⚗ Cambridge (CIE) A Level Chemistry
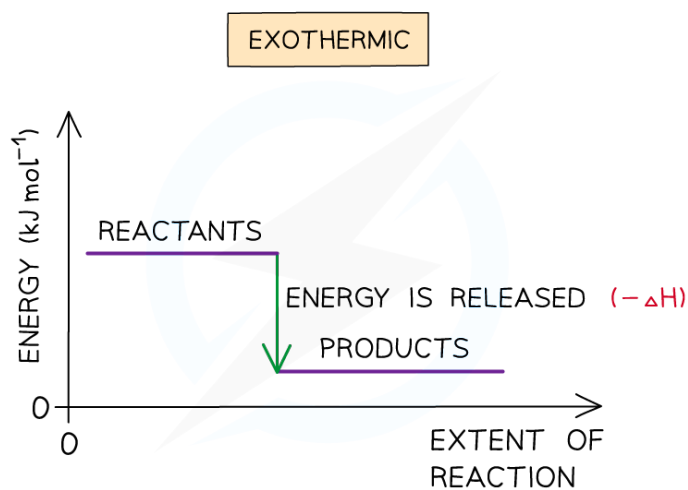
Enthalpy Change, ΔH

Contents

Enthalpy Changes

- 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

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 on a thermometer

  - The **temperature** 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, the rate may be too slow to observe any appreciable reaction

  - In this case, the reaction is **kinetically** controlled

  - This means the reaction could have a high activation energy which is preventing the reaction from taking place.

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 **temperature** of the **system increases**

- There is an enthalpy increase during the reaction, so ΔH is positive

The enthalpy change during an endothermic reaction
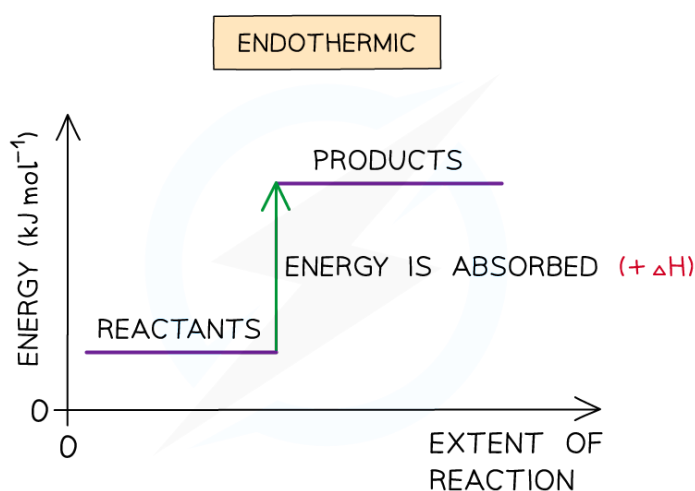
Endothermic reactions show a positive enthalpy change as energy is absorbed

💡

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:

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

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

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

Reaction Pathway Diagrams

- A reaction pathway diagram shows the energies of the reactants, the transition state(s) and the products of the reaction with time

    - They are sometimes called energy profile diagrams

- The **transition state** is a stage during the reaction at which chemical bonds are partially broken and formed

- The transition state is very unstable – it cannot be isolated and is higher in energy than the reactants and products

- The activation energy (E_a) is the energy needed to reach the transition state

- We can define the activation energy as '*the minimum amount of energy needed for reactant molecules to have a successful collision and start the reaction*'

