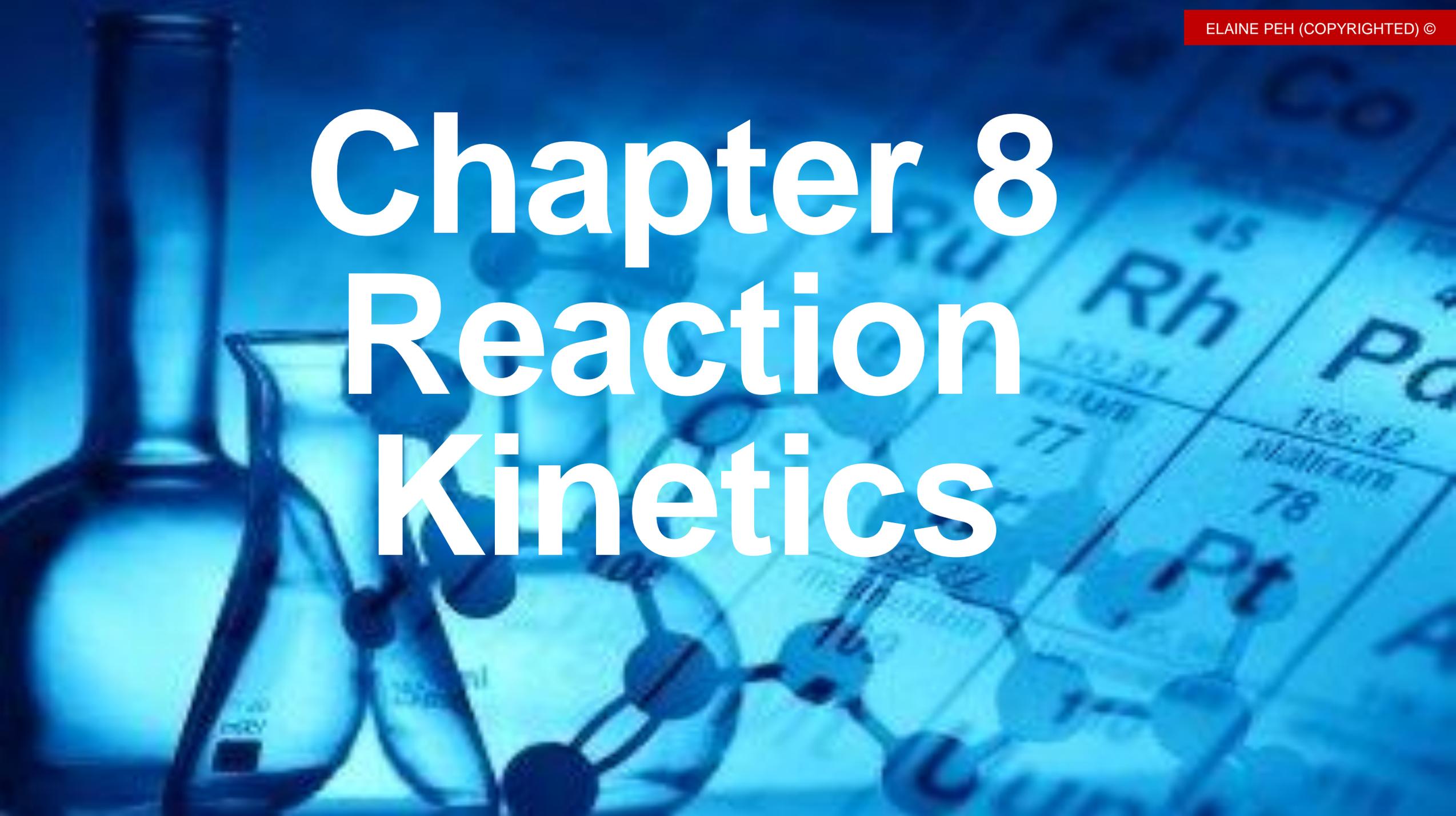


Chapter 8 Reaction Kinetics



CHAPTER ANALYSIS



FOCUS

- One of the major chapters
- 6 **key** concepts



EXAM

- Tested in both theory and practical



WEIGHTAGE

- Appears yearly in at least 1 question for theory paper

KEY CONCEPT

Reaction Kinetics Terminology

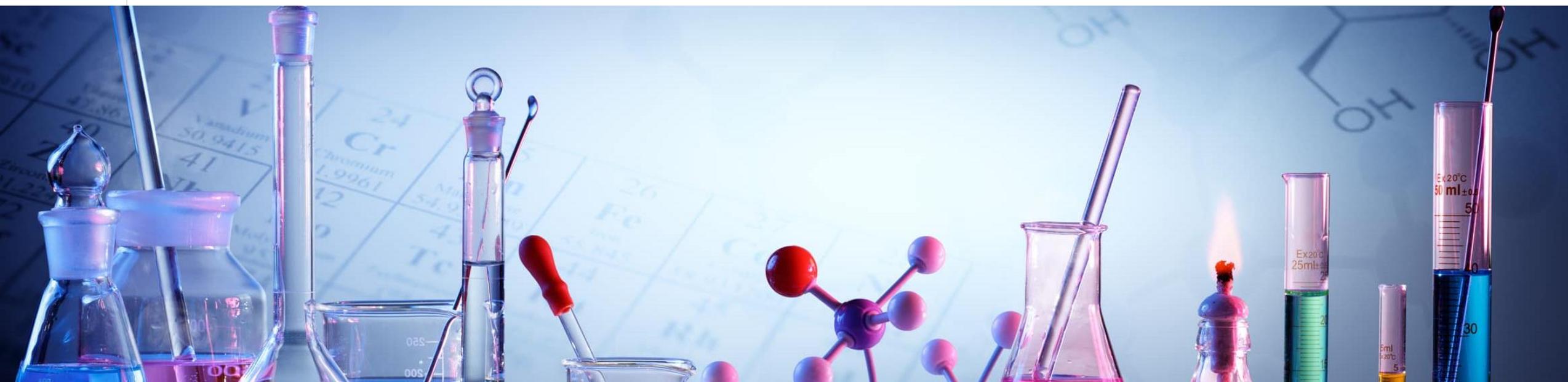
Rate Equation & Order of Reaction

Methods to determine Order of Reaction

Mechanism

Factors affecting Rate of Reaction

Experimental studies of Kinetics



Reaction Kinetics Terminology

RATE OF REACTION

$$\text{Rate} = \frac{\Delta \text{ of [reactant/product]}}{\text{time taken}}$$

Units = mol dm⁻³ s⁻¹, mol dm⁻³ min⁻¹, mol dm⁻³ h⁻¹

Note: When using $\Delta[\text{reactant}]$, rate will be (-)

Note: When using $\Delta[\text{product}]$, rate will be (+)

INSTANTANEOUS RATE

The rate at a **particular time**..

INITIAL RATE

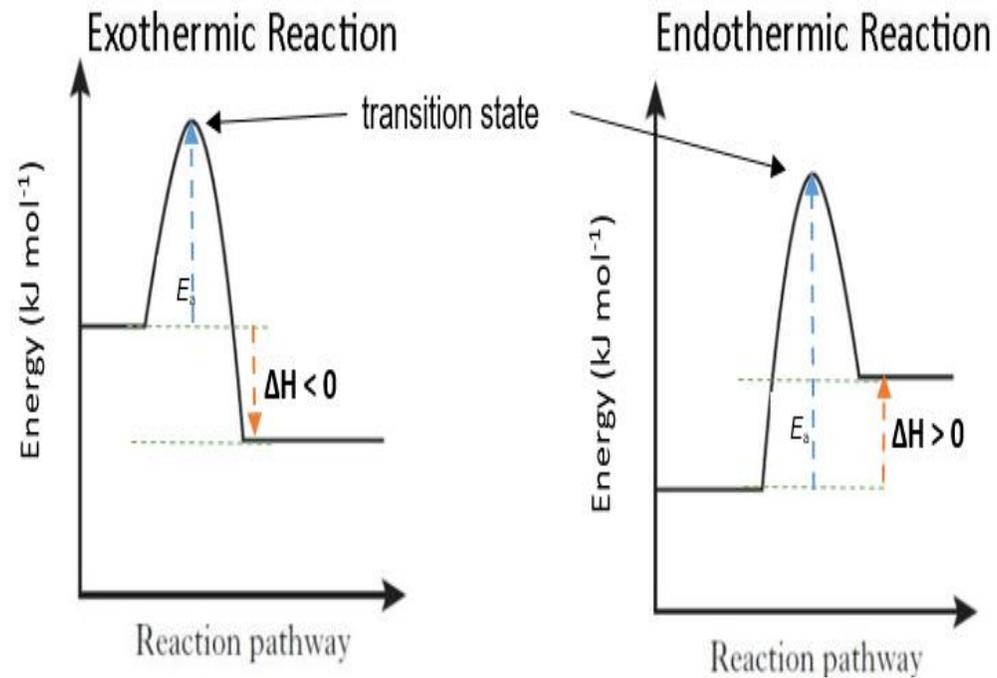
The **instantaneous rate** at **time=0**.

