

DP IB Chemistry: HL


Your notes

5.3 Bond Enthalpy

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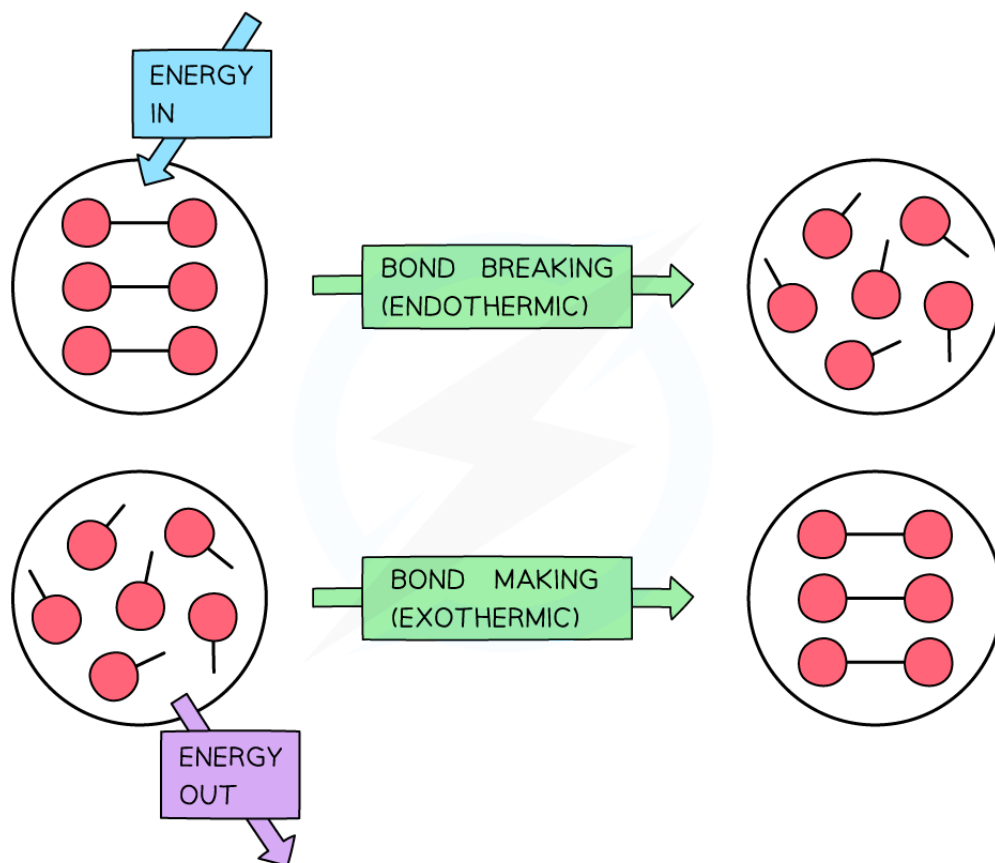


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5.3.1 Bond Enthalpy

Bonds & Energy

- 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



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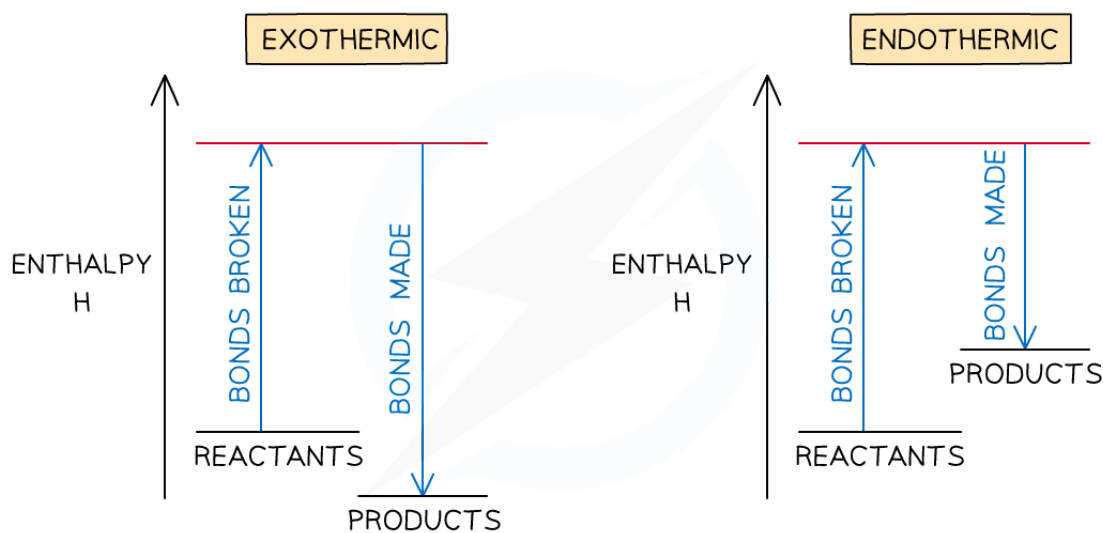
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To break bonds energy is required from the surroundings and to make new bonds energy is released from the reaction to the surroundings

