2.8   Measurement of enthalpy changes - Calorimetry

The science of measuring energy changes involving heat is known as **calorimetry** and the apparatus

used is known as a calorimeter. Various types of calorimeter are in use but they share the same basic

principle. The reaction or process under study is conducted and the temperature change compared with

that caused by a known reaction or other **calibration**. To illustrate the principles underlying the

measurements, we can consider various types of calorimeter. However, it is important to note

that as well as calorimetry, enthalpy changes can be measured by looking at how equilibrium

constants change with temperature or, for redox reactions, the variation of the

electrochemical properties of the reaction. These are discussed further in Chapter 4.

The bomb calorimeter

The energy changes that occur during reactions between solids or liquids with gases,

particularly combustion reactions with oxygen gas, can be measured in a **bomb calorimeter,**
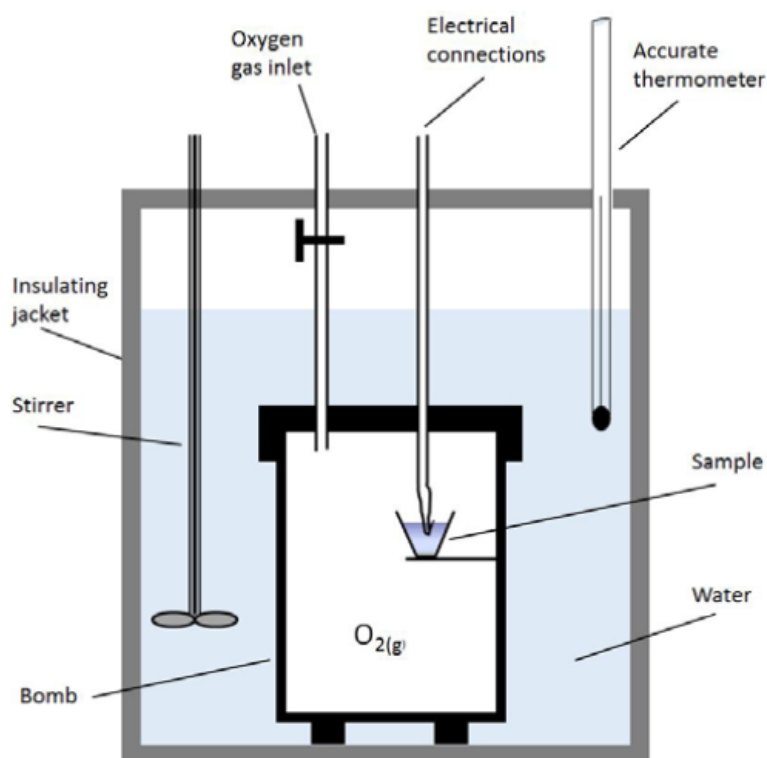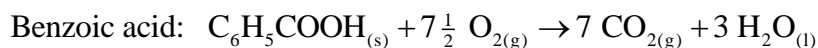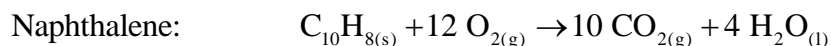
illustrated in Figure Web2.1.

Figure Web2.1 Schematic diagram of a bomb calorimeter for measuring energy in combustion reactions.

The reaction chamber or (totally misnamed!) 'bomb' which contains the substance under study is constructed from thick (~1 cm) stainless steel, ensuring that the products cannot escape. After pressurizing with oxygen gas, the reaction can be started by electrically heating a piece of wire in contact with the reactants. The heat given out during the reaction warms up both the metal of the calorimeter and the water that surrounds it. The temperature is measured precisely to ±0.001 °C or better. The temperature rise can be compared with that when a known mass of a compound with accurately known energy change undergoes reaction. Naphthalene or benzoic acid are commonly used for this purpose. The chemical changes involved in the reactions for calibrating the calorimeter are:

Naphthalene: $\qquad C_{10}H_{8(s)} + 12\ O_{2(g)} \rightarrow 10\ CO_{2(g)} + 4\ H_2O_{(l)}$

Benzoic acid: $\ C_6H_5COOH_{(s)} + 7\frac{1}{2}\ O_{2(g)} \rightarrow 7\ CO_{2(g)} + 3\ H_2O_{(l)}$

An alternative to using a standard reaction is to perform an electrical calibration. If an electric current I passes through the wire at a voltage V for time t, the energy delivered is given by $(I \times V \times t)$. An example is given in Example Web2.6.

