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Wadsö, Lars; Li, Xie

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PO Box 117
221 00 Lund
+46 46-222 00 00

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A Simple Rate Law Experiment Using a Custom-Built Isothermal Heat Conduction Calorimeter

Lars Wadsö*
Division of Building Materials, Lund University, 221 00 Lund, Sweden; **lars.wadso@byggtek.lth.se*

Xi Li
Applied Chemistry, Wuhan University of Technology, Wuhan, Hubei, China

Calorimetry is the measurement of heat and thermal power (heat production rate). Such measurements can be made with different types of calorimeters and are of interest in many fields of physics, chemistry, and biology, as almost all processes produce or consume heat. There are several experimental methods called "calorimetry" in use as educational tools. The most common are the (dis)solution calorimeter *(1–3),* the combustion bomb calorimeter *(4–5)* and the differential (temperature) scanning calorimeter (DSC) *(6–7).* One of us (LW) has previously published a paper in this *Journal* discussing how another type of calorimeter, the isothermal calorimeter, can be used as a versatile tool in many fields of science and in teaching *(8).* (See ref *9* for an earlier paper on such a calorimeter used commercially.) The present paper presents the design of an instrument for teaching and shows how this can be used to study both kinetics and thermodynamics of a chemical reaction.

In an isothermal (heat conduction) calorimeter the thermal power (heat production rate; sometimes improperly called heat flow) of a process is measured continuously at essentially constant temperature. The design of such instruments for teaching can be rather simple. The instruments can be used at the undergraduate and graduate levels to study topics as different as:

- Respiration of an insect in a biology course.
- Dissolution of salts in a general chemistry course.
- Pressure–volume effects in a physical chemistry course.
- Transformation of mechanical energy into heat in a physics course.

These examples show that isothermal calorimetry is an extremely general measurement technique; in contrast to other calorimetric techniques that often are limited to only one type of experiment. In an isothermal calorimeter one can, in principle, study any process (provided one can get the sample into the calorimeter and that the sample produces enough thermal power to be detectable by the instrument used).

An important difference between an isothermal calorimeter and solution or bomb calorimeters is that the former measures thermal power, whereas the other two primarily measure heat (the integral of thermal power). As heat (J or J mol^{-1}) is obtained from a simple integration of thermal power (W or W mol^{-1}) the isothermal approach is more general (going from heat to thermal power by differentiation is in practice much more difficult). Isothermal calorimetry therefore resolves processes in time and has a wider use than bomb or dissolution calorimeters.

Isothermal calorimetry and differential temperature scanning calorimetry are quite different techniques: the latter mainly studies processes that are induced by temperature changes, such as melting and glass transition. Note that, although DSC instruments can be run in isothermal mode, such instruments usually have significantly lower specific sensitivity (W/g) than dedicated isothermal calorimeters because DSC samples are usually significantly smaller than samples for isothermal calorimetry *(10).*

Isothermal calorimetry is a fundamental way of studying all types of reactions. The thermal power is proportional to the rate of a reaction and the produced heat is proportional to the amount that has reacted (the extent of reaction):

$$P = \frac{\mathrm{d}n}{\mathrm{d}t}\Delta H \qquad (1)$$

$$Q = -\left[n(0) - n(t)\right]\Delta H \qquad (2)$$

Here, n is the amount of reactant, P is the thermal power at time t, ΔH is the molar reaction enthalpy, and Q is the heat produced from time zero to time t (ΔH is as usual negative for exothermic processes; for such processes P and Q are here defined as positive). These two equations connect the rate and extent of reactions with thermal power and heat that are measured by an isothermal calorimeter. Isothermal calorimetry can thus be used both in kinetic and thermodynamic studies.

