

Reaction Kinetics

H 2 C H E M I S T R Y · 9 4 7 6

❖ The Importance of Reaction Kinetics

In Thermodynamics, we learned that $\Delta G < 0$ tells us a reaction is **thermodynamically feasible**. However, ΔG says nothing about the **rate**. Combustion of paper has $\Delta G < 0$ at room temperature, yet a stack of paper does not spontaneously catch fire.

For a reaction to occur, it must also be **kinetically feasible**.

Reaction kinetics is the study of how fast reactions proceed and what factors influence the rate.

Rate of reaction is defined as the change in concentration of a reactant or product per unit time.

$$\text{Rate} = \frac{\Delta[X]}{\Delta t} \quad \text{units: mol dm}^{-3} \text{ s}^{-1}$$

❖ COLLISION THEORY

For a reaction between two particles to occur, **two conditions** must be met:

- 1) The particles must collide in the **correct orientation**.
- 2) The particles must collide with **energy $\geq E_a$**

A collision satisfying both conditions is an **effective collision** and leads to a chemical reaction. Otherwise it is ineffective and the particles bounce apart unchanged.

The greater the **frequency of effective collisions**, the greater the rate of reaction.

❖ FACTORS AFFECTING RATE OF REACTION

Reaction rate is influenced by the following factors. Each factor affects rate by changing either the energy distribution of particles or how often they collide:

- Concentration / pressure of reactants
- Temperature
- Surface area of solid reactants
- Catalyst
- Light (photochemical reactions only)

1) Concentration / Pressure

For gases, increasing pressure \equiv increasing concentration ($pV = nRT$).

Increasing the concentration of a reactant increases the number of reactant particles per unit volume.

More particles in the same volume \rightarrow more collisions per second \rightarrow greater frequency of effective collisions \rightarrow faster rate.

❖ ANSWERING TECHNIQUE

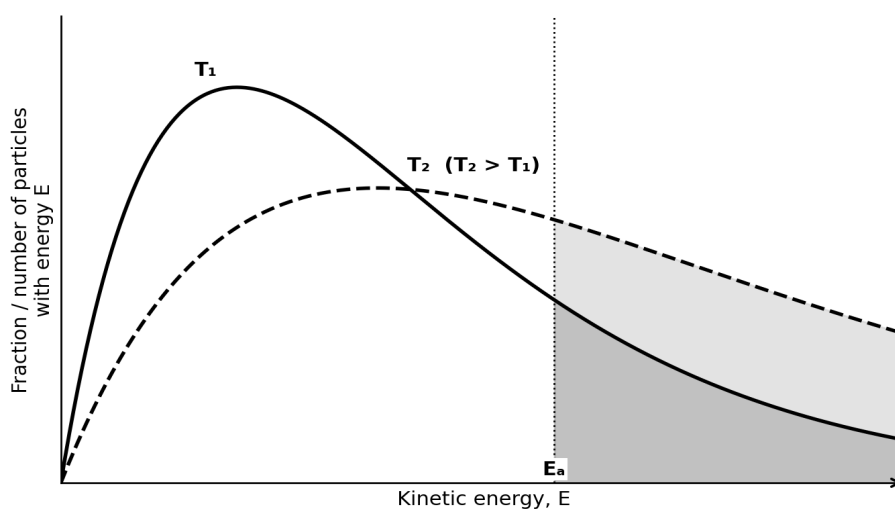
more particles \rightarrow more effective collisions \rightarrow faster rate.

As [reactant] increases, the number of reactant particles per unit volume increases.

The frequency of effective collisions increases. Hence, **rate of reaction increases.**

2) Temperature (MOST COMMON)

Increasing temperature increases the average kinetic energy of the reactant particles. The Maxwell–Boltzmann distribution shifts: the curve flattens, broadens and moves rightwards.



◆ ANSWERING TECHNIQUE

Note:

ALWAYS reference the Boltzmann distribution when

As temperature increases, the average kinetic energy of the reactant particles increases.

The number of particles with energy $\geq E_a$ increases as seen in the Boltzmann distribution curve increases. The frequency of effective collisions increases. Hence, **rate of reaction increases**.

3) Surface Area of Solid Reactant

Note:

Only relevant when at least one reactant is a solid.

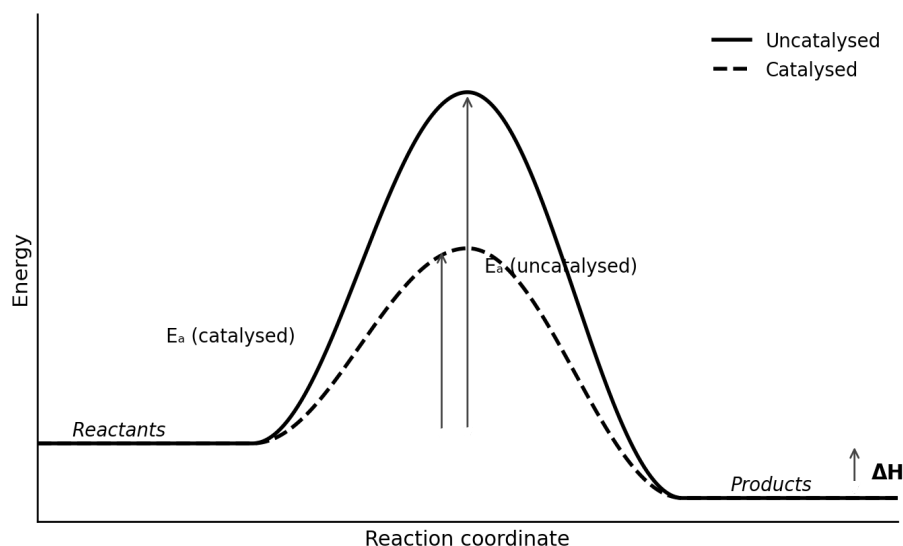
In a solid, only particles on the surface can come into contact with other reactants. Reducing particle size (e.g. powdering) dramatically increases the surface area of contact.

