CHEMICAL KINETICS (RATES OF REACTION)

Introduction Chemical kinetics is concerned with the dynamics of chemical reactions such as the way reactions take place and the rate (speed) of the process.

Collision theory

- particles must COLLIDE before a reaction can take place
- not all collisions lead to a reaction
- reactants must possess a minimum amount of energy - ACTIVATION ENERGY
+ - particles must approach each other in a certain relative way - STERIC EFFECT

Rate increase

to increase the rate one needs, according to collision theory, to have ...

more frequent collisions - increase particle speed   or
                                  have more particles present

more successful collisions - give particles more energy   or
                                    lower the activation energy

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- increase surface area
- increase pressure (gaseous reactions only)
- increase concentration
- increase temperature
- use a light source (certain reactions only)
- add a catalyst

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SURFACE AREA
- increasing surface area leads to more chances of a collision
- catalysts (in catalytic converters) are used in a finely divided form for this reason

+ *in many organic reactions you have two liquid layers, one aqueous, the other non-aqueous. Shaking the mixture improves the rate as an emulsion is often formed and the area of boundary layers is increased and more collisions can take place.*

Q.1 *What is the surface area of a cube of side 1cm?*

If you cut the cube in half, what is the new surface area ?

CONCENTRATION

Introduction   **Increasing concentration = more frequent collisions = increased rate**

| **LESS**
CONCENTRATED | | | **MORE**
CONCENTRATED |

LESS CONCENTRATED

SLOWER

MORE CONCENTRATED
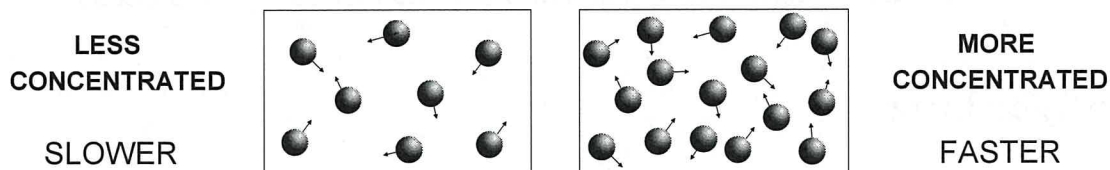
FASTER

Increasing the concentration of some reactants can have a greater effect than increasing the concentration of other reactants.

Rate   Reactions start off at their fastest then slow as the reactant concentration drops.

*eg*   In the reaction   **A + 2B —> C**   the concentrations might change as shown

• the steeper the curve the faster the rate of the reaction
• reactions start off quickly because of the greater likelihood of collisions
• reactions slow down with time because there are fewer reactants to collide
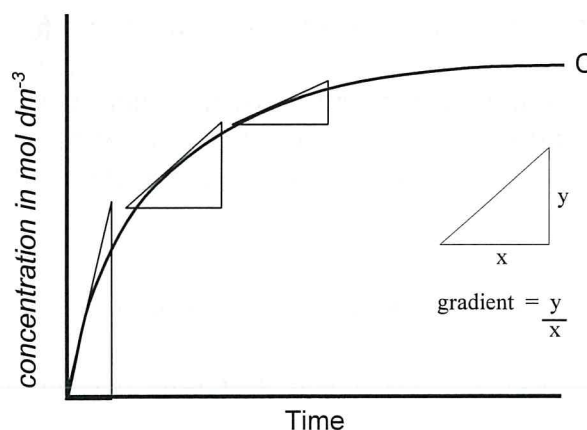
Reactants (A and B)
Concentration decreases with time

Products (C)
Concentration increases with time
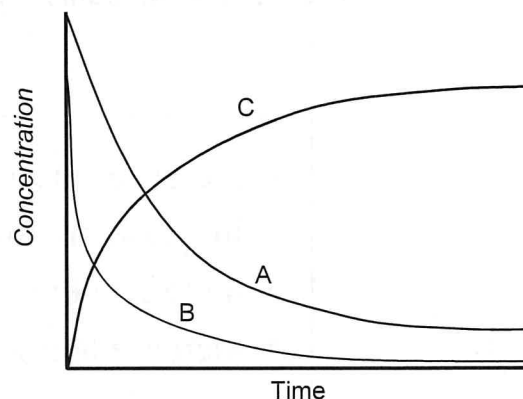
• the **rate of change** of concentration is found from the **slope** or **gradient**
• the slope at the start of the reaction will give the INITIAL RATE
• the slope gets less (showing the rate is slowing down) as the reaction proceeds

$$\text{gradient} = \frac{y}{x}$$

PRESSURE • increasing the pressure makes gas particles get closer together

• this increases the frequency of collisions so the reaction rate increases

• many industrial processes occur at high pressure to increase the rate but it also can affect the position of equilibrium - *see Chemical Equilibrium*

LOW
PRESSURE

SLOWER
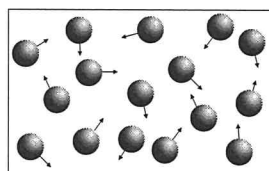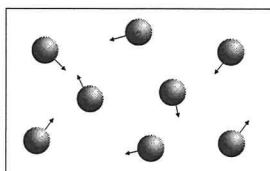
HIGH
PRESSURE

FASTER

*The greater the pressure, the more frequent th*e collisions

TEMPERATURE

Effect   **increasing the temperature increases the rate** of a reaction
• **particles get more energy** so they can overcome the energy barrier
• **particle speeds increase** so collisions are more frequent

Distribution of molecular velocities and energies

Introduction Because of the many collisions taking place, there is a **spread of molecular velocities and energies**. Experiments indicated that ...

• no particles have zero velocity
• some have very low and some have very high velocities
• most have intermediate velocities.