Example reaction pathway diagram
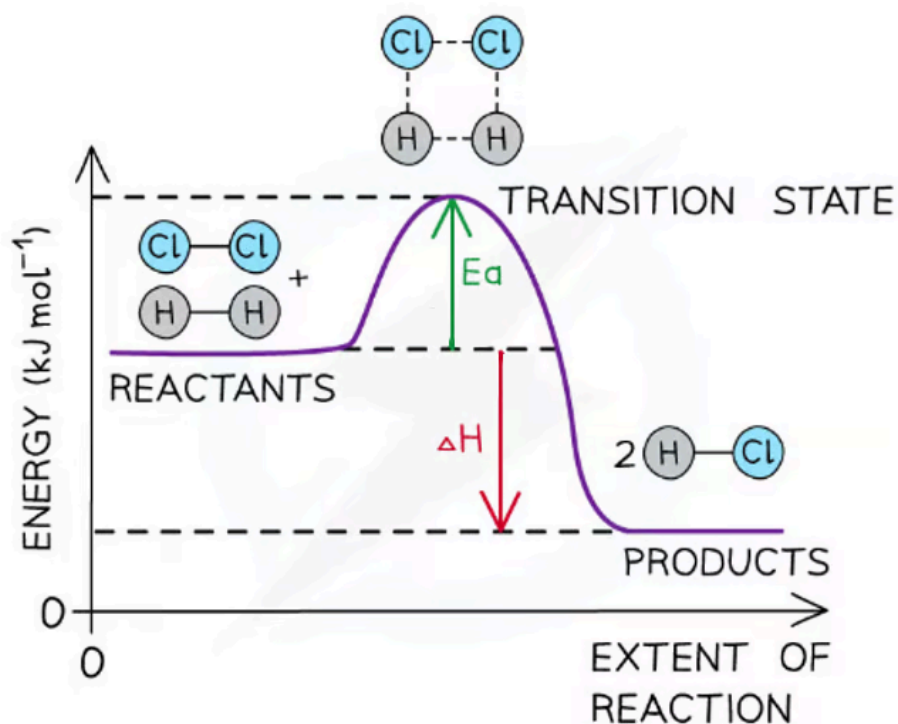
The reaction pathway diagram for the reaction of hydrogen with chlorine to form hydrogen chloride gas
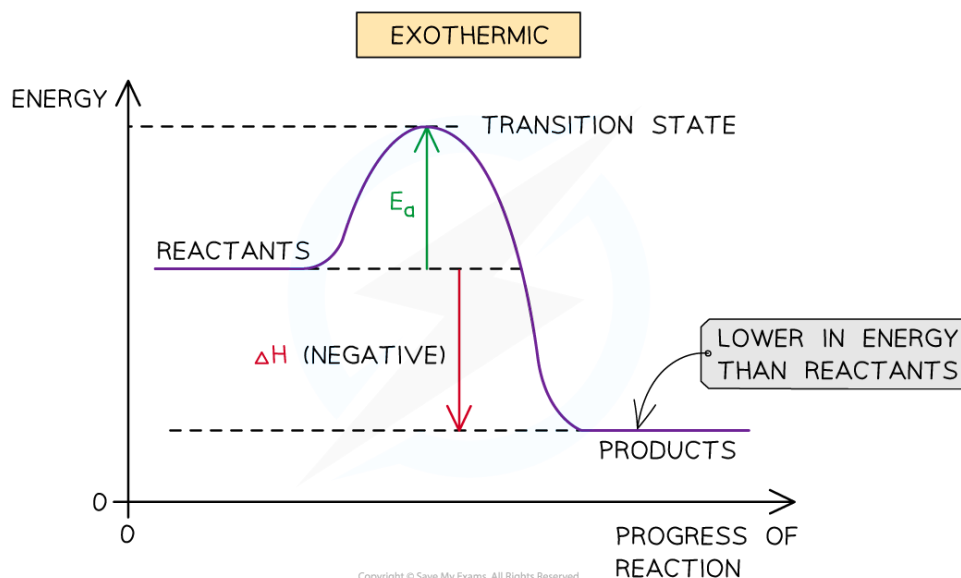
Exothermic reaction

- 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 pathway diagram for exothermic reactions