More surface particles exposed \rightarrow more frequent collisions with the surrounding reactant \rightarrow greater frequency of effective collisions \rightarrow **rate of reaction increases**.

4) Catalyst

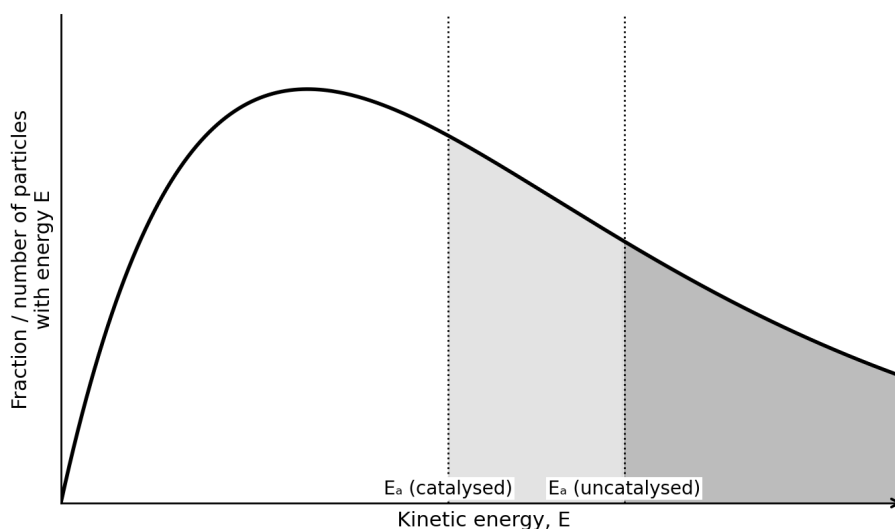
A catalyst is **not consumed** and does **NOT** change ΔH of the reaction.

A **catalyst** speeds up the rate of a reaction by providing an alternative pathway with **lower activation energy**. It is not used up, and it does not affect ΔH .



Energy profile diagram. The catalysed pathway (dashed) has a lower E_a than the uncatalysed pathway (solid). ΔH is unchanged.

On the Boltzmann distribution, lowering E_a increases the number of particles able to react:



Boltzmann distribution: a catalyst lowers E_a , increasing the fraction of particles with $K.E. \geq E_a$.

❖ ANSWERING TECHNIQUE

A catalyst provides an alternative pathway with lower activation energy E_a .

The number of particles with energy $\geq E_a$ as seen in the Boltzmann distribution curve increases. The frequency of effective collisions increases. Hence, **rate of reaction increases**.

❖ TYPES OF CATALYSTS

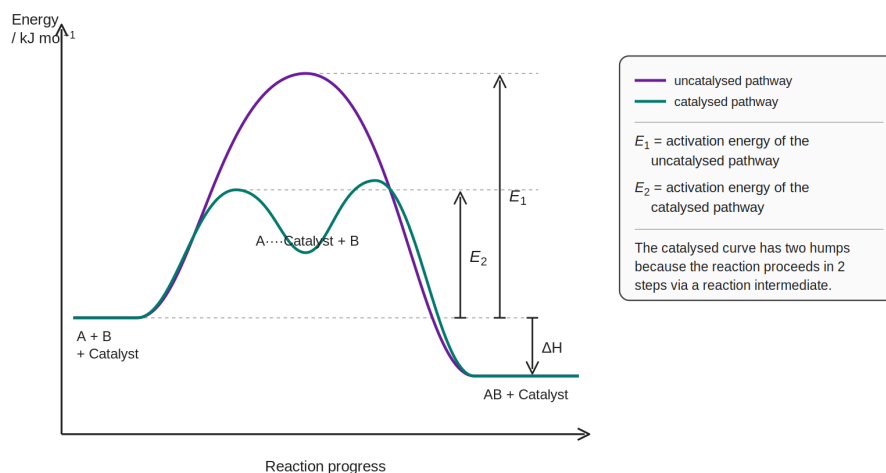
	Homogeneous	Heterogeneous
Phase	Same phase as reactants	Different phase from reactants
Mechanism	Forms an intermediate with reactant which then reacts to product + regenerated catalyst	Reactants adsorb onto catalyst surface, react, then desorb as product
Example	$\text{Fe}^{2+}(\text{aq})$ catalysing $\text{S}_2\text{O}_8^{2-}(\text{aq}) + 2\text{I}^-(\text{aq}) \rightarrow 2\text{SO}_4^{2-}(\text{aq}) + \text{I}_2(\text{aq})$	$\text{Fe}(\text{s})$ catalysing $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$ (Haber process)

1) Homogenous Catalyst

The catalyst and reactants are in the same phase.

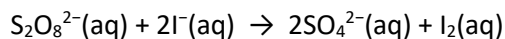
The reaction usually occurs through 2 steps due to the formation of an intermediate first before the catalyst is regenerated and the product is formed.

Hence, the energy profile diagram will show two humps, with the first hump being larger.



Common use of Homogenous Catalyst

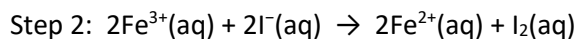
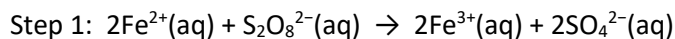
Reaction of Iodide and Peroxodisulfate Ions



Due to the electronic **repulsion** between the negatively charged $\text{S}_2\text{O}_8^{2-}$ and I^- ions, the reaction has **high activation energy**. This results in a very slow reaction.

Ions such as $\text{Fe}^{2+}(\text{aq})$ act as **homogeneous catalysts** by providing an alternative reaction pathway of lower activation energy.