Number of
particles with
a given energy

MAXWELL - BOLTZMANN
DISTRIBUTION CURVE

0

Energy E_a T
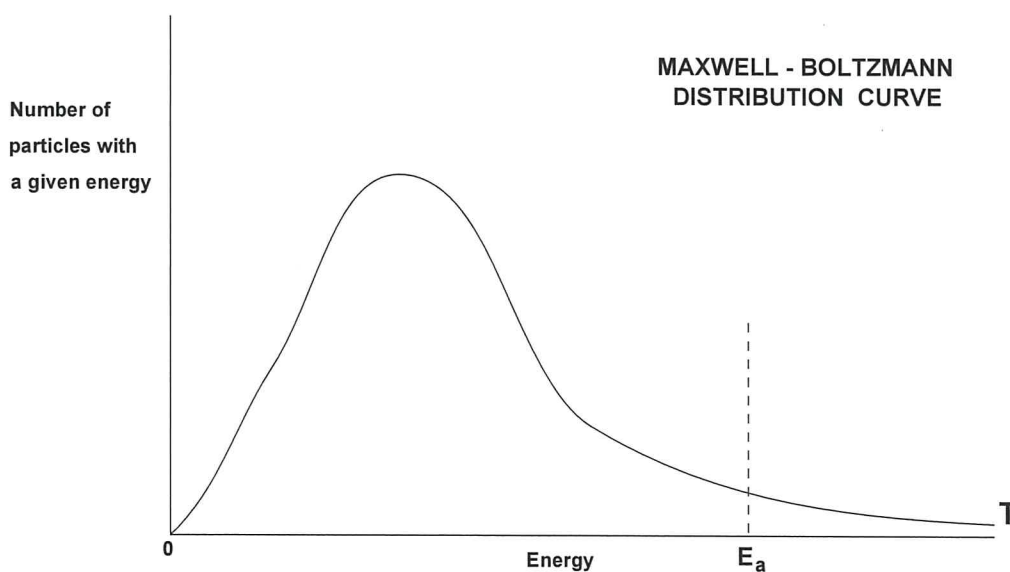
Significance E_a corresponds to the **Activation Energy**. The area under the curve beyond this value is proportional to the number of particles with energy greater than E_a

Increasing the temperature alters the distribution;

- get a **shift to higher energies/velocities**
- **curve gets broader and flatter** due to the greater spread of values
- **area under the curve stays constant**- corresponds to the total no. of particles

MAXWELL - BOLTZMANN DISTRIBUTION CURVE
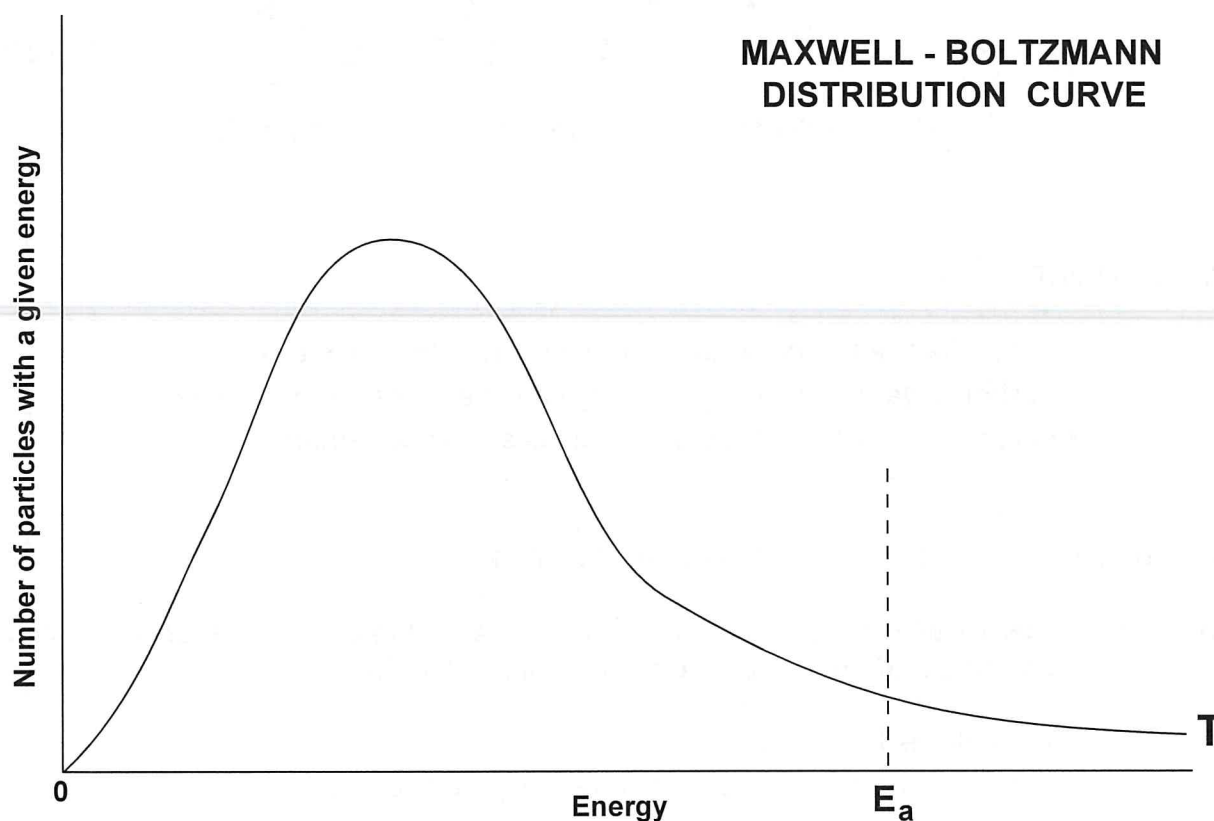
Q.2   *Superimpose the curves you get at a higher (T_2) and a lower (T_1) temperature.*

