# The Isothermal Heat Conduction Calorimeter: A Versatile Instrument for Studying Processes in Physics, Chemistry, and Biology

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Nearly all physical, chemical, and biological processes produce or consume heat. Processes that produce heat are called exothermic and processes that consume heat are called endothermic. Devices that measure heat are called calorimeters. The results of calorimetric measurements may usually be treated with thermodynamics and thus be used in a broader perspective.

In this paper we describe a simple but sensitive isothermal heat-conduction calorimeter and present five experiments for students to illustrate its use. Experiments are made at essentially isothermal conditions because the heat produced in the sample is conducted away through heat flow sensors into an isothermal heat sink. Wadsö (*1*) has reviewed current trends in isothermal heat-conduction calorimetry, a technique widely used in research but relatively unknown in chemical education.

In heat-conduction calorimetry, the instantaneous thermal power, $P = dQ/dt$, generated within a sample is measured by means of a heat-flow sensor located between the sample and

a heat sink (*2, 3*). The time integration of the thermal power signal gives the total heat, $Q$, associated with a chemical process or reaction. In adiabatic calorimetry, a chemical process occurring in an adiabatically shielded vessel of known heat capacity, $C$, releases or absorbs heat, $Q$, and causes a temperature change $\Delta T = Q/C$. Figures 1 and 2 compare and contrast these two calorimetric methods.

That isothermal heat-conduction calorimeters are not common in teaching today is somewhat surprising. In introductory courses, simple adiabatic calorimeters constructed from Styrofoam cups and thermometers are often used to measure reaction enthalpies or heat capacities, whereas in advanced laboratories differential scanning calorimetry and adiabatic bomb calorimetry are usually the thermal methods of choice. Isothermal heat conduction calorimeters are often equipped with titrators for stepwise addition of solution reagents to obtain *isothermal titration calorimeters*, widely used in biophysical chemistry to measure protein–ligand binding con-
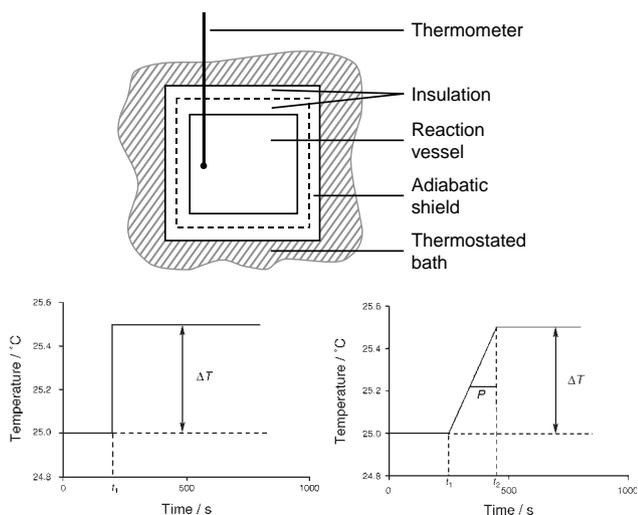


Figure 1. Top: Adiabatic shield calorimeter, principle of design. Left: a temperature-versus-time curve following a short heat pulse released at time $t_1$. Right: temperature-versus-time curve following a constant heat production rate $P$ between $t_1$ and $t_2$. $P$ is directly proportional to the slope of the curve (*2, 3*).
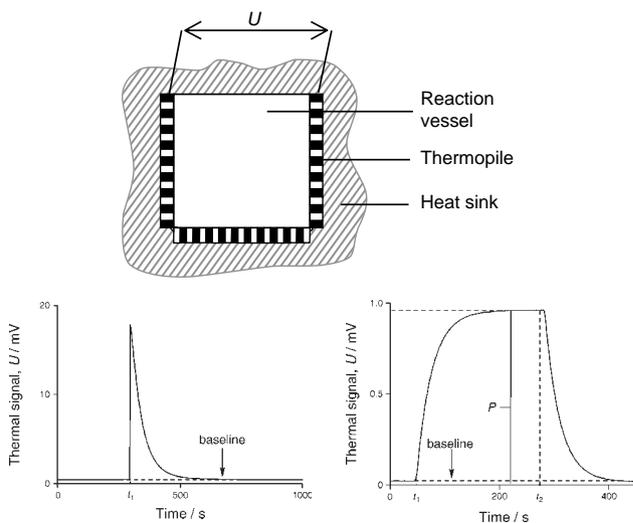


Figure 2. Top: Thermopile heat conduction calorimeter, principle of design. Left: a potential-versus-time curve following a short heat pulse released at time $t_1$. Right: a potential against time curve following a constant heat production rate $P$ between $t_1$ and $t_2$. The baseline displacement is directly proportional to $P$. In both cases the heat quantities released are proportional to the areas under the curves (*2, 3*).

stants (1). In industry there is a rapid development of so-called "monitoring calorimetry" based on the heat-flow calorimeter principle, and many such applications can easily be transformed into interesting student experiments as we show below.