Mechanism



Fe^{2+} will first react with $\text{S}_2\text{O}_8^{2-}$ ion, undergoing oxidation in step 1 to form Fe^{3+}

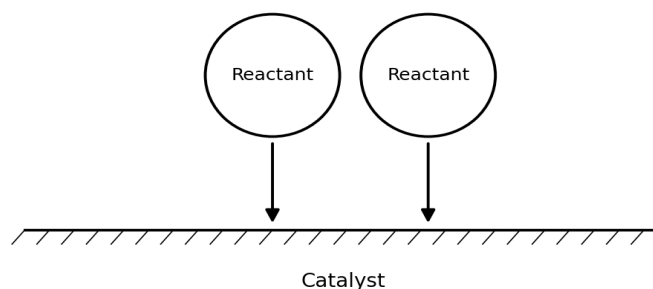
Fe^{3+} will then react with I^- to regenerate Fe^{2+} catalyst.

Both steps consist of reactions between ions of opposite charges, eliminating the electronic repulsion that caused the slow rate of reaction between $\text{S}_2\text{O}_8^{2-}$ and I^- ions, helping lower activation energy.

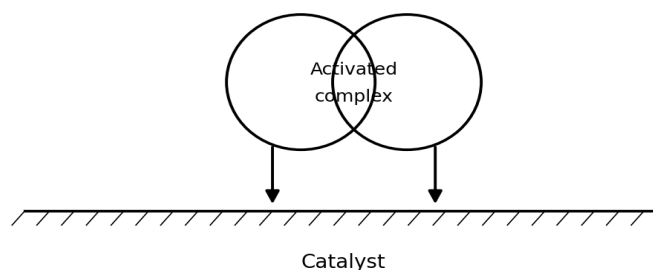
1) Heterogeneous Catalyst.

The catalyst and reactants are in the different phases.

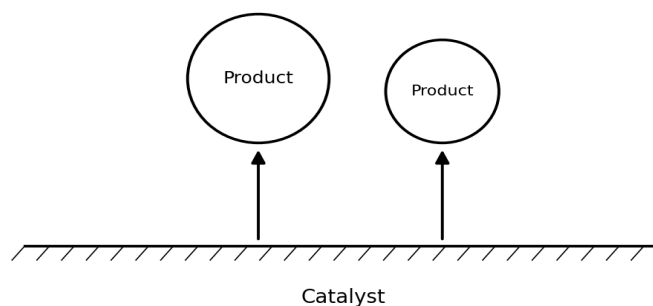
Step 1: Adsorption of reactant particles onto the surface of the catalyst. Weak interactions form between the reactant and catalyst.



Step 2: Reaction at the surface occurs at a faster rate as reactant molecules are brought closer together and existing interactions in the reactant molecules are weakened (lower E_a).



Step 3: Desorption of products from the catalyst surface. Catalyst is regenerated.



Catalysis at the solid metal surface involves the adsorption of reactant molecules on the surface catalyst atoms. This has the effect of increasing the concentration of the reactants at the catalyst surface and also weakening of the bonds in the reactant molecules, i.e. activation energy is lowered.

CASE STUDY: AUTOCATALYST

Autocatalysis is a process where a product formed in the chemical reaction serves as a catalyst and increases the rate of reaction.

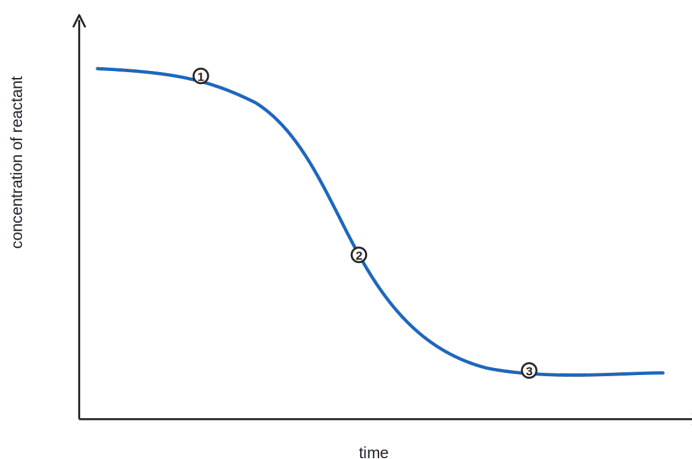
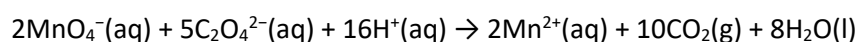
Initially, an autocatalyzed reaction is very slow, due to high activation energy of the reaction.

As time progresses, the rate of reaction will rapidly increase to a maximum due to the formation of the product which serves as a catalyst.

After the rate reaches a maximum, the reaction begins to slow down as the concentration of the reactants has decreased.

Common Example of Autocatalyst

Reaction of manganate(VII) and ethanedioate ions in acidic medium



- 1) Electronic repulsion between the two negatively charged MnO_4^- and $\text{C}_2\text{O}_4^{2-}$ ions will cause effective collisions to be difficult resulting in the activation energy of the reaction to be high
- 2) As reaction progresses, sufficient amounts of Mn^{2+} is formed and the rate of reaction increases as Mn^{2+} will act as a homogenous catalyst for the reaction. Rate of reaction increases until a maximum.
- 3) Rate of reaction will decrease as the concentration of the reactants have decreased significantly.

◆ KINETICS

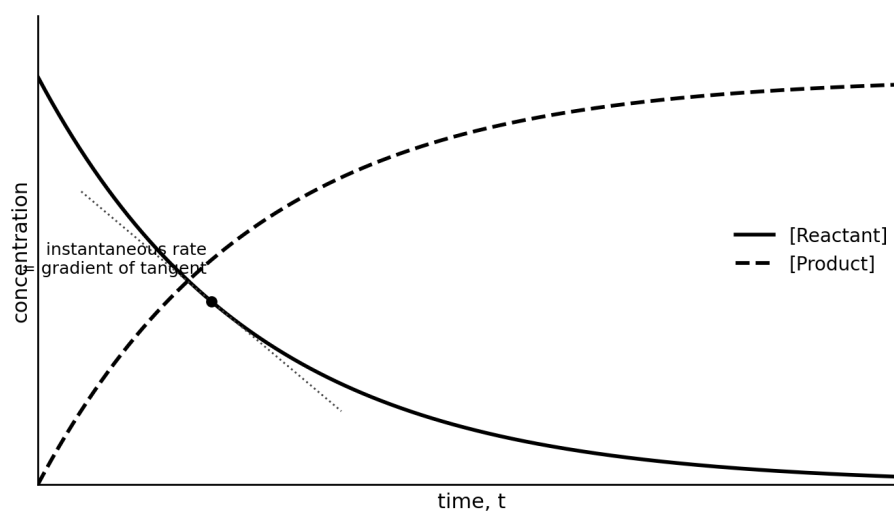
Rate Definitions

Average rate over a time interval = $\frac{\text{total } \Delta[\text{reactant/product}]}{\Delta t}$

Instantaneous rate at time t = gradient of the tangent of the curve at t

Initial rate = gradient of the tangent of the curve at t=0

Rate is a positive quantity.