Explanation • increasing the temperature gives more particles with energy greater than E_a
- more reactants can overcome the energy barrier associated and form products
- a small rise in temperature can lead to a large increase in rate

The Effect of Temperature on the Rate of a Reaction
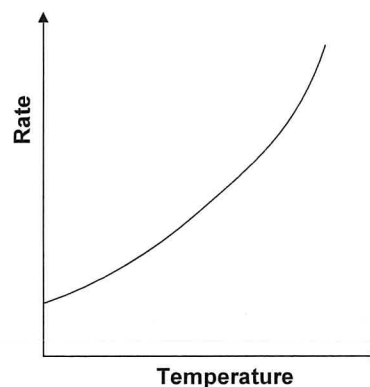
Energy Profiles   During a reaction the energy of the system rises to a maximum, then falls
There are two possibilities.

• energy falls below the original value
• overall release of energy

EXOTHERMIC REACTION
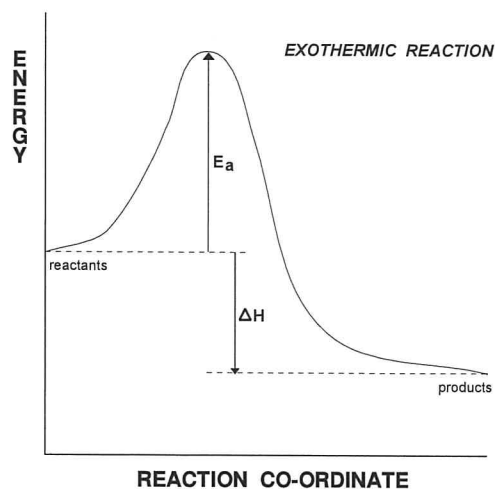
• energy rises above the original
• overall absorption of energy

ENDOTHERMIC REACTION
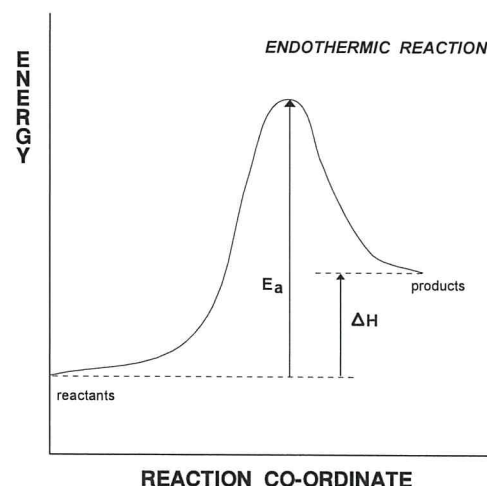
LIGHT   • shining a suitable light source onto some reactants increases the rate of reaction
• the light - often U.V. - provides energy to break bonds and initiate a reaction
• the greater the intensity of the light, the greater the effect

Examples   • the reaction between methane and chlorine - *see organic notes on alkanes*
• the reaction between hydrogen and chlorine

Equation $H_2(g)$ + $Cl_2(g)$ ⎯⎯⎯⎯⎯> $2HCl(g)$

Bond enthalpies   H-H ....**436**.... $kJ\ mol^{-1}$ Cl-Cl ....**242**.... $kJ\ mol^{-1}$

Mechanism Cl_2 ⎯⎯⎯> $2Cl•$ - - - - - - - - - - - *initiation*

H_2 + $Cl•$ ⎯⎯⎯> HCl + $H•$ - - - - - *propagation*
$H•$ + Cl_2 ⎯⎯⎯> HCl + $Cl•$

$2Cl•$ ⎯⎯⎯> Cl_2 - - - - - - - - - - - *termination*
$2H•$ ⎯⎯⎯> H_2
$H•$ + $Cl•$ ⎯⎯⎯> HCl
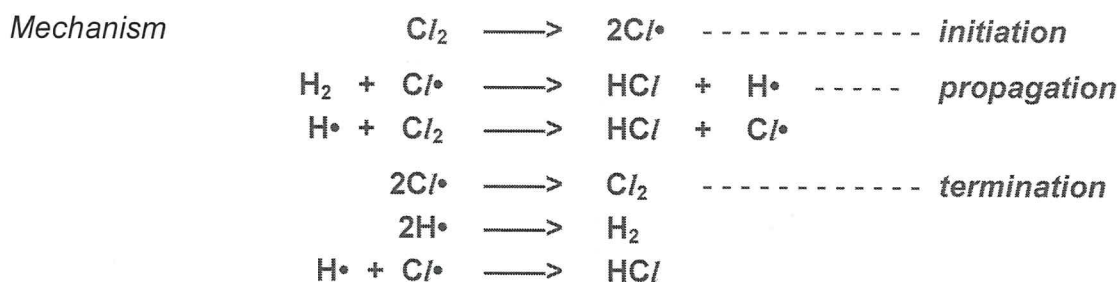
CATALYSTS

Operation   • provide an **alternative reaction pathway with a lower Activation Energy**