- 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

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:



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Bond enthalpy profiles



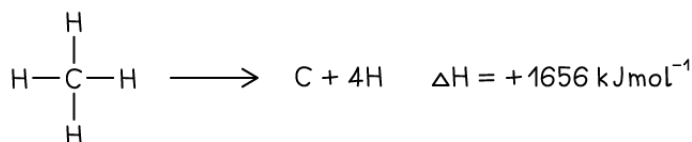
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Bond Enthalpy

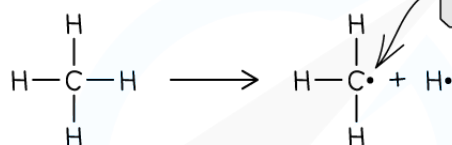
Average bond energy

- 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'



FIRST STEP



THE REMAINING Hs ARE HELD MORE STRONGLY

SECOND STEP



IT TAKES MORE ENERGY TO REMOVE MORE H ATOMS

$$\text{AVERAGE BOND ENTHALPY} \quad \Delta H = \frac{+1656}{4} = +414 \text{ kJ mol}^{-1}$$

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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**

 **Examiner Tip**

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**'



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5.3.2 Bond Enthalpy Calculations

Bond Enthalpy Calculations

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

$$\Delta H_r^\ominus = \text{ENTHALPY CHANGE FOR BONDS BROKEN} + \text{ENTHALPY CHANGE FOR BONDS FORMED}$$

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Formula for calculating the standard enthalpy change of reaction using bond energies

- These two worked examples show how to lay out your calculation

Worked example

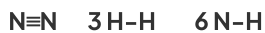
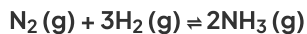
Calculate the enthalpy of reaction for the Haber process reaction. The relevant bond energies are given in the table below:

| Bond | Average Bond Energy (kJ mol ⁻¹) |
|-------|--|
| N ≡ N | 945 |
| H - H | 436 |
| N - H | 391 |

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Answer:

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



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

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

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

Step 3: Calculate the standard enthalpy of reaction

$$\begin{aligned} \Delta H_r^\ominus &= \text{enthalpy change for bonds broken} + \text{enthalpy change for bonds formed} \\ &= (+2253 \text{ kJ mol}^{-1}) + (-2346 \text{ kJ mol}^{-1}) \\ &= -93 \text{ kJ mol}^{-1} \end{aligned}$$



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Worked example

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



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 |

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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:



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}) |
|--|--|
| $1 \times \text{C} \equiv \text{C} = 1 \times 839 = 839$ | $2 \times \text{O}-\text{H} = 2 \times 463 = 926$ |
| $2 \times \text{C}-\text{H} = 2 \times 414 = 828$ | $4 \times \text{C}=\text{O} = 4 \times 804 = 3216$ |
| $2\frac{1}{2} \times \text{O}=\text{O} = 2\frac{1}{2} \times 498 = 1245$ | |
| Total = +2912 | Total = -4142 |

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$\Delta H_r^\ominus =$ enthalpy change for bonds broken + enthalpy change for bonds formed

