REACTION KINETICS TUTORIAL

A. BASIC CONCEPTS (QUALITATIVE KINETICS)

Section A1: Boltzmann distribution

1 Explain, using collision theory, how the following changes can affect the initial reaction rate of a gaseous system.

Illustrate your answer with the Boltzmann distribution curve for parts (ii) and (iii).

(i) increasing the pressure

There is greater no of particle per unit volume leading to <u>greater collision</u> <u>frequency</u> therefore <u>frequency of effective collision increases</u> leading to <u>increase</u> in rate.

Note: Assumption made that increase in total pressure comes from smaller volume.

(ii) decreasing the temperature



Kinetic Energy

As the temperature decreases, the average kinetic energy of the particles decreases.

There are less particles with kinetic energy equal or greater than the activation energy as shown in the Boltzmann distribution.

This result in lower frequency of effective collisions. Hence rate of reaction decreases.

(iii) addition of a catalyst



In the presence of catalyst, the reaction proceeds with an alternative reaction pathway of lower activation $energy(E_a')$.

There are more particles with kinetic energy equal or greater than the lowered activation energy as shown in the Boltzmann distribution curve.

This result in greater frequency of effective collisions. Hence rate of reaction increases.

- 2 Which statement best explains why a small increase in temperature leads to a significant increase in the rate of a gaseous reaction?
 - A The frequency of collisions between the molecules is greater at a higher temperature.
 - **B** The activation energy of the reaction is lower when the gases are at a higher temperature.
 - **C** The average kinetic energy of the molecules is greater at a higher temperature.
 - **D** The frequency of effective collisions between molecules with kinetic energy greater than the activation energy is greater at a higher temperature

Ans: D

When temperature of the reaction increases, average kinetic energy of the reacting molecules increases. The fraction of molecules with $K.E \ge E_a$ decreases as shown in the Boltzmann distribution. The frequency of effective collisions increases hence rate of reaction increases.

Section A2: Catalysis

- 3 Which is a correct statement about the effect of a homogeneous catalyst?
 - A It does not appear in the rate equation for the reaction.
 - **B** It causes the reaction to proceed via a different mechanism.
 - **C** It increases the rate constant of the forward reaction but not that of the backward reaction.
 - **D** It increases the kinetic energy of the reactant particles and therefore the frequency of effective collision.

Ans: B

Due to the involvement of the homogenous catalyst, the **alternative pathway** will require one additional step to complete the reaction. This is because there can only be a maximum of two colliding particles in a particular step as probability of effective collision between 3 or more particles are hardly likely.

4 Answer the following questions based on the energy profile diagram shown below:



(a) Does the graph represent an endothermic or exothermic reaction?

The graph represents an endothermic reaction, $\Delta H = +ve$

(b) Label the position of the reactants, products, and transition state.



(c) Determine the heat of reaction, ΔH , (enthalpy change) for this reaction.

 $\Delta H = +50 \text{ kJ.} (100 \text{ kJ} - 50 \text{ kJ})$

(d) Determine the activation energy, $E_a(f)$ for forward reaction.

 $E_a(f) = +200 \text{ kJ}.$ Activation energy is the amount of energy required to go from the energy level of the reactants (50 kJ) to the highest energy point on the graph, the activated complex (250 kJ).

(e) Determine the activation energy, E_a(b) for backward reaction. Hence explain why this reaction could be reversible.

 $E_a(b) = 150$ kJ. The 200kJ of activation energy supplied enable both the forward and backward reaction to take place, hence resulting it potentially a reversible reaction.

(f) Sketch how the energy profile will change, if any, if a homogeneous catalyst is added to the reaction system.



The reaction would become a 2 steps reaction with lowered E_a . Does not matter step 1 or 2 has the lower E_a . ΔH remains unchanged.

(g) Describe how a heterogeneous catalyst can increase effective collision between gaseous reactants by referring to the collision theory.

The gaseous reactants are **<u>adsorbed</u>** on the surface of the solid catalyst. This interaction increases the proximity of the reacting gas particles hence increases frequency of collision. This interaction also <u>weakens the existing inter-atomic</u> <u>**bonds**</u> within the reacting gas molecules thus <u>reduces the activation energy</u> for the reaction. <u>Products, once formed, leave the active sites (desorption)</u>, making the active sites available for other gaseous reactants.

Thus, effective collision of this reaction increases, leading to an increase in rate of reaction.

5 The reaction represented by the following equation was carried out.

 MnO_4^- (aq) + 5 $C_2O_4^{2-}$ (aq) + 16 $H^+ \rightarrow Mn^{2+}$ (aq) + 10 CO_2 (g) + 8 H_2O (l)

Which graph best shows the relationship between volume of CO_2 collected over time from mixing of the reactants?