Number of particles

Maxwell-Boltzman Distribution Curve

WITH CATALYST   WITHOUT CATALYST

0   E_a E_a **Energy**
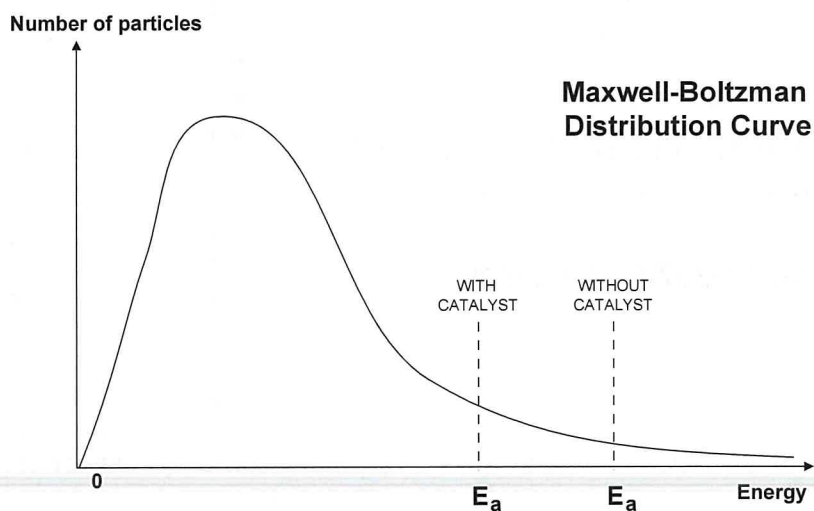
Lowering E_a results in there being a greater area under the curve showing that more molecules have energies in excess of the Activation Energy

• decreasing the Activation Energy means that more particles will have sufficient energy to overcome the energy barrier and react

• using catalysts avoids the need to supply extra heat - safer and cheaper

• catalysts **remain chemically unchanged at the end** of the reaction.

ENERGY

Energy profile for non-catalysed reaction

E_a

E_a

Each of the steps has a lower activation energy than the single reaction without a catalyst

reactants

ΔH

products

REACTION CO-ORDINATE
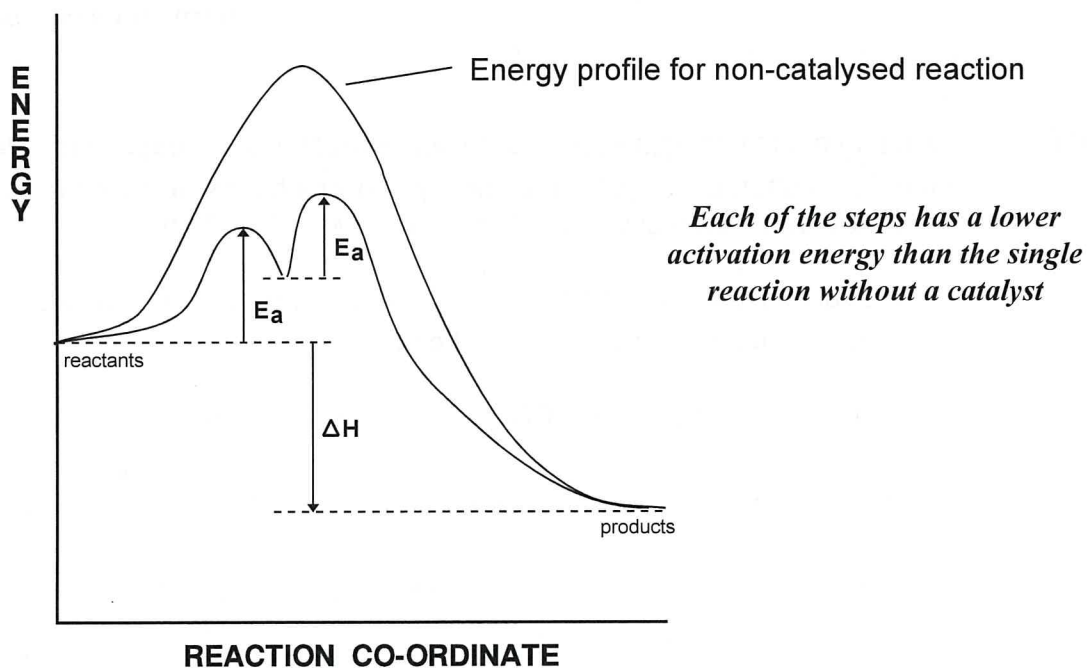
Types   **Homogeneous Catalysts**   **Heterogeneous Catalysts**
                 same phase as reactants   different phase to reactants

Uses

- widely used in industry where an increase in temperature would result in a lower yield due to a shift in equilibrium (e.g. Haber and Contact Processes)

- **CATALYSTS DO NOT AFFECT THE POSITION OF ANY EQUILIBRIUM** but they **do affect the rate at which equilibrium is attained**.

- a lot is spent on research into more effective catalysts - savings can be dramatic
- catalysts need to be changed regularly as they get 'poisoned' by other chemicals
- catalysts are used in a finely divided state to increase the surface area

Catalysts...

- allow reactions to take place at lower temperatures   SAVE ENERGY
    REDUCE CO_2 OUTPUT

- enable different reactions to be used   BETTER ATOM ECONOMY
    REDUCE WASTE

- are often enzymes   GENERATE SPECIFIC PRODUCTS
    OPERATE EFFECTIVELY AT ROOM TEMPERATURES

- have great economic importance in industry   POLY(ETHENE)
    SULPHURIC ACID
    AMMONIA
    ETHANOL PRODUCTION

- can reduce pollution   CATALYTIC CONVERTERS IN CARS

HETEROGENEOUS CATALYSIS
Catalyst is in a **different phase to the reactants**
e.g. a solid catalyst in a gaseous reaction

Action
- takes place at **active sites** on the **surface** of a solid
- gases are **adsorbed onto the surface**
- form weak bonds between gas and metal atoms

*Catalysis is thought to work in **three stages** as follows ...*

Adsorption • formation of bonds with surface weakens bonds in gas molecules makes a subsequent reaction easier

Reaction • adsorbed gases may be held on the surface increases chances of favourable collisions

Desorption • the products are then released from the active sites

> **HARD** **H**etero = **A**dsorption + **R**eaction + **D**esorption

The **strength of adsorption is critical** ...