It should be clear from Figure Web2.1 that the reaction inside the chamber occurs with no change in volume. Equation 2.9 shows that the energy change measured is therefore the change in internal energy, $\Delta_c U$. This value can be readily converted to $\Delta_c H$ using the definition implicit from Equation 2.11.

$$\Delta_c H = \Delta_c U + \Delta_c(pV)$$

We can simplify the final term by assuming ideal gas behaviour (Section 1.4) so that

$$\Delta_c(pV) = (pV)_{products} - (pV)_{reactants} = (n_{gas}RT)_{products} - (n_{gas}RT)_{reactants}$$

or

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$$\Delta(pV) = \Delta n_{gas}RT$$

where Δn_{gas} is the change in number of moles of gas. Hence,

$$\Delta_c H = \Delta_c U + \Delta n_{gas}RT$$

where Δn_{gas} is the change in the number of moles of gas during the reaction. The assumption of ideal gas behaviour is reasonable for pressures up to several hundred bar. Also reasonable is the assumption that any volume changes in the solid or liquid components are negligible. The methods involved are best illustrated by looking at some experimental data as in Example Web2.6.

Note that in order to calculate $\Delta_c H$, we need to know Δn_{gas} and hence the exact chemical equation for the reaction. This is straightforward when the substance of interest contains only C, H and oxygen. However, if other elements such as nitrogen or phosphorus are present which can form products in different oxidation states, careful analysis of the products is needed to establish the stoichiometry.

Example Web2.6. The combustion of 0.6475 g of naphthalene in a bomb pressurized with oxygen at 25 °C resulted in a temperature increase of 2.424 °C. Under the same conditions, passage of an electric current of 1.500 A at 15.00 V for 15.00 min raised the temperature by 1.890 °C. Calculate $\Delta_c U$ and $\Delta_c H$ for naphthalene.

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First, we need to consider the calibration.

Energy supplied $= I \times V \times t = 1.500$ A $\times 15.00$ V $\times (15.00 \times 60)$ s $= 20250$ J

This caused a temperature rise of 1.890 K. From this, we can find the amount of energy needed to change the temperature by 1 K. This is equivalent to the heat capacity of the whole calorimeter, $C_{calorimeter}$.

$$C_{\text{calorimeter}} = \frac{\text{energy supplied}}{\text{temperature change}} = \frac{20\,250\,\text{J}}{1.890\,\text{K}} = +10\,710 \ \text{J K}^{-1}$$

This value tells us that a temperature rise of 1 K in the calorimeter is equivalent to a release of 10.71 kJ of energy.

Now considering the data for naphthalene. The temperature rise was 2.424 K so the energy released can be found from

$$\text{Energy released} = C_{\text{calorimeter}} \times \text{temperature rise}$$

$$= 10710 \ \text{J K}^{-1} \times 2.424 \ \text{K}$$

$$= 25\,970 \ \text{J}$$

This came from 0.6475 g of naphthalene. The molar mass is 128.2 g mol^{-1} so

$$0.6475 \ \text{g is equivalent to} \ \frac{0.6475 \ \text{g}}{128.2 \ \text{g mol}^{-1}} = 5.051 \times 10^{-3} \ \text{mol}.$$

Therefore the combustion of 5.051×10^{-3} mol releases 25 970 J so 1 mol releases

$$\text{Energy released} = \frac{25970 \ \text{J}}{5.051 \times 10^{-3} \ \text{mol}} = 5.142 \times 10^{6} \ \text{J mol}^{-1}$$

Since the reaction is conducted at constant volume, the energy released is equivalent to the change in internal energy. The reaction is exothermic and energy is evolved from the combustion to raise the temperature of the calorimeter. The change in internal energy of the system therefore has a *negative* value.

$$\Delta_c U = -\,5.142 \times 10^{6} \ \text{J mol}^{-1} = -5143 \ \text{kJ mol}^{-1}$$

To find the enthalpy change using Equation 2.22, we need to know the change in the number of moles of gas Δn_{gas}. The balanced equation for the combustion reaction is

$$\text{C}_{10}\text{H}_{8(s)} + 12 \ \text{O}_{2(g)} \rightarrow 10 \ \text{CO}_{2(g)} + 4 \ \text{H}_2\text{O}_{(l)}$$
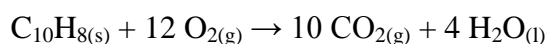
so considering only the gaseous components,

$$\Delta n_{\text{gas}} = n_{\text{gas}}(\text{products}) - n_{\text{gas}}(\text{reactants}) = 10 - 12 = -2 \ \text{mol}$$

