appear from the following description.

To the accomplishment of the foregoing and related ends, said invention, then, comprises the features hereinafter fully described and particularly pointed out in the claims, the following description and the annexed drawing setting forth in detail certain illustrative embodiments of the invention, these being indicative, however, of but a few of the various ways in which the principle of the invention may be employed.

In said annexed drawing:

Fig. 1 is a perspective view, partly broken, showing an illustrative embodiment of the invention; and

Fig. 2 is a wiring diagram thereof.

In its general features, the construction involves a double wall flask on the order of a silvered Dewar flask within which the sample to be tested is contained, also precision temperature-indicating means, temperature control means and stirring means, the flask being surrounded by heat insulation and a temperature-controlled or constant temperature air bath.

In the form of device illustrated in the drawing, there is shown a silvered Dewar flask **2** with a cover **3**, which may be of plastic material. The cover supports a U-shaped glass tube upon which is carried lead wires **4** to resistance-heating wires **5**, such as of Nichrome, these extending across from leg to leg of the glass tube. A pyrometer-type temperature detector **6** is provided. This may be of conventional bi-metallic type. But we prefer the construction which involves a small bead of sintered metal oxides, such as the commercial "thermistor" of the Western Electric Co. It is supported by a glass tube **7** suspended from the cover, and lead wires **8** are connected between the thermistor and indicating instrumental means outside, such as a usual galvanometer-type indicator. Connected onto the U-tube are tubes **9**, such as of pliant plastic, through which a cooling fluid may be supplied. A stirrer propeller **10** is supported in the flask by shaft **11** from its drive motor **12**. The flask is surrounded by thick insulation **14**, which may be of cellular

type, as santocel, vermiculite, and the like. This is surrounded by a sheet metal container wall **15**, with a cover **16**; and this assemblage is supported within an air bath container **18** providing constant temperature surrounding. The air bath container **18** is provided with a heating means **19**, in the form of a bulb preferably, the incandescent member there being protected by a glass envelope, and cooling means is provided in the form of a radiator **20** which is supplied with cooling fluid, and opposite the radiator and heater a fan **21** is arranged, being driven by a motor **22** outside the cabinet. Thermometer **23** projects into the cabinet, its scale being readable outside. A bi-metallic thermo-regulator **25** is arranged also in the cabinet, and this includes a relay-casing **25'** outside; and a steel rod **24** between it and the fan motor **22** directs constant vibration from the motor to the relay-casing and keeps it sensitive against sticking and undue inertia.

As illustrated in the wiring diagram of Fig. 2, the supply circuit for the heater **5** comprises a storage battery B and a double-pole double-throw switch designated at S. A clock timer T and an auxiliary resistor *r* are also connected to terminals of such switch, and it will be clear from the diagram that the switch is operative in one position to connect the heater **5** across the battery and simultaneously to close the circuit of the timer T for energization of the latter from a conventional source of supply. In its other position, the switch opens the timer circuit, disconnects the heater **5** from the battery, and connects resistor *r* across the battery. The latter action maintains a constant load on the battery when the heater **5** is de-energized and thereby serves to keep the battery "warm" between heating cycles. A voltmeter **26** is connected across the heater **5** and an ammeter **27** is provided in series to measure the current flow.

Thermistor **6** is connected across one branch or leg of a Wheatstone bridge designated generally by reference numeral **28**, fixed resistors **29** and **30** and variable resistor **31** forming the other legs of the bridge respectively. The bridge is energized by means of a further battery B_1 connected across two opposite terminals thereof, and a galvanometer **32** is connected across the remaining bridge terminals. The resistance of the thermistor is measured in conventional manner, that is, by adjusting the variable resistor **31** in the adjoining leg until the galvanometer reads zero and then computing the resistance of the thermistor from the known resistance values of the other legs of the bridge.