The Calorimeter Design

We have designed a custom-built instrument with four calorimeters housed in an insulated box. The instrument can also be built with fewer calorimeters, although because many interesting educational calorimetric experiments take at least four hours to perform, it is an advantage if more than one experiment can be run in parallel. For example, if some of the experiments fail, or to vary the experimental parameters, or to calculate mean and standard deviation of the result, additional calorimeters can meet these needs. The instrument is not actively thermostated and the quality of the results depends to some extent on the temperature stability of the environment. We have tested it in laboratories and offices in which the temperature may change a few degrees during the day (no air conditioning) and found that it gives satisfactory performance. However, it should be protected from large temperature changes and should not, for example, be placed where the sun may reach it. Note that this type of calorimeter can be built in many different ways and we only give a general description of our design.

As shown in Figure 1, each calorimeter has two heat flow sensors (PT3-12-30, Melcor, Trenton NJ, USA) placed on an aluminum block that serves as a heat sink (the dimensions are 50 × 50 × 100 mm). These are thermocouple plates (Peltier devices) that are mostly used for cooling electronics. In this application we use them the opposite way by measuring the weak Seebeck- effect voltages that are proportional to the heat flow between the sample and the heat sink (as both heat flow and voltage are proportional to the temperature difference over a thermocouple plate). Note that the temperature differences are so low (typically in the order of 0.01 K) in a well-designed experiment that the situation is essentially isothermal. (The term "isothermal calorimetry" does not imply that the sample is at thermodynamically isothermal conditions, only that the sample temperature is constant enough so that one gets the same result as one would get from a truly isothermal experiment.)

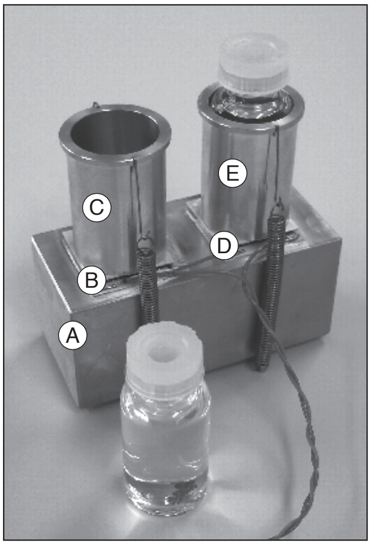

Figure 1. Setup of a calorimetric unit showing two glass vials with reusable plastic caps. (A) Heat sink; (B) Sample heat flow sensor; (C) Sample vial holder; (D) Reference heat flow sensor; (E) Reference vial holder. The heat flow sensors (placed between the vial holders and the aluminum heat sink) are connected so that the reference signal is subtracted from the sample signal.

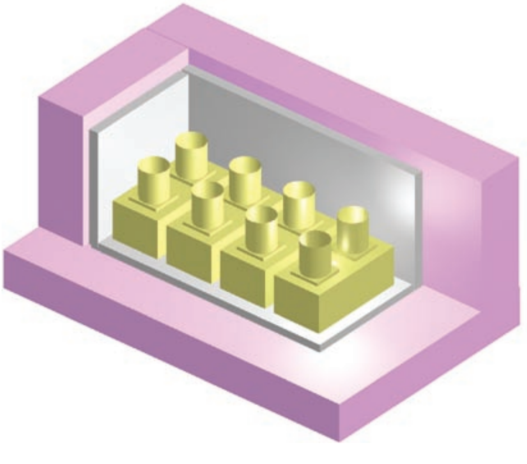

Figure 2. Cutaway diagram of a box showing four calorimeters in one unit surrounded by 10-mm aluminum plates and 50-mm insulation.

An aluminum vial holder with an inner diameter only slightly larger than the vials is placed on each heat flow sensor. This vial holder can be held in place by fastening it with a heat conducting adhesive or with heat sink paste, or by springs as we have done (Figure 1). One heat flow sensor is used for the sample and the other for an inert reference; the measured signal is the difference between these two signals.