Concentration vs time

The Rate Equation

Order of reaction can **ONLY** be determined experimentally — never read it off the stoichiometry.

Do not assume that $x = a$ and $y = b$.

The equation is...

Rate =

and not

Rate equation =

Given $aA + bB \rightarrow \text{Products}$,

$$\text{Rate} = k[A]^x[B]^y$$

x = order of reaction with respect to A

y = order with respect to B,

k = rate constant.

Overall order of reaction = x + y.

x and y are typically 0, 1, or 2 in H2 Chemistry.

To find the value of x and y, we need to find the **slow** step

The **slow** step = **rate determining** step

Only the **slow** step will affect the rate of reaction.

The coefficients of **A** and **B** in the slow step will be the value of x and y respectively.

The **slow** step is the step with the highest activation energy.

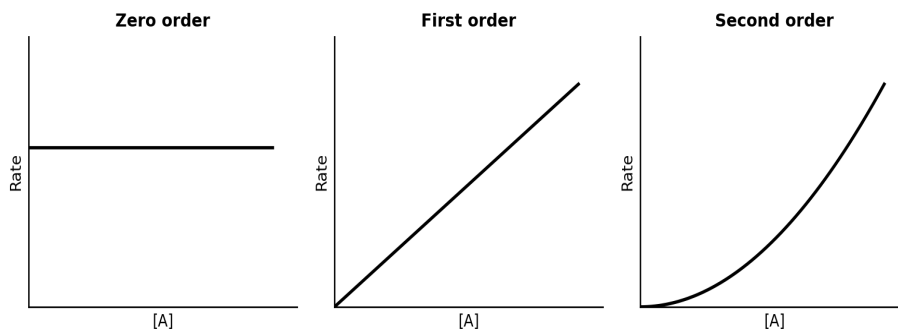
Order of Reaction with Respect to a Reactant

These two definitions are commonly tested.

Order of reaction with respect to a reactant is the power of the concentration of the reactant in the experimentally determined rate equation

OVERALL Order of reaction is the **sum** of the orders of reaction with respect to the reactants which are the powers of the concentrations of the reactants in the experimentally determined rate equation

Order	Effect on Rate when [reactant] doubles
Zero	No effect — rate unchanged.
First	Rate doubles (rate \propto [reactant])
Second	Rate quadruples (rate \propto [reactant] ²)



Rate Constant, k

Factors affecting Rate Constant, k

	Effect on Rate Constant, k
Temperature	Increases as temperature increases
Catalyst	Increases when catalyst is added

Units of the Rate constant, k

Rate is always $\text{mol dm}^{-3} \text{s}^{-1}$.
Solve for the units of k by

$$\frac{\text{mol dm}^{-3} \text{s}^{-1}}{(\text{mol dm}^{-3})^{\text{overall order}}}$$

Overall Order	Units of k
0	$\text{mol dm}^{-3} \text{s}^{-1}$
1	s^{-1}
2	$\text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$
3	$\text{mol}^{-2} \text{dm}^6 \text{s}^{-1}$

❖ REACTION MECHANISM AND RATE EQUATION

A reaction usually proceeds in several steps. The slowest step determines the overall rate.

The rate equation is determined entirely by the species in the slow step.

If the slow step contains intermediate species, we do not write the **intermediate species** but the **species that produced the intermediate**.

There are two ways for us to figure out the slow step of the reaction.

1) Initial Rates Data

2) Graphical Method

Initial Rates Data

For these types of questions, it is usually very simple.

The experiment is repeated multiple times with the concentration of the reactants changed. A table consisting of the concentration of the reactants and rate of reaction is provided.

We will then be able to use the **ratio** of the **change in concentration** of a reactant and the **change in rate of reaction** to calculate the **order of reaction with respect to the reactant**.

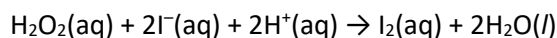
If we recall...

Order	Effect on Rate when [reactant] doubles
Zero	No effect — rate unchanged.
First	Rate doubles (rate \propto [reactant])
Second	Rate quadruples (rate \propto [reactant] ²)

This means that through the ratio, we are able to determine whether the order of reaction w.r.t the reactant is zero, first or second.

EXAMPLE 1

Hydrogen peroxide reacts with acidified iodide ions, liberating iodine.



In investigations of this reaction, the following results were obtained.

experiment	initial concentrations of reactants / mol dm ⁻³			initial rate of formation of I ₂ / mol dm ⁻³ s ⁻¹
	[H ₂ O ₂]	[I ⁻]	[H ⁺]	
1	0.010	0.010	0.010	2.0 × 10 ⁻⁶
2	0.030	0.010	0.010	6.0 × 10 ⁻⁶
3	0.030	0.020	0.010	1.2 × 10 ⁻⁵
4	0.030	0.040	0.020	2.4 × 10 ⁻⁵

(a) Deduce the orders of reaction with respect to H₂O₂, I⁻ and H⁺.

Inspection method:

Comparing experiments 1 and 2, where [I⁻] and [H⁺] are kept constant,

When **[H₂O₂] is tripled, initial rate is tripled.**

∴ the reaction is **1st order** with respect to **H₂O₂**.