This is an autocatalysis reaction. (Mn^{2+} is the catalyst), the gradient of vol vs time graph represents the rate of reaction.

- (1) At the beginning of the reaction, the rate is slow (gentle gradient) because the collision of two negatively charged reactants experiences repulsion making effective collision between the two reactants difficult. Therefore, volume of CO₂ produced is increasing at a slower rate.
- (2) Once a certain amount of Mn²⁺ has been formed, the reaction rate increases (steeper gradient). More CO₂ is being produced.
- (3) Reaction rate falls (gentle gradient) as the concentration of the reactants decreased to a low level. Therefore, the volume of CO₂ will remain constant.

6 The rate of decomposition of aqueous H_2O_2 increases in the presence of the enzyme, catalase.

$$2H_2O_2 \longrightarrow 2H_2O + O_2$$

The following graph was obtained in a study to investigate the effect of catalase on the rate of decomposition of H_2O_2 .



The steps predicted for this enzymatic decomposition of H₂O₂ are shown below.

catalase + H_2O_2 \iff catalase - H_2O_2 complex slow step

Catalase– H_2O_2 complex \longrightarrow $H_2O + O_2$ + catalase fast step

Which statements about the enzymatic decomposition of H₂O₂ are correct?

- **1** At low [H₂O₂], the rate of decomposition increases with increasing concentration of catalase used.
- 2 Catalase lowers the activation energy of the decomposition by forming temporary bonds with H₂O₂ molecules.
- 3 At high $[H_2O_2]$, all the active sites of the catalase enzyme are saturated with H_2O_2 molecules.
- A 1, 2 and 3
- **B** 1 and 2 only
- C 2 and 3 only
- D 1 only

Ans: A

Slow step involves the reaction between catalase and H_2O_2 . At low $[H_2O_2]$, the rate of reaction increases proportionally with H_2O_2 and catalase concentration. Hence statement 1 is correct.

The attractive forces between the reactant (substrate) molecule and the enzyme weakens the bonds within the substrate molecule, thereby lowering the activation energy and increasing the rate of reaction. Hence statement 2 is correct.

At high [substrate], all the active sites of the enzyme are saturated. Any increase in the substrate concentration cannot increase the rate of reaction. The rate of reaction no longer depends on the substrate concentration and is zero-order with respect to the substrate. Hence statement 3 is correct.

B. QUANTITATIVE KINETICS

Section B1: The Rate Equation

- 7 (a) Define the following terms with the help of a rate equation.
 - (i) Order of reaction and overall order of reaction

Write rate eqn to define these two terms Note: rate eqn: rate = $k[A]^{x}[B]^{y}$ Where x is the order of reaction w.r.t A and y is the order of reaction w.r.t B. Overall order of reaction = x + y

(ii) Rate constant

k = proportionality constant that depends on the nature of reacting particles.

(b) Consider the following reaction:

 $N_2(g) + 3 H_2(g) \rightarrow 2 NH_3(g)$

If the rate of loss of hydrogen gas is 0.03 mol dm $^{-3}$ s $^{-1}$, calculate the rate of production of ammonia.

Rate of production of NH₃ = $\frac{2}{3} \times 0.03$ = 0.02 mol dm⁻³ s⁻¹

8 (a) Given the following equation and rate equation,

 $2A(g) + B(g) \rightarrow C(g) + D(g)$ Rate = k[A][B]

Predict how would the rate change when the following changes are made.

(i) Partial pressures of both A and B are doubled

Partial pressures of each reactant are doubled by putting in twice the amount each of A and B. Concentrations of both A and B are doubled, therefore rate is 4 times of the original.

(ii) Partial pressure of A doubles but that of B remains constant

Only conc of A is doubled therefore rate is 2 times of the original.

(iii) Volume of the reaction vessel is doubled

(iv) Addition of an inert gas causing a doubling of the overall pressure

Pressure is increased by increasing the amount of gaseous particles, volume of reaction vessel stays the same. Conc of each reactant stay the same, therefore rate will not be affected.

(v) Temperature of the reaction system is raised

Value for rate constant, k, will increase, causing increase in rate.

(vi) A catalyst is added.

Value for rate constant, k, will increase causing rate of reaction to increase.

Section B2: Mechanisms

9 Nitrogen monoxide reacts with hydrogen gas to produce nitrogen gas and water vapour.

The mechanism is believed to be:

 $\begin{array}{l} \mbox{Step 1: } 2NO \rightarrow N_2O_2 \\ \mbox{Step 2: } N_2O_2 + H_2 \rightarrow N_2O + H_2O \\ \mbox{Step 3: } N_2O + H_2 \rightarrow N_2 + H_2O \end{array}$

(a) Write the overall balanced equation.