Too weak   little adsorption - molecules will not bond to surface

Too strong molecules are held tightly and remain on the surface thus blocking reactive sites and preventing further reaction

Just right   reactants are attracted yet products can leave to open up active sites

Rate   Catalysis of gaseous reactions can lead to an increase in rate in several ways ...
- one species is adsorbed onto the surface so is more likely to undergo a collision
- one species is held in a favourable position for reaction to occur
- adsorption onto the surface allows bonds to break and fragments react quicker
- two reactants are adsorbed alongside each other give a greater concentration

Format
- used in a **finely divided** form   increases the surface area provides more collision sites.

- mounted in a **support** medium   maximises surface area to reduce costs

Examples
• Metals	Ni, Pt	hydrogenation reactions
	Fe	Haber Process
• Oxides	Al_2O_3	dehydration reactions
	V_2O_5	Contact Process

HOMOGENEOUS CATALYSIS
Catalyst and reactants are in the **same phase**

- reaction proceeds through an **intermediate** species with **lower energy**
- there is usually more than one reaction step
- transition metal ions often involved - **oxidation state changes** during reaction

Examples

Acids   e.g.   hydrolysis of esters

Gases   **OZONE** in the atmosphere breaks down naturally as follows ...

$$O_3 \longrightarrow O\bullet + O_2$$

It breaks down more easily in the presence of chlorofluorcarbons (CFC's).

There is a series of complex reactions but the basic process is :-

- *CFC's break down in the presence of UV light to form chlorine radicals* $CCl_2F_2 \longrightarrow Cl\bullet + \bullet CClF_2$

- *chlorine radicals then react with ozone* $O_3 + Cl\bullet \longrightarrow ClO\bullet + O_2$

- *chlorine radicals are regenerated* $ClO\bullet + O \longrightarrow O_2 + Cl\bullet$

Overall, chlorine radicals are not used up so a small amount of CFC's can destroy thousands of ozone molecules before the termination stage

THERMODYNAMICS

First Law Energy can be neither created nor destroyed but It can be converted from one form to another.

- all chemical reactions are accompanied by some form of energy change
- changes can be very obvious *(gas burning)* but in many cases it goes unnoticed

Enthalpy
- a measure of the heat content of a substance at constant pressure
- you cannot measure the actual enthalpy of a substance
- you can measure an ENTHALPY CHANGE at CONSTANT PRESSURE
- written as the symbol ΔH , "delta H"

Enthalpy change (ΔH) = Enthalpy of products - Enthalpy of reactants

EXOTHERMIC REACTION

ENDOTHERMIC REACTION

ENTHALPY

E_a

reactants

ΔH

products

REACTION CO-ORDINATE

ENTHALPY

E_a

products

ΔH

reactants

REACTION CO-ORDINATE
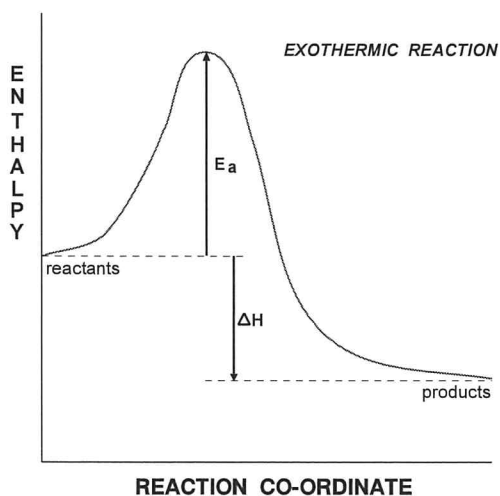
Enthalpy of reactants > products

$$\Delta H = - \text{ive}$$

EXOTHERMIC *Heat given out*
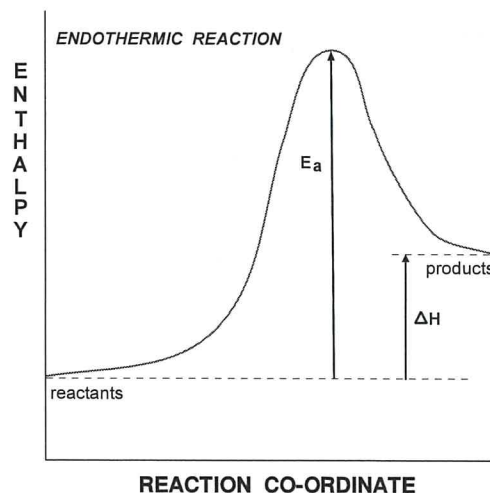
Enthalpy of reactants < products

$$\Delta H = + \text{ive}$$

ENDOTHERMIC *Heat absorbed*

Examples

EXOTHERMIC
- **combustion** of fuels $CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$
- **respiration** $C_6H_{12}O_6 + 6O_2 \longrightarrow 6CO_2 + 6H_2O$
  (oxidation of carbohydrates such as glucose)
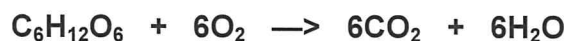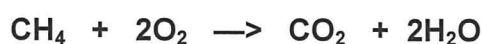
ENDOTHERMIC
- **photosynthesis** $6CO_2 + 6H_2O \longrightarrow C_6H_{12}O_6 + 6O_2$
- **thermal decomposition** $CaCO_3 \longrightarrow CaO + CO_2$
  of calcium carbonate
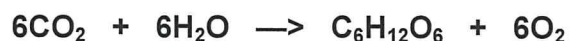
Standard Enthalpy Changes

- enthalpy values vary with the conditions - so standard conditions are needed
- a substance will then be in its **standard state** ...