Exothermic reaction pathway diagrams always have the products lower in energy than the reactants
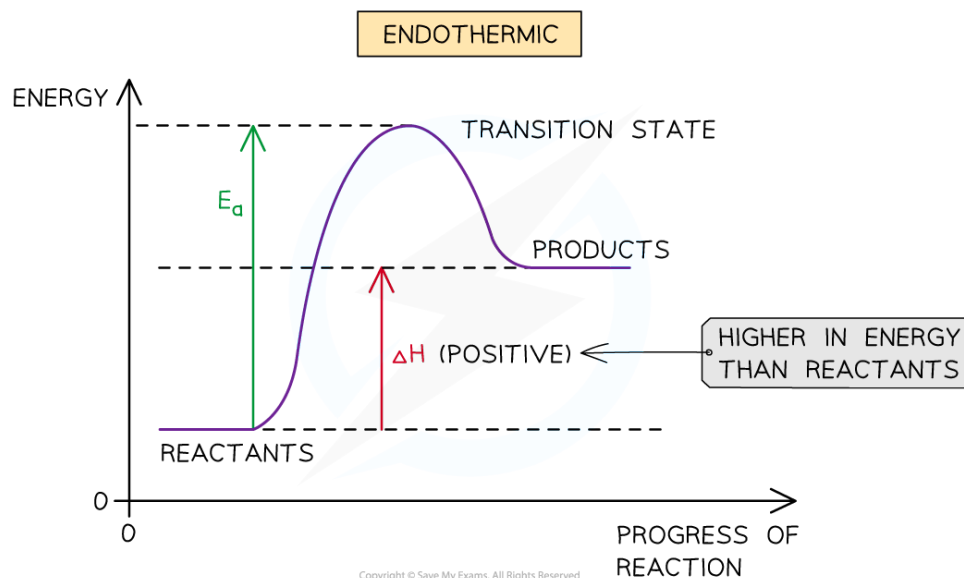
Endothermic reaction

- In an endothermic reaction, the reactants are lower in energy than the products

- The reactants are therefore further away in energy to the transition state

- This means that endothermic reactions have a higher activation energy compared to exothermic reactions

The reaction pathway diagram for endothermic reactions

Endothermic reaction pathway diagrams always have the products higher in energy than the reactants

Worked Example

Drawing energy level diagrams of the combustion of methane

The E_a and ΔH for the complete combustion of methane are +2653 kJ mol^{-1} and –890 kJ mol^{-1} respectively.
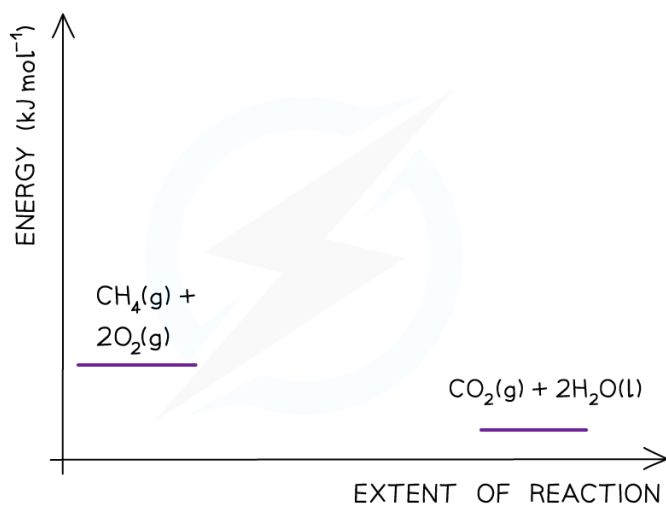
Draw the reaction pathway diagram for this reaction

Answer

- **Step 1:** The chemical equation for the complete combustion of methane is:
$$CH_4\ (g) + 2O_2\ (g) \rightarrow CO_2\ (g) + 2H_2O\ (l)$$

- **Step 2:** Combustion reactions are always exothermic (ΔH is negative) so the reactants should be drawn higher in energy than the products

- **Step 3:** Draw the curve in the energy level diagram, clearly showing the transition state
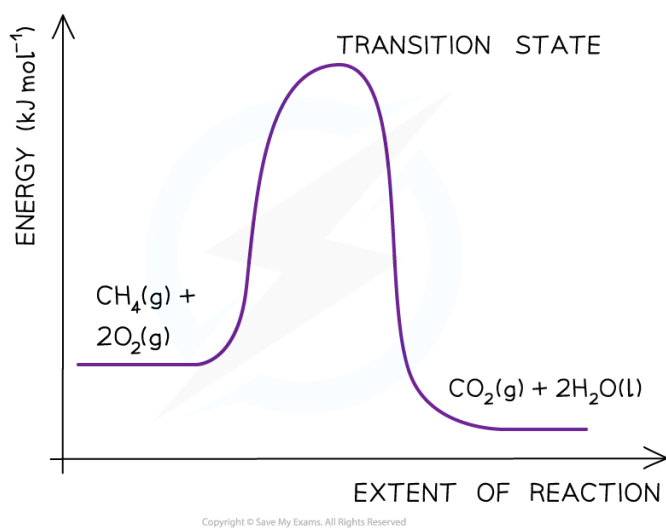
- **Step 4:** Draw arrows to show the E_a and ΔH including their values

Worked Example

Determining the activation energy

Determine, using the reaction pathway diagram, the E_a for the forward and backward reaction.