## The Isothermal Heat-Flow Calorimeter

Here we describe the basic components of a simple isothermal calorimeter, present a simple theory for how it works, and end with some notes on how to use it. It is not our goal to describe in detail how to construct a heat-conduction calorimeter or to focus on one level of laboratory instruction in chemistry or any other field. Two of us (Wadsö and Hofelich) have designed inexpensive heat-conduction calorimeters based on the general concepts described below, and both of them are commercially available (4, 5).

A heat-conduction calorimeter consists of a sample and its holder in thermal contact only with a heat-flow sensor, which in turn is mounted on a heat sink. The sample–sensor–heat sink unit is placed in a constant-temperature bath or an insulated container. Some terms related to the apparatus are defined in the box below.

The heat-flow sensors used in this type of calorimeter (and in most commercial heat-conduction calorimeters) are thermocouple plates (TCPs). One TCP is made up of a large number of thermocouples made of p- and n-doped bismuth telluride, connected in series electrically to give high output voltages but in parallel thermally to give a high ratio of output voltage to temperature difference over the TCP. They

work by the Seebeck effect (6), in which a voltage difference $\Delta U$ is generated across two different conductor or semiconductor materials when a temperature difference $\Delta T$ is applied across two junctions of the materials. The Seebeck coefficient $a$ (V K$^{-1}$) for a single thermocouple is defined by $\Delta U = a\Delta T$. For a TCP we may define a device Seebeck coefficient, $E = Na$, where $N$ is the number of thermocouples in a TCP.[1]

Two properties of a TCP determine its sensitivity: the device thermal conductance $K$ (W/K) and the device Seebeck coefficient, $E$ (V/K). These two coefficients relate the heat flow rate through the TCP and the voltage produced by the TCP, respectively, to the temperature difference between the sample and the heat sink. The ratio of the two will give the heat flow rate per voltage output—that is, the calibration coefficient, $\varepsilon$—of an ideal calorimeter:

$$\varepsilon = K/E \qquad (1)$$

For a real calorimeter some heat will be lost through heat-flow paths other than the TCP, so a measured calibration coefficient will be somewhat higher than the one calculated with eq 1. Note that the inverse of the calibration coefficient is often called the sensitivity of the instrument. It will have units of V/W.

The output voltage $U(t)$ from the heat-flow sensor may be converted into heat-flow rate through the sensor by multiplying by the calibration coefficient $\varepsilon$. At steady-state conditions the thermal power $P(t)$ produced in the sample equals the heat-flow rate through the sensor and we have

$$P(t) = \varepsilon * U(t) \qquad (2)$$

The calibration coefficient is usually found from electrical calibrations, as discussed below.

Equation 2 is sufficient for measurements when the thermal power only changes slowly or if we are only interested in the total heat. If we are interested in the kinetics of rapidly changing processes, eq 2 must be generalized with a term that takes account of changes in the heat content of the sample. The Tian equation is employed for this purpose (1):

$$P(t) = \varepsilon[U(t) + \tau*(\mathrm{d}U(t)/\mathrm{d}t)] \qquad (3)$$

Here $\tau$, the time constant of the calorimeter is approximately given by

$$\tau = C/K \qquad (4)$$

where $C$ is the heat capacity of the sample and its holder cup. Note that the heat capacity of the sample only influences the time constant; the calibration coefficient is not changed. This is in contrast to adiabatic calorimetry in which the measured total heat $Q$ for a process is proportional to the total heat capacity of sample and container.

With eq 3, if the signal $U(t)$ is numerically differentiated to give d$U$/d$t$, we may calculate the instantaneous thermal power $P(t)$ produced in the sample and thus compensate for the finite time constant of the calorimeter. The total heat associated with a process is obtained by integrating the thermal power over the duration of the process.

In Table 1 we give representative values of the most important parameters of a typical heat-flow calorimeter. They are based on the use of thermocouple plates of the type CP1.4-71-045L from Melcor (Trenton, NJ), but most TCPs would be satisfactory (7).

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**Terms Related to the Isothermal Heat-Conduction Calorimeter**

| Symbol | Definition | Units |
|---|---|---|
| $C$ | heat capacity of sample | J/K |
| $a$ | Seebeck coefficient of TCP | V/K |
| $E$ | Seebeck TCP voltage ($Na_s$) | V/K |
| $I$ | electrical current through heater | A |
| $K$ | heat conductance of TCP | W/K |
| $P$ | thermal power produced in sample | W |
| $R$ | electrical resistance of heater | Ω |
| $U$ | output voltage from TCP | V |
| $\Delta T$ | temperature difference over TCP | K |
| $\varepsilon$ | calibration coefficient | W/V |
| $\tau$ | time constant | s |

The TCP (thermocouple plate) is the heat-flow sensor used in the calorimeter.