$$= (+2912 \text{ kJ mol}^{-1}) + (-4142 \text{ kJ mol}^{-1})$$

$$= -1230 \text{ kJ mol}^{-1}$$

Examiner Tip

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



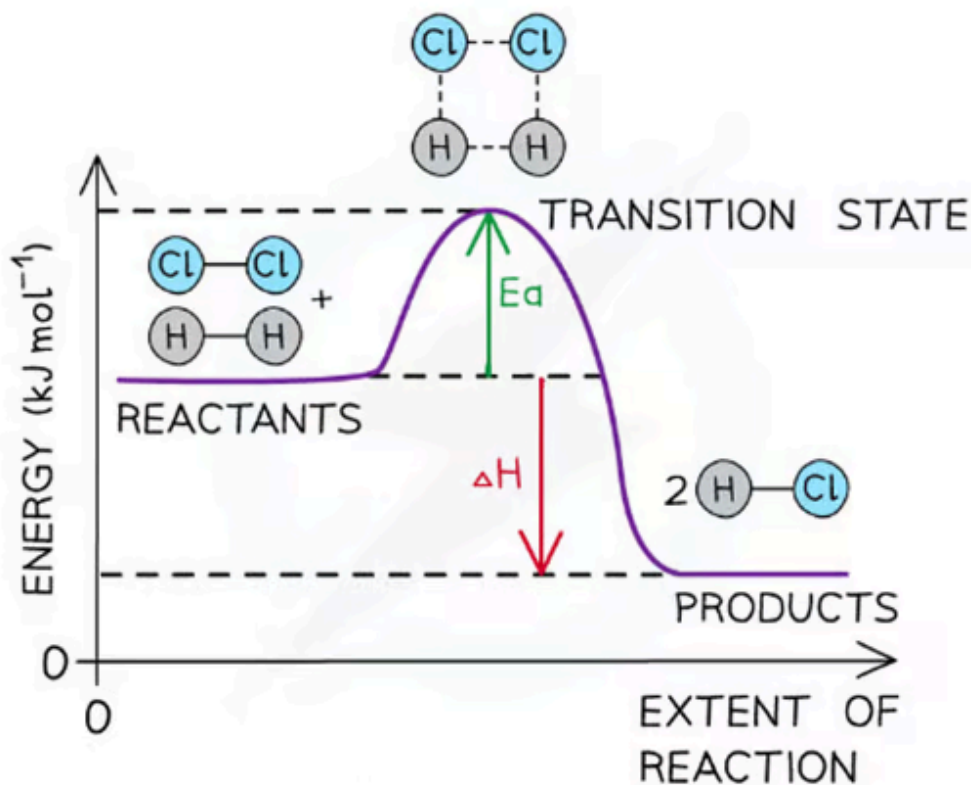
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5.3.3 Energy Profiles

Energy Profiles

- An energy profile or energy level diagram is a diagram that shows the energies of the reactants, the **transition state(s)** and the products of the reaction with time
 - 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'



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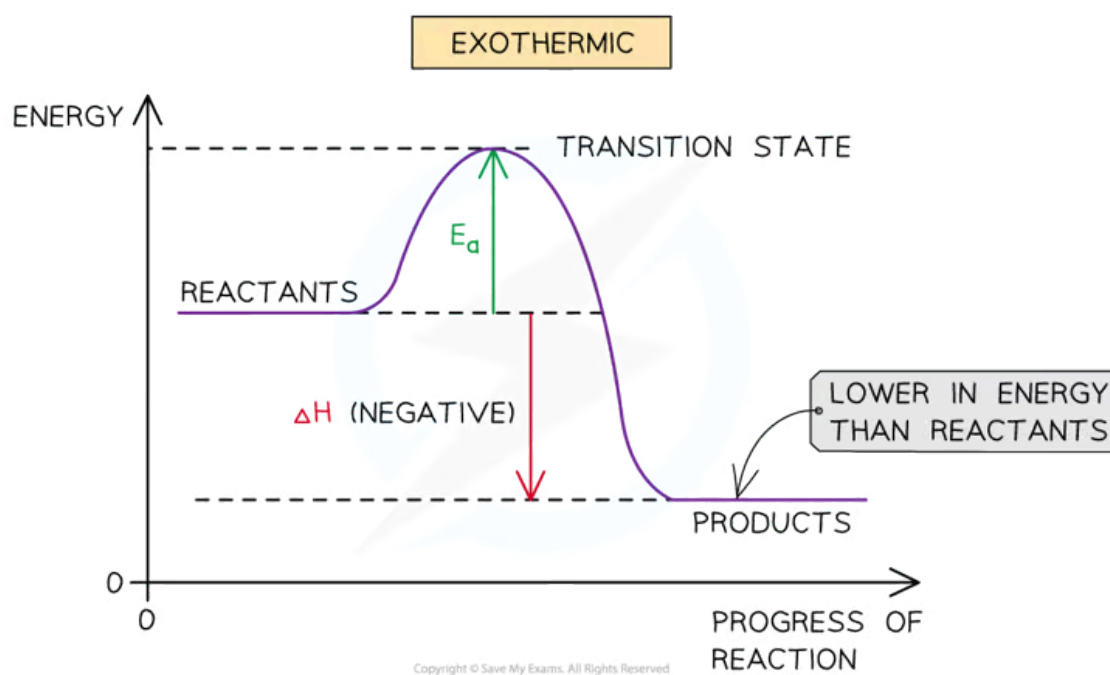
The energy level diagram for the reaction of hydrogen with chlorine to form hydrogen chloride gas