ACTIVATION ENERGY

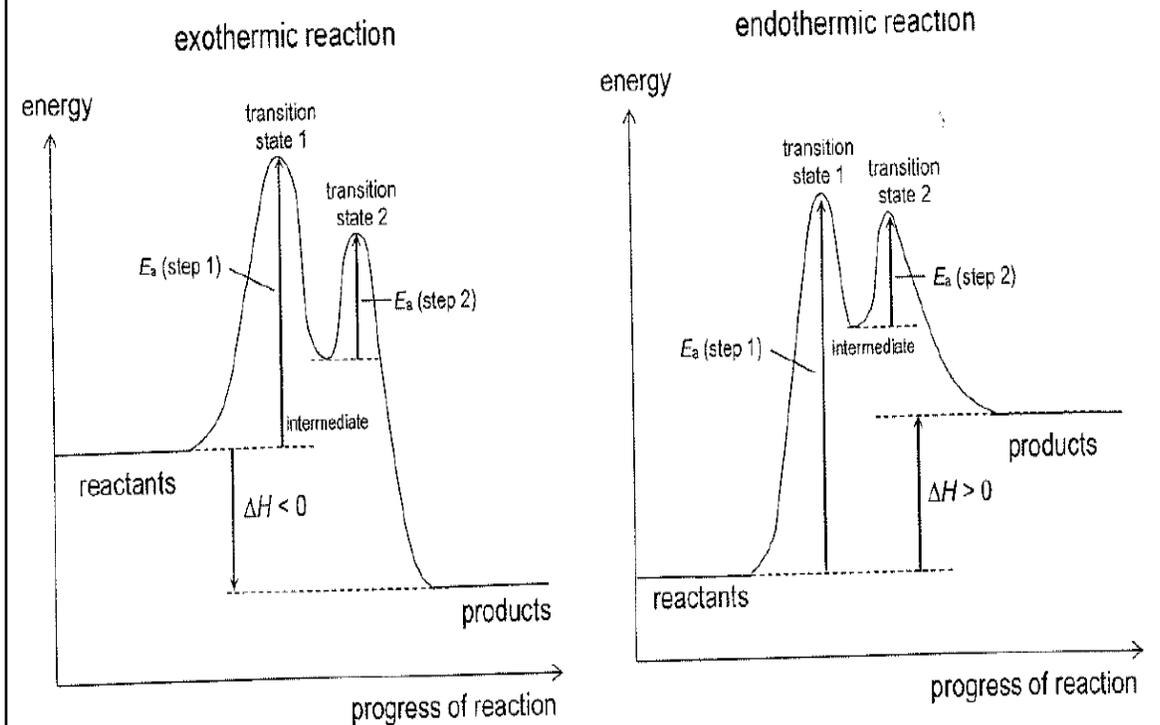
Minimum energy which reacting particles must **possess** in order to **overcome** the **activation energy barrier** before becoming **products**.

ENERGY PROFILE DIAGRAM

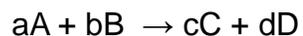
In a Single-Step Reaction



In a Multiple-Steps Reaction



RATE EQUATION



$$\text{Rate} = k[A]^a[B]^b$$

- k = rate constant
- a = order of reaction with respect to A
- b = order of reaction with respect to B
- $a+b$ = overall order of reaction

Note: Stoichiometric equation is the overall chemical equation, rate equation involves only the rate determine step (the slow step).

RATE CONSTANT

- Rate Constant (k) is the constant of proportionality in the reaction.
- It is affected by both temperature and catalyst.
- The larger the k , the faster the reaction.

Rate Equation & Order of Reaction

ORDER OF REACTION

- The **order of reaction** with respect to a **given reactant** is the **power** to which the concentration of the reactant is raised to in the experimentally determined rate equation.
- The **overall order of reaction** is the **sum of the powers** of all the **reactant's order** in the experimentally determined rate equation.

ZERO ORDER REACTION

$$\text{Rate} = k[A]^0 = k$$

- Rate is **independent** to the reactant's concentration.
- $k = \text{mol dm}^{-3} \text{ s}^{-1}$

Rate Equation & Order of Reaction

Rate Equation & Order of Reaction

FIRST ORDER REACTION

$$\text{Rate} = k[A]^1$$

- Rate is **directly proportional** to the reactant's concentration.
- $k = \text{s}^{-1}$
- Constant half-life

Note: it is the only reaction with constant $t_{1/2}$

HALF LIFE

Time taken for the [A] to decrease to half its initial value

$$\frac{\text{final [reactant]}}{\text{initial [reactant]}} = \frac{1}{2^n}$$

$n = \text{number of half-lives}$

SECOND ORDER REACTION

- Rate is **proportional** to the concentration of a **single reactant raised to the power of two** or to the **product of the concentrations of two reactants**.
- $k = \text{mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ (2nd order)

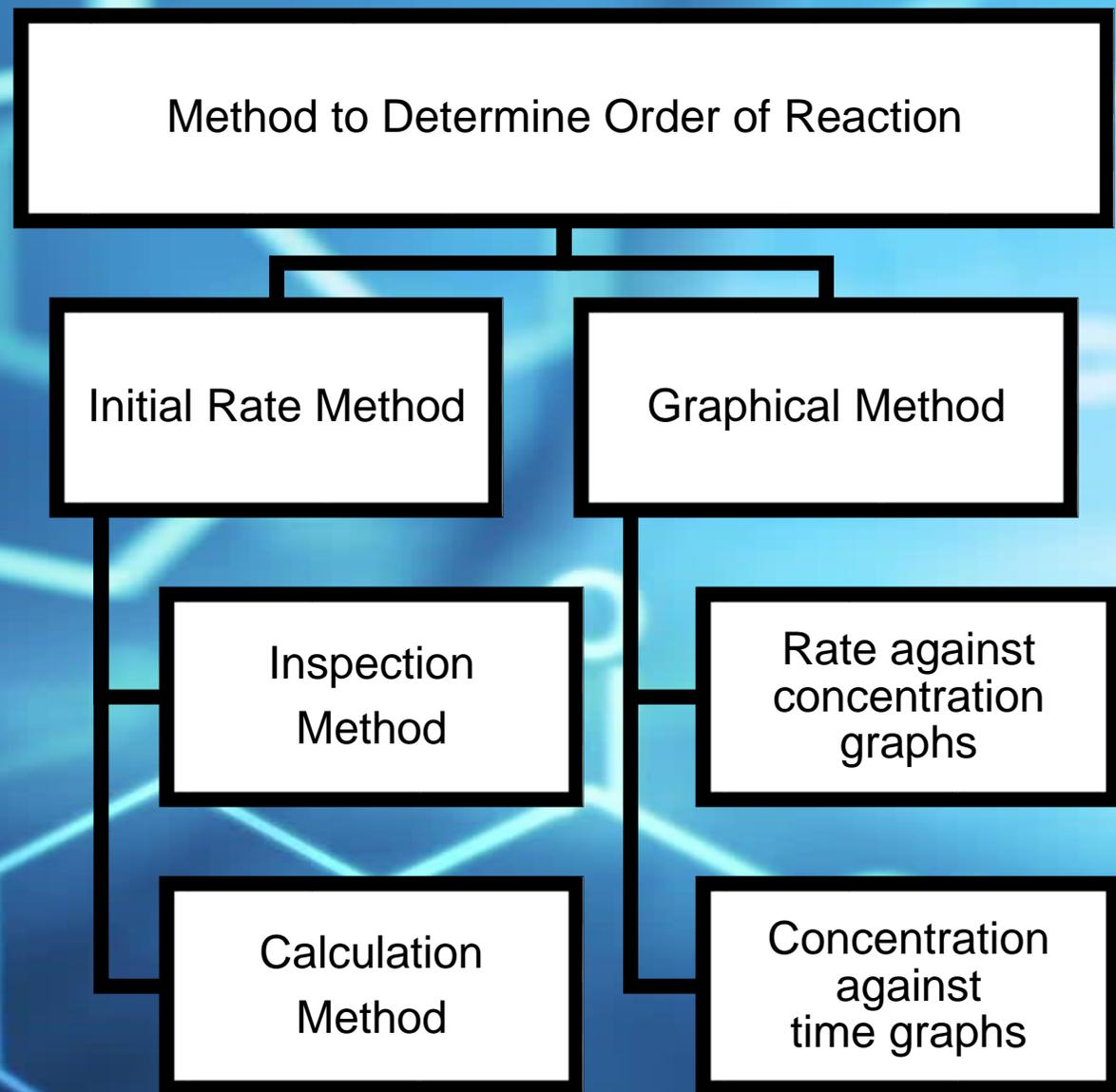
$$\text{Rate} = k[\text{A}]^2 = k[\text{A}][\text{B}]$$

