A2 CHEMISTRY 9701

Crash Course

PROSPERITY ACADEMY

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REACTION KINETICS

COMPLETE NOTES

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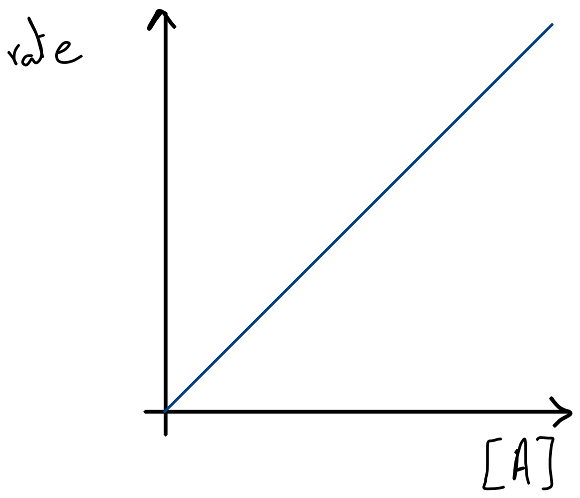
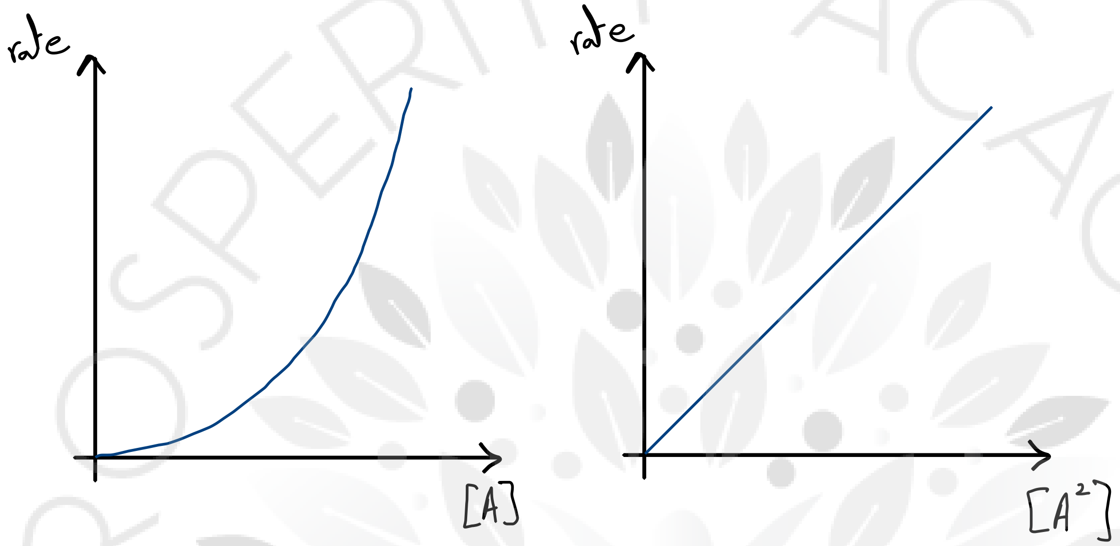
Reaction Kinetics:-

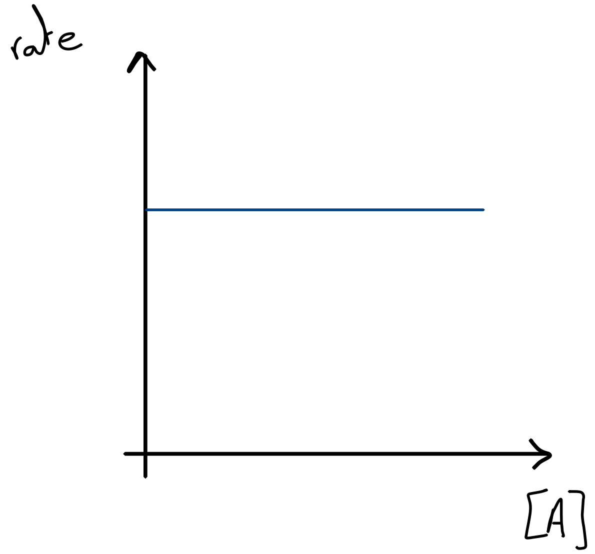
Rate - concentration graphs:-



rate $\propto$ [A]
(1st order w.r.t to [A])



rate $\propto [A]^2$
(2nd order w.r.t [A])



rate unaffected by [A]

Order of reaction:- The power to which a concentration term is raised

- cannot be determined from equation unless mechanism is known
- we determine it experimentally by varying the concentration of one reactant while keeping others constant

e.g. $rate = K[A]^2[B]^1$ (The units of rate are $mol\ dm^{-3}\ s^{-1}$)