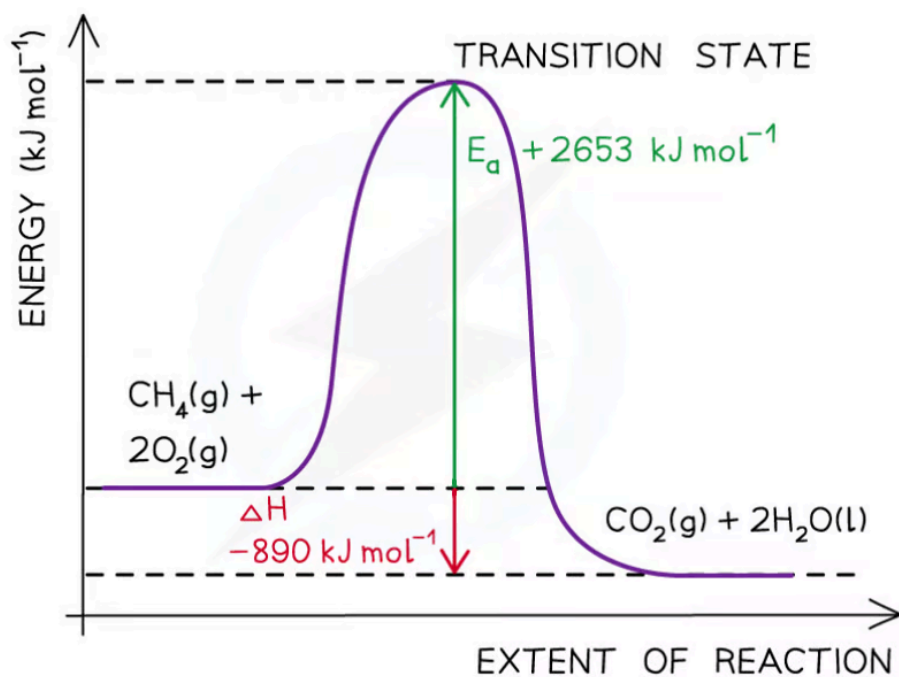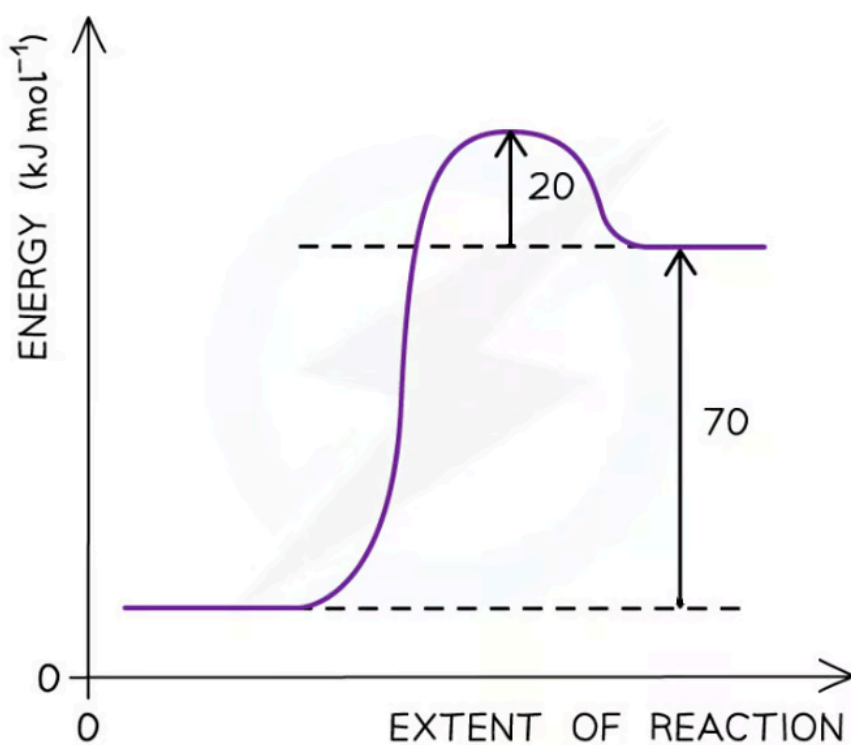Copyright © Save My Exams. All Rights Reserved