PSEUDO FIRST ORDER REACTION

- When a 2nd order kinetics is approximated to a 1st order kinetics whereby all the other reactants are in large excess except the one being studied
- It only occurs if:
 - 1) presence of large excess of a reactant
 - 2) solvent used is also the reactant
 - 3) presence of a catalyst in the rate equation

Rate Equation & Order of Reaction

Determine Order of Reaction



METHOD 1: INITIAL RATE METHOD

Comparing the **initial rates** of reactions at **different known initial concentrations**

| Experiment Number | [A] / mol dm ⁻³ | [B] / mol dm ⁻³ | [C] / mol dm ⁻³ | Initial rate / mol dm ⁻³ s ⁻¹ |
|-------------------|----------------------------|----------------------------|----------------------------|-----------------------------------------------------|
| 1 | 0.100 | 0.100 | 0.100 | 4.0 x 10 ⁻⁵ |
| 2 | 0.100 | 0.200 | 0.100 | 4.0 x 10 ⁻⁵ |
| 3 | 0.100 | 0.200 | 0.200 | 8.0 x 10 ⁻⁵ |
| 4 | 0.200 | 0.100 | 0.100 | 16.0 x 10 ⁻⁵ |

1a) INSPECTION METHOD (USING WORDS)

To find order of reaction w.r.t. A:

We use experiment 1 and 4 as [B] and [C] are constant

[A] doubles from 0.100 mol dm⁻³ to 0.200 mol dm⁻³

Initial rate quadruple

This indicate that rate is proportional to [A]²

Hence reaction is 2nd order w.r.t. A

To find order of reaction w.r.t. B:

We use experiment 1 and 2 as [A] and [C] are constant

[A] doubles from 0.100 mol dm⁻³ to 0.200 mol dm⁻³

Initial rate remains the same

This indicate that rate is independent of [B]

Hence reaction is 0 order w.r.t. B

To find order of reaction w.r.t. C:

We use experiment 2 and 3 as [A] and [B] are constant

[C] doubles from 0.100 mol dm⁻³ to 0.200 mol dm⁻³

Initial rate doubles

This indicate that rate is proportional to [C]

Hence reaction is 1st order w.r.t. C

METHOD 1: INITIAL RATE METHOD

Comparing the **initial rates** of reactions at **different known initial concentrations**

| Experiment Number | [A] / mol dm ⁻³ | [B] / mol dm ⁻³ | [C] / mol dm ⁻³ | Initial rate / mol dm ⁻³ s ⁻¹ |
|-------------------|----------------------------|----------------------------|----------------------------|-----------------------------------------------------|
| 1 | 0.100 | 0.100 | 0.100 | 4.0 × 10 ⁻⁵ |
| 2 | 0.100 | 0.200 | 0.100 | 4.0 × 10 ⁻⁵ |
| 3 | 0.100 | 0.200 | 0.200 | 8.0 × 10 ⁻⁵ |
| 4 | 0.200 | 0.100 | 0.100 | 16.0 × 10 ⁻⁵ |

1b) CALCULATIONS METHOD

To find order of reaction w.r.t. A:

We use experiment 1 and 4 as [B] and [C] are constant

$$\frac{rate_4}{rate_1} = \frac{k [0.200]^a [0.100]^b [0.100]^c}{k [0.100]^a [0.100]^b [0.100]^c}$$

$$\frac{16 \times 10^{-5}}{4 \times 10^{-5}} = \frac{[0.200]^a}{[0.100]^a}$$

$$4 = 2^a$$

$$a = 2$$

Hence reaction is 2nd order w.r.t. A

To find order of reaction w.r.t. B:

We use experiment 1 and 2 as [A] and [C] are constant

$$\frac{rate_2}{rate_1} = \frac{k [0.100]^a [0.200]^b [0.100]^c}{k [0.100]^a [0.100]^b [0.100]^c}$$

$$\frac{4 \times 10^{-5}}{4 \times 10^{-5}} = \frac{[0.200]^b}{[0.100]^b}$$

$$1 = 2^b$$

$$b = 0$$

Hence reaction is 0 order w.r.t. B

To find order of reaction w.r.t. C:

We use experiment 2 and 3 as [A] and [B] are constant

$$\frac{rate_3}{rate_2} = \frac{k [0.100]^a [0.200]^b [0.200]^c}{k [0.100]^a [0.200]^b [0.100]^c}$$

$$\frac{8 \times 10^{-5}}{4 \times 10^{-5}} = \frac{[0.200]^c}{[0.100]^c}$$

$$2 = 2^c$$

$$c = 1$$

Hence reaction is 1st order w.r.t. C

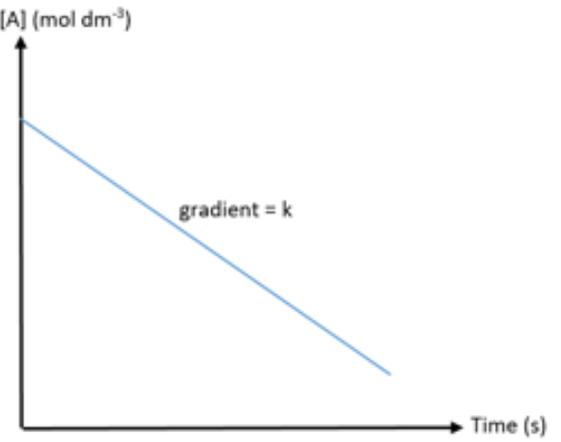
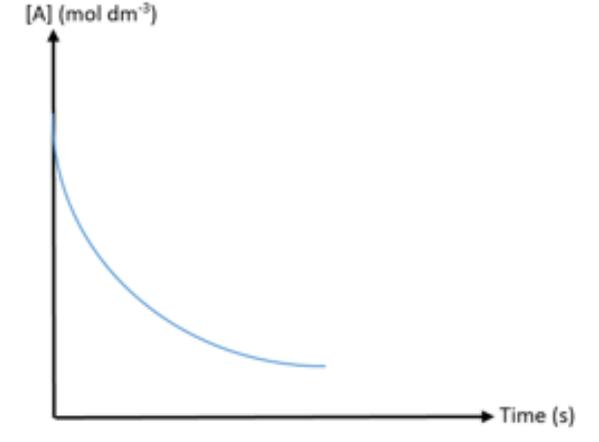
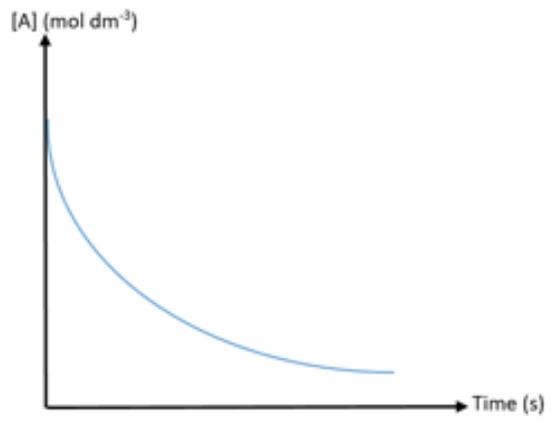
METHOD 2: GRAPHICAL METHOD (plotting of graphs)

