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Temperature changes within samples in heat conduction calorimeters

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Abstract

So-called isothermal calorimeters are often built on the heat conduction principle. This may sound as a contradiction, as heat conduction is a result of non-isothermal conditions, but most measurements with microcalorimeters and other such instruments are essentially isothermal as the temperature differences within the instruments are in the order of 10 mK. This paper presents simple methods to estimate the temperature changes within a sample in a heat conduction calorimeter during a measurement. It also shows that the determination of activation energy is normally not disturbed by these small temperature changes. In addition to the heat production rate in the sample, the thermal properties of the sample and the calorimeter are needed as input to the calculations. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Calorimeters; Conduction; Isothermal

1. Introduction

Heat conduction calorimeters are currently the most common type of non-scanning calorimeters. They are used at universities and industrial laboratories for both applied and fundamental measurements. In a heat conduction calorimeter, heat flow sensors made from thermocouples are placed between the sample and a heat sink. The heat produced in the sample is conducted through the heat flow sensors, through the heat sink, and out into a thermostat that surrounds the instrument. As the heat is conducted away from the sample, the temperature changes in the instrument will be low compared to in adiabatic types of calorimeters where the sample is insulated to prevent the heat from escaping. In the following, temperature changes are always referred to the temperature of the thermostat surrounding the calorimeter, i.e. there is no temperature change when there is no heat production as the whole calorimeter then has the same temperature as the thermostat.

The term isothermal calorimeter is not well-defined, but is commonly used for calorimeters designed for work under (essentially) isothermal conditions [1] or for instruments where the calorimetric sample is maintained under isothermal conditions [2]. As the temperature change during a measurement not only depends on the instrument, but also on the sample, I propose the following more pragmatic definition: an isothermal measurement takes place at conditions where the temperature changes are so small so that the result of the measurement is the same as if there had been perfectly constant temperature conditions. We thus allow an isothermal measurement to be

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Nomenclature

D	sample diameter (m)
E_a	activation energy (J/mol)
H	sample height (m)
k	thermal conductance (W/K)
P	thermal power, heat flow rate (W)
q	volumetric heat production rate (W/m^3)
R	gas constant (J/mol/K)
T	temperature (K)
Greek letter	
λ	thermal conductivity of sample (W/m/K)
1	sample
2	heat flow sensor
3	external insulation

slightly non-isothermal as long as it does not influence the result.

It is the aim of this paper to derive simple methods to calculate temperature changes within samples with continuous heat production (stability measurements etc.) in heat conduction calorimeters. As it will be shown that this temperature difference is very small in a well-designed experiment, heat conduction calorimetry may often be termed an (essentially) isothermal measurement technique. However, there are cases where significant temperature increases will occur, and these may be found with the described methods.

One practical concern with temperature changes (or self heating) in a calorimetric sample is the calculation of activation energy. This is done by comparing the thermal powers from a process being measured at different temperatures. When the temperature is raised, the reaction rate and the thermal power will increase and, consequently, the over-temperature of the sample will also be higher. Thus, the reaction rates at high temperatures will be attributed to too low temperatures, e.g. if we have a temperature increase of 1 K in the sample, when the thermostat of the calorimeter is at 80°C, the actual temperature of the sample is 81°C. This may give rise to significant errors in the determination of the activation energy. On the other hand, if the over-temperature is 10 mK — which is more common — the error made will be very small.

Another case where the temperature increase in a sample could be a problem is during stability measurements of explosives. To accelerate the degradation of an explosive compound, measurements are usually made at 70–80°C and may produce quite high thermal powers. As many solid explosives have low thermal conductivities, the internal temperature gradient in a sample will be much more pronounced than in many other types of experiments. This could potentially (but not in practice, except in extreme cases, as will be shown below) cause a run-away reaction.

The standard heat transfer equations and standard computer methods used in this paper are described by Hagen [3] and others.

The following indices are used for the three main heat flow resistances in a heat conduction calorimeter.

2. Heat conduction calorimeters

In a heat conduction calorimeter, the heat produced in the sample is conducted away from the sample through heat flow sensors and out into a thermostated environment, most commonly a water bath. Fig. 1 shows a basic thermal model of a heat conduction calorimeter. One aim of this paper is to calculate the temperature difference between the center of a sample and the thermostat bath; when there is a constant heat production in the sample. On its way from the sample to the thermostat, the heat has to pass through three main resistances to heat flow

1. The sample with diameter D and thermal conductivity λ.
2. The heat flow sensors (thermocouple plates) represented by the thermal conductance k_2.
3. A heat flow resistance separating the heat sink and the thermostated bath; here called the external insulation (k_3).