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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



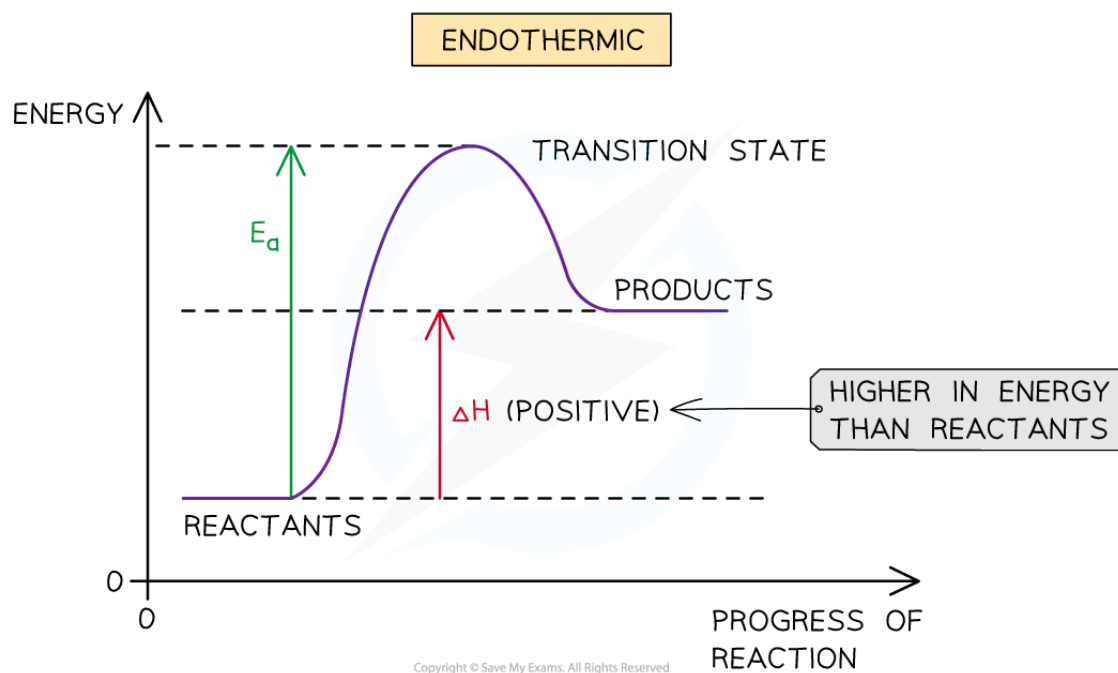
The energy level diagram for exothermic reactions

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



Your notes



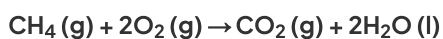
The energy level diagram for endothermic reactions

 **Worked example**

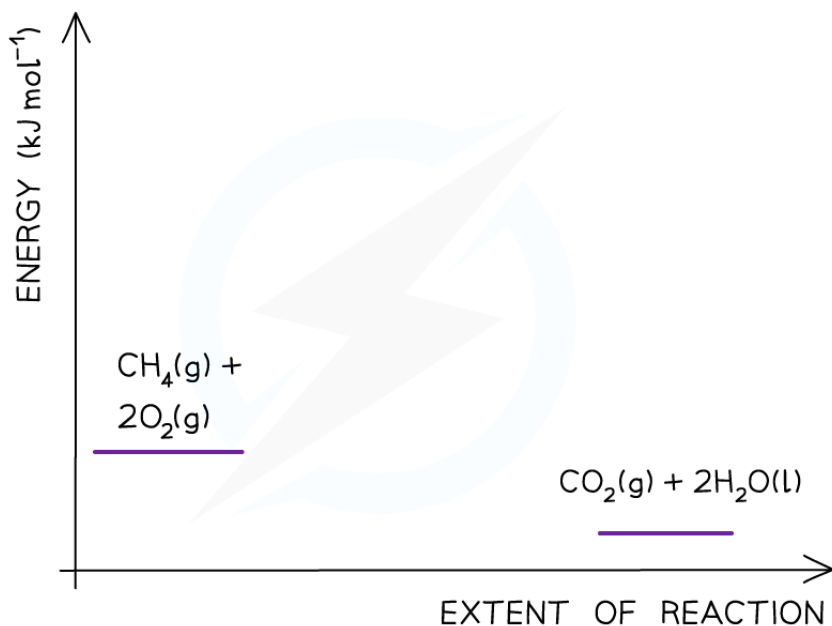
The enthalpy of combustion for methane is -890 kJ mol^{-1} and the activation energy is $+2653 \text{ kJ mol}^{-1}$.
 1 Draw a labelled energy level diagram for this reaction.