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**Table 1. Parameters of Student Heat-Flow Calorimeter Designed at Lund University**

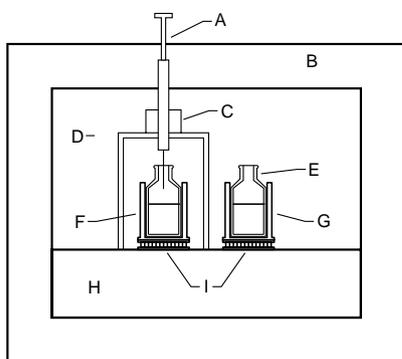| Parameter | Value |
|---|---|
| Calibration coefficient, $\varepsilon$ | 15 W/V |
| Time constant, $\tau$ | 30 s (empty cup)<br>65 s (empty glass ampoule)<br>165 s (glass ampoule with water) |
| $K$ (heat flow sensor) | 0.40 W/K |
| $E$ (heat flow sensor) | 0.030 V/K |

Figure 3. Schematic representation of a simple isothermal heat conduction calorimeter. A: syringe; B: insulation jacket; C: syringe holder; D: U-shaped holder; E: glass ampoule; F: sample aluminum cup; G: reference aluminum cup; H: heat sink; I: thermocouple plate (TCP).

## The Instrument

As Figure 3 shows, a basic instrument is quite simple in its design. There are two identical heat-flow sensors, one for the sample measurement and the other for a reference. On top of the sensors aluminum cups are mounted into which the ampoules with the sample and the reference are inserted for a measurement. The sensors are in intimate thermal contact with a relatively large aluminum heat sink. A syringe is mounted above the sample cup to enable introduction of a solution or liquid as a reagent. The whole instrument is shielded from the surroundings by an insulation jacket.

The voltage from the reference heat flow sensor is subtracted from the voltage from the measurement heat-flow sensor (differential coupling). Heat that enters through the jacket will influence the measurement and the reference sides identically and will thus produce no net signal. Only a signal produced by the sample will be recorded.

We use inexpensive glass vials as ampoules because these have uniform outside diameters. For many student experiments the vials can be closed with ordinary rubber stoppers, but aluminum shrink caps with rubber seals may also be used. It is easy to arrange for the introduction of gas, liquid, solid, or living samples by inserting different devices through the rubber seal.

It is advantageous for the calorimeter to be equipped with a thermostating position where a sample may be held for some time before being introduced into thermal contact with the TCPs.

## Calibration of the Instrument

Isothermal calorimeters are usually calibrated electrically with a resistance heater inserted into the measurement ampoule or attached to the ampoule holder. When a current is passed through the resistance the produced thermal power may be calculated by

$$P = I^2R = V^2/R \qquad (5)$$

where $V = IR$ is the voltage drop across the resistor. When a steady-state output is obtained, the calibration coefficient may be obtained from eqs 1, 2, and 5:

$$\varepsilon = I^2R/U \qquad (6)$$

where $U$ is the steady-state voltage output from the TCP. It

is also possible to calibrate with thermal power pulses, typically 200 s long, integrating the voltage output.

One may also calibrate an isothermal calorimeter by doing an experiment in which the produced thermal power or heat is well known. Especially for systems such as chemical dissolution, in which it can be difficult to arrange for the heat to be produced in a similar way in both the measurement and an electrical calibration, such calibrations or tests are very useful. For the experiments described in this paper electrical calibration is sufficient.

## Practical Notes

To utilize the reference it is essential that the measurement and the reference sides are arranged in the same way; most importantly, the reference side needs to have a heat capacity similar to that of the measurement side. The easiest way to accomplish this is to charge the reference ampoule with a sample as similar as possible to the measurement sample, but without any heat production (see the experiments described below).

In the student experiments described here it is not necessary to make the Tian correction (eq 3). It may still be instructive to do so, as this will sharpen peaks.

From the calibration coefficient it is easy to calculate what type of data acquisition system is needed. Let us assume that we have a data logger with a least significant bit of 1 mV and a maximal voltage of ±60 mV (typical of an inexpensive thermocouple logger). From eq 3 the corresponding thermal powers may be calculated: 15 mW and 0.9 W, respectively. As 1 mV was the limit of detectability of the logger, we can state that a calorimeter of the present type that uses this logger can measure thermal powers from below 0.1 mW up to 900 mW, and the same on the negative side.

The sample has to have a slightly different temperature from that of the heat sink; otherwise there would not be any signal from the heat-flow sensor. The relation between the produced thermal power and the temperature difference at steady state is

$$\Delta T = P/K \qquad (7)$$

When a measurement using this calorimeter with an insulation jacket is run for a long time with high thermal power or ambient temperature different from that of the calorimeter, the calorimeter temperature may change somewhat during the measurement. However, for the experiments described here these temperature changes will never be greater than 0.1 K.