The vial holder measures 27.50 mm i.d., which makes it possible to use two types of 20 mL vials: calorimetric glass vials (Thermometric AB, Järfälla, Sweden) or polyethylene scintillation vials (e.g., article no. 3071401 by Zinsser Analytic, Germany). The glass vials can be sealed with silicone rubber stoppers, aluminum caps, or reusable polyethylene caps; the scintillation vials come with a polyethylene screw cap.

Figure 2 shows four calorimeters positioned in a box constructed of 50-mm polystyrene foam covered with 10-mm aluminum plates on the inside. Eight holes were cut through the aluminum and insulation above the eight vial holders. These holes allow access to a sample during an experiment and accommodate tubes connected to the vials. During experiments these holes are filled with plugs made from soft packaging foam.

The voltage signals from the four calorimeters were collected by a multichannel logger (ADC-24, Pico Technology Ltd., St. Neots, UK) on its most sensitive range (±39 mV, accuracy 0.1%). This data logger connects to and gets its electrical power from the USB connection to a computer so there are no high voltages in the calorimeter.

The main difference between this student calorimeter and a commercial isothermal calorimeter is that the present instrument is not actively thermostated. Incorporating the following experimental conditions will help ensure that students can obtain reproducible results:

1. It is absolutely necessary to employ a reference. As the signal from the reference is subtracted from the sample signal, external thermal disturbances that enter the calorimeter will be greatly reduced because they influence sample and reference similarly. To get this effect it is important to charge the reference with an inert sample of similar heat capacity as the sample. In the experiment with an aqueous solution described below, an equal mass of water in the reference should be used.
2. To get this type of calorimeter to work well without a thermostat the heat sink should have a high heat capacity, and the calorimeters should be placed in an insulated box with a metal container on the inside. The insulation decreases the influence of the room temperature and the metal container distributes thermal disturbances evenly in the instrument so that the references can be more effective.
3. The vial holder must be made of a material with high thermal conductivity, such as aluminum. It must also be as high as the vial so that it collects the heat that is produced in the whole vial and conducts that heat to the heat flow sensor.

The calorimeter is calibrated using electrical heaters. These were precision resistors of 100.0 ± 0.1 Ω connected to a stable voltage source (a dry cell battery will suffice). The current can be calculated by measuring the voltage over an external resistance. Calibrations are made by first measuring a baseline, then turning on the constant current and waiting until the signal reaches a constant value, and finally turning off the current and waiting for a final baseline. The calibration coefficient is the ratio of the thermal power produced in the heater resistor to the increase in the voltage signal above the baselines. If the measured voltage from an experiment is multiplied by the calibration coefficient the result is the thermal power (See the Calibration section of the online supplement):

$$P = \varepsilon(U - U_0) \tag{3}$$

Here, P is the thermal power, ε is the calibration coefficient, U the voltage from the heat flow sensor, and U_0 the baseline voltage. Note that it is necessary in all applications to subtract the baseline (the signal when no heat is produced) as this in practice may be significantly different from zero.

For some experiments, mainly kinetic ones, one needs to make a correction for the thermal inertia of the instrument, namely, that the measured signal lags behind the true signal. This correction is made with the Tian equation (named after the French chemist Albert Tian who developed heat conduction calorimeters in the 1920s):

$$P_c = P + \tau\frac{dP}{dt} \tag{4}$$

Here, P_c is the corrected thermal power and τ is the time constant. (See the Calibration section of the online supplement.) The present calorimeter design with vials containing 20 mL water has a rather high time constant of about 700 s. For the experiment described below the reaction enthalpy was overestimated by about 5% when no Tian equation correction was made, although the rate constant was essentially correct. Note that the use of the Tian equation correction increases the noise in the signal and that it is necessary to apply noise reduction afterwards if data are collected at a high rate.

A Rate Law Experiment

The rates of chemical reactions can be described by rate equations. As there is a direct connection between rate and thermal power (eq 1) isothermal calorimetry is a general method to study reaction kinetics. We provide here an example of a calorimetric experiment with a robust first-order reaction: the alkaline hydrolysis of propyl paraben (propyl 4-hydroxybenzoate, $C_{10}H_{12}O_3$, molar mass 180.203 g mol^{-1}, CAS 94-13-3) *(11)*.