Hence,
$$\Delta_c H = \Delta_c U + \Delta n_{\text{gas}} RT$$

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$$= -5142 \times 10^3 \text{ J mol}^{-1} + (-2 \text{ mol}) \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times$$

$$298.15 \text{ K})$$

$$= -5\ 147 \times 10^3 \text{ J mol}^{-1}$$

$$= -5147 \text{ kJ mol}^{-1}$$

Hence, $\qquad \Delta_c U = -5142 \text{ kJ mol}^{-1}$ and $\Delta_c H = -5147 \text{ kJ mol}^{-1}$

The difference between the internal energy and enthalpy is relatively small in this case.

A bomb calorimeter is not suitable for measuring the properties of reactions involving only gases but this can be carried out in a modification known as a *flame calorimeter,* illustrated in Figure Web2.2. The gases under study are fed at a known, constant rate to a jet where the reaction occurs. The gases pass through a coil immersed in water so that they are at a known, constant temperature when they reach the reaction site. The energy released in the reaction heats a water bath in the same way as with a bomb calorimeter. The masses of the two gases are usually measured from the volume that flows in a given time and the ideal gas equation, Equation 1.1. Calibration is also performed here either with a standard reaction or by electrical means. Here, the reaction is conducted at constant pressure and so measures the enthalpy change directly, as illustrated in Example Web2.7.
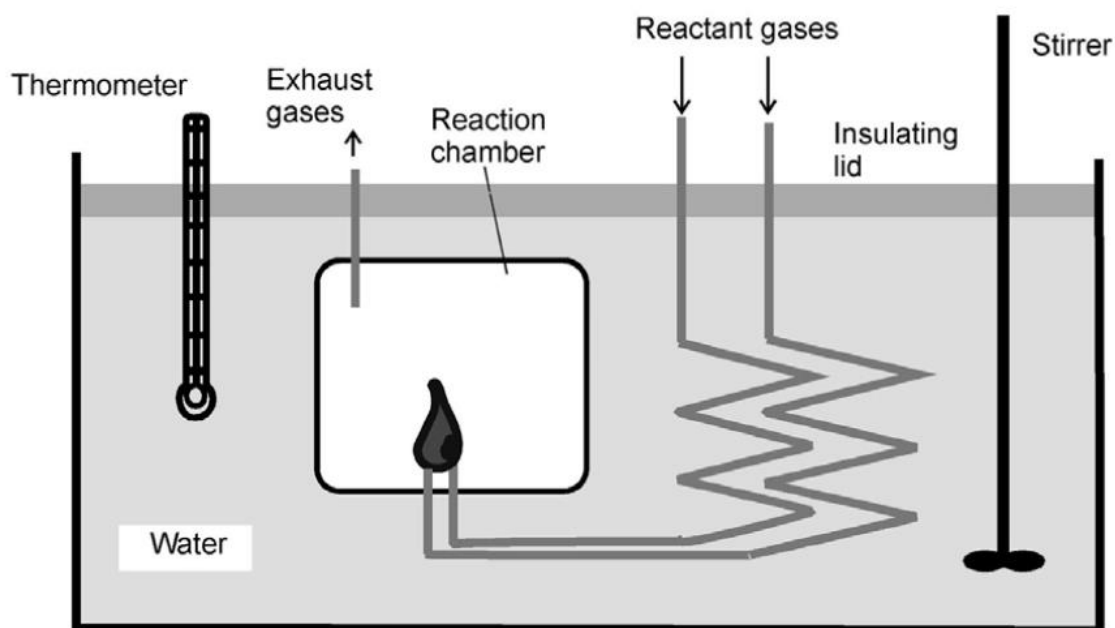
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Figure Web2.2 Schematic diagram of a flame calorimeter for measuring energy in gas phase reactions.

Example Web2.7. The combustion at 25 °C of 2.900 g of butane gas, C_4H_{10}, raised the temperature of a calorimeter by 11.470 °C. The enthalpy of combustion at 25 °C of butane is −2877.1 kJ mol^{-1}.

The gas flow was then changed to 2-methylpropane. Combustion of 1.162 g at 25 °C caused a temperature rise of 4.575 °C. Calculate the enthalpy change of combustion of 2-methyl propane.

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The molar mass of *n*-butane is 58.12 g mol^{-1}. Hence 2.900 g is 0.0499 mol, so

energy change = 0.0499 mol × −2877.1 kJ mol^{-1} = −143.55 kJ.

