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STUDIES OF THERMOKINETICS IN AN ADIABATIC CALORIMETER

I. Design and testing of an adiabatic automatic calorimeter

*S. Zhan, J. Liu**, *Z. Qin and Y. Deng*

Department of Chemistry, Sichuan University, Chengdu 610064, P. R. China

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Abstract

An adiabatic calorimeter in which automation of the control of the adiabatic condition and the thermogram recording is achieved in a simple way has been designed for studies of both thermochemistry and thermokinetics. A new method for specific heat measurements has been proposed and specific heats of *n*-heptane were measured to test the reliability of this calorimeter.

Keywords: adiabatic calorimeter, calorimetry, specific heat

Introduction

Adiabatic calorimeters have long been widely used to measure heat effects and determine thermodynamic functions. In recent years, they have also been used to determine the rate constants of chemical or biochemical reactions and have become important tools for studies of thermokinetics [1–3]. For an adiabatic calorimeter system, the automation of temperature measurement is a prerequisite for thermokinetic research.

Here, an adiabatic automatic calorimeter is reported, in which the automation of temperature measurement is achieved by using a recording system, and the temperature of the adiabatic shield can be controlled automatically with a system consisting of a thermopile, a regulator and a modified precision thermostat. It can therefore be used to study the thermokinetics of chemical or biochemical reactions and also thermochemistry.

A new method for specific heat measurements is proposed. The specific heats of *n*-heptane at 20.0 and 25.0°C have been measured to test the reliability of this calorimeter and to verify the validity of the method for specific heat measurements.

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* Author to whom correspondence should be addressed

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Design of an adiabatic automatic calorimeter

Calorimeter

As shown in Fig. 1, this calorimeter consists basically of three parts: a calorimetric system, an adiabatic shield and an aluminium thermostated block. The vessel in the calorimetric system, 50 mm in diameter and 175 mm in height, is made of copper (99.95% purity), its wall is 1.5 mm thick with a gold-plated inner surface and a polished outer surface, and its effective capacity is about 150 ml.

The large cross-section and capacity of the vessel are convenient for the location of other devices in it, such as a stirring tube, an injection tube and so on, which are important for thermokinetic research.

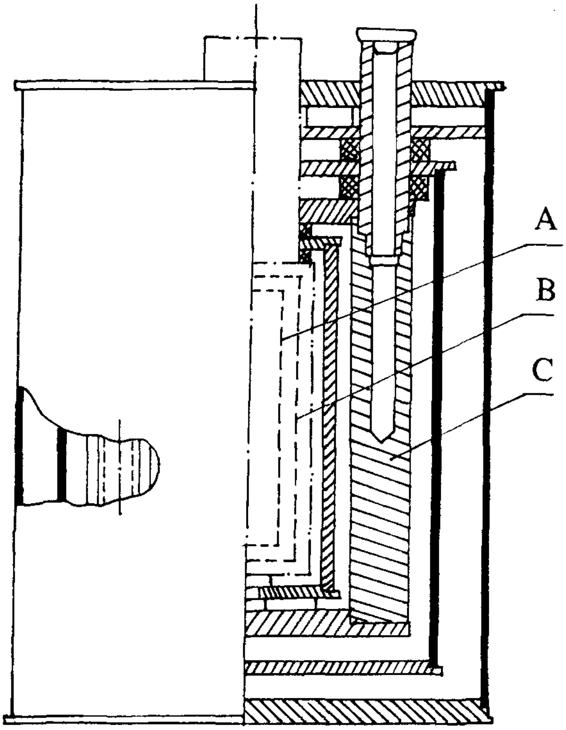

Fig. 1 Schematic diagram of the adiabatic calorimeter. A. calorimetric system; B. adiabatic shield; C. thermostated aluminium block

Automatic control of temperature of adiabatic shield

The problem of controlling the temperature of the adiabatic shield for studies of thermokinetics differs from the problem for thermodynamics, such as heat capacity measurement. The calorimetric system may be cooled down while an endothermic reaction is taking place, and provisions should be made to adjust the temperature of the shield automatically and rapidly, so as to follow the fall or rise of temperature in the calorimetric system.

