Edexcel International AS Chemistry

Your notes

Energetics

Contents

Your notes

Enthalpy Level Diagrams

- The total chemical energy inside a substance is called the **enthalpy** (or heat content)
- When chemical reactions take place, changes in chemical energy take place and therefore the enthalpy changes
- An **enthalpy change** is represented by the symbol ΔH (Δ= change; H = enthalpy)
- An enthalpy change can be positive or negative

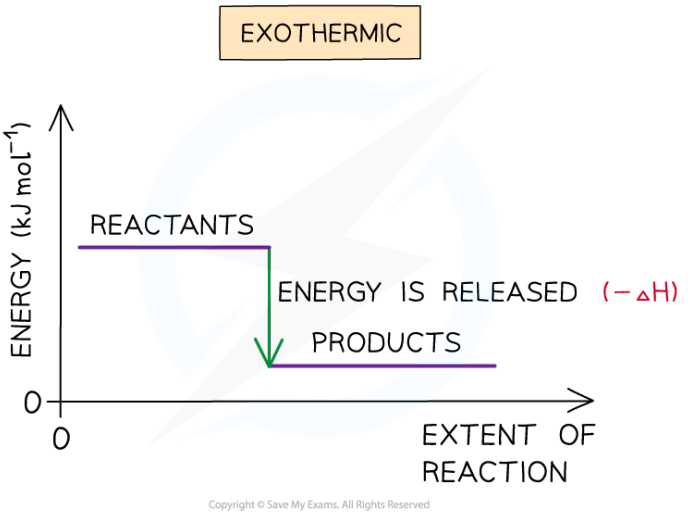
Examiner Tips and Tricks

Activation energy is not shown in enthalpy level diagrams

Activation is shown in reaction profile diagrams

Exothermic reactions

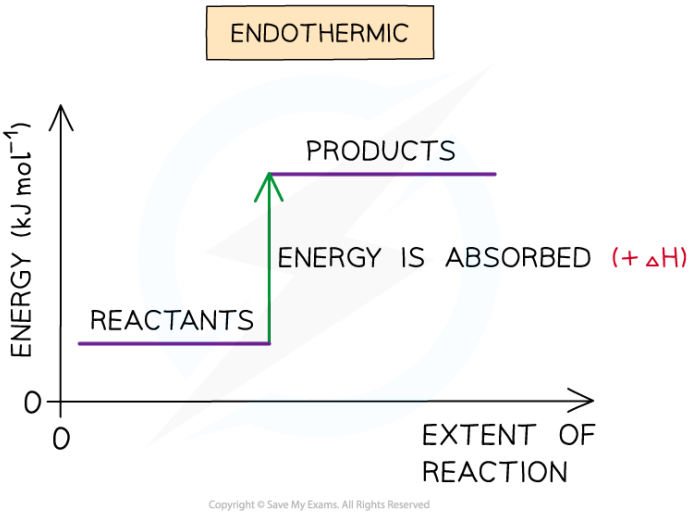
- A reaction is exothermic when the products have less energy than the reactants
- Heat energy is **given off** by the reaction **to the surroundings**
  - The **temperature** of the **environment increases** - this can be measured with a thermometer
  - The **energy** of the **system decreases**
- There is an enthalpy decrease during the reaction so ΔH is negative
- Exothermic reactions are **thermodynamically** possible (because the enthalpy of the reactants is **higher** than that of the products)
- However, if the rate is too slow, the reaction may not occur
  - In this case the reaction is **kinetically** controlled



The enthalpy change during an exothermic reaction

Endothermic reactions

- A reaction is endothermic when the products have more energy than the reactants
- Heat energy is **absorbed by** the reaction **from** the **surroundings**
  - The **temperature** of the **environment decreases** - this can be measured with a thermometer
  - The **energy** of the **system increases**
- There is an enthalpy increase during the reaction so ΔH is positive



The enthalpy change during an endothermic reaction

Examiner Tips and Tricks

It is important to specify the physical states of each species in an equation when dealing with enthalpy changes as any changes in state can cause very large changes of enthalpy. For example:

$$NaCl\,(s) \rightarrow Na^{+}\,(aq) + Cl^{-}\,(aq) \quad \Delta H = +4\ kJ\ mol^{-1}$$

$$NaCl\,(g) \rightarrow Na^{+}\,(g) + Cl^{-}\,(g) \quad \Delta H = +500\ kJ\ mol^{-1}$$

Also, remember that the **system** is the substances **that are reacting** (i.e. the reaction itself) and the **surroundings is everything else** (e.g. the flask the reaction is taking place in).

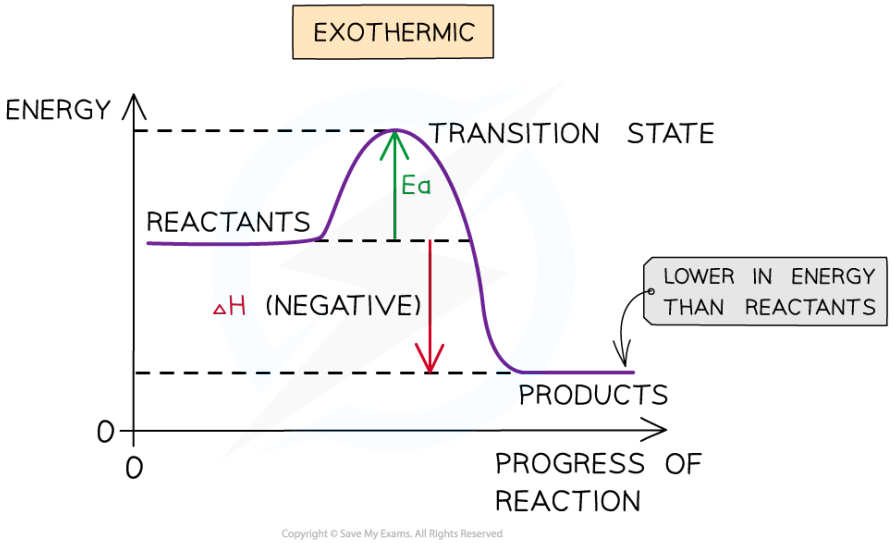
Your notes

Reaction profile diagrams

- Reaction profile diagrams are similar to enthalpy level diagrams
  - The difference between the energy level of the reactants and the energy level of the products is still the overall enthalpy change of the reaction, ΔH
- The main differences are that they include information about:
  - The activation energy, E_a, of the reaction
    - **Activation energy** can be defined as '*the minimum amount of energy needed for reactant molecules to have a successful collision and start the reaction*'
    - This is the difference between the energy level of the reactants and the peak of the curve
  - Possible transition states
    - The peak of the curve indicates a transition state
    - The **transition state** is a stage during the reaction at which chemical bonds are partially broken and formed
    - The transition state is very unstable – a molecule in the transition state cannot be isolated and is higher in energy than the reactants and products