2a) RATE AGAINST CONCENTRATION

| 1) Rate against concentration graphs | | |
|------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| 0 order Rate = k | 1 st order Rate = k[A] | 2 nd order Rate = k[A] ² |
| <p>Rate (mol dm⁻³ s⁻¹)</p> <p>k</p> <p>Rate = k</p> <p>[A] (mol dm⁻³)</p> | <p>Rate (mol dm⁻³ s⁻¹)</p> <p>gradient = k</p> <p>[A] (mol dm⁻³)</p> | <p>Rate (mol dm⁻³ s⁻¹)</p> <p>[A] (mol dm⁻³)</p> <p>Rate (mol dm⁻³ s⁻¹)</p> <p>gradient = k</p> <p>[A]² (mol dm⁻³)²</p> <p><i>Note: take not of the axis, a 2nd order reaction can also have a straight line graph</i></p> |
| <p>Determine the order of reaction by looking at the shape of the graph</p> | | |

METHOD 2: GRAPHICAL METHOD (plotting of graphs)

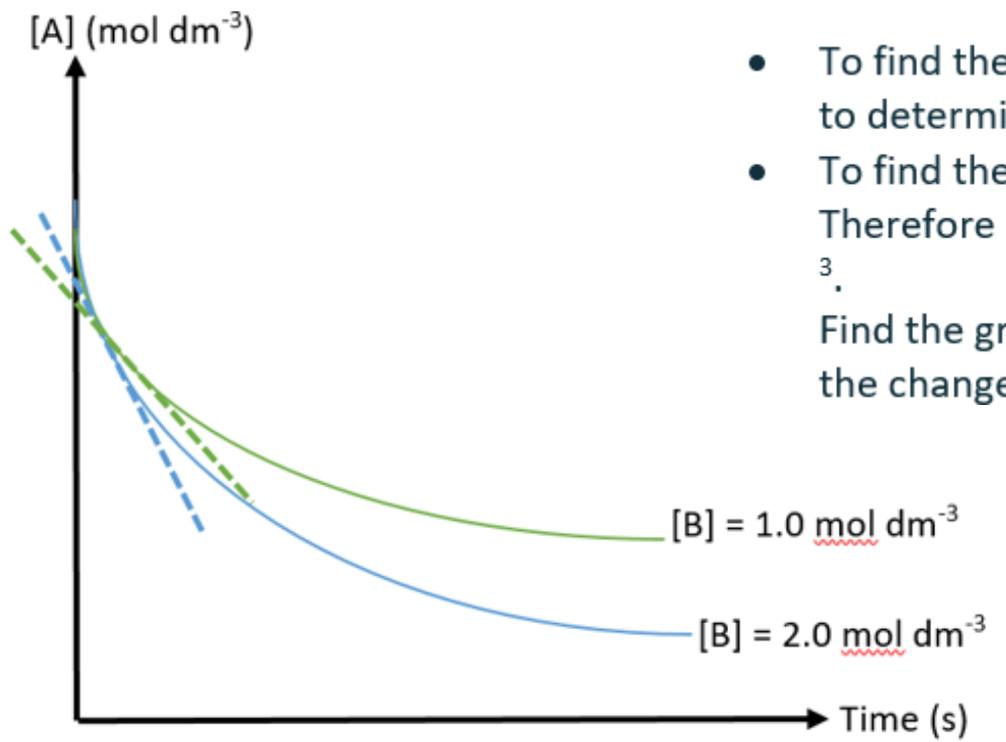
2b) CONCENTRATION AGAINST TIME

| 2) Concentration against time graphs | | |
|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------|
| 0 order Rate = k | 1 st order Rate = $k[A]$ | 2 nd order Rate = $k[A]^2$ |
|  <p>[A] (mol dm⁻³)</p> <p>Time (s)</p> <p>gradient = k</p> |  <p>[A] (mol dm⁻³)</p> <p>Time (s)</p> |  <p>[A] (mol dm⁻³)</p> <p>Time (s)</p> |
| <p>If graph is straight line, rate is constant; order of reaction with respect to reactant is 0.</p> <p>If graph is curve, determine the half-life from the curve.</p> <ul style="list-style-type: none"> • If half-life is constant, order of reaction with respect to reactant is 1. • If half-life is not constant, order of reaction with respect to reactant is 2. | | |

METHOD 2: GRAPHICAL METHOD (plotting of graphs)

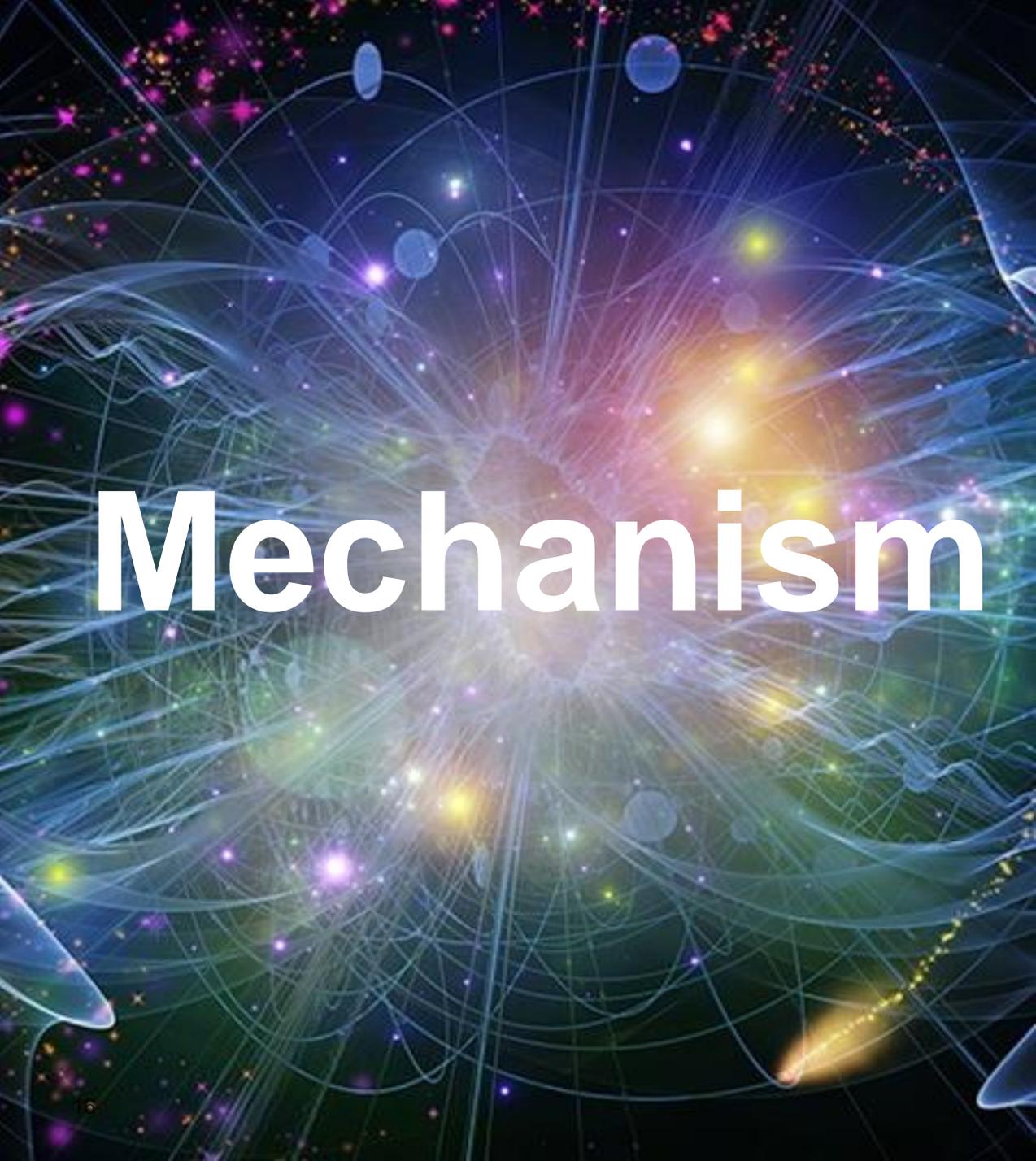
2b) CONCENTRATION AGAINST TIME

This can also be used to find the order of reaction with respect to **two** reactants