Comparing experiments 2 and 3, where [H₂O₂] and [H⁺] are kept constant,

When **[I⁻] is doubled, initial rate is doubled,**

∴ the reaction is **1st order** with respect to **I⁻**.

Comparing experiments 3 and 4, where [H₂O₂] is kept constant,

When **[I⁻] is doubled** and **[H⁺] is doubled, initial rate is doubled.** Since the reaction is 1st order with respect to I⁻, **doubling [I⁻] would double the rate,** hence **doubling [H⁺] did not change the initial rate.**

∴ the reaction is **zero order** with respect to H⁺.

Mathematical Method :

$$\frac{\text{rate}_3}{\text{rate}_4} = \frac{k[\text{H}_2\text{O}_2][\text{I}^-][\text{H}^+]^x}{k[\text{H}_2\text{O}_2][\text{I}^-][\text{H}^+]^x}$$

$$\frac{1.2 \times 10^{-5}}{2.4 \times 10^{-5}} = \frac{k(0.030)(0.020)(0.010)^x}{k(0.030)(0.040)(0.020)^x}$$

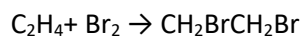
$$\left(\frac{1}{2}\right)^z = 1$$

$$z = 0$$

∴ the reaction is **zero order** with respect to H⁺.

EXAMPLE 2

Hydrogen peroxide reacts with acidified iodide ions, liberating iodine.



In investigations of this reaction, the following results were obtained.

experiment	initial concentrations of reactants / mol dm ⁻³			Time taken for Br ₂ to disappear.
	Volume of C ₂ H ₄ in CCl ₄ /cm ³	Volume of Br ₂ in CCl ₄ /cm ³	Volume of CCl ₄ /cm ³	
1	20	20	0	15
2	12	20	8	25
3	20	10	10	15
4	40	20	20	T ₄

(a) Explain why was varying volumes of CCl₄ used

This is to ensure that the volume of each mixture is 40cm³. This ensures that the concentration of each reactant to be directly proportional to its volume. Comparison of volume is equal to comparison of concentration.

(b) Deduce the orders of reaction with respect to C₂H₄ and Br₂

Inspection method:

Comparing experiments 1 and 3, where volume of C₂H₄ is kept constant,

When **volume of Br₂ is halved, time taken** remain constant.

∴ the reaction is **1st order** with respect to **H₂O₂**.

Mathematical Method :

$$\frac{rate_1}{rate_2} = \frac{k[\text{Br}_2][\text{C}_2\text{H}_4]^x}{k[\text{Br}_2][\text{C}_2\text{H}_4]^x}$$

$$\frac{1}{25} = \frac{k(20)(20)^x}{k(20)(12)^x}$$

$$\left(\frac{5}{3}\right)^x = \left(\frac{5}{3}\right)$$

$$x = 1$$

∴ the reaction is **first order** with respect to C₂H₄.

GRAPHICAL METHOD

The second type of question involve the use of graphs. Typically, the graph given is a **Concentration** against **Time** graph. To calculate the rate of reaction at any point, we will...

- Draw a tangent at that point
- Find gradient of the tangent.

The values of the rate of reactions will then allow us to calculate the order of reaction with respect to a reactant.

Half-Life of First-Order Reactions

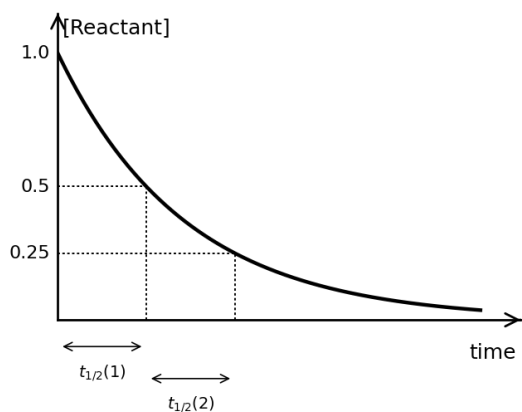
Constant $t_{1/2}$ is the key indicator of first-order kinetics. Use this to determine order graphically.

Half-life, $t_{1/2}$, is defined as the time taken for the concentration of the reactant to fall to half its initial concentration.

For a **first-order** reaction, the half-life is constant.

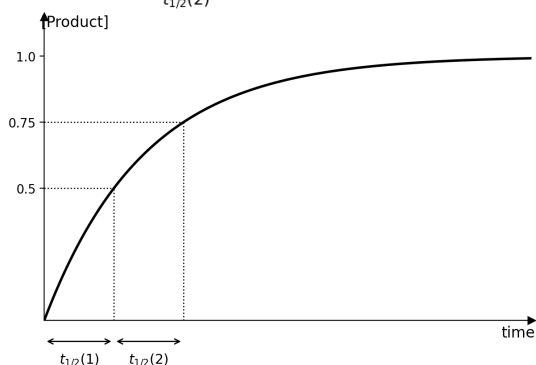
If concentration against time graph produces a constant half-life, reaction is first order.