Answer:

Step 1: The chemical equation for the complete combustion of methane is:

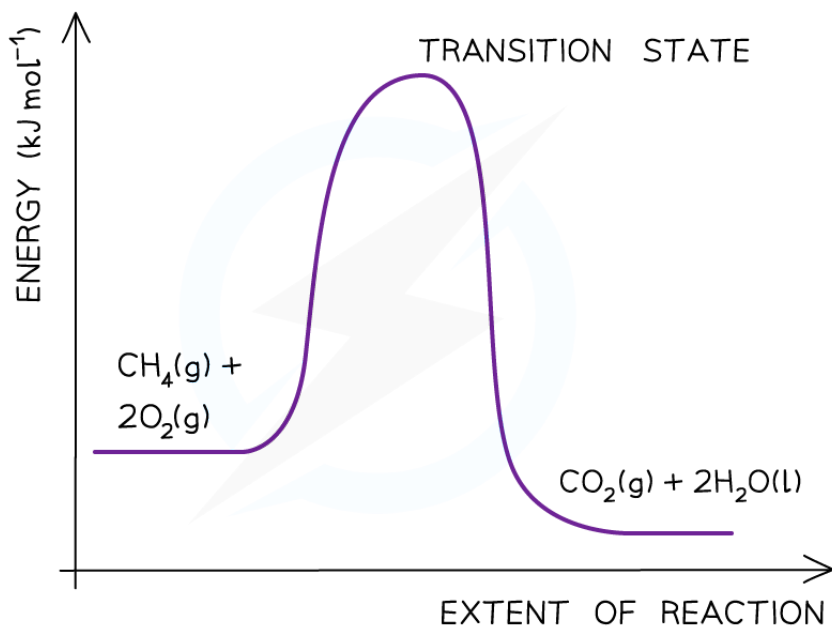


Step 2: Combustion reactions are always exothermic (ΔH is negative) so the reactants should be drawn higher in energy than the products



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Step 3: Draw the curve in the energy level diagram clearly showing the transition state