Pressure:- **100 kPa** (1 atm)   *A stated temperature*:- usually **298K** (25°C)

- as a guide, just think of a substance under normal laboratory conditions
- assign the correct subscript [e.g. (g), (l) or (s)] to indicate which state it is in
- any solutions are of concentration 1 mol dm^{-3}
- to tell if standard conditions are used we modify the symbol for ΔH .

Enthalpy Change   **Standard Enthalpy Change (at 298K)**

$$\Delta H \qquad\qquad\qquad \Delta H^{\ominus}_{298}$$

Standard Enthalpy Change of Combustion (ΔH°_c)

Definition   The enthalpy change when ONE MOLE of a substance undergoes complete combustion under standard conditions. All reactants and products are in their standard states.

Values   **Always exothermic**

Example(s) $C_{(graphite)}$ **+** $O_{2(g)}$ ⟶ $CO_{2(g)}$

$C_2H_5OH_{(l)}$ **+** $3O_{2(g)}$ ⟶ $2CO_{2(g)}$ **+** $3H_2O_{(l)}$
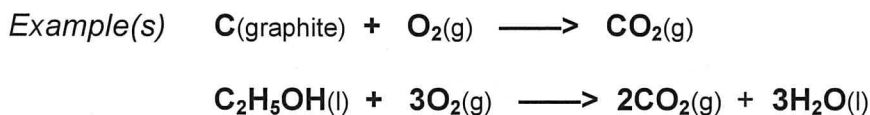
Notes   *To aid balancing the equation, remember that you get one carbon dioxide molecule for every carbon atom in the original molecule and a water molecule for every two hydrogen atoms. Having done this, go back and balance the oxygen.*

Q.1   *Write equations representing the standard enthalpy change of combustion of...*

methane

methanol

cyclohexane

hydrogen

carbon

Standard Enthalpy Change of Formation (ΔH°_f)

Definition   The enthalpy change when ONE MOLE of a compound is formed in its standard state from its elements in their standard states.

Values   Usually, but not exclusively, **exothermic**

Example(s) $2C_{(graphite)}$ **+** $\frac{1}{2}O_{2(g)}$ **+** $3H_{2(g)}$ ———> $C_2H_5OH_{(l)}$

Notes
- Elements In their standard states have zero enthalpy of formation.
- Carbon is usually taken as the graphite allotrope.

Q.2   *Construct equations representing the standard enthalpy change of formation of*

methane

sulphuric acid

sodium chloride

water

carbon dioxide

Q.3   *What do you notice about the equations for..*
- *the standard enthalpy change of combustion of hydrogen and the standard enthalpy change of formation of water?*

- *the standard enthalpy change of combustion of carbon and the standard enthalpy change of formation of carbon dioxide?*

Enthalpy of Neutralisation

Definition   Enthalpy change when ONE MOLE of water is formed from its ions in dilute soln.

Values   **Exothermic**

Equation $H^+_{(aq)}$ **+** $OH^-_{(aq)}$ ———> $H_2O_{(l)}$

Notes   A value of $-57 kJ\ mol^{-1}$ is obtained when strong acids react with strong alkalis.

Bond Dissociation Enthalpy (Energy)

Definition Energy required to break ONE MOLE of gaseous bonds to form gaseous atoms.

Values **Endothermic** *Energy must be put in to break any chemical bond*

Example $Cl_2(g) \longrightarrow 2Cl(g)$

Notes
- the strength of a bond depends on its environment so MEAN values are quoted
- making a bond is an exothermic process as it is the opposite of breaking a bond
- for diatomic gases, the bond enthalpy is twice the enthalpy of atomisation
- the smaller the bond enthalpy, the weaker the bond and the easier it is to break

Some mean bond enthalpies (in kJ mol^{-1})
(values may differ slightly in other texts)

H-H	436	H-F	562	N-N	163		
C-C	346	H-Cl	431	N=N	409		
C=C	611	H-Br	366	N≡N	944		
C≡C	837	H-I	299	P-P	172		
C-O	360	H-N	388	F-F	158		
C=O	743	H-O	463	Cl-Cl	242		
C-H	413	H-S	338	Br-Br	193		
C-N	305	H-Si	318	I-I	151		
C-F	484	P-H	322	S-S	264		
C-Cl	338	O-O	146	Si-S	176		
C-Br	276	O=O	496	Si-O	374		

HESS'S LAW "The enthalpy change is independent of the path taken"
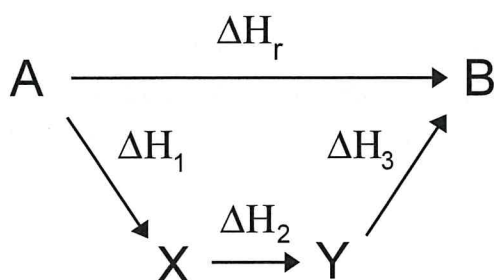
$$\Delta H_r = \Delta H_1 + \Delta H_2 + \Delta H_3$$

- applying Hess's Law enables one to calculate enthalpy changes from other data
- used for calculating changes which can't be measured directly - *Lattice Enthalpy*
- used for calculating - enthalpy change of reaction from bond enthalpy
  - enthalpy change of reaction from $\Delta H°_c$
  - enthalpy change of formation from $\Delta H°_f$

Enthalpy change of reaction from average bond enthalpies

Theory   Imagine that, during a reaction, all the bonds of reacting species are broken and the individual atoms join up again but in the form of products. The overall energy change will depend on the difference between the energy required to break the bonds and that released as bonds are made.