K: rate constant, rate is 2nd order w.r.t [A] and 1st order w.r.t [B] and 3rd order in total

- K (rate constant) increases with temperature

4 (a) Chlorine dioxide undergoes the following reaction in aqueous solution.

$$2ClO_2 + 2OH^- \rightarrow ClO_2^- + ClO_3^- + H_2O$$

The initial rate of the reaction was measured at different initial concentrations of ClO_2 and OH^-. The table shows the results obtained.

experiment	$[ClO_2]$ / $mol\,dm^{-3}$	$[OH^-]$ / $mol\,dm^{-3}$	initial rate / $mol\,dm^{-3}\,s^{-1}$
1	1.25×10^{-2}	1.30×10^{-3}	2.33×10^{-4}
2	2.50×10^{-2}	1.30×10^{-3}	9.34×10^{-4}
3	2.50×10^{-2}	2.60×10^{-3}	1.87×10^{-3}

(i) Use the data in the table to determine the rate equation, showing the order with respect to each reactant. Show your reasoning.

Comparing experiments 1 and 2, the $[ClO_2]$ increased by a factor of $2.5\times10^{-2}/1.25\times10^{-2} = 2$ while the rate constant increased by a factor of $9.34\times10^{-4}/2.33\times10^{-4} = 4$ so the rate is 2nd order w.r.t to $[ClO_2]$. Comparing experiments 2 and 3, the $[OH^-]$ increased by a factor of $2.6\times10^{-3}/1.30\times10^{-3} = 2$ while the rate constant increased by a factor of $1.87\times10^{-3}/9.34\times10^{-4} = 2$ so the rate is 1st order w.r.t $[OH^-]$

rate equation = $K[ClO_2]^2[OH^-]$

[3]

(ii) Calculate the value of the rate constant, k, using the data from experiment 2. State its units.

$9.34\times10^{-4} = K(2.50\times10^{-2})^2(1.30\times10^{-3})$

$K = 1149.5$

$mol\,dm^{-3}s^{-1} = K(mol\,dm^{-3})^2(mol\,dm^{-3})$

$\cancel{mol\,dm^{-3}}\,s^{-1} = K(mol^{\cancel{3}}\,dm^{-\cancel{6}})$ $\Rightarrow K = dm^6\,mol^{-2}\,s^{-1}$

k = 1150 units $dm^6\,mol^{-2}\,s^{-1}$ [2]

Same units as this as equation same

(d) NO reacts readily with oxygen.

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

The table shows how the initial rate of this reaction at 25 °C depends on the initial concentrations of the reactants.

initial concentration / $mol\,dm^{-3}$		initial rate / $mol\,dm^{-3}\,s^{-1}$
$[NO(g)]$	$[O_2(g)]$	
0.100	0.0500	3.50
0.0500	0.100	1.75
0.0500	0.0500	0.875

(i) Deduce the order of reaction with respect to each reactant. Explain your reasoning.

order with respect to $[NO(g)]$ Comparing experiment 1 & 3, when $[NO]$ increased by a factor of $\frac{0.100}{0.0500} = 2$ from expt 3 to 1, the rate increased by $\frac{3.50}{0.875} = 4$ so 2nd order w.r.t $[NO]$

order with respect to $[O_2(g)]$ Comparing expt 2 & 3, when $[O_2]$ increased by a factor of $\frac{0.1}{0.05} = 2$ from expt 3 to 2, the rate increased by $\frac{1.75}{0.875} = 2$ so 1st order w.r.t $[O_2]$

[2]

(ii) State the rate equation for this reaction. Use the rate equation to calculate the rate constant. Include the units for the rate constant in your answer.

rate = $K[NO_{(g)}]^2[O_{2(g)}]$

$0.875 = K(0.05)^2(0.05)$

$K = 7000$

rate constant, k = 7.00×10^3

units of k = $dm^6\,mol^{-2}\,s^{-1}$

[3]

Deducing mechanism from order:-

- Only reactants involved in or up till the slowest step will appear in the rate equation.

- The order of a concentration term tells us how many molecules of a particular reactant were involved in the mechanism till the slow step.

Q. Work out the rate equations from the following mechanisms:-

a) $A + B + C \rightarrow ABC$

Mechanism:- $A + B \rightarrow AB$ slow
$AB + C \rightarrow ABC$ fast

rate $= K[A][B]$

b) $A + B + C \rightarrow ABC$

Mechanism:- $A + B \rightarrow AB$ fast
$AB + C \rightarrow ABC$ slow

rate $= K[A][B][C]$

c) $2A + B \rightarrow C$

Mechanism:- $2A \rightarrow X$ slow
$X + B \rightarrow C$ fast

rate $= K[A]^2$

(d) The reaction between X and Y was studied.

$$2X + Y \rightarrow Z$$

The following sequence of steps is a proposed mechanism for the reaction.

step 1 $2X \rightarrow V$ slow
step 2 $V + Y \rightarrow Z$ fast

The general form of the rate equation for this reaction is as follows.

$$\text{rate} = k[X]^m[Y]^n$$

Step 1 is the slower step in the mechanism.