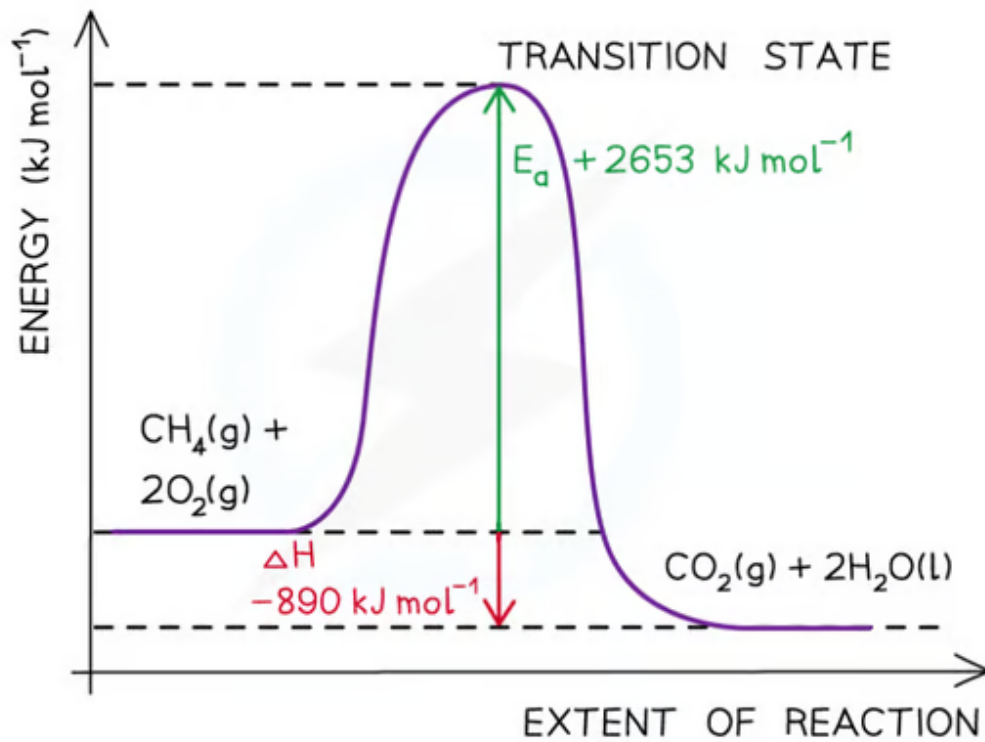


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Step 4: Draw arrows to show the E_a and ΔH including their values



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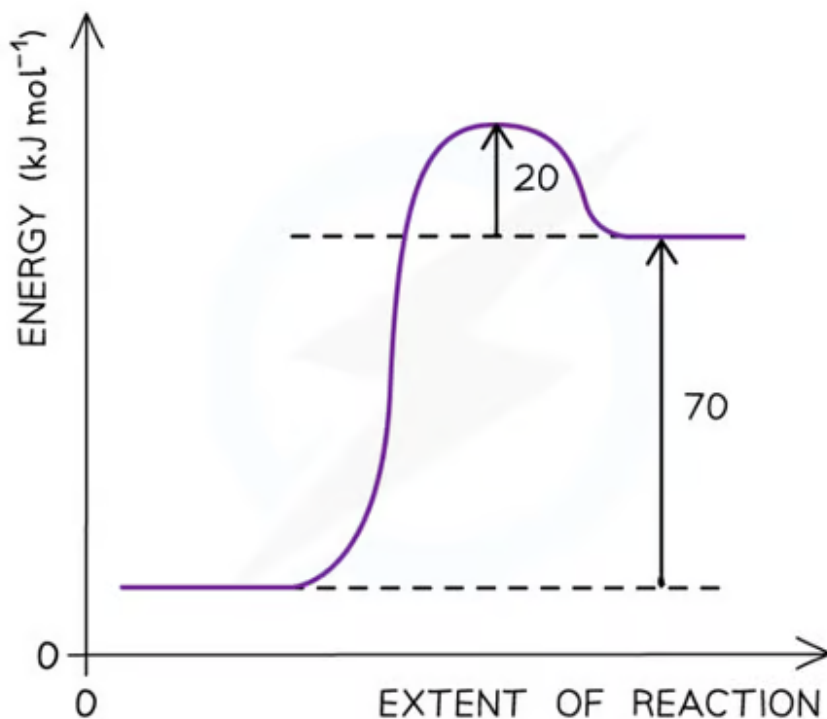




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Worked example

Use the energy level diagram below to identify the activation energy, E_a , for the reaction



The reaction pathway diagram for a reversible reaction

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) = $(+70 \text{ kJ mol}^{-1}) + (+20 \text{ kJ mol}^{-1}) = +90 \text{ kJ mol}^{-1}$

Examiner Tip

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

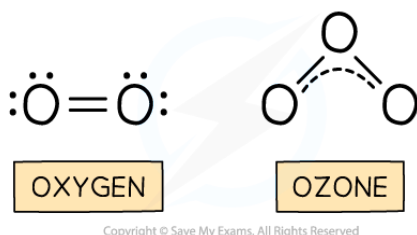


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5.3.4 Case Study: Ozone

Case study: Ozone & Bond Strength

- A study of **bond enthalpy** can explain why ozone and oxygen in the atmosphere play very different roles in the flow of energy
- These processes have a profound effect on the amount of solar radiation reaching ground level
- The structure of oxygen and ozone molecules influences the amount of energy needed to break their bonds:

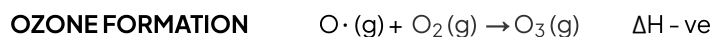


The structure of oxygen and ozone

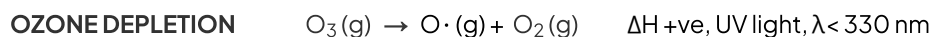
- The double bond in oxygen is stronger than the **delocalised π bonds** in ozone
 - We say the **bond order** of oxygen is **2** and the **bond order** of ozone is **1.5**
 - Both bonds are broken by ultraviolet radiation but the bond in oxygen requires radiation of higher energy and shorter wavelength than the bond in ozone
- High energy UV radiation in the stratosphere breaks the oxygen-oxygen double bond creating oxygen atoms