Exothermic reaction profiles

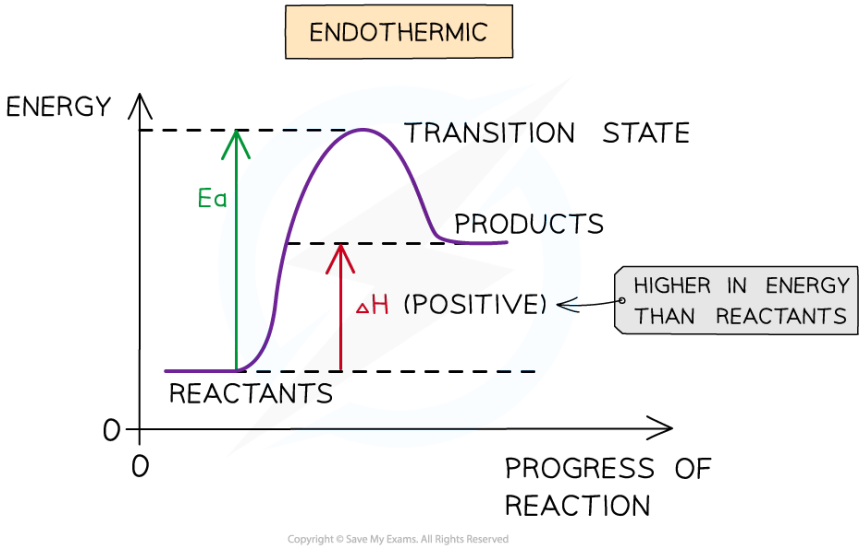
- In an exothermic reaction, the reactants are higher in energy than the products
- The reactants are therefore closer in energy to the transition state
- This means that exothermic reactions have a lower activation energy compared to endothermic reactions



The reaction profile diagram for a general exothermic reaction

Endothermic reaction profiles

- In an endothermic reaction, the reactants are lower in energy than the products
- The reactants are therefore further away in energy from the transition state
- This means that endothermic reactions have a higher activation energy compared to exothermic reactions



The reaction profile diagram for a general endothermic reaction

Your notes

Your notes

Enthalpy Change – Definitions

- To be able to compare the changes in enthalpy between reactions, all thermodynamic measurements are carried out under standard conditions
- These standard conditions are:
  - A **pressure** of 100 kPa (you may see some older exam questions that use a figure of 101 kPa; the exact figure is 101 325 Pa, but it has been simplified in the current syllabus for problem-solving purposes)
  - A **temperature** of 298 K (25 ^{o}C)
  - Each substance involved in the reaction is in its **standard physical state** (solid, liquid or gas)
- To show that a reaction has been carried out under standard conditions, the symbol '≡' is used
  - $\Delta H^{\equiv}$ = the standard enthalpy change
- There are a number of standard definitions relating to enthalpy changes that you are expected to know

Enthalpy Definitions Table

Your notes

Standard Enthalpy Change of ...	Definition	Symbol	Exothermic / Endothermic
Reaction	The enthalpy change when the reactants in the **stoichiometric equation** react to give the products under standard conditions	$\Delta H_r^{\ominus}$	Both
Formation	The enthalpy change when **one mole** of a compound is **formed** from its **elements** under standard conditions	$\Delta H_f^{\ominus}$	Both
Combustion	The enthalpy change when **one mole** of a substance is **burnt** in excess oxygen under standard conditions	$\Delta H_c^{\ominus}$	Exothermic
Neutralisation	The enthalpy change when **one mole** of **water** is **formed** by reacting an acid and alkali under standard conditions	$\Delta H_{neut}^{\ominus}$	Exothermic

- A further definition that is expected knowledge, although less used at AS level, is:
  - **Standard enthalpy of atomisation** - the enthalpy change when **one mole** of **gaseous atoms** is formed from an element in its standard state, under standard conditions

Examiner Tips and Tricks

You will see various enthalpy change symbols used with subtle changes, e.g.

$\Delta H_c^{\equiv}$ or $\Delta_c H^{\equiv}$ for enthalpy of combustion

Whichever symbol you use must have the following basic points:

- Δ to represent change
- H to represent enthlalpy
- $\equiv$ to respresent standard conditions
- A symbol to represent the type of enthalpy change occurring, e.g.
  - c for combustion
  - f for formation

- neut for neutralisation
- r for reaction

Your notes

Worked Example

Calculating the enthalpy change of reaction

One mole water is formed from hydrogen and oxygen, releasing 286 kJ of energy

$$H_2(g) + ½O_2(g) \rightarrow H_2O(l) \quad \Delta H_r^{\ominus} = -286 \text{ kJ mol}^{-1}$$

Calculate $\Delta H_r^{\ominus}$ for the reaction below:

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$$

Answer

- Since two moles of water molecules are formed in the question above, the energy released is simply:
- $\Delta H_r^{\ominus} = 2 \text{ mol} \times (-286 \text{ kJ mol}^{-1}) = -572 \text{ kJ mol}^{-1}$

Worked Example

Calculating the enthalpy change

Calculate $\Delta H_f^{\ominus}$ for the reaction below, given that $\Delta H_f^{\ominus} [Fe_2O_3(s)] = -824.2 \text{ kJ mol}^{-1}$

$$4Fe(s) + 3\,O_2(g) \rightarrow 2\,Fe_2O_3(s)$$

Answer

- Since two moles of Fe_2O_3 (s) are formed the total change in enthalpy for the reaction above is:
  - $\Delta H_f^{\ominus} = 2 \times (-824.2 \text{ kJ mol}^{-1}) = -1648 \text{ kJ}$

Worked Example

Calculating enthalpy changes

Identify each of the following as $\Delta H_r^{\ominus}$, $\Delta H_f^{\ominus}$, $\Delta H_c^{\ominus}$ or $\Delta H_{neut}^{\ominus}$

1. $MgCO_3(s) \rightarrow MgO(s) + CO_2(g)$
2. $C \text{ (graphite)} + O_2(g) \rightarrow CO_2(g)$
3. $HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$

Answer

Answer 1: $\Delta H_r^{\ominus}$

Answer 2: $\Delta H_f^{\ominus}$ as one mole of CO_2 is formed from its elements in standard state *and* $\Delta H_c^{\ominus}$ as one mole of carbon is burnt in oxygen

Answer 3: $\Delta H_{neut}^{\ominus}$ as one mole of water is formed from the reaction between an acid and an alkali

Examiner Tips and Tricks

The $\Delta H_f^{\ominus}$ of an **element** in its standard state is zero.