Deduce the values of m and n in the rate equation.

m = 2 n = 0 [1]

(ii) The equation for the reaction between ClO_2 and F_2 is shown.

$$2ClO_2 + F_2 \rightarrow 2ClO_2F$$

$$\text{rate} = k[ClO_2][F_2]$$

The mechanism for this reaction has two steps.

Suggest equations for the **two** steps of this mechanism, stating which of the two steps is the rate-determining step.

step 1 $ClO_2 + F_2 \rightarrow ClO_2F + F$

step 2 $ClO_2F + F \rightarrow ClO_2F$

rate-determining step = 1 [2]

(e) By considering the rate equation, explain why the rate increases with increasing temperature.

increasing temperature increases K so rate increases [1]

The rate equation for this reaction is given.

$$\text{rate} = k[NO]^2[H_2]$$

(f) The reaction is believed to proceed in three steps.

2 molecules of NO
1 molecule of H_2

1 $2NO \rightarrow N_2O_2$

2 $N_2O_2 + H_2 \rightarrow N_2O + H_2O$ slow

3 $N_2O + H_2 \rightarrow N_2 + H_2O$

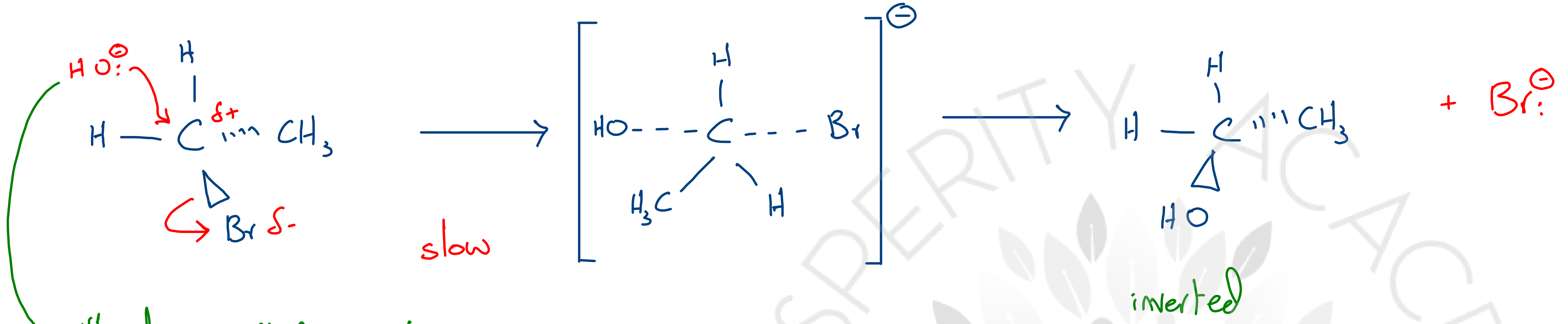
(i) Deduce which of the three steps is the rate-determining step.

2 [1]

(ii) Explain your answer to **(i)**.

The rate equation tells us that 2 molecules of NO and 1 molecule of H_2 is involved till the rate determining step so rate determining step will be step 2. [1]

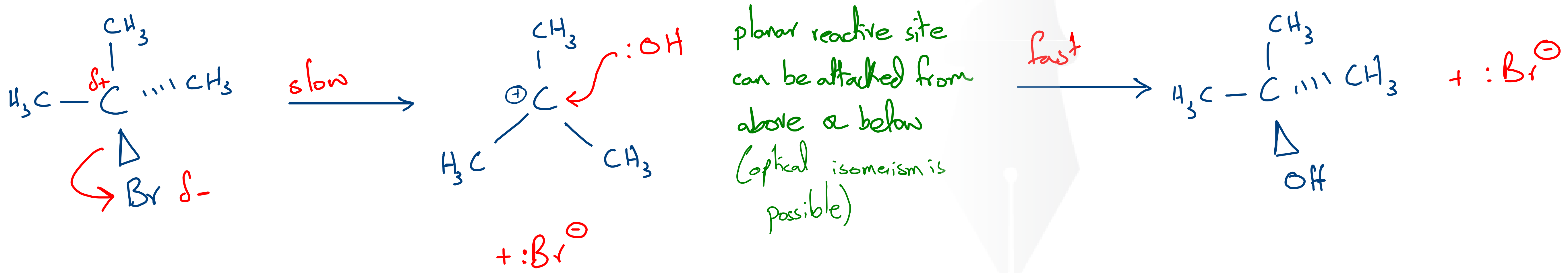
S_N2 mechanism:- OH^- substitution into primary halogenoalkane



will always attack opposite leaving group (optical isomerism not possible)

- As 1 OH^- and 1 halogenoalkane molecule took part in this reaction till the slow step, rate is 1st order w.r.t both
- rate = $K[OH^-][CH_3CH_2Br]$
- 2 molecules involved till RDS so that's why S_N2.