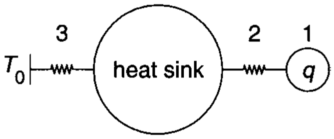

Fig. 1. Thermal model of a heat conduction calorimeter with a constant temperature thermostat (0), an external insulation (3), heat flow sensors (2), and a sample (1) (cf. the text). The sample is modeled as a cylinder with a volumetric heat production rate q. The heat capacity of the heat sink is comparatively high (not used in the steady-state calculations).

Table 1
Data for the five calorimetric constructions used as examples (cf. nomenclature and text)[a]

	A	B	C	D	E
Diameter of sample, D (mm)	12	25	25	70	12
Height of sample, H (mm)	25	40	40	75	25
Volume of sample (ml)	3	20	20	300	3
Conductance of heat flow sensor, k_2 (W/K)	0.11	1.3	0.33	0.11	0.0011
External conductance, k_3 (W/K)	0.5	0.6	2	0.5	0.5
Measuring range (maximum P) (mW)	3	3	60	–	–

[a] The thermal conductances of the thermocouple plates were calculated from equations given by the manufacturer (Melcor, Trenton, NJ, USA). The external conductances were calculated from the thermal conductance of air and the air gap geometries (for calorimeter C, this is instead the heat conductance of the insulation).

Table 1 gives data for five different calorimetric constructions. The first three are real commercial designs and the latter two are possible — but not recommended — variations of calorimeter A.

A. A 2277-201 ampoule microcalorimeter for the 2277 TAM system (Thermometric AB, Järfälla, Sweden [4,5]) with a 3 ml ampoule. This is highly sensitive instrument that is often used for stability measurements. The external insulation consists of an air gap between the heat sink and the thermostated bath. It can measure thermal powers up to 3 mW.
B. A 2230-000 ampoule microcalorimeter for the 2277 TAM system (Thermometric AB, Järfälla, Sweden [5]). It is similar to calorimeter A, but has a 20 ml ampoule.
C. An isothermal heat flow calorimeter built on a slightly different principle than the microcalorimeters A and B as it does not have an air gap that protects it from a thermostated bath, but instead an insulation that protects it from an air thermostat [6,7]. It uses the same 20 ml ampoules as calorimeter B, but measures thermal powers up to 60 mW.
D. A fictive calorimeter with the same data as A, except that the sample is 100 times larger.
E. A fictive calorimeter with the same data as A, except that the heat flow sensor has 100 times lower heat conductance.

The following assumptions or simplifications have been made in the calculations:

- Throughout the paper it is assumed that the temperature in the sample increases (exothermic processes). The methods derived will, however, work just as well for endothermic processes that lowers the sample temperature.
- The sample is cylindrical and the heat flow through the sample is in the radial direction only.
- The thermal resistances of the aluminum parts of the calorimeters (ampoule holder and heat sink) have been neglected as they are comparatively low.
- The thermostated environment surrounding the calorimeters has constant temperature. For calorimeters A and B, the actual water thermostat has a temperature stability of 0.1 mK over 24 h [5]. The same figure for the air thermostat of calorimeter C is 20 mK [7].
- All calculations are made at steady-state. Therefore, heat capacities are not used in the calculations.
- As the differential twin arrangement used on most heat conduction calorimeters will not influence the steady-state temperature increase, all calculations has been done for single calorimeters.

3. Calculations and discussions

3.1. Constant thermal power

When there is a heat flow P (W), the resulting temperature difference over a thermal conductance k (W/K) is

$$\Delta T = \frac{P}{k} \tag{1}$$

This equation may be used to calculate the temperature differences over the heat flow sensors and the external insulation if the conductances are known.

The temperature difference within a sample is caused by the heat production in the whole volume of the cylindrical sample. Consider a cylindrical sample with diameter D(m) and height H(m) with heat flow in the radial direction only. Note that at any internal radius r all the heat that is produced inside that radius has to flow out, and that this heat flow must be proportional to the temperature gradient (Fourier's law of heat conduction)

$$qH\pi r^2 = -H2\pi r\lambda \frac{dT}{dr} \tag{2}$$

Here, λ (W/m/K) is the thermal conductivity of the sample and q (W/m^3) is the volumetric heat production rate. The solution to this differential equation gives the temperature difference ΔT_1 (K) between the sample center and the sample surface

$$\Delta T_1 = \frac{P}{4\pi\lambda H} \tag{3}$$

Here, the thermal power P (W) produced in the whole sample was used instead of q

$$P = \frac{q\pi D^2 H}{4} \tag{4}$$

Note that the temperature difference calculated by Eq. (2) is not dependent on the diameter D of the sample. The diameter does, however, enter into the equation through the thermal power P (increasing D with constant q will increase P). Note also that the temperature difference over the sample calculated with Eq. (2) is lower than for the case, where the heat is produced only in the center of the sample.