Before experimental operation, the temperature of the adiabatic shield should controlled so as to be 2.0–3.0 deg higher than that of the aluminium block. The temperature of the block can be controlled precisely by a thermostat at will, the temperature of the adiabatic shield can be controlled by manual adjustment of the current to the heater surrounding the shield, and a bridge is used to measure the temperature of the shield.

While a thermal change is proceeding, the temperature of the shield can be adjusted by an automatic adiabatic-shield-control system, which is composed of a thermopile between the shield and the calorimeter system, a regulator and a modified precision thermostat. The thermopile is made of 40 junctions of chromel–constantan wires (ø 0.60 mm) having a sensitivity of about 2400 μV/deg. The schematic diagram of this control system is shown in Fig. 2.

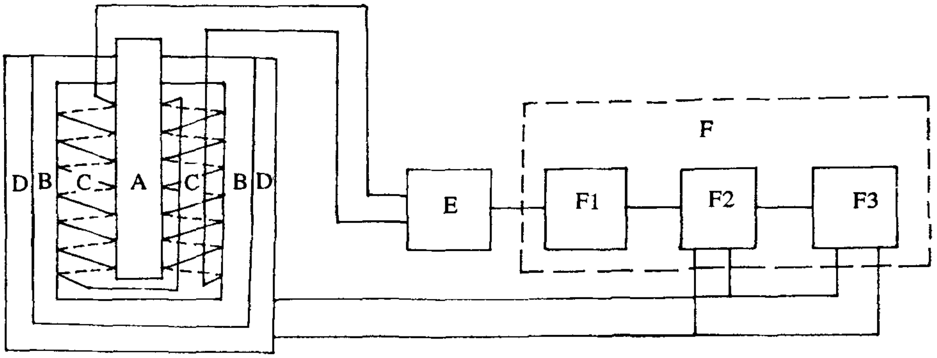

Fig. 2 Schematic diagram of the adiabatic-shield-control system. A. calorimetric system; B. adiabatic shield; C. thermopile; D. shield heater; E. regulator; F. modified precision thermostat; F1. three-mode controller (PID); F2. silicon-controlled trigger; F3. silicon-controlled executor

When the temperature of the calorimetric system is equal to that of the shield, there is no thermo-EMF output from the thermopile, and the photopen of the regulator, which was described in detail in a previous paper [4], will not move, so a line parallel to the time axis is recorded. If there is a certain temperature difference between the calorimetric system and the adiabatic shield, the thermo-EMF output will make the photopen move a certain distance, proportional to the temperature difference. This movement will cause the adjustable arm of a bridge circuit in the regulator to move, and then, a non-equilibrium potential signal proportional to the temperature difference will be produced. After being amplified, this signal is used to actuate a three-mode controller (proportional, integral and derivative). By means of a silicon-controlled trigger, the current output from the three-mode controller will operate a silicon-controlled executor, which will regulate the heating current to change the shield temperature. Thus, automation of the control of the adiabatic condition is attained.

A heat-exchange graph, describing the dynamic controlling process of the adiabatic condition, is recorded directly by the photopen, according to which the accuracy of this control system can be calculated quantitatively.

For this calorimeter, the value of the cooling constant is about 1.6×10^{-5} s^{-1}, the cumulative temperature difference of the adiabatic-shield-control system is smaller than 0.05 deg, and the corrected value of the heat exchange can be neglected.

Automatic thermoanalytical information recording

The system recording the thermoanalytical information consists of a recorder with a photopen [4] and a high-precision non-equilibrium bridge, one arm of which is a copper resistance thermometer wound non-inductively on the outside of a steel attaching sleeve for the temperature measurements in the calorimeter system. The copper resistance thermometer is calibrated against a certified platinum resistance thermometer.

