Chapter 5

Energy change and reactions

Topic 5 of the Nuffield course introduces the ideas of thermodynamics, which is the study of energy and its interconversions. We are starting to investigate one of the most interesting and difficult questions chemists can ask: *What makes a reaction take place?* This topic does not give us all of the tools we need to answer this question, but starts us on the road to a rigorous answer, which can be employed to great effect in chemical and biochemical systems. The parts of thermodynamics specific to chemistry are called, interestingly, thermochemistry. There are three laws of thermodynamics, which are called the 'first', 'second' and 'third' laws.

- First law: Energy and matter are conserved[1] (this is just a restatement of the law of conservation of energy).
- Second law: In any spontaneous process, there is always an increase in the disorder (entropy) of the universe[2].
- Third law: The disorder (entropy) of a perfect crystal at 0 K is 0[3]. There is no such thing as a perfect crystal, and 0 K is unattainable.

In this topic we are interested only in the application of the first law.

5.1 Measuring heat energy changes

In the two experiments in this topic you measure enthalpy changes using a simple technique, which is called **calorimetry** (after an inferior unit of energy, the calorie). Your reaction occurs and heats a known volume of water. You measure the

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[1] $\Delta U = Q + W$ is the mathematical statement of this. Do not remember this.

[2] $\Delta S_{total} > 0$

[3] $S(0) = 0$

temperature rise of the water, and assuming that the changes in other aspects are negligible, can use the specific heat capacity of water to work out how much heat energy was released or consumed by the reaction.

In an exothermic reaction the temperature of the surroundings would _______. In an endothermic reaction the temperature of the surroundings would _______.

The **specific heat capacity** of a substance is the energy required to raise the temperature of 1 g by 1 K. For water this is about 4.2 J g^{-1} K^{-1}. The energy exchanged between the reactants and surroundings is given by

$$Q = cm\Delta T \tag{5.1}$$

This does not give a measure which would be worth telling your friends about however. For that you need to convert to a more general format. Work out how many moles of substance you used, then scale that up to one mole. For instance, if you had performed a solution reaction which released 200 J, and used 25 $cm^3$of a 0.25 M solution, how many moles have you used?

$$\text{Moles} = \frac{25}{1000} \times 0.25 = 6.25 \times 10^{-3} \tag{5.2}$$

How do you scale your 200 J value up from 6.25×10^{-3} moles to 1 moles?

$$\Delta H = -\frac{200}{6.25 \times 10^{-3}} = -32000 \text{ J mol}^{-1} = -32.0 \text{ kJ mol}^{-1} \tag{5.3}$$

As the reaction has given out heat energy, exothermic, this value is negative (the reaction system has lost heat energy). The value ΔH is the **enthalpy change** or

The energy exchanged with the surroundings at constant pressure.

What does that mean? The reaction mixture is referred to as the **system**, and the assumption is that at the start and end of the reaction the temperature of the system is the same. All the heat energy has been exchanged with the surroundings of the experiment. The **surroundings** includes the apparatus. You can get away with measuring the temperature of the reaction solution in your experiment by assuming that all of the heat energy generated in there is later exchanged with the surroundings, and the temperature of your reaction mixture returns to its original value.

The value of ΔH relates to the quantities given in an equation. In order to be able to share this data with other scientists, **standard conditions** are defined. Look on page 102 to complete the list of standard conditions

- Physical state of reagents ...

- Solution concentrations are __________
- Temperature is __________ K
- Pressure is __________ atmosphere

The **standard enthalpy change of formation** of, for instance, water, is the enthalpy change accompanying the formation of one mole of water from its elements (under standard conditions), $\Delta H_f^\ominus$ is

$$H_2(g) + \frac{1}{2}\,O_2(g) \longrightarrow H_2O(l) \qquad \Delta H_f^\ominus[H_2O(l)] = -285.6\ \text{kJ mol}^{-1} \tag{5.4}$$

5.2 Hess's Law

Hess's Law is an application of the first law. It states that it does not matter by which route you make a chemical from other chemicals - the overall enthalpy change will always be the same. **The total enthalpy change accompanying a chemical change is independent of the route by which the chemical change takes place**.

The value of this is that it is possible to calculate the enthalpy changes for reactions which would be impossible to measure.

5.2.1 Applications of Hess's Law

The bombardier beetle, *Stenaptinus insignis* uses an explosive charge of quinone to defend itself. Hydroquinone is oxidised by hydrogen peroxide to produce quinone and water:

$$C_6H_4(OH)_2(aq) + H_2O_2(aq) \longrightarrow C_6H_4O_2(aq) + 2H_2O(l) \tag{5.5}$$

It is possible to calculate the enthalpy change for this reaction, given that

Reaction	$\Delta H^{\ominus}$ kJ mol^{-1}
$C_6H_4(OH)_2(aq) \longrightarrow C_6H_4O_2(aq) + H_2(g)$	-177.4
$H_2(g) + O_2(g) \longrightarrow H_2O_2(aq)$	-191.2
$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(g)$	-241.8
$H_2O(g) \longrightarrow H_2O(l)$	-43.8

You should get something like -557.4 kJ mol^{-1}. Why do you think this is an effective defence strategy?

Calculate $\Delta H_f^\ominus$ for glucose being produced in photosynthesis.

Species	$\Delta H_f^\ominus$ kJ mol^{-1}
CO_2	-393.5
H_2O	-285.8
$C_6H_{12}O_6$	-1274.5
O_2	???

Equation:

What is $\Delta H_f^\ominus$ for the formation of oxygen?

Can you construct a Hess cycle to show $\Delta H_f^\ominus = +2801.3$ kJ mol^{-1} for the production of glucose?

You will get plenty of practice using Hess cycles! Standard enthalpies of formation can help us to work out the standard enthalpy changes of reaction, without doing an experiment.