Chapter 25: Thermochemistry

Thermochemistry focuses on how **energy, usually in the form of heat, flows between the system and its surroundings.**

System = refers to the chemicals involved in a reaction.

Surroundings = refer to everything that is not the chemicals themselves (e.g. the conical flask, the thermometer in the flask, the air around it, the laboratory you are conducting the experiment in).

Enthalpy is the total heat content of a system at constant pressure.

Enthalpy change (ΔH) is the amount of heat energy absorbed or released by a system during a process (such as a chemical reaction or phase change) at constant pressure.

As we know, chemical reactions involve both bond-breaking and bond-making. **Energy is required to break a bond, and energy is released when a bond is formed.**

Therefore, enthalpy changes for chemical reactions depend on the balance between the total energy required to break bonds and the total energy released when new bonds are formed.

Enthalpy = H. Change in enthalpy = ΔH (measured in (kJ/mol or kJ mol^{-1})

A standard enthalpy change of reaction $\Delta H^{\ominus}$ refers to the enthalpy change (the amount of heat energy absorbed or released by a system) that occurs when a reaction takes place under standard conditions, with all reactants and products in their standard states.

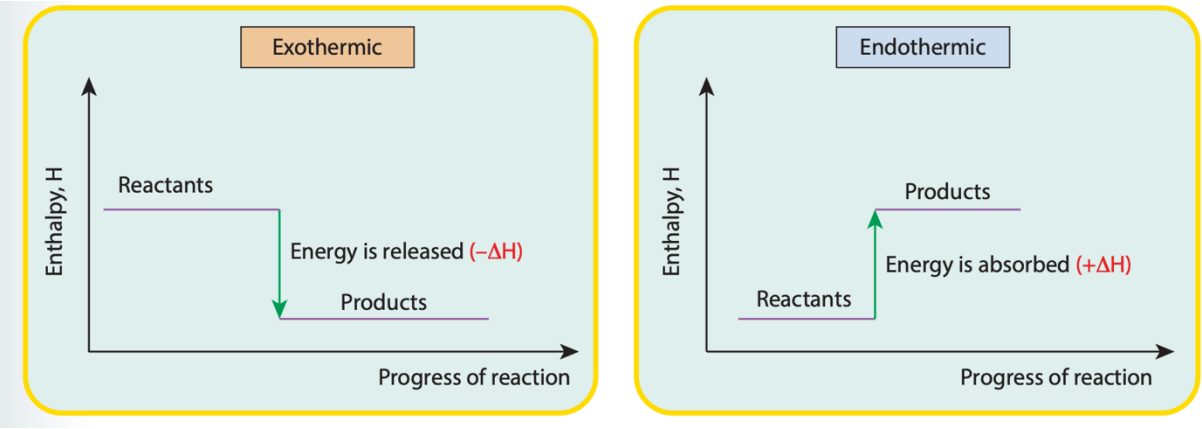
Exothermic reactions

- **Exothermic** reactions are chemical reactions that **release energy to the surroundings** in the form of heat.
- This causes the temperature of the surroundings to increase (e.g. the reaction vessel feels warm to touch).
- More energy is released in forming bonds than is absorbed in breaking bonds.
- A **negative value** for ΔH indicates an **exothermic** reaction since the **system loses energy.**

Endothermic reactions

- Chemical reactions that **absorb energy** from the surroundings in the form of heat.
- This causes the temperature of the surroundings to decrease (e.g. the reaction vessel feels cool to touch).
- Less energy is released in forming bonds than is absorbed in breaking bonds.
- A **positive value** for ∆H indicates an **endothermic** reaction, since the **system gains energy.**

Enthalpy diagrams



Processes of energy transfer

The law of conservation of energy states that energy can neither be created nor destroyed but simply changed from one form to another.

This principle underpins all thermochemical processes

Rusting of iron: Exothermic – energy released

Respiration: Exothermic – energy released

Photosynthesis: Endothermic **–** energy absorbed by plant

Thermal decomposition: Breakdown of a chemical caused by heat – endothermic reaction: energy is transferred from the surroundings to the system.