## Examples of Student Experiments

### Physics: Heat Capacity of Solids

Specific heat capacity, $c$, the heat needed to change the temperature of one unit mass one degree, is a basic property of all substances and materials. In this experiment we drop small solid samples of known mass and a temperature different from that of the calorimeter into the measurement ampoule holder. The excess heat transferred to the ampoule holder produces a peak that may be integrated to give the heat capacity of the sample. This method, referred to as *drop calorimetry*, is widely used for measuring the temperature dependence of heat capacities of both solids (8) and levitated liquid metals (9) at high temperatures.
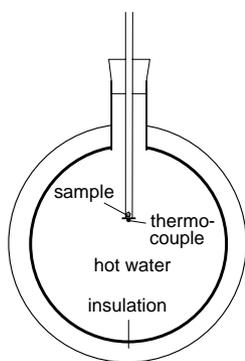
Figure 4. Schematic diagram of device used for heat capacity measurements.
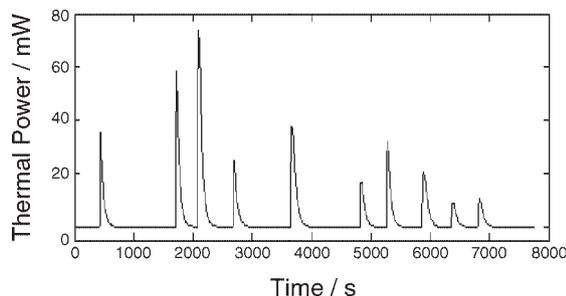


Figure 5. Calorimetric result from measurement of heat capacities. The peaks (from left to right) correspond to samples 1–10 in Table 2.
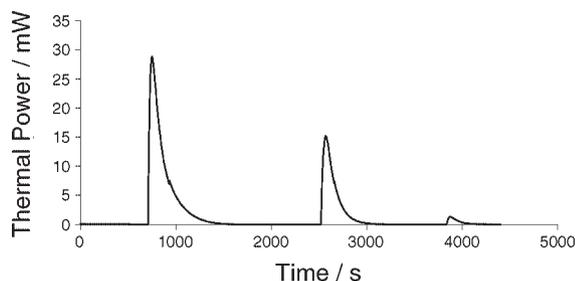


Figure 6. Acid–base titration. Exothermal signals generated from titration of tris(hydroxymethyl)aminomethane (THAM) in a saturated aqueous solution with 3.0 M HCl. Each peak represents three drops of titrant.

One way to transfer the sample into the calorimeter quickly is to equip a flask as shown in Figure 4. To drop the sample into the calorimeter one turns the flask upside down carefully so that the sample falls into a plastic guide tube and down into the calorimeter.

Figure 5 and Table 2 give the results of a measurement series with four small samples of aluminum and six samples of brick. Each peak, which corresponds to a sample that has been dropped into the calorimeter, may be integrated to give a heat $Q$. As we also know the sample masses, $m$, and the temperature changes, $\Delta T$, the equation for calculating the heat capacity is

$$C = Q/(m\Delta T) \qquad (8)$$

If a sample is dropped before the signal from the previous

**Table 2. Heat Capacity Data**

| | Sample | Mass/ mg | $Q$/J | $T_{sample}$/ °C | $c$/(J g$^{-1}$ K$^{-1}$) | |
|---|---|---|---|---|---|---|
| | | | | | Exptl | Lit. |
| 1 | aluminum | 93 | 2.15 | 50.5 | 0.850 | |
| 2 | aluminum | 164 | 3.60 | 49.4 | 0.838 | |
| 3 | aluminum | 275 | 5.88 | 49.0 | 0.829 | |
| 4 | aluminum | 84 | 1.53 | 44.2 | 0.867 | |
| | | | | Mean | $0.85 \pm 0.02$ | 0.90 |
| 5 | brick | 180 | 3.61 | 51.4 | 0.711 | |
| 6 | brick | 77 | 1.44 | 49.9 | 0.700 | |
| 7 | brick | 120 | 2.26 | 49.1 | 0.727 | |
| 8 | brick | 129 | 2.14 | 48.3 | 0.661 | |
| 9 | brick | 49 | 0.86 | 47.4 | 0.727 | |
| 10 | brick | 60 | 1.00 | 46.9 | 0.703 | |
| | | | | Mean | $0.70 \pm 0.02$ | 0.75 |

NOTE: the calorimeter temperature was 23.2 °C during all measurements.

sample has reached the baseline, one may use the Tian equation to try to resolve the peaks.
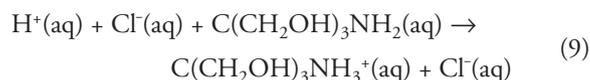
Table 2 gives the data for the samples. Both results are low. This probably reflects that the samples may lose some heat when they fall down into the calorimeter and some heat is lost through natural convection when the warm sample is in the cold calorimeter cup.