Parabens are esters of 4-hydroxy benzoic acids that are used as preservatives in shampoos, skin products, deodorants, toothpastes, and so on. The most common ones are methyl paraben, ethyl paraben, and propyl paraben. Often more than one paraben is used, as combinations of them are more effective as preservatives.

Parabens can be degraded by both acid and base hydrolysis. As this experiment takes place under alkaline conditions the acid that is formed by the hydrolysis is immediately neutralized. The reaction can thus be seen as being composed of two processes: hydrolysis and neutralization, as shown in Figure 3. The neutralization is an almost instantaneous process, so it is the rate constant of the hydrolysis that is measured in the present experiment. It is interesting to note that hydrolysis of esters generally has low enthalpy changes; for example, the enthalpy of ethyl acetate hydrolysis in aqueous solution is 3.7 kJ mol^{-1} *(12)*. Neutralization processes have much higher enthalpies; the enthalpy of protonation of hydroxyl ions in aqueous solutions at infinite dilution is −55.81 kJ mol^{-1} *(13)*. Therefore, most of the heat from the studied process originates from the neutralization. Measuring only the hydrolysis part of the reaction can be done by acid hydrolysis; however in the case of a paraben, this is complicated by the fact that the formed 4-hydroxybenzoic acid reacts further to form phenol under acid conditions *(11)*.

Make the measurement by dissolving 150–250 mg of propyl paraben in 20 mL of 0.5 M NaOH(aq) and shaking until all the paraben is dissolved. This gives a molar ratio paraben/hydroxide ions of ~0.1. Glass vials should be used to see that the substance is fully dissolved. The vials are then placed in the calorimeter and measured for 3–15 h. (See the guides for teachers and students in the online supplement.) Figure 4 shows the result of an experiment. The alkaline hydrolysis rate constant is proportional to the hydroxide ion concentration *(14)* and the experiment can also be conducted with, for example, 1 M or 0.2 M NaOH. However, already with 0.1 M NaOH the solubility of propyl paraben is lowered so much that it is not possible to perform the experiment as described above.

A first-order rate equation for the present 1:1 reaction (Figure 3) written for the reactant (in our case, propyl paraben) has the following general solution:

$$n(t) = n(0)\,e^{-kt} \tag{5}$$

Here, $n(t)$ and $n(0)$ are the amounts of reactant at time t and when the experiment starts, respectively; k (s^{-1}) is the rate constant. Note that eq 5 is written in terms of moles and that $n(t)/n(0)$ is the extent of reaction (cf. ref *15*). We can write an equation suitable for evaluation of calorimetric results by taking the derivative of eq 5 and substituting the rate dn/dt with thermal power divided by molar reaction enthalpy obtained from eq 1:

$$P = -k\,\Delta H\,n(0)\,e^{-kt} \tag{6}$$

Note that the expression $k\ \Delta H\ n(0)$ is $P(0)$, the ther-

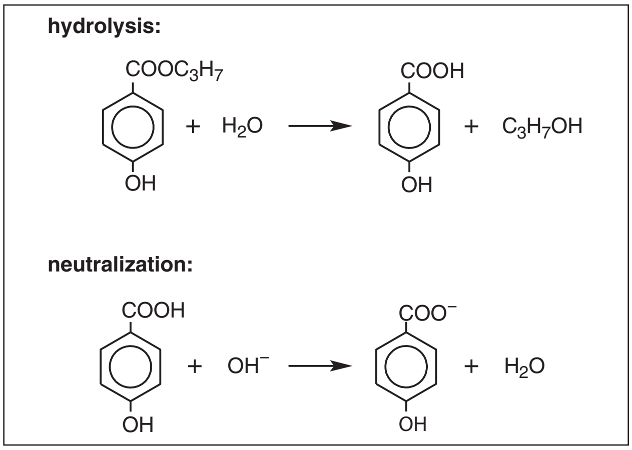

Figure 3. The hydrolysis of propyl paraben (propyl 4-hydroxybenzoate) to 4-hydroxybenzoic acid and propanol, followed by the neutralization of the acid.