Physical changes: Can be exothermic or endothermic – involve losing/gaining energy to/from surroundings

Bond enthalpy

Bond enthalpies can be used to calculate ΔH by focusing on the energy required to break bonds and the energy released when new bonds are formed.

Bond enthalpy (also known as bond energy) is the average energy required to break one mole of a particular type of covalent bond into separate atoms when all chemical species are in the gaseous state.

- Bond enthalpy values are averages because the energy required to break a specific bond can vary depending on its chemical environment.

Calculate the value of ΔH using average bond enthalpy values

Since breaking bonds requires energy, it's an endothermic process (+ΔH).

Since forming bonds releases energy, it's an exothermic process (−ΔH).

Step 1: Draw out the full structure of all reactants and products.

Step 2: Identify the bonds that have been broken in the reactants.

Step 3: Add bond enthalpy values to find the combined bond enthalpies for all bonds broken. Since bonds are being broken, this value is positive.

Step 4: Identify the bonds that have been formed in the products.

Step 5: Add bond enthalpy values (provided) to find the combined bond enthalpies for all bonds formed. Since bonds are being formed, this value is negative.

Step 6: Calculate ΔH by adding the values from steps 3 and 5 together.

If the answer to step 6 is negative, the reaction is exothermic. If the value is positive, this reaction is endothermic.

Enthalpy changes of neutralisation

The enthalpy change of neutralisation ($\Delta H^{\ominus}_{n}$) is the enthalpy change (the amount of heat energy absorbed or released by a system) when one mole of H^+ ions from an acid reacts with one mole of OH^- ions from a base to form one mole of water (under standard conditions).

- Neutralisation reactions are exothermic.
- There is a transfer of energy from the system to the surroundings.
- The temperature rises.
- For any strong acid and strong base, the ΔH is approx. −57 kJ mol^{-1}.

Calorimetry

Calorimetry is the process of experimentally measuring the amount of heat energy released or absorbed in a physical or chemical change.

A calorimeter is any device or apparatus used to measure the amount of heat exchanged between a system and its surroundings.

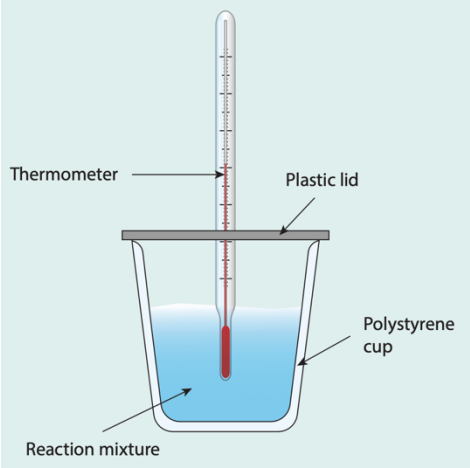
Experiment 23: Investigate, using primary data, how to determine ΔH for a suitable neutralisation reaction

A known number of moles of a strong acid is mixed with a known number of moles of a strong base, e.g. HCl + NaOH → NaCl + H_2O

The temperature of the acid and base is recorded separately. They are then carefully mixed – in a polystyrene cup – and the mixture is stirred, the lid of the polystyrene cup is replaced, and the change in temperature measured (using a thermometer).

If a strong acid & base are used the temperature will rise – this is an exothermic reaction.

Using more concentrated solutions results in a bigger temperature rise and less percentage error.



Sources of error

The polystyrene coffee cup is not a perfect insulator (it does allow some heat loss to the surroundings). This heat loss results in the maximum recorded temperature being lower than the true value.

The specific heat capacity of the solution is assumed to be the same as that of pure water (this is a simplification).

Possible improvements

• To improve insulation, two polystyrene cups could be used – one nestled inside the other.

• A thermometer that reads to 0.1°C could be used to improve accuracy.

• Using burettes (or pipettes) rather than graduated cylinders to measure the acid and base would make the volumes more accurate.

Once the temperature change is recorded, the enthalpy change is calculated using the formula m × c × Δt.