- To find the order of reaction w.r.t [A], do the normal method of using the half-life to determine.
- To find the order of reaction w.r.t [B], [A] have to be constant while [B] changes. Therefore have to use both graph when [B] = 1 mol dm⁻³ and when [B] = 2 mol dm⁻³. Find the gradient of each individual graph to get the initial rate, and compare with the changes in [B] to determine the order of reaction w.r.t [B].

| | When [B] doubles | |
|--------------------------------------------|----------------------------------------------|-------------------------------------------------|
| Initial rate remains constant = zero order | Initial rate doubles = 1 st order | Initial rate quadrupled = 2 nd order |



Mechanism

RATE-DETERMINING STEP

It is the slowest step in the reaction mechanism.

SINGLE-STEP REACTION

- A reaction that only consist of one elementary step
- The reaction mechanism only have **one** step, which the **rate-determining step**
- The **rate equation** is **identical to the stoichiometric equation**

MULTIPLE-STEP REACTION

- A reaction that take place by two or more steps
- The reaction mechanism consist of two or more elementary steps
- The **rate equation** is **not identical to the stoichiometric equation**
- The **rate equation** is obtained from the **rate-determining step**, the slowest step in the reaction mechanism with the highest E_a

Mechanism

METHOD 1

Deducing the Rate Equation from Reaction Mechanism

1. **Single-Step Reactions** – the rate equation can be deduced directly from the stoichiometric equation
2. **Multiple-Steps Reactions**
 - (A) Mechanism with Step 1 as the slow step

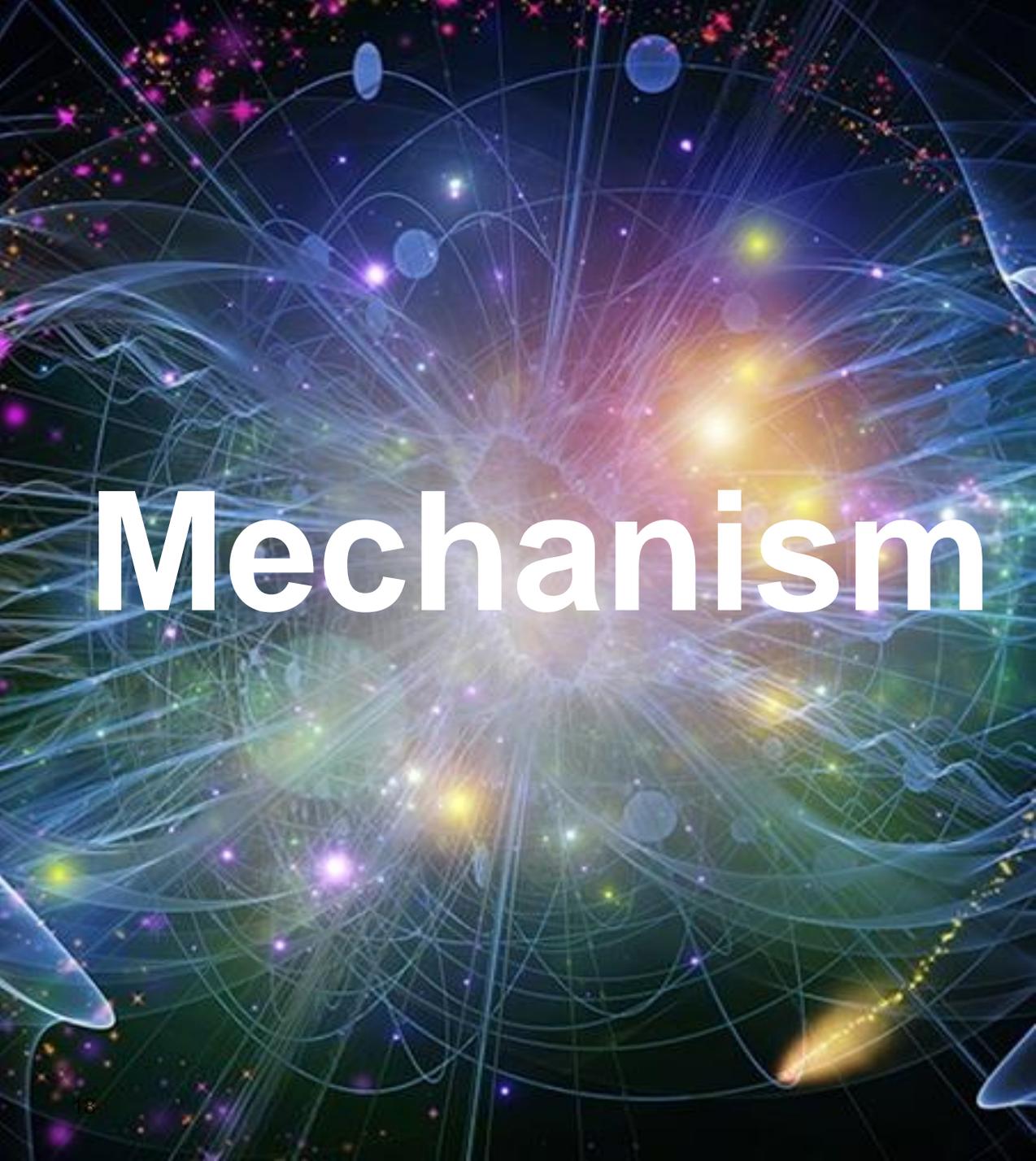
Only the reactant that appears in Step 1 will be included in the rate equation

| | |
|-------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Stoichiometric Equation | $2\text{N}_2\text{O} \rightarrow 2\text{N}_2 + \text{O}_2$ |
| Reaction Mechanism | Step 1: $\text{N}_2\text{O} \rightarrow \text{N}_2 + \text{O}$ (slow) Step 2: $\text{N}_2\text{O} + \text{O} \rightarrow \text{N}_2 + \text{O}_2$ (fast) |
| Rate Equation | Rate = $k[\text{N}_2\text{O}]$ |

(B) Mechanism with Step 1 **NOT** the slow step

Take into account the reactant that appears in the slow step and any **fast step before** the slow step. Do not include the intermediates

| | |
|-------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------|
| Stoichiometric Equation | $2\text{NO} + \text{Cl}_2 \rightarrow 2\text{NOCl}$ |
| Reaction Mechanism | Step 1: $\text{NO} + \text{Cl}_2 \rightarrow \text{NOCl}_2$ (fast) Step 2: $\text{NO} + \text{NOCl}_2 \rightarrow 2\text{NOCl}$ (slow) |
| Rate Equation | Rate = $k[\text{NO}]^2[\text{Cl}_2]$ <i>Note: NOCl_2 is an intermediate and thus do not include in the rate equation</i> |