Answer

- The E_a is the energy difference from the energy level of the reactants to the top of the 'hump'
- E_a (forward reaction) = (+70 kJ mol^{-1}) + (+ 20 kJ mol^{-1}) = **+90 kJ mol^{-1}**
- As the question is asking for the **reverse reaction,** the E_a is the energy difference from the energy level of the products to the 'hump'
- **E_a (reverse reaction) = +20 kJ mol^{-1}**

Examiner Tips and Tricks

- The activation energy is the energy difference from **reactants** to the **transition state.**
- The enthalpy change of the reaction is the energy difference from **reactants** to **products.**
- Remember to label the axis of the reaction pathway diagrams!

Defining Enthalpy Changes

- To fairly compare the changes in enthalpy between reactions, all reactions should be carried out under standard conditions

- These standard conditions are:

  - A **pressure** of 101 kPa

  - A **temperature** of 298 K (25 ^{o}C)

  - Each substance involved in the reaction is in its normal physical state (solid, gas or liquid)

- To show that a reaction has been carried out under standard conditions, the symbol θ is used

  - ΔH^{θ} = the standard enthalpy change

- These are a number of key definitions for common language relating to enthalpy change that all chemists need to know

Enthalpy definitions

- All standard enthalpies are performed under standard conditions

- **Standard enthalpy change of reaction,** ΔH^{θ}_{r}

  - The enthalpy change when the reactants in the **stoichiometric equation** react to form the products, with all species in their standard states

  - Can be **both** exothermic and endothermic

- **Standard enthalpy change of formation,** ΔH^{θ}_{f}

  - The enthalpy change when **one mole** of a compound is **formed** from its **elements** in their standard states

  - Can be **both** exothermic and endothermic

- **Standard enthalpy change of combustion,** ΔH^{θ}_{c}

  - The enthalpy change when **one mole** of a substance, in its standard state, is **burnt** in excess oxygen

  - It is an **exothermic** change

- **Standard enthalpy change of neutralisation,** ΔH^{θ}_{neut}

  - The enthalpy change when **one mole** of **water** is **formed** by reacting an acid and an alkali
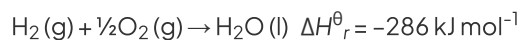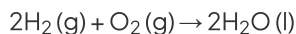
  - It is an **exothermic** change

Worked Example

Calculating the enthalpy change of reaction of water

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

$$H_2\,(g) + \tfrac{1}{2}O_2\,(g) \rightarrow H_2O\,(l) \quad \Delta H^{\theta}_r = -286 \text{ kJ mol}^{-1}$$

Calculate ΔH_r for the reaction below:

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

Answer

- The ΔH^{θ}_r value of –286 kJ mol^{-1} is for one mole of water being formed
- Two moles of water molecules are formed for the equation in question
- So, the energy released is simply:

  - ΔH_r = 2 mol x (–286 kJ mol^{-1})
  - ΔH_r = –572 kJ mol^{-1}

Worked Example

Calculating the enthalpy change of formation

Calculate ΔH^{θ}_f of the reaction below:

$$4Fe\,(s) + 3O_2\,(g) \rightarrow 2Fe_2O_3\,(s) \quad \Delta H^{\theta}_f\,[Fe_2O_3\,(s)] = -824.2 \text{ kJ mol}^{-1}$$

Answer

- The ΔH^{θ}_f value of –824.2 kJ mol^{-1} is for one mole of Fe_2O_3 (s) being formed
- Two moles of Fe_2O_3 (s) are formed for the equation in question
- So, the energy released is simply:

  - ΔH^{θ}_f = 2 mol x (–824.2 kJ mol^{-1})
  - ΔH^{θ}_f = –1648.4 kJ mol^{-1}

Worked Example

Calculating enthalpy changes

Identify each of the following as ΔH^{θ}_r, ΔH^{θ}_f, ΔH^{θ}_c or ΔH^{θ}_{neut}:

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

Answers:

Answer 1

- It cannot be ΔH^{θ}_f as there is more than one compound being formed
- It cannot be ΔH^{θ}_c as there is no reaction with oxygen
- It cannot be ΔH^{θ}_{neut} as there is no acid or alkali involved
- This is just a chemical reaction, therefore, it is ΔH^{θ}_r