$$t_{1/2} = \frac{\ln 2}{k}$$



For the reactant time graph,

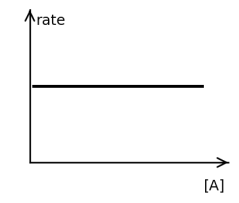
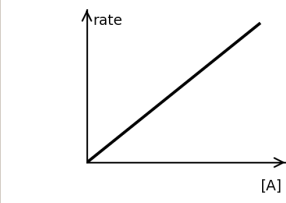
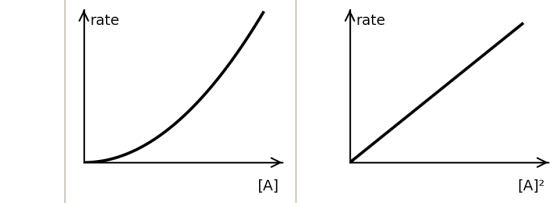
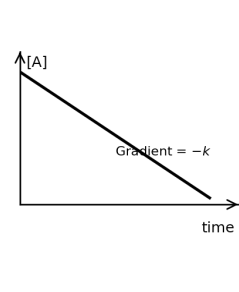
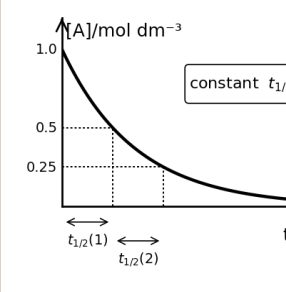
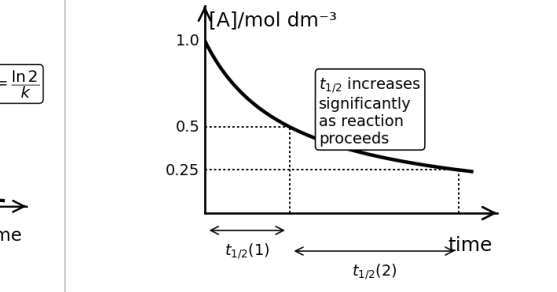
- first half-life ($t_{1/2}(1)$) is the time for the concentration to fall from 1.0 mol dm^{-3} to 0.5 mol dm^{-3} .
- second half-life ($t_{1/2}(2)$) is the time for the concentration to fall from 0.5 mol dm^{-3} to 0.25 mol dm^{-3} .



For the product time graph,

- first half-life ($t_{1/2}(1)$) is the time for the concentration to increase from 0.0 mol dm^{-3} to 0.5 mol dm^{-3} .
- second half-life ($t_{1/2}(2)$) is the time for the increase to fall from 0.5 mol dm^{-3} to 0.75 mol dm^{-3} .

Time	0	1 st $t_{1/2}$	2 nd $t_{1/2}$	3 rd $t_{1/2}$
[reactant]	100%	50%	25%	12.5%
[product]	0%	50%	75%	87.5%

Order of reaction	0	1	2
Example	$A \rightarrow \text{products}$	$A \rightarrow \text{products}$	$2A \rightarrow \text{products}$
Rate equation	Rate = $k [A]^0$	Rate = $k [A]$	Rate = $k [A]^2$
Units of k	$\text{mol dm}^{-3} \text{t}^{-1}$	t^{-1}	$\text{mol}^{-1} \text{dm}^3 \text{t}^{-1}$
Graph of rate vs [A]			
Graph of [A] vs time Gradient = rate of reaction			
Notes	Rate of reaction is unaffected by concentration of reactants. Gradient of conc vs time graph is constant.	Rate of reaction decreases as [reactants] decreases. Gradient of conc vs time graph decreases with time. Half-life is constant, $t_{1/2} = \frac{\ln 2}{k}$	Rate of reaction decreases sharply as concentration of reactants decreases. Gradient of conc vs time graph decreases sharply with time. Half-life increases more than proportionately as the reaction proceeds.

EXAMPLE 3 [N2013/3/5(c),(d)]

The Harcourt and Esson reaction is that between hydrogen peroxide and acidified potassium iodide. The rate of reaction can be followed by measuring the amount of iodine produced after various times, from which the concentration of H_2O_2 remaining can be calculated.

The following reaction mixture was prepared for experiment 1.

initial $[\text{H}^+]$	$0.200 \text{ mol dm}^{-3}$
initial $[\text{I}^-]$	$0.200 \text{ mol dm}^{-3}$
initial $[\text{H}_2\text{O}_2]$	$0.0200 \text{ mol dm}^{-3}$

The following table shows $[\text{H}_2\text{O}_2]$ at various times.

time /s	$[\text{H}_2\text{O}_2]$ / mol dm^{-3}
0	0.0200
80	0.0167
183	0.0135
315	0.0103
490	0.0071
760	0.0039

- (i) Plot these data on suitable axes below.
- (ii) Use your graph to determine
- (1) the order of reaction with respect to $[\text{H}_2\text{O}_2]$,
 - (2) the initial rate, in $\text{mol dm}^{-3} \text{ s}^{-1}$.

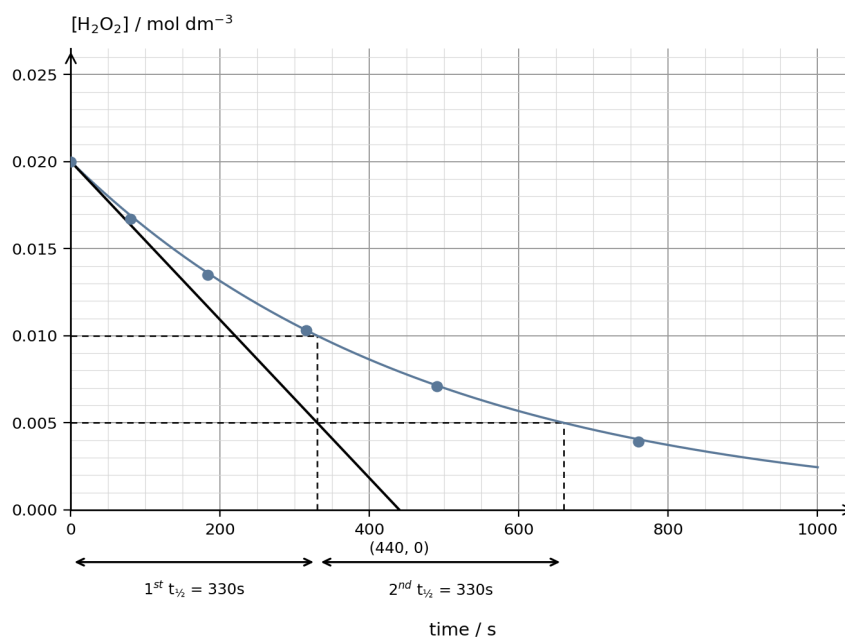
showing all your working and drawing clearly any construction lines on your graph.