Mechanism

METHOD 2

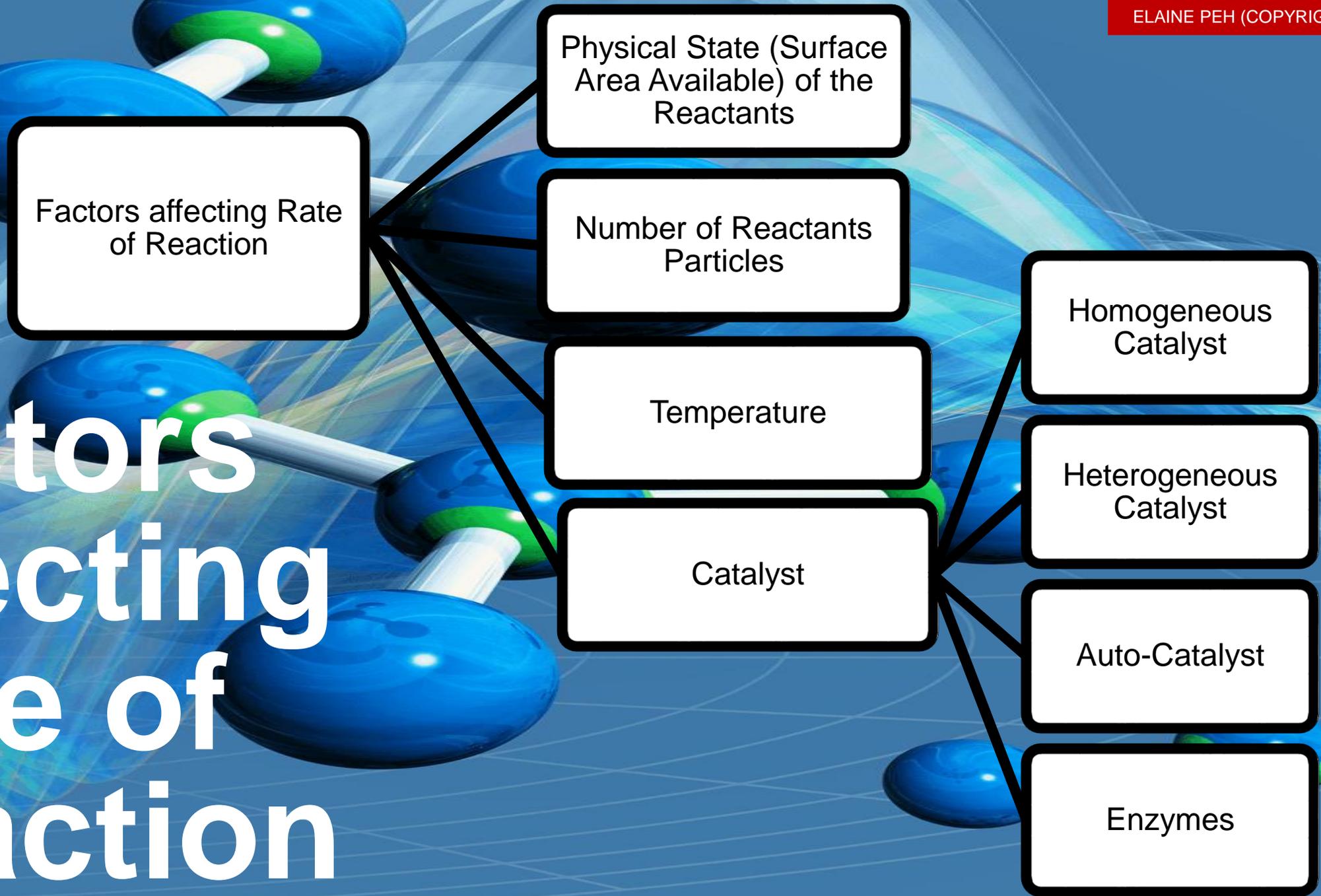
Deducing Reaction Mechanism from the Rate Equation

Step 1 – If the question did not specify which step is the slow step, try to make Step 1 in the reaction mechanism as the slow step using the rate equation

Step 2 – Subtract the reactants in the slow step from the stoichiometric equation to get the reactants and intermediates required for the remaining fast step

Step 3 – Write out the equation with reference to the products from the stoichiometric equation

Factors affecting Rate of Reaction



COLLISION THEORY

A chemical reaction only occurs if (1) particles collide (2) the collision occur with sufficient energy to overcome E_a (3) collision must be at the correct orientation → **Effective Collision**

FACTOR 1: Physical State (Surface Area Available) of the Reactants

The **more finely divided** the reactant is → the **greater its surface area** → the **number of collision sites** increase → the **frequency of collision** increase → the **frequency of effective collision** increase → rate **increase**

Note: this applies for solids

FACTOR 2: Number of Reactants Particles

When **concentration** increase, the **number of reactant particles per unit volume increase** → the number of sites for collision increase → the **frequency of collision** increase → the **frequency of effective collision** increase → rate **increase**

*Note: for liquids, and the order of reaction w.r.t the reactant is **NOT** zero.*

When **pressure** increase, the **number of gaseous reactant particles per unit volume increase** → the number of sites for collision increase → the **frequency of collision** increase → the **frequency of effective collision** increase → rate **increase**

Note: for gases



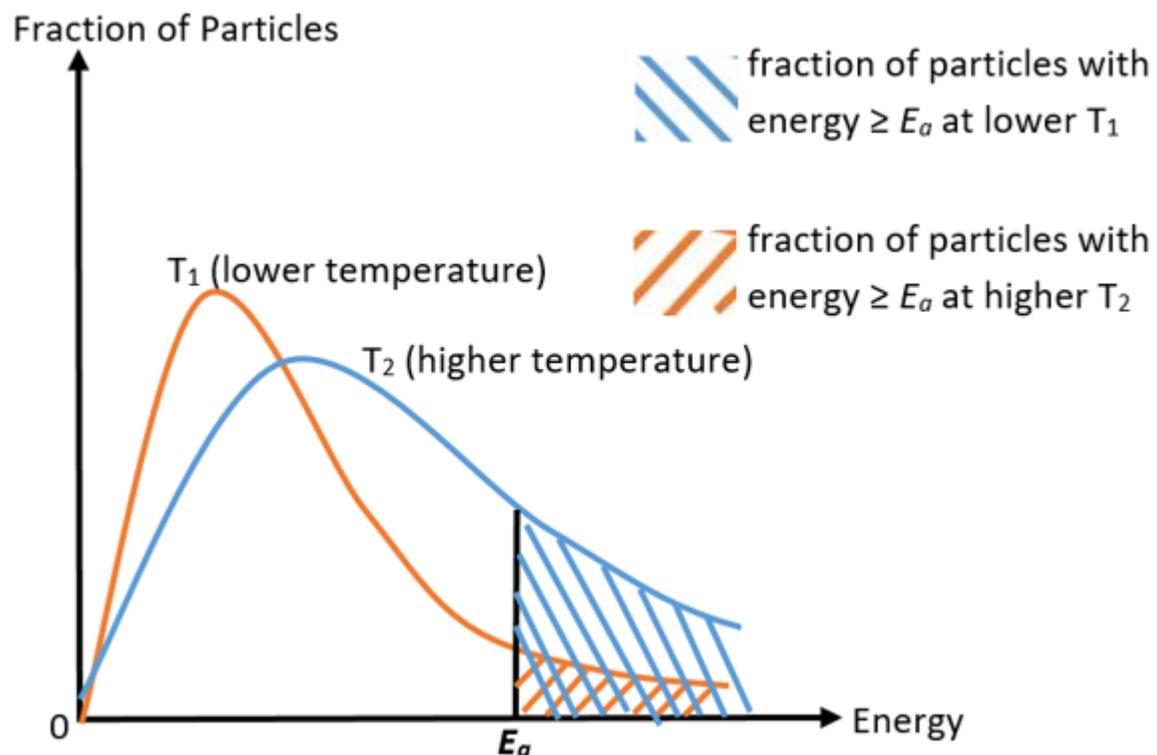
Factors affecting Rate of Reaction

FACTOR 3: Temperature

When **temperature** increase, the **average kinetic energy of reactant particles increase** hence **increases the fraction of particles with energy $\geq E_a$** → the **frequency of collision** also increase → the **frequency of effective collision** increase → **rate increase**

Note: a change in temperature usually increases the rate of reaction significantly, as temperature also affects the rate constant.