S_N1 mechanism:- OH^- substitution into tertiary halogenoalkane



- As only 1 halogenoalkane molecule is involved up till the RDS, the rate is 1st order w.r.t to it
- rate = $K[(CH_3)_3CBr]$ – 1 molecule involved till RDS that is why S_N1

4 (a) Ethanal, CH_3CHO, dimerises in alkaline solution according to the following equation.

$$2CH_3CHO \rightarrow CH_3CH(OH)CH_2CHO$$

The initial rate of this reaction was measured, starting with different concentrations of CH_3CHO and OH^-. The following results were obtained.

$[CH_3CHO]$ / mol dm^{-3}	$[OH^-]$ / mol dm^{-3}	initial rate of reaction (relative values)
0.10	0.015	1
0.20	0.015	2
0.40	0.030	8

2x 2x 2x 2x 2x = 4 2x

(i) Deduce the order of the reaction with respect to CH_3CHO.

1st order [1]

(ii) Deduce the order of the reaction with respect to OH^-.

1st order [1]

(iii) State the overall rate equation for this reaction.

rate = $[CH_3CHO][OH^-]$ [1]

(iv) State the units for the rate constant, k.

$mol\,dm^{-3}s^{-1} = mol^2dm^{-6} \times K$

$K = dm^3\,mol^{-1}s^{-1}$

$dm^3\ mol^{-1}\ s^{-1}$ [1]

(v) Calculate the initial rate of reaction (relative value) for a reaction where the $[CH_3CHO]$ is 0.30 mol dm^{-3} and $[OH^-]$ is 0.030 mol dm^{-3}.

Using expt 3

$[CH_3CHO]$ decreased by $\frac{0.30}{0.40} = \frac{3}{4}$

so rate must also decrease by $3/4$ so $8 \times \frac{3}{4} = \boxed{6}$

Ans

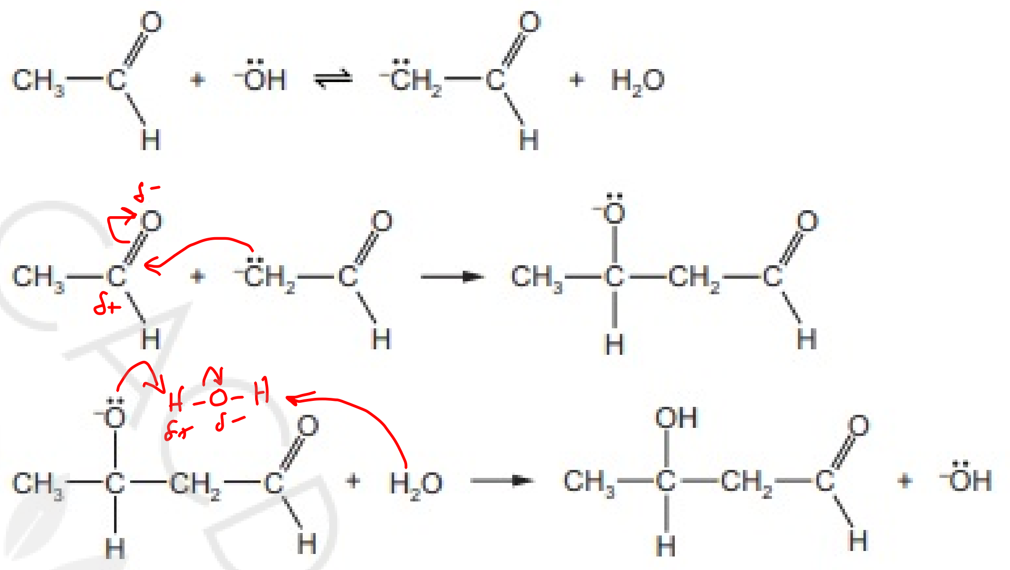
[1]

(b) (i) A three-step mechanism has been proposed for the reaction in (a).

step 1

step 2

step 3



Using your rate equation in (iii), predict which is the rate-determining step. Explain your answer.

rate-determining step 1

explanation 1 molecule of CH_3CHO and 1 molecule of H_2 must be involved till RDS according to rate equation [2]

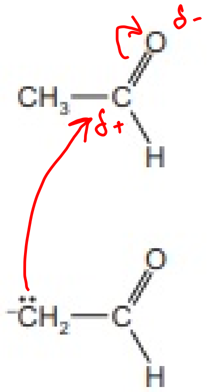
(ii) Describe the chemical behaviour of CH_3CHO in step 1.