Net Reaction: 2 NO + 2 H₂ \rightarrow N₂ + 2 H₂O

(b) Identify any reaction intermediates.

To identify the reaction intermediates, look for substances that first appear on the product side of the equation, but then appear in the next step as a reactant. In this example there are **two reaction intermediates:** N_2O_2 and N_2O .

10 The proposed mechanisms of two reactions are as shown below.

In each case, determine the:

- (a) Rate equation
- (b) order of reaction with respect to each reactant
- (c) units for the rate constant

(i) $A + B \rightarrow C$ single step

Rate = k[A][B]First order w.r.t A, first order w.r.t B Units of k: mol⁻¹ dm³ t⁻¹

(ii) $S + R \rightarrow P$

 $S + H^+ = SH^+$ fast $SH^+ + R \rightarrow P + H^+$ slow

Notice that H⁺ is used and regenerated. Therefore, H⁺ must assume the role of a catalyst. Rate = $k[SH^+][R]$ but SH⁺ is not a reactant, it is an intermediate. Since [SH⁺] is proportional to [S] and [H⁺] from step 1, therefore rate = $k'[S][H^+][R]$ units of $k' = mol^{-2} dm^6 t^{-1}$ **11** The mechanism for a given reaction is shown below.

Step 1 : 2A 🔫 C	fast
Step 2 : $\mathbf{C} + \mathbf{B} \rightarrow \mathbf{D}$	slow
Step 3 : $\mathbf{D} + \mathbf{B} \rightarrow \mathbf{A}_2 \mathbf{B}_2$	fast

What conclusion(s) can be drawn from the information given above?

- 1 rate = $k[A]^{2}[B]$
- **2** The overall equation is $2\mathbf{A} + 2\mathbf{B} \rightarrow \mathbf{A}_2\mathbf{B}_2$.
- **3** The rate of formation of A_2B_2 is proportional to the initial concentration of **B**.

2 and 3 only С D 1 only 1 and 2 only 1, 2 and 3 В Α Ans: A From slow step, Rate = k[B][C]From fast step, $[C] = [A]^2$ Rate = $k[B][A]^2$ = C 2A fast $C + B \rightarrow D$ slow $\mathbf{D} + \mathbf{B} \rightarrow \mathbf{A}_2 \mathbf{B}_2$ fast Overall: $2\mathbf{A} + 2\mathbf{B} \rightarrow \mathbf{A}_2\mathbf{B}_2$.

Rate is first order w.r.t to [B] therefore rate \propto [B]

12 [N2021/1/13]

Hydrogen reacts with gaseous bromine to form hydrogen bromide:

 $H_2(g) + Br_2(g) \rightarrow 2HBr(g)$

It also reacts with gaseous iodine to form hydrogen iodide:

 $H_2(g) + I_2(g) \rightarrow 2HI(g)$

For the first reaction, the rate equation is

rate = $\frac{k_1[H_2][Br_2]^{1.5}}{[Br_2] + k_2[HBr]}$

For the second reaction, the rate equation is

rate = $k[H_2][I_2]$

 k_1 , k_2 and k represent rate constants.

What can be deduced based on this information only?

- 1 For the hydrogen / bromine reaction, the formation of HBr slows down the rate of the forward reaction.
- 2 Only the hydrogen and iodine reaction could be a single-step reaction.
- **3** Doubling the concentration of the halogen in each reaction doubles each rate of reaction.

Α	1, 2 and 3	С	2 and 3 only
в	1 and 2 only	D	1 only

Ans: B (1 and 2 only)

Option 1: Correct

From the given rate equation for the hydrogen / bromine reaction, rate decreases as [HBr] increases.

Option 2: Correct

If the reaction is a single-step reaction, the overall equation will also be the rate-determining step of the mechanism. Hence, the stoichiometry coefficient in the overall equation will coincide with the order shown in the rate equation. This is seen in the hydrogen / iodine reaction but not in the hydrogen / bromine reaction.

Option 3: Wrong

Rate is doubled for when concentration of iodine is doubled but not for concentration of bromine.

Section B3: Inspection Method (Initial Rate Method)

13 In acid medium, bromate ions, BrO_3^- , oxidize bromide ions to bromine:

$$BrO_3^-(aq) + 5Br^-(aq) + 6H^+(aq) \rightarrow 3Br_2(aq) + 3H_2O(I)$$

brown

A series of experiments were conducted, involving different volumes of each of the reagents, 1 mol dm⁻³ BrO₃⁻, 1 mol dm⁻³ Br⁻ and 1 mol dm⁻³ H⁺. The time taken for the first appearance of Br₂ was determined.