Calculating ΔH for a neutralisation reaction

Step 1: Calculate the heat energy transferred.

$$q = m \times c \times \Delta t$$

q = heat energy transferred (heat energy absorbed or released)

m = mass of solution (in kilograms)

c = specific heat *capacity (the amount of heat required to raise the temperature of 1 kg of that substance by 1 kelvin)*

Δt = change in temperature (which can be calculated by final temperature minus initial temperature)

Step 2: Work out how many moles caused this heat change.

Step 3: Calculate the heat change for one mole.

Step 4: Check the sign of ΔH.

Note:
If heat capacity, C, is given, then the equation is q = C x Δt
If the acid is diprotic, divide your final answer by 2.

Enthalpy changes of formation

The standard enthalpy change of formation, $\Delta H^{\ominus}_f$, is the enthalpy change (the amount of heat energy absorbed or released by a system) when one mole of a compound is formed from its elements in their standard states under standard conditions.

Writing formation equations

Step 1: Write the formula for one mole of the compound on the product side of the equation.

Step 2: On the reactant side, write the elements that the compound is formed from.

Step 3: Balance the equation.

Calculating enthalpies of reaction

$$\Delta H^\circ_{reaction} = \sum \Delta H^\circ_f(products) - \sum \Delta H^\circ_f(reactants)$$

Where ∑ means the 'sum of'.

Note that the enthalpy of formation of any element in its standard state is zero.

Enthalpy changes of combustion

Combustion reactions refer to the burning of a fuel in oxygen. They are exothermic reactions.

The standard enthalpy of combustion ($\Delta H^{\ominus}_c$) is the enthalpy change when one mole of a substance is completely burnt in excess oxygen under standard conditions.

Writing combustion equations

Hydrocarbons and primary alcohols burn in oxygen to produce carbon dioxide and water vapour.

Step 1: Write the formula for one mole of the hydrocarbon or alcohol.

Step 2: Since all fuels burn in oxygen, add oxygen to the reactants.

Step 3: All hydrocarbons and primary alcohols burn to produce carbon dioxide and water. Write these as products.

Step 4: Balance the equation (remember the order CHO).

Explaining trends

- As the size of the hydrocarbon molecule increases, the ΔH becomes more negative = more energy is released during the combustion of larger hydrocarbons.
- Although the energy required to break bonds increases as hydrocarbons become larger, the energy released when larger hydrocarbons react to form carbon dioxide and water is significantly greater.
- This is also true for alkenes and alkynes and alcohols: the larger the molecule, the greater the energy released.

Experiment 24: Investigate the energy change of combustion of a series of alcohols (EI)

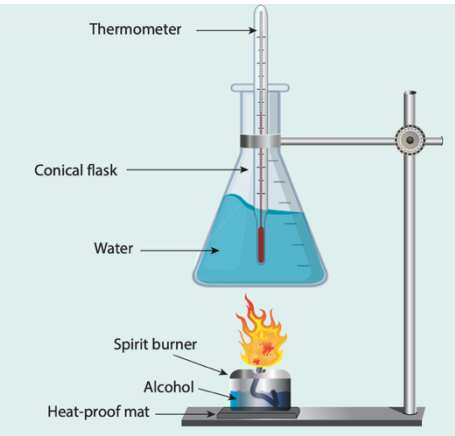
• Measure and record the initial mass of the spirit burner containing the alcohol (including its cap).

• A known volume of water is measured into a conical flask.

• The temperature of the water is measured and recorded.

• The spirit burner is placed on a heat-proof mat.

• The apparatus is arranged as shown.



• The cap of the spirit burner is removed and the wick lit.

• The alcohol is burnt until a certain temperature increase is achieved – e.g. the temperature rises by 40°C.

• The water is continuously stirred to ensure an even distribution of heat.

• When the temperature increase is reached, the spirit burner cap is replaced to extinguish the flame.

• Once cool, the final mass of the spirit burner is measured to determine the mass of alcohol burned.

• This is repeated using separate spirit burners each containing a different alcohol.

Safety

• Alcohols are flammable.
• Light the wick with a lit splint.

Once the mass of water, mass of fuel (i.e. alcohol) burnt and temperature change are recorded, the ΔH is calculated using the equation $q = m \times c \times \Delta t$.