Brønsted Lowry acid [1]

(c) Name the mechanism occurring in steps 2 and 3.

nucleophilic addition [1]

(d) Using the diagram below, show the mechanism for step 2 showing the relevant curly arrows and dipoles.



[2]

(b) The rate of this reaction was measured at different initial concentrations of the two reagents. The table shows the results obtained.

experiment	$[C_6H_5CHClCH_3]$ / mol dm^{-3}	$[OH^-]$ / mol dm^{-3}	relative rate
1	0.05	0.10	0.5
2	0.10	0.20	1.0
3	0.15	0.10	1.5
4	0.20	0.15	to be calculated

2x 2x 3x 2x 3x

(i) Deduce the order of reaction with respect to each of $[C_6H_5CHClCH_3]$ and $[OH^-]$. Explain your reasoning.

order with respect to $[C_6H_5CHClCH_3]$ ....1 st order....

....

order with respect to $[OH^-]$ ....zero order....

.... [2]

(ii) Write the rate equation for this reaction, stating the units of the rate constant, k.

rate = ...$K\,[C_6H_5CHClCH_3]$.... mol dm^{-3} s^{-1}

units of k = ...s^{-1}....

this means its S_N1 [1]

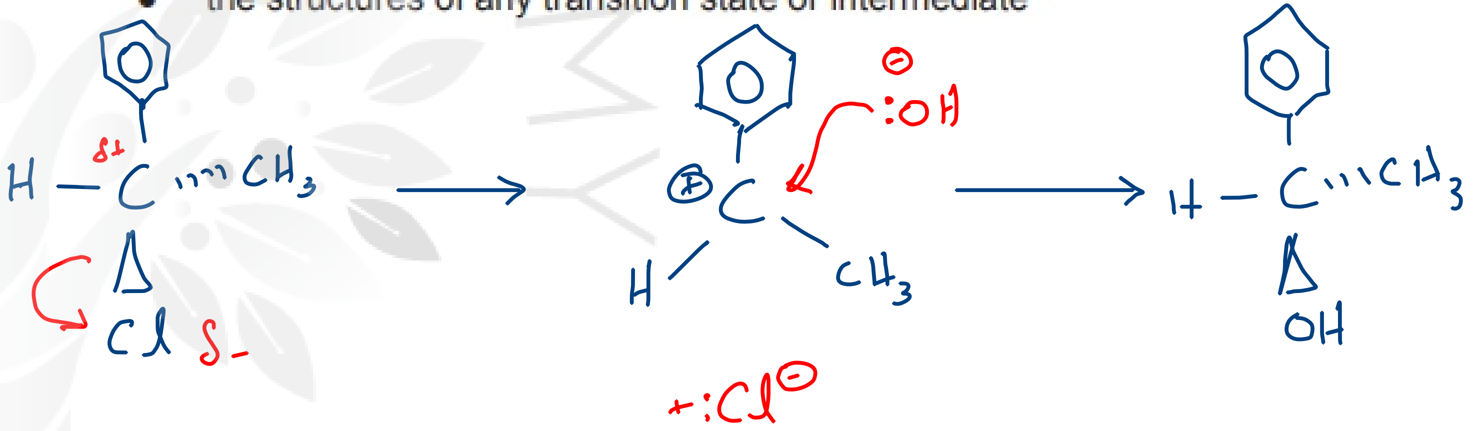
(iii) Calculate the relative rate for experiment 4.

Comparing 2 & 4   1×2

relative rate for experiment 4 = ...2.0.... [1]

(c) (i) Use your answers in **(b)(i)** to help you to draw the mechanism for the reaction of 1-chloro-1-phenylethane with hydroxide ions, including the following.

- all relevant lone pairs and dipoles
- curly arrows to show the movement of electron pairs
- the structures of any transition state or intermediate



[3]

(ii) This reaction was carried out using a single optical isomer of 1-chloro-1-phenylethane.

Use your mechanism in **(i)** to predict whether the product will be a single optical isomer or a mixture of two optical isomers. Explain your answer.

It will be a mixture of 2 optical isomers as planar reactive site can be attacked from above or below [1]

Important information for this question

- In this question (pr) means 'a solution in propanone'.
- Sodium iodide is soluble in propanone giving $Na^+(pr)$ and $I^-(pr)$.
- Sodium chloride is insoluble in propanone.