	Vo	lume of r	eagent /	Total Time take		
Mixture	BrO_3^-	Br⁻	H⁺	Water	volume / cm ³	for brown Br ₂ to appear / s
1	100	500	600	800	2000	305
1'	50	250	300	400	1000	305
2	50	250	600	100	1000	77
3	100	250	600	50	1000	38
4	50	125	600	225	1000	149

- (a) Data for mixture 1' is derived from mixture 1.
 - Explain the purpose of halving every volume of the reagent used for mixture 1.
 - Explain why the time taken for brown Br₂ to appear is not halved.

This is because total volume of reaction mixture 1 is doubled of the reaction mixtures 2,3 and 4, hence, in order for the volume of each reactant to be proportional to its concentration, volume of each reactant for reaction mixture 1 should be halved to obtain the same total volume as mixture 2, 3 and 4.

Rate depends on concentration of the reactant in the mixture. The concentration of each reactant in a mixture remains unchanged when all volumes are reduced by the same extent, thus the rate is not affected.

(b) Using the above data, determine how the initial rate depends on the concentration of BrO₃⁻, Br⁻ and H⁺. Hence determine the rate equation.

conc of each reactant in the mixture \propto vol of each reactant in the mixture as total volume kept the same for all reaction mixture.

Compare expt 1' and 2 where volume of BrO_3^- and Br^- are the same, when $[H^+]_{expt}_2 = 2 \times [H^+]_{expt 1}$, (rate)_{expt 2} = 4 × (rate)_{expt 1}, therefore order w.r.t H⁺ is 2.

Compare expt 2 and 3 where the volume of H⁺ and Br⁻ are the same, when $[BrO_{3}^{-}]_{expt3} = 2 \times [BrO_{3}^{-}]_{expt2}$, (rate)_{expt3} = 2 × (rate)_{expt2}, therefore order w.r.t BrO₃⁻ is 1.

Compare expt 2 and 4 where the volume of H⁺ and BrO_3^- are the same, when $[Br^-]_{expt 2} = 2 \times [Br^-]_{expt 4}$, (rate)_{expt 2} = 2 × (rate)_{expt 4}, therefore order w.r.t Br⁻ is 1.

Rate eqn: rate = $k [H^+]^2 [BrO_3^-] [Br^-]$

(c) Explain why water is added.

This is to keep the total volume constant across the experiments so that conc of each reactant is proportional to the volume of reactant present. comparison of volume is equivalent to comparison of conc.

14 An experiment was carried out to investigate the initial rate of reaction between ammonia peroxodisulfate, (NH₄)₂S₂O₈, an oxidizing agent, and potassium iodide, KI.

$$S_2O_8^{2-}(aq) + 2I^{-}(aq) \rightarrow 2SO_4^{2-}(aq) + I_2(aq)$$

The initial concentrations of the $(NH_4)_2S_2O_8$ and KI solutions in the mixture, together with the time taken for the mixture to darken for the various experimental runs are given below:

Experiment	Initial concentration of (NH ₄) ₂ S ₂ O ₈ / mol dm ⁻³	Initial concentration of KI / mol dm ⁻³	Time taken to darken/ s
1	0.10	0.20	35
2	0.05	0.20	70
3	0.10	0.067	105
4	0.02	0.75	?

Which statements about the reaction is/are true?

- 1 The reaction involves the formation of an intermediate.
- 2 The time taken for the mixture to darken in Experiment 4 is 47s.
- 3 The slow step involves the reaction between 1 mole of $(NH_4)_2S_2O_8$ and 1 mole of KI.
- A 1, 2 and 3 B 1 and 2 only C 2 and 3 only D 1 only

Ans: A

Since we are monitoring time taken for a fixed amount of I2 to be formed,

rate
$$\propto \frac{1}{\text{time taken}}$$

Comparing expt 1 & 2, [KI] remain constant and $[(NH_4)_2S_2O_8] \times 2$, rate also $\times 2$. Hence it is first order w.r.t $(NH_4)_2S_2O_8$.

Comparing expt 1 & 3, $[(NH_4)_2S_2O_8]$ remain constant and $[KI] \times 3$, rate also $\times 3$. Hence it is first order w.r.t KI.

Rate = $k[(NH_4)_2S_2O_8][KI]$, statement 3 is correct.

Since the overall reaction involves 2 mol of KI, the second mol of KI must be involved in another step after the slow step. Hence the reaction involves an intermediate. Statement 1 is correct.