Possible reasons for inaccurate results

• The makeshift calorimeter used (a conical flask containing water) is not a very good calorimeter. It is not insulated, or covered. This leads to significant heat loss to the surroundings. (A metal calorimeter – e.g. a copper calorimeter – would be more suitable, and the calorimeter should be covered.)

• Incomplete combustion of the alcohol. If the alcohol doesn't combust completely, carbon monoxide (CO) and carbon soot may be produced instead of carbon dioxide. You would see the carbon soot as a black layer inside the flask.

• The wick may not have been lit immediately. As a result, some of the alcohol may have evaporated before combustion began, leading to less alcohol being burnt.

• The values given in this page are standard values – i.e. values obtained under a standard set of conditions of temperature and pressure. The lab conditions for your experiment may differ from standard conditions.

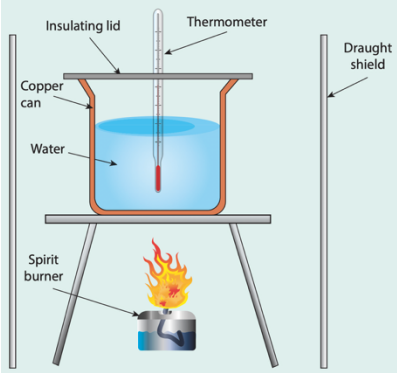
• Air movement in the lab can carry heat away from the flame and the conical flask, reducing the efficiency of heat transfer to the water.

Possible improvements

• Use a metal calorimeter with a lid.

• Light the wick immediately after removing the cap of the spirit burner.

• Place draught shields around the experiment as they can reduce heat loss.



Calculate the ΔH of combustion of alcohols

Step 1: Calculate the heat energy transferred.

$$q = m \times c \times \Delta t$$

Step 2: Work out how many moles caused this heat change.

Step 3: Calculate the heat change for one mole.

Step 4: Check the sign of ΔH.

Hess's Law

Hess's law states that the total enthalpy change for a chemical reaction is independent of the path taken (i.e. it's the same whether the reaction takes place in one or more stages).

Step 1: Write your 'star equation'. (Your star equation is the equation whose ΔH you are trying to calculate).

Step 2: Change the given equations to most closely resemble the star equation.

Step 3: Circle the star equation. Make sure everything else 'cancels'.

Step 4: Add the ΔH values together.

Example:

Using the following data, calculate ΔH for the combustion of C_8H_{18}.

(1) $8C + 9H_2 \longrightarrow C_8H_{18}$ $\Delta H = -250.3 kJ\ mol^{-1}$

(2) $C + O_2 \longrightarrow CO_2$ $\Delta H = -393.5 kJ\ mol^{-1}$

(3) $H_2 + ½O_2 \longrightarrow H_2O$ $\Delta H = -285.8 kJ\ mol^{-1}$

Step 1

A hydrocarbon burns in oxygen to produce carbon dioxide and water. (Be sure to balance the equation!)

$$\bigstar C_8H_{18} + 12½O_2 \longrightarrow 8CO_2 + 9H_2O \bigstar$$

Step 2

(1) ↩ $C_8H_{18} \longrightarrow 8C + 9H_2$ $\Delta H = +250.3 kJ\ mol^{-1}$

(2) x8 $8C + 8O_2 \longrightarrow 8CO_2$ $\Delta H = -393.5(8) kJ\ mol^{-1}$

(3) x9 $9H_2 + 4½O_2 \longrightarrow 9H_2O$ $\Delta H = -285.8(9) kJ\ mol^{-1}$

Step 3

(1) ↩ $C_8H_{18} \longrightarrow 8C + 9H_2$ $\Delta H = +250.3 kJ\ mol^{-1}$

(2) x8 $8C + 8O_2 \longrightarrow 8CO_2$ $\Delta H = -3148 kJ\ mol^{-1}$

(3) x9 $9H_2 + 4½O_2 \longrightarrow 9H_2O$ $\Delta H = -2572.2 kJ\ mol^{-1}$

Step 4

$\Delta H = +250.3 - 3148 - 2572.2 =$ **$-5469.9 kJ\ mol^{-1}$**