Answer 2

- ΔH^{θ}_f as one mole of CO_2 is formed from its elements in their standard states **AND** ΔH^{θ}_c as one mole of carbon is burnt completely in oxygen

Answer 3

- $\Delta H_{neut}^{\equiv}$ as one mole of water is formed from the reaction of an acid and alkali

💡

Examiner Tips and Tricks

The ΔH^{θ}_f of an **element** in its standard state is zero. For example, ΔH^{θ}_f of O_2 (g) is 0 kJ mol^{-1}

Enthalpy & Bond Energies

- During a reaction, enthalpy changes take place because bonds are being broken and formed

- Energy (in the form of heat) is needed to overcome attractive forces between atoms

- **Bond breaking** is therefore **endothermic**

- Energy is released from the reaction to the surroundings (in the form of heat) when new bonds are formed

- **Bond forming** is therefore **exothermic**

Making and breaking bonds
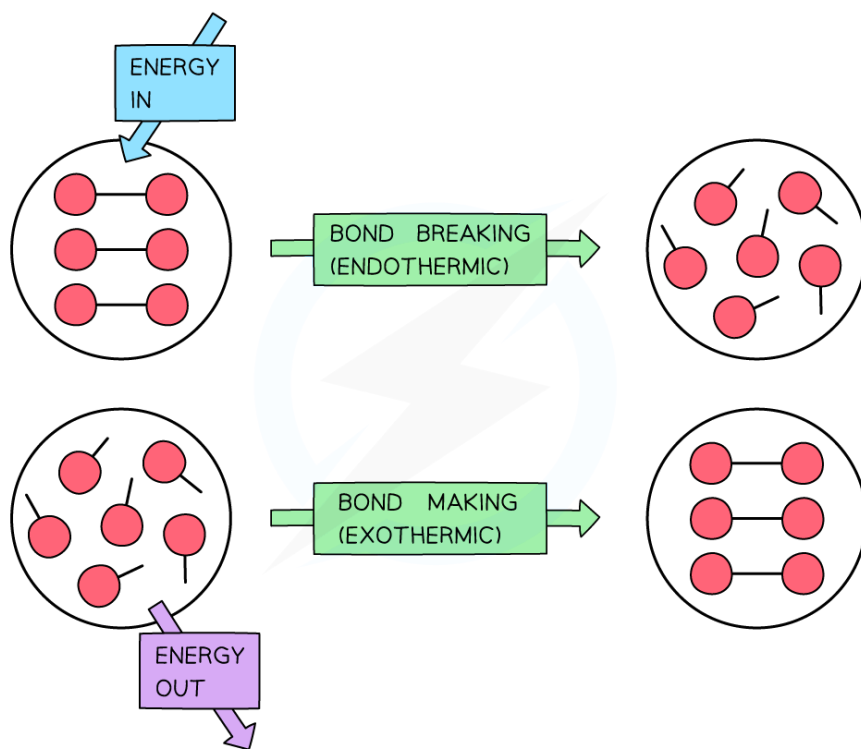
Breaking bonds requires energy from the surroundings and making bonds releases energy to the surroundings

- If more energy is required to break bonds than energy is released when new bonds are formed, the reaction is **endothermic**

- If more energy is released when new bonds are formed than energy is required to break bonds, the reaction is **exothermic**

- In reality, only some bonds in the reactants are broken and then new ones are formed
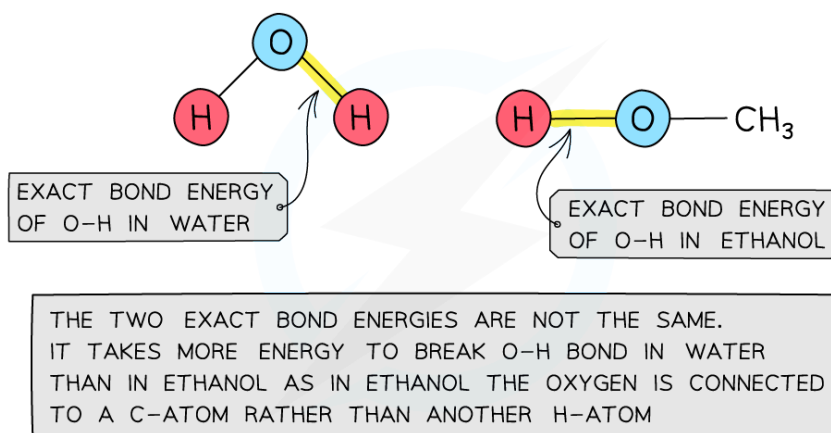
Enthalpy Calculations