Using expt 1 data, $\frac{1}{35} = k (0.1)(0.2), k = 1.429$

Using the value of k for expt 4 (since same temperature condition),

 $\frac{1}{\text{time taken}} = 1.429(0.02)(0.750),$

Time taken = 46.7s, statement 2 is correct.

15 The following data was collected for the gas-phase reaction between nitrogen monoxide and hydrogen at 700°C.

Expt No.	[NO] _{initial} / mol dm ⁻³	[H ₂] _{initial} / mol dm ⁻³	Initial rate of reaction / mol dm ⁻³ s ⁻¹
1	0.002	0.012	0.0033
2	0.004	0.012	0.0132
3	0.008	0.012	0.0528
4	0.010	0.012	0.0825
5	0.012	0.012	0.119
6	0.012	0.0020	0.0198
7	0.029	To be calculated	1.33

$2NO(g) + 2H_2(g)$	── N₂(g) +	2H ₂ O(g)	ΔH _{reactior}
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(a) How is the rate of appearance of N₂ related to the rate of disappearance of hydrogen?

Rate of appearance of $N_2 = \frac{1}{2} \times$ rate of disappearance of H_2 .

(b) (i) Determine the order of reaction with respect to H_2 by making use of suitable pairs of data from the table above.

Compare expt 5 and 6 where conc of NO is the same When $[H_2]_{expt 5} = 6 \times [H_2]_{expt 6}$, $(rate)_{expt 5} = 6 \times (rate)_{expt 6}$, \therefore the order w.r.t H₂ is 1.

(ii) Determine the order of reaction with respect to NO by plotting a suitable graph by making use of the data from experiments 1 to 5.



Graph A: rate is plotted against [NO]_{initial}, rate is \times 4 when [NO] \times 2, therefore it is 2nd order w.r.t NO.

ALTERNATIVE: Plot Graph B: rate vs $[NO]^2$ initial, in this case a linear graph that shows directly proportional relationship will be obtained. \therefore order w.r.t NO is 2

(iii) Hence derive the rate law or otherwise known as the rate equation.

Therefore rate law: rate = $k [NO]^2 [H_2]^1$

(c) Calculate the value of the rate constant and state its units.

Using expt 5 as an example: Rate = $0.119 = k(0.012)^2(0.0120)$ k= 6.89×10^4

Or use graph A and extrapolate to obtain rate at a particular [NO] with $[H_2]=0.012$, then substitute into rate equation to obtain the value of k.

Units: mol⁻² dm⁶ s⁻¹

(d) Calculate the initial concentration of H_2 for experiment 7.

Substitute value of k obtained from part (c) into the rate equation to solve for the initial $[H_2]$ in expt 7.

Rate = $1.33 = 6.89 \times 10^4 (0.029)^2$ [H₂] [H₂] = 0.0230 mol dm⁻³

(e) Using the rate equation and the overall equation, the following three-step mechanism for the reaction was suggested. X and Y are intermediate species.

Step 1:	NO + NO 🗧	X 🚍
Step 2:	$\textbf{X} + H_2 \ \rightarrow$	Y
Step 3:	$\mathbf{Y} + \mathbf{H}_2 \ \rightarrow \ \ $	N ₂ + 2H ₂ O

Suggest which one of the three steps is the rate-determining step.

Explain your answer.

Rate eqn suggests that 2 moles of NO and 1 mole of H_2 are involved in the slow step but none of the above steps seem to be consistent with the rate eqn.

Step 1 is not the slow step as only 2 mol of NO collide. The rate equation would be rate = $k[NO]^2$ if step 1 is slow.

Step 2 could be the slow step. Rate = $k[X][H_2]$. But since X is an intermediate (thus cannot appear in slow step), X can be expressed as $k'[NO]^2$, since it is formed from 2 mol of NO. Rate eqn would thus be Rate = $k[NO]^2[H_2]$, consistent with what is in part (b)

(f) Given that the bond energy of NO is 420 kJ mol⁻¹, Determine the enthalpy change of this reaction, ΔH_{reaction} by making use of suitable data from the Data Booklet.