(c) The rate of this reaction was measured at different initial concentrations of the two reagents. The table shows the results obtained.

experiment	$[CH_3CH_2CHClCH_3]$ / mol dm^{-3}	$[I^-]$ / mol dm^{-3}	relative rate
1	0.06	0.03	3
2	0.10	0.03	5
3	0.06	0.05	5
4	0.08	0.04	to be calculated

(i) Deduce the order of reaction with respect to each of $[CH_3CH_2CHClCH_3]$ and $[I^-]$. Explain your reasoning.

order with respect to $[CH_3CH_2CHClCH_3]$ .... 1st order

....

order with respect to $[I^-]$ .... 1st order

.... [2]

(ii) Write the rate equation for this reaction, stating the units of the rate constant, k.

rate = $k[CH_3CH_2CHClCH_3][I^-]$ .... mol dm^{-3} s^{-1}

units of k = $dm^3\ mol^{-1}\ s^{-1}$ .... [1]

so S_N2

(iii) Calculate the relative rate for experiment 4.

Comparing 1 & 4

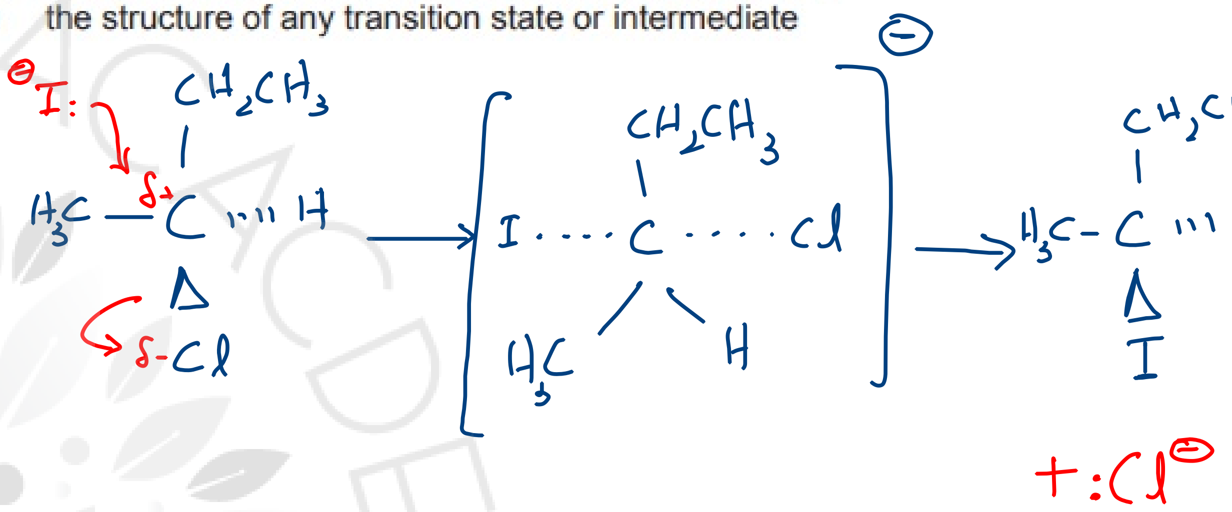
$\uparrow [CH_3CH_2CHClCH_3] = \frac{0.08}{0.06} = \frac{4}{3}$ $\uparrow [I^-] = \frac{0.04}{0.03} = \frac{4}{3}$

$\uparrow rate = 3 \times \frac{4}{3} \times \frac{4}{3} = 5.333$

relative rate for experiment 4 = ... 5.3 .... [1]

(d) (i) Suggest the mechanism for the reaction of 2-chlorobutane with iodide ions. Draw out the steps involved, including the following.

- all relevant lone pairs and dipoles
- curly arrows to show the movement of electron pairs
- the structure of any transition state or intermediate



[3]

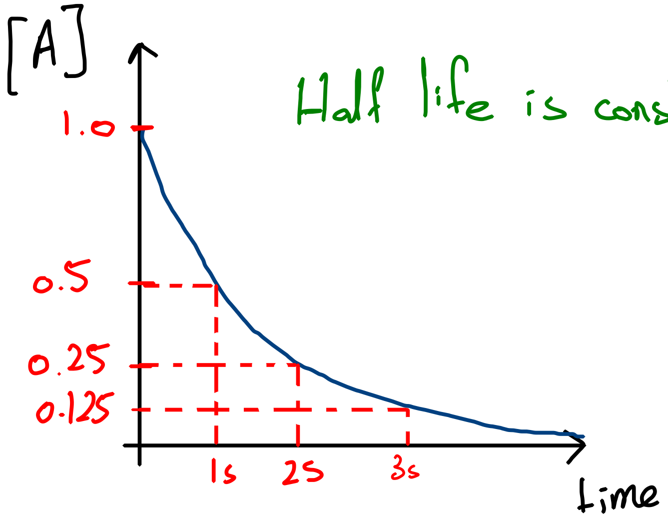
(ii) This reaction was carried out using a single optical isomer of 2-chlorobutane.