Exact bond energy

- The amount of energy required to break one mole of a **specific** covalent bond in the gas phase is called the bond dissociation energy

- Bond dissociation energy (E) is also known as **exact bond energy** or *bond enthalpy*

- The type of bond broken is put in brackets after E

    - E.g. EE(H-H) is the bond energy of a mole of single bonds between two hydrogen atoms

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**

- Since bond energies cannot be determined directly, **enthalpy cycles** are used to calculate the average bond energy

How bond energies are affected by other atoms in the molecule

EXACT BOND ENERGY OF O–H IN WATER

EXACT BOND ENERGY OF O–H IN ETHANOL

THE TWO EXACT BOND ENERGIES ARE NOT THE SAME. IT TAKES MORE ENERGY TO BREAK O–H BOND IN WATER THAN IN ETHANOL AS IN ETHANOL THE OXYGEN IS CONNECTED TO A C–ATOM RATHER THAN ANOTHER H–ATOM

Bond energies are affected by other atoms in the molecule

Calculating enthalpy change from bond energies

- Bond energies are used to find the $\Delta H_r^{\ominus}$ of a reaction when this cannot be done experimentally

    - E.g. the Haber Process

- The equation to calculate the standard enthalpy change of reaction using bond energies is:

ΔH^{θ}_r = enthalpy change for bonds broken + enthalpy change for bonds formed
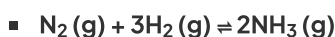
Worked Example

Calculate the enthalpy change of reaction the Haber process reaction.

The relevant bond energies are given in the table.

Bond	Average bond energy kJ mol^{-1}
N $\equiv$ 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)
- **Step 2:** Set out the calculation as a balance sheet:

Bonds broken kJ mol^{-1}	Bonds formed kJ mol^{-1}
1 x N $\equiv$ N = 1 x 945 = 945 3 x H–H = 3 x 436 = 1308	6 x N–H = 6 x 391 = 2346
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:

  - ΔH^{θ}_r = enthalpy change for bonds broken + enthalpy change for bonds formed
  - ΔH^{θ}_r = (+2253 kJ mol^{-1}) + (–2346 kJ mol^{-1})
  - ΔH^{θ}_r = –93 kJ mol^{-1}

Worked Example

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

$$2H–C \equiv C–H + 5O{=}O \rightarrow 2H–O–H + 4O{=}C{=}O$$
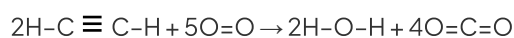
Calculate, using the average bond enthalpies given in the table, the enthalpy of combustion of ethyne.

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:
    $$H–C≡C–H + 2½ O=O → H–O–H + 2O=C=O$$

- **Step 2:** Set out the calculation as a balance sheet:

Bonds broken kJ mol^{-1}	Bonds formed kJ mol^{-1}
1 x C ≡ C = 1 x 839 = 839 2 x C–H = 2 x 414 = 828 2½ x O=O = 2½ x 498 = 1245	2 x O–H = 2 x 463 = 926 4 x C=O = 4 x 804 = 3216
Total = **+2912**	Total = **–4142**