Maxwell-Boltzmann distribution curve:



Things to note when drawing the Maxwell-boltzmann curve:

- The **peak shift right** as **temperature increase** and **shift left** as **temperature decrease**
- The **distribution curve broadens** when there is a **greater spread of kinetic energies** as **temperature increase**
- **Shaded area** = fraction of particles with energy $\geq E_a$

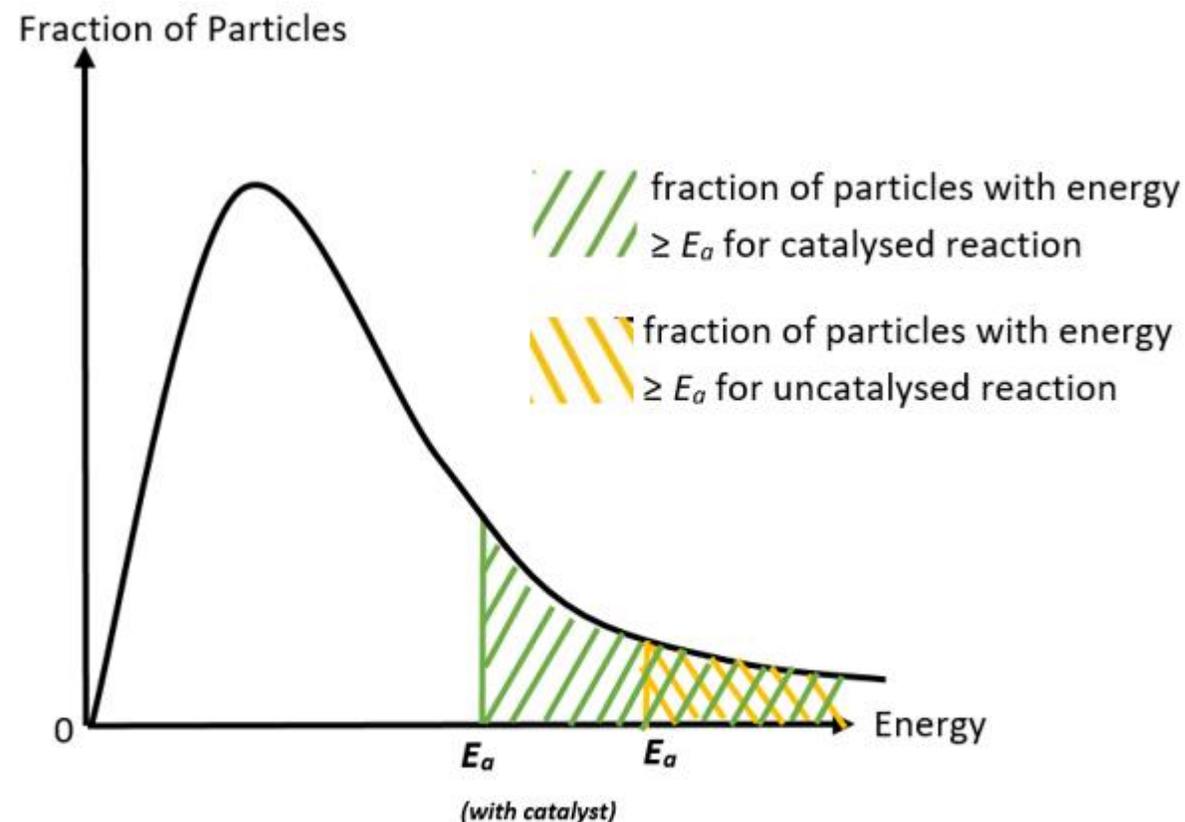
FACTOR 4: Catalyst

Catalyst provides an alternative reaction pathway with a lower E_a → therefore this increases the fraction of particles with energy $\geq E_a$ → the frequency of effective collision increase → rate increase

Properties of a Catalyst:

1. Remained unchanged in quantity at the end of the reaction
2. Just a small amount is usually sufficient to bring about a rapid increase in the rate of reaction
3. Increases the rate constant
4. It alters the reaction mechanism and hence the order and rate equation

Note: catalyst never appear in the stoichiometric equation, but they may appear in the rate equation if they take part in the rate determining step

Maxwell-Boltzmann distribution curve

Note: the graph remains unchanged, only the E_a changes

FACTOR 4: Catalyst

Types of Catalyst:

1. Homogeneous Catalyst – catalyst and reactants are of the same phase
2. Heterogeneous Catalyst – catalyst and reactants are of different phase
3. Auto-Catalyst – product of the reaction act as the catalyst
4. Enzymes – proteins in a biological system

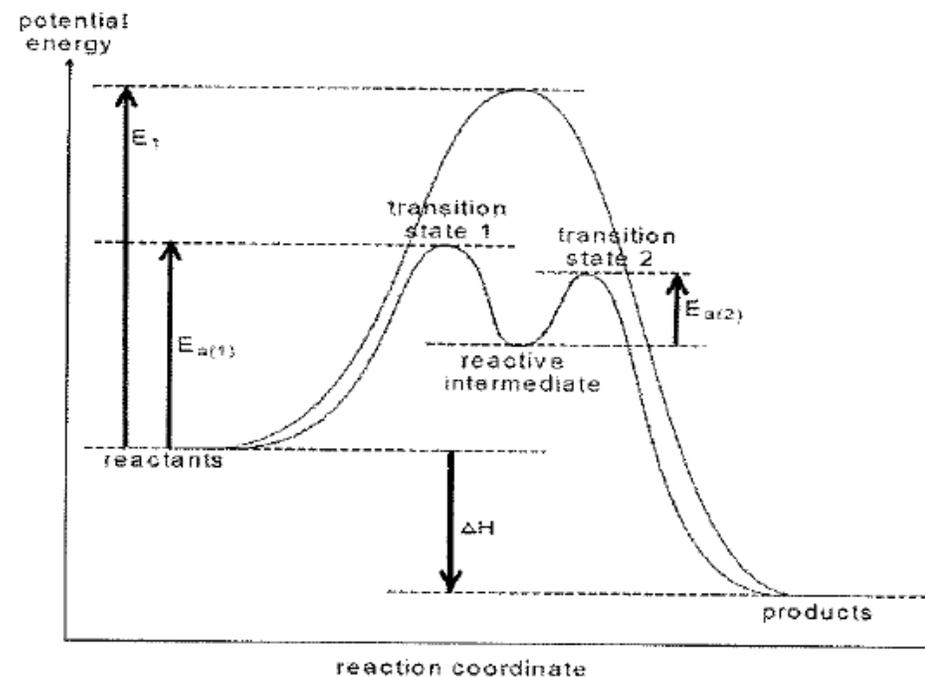
FACTOR 4: Catalyst – Homogeneous Catalyst

Mode of Action:

Step 1 – It **takes part** in the chemical reaction by converting into an intermediate

Step 2 – The intermediate then undergoes the reaction to form the products and the **catalyst is regenerated**

Energy Profile Diagram for Homogenous Catalyst



E_1 = activation energy of uncatyalsed reaction

$E_{a(1)}$ = activation energy of first step of catalysed reaction

$E_{a(2)}$ = activation energy of second step of catalysed reaction

FACTOR 4: Catalyst – Heterogeneous Catalyst

Mode of Action:

Step 1 – The reactants **adsorbed** onto the active site on the **surface of the catalyst**.