When the temperature of the calorimetric system remains constant, the resistance of the copper resistance thermometer also remains constant and the signal output from the non-equilibrium bridge does not change. Thus, a line parallel to the time axis is drawn by the photopen of the recorder. When a heat effect is generated in the calorimetric vessel, the temperature of the calorimeter system will change, accompanying which the resistance of the copper resistance thermometer will change, and thus the non-equilibrium potential output from the bridge will change. The potential output at time *t*, proportional to the temperature change in the calorimetric system, can be recorded precisely and continuously by the photopen of the recorder. Finally, a thermal curves representing the process of temperature change of the calorimetric system, can be obtained.

Automation of the thermogram recording makes experimental operation easy and results in the possibility of the study of thermokinetics with this adiabatic calorimeter.

Testing of the adiabatic calorimeter

In order to test the reliability of the adiabatic calorimeter, and especially the effectiveness of the adiabatic-shield-control system and the system recording, the thermoanalytical information of the specific heats of *n*-heptane at 20.0 and 25.0°C were measured with this calorimeter.

Formula for specific heat ratio

The specific heats of most substances have been measured with adiabatic calorimeters. According to the traditional method for specific heat measurements [4], the resistance thermometer for temperature measurements must be calibrated, and the difference between the calorimetric states of the empty vessel and that of the vessel containing a sample in the measuring processes is the main source of error for specific heat measurements. For this case, a formula for measurement of the specific heat ratio with an adiabatic calorimeter is suggested.

The peak-height Δ at time t for a curve measured with an adiabatic calorimeter is proportional to the temperature difference of the calorimetric system, i.e.

$$\Delta = G(T-T_o) \tag{1}$$

where G is the proportionality constant, and T and T_o are the temperature at time t and the initial temperature of the calorimetric system, respectively.

If the calorimetric vessel, containing m_i (g) of sample i, is heated with a constant power, the total electric energy Q_i(J) and the final peak height Δ_∞ (mm) can be measured. It is clear that

$$\Lambda_i = Q_i / \Delta_\infty \tag{2}$$

and

$$G\Lambda_i = m_iC_i + G\Delta_o \tag{3}$$

where Λ_o and Λ_i are the heat-capacity constants of the empty vessels and the vessel containing m_i (g) of sample i, respectively, and C_i is the specific heat of the sample at constant pressure.

According to Eq. (2), the heat capacity constants of the vessel containing m_1 and m_2 (g) of reference substance and m_3 (g) of sample can be determined by means of electric calibration.

Then, according to Eq (3), we have:

$$G\Lambda_1 = m_1C_R + G\Lambda_o \tag{4}$$

$$G\Lambda_2 = m_2C_R + G\Lambda_o \tag{5}$$

$$G\Lambda_3 = m_3C_S + G\Lambda_o \tag{6}$$

where C_R and C_S are the specific heats at constant pressure of the reference substance and the sample, respectively.

From Eqs (4–6), it can be proved that

$$r_C = \frac{C_S}{C_R} = \frac{m_1}{m_3} + \frac{(m_2 - m_1)}{m_3} \cdot \frac{(\Lambda_3 - \Lambda_1)}{(\Lambda_2 - \Lambda_1)} \tag{7}$$

where r_C is the specific heat ratio.

Therefore, in the light of Eq. (7), the specific heat of the sample can be calculated on the basis of the known accurate value of specific heat of the reference substance through three experimental measurements.

Experimental

The specific heats of *n*-heptane at a pressure of 1 atm were measured at 20.0 and 25.0°C in this work, with water as the reference substance.

The water was deionized and air-free, while the *n*-heptane was of chromatographic grade and its purity was higher than 99.99%.

