### 1.4 Energetics

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

If an enthalpy change occurs then energy is transferred between *system* and *surroundings.* The system is the chemicals and the surroundings is everything outside the chemicals.

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

In an endothermic change, 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 energy 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 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. Symbol $\Delta H^\circ$  

Mg (s) + Cl₂ (g) $\rightarrow$ MgCl₂ (s)  
2Fe (s) + 1.5 O₂ (g) $\rightarrow$ Fe₂O₃ (s)  

The enthalpy of formation of an element = 0 kJ mol⁻¹

#### 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. Symbol $\Delta H^\circ$  

CH₄ (g) + 2O₂ (g) $\rightarrow$ CO₂ (g) + 2 H₂O (l)  

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

When an enthalpy change is measured at standard conditions the symbol $\Delta H^\circ$ is used.  

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

- 100 kPa pressure
- 298 K (room temperature or 25°C)
- Solutions at 1 mol dm⁻³
- all substances should have their normal state at 298K
Measuring the Enthalpy Change for a Reaction Experimentally

Calorimetric method

For a reaction in solution we use the following equation

\[
Q (J) = m (g) \times c_p (J g^{-1} K^{-1}) \times \Delta T (K)
\]

This equation will only give the energy for the actual quantities used. Normally this value is converted into the energy change per mole of one of the reactants. (The enthalpy change of reaction, \(\Delta H_r\))

Calorimetric method

One type of experiment is one in which substances are mixed in an insulated container and the temperature rise measured.

To counteract this we take readings at regular time intervals and extrapolate the temperature curve/line back to the time the reactants were added together.

We also take the temperature of the reactants for a few minutes before they are added together to get a better average temperature. If the two reactants are solutions then the temperature of both solutions need to be measured before addition and an average temperature is used.

Errors in this method

• energy transfer from surroundings (usually loss)
• approximation in specific heat capacity of solution. The method assumes all solutions have the heat capacity of water.
• neglecting the specific heat capacity of the calorimeter- we ignore any energy absorbed by the apparatus.
• reaction or dissolving may be incomplete or slow.
• density of solution is taken to be the same as water.

General method

• washes the equipment (cup and pipettes etc) with the solutions to be used
• dry the cup after washing
• put polystyrene cup in a beaker for insulation and support
• Measure out desired volumes of solutions with volumetric pipettes and transfer to insulated cup
• clamp thermometer into place making sure the thermometer bulb is immersed in solution
• measure the initial temperatures of the solution or both solutions if 2 are used. Do this every minute for 2-3 minutes
• At minute 3 transfer second reagent to cup. If a solid reagent is used then add the solution to the cup first and then add the solid weighed out on a balance.
• If using a solid reagent then use ‘before and after’ weighing method
• stirs mixture (ensures that all of the solution is at the same temperature)
• Record temperature every minute after addition for several minutes

If the reaction is slow then the exact temperature rise can be difficult to obtain as cooling occurs simultaneously with the reaction.

Read question carefully. It may be necessary to describe:
• Method
• Drawing of graph with extrapolation
• Description of the calculation

Practical

This could be a solid dissolving or reacting in a solution or it could be two solutions reacting together

One type of experiment is one in which substances are mixed in an insulated container and the temperature rise measured.

If the reaction is slow then the exact temperature rise can be difficult to obtain as cooling occurs simultaneously with the reaction.
Calculating the enthalpy change of reaction, \( \Delta H \) from experimental data

**General method**

1. Using \( q = m \times c_p \times \Delta T \) calculate energy change for quantities used.
2. Work out the moles of the reactants used.
3. Divide \( q \) by the number of moles of the reactant not in excess to give \( \Delta H \).
4. Add a sign and unit (divide by a thousand to convert J mol\(^{-1}\) to kJ mol\(^{-1}\)).

The heat capacity of water is 4.18 J g\(^{-1}\)K\(^{-1}\). In any reaction where the reactants are dissolved in water we assume that the heat capacity is the same as pure water.

Also assume that the solutions have the density of water, which is 1 g cm\(^{-3}\). E.g 25 cm\(^3\) will weigh 25 g.

**Example 1.** Calculate the enthalpy change of reaction for the reaction where 25.0 cm\(^3\) of 0.200 mol dm\(^{-3}\) copper sulfate was reacted with 0.0100 mol (excess of zinc). The temperature increased 7.0 °C.

**Step 1:** Calculate the energy change for the amount of reactants in the calorimeter.

\[
Q = m \times c_p \times \Delta T
\]

\[
Q = 25 \times 4.18 \times 7
\]

\[
Q = 731.5 \text{ J}
\]

**Step 2:** Calculate the number of moles of the reactant not in excess.

\[
\text{moles of CuSO}_4 = \text{conc} \times \text{vol}
\]

\[
= 0.20 \times 25/1000
\]

\[
= 0.005 \text{ mol}
\]

If you are not told what is in excess, then you need to work out the moles of both reactants and work out using the balanced equation which one is in excess.

