3.11 Introduction to Energy and Enthalpy Changes

Why do we study energy changes during a reaction?

Because it helps us to answer many questions including
a) why chemical reactions occur
b) why a certain reaction is more likely to occur than another
c) why the overall energy change accompanying a chemical change is independent of the route by which the change is achieved

Energy, Enthalpy and Heat

We can sometimes get bogged down in Chemistry with definitions, but they are important. We often use interchangeably the words ‘heat’ ‘energy’ and ‘enthalpy’ but they all mean different things. Most A-level students will have a reasonable understanding of energy and heat but enthalpy will be for many a new term and is more difficult to define.

In chemical reactions energy will be most often seen as Heat energy which will cause the temperature to change. Energy, however, can be transferred in other forms than just heat energy.

We often use the words **system** and **surroundings**. The word **system** means all the chemicals both reactants and products. The surroundings is everything else in the universe outside of the system. Energy can be transferred between the system and surroundings in both directions.

Definitions.

**Energy** is the ability of a system to do work.

**Work** is the energy transfer that is the result of a force moving an object through a distance.

**Heat** is the energy transfer that is a result of a temperature difference between system and surroundings.

In the above exploding hydrogen balloon reaction, the system is the hydrogen in the balloon and the oxygen in the air. These substances contain an internal energy. The internal energy of the system will be a combination of kinetic energy of the moving particles and the potential energy stored in the chemical bonds. During the reaction some of the internal energy will be converted into heat energy passed into the surroundings and also work. The expanding gases will have done some work pushing other molecules out of the way. The internal energy of the system will have decreased.

The above process can be represented by the following equation:

\[
\text{Change in internal energy} = \text{heat added to the system} + \text{work done to the system}
\]

These would be negative values if heat energy was transferred away from the system or if work was done by the system.

The problem with this equation is that it is difficult to measure internal energy and the work done to the system. It is relatively easy to measure the heat added to the system though. So how does Enthalpy fit into this?
Enthalpy change

**Definition:** Enthalpy change ($\Delta H$) is the amount of heat energy taken in or given out during any change in a system provided the pressure is constant.

Why is the condition **pressure is constant** important in this definition? To fully answer this we have to do some quite complicated maths - if you are interested look at page 4. However, when the maths is done if pressure is constant we can just look at the heat transferred (which is easy to measure) and ignore the work done. So in this case enthalpy is something similar to the internal energy of the system. When heat energy is transferred away from the system the enthalpy change ($\Delta H$) (like internal energy change) will be negative.

$$\Delta H = H_{\text{products}} - H_{\text{reactants}}$$

Like internal energy, enthalpy is difficult to measure but it is easy to measure enthalpy change by measuring the amount of heat transferred during a reaction.

In an exothermic change heat energy is transferred from the system (chemicals) to the surroundings. The products have less enthalpy than the reactants.

In an endothermic change, heat energy is transferred from the surroundings to the system (chemicals). They require an input of heat energy e.g. thermal decomposition of calcium carbonate. The products have more enthalpy than the reactants.

Common oxidation exothermic processes are the combustion of fuels and the oxidation of carbohydrates such as glucose in respiration.
Standard Enthalpy change definitions

There are lots of enthalpy changes that we use in chemistry that can be further defined for specific reactions and processes. Listed below are some common enthalpy changes that are often met at A-level. They need exact definitions so scientists can know what the value quoted exactly refers to. Particular attention has to be paid to what substance the amount in moles refers to.

**Standard enthalpy change of Formation**

The standard enthalpy change of formation of a compound is the enthalpy change when 1 mole of the compound is formed from its elements under standard conditions (298K and 100kpa), all reactants and products being in their standard states.

\[ \Delta H \]

**Standard enthalpy change of Combustion**

The standard enthalpy of combustion of a substance is defined as the enthalpy change that occurs when one mole of a substance is combusted completely in oxygen under standard conditions. (298K and 100kpa), all reactants and products being in their standard states.

\[ \Delta H \]

**Definition: Enthalpy change of reaction** is the enthalpy change when the number of moles of reactants as specified in the balanced equation react together.