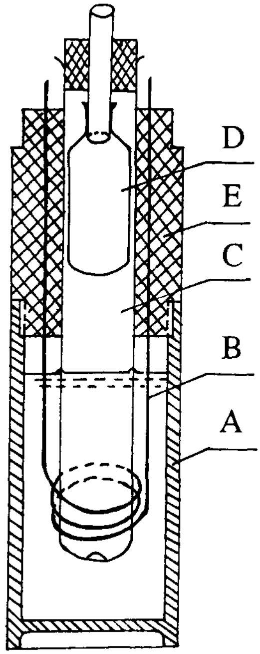

Fig. 3 Assembly of the vessel, the heater and the stirrer. A. calorimetric vessel; B. heater for electric calibration; C. glass tube for stirring; D. balloon; E. connecting tube

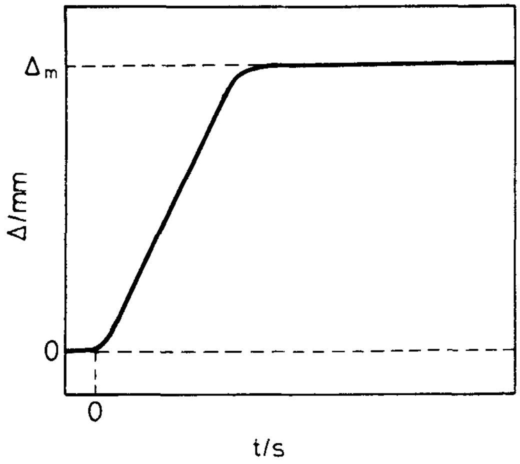

Fig. 4 Calorimetric curve of a constant power heating process

Experiments were undertaken in the adiabatic calorimeter designed in this work. The assembly of the calorimeter vessel, the heater for electric calibration and the glass tube for stirring are shown in Fig. 3. The constant heating power was provided with an electric calibration system, which was described previously [4]. The glass tube for stirring was connected to an air-compression micropump, which circulates once every 6 s, the container was stirred throughout the experimental process, and the adiabatic compensation was applied to reduce the effect of the stirring heat to a minimum. The calorimetric curve of the constant power heating is shown in Fig. 4.

Results and discussion

The measured results for the specific heats of *n*-heptane are listed in Table 1. The experimental data and the calculated value from a single experiment are given in Table 2.

Table 1 Comparison of the measured values with the reported values of the specific heats of *n*-heptane

Temperature / °C	20.0	25.0	
C_P	2.046	2.227	this paper
($J \cdot g^{-1} \cdot K^{-1}$)	2.050	2.242	literature [5, 6]

The measured values in this work are in agreement with those given in the literature [5, 6], which verifies the correctness of the formula for the specific heat ratio proposed in this paper. With this method, many system errors can be eliminated and smaller specific heats of some substances can be accurately de-

Table 2 Experimental data and calculated value from a measurement of the specific heat of *n*-heptane at 20.0°C

No.	1	2	3
m_i / g	70.30	139.2	141.46
Λ_i / J·mm^{-1}	3.168	4.178	3.153
C_R / J·g^{-1}·K^{-1} [5]		4.1799	
C_S / J·g^{-1}·K^{-1} [5]		2.046	

termined. Furthermore, this method is especially suitable for measurement of the specific heat ratio of homologues, whose physical properties are very similar to each other.

Conclusions

An adiabatic automatic calorimeter for the purpose of thermokinetic studies was designed in this work. A formula for the specific heat ratio is proposed and the specific heats of *n*-heptane at 20 and 25°C were measured to test the reliability of the calorimeter. The experimental results showed that the controlling system for adiabatic conditions is very effective and the curve which represents the process of temperature change of the calorimetric system can be recorded automatically. This adiabatic calorimeter can therefore be used to study the thermokinetics of chemical or biochemical reactions, which will be reported in a later article, as well as thermochemistry.

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Zusammenfassung — Zur Untersuchung von sowohl Thermochemie als auch Thermokinetik wurde ein adiabatisches Kalorimeter entwickelt, in welchem die Automatisierung der Überwachung der adiabatischen Bedingungen und der Thermogrammaufzeichnung auf einfache Weise erreicht werden. Es wird eine neue Methode für die Messung der spezifischen Wärme vorgeschlagen und zum Testen der Zuverlässigkeit dieses Kalorimeters die spezifische Wärme von *n*-Heptan bestimmt.