energy released making bonds > energy used to break bonds ... EXOTHERMIC

energy used to break bonds > energy released making bonds ... ENDOTHERMIC

Example   *Calculate the enthalpy change for the hydrogenation of ethene*

$$\Delta H_2$$
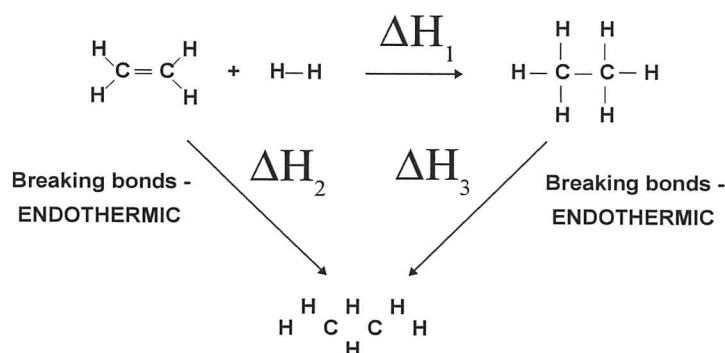
$$
\begin{aligned}
1 \times \ C=C \ \text{bond @ 611} &= \ 611 \\
4 \times \ C-H \ \text{bonds @ 413} &= \ 1652 \\
1 \times \ H-H \ \text{bond @ 436} &= \ \ 436 \\
\end{aligned}
$$

Total energy required to BREAK bonds of reactants = 2699 kJ mol^{-1}

$$\Delta H_3$$

$$
\begin{aligned}
1 \times \ C-C \ \text{bond} \ \ \text{@ 346} &= \ \ 346 \\
6 \times \ C-H \ \text{bonds} \ \text{@ 413} &= \ 2478 \\
\end{aligned}
$$

Total energy required to BREAK bonds of products = 2824 kJ mol^{-1}

Applying HESS'S LAW $\Delta H_1 = \Delta H_2 - \Delta H_3$

$$= 2699 - 2824 \qquad = -125\text{kJ}$$

Q.4   *Using the average bond enthalpies in your notes, calculate the standard enthalpy changes of reaction for the following reactions.*

a) $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(g)$

b) $CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(g)$

c) $H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$

d) $C_2H_5OH(g) + HBr(g) \longrightarrow C_2H_5Br(g) + H_2O(g)$

Enthalpy change of reaction from enthalpy changes of combustion and formation

Formation   If you formed the products from their elements you should need the same amounts of every substance as if you formed the reactants from their elements.

By applying Hess's Law ...

$$A \xrightarrow{\Delta H_r} B$$

ΔH_f ΔH_f

ELEMENTS

ELEMENTS

ΔH_f

REACTANTS

ΔH_f

ΔH_r
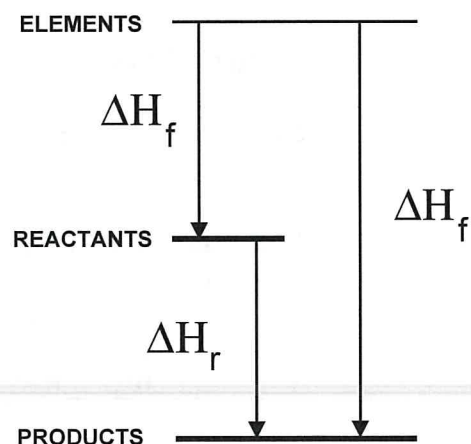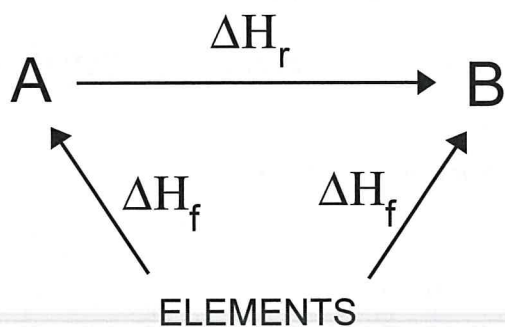
PRODUCTS

$$\Delta H_r = \sum \Delta H_{f\ (PRODUCTS)} - \sum \Delta H_{f\ (REACTANTS)}$$

example   *Calculate the standard enthalpy change for the following reaction, given that the standard enthalpies of formation of water, nitrogen dioxide and nitric acid are -286, +33 and -173 kJ mol^{-1} respectively.   [oxygen's value is ZERO as it is an element]*

$$2H_2O(l) \ + \ 4NO_2(g) \ + \ O_2(g) \ \longrightarrow \ 4HNO_3(l)$$
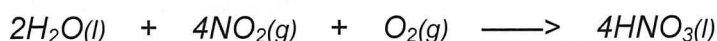
applying Hess's Law ... $\Delta H°_r =$ *[4(-173)] - [2(-286) + 4(+33) + 0]   = -252 kJ*

Q.5   *If the standard enthalpy changes of formation of SO$_2$(g) and SO$_3$(g) are -296 and -395 kJ mol^{-1} respectively, calculate the enthalpy change of reaction of ...   2SO$_2$(g) + O$_2$(g) $\longrightarrow$ 2SO$_3$(g)*

Combustion   If you burned all the products you should get the same amounts of CO_2 and H_2O etc. as if you burned the reactants.