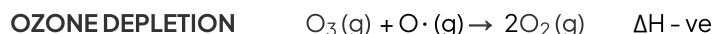
- These oxygen atoms have unpaired electrons- they are known as **free radicals**
- The **free radicals** are highly reactive and quickly attack oxygen molecules forming ozone in an **exothermic** reaction, which raises the temperature of the stratosphere



- Ozone requires less energy to break than oxygen
- It produces an oxygen molecule and an oxygen free radical:



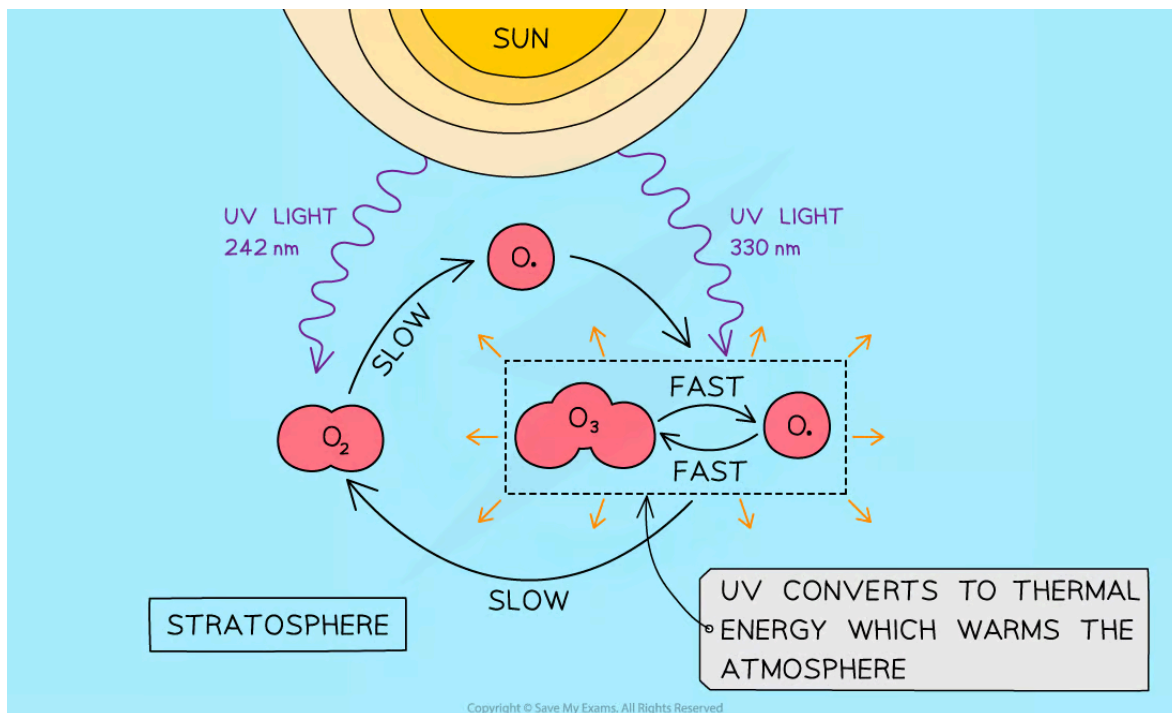
- The radical reacts with another ozone molecule making two molecules of oxygen in an **exothermic** reaction





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- The temperature in the stratosphere is maintained by the balance of ozone formation and ozone depletion in a process known as the Chapman Cycle
- It is not a closed system as matter and energy flow in and out, but it is what is called a **steady state**



The Chapman cycle

- Unfortunately, chemicals we have introduced into the atmosphere have interfered with this steady state resulting in ozone depleting at a faster rate than it is replaced
- Amongst these chemicals are **chlorofluorocarbons (CFCs)** found in refrigerants, propellants and solvents
- **CFCs** are greatly damaging to stratospheric ozone and have been largely replaced by safer alternatives following the 1985 Montreal Protocol
- The depletion of ozone has allowed greater amounts of harmful **UV light** to reach the surface of the Earth
- **UV light** has been linked to greater incidence of skin cancer and cataracts as well as the destruction of phytoplankton and reduced plant growth