The manner of use of the apparatus will be readily understood. For instance, to determine the specific heat of a liquid, a sample of 100 ml. volume of which the specific heat is desired, is supplied to a flask which is set in the constant temperature air bath overnight. The flask containing the sample is then weighed, and the sample poured into the Dewar flask. Re-weighing of a flask allows calculation of the sample weight by difference. The sample is now in the Dewar, and is at the temperature at which the specific heat is desired. The specific heat of a material varies with the temperature of measurement. Generally the specific heat increases as the temperature increases. The present apparatus is usable to measure at different temperatures. The temperature at which the specific heat is desired is that at which the data is to be taken, that of the constant-temperature box. The liquid must be cooled slightly and heated slightly to allow calculation of the calories of heat necessary to raise the temperature of the liquid one degree at this temperature. The sample is then first cooled by circulating cooled methanol through the U-tube inside the Dewar, followed by vacuum to dry the U-tube. The sample should be cooled at least a degree or a degree and a half below the specific heat temperature. If cooled too much, it can be reheated up to within a degree and a half of the specific heat tem-

perature by the Nichrome heater control. The stirrer has remained on overnight, to eliminate irregular stirring-rates during warm-up of the stirrer. Irregular stirring-rate is mainly due to changes in viscosity of the lubricating oil in the stirrer motor when the stirrer is started cold. The stirrer motor is outside the constant-temperature box, and hence by allowing a long time preliminary run for warm-up, extraneous error is avoided. With the sample at the starting temperature now, the run is started. The resistance of the thermistor is taken at one-minute intervals, by adjustment of the bridge circuit in the usual manner indicated above and read to the nearest 0.05 minute as the sample temperature increases with stirring to within 0.6° C. to 0.7° C. of the specific heat temperature. The heater and the timer T are then simultaneously started by actuation of the control switch S. The voltage and current of the thus energized heating circuit are indicated by the instruments **26** and **27** respectively and recorded. After ten minutes the heater and timer are turned off and thereafter the resistance of the thermistor is again determined as before at time intervals. The timer afore-indicated is concerned with the length of heating cycle. Another timer is run continuously from beginning to end of the test, for time-temperature data. The temperature of the constant temperature box, which should be at the temperature at which the specific heat is desired, is also important. Using the calibration curve for the thermistor, the resistance readings are converted to degrees centigrade. The change of resistance of the thermistor is not linear with temperature, but the conversion of resistance readings to temperature will give a straight line plot of temperature vs. time. Determinations wherein the time-temperature plot is not a straight line indicate that isothermal conditions were not attained or an irreproducible run. These runs should be discarded. The slopes of the time-temperature plots will be different before and after the heating cycle. It is desirable to plot the graphs on paper ruled to the nearest 0.02 of a degree, with estimation to the nearest 0.002 and time ruled to the nearest tenth of a minute and estimate to the hundredth of a minute. The two lines that is, representing the time-temperature plot obtained for a predetermined time prior to the ten minute heating period and the similar plot obtained after expiration of such period, can be extrapolated to the midpoint of the heating cycle, and the temperature rise ΔT measured between the two lines at such point, the rise being obtained to the thousandth of a degree. The amperage, voltage, time and sample weight are similarly determined to four digits. The formulas used for calculation of the specific heat Cp and K, the calorimeter constant, are given below. A repeat determination can be made upon the same sample, by cooling it to about one degree centigrade below the temperature at which the specific heat is desired, and repeating the procedure. The ammeter is connected in series with the heater on the supply side of the voltmeter, necessitating a voltmeter-current correction factor to be subtracted from the readings of the ammeter. The general formula for the current correction is voltmeter reading in volts divided by the voltmeter resistance in ohms=the correction in amps. This correction for instance where the voltmeter resistance is 1500 ohms is

$$\frac{\text{Volts}}{1500}=\text{amps}$$

The adaptation of the apparatus and method to other thermal determinations will be obvious. The reproducibility should remain on the same order.