### General Chemistry: Acid–Base Titration

Using heat-conduction calorimeters, thermal titrations carried out when one reactant is incrementally added to another enable the measurement of the heat evolved in fast reactions. This method has been widely used in biochemical systems to determine both the enthalpy change and the binding constant for the formation of enzyme–substrate complexes (*1*). Performing a thermal titration in this calorimeter requires only microliters of the titrating solution. In this experiment, a small sample of reagent A, either solution or solid, is placed in the vial and the titrating reagent B is held in a 1000-μL syringe mounted above the vial. Single drops of B are added to the vial, and the thermal signal generated from each addition is recorded.

We start by placing 15–16 mg of tris(hydroxymethyl)-aminomethane, C(CH$_2$OH)$_3$NH$_2$ (THAM), in a saturated aqueous solution in a glass vial and position the vial in the aluminum cup. The glass vial is covered with a paraffin film. A 1000-μL syringe is filled with the titrant, 3.0 M HCl. The syringe is secured into the sliding top (Fig. 3) so that the tip of the syringe punctures the film and is in the vial. The system is then allowed to reach thermal equilibrium.

As the first drops of titrant are delivered, a large exothermic signal is seen (Fig. 6). Two or three drops are delivered after the signal returns to the baseline. Drops of titrant are released until the expected equivalent molar volume is achieved indicating that the endpoint is reached. The titration proceeds according to (*10*):

$$\text{H}^+(\text{aq}) + \text{Cl}^-(\text{aq}) + \text{C(CH}_2\text{OH)}_3\text{NH}_2(\text{aq}) \rightarrow$$
$$\text{C(CH}_2\text{OH)}_3\text{NH}_3^+(\text{aq}) + \text{Cl}^-(\text{aq}) \qquad (9)$$

The volume of HCl required to neutralize all of the THAM is used to determine the enthalpy of reaction for this titration. At any intermediate point in the titration the ratio of the

added volume to the total volume of HCl equals the ratio of the added number of drops to the total number of drops.

The number of moles, $n_i$, in each drop of titrant is

$$n_{i(HCl)} = V_{i(HCl)} \times M_{HCl}$$

Each peak, corresponding to the $i$th drop of the titrant, is integrated to give the heat $Q_i$. The total heat in all peaks before the endpoint, $\Sigma_i Q_i$, divided by the moles of titrant added before the endpoint, $\Sigma_i n_i$, gives the enthalpy of the process:

$$\Delta_r H = \Sigma_i Q_i / \Sigma_i n_i \qquad (10)$$

Another method of calculating the enthalpy of reaction is to employ the moles of THAM used:

$$\Delta_r H = \Sigma_i Q_i / \Sigma_i n_{THAM} \qquad (11)$$

Using the literature value for the enthalpies of formation of all reactants and products, Hess's law is used to calculate the $\Delta_r H$. We assumed no concentration dependence for the $\Delta_f H(s)$. Table 3 gives data for four runs.

Possible sources of error include non-reproducible release of drops from the syringe. When using the moles of titrant to calculate the heat of reaction, if the endpoint is passed, there may be an excess of titrant present. The added titrant will give off a thermal signal but some of the signal may result from dilution of the titrant and not from the initial reaction.

*Physical Chemistry: Enthalpy of Vaporization of Solvents*

The heat-conduction calorimeter provides an easy method for determining the enthalpy of vaporization of volatile organic solvents. As only one drop of the solvent is released into the aluminum cup, the thermopile reads the endothermic event as the solvent evaporates and the thermal signal is gathered. By measuring the volume of a drop of solvent and calculating the mass of the drop from the solvent's density, we can compute the molar enthalpy of vaporization of the solvent.

Hexane, ethanol, and isopropanol are the three organic solvents used in this experiment. We start by filling a syringe with approximately 50 µL of hexane. The syringe is then mounted on the sliding top. The syringe may be lowered a few millimeters into the unsealed cup, but it should not touch the sides or the bottom of the cup. The insulating box is placed back on the calorimeter and thermal equilibrium is attained.

After recording a baseline for the experiment, the syringe plunger is displaced until a signal indicates that a drop disengaged from the syringe and fell into the ampoule. An endothermic signal is observed until the liquid is vaporized. The displacement of the plunger indicates the volume of the drop. This volume and the density of the liquid can be used to calculate the mass of the drop. The measurement is repeated two more times for hexane and then repeated for ethanol and isopropanol. Figure 7 shows typical thermal signals received for hexane.

To reduce the relative error, an alternative method would be to release several drops instead of only one. Each time it would be necessary to wait until the signal returned to the baseline. The sum of all signals could be used together with the total volume. Because the density and surface tension are the same for each droplet, the volume of a drop will be highly reproducible. Therefore, the total volume can be divided by the number of drops to obtain the volume of a single drop.