For example, $\Delta H_f^{\ominus}$ of $O_2(g)$ is 0 kJ mol^{-1}

Your notes

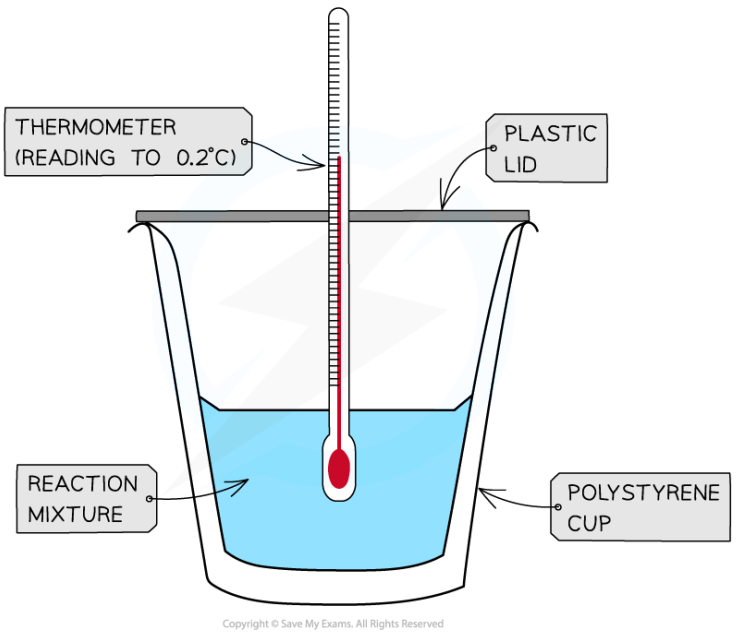
Your notes

Using Calorimetry

- **Calorimetry** is the measurement enthalpy changes in chemical reactions
- There are two types of calorimetry experiments you need to know:
  - **Enthalpy** changes of **reactions in solution**, e.g. displacement and neutralisation
  - **Enthalpy** changes of **combustion**
- In both cases, you should be able to give an outline of the experiment and be able to process experimental data using calculations or graphical methods

Enthalpy changes for reactions in solution

- The principle of these calorimetry experiments is to carry out the reaction with an excess of one reagent and measure the temperature change over the course of a few minutes
- The apparatus needed to carry out an enthalpy of reaction in solution calorimetry experiment is shown below
  - A **calorimeter** can be made up of a **polystyrene drinking cup**, a **vacuum flask** or **metal can**



A polystyrene cup can act as a calorimeter to find enthalpy changes in a chemical reaction

The energy needed to raise the temperature of 1 g of a substance by 1 K is called the **specific heat capacity** (c) of the liquid The **specific heat capacity** of water is 4.18 J g^{-1} K^{-1} The energy transferred as heat can be calculated by:

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

q = THE HEAT TRANSFERRED, J
m = THE MASS OF WATER, g
c = THE SPECIFIC HEAT CAPACITY, $J\,g^{-1}K^{-1}$
ΔT = THE TEMPERATURE CHANGE, K

Equation for calculating energy transferred in a calorimeter

Sample method for a displacement reaction

1. Using a measuring cylinder place 25 cm^3 of the 1.0 mol dm^{-3} copper(II) sulphate solution into the polystyrene cup
2. Weigh about 6 g of zinc powder - as this is an excess there is no need to be very accurate
3. Draw a table to record the initial temperature and then the temperature and time every half minute up to 9.5 minutes
4. Put a thermometer or temperature probe in the cup, stir, and record the temperature every half minute for 2.5 minutes
5. At precisely 3 minutes, add the zinc powder to the cup (DO NOT RECORD THE TEMPERATURE AT 3 MINUTES)
6. Continue stirring and record the temperature for an additional 6 minutes

- For the purposes of the calculations, some assumptions are made about the experiment:
  - That the specific heat capacity of the solution is the same as pure water, i.e. **4.18 $J\,g^{-1}K^{-1}$**
  - That the density of the solution is the same as pure water, i.e. **1 $g\,cm^{-3}$**
  - The specific heat capacity of the container is ignored
  - The reaction is complete
  - There are negligible heat losses

Examiner Tips and Tricks

As well as any assumptions made for the experiment, you can be expected to comment on:

- Sources of error, e.g. incorrect masses or volumes of chemicals, heat loss to the surroundings, etc.
- Uncertainty, e.g. measurements for mass, volume and temperature

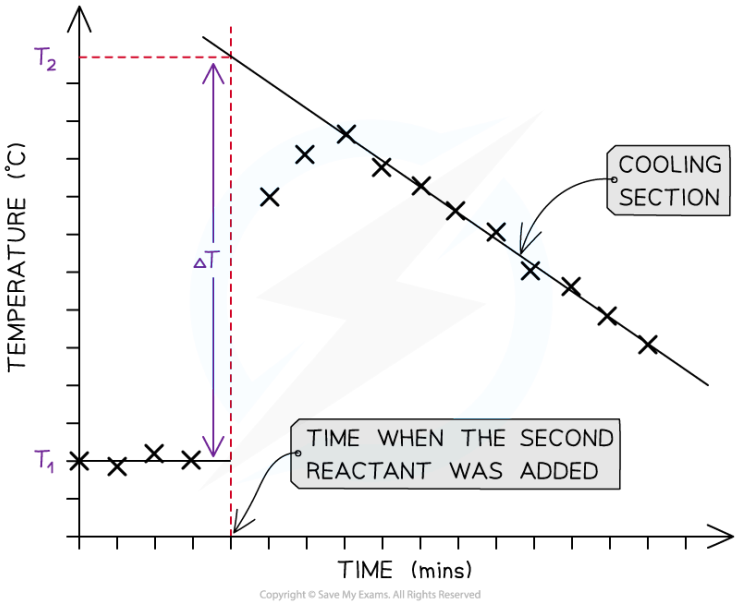
Your notes

- Be aware that you will have to double the uncertainty reading for temperature as the calculation requires an initial and final temperature to determine the temperature change

Your notes

Temperature correction graphs

- For reactions which are not instantaneous there may be a delay before the maximum temperature is reached
- During that delay the substances themselves may be losing heat to the surroundings, so that the true maximum temperature is never actually reached
- To overcome this problem we can use graphical analysis to determine the maximum enthalpy change



A temperature correction graph for a metal displacement reaction between zinc and copper sulfate solution. The zinc is added after 4 minutes

The steps to make a temperature correction graph are:

1. Take a temperature reading before adding the reactants for a few minutes to get a steady value
2. Add the second reactant and continue recording the temperature and time
3. Plot the graph and **extrapolate** the cooling part of the graph until you intersect the time at which the second reactant was added

Analysis

- Use both extrapolated lines to calculate ΔT as shown on the graph
- Use the equation $q = mc\Delta T$ to calculate the energy transferred
  - q = energy transferred

- m = mass - this will be the mass of the 25 cm^3 solution which will be 25 g (assuming a density of 1 g cm^{-3})
- c = specific heat capacity - this will be assumed to be 4.18 J g^{-1} K^{-1}, which is the specific heat capacity of water
- ΔT = the temperature change from the graph

- Convert your value for energy transferred from J into kJ
- Then use the equation $\Delta H = \frac{q}{n}$ to calculate the enthalpy change for the reaction
  - q = energy transferred
  - n = number of moles - this would be the number of moles of the **limiting reagent**, which means that you will have an extra calculation to do to determine whether this is the zinc or the copper sulfate
- Remember that in the example above, the temperature of the reaction mixture increased which means that the reaction is exothermic and should, therefore, have a negative value

Worked Example

Enthalpy of neutralisation calculation

The initial temperature of 25.0 cm^3 of sodium hydroxide and 50.0 cm^3 of sulfuric acid was measured every 30 seconds for 3 minutes. The two liquids were then mixed and the temperature of the resulting solution was taken every 30 seconds for 5 minutes. A temperature correction graph of the results was plotted and the temperature change was determined to be 6.5 °C.