With operations near or below room temperature, constant circulation of ice water through the radiator near the fan, together with intermittent heating by the light-bulb gives particularly satisfactory temperature control; and with the relay, which turns the current on and off to the light-bulb, subjected to continuous vibration from the fan motor, as afore-described, the sensitivity of control is remarkably close. The heat capacity of a system is defined as the heat input divided by the temperature rise. Since here the heat is electrical, it is easily measured by the product of voltage, amperage, and time, thereby giving value in joules, and by dividing this by 4.185, this is changed to calories. The heat capacity of a system is also defined as the product of the specific heat and the weight of the system. For these reasons,

$$\frac{(V)(A)(t)}{4.185(\Delta T)}$$

can be equated to $Cp(W)+K$ where Cp (W) is the contribution to the heat capacity from the unknown sample of weight W, and K is the contribution to the heat capacity from the calorimeter assembly, determined by using pure benzene. The solution of this equation for Cp gives

$$Cp=\frac{(V)(A)(t)}{4.185(\Delta T)(W)}=\frac{K}{W}$$

The formula for determination of specific heat is

$$Cp=\frac{(V)(A)(t)}{4.185\Delta T(W)}-\frac{K}{W}$$

and

$$A=Ao-\frac{V}{\text{Voltmeter resistance}}$$

where:

V=voltage during heating cycle
Ao=amperage registered during heating cycle
t=time in seconds of heating cycle
ΔT=temperature rise in degrees centigrade during heating cycle
W=weight in grams of sample
K=calorimeter constant

K, the calorimeter constant was determined using Mallinchrodt Reagant Grade Benzene by the identical method with application of the formula

$$K=\frac{(V)(A)(t)}{4.185(\Delta T)}-W(Cp)$$

where

Cp=specific heat of benzene from Specific Heat of Liquids, Burlew, J. A. C. S. 62, 681, 690, 696 (40)

Other modes of applying the principle of the invention may be employed, change being made as regards the details described, provided the features stated in any of the following claims or the equivalent of such be employed.

We therefore particularly point out and distinctly claim as our invention:

1. In a calorimeter, the combination of a silvered Dewar flask, a cover therefor, a stirrer with drive-shaft extending through the cover, a thermistor having lead wires extending through the cover, a glass support for the thermistor projecting into the flask, a U-shaped glass tube in the flask, resistance wire heating means carried by said tube, connections for circulation of coolant through said tube, heat-insulation surrounding said flask, a container about the insulation, an air-bath chamber surrounding said container, a cooling radiator and motor-driven circulator fan and a heater in said chamber, a bimetallic thermo-regulator in heat-exchange relationship with said chamber, a relay controlling said heater, and relay-sensitizing means including a rod transmitting vibrations from the circulator fan motor to the relay.

2. In a calorimeter, the combination of a silvered Dewar flask, a cover therefor, and within the flask a stirrer, a thermistor and a U-shaped glass tube with resistance wire heating means, connections for circulation of coolant through said tube, heat-insulation surrounding said flask, a container about the insulation, an air-bath chamber surrounding said container, a cooling radiator and motor-driven circulator fan and a heater in said chamber, a bimetallic thermo-regulator and a relay controlling said heater, in heat-exchange relationship with said cham-

ber, relay-sensitizing means including a rod transmitting vibrations from the circulator fan motor to the relay.

3. In a calorimeter, the combination of a silvered Dewar flask, a cover therefor, and within the flask a stirrer, a thermistor and a U-shaped glass tube with resistance wire heating means carried by the tube, connections for circulation of coolant through said tube, heat-insulation surrounding said flask, a container about the insulation, an air-bath chamber surrounding said container, a motor driven circulator fan and cooling means and heating means in said chamber, a thermo-regulator in heat-exchange relationship with said chamber, a relay controlling the heating means, and relay-sensitizing means including a connection transmitting vibrations from the circulator fan motor to the relay.

4. In a calorimeter, the combination of a silvered Dewar flask, a cover therefor, a stirrer within the flask with drive shaft extending through the cover, a thermistor and a U-shaped glass tube in the flask with resistance-wire heating means carried by said tube, connections for circulation of coolant through said tube, and a heat-insulating container surrounding said flask.

5. In a calorimeter, the combination of a silvered Dewar flask, a cover therefor, temperature-measuring means in the flask, and temperature controlling means in the flask including a tube supporting a resistance wire heater, and connections for circulating a coolant through the tube.

6. In a calorimeter, the combination of an insulated container, a cover therefor, temperature-measuring means in the container, and temperature-controlling means in the container including a tube supporting a resistance wire heater and connections for circulating a coolant through the tube.

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