Thus, a temperature rise of 11.470 K was caused by −143.6 kJ. Hence, a 1 K rise results from an energy change of

$$C_{\text{calorimeter}} = \frac{-143.6 \text{ kJ}}{11.470 \text{ K}} = -12.52 \text{ kJ K}^{-1}.$$

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The temperature rise generated by the combustion of 2-methyl propane is therefore equivalent to an energy change of

$$-12.52 \text{ kJ K}^{-1} \times 4.575 \text{ K} = -57.28 \text{ kJ}$$

which occurs from 1.162 g or $\dfrac{1.162 \text{ g}}{58.1 \text{ g mol}^{-1}} = 0.0200 \text{ mol}$

Hence,
$$\Delta_c H = \frac{-57.28 \text{ kJ}}{0.0200 \text{ mol}} = -2864 \text{ kJ mol}^{-1}$$

Hess's law shows that the difference in the two enthalpies of combustion is equivalent to the enthalpy of isomerization for the two isomers of butane.

Solution calorimetry

Solution calorimeters are used for measuring heat changes during reactions that occur in solution and are illustrated in Figure Web2.3. They allow two (or more) reactants to be separately placed inside an insulated, thermostatted chamber until thermal equilibrium is reached. The reactants can then be rapidly mixed to start the reaction, either by tilting the reaction vessel, tipping the cup or, in more sophisticated versions, using a magnet to raise or break a glass seal between the chambers.
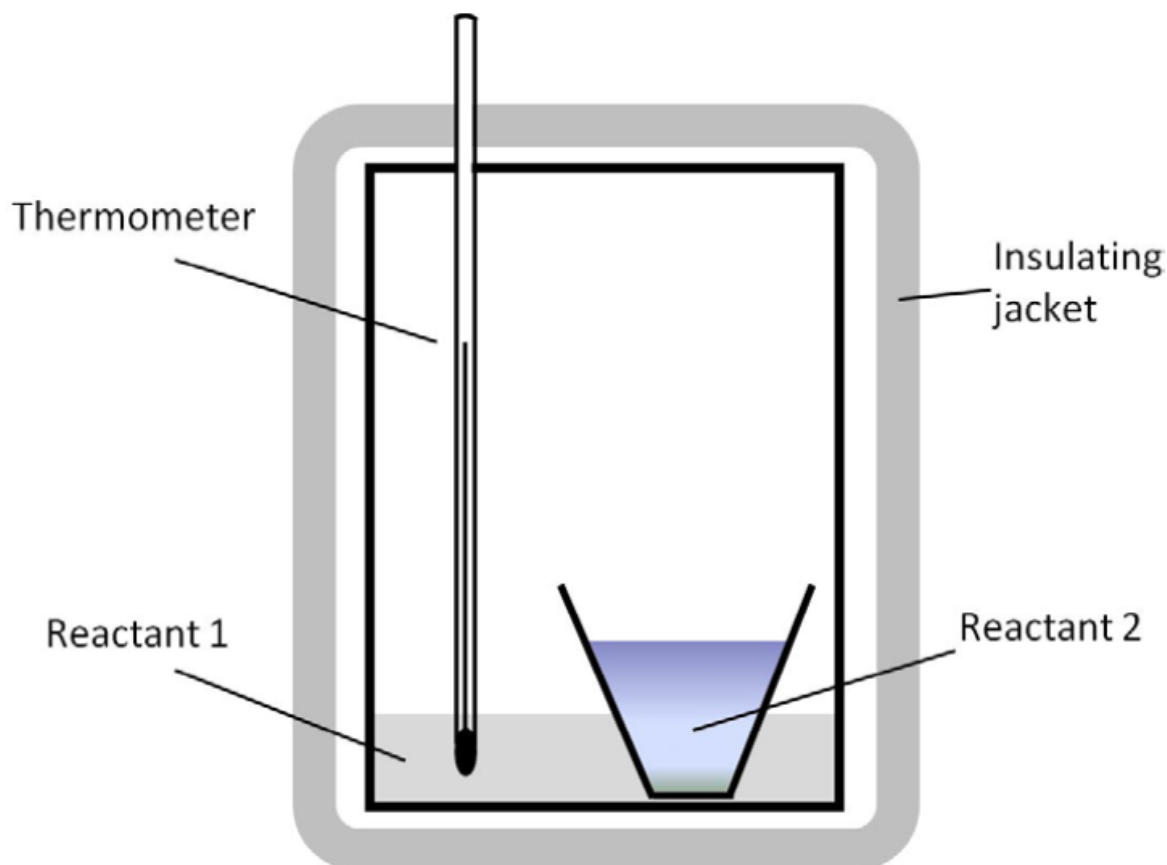
Figure Web2.3. Schematic diagram of a calorimeter suitable for measuring enthalpy changes for reactions in solution. The reactants are kept separate until the experiment starts.