Since all reactants and products are in gaseous state,

 $\Delta H_{\text{reaction}} = \sum BE(\text{reactants}) - \sum BE(\text{products})$ = [2×420+ 2×436] - [944 + 4×460] = -1072 kJ mol⁻¹

Section B4.1: Graphical Method – Initial Rate vs Continuous

- 16 (a) A reaction is found to be first order with respect to reactant **A**.
 - (i) Give the rate equation of this reaction, assuming that A is the only reactant.

rate = k[A]

- (ii) Given that half-life of reactant A is 10 mins, sketch the following graphs:
 - concentration of A vs time graph (continuous method) and
 - rate vs concentration of A (initial rate method)



- (b) If reaction is second order with respect to A,
 - (i) Give the rate equation of this reaction, assuming that A is the only reactant.

rate = $k[A]^2$

- (ii) Sketch the following graph
 - concentration of A vs time graph (continuous method) and
 - rate vs concentration of A (initial rate method)



(iii) How would you modify the axis of the rate vs concentration graph to obtain a linear graph?



- (c) If reaction is zero order with respect to A
 - (i) Give the rate equation of this reaction, assuming that A is the only reactant.

Rate = $k [A]^0$

- (ii) Sketch the following graph
 - concentration of A vs time graph (continuous method) and
 - rate vs concentration of A (initial rate method)



Section B4.2: Graphical Method – Continuous Method

17 The following reaction is monitored by measuring the changes in total pressure during the reaction, with initial pressure of O_2 at 300 kPa.

$$3O_2(g) \rightarrow 2O_3(g)$$

Time /s	15	30	45	60	75	90	∞
P _{total} / kPa	278	267	257	250	240	238	

(a) Work out the total pressure at time infinity. At time infinity, all O_2 is used up to form O_3 ,

thus final total pressure = $\frac{2}{3} \times 300$ kPa = 200 kPa.

Since all are gases under the same condition, we can use the mole for direct comparison (as molar volume are the same)

(b) Given that $P_{O2} = 3P_{total} - 600kPa$, determine the order of reaction with respect to oxygen with the aid of a suitable graph.



Calculate the P_{02} at different time in the above table and plot P_{02} vs time graph. *Note, we cannot find 2 consecutive half-life from the graph.

As the reaction proceeds, P_{O2} decreases and hence $[O_2]$ decreases. It is observed that the reaction has a <u>constant half-life of 60s.</u>

Hence it is first order w.r.t O₂.

(c) Determine the value of rate constant, stating its units.

Since this is overall first order reaction, $t_{1/2} = \frac{\ln 2}{k}$

$$k = \frac{\ln 2}{60} = 1.16 \times 10^{-2} \text{ s}^{-1}$$

18 Hydrogen peroxide of original concentration 3.0 mol dm⁻³ was placed in a contaminated bottle some time ago. The student was then asked to determine how long the hydrogen peroxide had been stored in the bottle. In order for the student to find out how long the H_2O_2 is stored in the bottle, the kinetics of decomposition of H_2O_2 must be followed to determine its half-life.

The rate of decomposition of hydrogen peroxide was investigated by monitoring remaining H_2O_2 with time.

$$2 H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$$

The remaining H_2O_2 can be determined by withdrawing 10 cm³ portions of H_2O_2 solution at regular time intervals and titrating it with acidified 0.1 mol dm⁻³ KMnO₄(aq). This is known as the **titrimetric method**.

The following results were obtained:

Time / min	Volume of 0.1 mol dm ⁻³ KMnO₄(aq) / cm ³
0	30.0
5	23.4
10	18.3
15	14.2
20	11.1
25	8.7
30	6.8

(a) Identify the type of reaction H_2O_2 has undergone when it decomposes to form O_2 and H_2O . Illustrate type of reaction by <u>making specific reference to H_2O_2 </u>.

O in H_2O_2 is -1 oxidation state, it is oxidized to 0 oxidation state in O_2 and reduced to - 2 in H_2O . Therefore, O in H_2O_2 undergoes disproportionation reaction.

(b) The remaining H_2O_2 is titrated against KMnO₄, construct a balanced equation between the two reactants. Identify the oxidizing and reducing agent in this reaction.

 $6H^+ + 2MnO_4^- + 5H_2O_2 \rightarrow 5O_2 + 2Mn^{2+} + 8H_2O$ KMnO₄ – oxidizing agent; H_2O_2 – reducing agent (c) By drawing a suitable graph on the graph paper, determine the order of reaction with respect to H_2O_2 . Write the rate equation (rate law) for the decomposition of H_2O_2 and calculate the rate constant and half-life.



Every 2 mol of H_2O_2 reacts with 5 mol of KMnO₄ The greater the volume of KMnO₄ required for titration, the greater the amount of H_2O_2 in the 10cm³ of the withdrawn sample.

As all the titrations are using a fixed volume of 10 cm^3 sample, vol of KMnO₄ is proportional to [H₂O₂] in the withdrawn sample.

Graph of Vol KMnO₄ vs time is proportional to graph of $[H_2O_2]$ vs time As the reaction proceeds, $[H_2O_2]$ decreases.