Calculate the energy transferred during this reaction.

Answer

- $q = m \times c \times \Delta T$
  - m (of resulting solution) = 25.0 + 50.0 = 75.0 g
  - c (of water) = 4.18 J g^{-1} °C^{-1}
  - ΔT (of water) = 6.5 °C
  - q = 75.0 x 4.18 x 6.5 = 2038 J

Examiner Tips and Tricks

It is more likely that you would be asked to calculate the enthalpy change for this neutralisation reaction

Your notes

1. Calculate the number of moles of NaOH and H_2SO_4 to determine which reactant is the **limiting reagent**
2. Calculate the enthalpy change by dividing the energy transferred by the number of moles of the limiting reagent

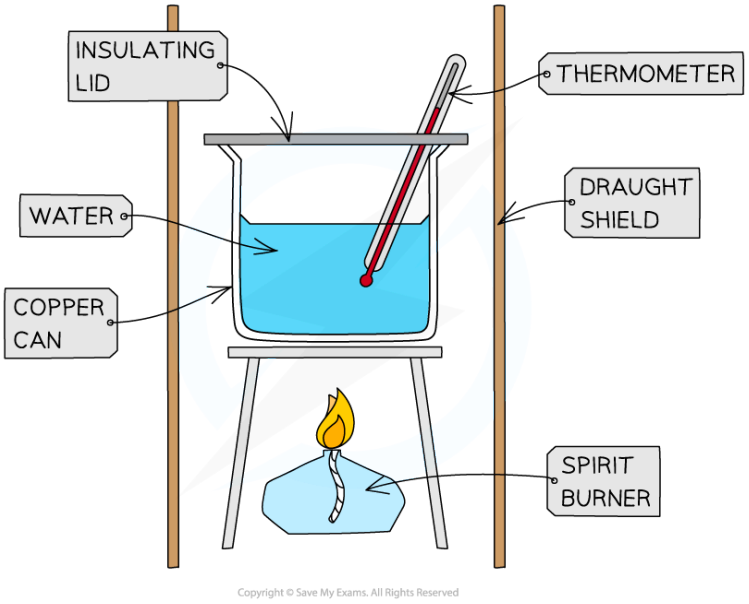
Another twist to this calculation could be for the NaOH and H_2SO_4 to have different initial temperatures

- In this case, you work out the energy transferred for the NaOH and for the H_2SO_4 separately and then add them together
- After that you follow steps 1 and 2 above to calculate the enthalpy change

Your notes

Enthalpy of combustion

- The principle here is to use the heat released by a combustion reaction to increase the heat content of water
- A typical simple calorimeter is used to measure the temperature changes to the water

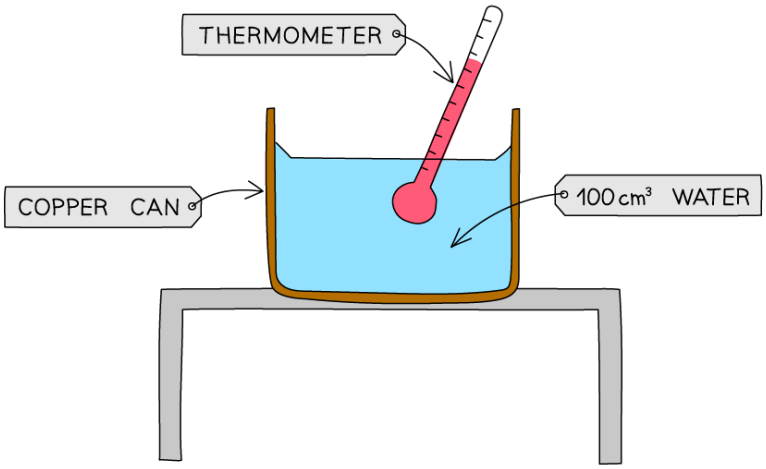


A simple combustion calorimeter

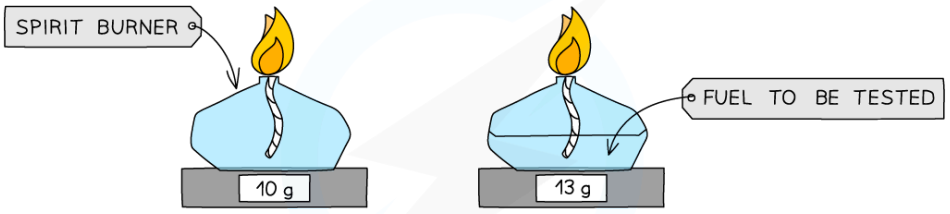
- To complete this experiment, the following steps will need to be completed:

Your notes

1 FILL COPPER CAN WITH 100 cm^3 OF WATER. RECORD INITIAL TEMPERATURE WITH THERMOMETER.



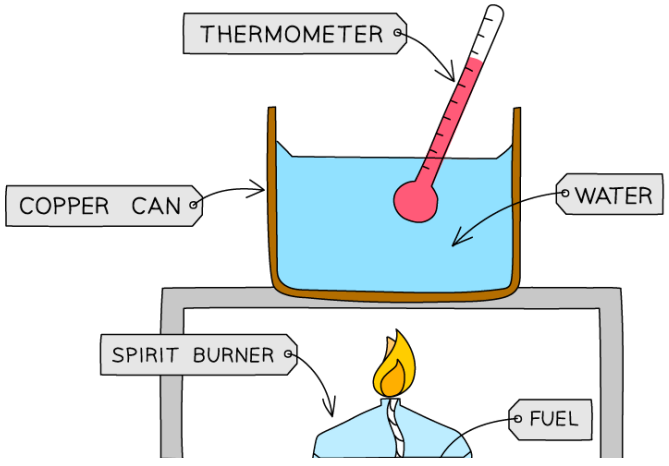
2 MEASURE AND RECORD THE MASS OF AN EMPTY SPIRIT BURNER. ADD FUEL AND RECORD MASS



3 LIGHT THE WICK. HEAT WATER (STIRRING CONSTANTLY) FOR SET TIME/UNTIL FUEL IS COMPLETELY BURNT.

RECORD TEMPERATURE OF WATER.

MEASURE MASS OF BURNER + ANY REMAINING FUEL. SUBTRACT TO FIND MASS OF FUEL BURNT.