As the thermal conductances of the heat flow sensors and the external insulation are known, the temperature difference between the center of the sample and the thermostated bath is found by adding three temperature differences (Eqs. (1) and (3))

$$\Delta T = P\left(\frac{1}{4\pi\lambda H} + \frac{1}{k_2} + \frac{1}{k_3}\right) \tag{5}$$

From Eq. (5) it is seen that an equivalent thermal conductance k_1 can be attributed to the sample (only at steady-state)

$$k_1 = 4\pi\lambda H \tag{6}$$

Table 2 gives ΔT-values for calorimeter designs A–E when the ampoules are charged with a material with a thermal conductivity, $\lambda = 0.17$ W/m/K and a volumetric heat production rate $q = 35$ J/m^3 (corresponding to a thermal power of 100 μW in calorimeter A). These values are typical of a nitrocellulose explosive; a material with quite low thermal conductivity, and thus a comparatively high temperature increase ΔT_1. Stability measurements on propellants and other explosives are often made with calorimeters of type A [8–10].

Table 2
Temperature differences (mK) between the center of a sample and the thermostat calculated with Eq. (5)

	A	B	C	D	E
$q = 35$ J/m^3	3	10	10	200	90
At maximum P	90	40	900	–	–

Table 2 also gives ΔT-values for the three real calorimeters A, B and C, when the thermal power is at its maximum values of 3, 3, and 60 mW, respectively. The temperature increases are low for calorimeters A and B, but for calorimeter C it is almost 1 K. The upper thermal power range of this calorimeter should, therefore, be used with caution for measurements where it is important that one knows the true temperature of the measurement. For other types of measurements this may not be a problem, e.g. in a titration experiment the thermal power during a peak may be high, but return back to the same state (baseline) as before the injection, giving a correct total heat of the peak.

If one is running samples with high heat production rates it may be tempting to increase the range of a heat conduction calorimeter by introducing a voltage divider between the heat flow sensors and the amplifier. With such a change one can measure higher thermal powers, but this will inevitably result in larger temperature changes in the sample (Eq. (5)). Two better options that does not result in larger temperature increases are

- To reduce the size of the sample.
- To make mechanical changes to the calorimeter to increase the thermal conductances k_1–k_3; e.g. by increasing the H/D ratio of the sample (increases k_1) or by adding a thermal conductance in parallel to the heat flow sensor (increases k_2).

3.2. Run-away reactions

A case of practical interest for those working with energetic materials is if self heating of a sample in a heat conduction calorimeter can cause a run-away reaction. To study this problem we assume that a sample has a heat production rate q that follows an Arrhenius equation

$$q(T) = A\exp\left(\frac{-E_a}{RT}\right) \tag{7}$$

Here, E_a (J/mol) is the activation energy, R (8.31 J/mol/K) is the gas constant, and T (K) is the temperature. The constant A is then

$$A = \frac{q_r}{\exp(-E_a/RT_r)} \tag{8}$$

Here, q_r is the volumetric heat production rate at a reference temperature T_r. A total steady-state thermal conductance k may be defined as (cf. Eqs. (5) and (6))

$$\frac{1}{k} = \frac{1}{k_1} + \frac{1}{k_2} + \frac{1}{k_3} \tag{9}$$

During a steady-state experiment, the temperature of the thermostat (T_0) and the temperature of the center of the sample (T) will be constant as the thermal power produced by the sample will equal to the heat flow rate from the sample (Eqs. (7)–(9))

$$A\exp\left(\frac{-E_a}{RT}\right)\frac{\pi D^2 H}{4} = k(T - T_0) \tag{10}$$

Eq. (10) does not have an analytical solution, but it can be solved numerically. This has been done with a MATLAB 5 (MathWorks, Natick, MA, USA) equation solver for two volumetric heat production rates: $q_r = 35$ and $1050\ \mathrm{W/m^3}$ at $T_r = 80°\mathrm{C} = 353.2\ \mathrm{K}$ (100 μW and 3 mW, respectively, in calorimeter A). The activation energy was 120 kJ/mol. Fig. 2 shows the temperature increases for calorimeters A–E for the two cases. It is seen that only for calorimeters D and E do we get a run-away reaction, and then only at the highest heat production rate. Note that calorimeters D and E are poor heat conduction calorimeters; they would more properly be termed as semi-adiabatic calorimeters. For normal heat conduction calorimeters; one will only get a run-away reaction if one performs a measurement at a temperature close to the temperature where one would get a run-away reaction even if the sample was not in the calorimeter.