Use your mechanism in **(i)** to predict whether the product will be a single optical isomer or a mixture of two optical isomers. Explain your answer.

single optical isomer as I^- can only attack from opposite side of Cl.
.... [1]

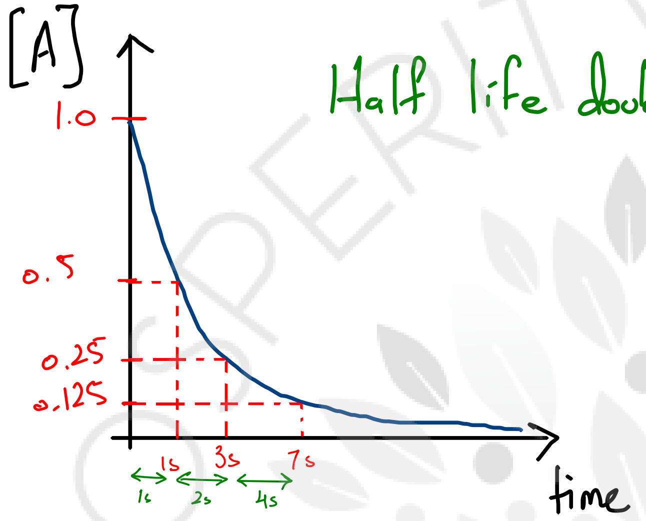
Concentration - Time Graphs:-

rate can be found out using |gradient|



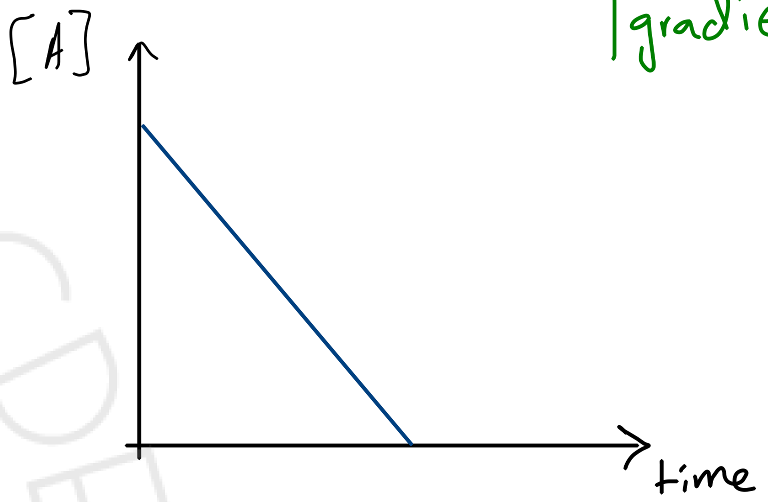
Half life is constant

rate is 1st order w.r.t [A]



Half life doubles

rate is 2nd order w.r.t [A]



rate is zero w.r.t [A]
rate is constant

Half life for 1st order graphs:-

- time taken for concentration of reactant to be halved

$$t_{1/2} = \frac{0.693}{K}$$

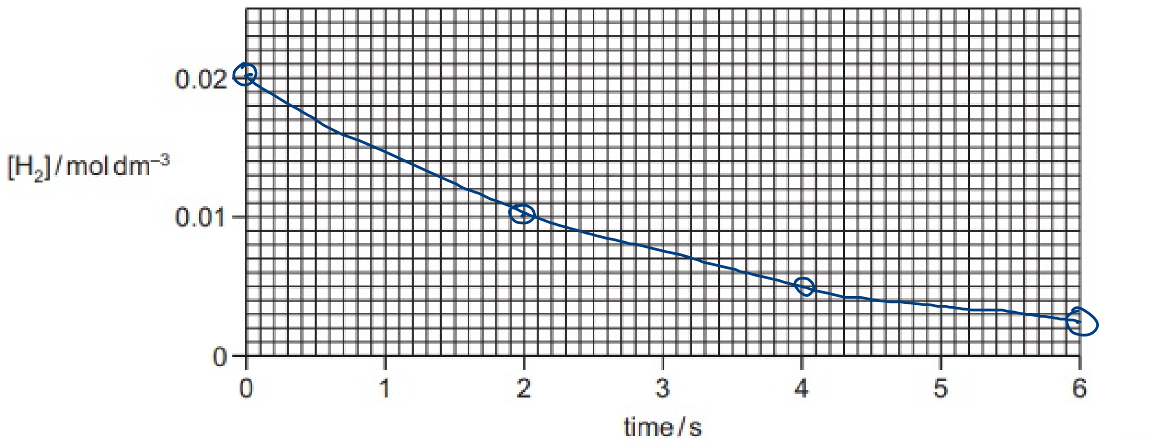
K = rate constant
Will Only work when 1st order

(g) A third experiment is performed under different conditions. A small amount of $H_2(g)$ of concentration 0.0200 mol dm^{-3} is mixed with a large excess of NO(g). The concentration of $H_2(g)$ is found to have a constant half-life of 2.00 seconds under the conditions used.