**Table 3. Titration of C(CH₂OH)₃NH₂ (THAM) with 3 M HCl**

| Run | $Q$/J | HCl/mol | $\Delta_r H^a$/ (kJ mol⁻¹) | Error (%) | THAM / mol | $\Delta_r H^b$/ (kJ mol⁻¹) | Error (%) |
|---|---|---|---|---|---|---|---|
| 1 | -13.2 | 2.79E-04 | -47.3 | 0.2 | 2.72E-04 | -48.5 | 2 |
| 2 | -7.3 | 1.89E-04 | -38.5 | -19 | 1.49E-04 | -49.1 | 4 |
| 3 | -7.7 | 1.89E-04 | -40.5 | -15 | 1.49E-04 | -51.6 | 9 |
| 4 | -8.2 | 1.55E-04 | -52.6 | 11 | 1.57E-04 | -52.0 | 10 |

$^a\Delta_r H$ as defined in eq 10; $^b\Delta_r H$ as defined in eq 11; lit. value -47.4 kJ mol⁻¹ (10).

**Table 4. Enthalpies of Vaporization**

| Compound | $\varepsilon^a$/ (W V⁻¹) | $Q_{total}$/ J | $\Delta_{vap}H$/(kJ/mol) | | Error (%) |
|---|---|---|---|---|---|
| | | | Exptl | Lit.$^b$ | |
| *n*-Hexane | 2.5 | 1.2 | 26.8 | 31.6 | -15 |
| Ethanol | 2.5 | 4.7 | 45.5 | 42.3 | 8 |
| Isopropanol | 2.5 | 3.3 | 39.2 | 45.4 | -14 |

$^a$Values from calorimeter built at Drexel University.
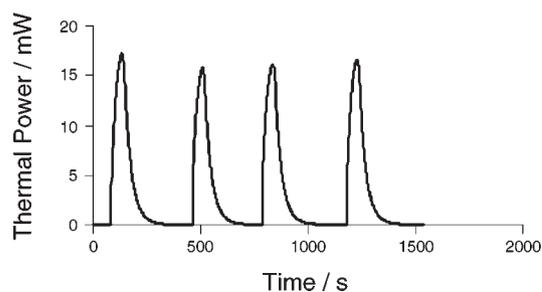$^b$*CRC Handbook of Chemistry and Physics*, 77th edition.



Figure 7. Endothermal signals for the vaporization of *n*-hexane. Each peak corresponds to the thermal signal resulting from the release of one drop of solvent.
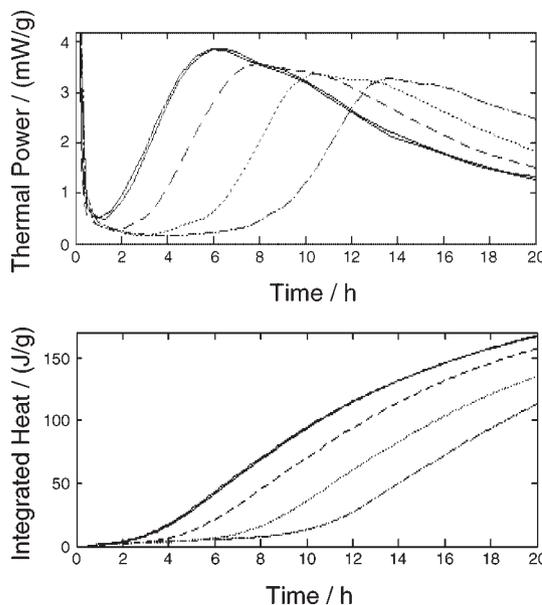


Figure 8. Results from cement hydration experiments. The two co-inciding curves to the left in both figures show the results for cement paste without any plasticizing agent. The other three curves are (from left to right) with 1.5, 3.0, and 4.5% (of the cement mass) of a melamine-based plasticizing agent. Top: primary data from the calorimeter. Bottom: graph of the integrated curves.

We then use the calibration coefficient from the calibration experiment to convert the voltage ($U$) to a thermal signal ($dQ/dt$). Integration of the area under each thermal signal curve gives the heat signal ($Q$). Using the measured heats and the amount of solvent in each drop, the molar enthalpy of vaporization is found:

$$\Delta_{vap}H = \frac{\epsilon \int U dt}{n} \qquad (12)$$

Here, $n$, is the number of moles of solvent.

A summary of $\Delta_{vap}H$ values for hexane, ethanol, and isopropanol is shown in Table 4. All calculated values for $\Delta_{vap}H$, with the exception of that for ethanol, fall below the expected literature value for each solvent at 25 °C. A source of error may arise at the tip of the syringe. After the release of a drop, if a partial drop of the volatile solvent is formed at the syringe tip, this volume may evaporate before reaching the sample cup. The total volume of solvent dispensed from the syringe may actually be larger than the volume that came into thermal contact with the thermopile. Using an extremely fine-tipped needle would help to diminish the loss of volatile solvent. Another option would be to use an inexpensive syringe pump and mount the syringe needle so that it touches the bottom of the ampoule holder. All of the vapor would then evaporate from the surface.