3.3. Evaluation of the activation energy

To evaluate the activation energy of a process, one can make calorimetric measurements at different temperatures and then plot the logarithm of the thermal power (ln(P)) as a function of the inverse of the absolute temperature ($1/T$). The slope of the resulting line is proportional to the activation energy (cf. Eq. (7)). As discussed in the introduction, a practical aspect of the temperature increase in a calorimetric sample is that we may not know the true temperature of a measurement and this may cause errors in an

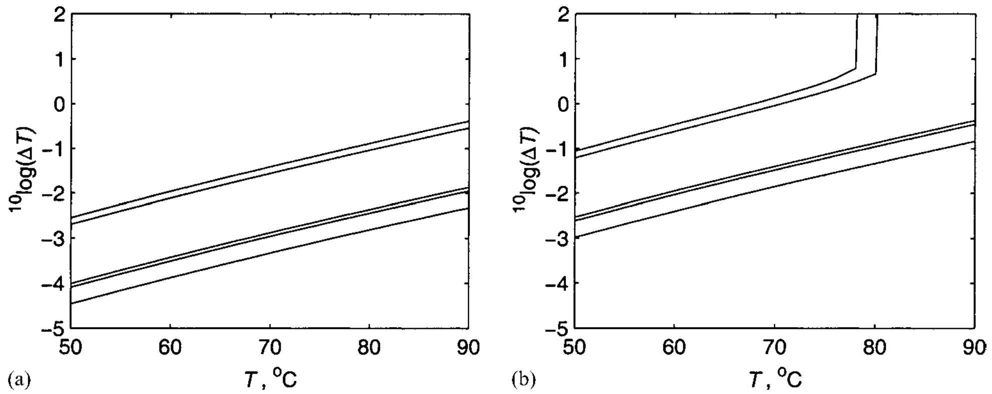

Fig. 2. Calculated temperature increases ΔT (not Arrhenius plots) for the five calorimeters with ampoules filled with the same reacting substance. In both figures the curves from the bottom and top are for calorimeters A, B, C, E, and D. (a) With a volumetric heat production rate of 35 W/m^3; (b) with a volumetric heat production rate of 1050 W/m^3.

Table 3
Calculated activation energies for the five calorimeters A–E, two true activation energies, and two columetric heat production rates[a]

q(J/m^3) (80°C)	True E_a(kJ/mol)	Calculated E_a(kJ/mol)				
		A	B	C	D	E
35	120	120.0	120.0	120.0	120.6	120.3
35	160	160.0	160.0	160.0	160.8	160.4
1050	120	120.3	(121.0)	121.1	r.a.	135.7
1050	160	160.4	(161.4)	161.5	r.a.	r.a.

[a] Values within parentheses includes calculated data points that should have been out of range for calorimeter B, and r.a. is run-away reaction.

evaluated activation energy. As the temperature increase will be higher at higher temperatures, we may even find that the activation energy is non-constant even if the true activation energy is independent of temperature.

To test this, Eq. (10) was solved at 50, 60, 70, and 80°C for calorimeters A–E, and for sample substances with two activation energies (120 and 160 kJ/mol) and two volumetric heat production rates (35 and 1050 W/m^3 at 80°C). The lower activation energy and the lower heat production rate is typical of many explosives. From the resulting $\ln(P)$ versus $1/T$ — plot, the activation energy was then evaluated by linear regression. Table 3 shows that the evaluated activation energies for calorimeters A–C are close to the true values. Even for the most extreme case (last line in Table 3) the evaluated activation energies are less than 1% wrong; a low uncertainty for an activation energy. At least in this respect it is quite safe to calculate activation energies from microcalorimetric data. If an evaluated activation energy is temperature dependent this is not an artifact of the method, but may instead reflect the properties of the studied process.

3.4. Unsteady-state

The above solutions are not strictly valid if the thermal power changes with time. However, from computer simulations (not presented here) I have found that for thermal power increase rates up to 10 μW/min in calorimeters A–C, the deviations from the above results are small. Note that an increasing thermal power, e.g. from an accelerating auto-catalytic reaction, will give a lower temperature in the sample than one would have at the same thermal power under steady-state conditions. Therefore, during a thermal power increase, the rate of the increase itself does not increase the thermal power further. When an exothermal thermal power is decreasing, the temperature of the sample will be higher than the steady-state temperature calculated from Eq. (5), but the temperature in the sample can never be higher than the steady-state temperature corresponding to the previous highest thermal power.

4. Conclusions

Temperature changes within a sample in a heat conduction calorimeter are normally so small that measurements with such instruments are essentially isothermal. The temperature changes will not significantly influence activation energies calculated from measurements of thermal power at different temperatures, nor will they activate energetic samples to give run-away reactions.

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