Further experiments were carried out changing $[\text{H}^+]$ and $[\text{I}^-]$, but keeping the initial $[\text{H}_2\text{O}_2]$ the same as before. The following results were obtained.

experiment	initial $[\text{H}^+]$ / mol dm^{-3}	initial $[\text{I}^-]$ / mol dm^{-3}	initial rate / $\text{mol dm}^{-3} \text{ s}^{-1}$
2	0.400	0.200	8.4×10^{-5}
3	0.300	0.200	6.3×10^{-5}
4	0.200	0.100	2.1×10^{-5}

- (iii) Determine the orders with respect to $[\text{H}^+]$ and $[\text{I}^-]$. Explain your reasoning.
- (iv) Hence, write the rate equation for the reaction, and calculate a value for the rate constant. Include units in your answer.

(i)



(ii) (1)

From the graph, 1st $t_{1/2} = 330$ s.

$$2^{\text{nd}} t_{1/2} = 330 \text{ s}$$

Since $t_{1/2}$ remains constant at 330s, reaction is first order with respect to H_2O_2 .

(2)

Initial rate = -gradient of tangent to graph at $t = 0$

$$= \frac{0.02}{440}$$

$$= \underline{4.55 \times 10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1}}$$

(iii) Comparing experiments 2 and 3.

When initial $[\text{H}^+] \times \frac{4}{3}$, initial rate $\times \frac{4}{3}$

Order of reaction with respect to $\text{H}^+ = 1$

From experiments 2 and 4,

$$\frac{\text{initial rate of experiment 2}}{\text{initial rate of experiment 4}} = \frac{8.4 \times 10^{-5}}{2.1 \times 10^{-5}} = \frac{k(0.400)(0.20)^a[\text{H}_2\text{O}_2]}{k(0.200)(0.10)^a[\text{H}_2\text{O}_2]}$$

$$2 = 2^a$$

$$\underline{a = 1}$$

reaction is first order with respect to I^-

(iv) rate = $k[\text{H}_2\text{O}_2][\text{I}^-][\text{H}^+]$

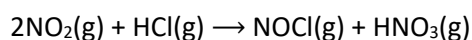
Using experimental data from 1st experiment,

$$8.4 \times 10^{-5} = k(0.0200)(0.400)(0.200)$$

$$k = \underline{0.0525 \text{ mol}^{-2} \text{ dm}^6 \text{ s}^{-1}}$$

EXAMPLE 4

Nitrogen dioxide undergoes the following gas phase reaction with hydrogen chloride.

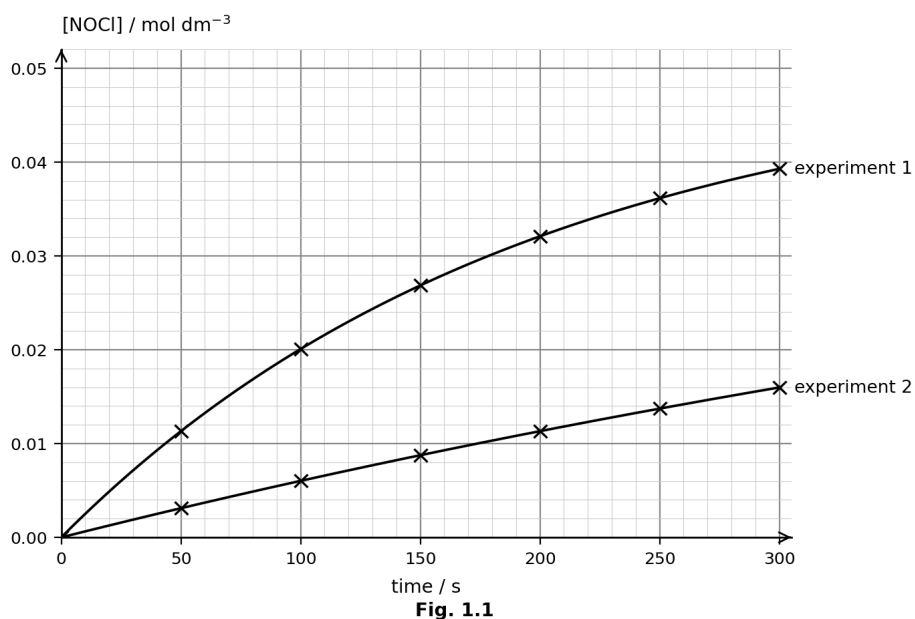


To study the kinetics for this reaction, three separate experiments were carried out in a vessel of fixed volume at a constant temperature of 500 K. The initial concentrations of NO_2 and HCl are shown below.

Table 1.1

experiment	initial $[\text{NO}_2]$ / mol dm^{-3}	initial $[\text{HCl}]$ / mol dm^{-3}
1	1.00	0.05
2	0.50	0.05
3	0.50	0.01

To monitor the progress of the reaction for each experiment, the total pressure in the vessel was measured at regular time intervals and the corresponding concentrations of NOCl were calculated. Fig. 1.1 shows how the concentration of NOCl varies with time for experiments 1 and 2.

