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Note

A Quasi-Adiabatic Reaction Calorimeter for Measurements in Liquids

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A quasi adiabatic reaction and solution calorimeter was constructed and tested using tris(hydroxymethyl)aminomethane dissolution in 0.1 mol dm^{-3} HCl as the reference (standard) process. The precision of the calorimeter amounts to approximately ± 1 per cent and its sensitivity to 4 J dm^{-3}.

The Type of Calorimeter

The calorimeter presented here has been designed for the measurements of the heats of reaction taking place in liquids by dissolution or admixing of solid or liquid reactants. Chemical reactions are usually typical energy sources whose energy evolution rate varies as the reaction proceeds. On the other hand, the liquids in which the reaction occurs are generally poor heat conductors. In such case the only choice is a quasi-adiabatic calorimeter for short processes[1] with vigourous stirring. The device described below can be used with an accuracy of 1 to 2 per cent for the enthalpy measurements of processes the duration of which does not exceed the order of magnitude of 10 minutes.

Apparatus

The cross section of the calorimetric device is presented in Figure 1. The calorimeter is immersed in a water bath whose temperature is controlled to within ± 0.1 °C. The hollow copper cylinder together with the brass tightening flanges is the calorimetric jacket (O). The heat transfer medium is the air under ambient pressure. The thermally active body (calorimetric body) is a glass bulb (B) which contains: the reaction liquid, two thin-walled tubes (filled with transformer oil) in which the heater (G) and thermistor (T) are situated, and the stirrer (M) to which the ampule (A) containing the reactant is fastened. The stirrer (M) is connected to an electromotor *via* a flexible steel shaft.

To initiate the reaction the ampule is broken on the glass spike (S) by moving the stainless steel cylinder (V) vertically. The spiral spring (IO) keeps the ampule rotating slightly above the spike; the adjustment of the lowermost position of the ampule is made by fixing the limiting ring (GP) at the proper height. To the neck of the glass bulb a brass ring (Z) with threaded outer side is sealed using epoxy adhesive Araldite AV 121 (Ciba product). This ring