**Step 3:** Calculate the enthalpy change per mole which is often called the enthalpy change of reaction

\[
\Delta H = \frac{Q}{\text{no of moles}}
\]

\[
= \frac{731.5}{0.005}
\]

\[
= 146300 \text{ J mol}^{-1}
\]

\[
= 146 \text{ kJ mol}^{-1} \text{ to 3 sf}
\]

Finally add in the sign to represent the energy change: if temp increases the reaction is exothermic and is given a minus sign e.g. \(-146 \text{ kJ mol}^{-1}\).

**Example 2.** 25.0 cm\(^3\) of 2.00 mol dm\(^{-3}\) HCl was neutralised by 25.0 cm\(^3\) of 2.00 mol dm\(^{-3}\) NaOH. The temperature increased 13.5 °C.

Calculate the enthalpy change per mole of HCl.

**Step 1:** Calculate the energy change for the amount of reactants in the calorimeter.

\[
Q = m \times c_p \times \Delta T
\]

\[
Q = 50 \times 4.18 \times 13.5
\]

\[
Q = 2821.5 \text{ J}
\]

**Step 2:** Calculate the number of moles of the HCl.

\[
\text{moles of HCl} = \text{conc} \times \text{vol}
\]

\[
= 2 \times 25/1000
\]

\[
= 0.05 \text{ mol}
\]

**Step 3:** Calculate \( \Delta H \) the enthalpy change per mole which might be called the enthalpy change of neutralisation

\[
\Delta H = \frac{Q}{\text{no of moles}}
\]

\[
= \frac{2821.5}{0.05}
\]

\[
= 56430 \text{ J mol}^{-1}
\]

\[
= -56.4 \text{ kJ mol}^{-1} \text{ to 3 sf}
\]

Exothermic and so is given a minus sign.
Measuring Enthalpies of Combustion Using Calorimetry

Enthalpies of combustion can be calculated by using calorimetry. Generally the fuel is burnt and the flame is used to heat up water in a metal cup.

**Example 3.** Calculate the enthalpy change of combustion for the reaction where 0.650g of propan-1-ol was completely combusted and used to heat up 150g of water from 20.1 to 45.5°C

Step 1: Calculate the energy change used to heat up the water.

\[ Q = m \times c_p \times \Delta T \]

\[ Q = 150 \times 4.18 \times 25.4 \]

\[ Q = 15925.8 \text{ J} \]

Note the mass is the mass of water in the calorimeter and not the alcohol

Step 2: Calculate the number of moles of alcohol combusted.

moles of propan-1-ol = mass/ \( M_r \)

= 0.650 / 60

= 0.01083 mol

Step 3: Calculate the enthalpy change per mole which is called \( \Delta c_H \) (the enthalpy change of combustion)

\[ \Delta H = Q / \text{no of moles} \]

\[ = 15925.8 / 0.01083 \]

\[ = 1470073 \text{ J mol}^{-1} \]

\[ = 1470 \text{ kJ mol}^{-1} \text{ to 3 sf} \]

Finally add in the sign to represent the energy change: if temp increases the reaction is exothermic and is given a minus sign eg \(-1470 \text{ kJ mol}^{-1}\)

Remember in these questions: sign, unit, same sig figs as data given.

Errors in this method

- Energy losses from calorimeter
- Incomplete combustion of fuel
- Incomplete transfer of energy
- Evaporation of fuel after weighing
- Heat capacity of calorimeter not included
- Measurements not carried out under standard conditions as \( \text{H}_2\text{O} \) is gas, not liquid, in this experiment
Hess’s Law

Hess’s law states that total enthalpy change for a reaction is independent of the route by which the chemical change takes place.

Hess’s law is a version of the first law of thermodynamics, which states that energy is always conserved.

On an energy level diagram the directions of the arrows can show the different routes a reaction can proceed by.

In this example one route is arrow ‘a’
The second route is shown by arrows $H$ plus arrow ‘b’

So $a = H + b$
And rearranged
$H = a - b$

Interconnecting reactions can also be shown diagrammatically.

So $a + H = c + d$
And rearranged
$H = c + d - a$

Often Hess’s law cycles are used to measure the enthalpy change for a reaction that cannot be measured directly by experiments. Instead alternative reactions are carried out that can be measured experimentally.

This Hess’s law is used to work out the enthalpy change to form a hydrated salt from an anhydrous salt.

This cannot be done experimentally because it is impossible to add the exact amount of water and it is not easy to measure the temperature change of a solid.

Instead both salts are dissolved in excess water to form a solution of copper sulfate. The temperature changes can be measured for these reactions.
Using Hess’s law to determine enthalpy changes from enthalpy changes of formation.