It is observed that the reaction has a constant half-life (~14 min), therefore order of reaction w.r.t H_2O_2 is 1.

- $k = \frac{\ln 2}{t_{1/2}}$ (Note this is only used if overall order is 1) k = 0.0495 min⁻¹
- (d) Suggest other ways this reaction can be monitored continuously to determine order of reaction with respect to H_2O_2 .

As O_2 is given off during decomposition (disproportionation of H_2O_2), rate of reaction can be monitored by measuring the

- increase in pressure with time under constant volume,
- increase in volume of gas with time under constant pressure or
- mass loss with time

(e) Calculate the concentration of the hydrogen peroxide at time t = 0. Hence estimate how long the solution had been in the contaminated bottle before it was analyzed by making use of the half-life determined in part (c).

At t = 0, amount of KMnO₄ required =
$$\frac{30}{1000} \times 0.1 = 0.003$$
 mol
At t = 0, amount of H₂O₂ in 10 cm³ sample = $\frac{5}{2} \times 0.003 = 0.0075$ mol
At t = 0, [H₂O₂] = $\frac{0.0075}{10/1000}$ = 0.75 mol dm⁻³

original $[H_2O_2] = 3.0 \text{ mol } dm^{-3}$

therefore duration of H_2O_2 stored in bottle = 2 × 14 min = 28 min.

OR

 $\frac{\text{final conc of reactant}}{\text{Initial conc of reactant}} = \frac{0.75}{3} = \frac{1}{4} = (\frac{1}{2})^2$, two half life has passed

Total time = no. of half-life \times duration of each half life = 2 \times 14 = 28min.

19 The following reaction is monitored by measuring the increase in pressure with time as O_2 is collected into a vessel of 0.05 dm³ using 100 cm³ each of H₂O₂ and I₂ solution for reaction.

$$H_2O_2$$
 (aq) + I_2 (aq) $\rightarrow 2I^-$ (aq) + O_2 (g)

The starting concentration of H_2O_2 and I_2 are 1.0 mol dm⁻³ and 0.005 mol dm⁻³ respectively.

Time /s	0	30	60	90	120	150	180
[O ₂] / mol dm ⁻³	0	0.003	0.006	0.0075	0.0084	0.0089	0.0094

(a) Determine the concentration of oxygen produced at time infinity.

At time infinity, all reactants are reacted completely. Hence, amount of O_2 produced depends on the amt of limiting agent used, which in this case is iodine Amount of $I_2 = \frac{100}{1000} \times 0.005 = 0.0005$ mol, Amount of $H_2O_2 = \frac{100}{1000} \times 1.0 = 0.1$ mol Since I_2 is the limiting reagent, amount of O_2 at time infinity = 0.0005 Concentration of O_2 at time $\infty = (\frac{0.0005}{0.050}) = 0.01$ mol dm⁻³



(b) With the aid of a suitable graph, determine the order with respect to iodine.

When [product] vs time graph is being analyzed, do note that first half-life, $t_{1/2}(1)$ corresponds to time needed to attain 50% yield while $t_{1/2}(2)$ is time taken to increase the product yield from 50% to 75%

As the reaction proceeds, $[I_2]$ decreases significantly while $[H_2O_2]$ remains approximately constant.

It is observed that reaction has a <u>constant half-life</u> (\approx 45sec) => it is first order to I₂. (Label your half-life clearly on your own graph)

(c) Suggest how the above experiment can be modified so that the order with respect to H_2O_2 can be determined. Your answer should also include details of how the order with respect to H_2O_2 can be deduced from the data collected.

Repeat experiment with 2.0 mol dm⁻³ of H_2O_2 and 0.005 mol dm⁻³ of I_2 (same conc). Method 1: compare gradient at time 0 to the original graph to determine the effect of H_2O_2 conc on rate. Method 2: compare the half-life magnitude to determine the effect of H_2O_2 on rate.

Section B4.3: Graphical Method – Combined Method

20 Quaternary ammonium ions can undergo Hofmann elimination in a single step mechanism as shown.



quaternary ammonium ion

The following concentrations of OH^- and $CH_3CH_2NR_3^+$ were used in *Experiment 1* and the half-life was found to be 10 s.

 $[OH^{-}] = 0.001 \text{ mol } dm^{-3}$ $[CH_3CH_2NR_3^+] = 0.100 \text{ mol } dm^{-3}$

What will be the half–life when the experiment is repeated with the following changes in concentrations?