**Enthalpy of atomisation**

The enthalpy of atomisation of an element is the enthalpy change when 1 mole of gaseous atoms is formed from the element in its standard state.

- Na (s) \( \rightarrow \) Na(g) \( [\Delta_{v}H = +148 \text{ kJ mol}^{-1}] \)
- \( \frac{1}{2} \text{O}_2 \) (g) \( \rightarrow \) O (g) \( [\Delta_{v}H = +249 \text{ kJ mol}^{-1}] \)

When an enthalpy change is measured at standard conditions the symbol \( \Delta \) is used.

Eg \( \Delta H \)

**Enthalpy changes are normally quoted at standard conditions.**

Standard conditions are:

- 100 kPa pressure
- 298 K (room temperature or 25°C)
- Solutions at 1mol dm\(^{-3}\)
- all substances should have their normal state at 298K

**Enthalpy of atomisation**

The enthalpy of atomisation of an element is the enthalpy change when 1 mole of gaseous atoms is formed from the element in its standard state.

\[ \Delta_{v}H \]

**Incomplete combustion** will lead to soot (carbon), carbon monoxide and water. It will be less exothermic than complete combustion.

**Standard enthalpy change definitions**

**Enthalpy change of Neutralisation**

The standard enthalpy change of neutralisation is the enthalpy change when solutions of an acid and an alkali react together under standard conditions to produce 1 mole of water.

Enthalpy changes of neutralisation are always exothermic. For reactions involving strong acids and alkalis, the values are similar, with values between -56 and -58 kJ mol\(^{-1}\)
Maths of Internal Energy and Enthalpy

Referring to the equation from page 1
Change in internal energy \( (U) = \) heat added to the system \( (q) + \) work done to the system \( (w) \)
\[
\Delta U = q + w \quad (1)
\]

Using some physic’s definitions work is defined as
Work\( (w) = \) force \( \times \) distance moved \( (2) \)

Pressure is defined as
Force = pressure \( \times \) area \( (3) \)

So combining equation (2) and (3) gives us
Work = pressure \( \times \) area \( \times \) distance moved

Which is the same as
Work = pressure \( \times \) change in volume

Using symbols
\[
w = - p \Delta V \quad (4)
\]
Given minus sign because work is being done by the system on the surroundings

Combining equations (1) and (4) give us
\[
\Delta U = q - p \Delta V \quad (5)
\]

Now moving on to Enthalpy \( (H) \). This is defined by this different equation
\[
H = U + pV \quad (6)
\]

For small changes in the enthalpy we can convert equation (6) into one that represents \( \Delta H \)
\[
\Delta H = \Delta U + p\Delta V + V\Delta p \quad (7)
\]

Now we can substitute the equation (5) defining \( \Delta U \) into equation (7)
\[
\Delta H = q - p\Delta V + p\Delta V + V\Delta p
\]
Simplify to
\[
\Delta H = q + V\Delta p \quad (8)
\]
If the change in pressure is zero then equation (8) simplifies to \( \Delta H = q \) which takes us back to the exam board definition of enthalpy change which is enthalpy change is the amount of heat energy taken in or given out during any change in a system provided the pressure is constant

So note that when the change if volume is zero we can say \( \Delta U = q \) and when change in pressure is zero we can say \( \Delta H = q \)

Why do we prefer to measure \( \Delta H \) rather than \( \Delta U \)?

1) It is more convenient to measure \( \Delta H \) in the lab because we can open vessels and maintain constant pressure.
2) In reactions where there is no volume change (ones that are just solids and liquids). \( \Delta H = \Delta U \)
3) In reactions involving a volume change, the difference in \( \Delta U \) is less than 5% if \( \Delta H \) is greater than 40kJ.