(i) Define the term *half-life*.

the time taken for reactant concentration to become half of its initial value. [1]

(ii) Use the axes below to construct a graph of the variation in the concentration of $H_2(g)$ during the first 6 seconds under the conditions used.



[2]

Catalysis:-

A catalyst increases the rate of reaction by providing an alternate reaction pathway with lower activation energy. The catalyst is chemically unchanged at the end of a reaction

Homogenous Catalyst:-

- It is in same phase (state) as reactants

e.g Ester Hydrolysis

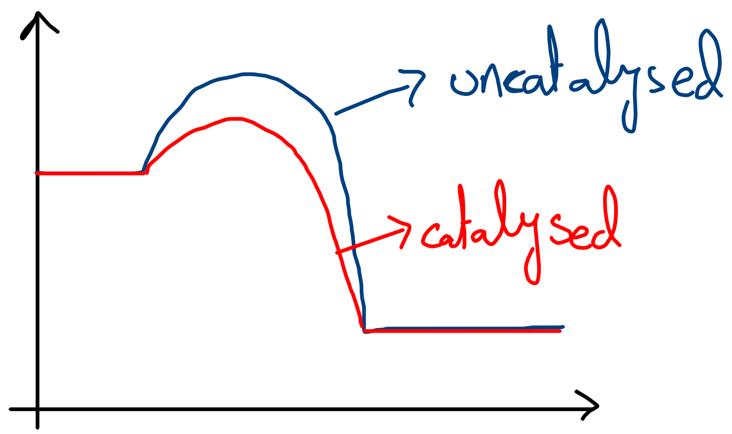
$$CH_3CO_2H_{(aq)} + CH_3CH_2OH_{(aq)} \xrightleftharpoons{H_2SO_4(aq)} CH_3CO_2CH_2CH_{3\,(aq)} + H_2O_{(l)}$$

e.g. Oxidation of Atmospheric SO_2 to SO_3 by NO_x

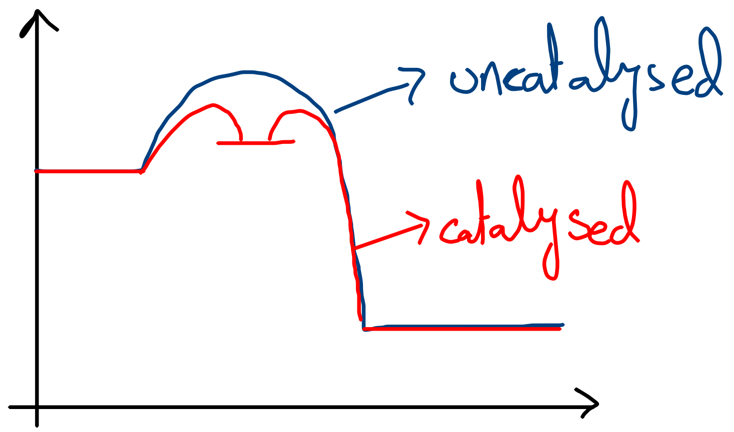
$$SO_{2(g)} + NO^{\bullet}_{2\,(g)} \longrightarrow SO_{3(g)} + NO^{\bullet}_{(g)}$$

$$NO^{\bullet}_{(g)} + \frac{1}{2}O_{2\,(g)} \longrightarrow NO_{2\,(g)}$$

Catalysed reaction graphs:-



if no intermediate



if intermediate is present

Heterogenous catalyst:-

- It is in different phase (state) as reactants

e.g. Haber process

$$N_{2\,(g)} + 3H_{2\,(g)} \xrightleftharpoons{Fe(s)} 2NH_{3}(g)$$

e.g Contact process

$$SO_{2\,(g)} + \frac{1}{2}O_{2\,(g)} \xrightleftharpoons{V_2O_5(s)} SO_{3\,(g)}$$

e.g. Catalytic Converters

$$2CO_{(g)} + 2NO_{(g)} \xrightarrow{Pt(s)/Pd(s)/Rh(s)} 2CO_{2(g)} + N_{2(g)}$$

e.g. Hydrogen peroxide decomposition

$$H_2O_{2\,(l)} \xrightarrow{MnO_2(s)} H_2O_{(l)} + \frac{1}{2}O_{2\,(g)}$$

e.g. Hydrogenation of Alkenes

$$CH_2=CH_{2(g)} + H_{2\,(g)} \xrightleftharpoons{Ni(s)} CH_3-CH_3$$

In heterogenous catalysis, reactant molecules form bonds to the catalyst that are stronger than their own bonds but weak enough to break later and form new ones

for e.g. Haber process