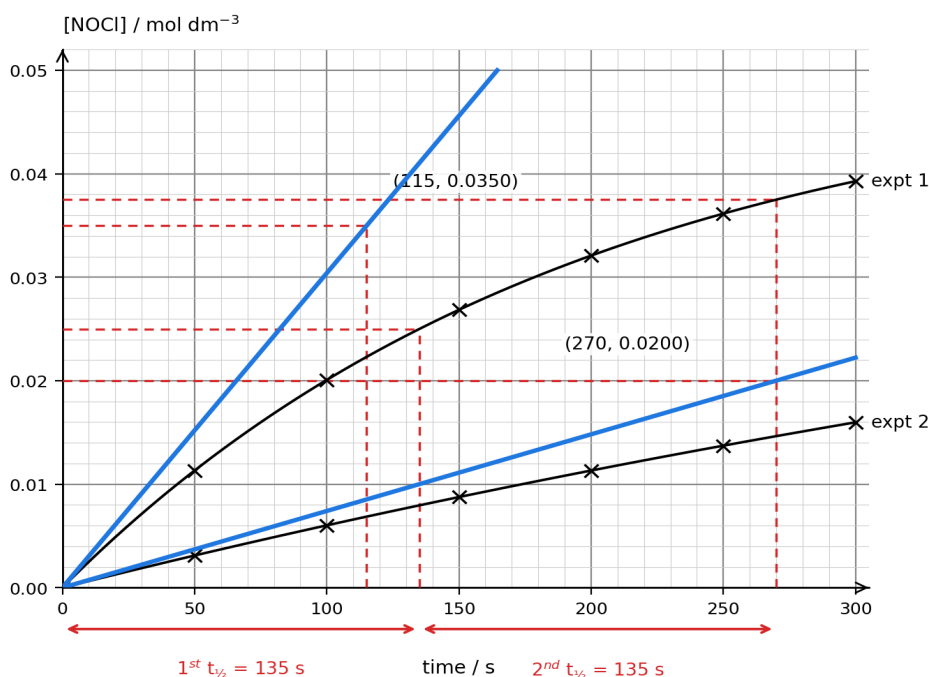


- (i) Using Fig. 1.1, determine the initial rate of reaction for experiments 1 and 2, showing your working clearly on the graph.

Hence, deduce the order of reaction with respect to NO_2 .

- (ii) State the final concentration of NOCl in the vessel for experiment 1 if the reaction were to proceed to completion.

- (iii) Hence, determine the order of reaction with respect to HCl . Show your working, including construction lines on Fig. 1.1.



$$\text{initial rate of reaction for experiment 1} = \frac{0.0350 - 0}{115 - 0} = 3.04 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$$

$$\text{initial rate of reaction for experiment 2} = \frac{0.0200 - 0}{270 - 0} = 7.41 \times 10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1}$$

$$\frac{\text{initial rate of expt 1}}{\text{initial rate of expt 2}} = \frac{3.04 \times 10^{-4}}{7.41 \times 10^{-5}} = 4.10 \approx 4$$

Comparing experiments 1 and 2, when $[\text{NO}_2]$ is **doubled**, rate of reaction **quadrupled**.
 reaction is second order with respect to NO_2 .

(ii) Final $[\text{NOCl}] = \underline{0.0500 \text{ mol dm}^{-3}}$ (as limiting reactant is HCl)

(iii) For experiment 1, final $[\text{NOCl}] = 0.05 \text{ mol dm}^{-3}$.

$$1^{\text{st}} t_{1/2} = \underline{135 \text{ s}}$$

time taken for $[\text{NOCl}]$ to increase from 0 mol dm^{-3} to $0.025 \text{ mol dm}^{-3}$

$$2^{\text{nd}} t_{1/2} = \underline{135 \text{ s}}$$

time taken for $[\text{HCl}]$ to decrease from $0.025 \text{ mol dm}^{-3}$ to $0.0125 \text{ mol dm}^{-3}$

Since $t_{1/2}$ remains constant at 135s, reaction is first order with respect to NOCl

❖ PSEUDO FIRST-ORDER REACTIONS

Given the reaction $X + Y \rightarrow Z$, where the rate equation is

$$\text{rate} = k[X][Y].$$

If Y is used in **large excess** compared to A, the $[Y] \gg [X]$, then **[Y] remains effectively constant** during the reaction as its decrease would be negligible.

The above rate equation can then be rewritten as:

$$\text{rate} = k'[X] \quad \text{where} \quad k' = k[Y]$$

The reaction follows **first-order kinetics** and thus we say that the reaction follows **pseudo first-order kinetics**.

$$t_{1/2} \text{ of X} = \frac{\ln 2}{k'}$$

$$t_{1/2} = \frac{\ln 2}{k'} = \frac{\ln 2}{k[Y]}$$

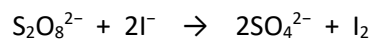
The table below shows how the $t_{1/2}$ of A is affected when [A] and [B] are changed.

experiment	[X] / mol dm ⁻³	[Y] / mol dm ⁻³	$t_{1/2}$ / min
1	0.01	1	10
2	0.02	1	10
3	0.01	2	5

By the $t_{1/2}$ equation, the value of $t_{1/2}$ is only affected by the **concentration of Y** and k which is only affected by **temperature** and **activation energy**.

Common types of Pseudo First-order Kinetics

(a) Presence of a Large Excess of a Reactant

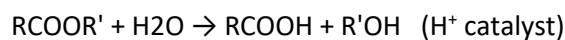


The rate equation is: **rate = $k[\text{S}_2\text{O}_8^{2-}][\text{I}^-]$**

If **initial $[\text{S}_2\text{O}_8^{2-}] \gg \text{initial } [\text{I}^-]$** , then $[\text{S}_2\text{O}_8^{2-}]$ will remain relatively constant throughout the reaction relative to the change in $[\text{I}^-]$.

Hence the rate equation : **rate = $k'[\text{I}^-]$** where **$k' = k[\text{S}_2\text{O}_8^{2-}]$**

(b) Presence of a Catalyst

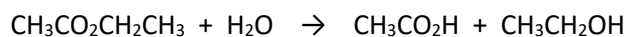


The rate equation is: **rate = $k[\text{H}^+][\text{RCOOR}']$**

H^+ is a catalyst. At the end of the reaction, it is **regenerated and remains chemically unchanged**. The $[\text{H}^+]$ will remain constant during the reaction.

Hence the rate equation: **rate = $k'[\text{RCOOR}']$** where **$k' = k[\text{H}^+]$**

(c) Solvent takes Part in Reaction



The rate equation is: **rate = $k[\text{CH}_3\text{CO}_2\text{CH}_2\text{CH}_3][\text{H}_2\text{O}]$**

H_2O is a reactant that takes part in the reaction. Since it is also a solvent, $[\text{H}_2\text{O}]$ remains essentially constant throughout the reaction.

Hence the rate equation can be modified as: **rate = $k'[\text{CH}_3\text{CO}_2\text{CH}_2\text{CH}_3]$** where **$k' = k[\text{H}_2\text{O}]$** . We now have a **pseudo first-order** reaction.