**Example 4.** Calculate the enthalpy change for this reaction

\[ \text{Al}_2\text{O}_3 (s) + 3 \text{ Mg} (s) \rightarrow 3 \text{ MgO} (s) + 2 \text{ Al} (s) \]

\[ \Delta H = \Sigma \Delta H \text{ products} - \Sigma \Delta H \text{ reactants} \]

\[ \Delta H = 3 \times \Delta H (\text{MgO}) - \Delta H (\text{Al}_2\text{O}_3) \]

\[ \Delta H = (3 \times -601.7) - (-1675.7) \]

\[ = -129.4 \text{ kJ mol}^{-1} \]

Remember elements have \( \Delta H = 0 \)

\[ \Delta H (\text{MgO}) = -601.7 \text{ kJ mol}^{-1} \]

\[ \Delta H (\text{Al}_2\text{O}_3) = -1675.7 \text{ kJ mol}^{-1} \]

Using Hess’s law to determine enthalpy changes from enthalpy changes of combustion.

**Example 5.** Using the following data to calculate the enthalpy of combustion of propene

\[ \Delta H_{\text{C}_3\text{H}_6(g)} = +20 \text{ kJ mol}^{-1} \]

\[ \Delta H_{\text{CO}_2(g)} = -394 \text{ kJ mol}^{-1} \]

\[ \Delta H_{\text{H}_2\text{O}(g)} = -242 \text{ kJ mol}^{-1} \]

\[ \text{C}_3\text{H}_6 + 4.5 \text{ O}_2 \rightarrow 3\text{CO}_2 + 3\text{H}_2\text{O} \]

\[ \Delta H = \Sigma \Delta H \text{ products} - \Sigma \Delta H \text{ reactants} \]

\[ \Delta H = [3 \times \Delta H (\text{CO}_2) + 3 \times \Delta H (\text{H}_2\text{O})] - \Delta H (\text{C}_3\text{H}_6) \]

\[ \Delta H = [3 \times (-394) + 3 \times (-242)] - 20 \]

\[ = -1928 \text{ kJ mol}^{-1} \]

Using Hess’s law to determine enthalpy changes from enthalpy changes of combustion.

**Example 6.** Using the following combustion data to calculate the enthalpy of reaction

\[ \text{CO} (g) + 2\text{H}_2 (g) \rightarrow \text{CH}_3\text{OH} (g) \]

\[ \Delta H_{\text{CO}(g)} = -283 \text{ kJ mol}^{-1} \]

\[ \Delta H_{\text{H}_2(g)} = -286 \text{ kJ mol}^{-1} \]

\[ \Delta H_{\text{CH}_3\text{OH}(g)} = -671 \text{ kJ mol}^{-1} \]

\[ \Delta H = \Sigma \Delta H \text{ reactants} - \Sigma \Delta H \text{ products} \]

\[ \Delta H = \Delta H (\text{CO}) + 2 \times \Delta H (\text{H}_2) - \Delta H (\text{CH}_3\text{OH}) \]

\[ \Delta H = -283 + 2 \times -286 - -671 \]

\[ = -184 \text{ kJ mol}^{-1} \]
Example 7. Calculate the enthalpy of formation of propene using the following enthalpy of combustion data

\[ 3\text{C} (s) + 3\text{H}_2 (g) \rightarrow \text{C}_3\text{H}_6 (g) \]

\[ \Delta \text{H} \text{C} (s) = -393 \text{kJ mol}^{-1} \quad \Delta \text{H} \text{H}_2 (g) = -286 \text{kJ mol}^{-1} \quad \Delta \text{H} \text{C}_3\text{H}_6 (g) = -2058 \text{kJ mol}^{-1} \]

\[ \Delta \text{H} = \Sigma \Delta \text{H} \text{ reactants} - \Sigma \Delta \text{H} \text{ products} \]

\[ \Delta \text{H} = 3 \times \Delta \text{H} \text{ (C)} + 3 \times \Delta \text{H} \text{ (H}_2) \ - \Delta \text{H} \text{ (C}_3\text{H}_6) \]

\[ \Delta \text{H} = 3 \times -393 + 3 \times -286 \ - 2058 \]

\[ = +21 \text{ kJ mol}^{-1} \]

**Mean Bond energies**

**Definition:** The mean bond energy is the enthalpy needed to break the covalent bond into gaseous atoms, averaged over different molecules.

We use values of mean bond energies because every single bond in a compound has a slightly different bond energy. E.g. In CH\textsubscript{4} there are 4 C-H bonds. Breaking each one will require a different amount of energy. However, we use an average value for the C-H bond for all hydrocarbons.