mal power at the start of the experiment. Taking the natural logarithm of both sides of eq 6 we obtain the following linear equation:

$$\ln P \;=\; \ln\left[-k\,\Delta H\,n_{\mathrm{A}}(0)\right] \;-\; k\,t \qquad (7)$$

Plotting $\ln P$ from an experiment as a function of time yields a straight line in which the slope is $-k$ and the intercept is $\ln(-k\,\Delta H\,n(0))$. Figure 5 shows an example of such a plot from a 15-h experiment. Observe that a section of the curve is linear: k and ΔH can be evaluated from this section. Conversely, the initial and final sections of the curve in Figure 5 are not linear. For the initial section of the curve this is because the signal from the calorimeter is disturbed by the introduction of the sample vial into the calorimeter. For the final section of the curve it is an effect of the low signal/noise ratio when the thermal powers are low. Table 1 gives the results of 12 measurements.

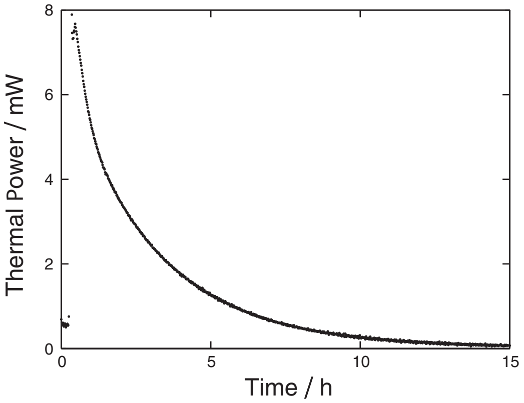

Figure 4. Primary calorimetric results from an experiment dissolving 219 mg of propyl paraben in 20 mL of 0.5 M NaOH(aq).

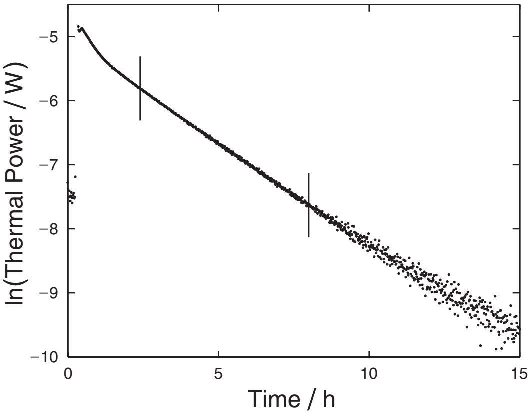

Figure 5. The results from Figure 4 (corrected using the Tian equation) plotted according to eq 7. The two vertical lines indicate typical starting points and endpoints for a linear regression. Part of the noise seen comes from the derivative in the Tian equation (eq 4): no noise reduction has been made.

Figure 5 shows that it is possible to get a linear curve already after about 3 h, so it should be possible to perform the measurement in a four-hour session. However, it can be difficult to judge whether the curve is linear without measuring for a longer time; we have found it convenient to let the measurements run overnight so that the students can obtain their results the next day.

Hazards

The calorimeter and the data logger are safe to use because they are only powered with low voltages through the USB computer connection. Propyl paraben is used as a preservative (e.g., in toothpaste) and is safe to use if standard lab precautions are observed. Concentrated sodium hydroxide solution is caustic; high temperatures result upon mixing sodium hydroxide with water. The strong hydroxide solution should be handled (filling, closing, and shaking of the vials) using protective coats, gloves, and safety glasses.