- **Note:** Values for bonds broken are positive (endothermic) and values for bonds formed are negative (exothermic)
- **Step 3:** Calculate the standard enthalpy of reaction:
    - ΔH^{θ}_r = enthalpy change for bonds broken + enthalpy change for bonds formed
    - ΔH^{θ}_r = (+2912 kJ mol^{-1}) + (–4142 kJ mol^{-1})
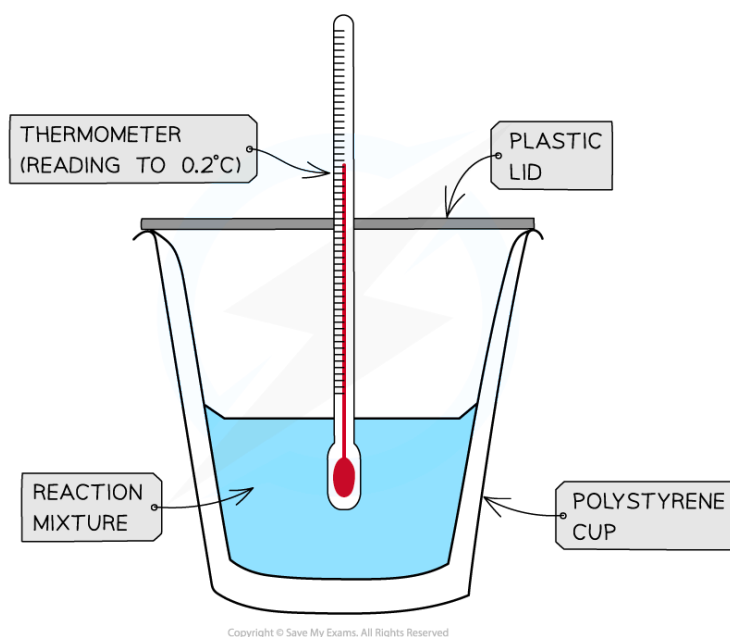   - ΔH^{θ}_r = –1230 kJ mol^{-1}

Measuring enthalpy changes

- **Calorimetry** is a technique used to measure changes in enthalpy of chemical reactions

- A **calorimeter** can be made up of a **polystyrene drinking cup**, a **vacuum flask** or **metal can**

Example calorimetry equipment

THERMOMETER
(READING TO 0.2°C)

PLASTIC
LID

REACTION
MIXTURE

POLYSTYRENE
CUP

Copyright © Save My Exams. All Rights Reserved

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

- The energy needed to increase the temperature of 1 g of a substance by 1 °C is called the **specific heat capacity** (c) of the liquid

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

- The energy transferred as heat can be calculated using the following equation:

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

- q = the heat transferred, J

  - m = the mass of water, g

  - c = the specific heat capacity, J g^{-1}°C^{-1} or J g^{-1}K^{-1}

  - T = the temperature change, °C

Worked Example

In a calorimetric 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, causing the temperature to rise from 25 °C to 68 °C.

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

Calculate the total energy released per gram of methane burnt.

Answer

- **Step 1:** Gather the necessary values for the $q = m \times c \times \Delta T$ equation:
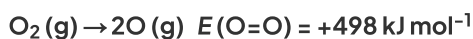
- m (of water) = 500 g
- c (of water) = 4.18 J g^{-1} K^{-1}
- ΔT (of water) = 68 °C – 25 °C = 43 °C = 43 K

  - The change in temperature in °C is equal to the change in temperature in K

- **Step 2:** Complete the calculation:

  - q = 500 x 4.18 x 43
  - q = 89 870 J
- **Step 3:** Conversion from 30% to 100%

  - The value of q calculated is only 30% of the total energy released by 2.50 g of methane
  - Total energy x 0.3 = 89 870 J
  - Total energy = 299 567 J
- **Step 4:** Calculate the energy released by 1.00 g of methane

  - The energy calculated is released by 2.50 g of methane
  - Energy released by 1.00 g of methane = $\dfrac{299567}{2.50}$
  - Energy released by 1.00 g of methane = 119 827 J
- **Step 5:** Convert the answer from J to kJ:

  - $\dfrac{119827}{1000}$ = 120 kJ (to 3 significant figures)

Examiner Tips and Tricks

- When new bonds are formed, the amount of energy released is equal to the amount of energy absorbed when the same bonds are broken
- For example:

$$O_2 \,(g) \rightarrow 2O \,(g) \quad E \,(O=O) = +498 \text{ kJ mol}^{-1}$$

$$2O \,(g) \rightarrow O_2 \,(g) \quad E \,(O=O) \; -498 \text{ kJ mol}^{-1}$$

- 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 then calculate any changes in enthalpy per mole of a reactant or product, the following relationship can be used:

$$\Delta H = -m \times c \times \Delta T$$

- When there is a rise in temperature, the value for ΔH becomes negative, suggesting that the reaction is exothermic
- When there is a fall in temperature, the value for ΔH becomes positive, suggesting that the reaction is endothermic
- Also, remember that ΔT is the same in °C and K!