	Half-life for <i>Experiment</i> 2 when [OH [–]] is doubled	Half-life for <i>Experiment 3</i> when [CH ₃ CH ₂ NR ₃ ⁺] is doubled
Α	10 s	10 s
В	10 s	5 s
С	5 s	10 s
D	5 s	5 s

Ans: B

Since it is a single step mechanism, rate = $[CH_3CH_2NR_3^+][OH^-]$. As $[CH_3CH_2NR_3^+]$ is much higher than $[OH^-]$, rate = $k'[OH^-]$ where $k' = k[CH_3CH_2NR_3^+]$

For expt 1,
$$t_{1/2} = \frac{\ln 2}{k'} = \frac{\ln 2}{k[CH_3CH_2NR_3^+]}$$

 $10 = \frac{\ln 2}{k[0.1]}$, $k = 0.6931 \text{ s}^{-1}$
For expt 2, when $[OH^-] \times 2$ while $[CH_3CH_2NR_3^+]$ is kept constant, $t_{1/2}$ is not affected.
For expt 3, when $[CH_3CH_2NR_3^+] \times 2$ while $[OH^-]$ is kept constant,

new $t_{1/2} = \frac{\ln 2}{0.6931 \times 0.2} = 5s$

Section C: First order reaction- Half life of reaction

21 Lead is the final product formed by a series of changes in which the rate-determining stage is the radioactive decay of uranium-238. This radioactive decay is a first order reaction with a half-life of 4.5×10^9 years.

What would be the age of the rock sample, originally lead-free, in which the molar proportion of uranium to lead is now 1:7?

Time	Amt of Uranium left	Amt of Lead formed	Mole ratio of U : Pb
0, Inital	1	0	1:0
One t _{1/2}	$1 \times \frac{1}{2} = \frac{1}{2}$	$\frac{1}{2}$	1 :1
Two t _{1/2}	$\frac{1}{2} \times \frac{1}{2} = \frac{1}{4}$	$\frac{1}{2} + \frac{1}{4} = \frac{3}{4}$	1:3
Three t _{1/2}	$\frac{1}{4} \times \frac{1}{2} = \frac{1}{8}$	$\frac{3}{4} + \frac{1}{8} = \frac{7}{8}$	1:7
Fourth t1/2	$\frac{1}{8} \times \frac{1}{2} = \frac{1}{16}$	$\frac{7}{8} + \frac{1}{16} = \frac{15}{16}$	1 : 15

Mole ratio of **U** : **Pb** = 1:7 \rightarrow 3 half lives Half-life = 4.5 × 10⁹ years Age of rock = 3 × 4.5 × 10⁹ years = 13.5 x 10⁹ years

22 The decomposition of benzene diazonium chloride is a first order reaction which proceeds according to the equation:

$$C_6H_5N_2Cl \rightarrow C_6H_5Cl + N_2$$

A solution gave 80 cm³ of N_2 on complete decomposition and it took 40 minutes for 40 cm³ of N_2 to be evolved. How long would it take for 70 cm³ of N_2 to be evolved?

Α	20 min	В	60 min	С	80 min	D	120 min
				-			

Ans: D

	t ₀	1 st t _{1/2}	2 nd t _{1/2}	3 rd t _{1/2}
[product]	0%	50%	75%	87.5%
Volume of N ₂ /cm ³	0	40	60	70
Time/ min	0	40	80	120

Time/min	0	15	40	80	8
[(CH ₃) ₃ COH]/ mol dm ⁻³	0	0.5	1.0	1.5	2.0

 $(CH_3)_3CBr \ + \ OH^- \ \rightarrow \ (CH_3)_3COH \ + \ Br^-$

What is the value of the rate constant?

A 8.66×10^{-3} **B** 1.73×10^{-2} **C** 2.77×10^{-2} **D** 4.62×10^{-2}

Ans: B

From the product vs time data, we can deduce the half life is constant at t = 40 mins.

Time	[Reactant]	[Product]
0	100%	0%
t ₁	50%	50%
t ₂	25%	75%
t ₃	12.5%	87.5%

When [product] vs time graph is being analyzed, do note that first half-life, $t_{1/2}(1)$ corresponds to time needed to attain 50% yield while $t_{1/2}(2)$ is time taken to increase the product yield from 50% to 75%

As the reaction proceeds, $[(CH_3)_3CBr]$ decreases significantly while $[OH^-]$ remains approximately constant. It is observed that the reaction has a <u>constant half-life of 40min</u>.

Hence it is first order w.r.t. (CH₃)₃CBr.

For overall first order reaction, $t_{1/2} = \frac{\ln 2}{k}$

$$k = \frac{\ln 2}{40} = 0.0173 \text{ min}^{-1}$$