Discussion

Table 1 gives the results of 12 measurements made by students. The agreement with literature values *(11)* is satisfactory. Note that the rate constant is temperature dependent, although the enthalpy is rather insensitive to such changes. The slightly lower rate constants are expected as the temperature was a few degrees lower in our experiment than in the literature experiment.

In the present experiment it is easier to get an accurate and precise value for the rate constant than for the enthalpy. This is because the rate constant is evaluated solely from the decay rate of the thermal power (the slope in eq 7), while such factors as calibration, Tian equation correction, weighing, and timing will influence the enthalpy determination (the intercept in eq 7).

There are many different ways to study kinetics and rate equations, however, nearly all of them are measurements of concentration as a function of time. Many rely on absorbance measurements in situ *(14, 16)* or the determination of concentrations in withdrawn aliquots, for example by HPLC *(17)*. For special reactions pH electrodes *(18)*, oxygen gas sensors *(19)*, pressure sensors *(20)*, and other equipment may be used. However, the use of an isothermal calorimeter that measures the thermal power that is proportional to the reaction rate is possibly the most general approach, as all reactions produce or consume heat that—at least in principle—can be measured. In

Table 1. Comparative Results of Students' Measurements

Source	ΔH/kJ mol^{-1}	k/s^{-1}
Group 1	-56 ± 1	$101 \pm 2 \times 10^{-6}$
Group 2	-58 ± 1	$95 \pm 3 \times 10^{-6}$
Group 3	-54 ± 4	$101 \pm 4 \times 10^{-6}$
All groups	-56 ± 3	$99 \pm 4 \times 10^{-6}$
Literature *(11)*, (25 °C)	-60.1	120×10^{-6}

Note: Each group of three students made four measurements at 21.7 °C for a total of 12 measurements: means and standard deviations are given; literature values are from ref *11*.

kinetic investigations it is also an advantage that the reaction rate is measured instead of measuring concentration. However, many reactions produce thermal power values that are too low to be precisely and accurately measurable by the simple calorimeter described here.

The present experiment involves the simultaneous measurement of reaction rate (a kinetic property) and reaction enthalpy (a thermodynamic property). We have used it in graduate courses for nonchemistry students to introduce kinetic concepts (reaction rate, rate equations, first-order reaction, rate constant), general chemistry concepts (neutralization, hydrolysis), and thermodynamic concepts (enthalpy, enthalpy difference). We have also used it to teach experiment design and error analysis, asking the students to list all possible sources of error (uncertainties) and then to make a sensitivity analysis for k and ΔH for each of these uncertainties. Some possibly important sources of error include:

- The mass of the reactant. (It is preferable to use a calibrated balance with a last digit of 0.1 mg).
- The freshness of the NaOH solution. (Use degassed water to make the solution; do not let the solution come in contact with CO_2.)
- Temperature differences between the solution and the calorimeter. (Store the solution in the same room as the calorimeter.)
- High temperature changes during the experiment. (Place the calorimeter in a room with a stable temperature; note that air conditioning may cause periodic disturbances, although these are often small and can usually be neglected.)

The experiment may be expanded in a number of ways, for example by:

- Measuring at different temperatures. (This changes the rate constant, yet the enthalpy is almost constant.)
- Using different parabens. (Methyl, ethyl, and propyl paraben have different rate constants, yet enthalpies similar to the neutralization enthalpy: see ref *11*).

It is common to measure concentrations and to determine the reaction rate using an *integrated rate plot* (ln[concentration] versus time). Urbansky *(21)* has shown that this can lead to serious errors in determining reaction orders if the reaction is not followed for enough half-lives (three is usually enough). In the present experiments it is typically possible to get a linear *rate plot* (ln[rate] versus time) over about eight half-lives. It is also possible to analyze the rate-versus-time data by nonlinear curve fitting (as has been recommended for integrated rate plots: see refs *22–23*), although for the present experiment it is a good idea to always start with the ln plot to see how much of the initial and final data needs to be discarded.

Acknowledgements

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