In general (if all substances are gases)

\[ \Delta \text{H} = \Sigma \text{ bond energies broken} - \Sigma \text{ bond energies made} \]

\[ \Delta \text{H reaction} \]

\[ \text{Reactants} \rightarrow \text{Products} \]

\[ \Sigma \text{bond energies broken in reactants} \rightarrow \Sigma \text{bond energies made in products} \]

\[ \text{Gaseous atoms of elements} \]

\[ \Delta \text{H values calculated using this method will be less accurate than using formation or combustion data because the mean bond energies are not exact} \]

These values are positive because energy is required to break a bond.

The definition only applies when the substances start and end in the gaseous state.
A more complicated example that may occur

Working out $\Delta H$ of a compound using bond enthalpies and other data

Example 8. Calculate the enthalpy of combustion of propene using the following mean bond enthalpy data.

$$
\Delta H = \Sigma \text{bond energies broken} - \Sigma \text{bond energies made}
$$

$$
= [E(C=C) + E(C-C) + 6 x E(C-H) + 4.5 x E(O=O)] - [6 x E(C=O) + 6 E(O-H)]
$$

$$
= [612 + 348 + (6 x 412) + (4.5 x 496)] - [(6 x 743) + (6 x 463)]
$$

$$
= -1572 \text{kJ mol}^{-1}
$$

Example 9. Calculate the enthalpy of formation of NH$_3$ using the following mean bond enthalpy data.

$$
\frac{1}{2}N_2 + 1.5H_2 \rightarrow NH_3
$$

$(\text{note the balancing is to agree with the definition of enthalpy of formation (i.e. one mole of product})$

$$
E(N≡N) = 944 \text{kJ mol}^{-1} \quad E(H-H) = 436 \text{kJ mol}^{-1} \quad E(N-H) = 388 \text{kJ mol}^{-1}
$$

$$
\Delta H = \Sigma \text{bond energies broken} - \Sigma \text{bond energies made}
$$

$$
= [0.5 x E(N≡N) + 1.5 x E(H-H)] - [3 x E(N-H)]
$$

$$
= [(0.5 x 944) + (1.5 x 436)] - [3 x 388]
$$

$$
= -38 \text{kJmol}^{-1}
$$

A more complicated example that may occur

Example 10. Calculate $\Delta H$ for propane, C$_3$H$_8$(g), given the following data.

$$
C(s) \rightarrow C(g) \quad a_tH = 715 \text{kJ mol}^{-1}
$$

$$
3C (s) + 4H_2 (g) \rightarrow C_3H_8(g),
$$

$$
\Delta H = \Sigma \Delta H \text{to turn elements into gaseous atoms} - \Sigma \Delta H \text{to turn compound into gaseous atoms}
$$

$$
\Delta H = (3x a_tH [C] + 4 x E[H-H]) - (2 x E[C-C]+ 8 x E[C-H])
$$

$$
= (3x715 + 4 x 436) - (2 x 348+ 8 x 412)
$$

$$
= -103 \text{kJ mol}^{-1}
$$
Enthalpies of Combustion in a Homologous Series

When comparing the enthalpies of combustion for successive members of a homologous series such as alkanes or alcohols there is a constant rise in the size of the enthalpies of combustion as the number of carbon atoms increases.

\[
\begin{align*}
\text{ethanol} & : & \text{H-C-C-O-H} + 3 \text{O}=\text{O} & \rightarrow & 2 \text{O}+\text{C}=\text{O} + 3 \text{H} \\
\text{Propan-1-ol} & : & \text{H-H-C-C-O-H} + 4.5 \text{O}=\text{O} & \rightarrow & 3 \text{O}+\text{C}=\text{O} + 4 \text{H} \\
\text{Butan-1-ol} & : & \text{H-H-H-C-C-O-O-O-H} + 6 \text{O}=\text{O} & \rightarrow & 4 \text{O}+\text{C}=\text{O} + 5 \text{H}
\end{align*}
\]

As one goes up the homologous series there is a constant amount and type of extra bonds being broken and made e.g. 1C-C, 2C-H and 1.5 O=O extra bonds broken and 2 C=O and 2 O-H extra bonds made, so the enthalpy of combustion increases by a constant amount.

\[
\begin{align*}
\text{H}_\text{c} &= -1365 \text{ kJ mol}^{-1} \\
\text{H}_\text{c} &= -2016 \text{ kJ mol}^{-1} \\
\text{H}_\text{c} &= -2677 \text{ kJ mol}^{-1}
\end{align*}
\]

If the results are worked out experimentally using a calorimeter the experimental results will be much lower than the calculated ones because there will be significant heat loss. There will also be incomplete combustion which will lead to less energy being released.

Remember that calculated values of enthalpy of combustions will be more accurate if calculated from enthalpy of formation data than if calculated from average bond enthalpies. This is because average bond enthalpy values are averaged values of the bond enthalpies from various compounds.