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Your notes

- It is important that you record the starting temperature, and the final temperature in order to complete the calculations
- You must also record the starting mass of the spirit burner and the final mass of the spirit burner, so that you can work out the mass of the fuel burned during the reaction
  - This will then be used to calculate the moles, which will be used to convert Q to an enthalpy change in your calculations

Key points to consider

- Not all the heat produced by the combustion reaction is transferred to the water
  - Some heat is lost to the surroundings
  - Some heat is absorbed by the calorimeter
- To minimise the heat losses the copper calorimeter should not be placed too far above the flame and a lid placed over the calorimeter
- Shielding can be used to reduce draughts
- In this experiment the main sources of error are
  - **Heat losses**
  - **Incomplete combustion**

Worked Example

Enthalpy of combustion

In a calorimetry experiment 2.50 g of methane is burnt in excess oxygen.

30% of the energy released during the combustion is absorbed by 500 g of water, the temperature of which rises from 25 °C to 68 °C.

The specific heat capacity of water is 4.18 J g^{-1} K^{-1}

What is the total energy released per gram of methane burnt?

Answer

Step 1:

- $q = m \times c \times \Delta T$
  - m (of water) = 500 g
  - c (of water) = 4.18 J g^{-1} $°C^{-1}$
  - ΔT (of water) = 68 °C - 25 °C = 43 °C

Step 2:

- $q = 500 \times 4.18 \times 43 = 89\,870$ J

Step 3:

- This is only 30% of the total energy released by methane
  - Total energy x 0.3 = 89 870 J
  - Total energy = 299 567 J

Step 4:

- This is released by 2.50 g of methane
  - Energy released by 1.00 g of methane = 299 567 ÷ 2.50 = 120 000 J g^{-1} (to 3 s.f.) or 120 kJ g^{-1}

Your notes

Calculating Enthalpy Changes

- Aqueous solutions of acid, alkalis and salts are assumed to be largely water so you can just use the m and c values of water when calculating the energy transferred.
- To calculate any changes in enthalpy per mole of a reactant or product the following relationship can be used:

$$\Delta H = \frac{q}{n} \text{ or } \frac{m \times c \times \Delta T}{n}$$

- When there is a rise in temperature, the value for ΔH becomes negative suggesting that the reaction is exothermic
  - This means that your value should be negative for an exothermic reaction, e.g. combustion
- When the temperature falls, the value for ΔH becomes positive suggesting that the reaction is endothermic
  - This means that your value should be positive for an endothermic reaction, e.g. ammonium salts dissolving in water

Worked Example

1.50 g of an organic liquid (M_r = 58.0) underwent complete combustion. The heat formed raised the temperature of 100 g of water from 20 °C to 75 °C.

Calculate the enthalpy of combustion for the organic liquid

Answer

Step 1: Calculate the energy released by the organic liquid

- $Q = mc\Delta T$
  - $Q = 100 \times 4.18 \times (75 - 20)$
  - $Q = 22990$ J
  - $Q = 22.99$ kJ

Step 2: Calculate the number of moles of the organic liquid

- Number of moles = $= \frac{mass}{molar\ mass} = \frac{1.50}{58.0} =$ 0.0259 moles (to 3s.f.)

Step 3: Calculate the enthalpy change of combustion

- $\Delta_c H^\theta = \frac{Q}{n} = \frac{22.99}{0.0259} =$ -887 kJ mol^{-1} (to 3s.f.)
  - Remember, combustion is an exothermic process and will, therefore, be a negative enthalpy change value

Your notes

Your notes

Hess Cycles – Construction

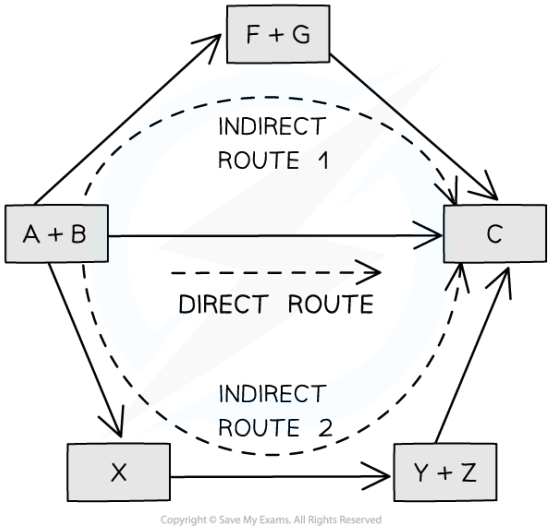
- In 1840, the Russian chemist Germain Hess formulated a law which went on to be known as **Hess's Law**
- This went on to form the basis of one of the laws of thermodynamics. The first law of thermodynamics relates to the **Law of Conservation of Energy**
- It is sometimes expressed in the following form:

Energy cannot be created or destroyed, it can only change form

- This means that in a **closed system**, the total amount of energy present is always constant
- Hess's law can be used to calculate the standard enthalpy change of a reaction from known standard enthalpy changes
- Hess's Law states that:

"The total enthalpy change in a chemical reaction is independent of the route by which the chemical reaction takes place as long as the initial and final conditions are the same."

- This means that whether the reaction takes place in one or two steps, the total enthalpy change of the reaction will still be the same



According to Hess' Law, the enthalpy change of the direct route, going from reactants (A+B) to product (C), is equal to the enthalpy change of the indirect routes

- Hess' Law is used to calculate enthalpy changes which can't be found experimentally using **calorimetry**, e.g.:

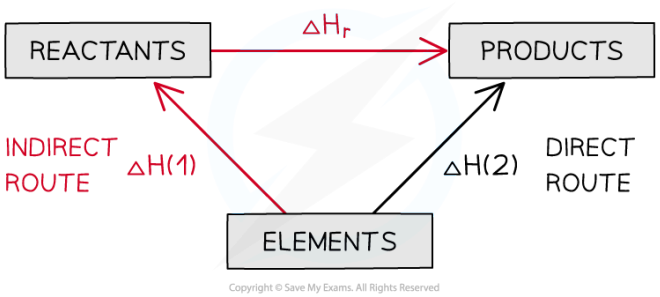
$$3C\,(s) + 4H_2\,(g) \rightarrow C_3H_8(g)$$

- $\Delta_f H$ (propane) can't be found experimentally as hydrogen and carbon don't react under standard conditions

Your notes

Calculating ΔH_r from ΔH_f using Hess's Law energy cycles

- You can see the relationships on the following diagram:



The enthalpy change from elements to products (direct route) is equal to the enthalpy change of elements forming reactants and then products (indirect route)

- The products can be formed:
  - Directly from the elements = ΔH_2
    OR
    Indirectly from the elements = $\Delta H_1 + \Delta H_r$
- **Equation**

$$\Delta H_2 = \Delta H_1 + \Delta H_r$$

- Therefore for energy to be conserved,

$$\Delta H_r = \Delta H_2 - \Delta H_1$$

Examiner Tips and Tricks

You do not need to learn Hess's Law word for word as it is not a syllabus requirement, but you do need to understand the principle as it provides the foundation for all the problem solving in Chemical Energetics