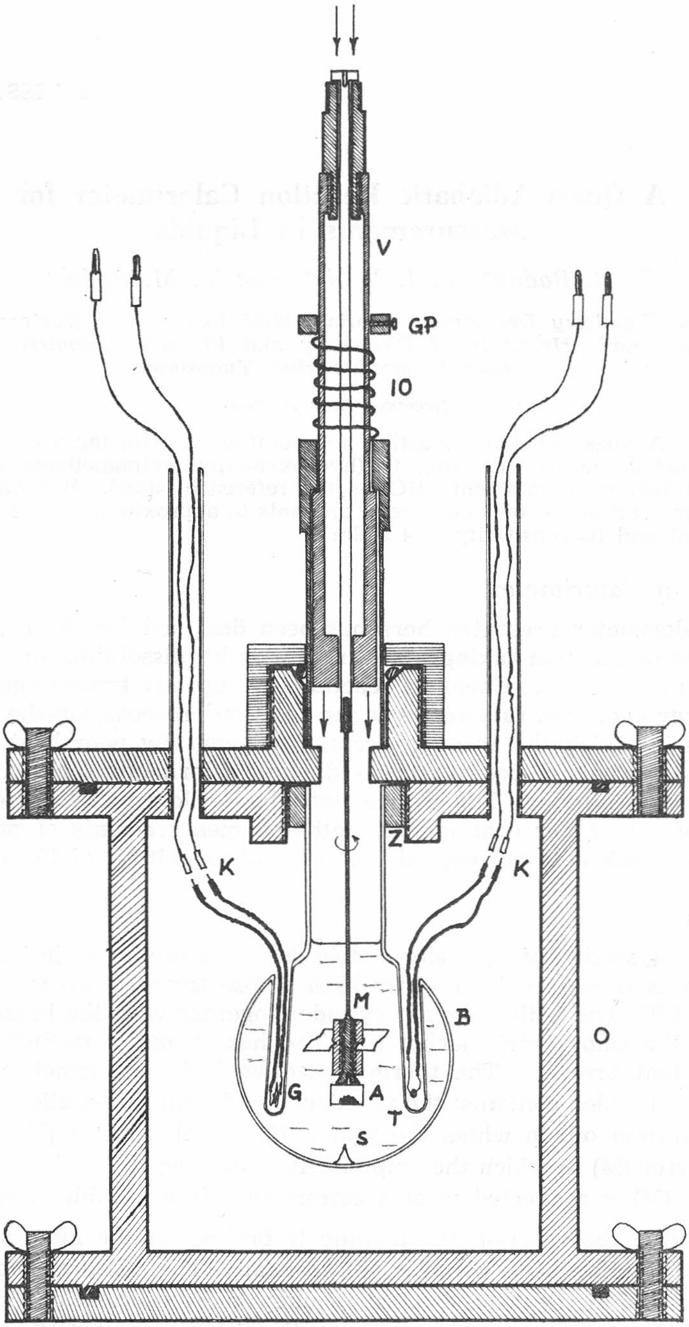

Figure 1. Cross section of the calorimeter

and the gold-plated connectors (K) enable a simple removal of the bulb and an easy exchange of the samples.

The thermistor thermometer (Philips, bead type of 4700 ohm at 25 °C) is a branch of the precision symmetric Wheatstone bridge. Instead of a null detector, a Beckman recorder, having a sensitivity of 1 mV for a full scale of 10 in, is connected to the bridge. The temperature changes of the calorimetric body are in this way, recorded as an »unbalance« signal of the bridge. (For small changes this signal is practically a linear function of the resistance).

Method

Measurements are performed in the following way. The calorimeter is thermostated for a long period of time at a continuous stirring of the liquid in (B). When the temperature of the body approaches that of the jacket, the thermistor resistance slowly changes and a straight line, with a slight slope against the abscissa, is recorded (initial period). The reaction is then initiated as described above (the main, or reaction period) and the temperature undergoes a rapid change. When the reaction is over a straight line is obtained again (the final period). In this way a typical S-shaped curve is obtained. Analyzing this curve by *e. g.* the Dickinson's method[2] one obtains the »true« temperature change of the calorimetric body, *i. e.* the change which would be obtained if the measurements were performed under ideally adiabatic conditions. The magnitude of the energy produced in the calorimetric body is determined by comparing the temperature change measured with the one induced by the electrical heater under identical conditions (mass, contents, rate of stirring).

Calibration

An essential part of the calorimeter is the calibration heater. Its purpose is to calibrate the measured heat effect of the chemical reaction by adding a known amount of electric energy. The heater is a thin insulated manganese wire folded many times and inserted into the capillary (G). In the calibration runs the current throught the heater is measured with a mA-meter of 0.2 per cent grade. By varying the current and the time of its flow one obtains different calorimetric S-curves which can be compared to a wide variety of chemical processes (differing in the maount of energy and/or energy evolution rate). Such a heater, however, has to meet two basic conditions:

- for a given current the temperature differences (ΔT) are directly proportional to the time (t) of current flow ($\Delta T \sim \Delta R = \mathrm{k} \cdot t$, where ΔR is the change of thermistor resistance and k the linear slope);
- within the whole calibration region* the heater is not sensitive to the energy evolution rate, *i. e.*, the relation

$$\frac{k_\mathrm{i}}{\mathrm{i}^2} = \mathrm{Const.}$$

where k_i is the slope for a given current i, applies to different currents.

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* The graphical method[2] applied with this type of calorimeters is based on a linear approximation of the Newton'cooling law which holds for small temperature differences. It could reliably be applied if the temperature differences do not exceed too much 1 K.[3]

In 40 calibration runs in which currents of 20, 30 and 35 mA through the calibration heater (resistance of 389.2 ohm) within the time range of 10 to 300 s, it was shown that the heater met both of the above conditions within the limits of error of 1.5 per cent. The range in which the measurements were performed was 10 to 50 Joules in a volume of 50 cm^3. The sensitivity of the device (using the 1 mV recorder) was 0.2 J, *i. e.*, 4×10^{-3} J cm^{-3} (about 1 millicalory per ml).