## Inorganic Chemistry and Material Science: Cement Hydration

Cement is a fine powder obtained from the burning and milling of limestone. When cement is mixed with water it hardens by a process called hydration to form a solid material usually called hardened cement paste. Concrete is the hardened mixture of cement, water, and aggregate (rocks) that is used in construction work.

To make an experiment, mix cement powder and water in a beaker. For a student experiment a water–cement ratio (w/c) of 0.5 is easy to mix. Sand may be added to the cement, especially at high w/c, to decrease the risk of water separation. Any additives should be completely dissolved in the water before the mixing. Charge a disposable ampoule with 5–15 g of cement paste and lower it directly into the calorimeter. As cement hydration is a comparatively slow process, the measurements should in most cases continue for about 20 h.

Figure 8 shows the result of some experiments with cement paste. All samples had the same w/c, 0.5, but different percentages of a common plasticizing agent were also added. Plasticizing agents are used to make high-performance cement with low water content less stiff to work with. A plasticizing agent reduces the internal friction in the cement paste when it is absorbed on the surface of the cement grains. Most plasticizing agents also retard the hydration. This is clearly seen in the experiments presented here where a higher percentage of plasticizing agent gives increased retardation. This is of practical importance because one may transport the concrete a longer time before it begins to set. On the other hand, increased retardation decreases the productivity at a work site, as it takes longer for the concrete to develop its strength.

Cement hydration is a highly exothermic reaction that, like many other solid-state reactions, cannot be described by the ordinary chemical rate equations (first order, second order, etc.). Still partly unknown processes such as diffusion or
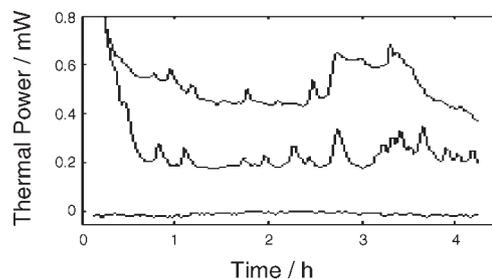


Figure 9. Thermal signals produced from insect metabolism. Each insect has a base (resting) metabolism; peaks correspond to the activity events.

precipitation from a supersaturated solution govern cement hydration. Typical of cement hydration is that it takes place in a number of stages: first some rapid initial processes (not seen in our measurement), then a lag period, then a rapidly increasing reaction rate after initialization, and finally a decreased reaction rate. Calorimetry is an excellent method to study such a complex process.

The rate of cement hydration is sensitive to a number of additives. For example, chlorides will accelerate the reaction and sugars will delay the setting or hinder it altogether. The rate of reaction is also sensitive to the w/c ratio, and there are a number of different cements on the market (slow hardening, standard, injection…). Temperature is of course another factor.

## Biology: Insect Metabolism

Isothermal calorimeters have been explored as a means of measuring the heat of metabolism of small insects. The rate of heat exchange between small insects and their environments is believed to be controlled by several factors: radiative heat gain, convective heat loss, metabolism, and evaporation. These properties vary with the size, shape, orientation, and surface properties of the insect (*11*).

Isothermal microcalorimeters offer a non-damaging way to monitor the metabolism of insects. To reduce the multiple sources of possible heat exchange, the heat measured from an insect scurrying in the vial is taken as the heat of metabolism. The heat measured is the sum of the heats from all of the insect processes that take place in the calorimeter.

The setup of this experiment involves placing an empty vial in the sample aluminum cup. A glass tube is secured in the sliding top above the glass vial. The insulating box is then placed on the system and the calorimeter is allowed to reach thermal equilibrium. Insects selected must be small enough to fit through the mouth of the vial, but large enough to register a thermal signal. In the examples shown in Figure 9, the base (resting) metabolism is shown along with the peaks corresponding to the activity events of the insects.

The integration of the peaks corresponding to the activity events gives the heat, $Q$. The total heat produced during the 4-hour measurement shown in the top curve in Figure 8 was approximately 7 J. An interesting question is: How much food would the insect need to produce this heat? An approximate value can be found by using the "burning" of glucose in oxygen as a model of metabolism:

$$C_6H_{12}O_6(s) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(\ell) \qquad (13)$$

$$m(C_6H_{12}O_6) = (Q \times 180 \text{ g/mol}_{glucose})/\Delta_r H_{m,glucose} \qquad (14)$$

where $\Delta_r H_m$ = –2813 kJ/mol. Thus, 7 J of heat corresponds to approximately 0.5 mg of glucose.

After performing this experiment, students may be interested in researching the many factors involved in the metabolism and heat transfer of living organisms. The above simple measurements may serve as a springboard for students to predict factors that would have to be considered for more accurate measurements and applications. A calorimeter would have to provide a means for air exchange and $CO_2$ exhaust, controlled thermal equilibrium of the humidified air, and easy removal of the holding vessels for autoclaving (12). The experiments may also be performed with other animals such as small fish, centipedes, and worms.