Calibration of this type of apparatus is often carried out using a neutralization reaction between a strong acid and a strong base in aqueous solution. Provided the acid and base are fully ionized, the reaction is the same for any combination.

$$H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(l)} \qquad \Delta_r H^\circ = -56.90 \text{ kJ mol}^{-1}.$$
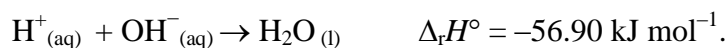
The other ions in solution do not take part in the reaction and so are unimportant.

The operation of this type of calorimeter is best illustrated by an example such as that in Example Web2.8.

Example Web2.8. The reaction between 50.0 cm^3 of 0.100 mol dm^3 hydrochloric acid solution and the same volume of 0.100 mol dm^{-3} sodium hydroxide solution in a solution calorimeter caused a temperature increase of 0.795 °C.

In a separate experiment, 100.0 cm^3 of water and 3.500 g of sodium carbonate decahydrate, $Na_2CO3•10H_2O$ were mixed in the calorimeter and the temperature decreased by 2.310 °C.

Calculate the enthalpy of solution for sodium carbonate decahydrate.

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50.0 cm^3 of 0.10 mol dm^3 HCl solution represents

$$\frac{50.0 \text{ cm}^3}{1000 \text{ cm}^3 \text{ dm}^{-3}} \times 0.100 \text{ mol dm}^{-3} = 5.00 \times 10^{-3} \text{ mol}$$

The enthalpy change is −56.90 kJ mol^{-1} so

$$\text{energy change} = 5.00 \times 10^{-3} \text{ mol} \times -56.90 \text{ kJ mol}^{-1}$$

$$= \text{-284.5 J.}$$

This raised the temperature by 0.795 °C. Hence, to find the amount of energy need to raise the temperature by 1 K, the so called 'heat capacity' of the calorimeter,

$$C_{\text{calorimeter}} = \frac{\text{-284.5 J}}{0.795 \text{ K}} = -358 \text{ J K}^{-1}.$$

So we know that an energy release of -358 J changes the temperature by 1 K.

Now considering $Na_2CO_3(s)·10 H_2O$, the temperature *decreases* by 2.310 K so that the enthalpy is absorbed and the enthalpy change is positive.

$$\text{energy absorbed} = \text{-2.310 K} \times \text{-358 J K}^{-1} = +826.7 \text{ J.}$$

This comes from 3.500 g corresponding to 0.0122 mol so

$$\text{Energy absorbed} = \frac{+826.7 \text{ J}}{0.0122 \text{ mol}} = +67\ 800 \text{ J mol}^{-1}.$$

In this case, the reaction is conducted at constant pressure so that the energy change corresponds directly to the enthalpy change of solution, $\Delta_{solution}H$.

$$\Delta_{solution}H = +67.8 \text{ kJ mol}^{-1}.$$

In this example, the same volume of solution was used for both experiments. If this is not the case, allowance must be made for the change in heat capacity.

These calorimeters use quite large amounts of chemicals. However, calorimetry can be carried out on other scales. For example, calorimeters the size of whole rooms have been built. The input of food and drink to a subject can be carefully controlled and the energy changes involved in their respiration and other living processes accurately measured. The 'calorific value' of individual foods can be measured by bomb calorimetry (Example Web2.5) but these 'whole room calorimeters' measure energy changes in a patient as they undergo their everyday lives, albeit at the expense of living in a sealed box for a length of time!

Isothermal titration calorimetry

At the other end of the scale is the isothermal titration calorimeter. Here the tiny energy changes in reactions of very small amounts of material are monitored during a titration *i.e.* a step-wise addition of one of the reagents. The method is most often applied to biochemical systems, for example, in measuring the interaction energies between proteins or between substrates and enzymes.