Checking

There are several »chemical standards« for the calibration of reaction calorimeters, *i. e.*, the chemical reactions with well established enthalpies can be found today. The suitable reaction in our case was the enthalpy of solution in 0.1 mol dm^{-3} HCl of tris-hydroxymethyl aminomethane, called »tris« or »tham«[4-6]. We applied the »tris« samples obtained from the Thermochemical Centre, Lund University (Lund, Sweden).[4] This reaction was used in order to check the compatibility and realibility of our calibration heater for the determination of the enthalpies of unknown chemical reactions.

The calorimetric S-curve of the dissolution of a known amout of »tris« in 0.1 mol dm^{-3} HCl was first recorded as described above. This measurement was followed by two runs with the calibration heater, one giving a smaller and the other a slightly larger heat effect. From these two calibrations the heat in the »tris« reaction was determined. The corresponding heat change was calculated (theoretical value) from the known enthalpy of »tris« dissolution in 0.1 mol dm^{-3} HCl, *i. e.*, —29.752 (±0.004) kJ mol^{-1} (or —245.76 ± 0.26 J g^{-1})[6] and the weighed amount of sample. The ratio of the calibration to the theoretical values was taken as the measure of usefulness of the heater and of the whole device.

The results of the checking are summarized in Table I. One can see that the standard deviation of the series of four different samples of »tris« did not exceed 1 per cent, whereas the error of individual measurement hardly exceeded 2 per cent.

Remarks

The accuracy and sensitivity obtained are acceptable, provided that the method of measurement with a recorder having the same limits of error, was applied. Both the accuracy and sensitivity could be increased considerably by applying the method of »timing-the-pass-through-zero«*, as it is currently done with the LKB 8700 Precision Calorimetry System designed by Sunner and Wadsö[7]. A further increase of sensitivity could be achieved by diminishing the size of the calorimetric body, the stirrer and the ampules. By meeting the requirements of safe stirring and solving other technical problems, one can hardly expect an increase in sensitivity exceeding the factor of two.

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* The method consists of the measurement of the change in thermistor resistance by using a sensitive null voltmeter (electronic galvanometer) in the bridge, pre-setting the resistance and timing the moment when the pointer of the meter passes through zero. Each measurement is followed by a new pre-setting and timing *etc.* The calorimetric S-curves are then drawn point-by-point from the data measured.

TABLE I

Intercomparison of the »tris« Enthalpy of Dissolution in 0.1 mol dm^{-3} HCl and the Values Obtained by Calibration Heater

Sample No.	Weight/mg of »tris«	Arbitr. ΔR/mm	Heater calibration data				Heat of reaction/J derived from		Ratio of values (Calibration / Theoretical)
			i/mA	t/s	Arbitr. ΔR/mm	Joule heat/J	Calibration value	Theoretical value	
1	80.0	124.5	30	30 75	66 161.5	10.508 26.271	20.111	19.661	1.023
2	100.4	153.5	30	60 100	130 216	21.016 35.028	24.814	24.674	1.006
3	139,9	217.5	30	70 112	154 251	24.520 40.282	34.767	34.382	1.011
4	174.7	268	30	100	218.5	35.028	42.963	42.934	1.001

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SAŽETAK

Kvazi-adijabatski kalorimetar za mjerenja u tekućinama

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Kvazi-adiabatski reakcijski kalorimetar bio je konstruiran i provjeren s pomoću reakcije otapanja tris(hidroksimetil)aminometana u O,1 M HCl. Preciznost opisanog kalorimetra iznosi oko ± 1%, a njegova osjetljivost je 4 J dm^{-3}.

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