Further studies in this area may include changing some of the factors for one species of insect, such as age, diet, or stage of development. Current experiments and applications in this field include using calorimetric thermograms to monitor insects' reactions toward toxic compounds and toward allelochemicals, including pheromones (13).

### Other Experiments

The five experiments presented here are a few examples of what one may do with an isothermal heat conduction calorimeter. There are probably few fields of science and technology where one could not devise student experiments with a heat conduction calorimeter. Other ideas include:

*Polymer science*: Curing reaction of a standard epoxy.

*Food science*: Microbiological growth in food.

*Material science*: Steel corrosion in different environments.

*Coatings technology*: Oxidation of linseed oils.

*Biotechnology*: Heat production in waste compost.

The calorimeter type described here has been used in both industry and universities for some time. Typical industrial uses are in the determination of the heat evolved upon mixing materials of both known and unknown origin (hazardous evaluation) and in the study of the effect of concrete additives on the hydration of cement paste. Other applications include studying microbiological growth in liquid foodstuffs (14) and aiding in trouble shooting catalyst impurities (15, 16). This type of instrument may also be used as an analytical tool, for example to determine the solubility from the break in the plot of heat versus moles added from a thermal titration.

### Conclusions

The isothermal heat-conduction calorimeter described here may serve as a springboard in widening the field of calorimetric techniques introduced to students. Forty-four thermodynamics researchers, in identifying important areas for development in the 21st century, describe dozens of applications of heat conduction calorimeters (17). By utilizing this isothermal calorimeter in undergraduate labs, students

may be offered a more versatile way of measuring a variety of heat changes. The experiments explored here, involving heat capacity measurements, reaction and vaporization enthalpies, cement hydration, and insect metabolism, are just a few of the many that are possible. The sensitive thermal signals invite discussion of what is physically taking place in a reaction and may lead students to develop experiments of their own. The use of the isothermal heat-conduction calorimeter offers students a window to one of the many analytic methods in research and industry that can be used to determine heat changes.

### Note

1. A useful discussion of the physical properties and operating formulas for thermoelectric devices can be found at *www.melcor.com./formula.htm* (accessed June 2001). At this Web site, the relationship between thermal conductivity and device thermal conductance is explained.

### Literature Cited

1. Wadsö, I. *Chem. Soc. Rev.* **1997**, *1997*, 79.
2. Wadsö, I. In *Solution Calorimetry*; Marsh, K. N.; O'Hare, P. A. G., Eds.; Blackwell: Oxford, 1994; Vol. IV, p 267.
3. Kemp, R. B. In *Handbook of Thermal Analysis and Calorimetry*; Brown, M. E., Ed.; Elsevier: Amsterdam, 1998; Vol. 1, pp 577–669.
4. Calorimetry Sciences Corporation, Inc., Provo, UT; *www.calscorp.com* (accessed Mar 2001).
5. Thermometric AB, Jarfalla, Sweden; *www.thermometric.com* (accessed Mar 2001).
6. Herwaarden, S. V. In *Thermal Sensors*; Meijer, G. C. M.; Herwaarden, A. W., Eds.; Institute of Physics: Bristol and Philadelphia, 1994; pp 102–116.
7. *Thermoelectric Handbook*; Melcor: Trenton, NJ; *www.melcor.com* (accessed Mar 2001).
8. Blachnik, R.; Besser, J.; Wallbrecht, P.; Dreyer, K. *Thermochim. Acta* **1996**, *271*, 85–92.
9. Frohberg, M. G. *Thermochim. Acta* **1999**, *337*, 7–17.
10. Eatough, D. J.; Christensen, J. J.; Izatt, R. M. *Experiments in Thermometric Titrimetry and Titration Calorimetry*; Brigham Young University Press: Provo, UT, 1974.
11. Casey, T. M. *Thermoregul. Heat-Exchange* **1988**, *20*, 119–146.
12. Kurtti, T. J.; Brooks, M. A.; Wensman, C.; Lovrien, R. *J. Therm. Biol.* **1979**, *4*, 129–136.
13. Lovrien, R. E.; Kurtti, T. J.; Tsang, R.; Brooks-Wallace, M. *J. Biochem. Biophys. Methods* **1981**, *5*, 307–318.
14. Wadso, L. *Int. Biodeter. Biodegrad.* **1998**, *42*, 25–28.
15. Hofelich, T. C.; Frurip, D. J.; Powers, J. B. *Process Safety Prog.* **1994**, *13*, 227–233.
16. Hofelich, T. C.; Prine, B. C.; Scheffler, N. E. *Process Safety Prog.* **1997**, *16*, 121–125.
17. *Chemical Thermodynamics*; Letcher, T., Ed.; Chemistry for the 21st Century Monograph; Blackwell Science: Malden, MA, 1999.