Hess Cycles – Calculations

Calculating ΔH_r from ΔH_f using Hess's Law energy cycles

- Knowing the enthalpy change of formation, ΔH_f, allows us to determine the overall enthalpy change of a reaction, ΔH_r
- To do this, we follow these steps:

1. Write the equation for the reaction
2. Write the elements with the correct **number of moles** and **state symbols** underneath
3. Draw **upwards pointing arrows** to each compound
4. Write the appropriate **values** on the arrows and **multiply** by the number of moles
5. In a cycle, go from the reactants to the products, changing the sign of the value if the arrow points in the opposite direction

Your notes

Worked Example

Calculating the enthalpy change of reaction

Use the information in the table to calculate the enthalpy change for this reaction:

$$NH_4NO_3(s) + ½C(s) \rightarrow N_2(g) + 2H_2O(g) + ½CO_2(g)$$

Substance	C (s)	N_2 (g)	H_2O(g)	CO_2 (g)	NH_4NO_3 (s)
$\Delta H_f^\ominus$ / kJ mol^{-1}	0	0	-242	-394	-365

Answer:

Step 1: Write the balanced equation

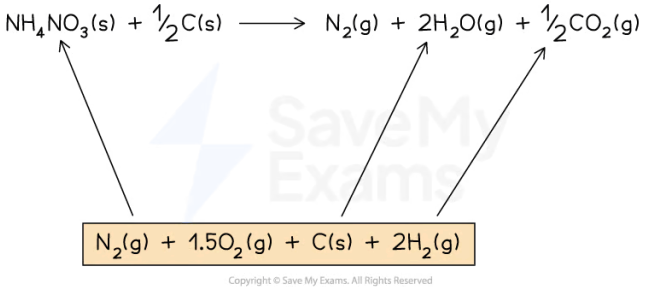
$$NH_4NO_3(s) + \frac{1}{2}C(s) \longrightarrow N_2(g) + 2H_2O(g) + \frac{1}{2}CO_2(g)$$

Step 2: Write the elements with the correct **number of moles** and **state symbols** underneath

$$NH_4NO_3(s) + \frac{1}{2}C(s) \longrightarrow N_2(g) + 2H_2O(g) + \frac{1}{2}CO_2(g)$$

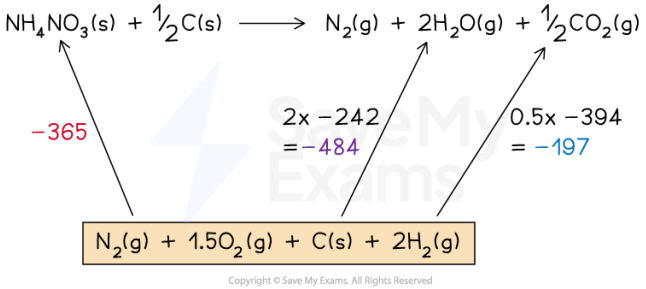
$$N_2(g) + 1.5O_2(g) + C(s) + 2H_2(g)$$

Step 3: Draw **upwards pointing arrows** to each compound

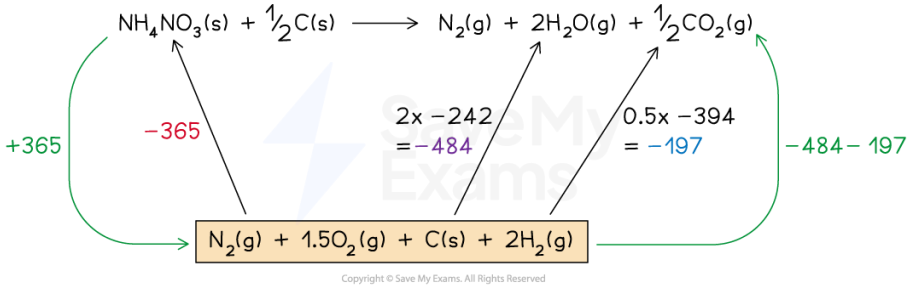


Your notes

Step 4: Write the appropriate **values** on the arrows and **multiply** by the number of moles



Step 5: In a cycle, go from the reactants to the products, changing the sign of the value if the arrow points in the opposite direction



$\Delta H_r^{\ominus}$ = +365 - 484 - 197 = **-316 kJ mol^{-1}**

- The sign on -365 needs reversing as the cycle goes in the opposite direction to the arrow pointing upwards
- There is no need to draw arrows from the elements to carbon and nitrogen as $\Delta H_f^{\ominus}$ is 0 for elements

Examiner Tips and Tricks

Keep your enthalpy values inside their own brackets so that you don't accidentally lose a minus sign

Your notes

Calculating ΔH_f from ΔH_c using Hess's Law energy cycles

- It can be difficult to find the enthalpy change of formation of compounds experimentally
- However, many enthalpy changes of combustion **can** be measured experimentally so these can be used to find the enthalpy of formation
- To do this, we follow these steps:
  1. Write the equation for the formation of the compound
  2. Write the combustion products **below** the equation
  3. Draw **downward pointing arrows** from each substance to its combustion products
  4. Write **values** on the arrows and multiply by the number of moles
  5. In a cycle, go from the reactants to the products, changing the sign of the value if the arrow points in the opposite direction

Worked Example

Calculating the enthalpy change of formation

Using the data provided, calculate the standard enthalpy change of formation, ΔH_f, of propanone.

$$3C(s) + 3H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow CH_3COCH_3(l)$$

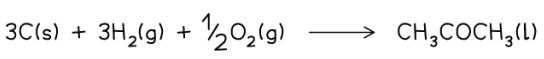
Substance	C (s)	H_2 (g)	CH_3COCH_3 (l)
$\Delta H_c^{\ominus}$ / kJ mol^{-1}	-394	-286	-1821

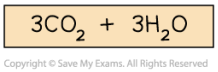
Answer:

- **Step 1:** Write the balanced equation

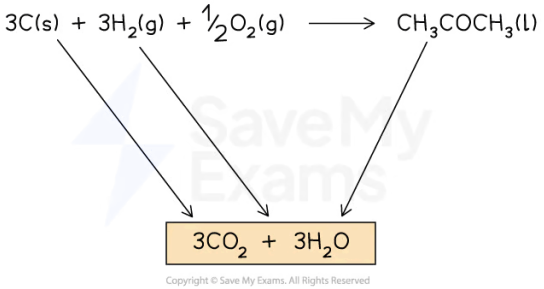
$$3C(s) + 3H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow CH_3COCH_3(l)$$