Applying Hess's Law ...
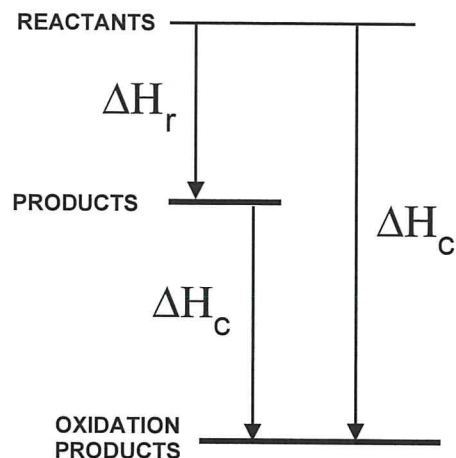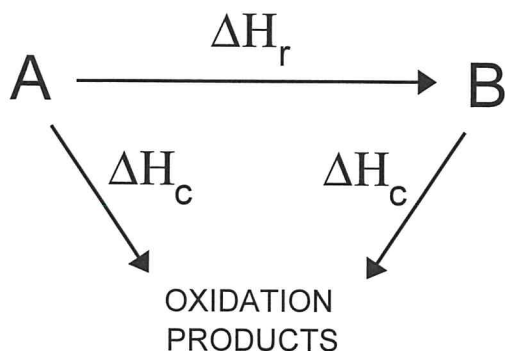
$$\Delta H_r = \sum \Delta H_{c\,(REACTANTS)} - \sum \Delta H_{c\,(PRODUCTS)}$$

example   *Calculate the standard enthalpy change of formation of methane, given that the standard enthalpies of combustion of carbon, hydrogen and methane are -394, -286 and -890 kJ mol^{-1} respectively.*

$$C_{(graphite)} + 2H_{2(g)} \longrightarrow CH_{4(g)}$$
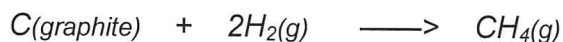
applying Hess's law ... $\Delta H^\circ_r = [\,(-394) + 2(-286)\,] - [\,(-890)\,] = -74\ kJ\ mol^{-1}$

Q.6   *Calculate the enthalpy change of reaction for* $H_2 + C_2H_4 \longrightarrow C_2H_6$
given that the enthalpy changes of combustion of H_2, C_2H_4 *and* C_2H_6 *are*
-286, -1409 and -1560 kJ mol^{-1} respectively.

Compare this value with that obtained using average bond enthalpies.

Measuring Enthalpy Changes

Calorimetry   • involves the practical determination of enthalpy changes
   • usually involves heating (or cooling) known amounts of water

water is heated up	reaction is EXOTHERMIC
water cools down	reaction is ENDOTHERMIC

Calculation   The energy required to change the temperature of a substance can be found;

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

where	q =	heat energy	kJ	
	m =	mass	kg	
	c =	Specific Heat Capacity	kJ K^{-1} kg^{-1}	[water is 4.18]
	ΔT =	change in temperature	K	

ΔT The value of ΔT is usually calculated graphically by measuring the temperature changes before, during and after a reaction.

Graphical method

The temperature is taken every half minute before mixing the reactants.

Reactants are mixed after 3 minutes.

Further readings are taken every half minute as the reaction mixture cools.

Extrapolate the lines as shown and calculate the value of ΔT.

Example 1   When 0.18g of hexane underwent complete combustion, it raised the temperature of 100g (0.1kg) water from 22°C to 47°C. Calculate its enthalpy of combustion.

Heat absorbed by the water (q)   = 0.1 x 4.18 x 25   =   10.45 kJ

Moles of hexane burned   = mass / M_r =   0.18 / 86
                                              =   0.00209

Enthalpy change   = heat energy / moles = − 10.45 / 0.00209

ANS   − 5000 kJ mol^{-1}

Example 2   25cm³ of 2.0M HCl was added to 25cm³ of 2.0M NaOH in an insulated beaker. The initial temperature of both solutions was 20°C. The reaction mixture was stirred to ensure mixing and the highest temperature reached by the solution was 33°C. Calculate the Molar Enthalpy of Neutralisation.

Temperature rise (ΔT)	=	306K - 293K	=	13K
Volume of resulting solution	=	50cm³	=	0.05 dm³
Equivalent mass of water	=	50g	=	0.05 kg
Heat absorbed by the water (q)	=	0.05 x 4.18 x 13	=	2.717 kJ
Moles of HCl reacting	=	2 x 25/1000	=	0.05 mol
Moles of NaOH reacting	=	2 x 25/1000	=	0.05 mol

Equation   NaOH + HCl ——> NaCl + H_2O

Moles of water produced   = 0.05 mol

Enthalpy change per mol (ΔH)   = − (heat energy / moles of water)

                                     = − 2.717 / 0.05

                         ANS   − 54.34 kJ mol ⁻¹

Q.7   *What is the usual value for the Molar Enthalpy of Neutralisation ?*

Why might the value calculated from the reaction between sodium hydroxide and ethanoic acid differ from the usual value?

Results from simple calorimetry experiments are seldom very accurate. Make a list of possible sources of error and suggests improvements to the experiment.

Enthalpy of Combustion of Alkanes

1. Write the equation representing the Standard Enthalpy Change of Combustion of heptane, C_7H_{16}.

    ....

2. Using the data, plot a graph of Enthalpy of Combustion against number of carbon atoms.

Compound	Enthalpy of Combustion / kJ mol^{-1}
CH_4	- 890
C_2H_6	- 1560
C_3H_8	- 2220
C_4H_{10}	- 2877
C_5H_{12}	- 3509
C_6H_{14}	- 4194
C_8H_{18}	- 5512

3. Use your graph to calculate the following

    a) the value of the Enthalpy Change of Combustion of heptane   ....

    b) an approximate value for the Enthalpy Change of Combustion of hydrogen   ....

4. State, giving reasons, any advantages of using butane as a household fuel.

    ....

    ....

    ....

5. State, giving reasons, any disadvantages of using butane as a household fuel.

    ....

    ....

    ....

6. Calculate the amount of heat produced when 1kg of the following undergo complete combustion.

    a) CH_4

    b) C_4H_{10}