The instrument (Figure Web2.4) contains two identical cells, made from an inert material that has high thermal conductivity which are surrounded by thermally insulating, adiabatic material. One is a reference cell that contains only the solvent in which the reaction is to be conducted. The sample cell contains a dilute solution of one of the components under study (*e.g.* an enzyme) together with a syringe through which accurately known amounts of

the second component (*e.g.* a substrate) in the solvent can be added. Each cell contains a heater and a sensitive thermocouple (an electrical device for measuring temperature). The instrument is designed to heat the cells in such a way to keep their temperatures identical and to monitor the energy supplied to the heaters. If an exothermic reaction occurs during the titration, energy will be given out and so less energy needed by the heater to keep the temperatures equal. The opposite is true if an endothermic reaction takes place. The required energy is plotted as the aliquots are added to give data such as that in Figure Web2.5, each 'peak' corresponding to a reduction in energy input from exothermic release of heat as each aliquot of substrate is added. As more substrate is added, more of the enzyme is used up and so the 'peaks' get smaller.
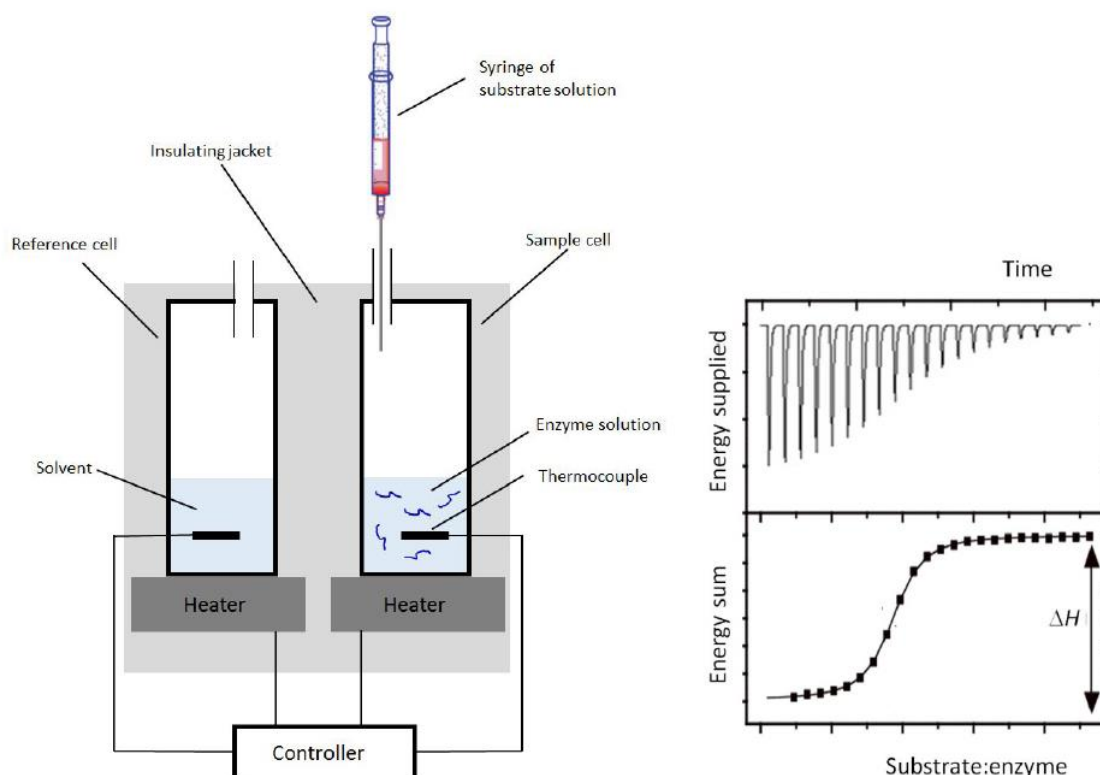

Figure Web2.4. Schematic diagram of an isothermal titration calorimeter. In this case the interaction of a substrate with an enzyme is being investigated.

Figure Web2.5. ITC data for an exothermic interaction – each peak results from addition of substrate from the syringe.

Analysis of the ITC data allows the determination of interaction energies and other thermodynamic parameters such as equilibrium binding constants. The titration is performed at constant pressure and temperature, so that direct measurements of enthalpy changes can be made. The size of the 'peaks' depends on the amount of energy released and this can be established by careful calibration with known reactions. Typical experiments involve micromolar amounts of the materials (or even less in some cases) and temperature changes of less than 0.1 mK can be measured. The technique is therefore useful when small amounts of material are available such as where medicinal chemists are interested in whether and how strongly a potential new drug interacts with a particular protein.