- **Step 2:** Write the combustion products **below** the equation

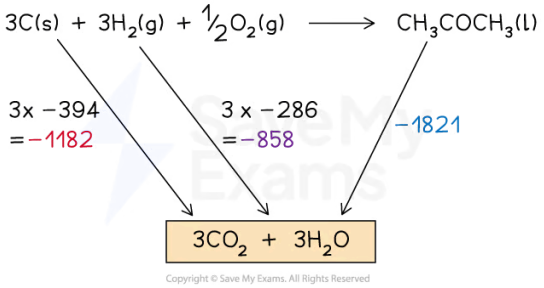




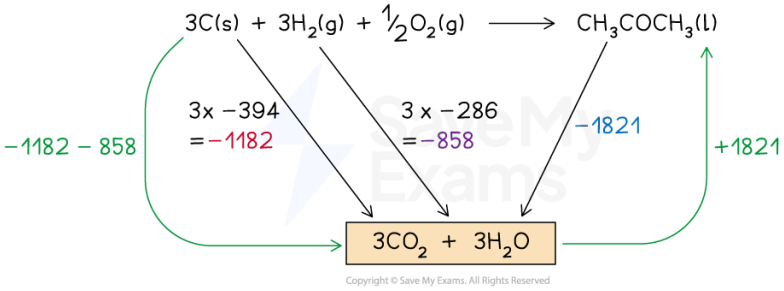
- **Step 3:** Draw **downward pointing arrows** from each substance to its combustion product



- **Step 4:** Write the appropriate **values** on the arrows and multiply by the number of moles



- **Step 5:** In a cycle, go from the reactants to the products, changing the sign of the value if the arrow points in the opposite direction



$\Delta H_f^{\ominus}$ = -1182 - 858 + 1821 = **-219 kJ mol^{-1}**

Your notes

- The sign on -1821 needs reversing as the cycle goes in the opposite direction to the arrow pointing to the combustion products

Your notes

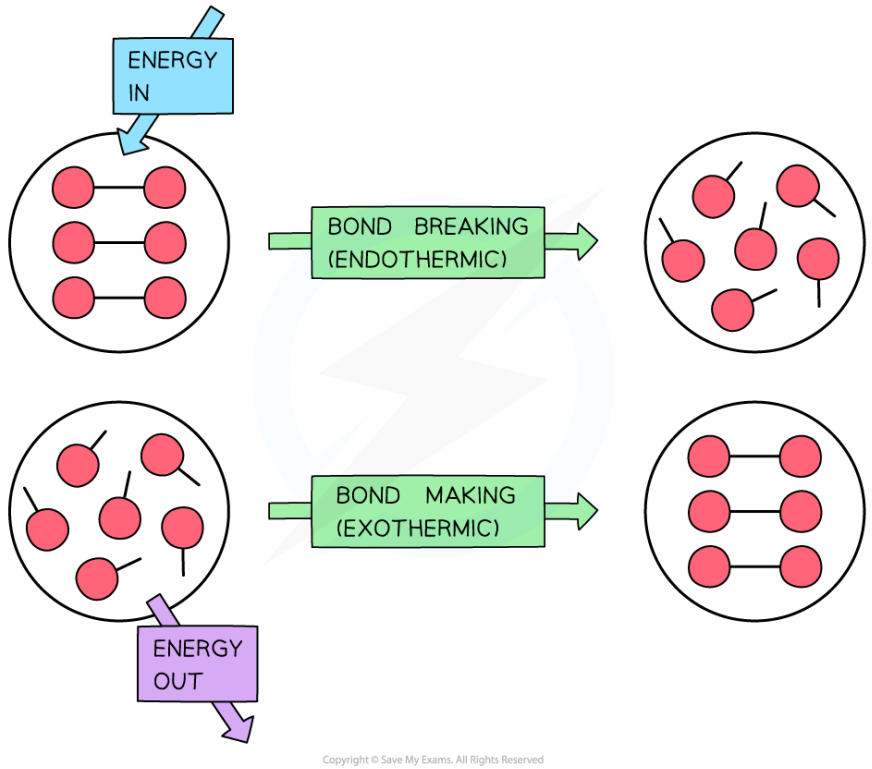
Examiner Tips and Tricks

Don't forget to make sure the number of atoms for each element is balanced when drawing your cycle.

Your notes

Bond Enthalpy – Definitions

- When bonds are broken or made **enthalpy changes** take place
  - A chemical bond is a force of attraction between two atoms
  - Breaking the bond requires the input of energy it is therefore an **endothermic** process
- The energy change required to break the bond depends on the atoms that form the bond
  - The energy required to break a particular bond is called the **bond dissociation enthalpy**
  - This is usually just shortened to **bond enthalpy** or **bond energy**
- Bond formation is the opposite of bond breaking and so energy is released when bonds are formed
  - It is therefore an **exothermic** process



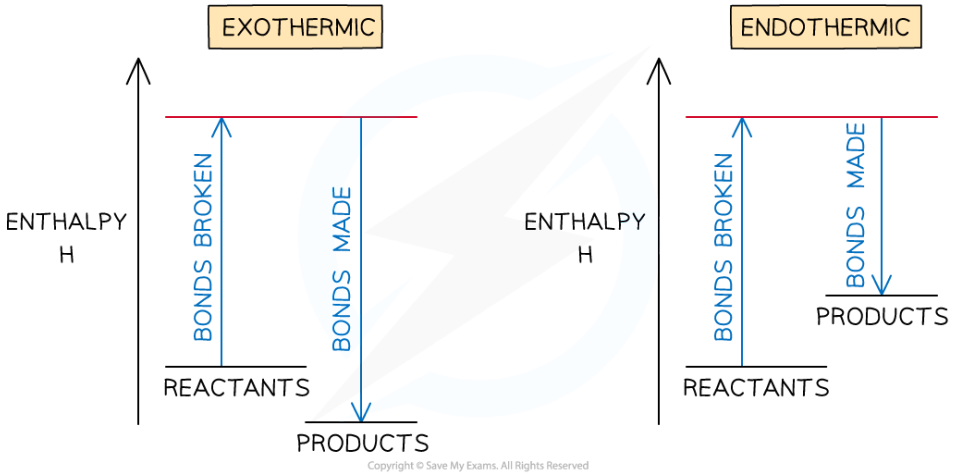
To break bonds energy is required from the surroundings and to make new bonds energy is released from the reaction to the surroundings

- The amount of energy released when a particular bond is formed has the same magnitude as the energy taken in when the bond is broken but has the opposite sign

Your notes

Overall enthalpy changes

- If more energy is released when new bonds are formed than energy is required to break bonds, the reaction is **exothermic**
  - The products are **more stable** than the reactants
- If more energy is required to break bonds than energy is released when new bonds are formed, the reaction is **endothermic**
  - The products are **less stable** than the reactants
- The relationship between bond breaking and bond making can be shown graphically like this:

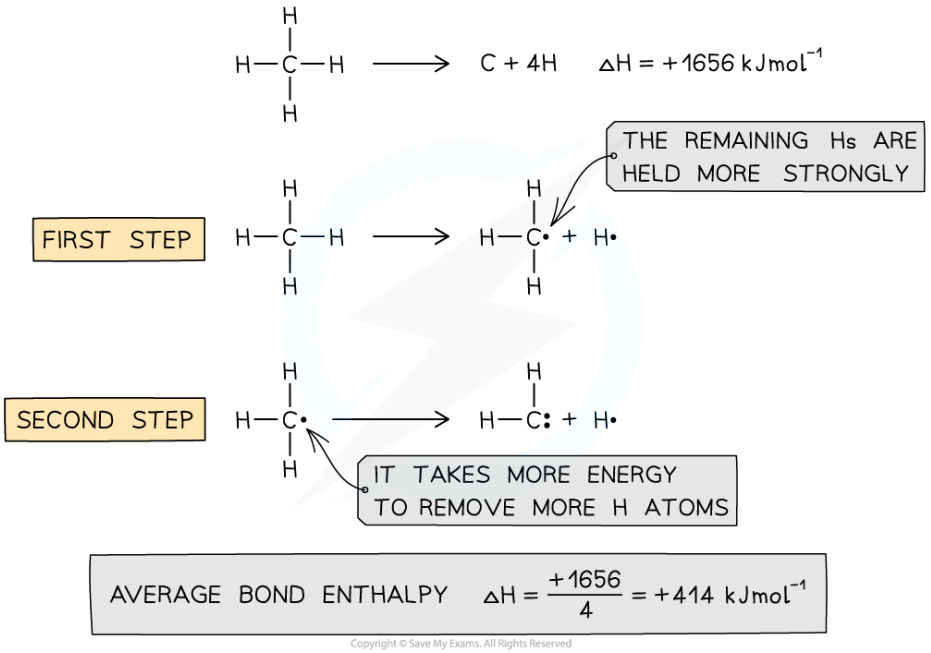


Bond enthalpy profiles

Average bond energy

- Bond energies are affected by other atoms in the molecule (the environment)
- Therefore, an average of a number of the **same type of bond** but in different environments is calculated
- This bond energy is known as the **average bond energy** and is defined as

'The energy needed to break one mole of bonds in a gaseous molecule averaged over similar compounds'



Average bond enthalpy of C-H in methane

- The **average bond enthalpy** of C-H is found by taking the **bond dissociation enthalpy** for the whole molecule and dividing it by the number of C-H bonds
- The first C-H bond is easier to break than the second as the remaining hydrogens are pulled more closely to the carbon
- However, since it is impossible to measure the energy of each C-H bond an average is taken
- This value is also compared with a range of similar compounds to obtain an accepted value for the **average bond enthalpy**
- Bond enthalpies can be used to predict which bonds will break first in a reaction
  - Bonds with high bond enthalpy values require more energy to break them
    - Reactions involving these types of bond often require heat and / or the use of a catalyst
  - Bonds with low bond enthalpy values require less energy to break them
    - Reactions involving these types of bonds are more likely to happen at room temperature
  - Therefore, bonds with lower bond enthalpy values are easier to break and are likely to be the first bonds to break in a reaction

Examiner Tips and Tricks

Your notes

A lot of students mix up endothermic / exothermic and bond breaking / bond making.

An easy way to remember is that **ENDOTHERMIC** leads to the poetic phrase the **'end o' the bond'**

Your notes

Bond Enthalpy – Calculations

- Bond energies are used to find the $\Delta H_r^{\ominus}$ of a reaction when this cannot be done experimentally
- The process is a step-by-step summation of the bond enthalpies of the all the molecules present finishing with this formula:

  $\Delta_r H^{\ominus}$ = enthalpy change for bonds broken + enthalpy change for bonds formed
- These two worked examples show how to lay out your calculation

Worked Example

Calculate the enthalpy of reaction for the Haber process reaction. The relevant bond energies are given in the table below:

Bond	Average Bond Energy ($kJ\ mol^{-1}$)
N ≡ N	945
H – H	436
N – H	391

Answer:

Step 1: The chemical equation for the Haber process is:

$$N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2NH_3\,(g)$$

N≡N 3 H–H 6 N–H

Step 2: Set out the calculation as a balance sheet as shown below:

Your notes

Bonds Broken (kJ mol^{-1})	Bonds formed (kJ mol^{-1})
$1 \times N \equiv N = 1 \times 945 = 945$ $3 \times H - H = 3 \times 436 = 1308$	$6 \times N - H = 6 \times 391$
Total = +2253	Total = −2346

Note! Values for bonds broken are positive (endothermic) and values for bonds formed are negative (exothermic)

Step 3: Calculate the standard enthalpy of reaction

- $\Delta_r H^{\ominus}$ = enthalpy change for bonds broken + enthalpy change for bonds formed
  - $\Delta_r H^{\ominus} = (+2253\ kJ\ mol^{-1}) + (-2346\ kJ\ mol^{-1})$
  - $\Delta_r H^{\ominus} = -93\ kJ\ mol^{-1}$

Worked Example

The complete combustion of ethyne, C_2H_2, is shown in the equation below:

$$2C_2H_2\,(g) + 5\,O_2\,(g) \rightarrow 2H_2O\,(g) + 4CO_2\,(g)$$

Using the average bond enthalpies given in the table, what is the enthalpy of combustion of ethyne?

Bond	Average Bond Energy (kJ mol^{-1})
C – H	414
C ≡ C	839
O = O	498
C = O	804
O – H	463
O – C	358

Answer:

Step 1: The enthalpy of combustion is the enthalpy change when **one mole** of a substance reacts in excess oxygen to produce water and carbon dioxide

The chemical reaction should be therefore simplified such that only **one mole** of **ethyne** reacts in excess oxygen:

$$H-C\equiv C-H + 2\tfrac{1}{2}\, O=O \rightarrow H-O-H + 2O=C=O$$

Step 2: Set out the calculation as a balance sheet as shown below:

Bonds Broken (kJ mol^{-1})	Bonds Formed (kJ mol^{-1})
$1 \times C \equiv C = 1 \times 839 = 839$ $2 \times C-H = 2 \times 414 = 828$ $2\frac{1}{2} \times O=O = 2\frac{1}{2} \times 498 = 1245$	$2 \times O-H = 2 \times 463 = 926$ $4 \times C=O = 4 \times 804 = 3216$
Total = +2912	Total = −4142

- $\Delta_r H^{\ominus}$ = enthalpy change for bonds broken + enthalpy change for bonds formed
  - $\Delta_r H^{\ominus} = (+2912 \text{ kJ mol}^{-1}) + (-4142 \text{ kJ mol}^{-1})$
  - $\Delta_r H^{\ominus} = -1230 \text{ kJ mol}^{-1}$

Examiner Tips and Tricks

The key to success in bond enthalpy calculations is to be very careful when accounting for every bond present. Always draw out the full displayed structures of the molecules so you don't miss any of the bonds.

Watch out for coefficients in the balanced equations as students often miss those, forget to multiply them by the bond enthalpies and get the answer wrong!

It is super important to show your steps because bond enthalpy calculations often carry 3 marks, 2 of which could be for workings if you get the final answer wrong

Your notes