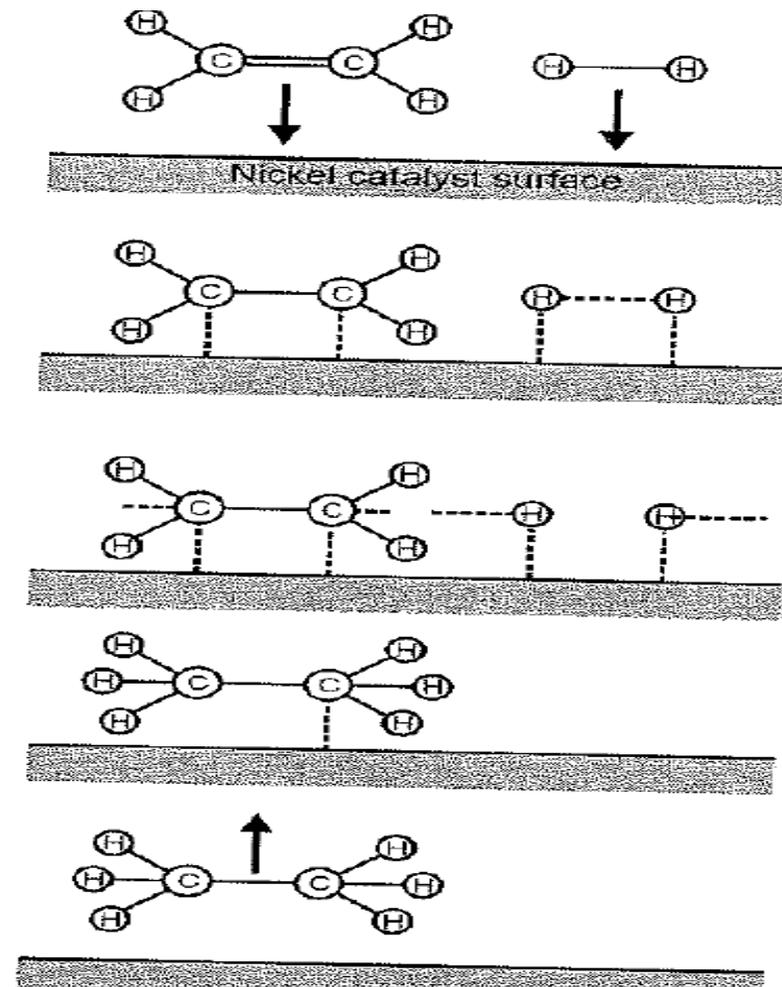
- Adsorption is facilitated by the **formation of weak bonds** between the active sites of the catalysts and the reactants

Step 2 – **Reaction between the reactants** at the surface of the catalyst.

- The **adsorption of the reactants** to the catalyst surface **weakens the covalent bonds** within the reactant molecules.
- This **decreases the activation energy** required for the reaction as lower amount of energy is now required to overcome the chemical bonds within the reactants.
- **Adsorption of the reactants** to the catalyst surface also **increases the local concentration of reactants**.

Step 3 – The products (and remaining reactants) then **desorbed** from the surface of the catalyst.

Haber Process, catalyse by Ni (s)



FACTOR 4: Catalyst – Auto-Catalyst

Mode of Action:

- The product acts as the catalyst.
- Initially the reaction will be slow as it is not catalysed (no products formed)
- As products formed, they act as the catalyst hence increasing the rate of reaction.
- Towards the end of the reaction, although a lot of product (catalysts) are present, the concentration of the reactants has decreased and hence the rate of reaction decrease.



Factors affecting Rate of Reaction

FACTOR 4: Catalyst – Enzymes

Mode of Action:

Step 1 – Substrates bind to the **active site** of the enzyme, forming an **enzyme-substrate complex**

- Only substrates of the **correct shape** can bind to the enzyme

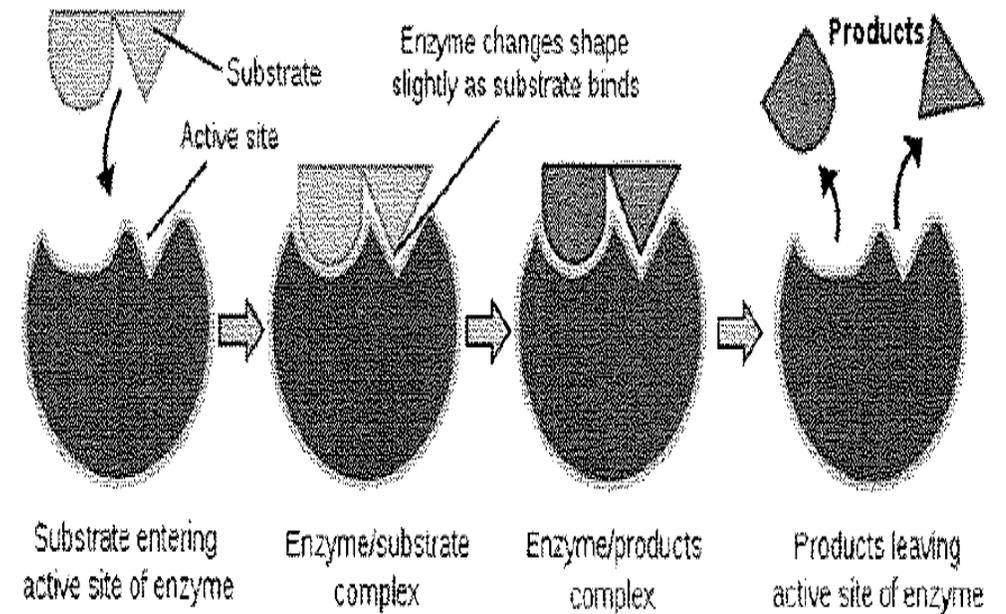
Step 2 – Reaction occur within the enzyme-substrate complex

- Similar to homogeneous catalyst, the **bonds within the reactant molecules are weakened during the formation of the enzyme-substrate complex**

Step 3 – The products then leave the enzyme

- As the **products** formed have a **different shape**, they are now unable to bind to the active sites of the enzymes, breaking the enzyme-substrate complex
- The enzyme is now free to accept another substrate for another reaction

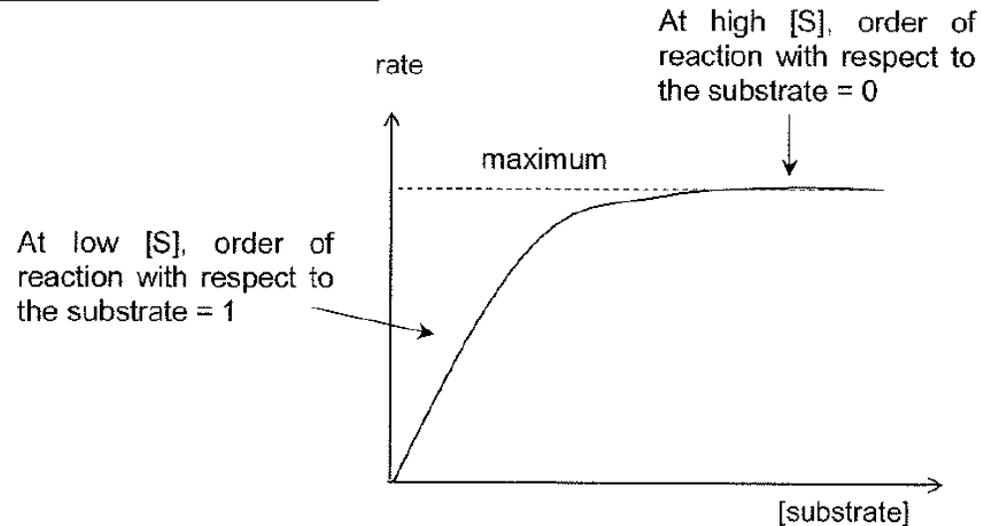
Lock & Key Model of Enzyme-Catalysed Reaction



FACTOR 4: Catalyst – Enzymes

Factors affecting enzyme-catalysed reaction:

1. Concentration of Substrate



- Graph is a straight line initially -> At low [substrate] not all active sites of the enzymes are occupied, hence reaction is 1st order w.r.t substrate
- Graph plateaus off -> At high [substrate] all active sites of the enzymes are occupied, hence any changes in [substrate] will not affect the rate and thus is zero order w.r.t substrate

2. Concentration of Enzyme

As [enzyme] is usually very small as compared to [substrate], rate of reaction is usually 1st order w.r.t enzyme

3. Temperature

Enzymes operate at an optimum temperature. Any temperature that is too high or too low will lower the rate.

4. pH

Enzymes only work well over a narrow pH range. Enzymes will be denatured outside the range of pH values.

5. Presence of inhibitors

Certain compounds have similar shape as the substrates hence they might compete with the substrate to bind to the active site of the enzymes

Experimental Studies of Kinetics

Continuous Rate Method

This method measures the changes in concentration over a period of time within the same set of experiment:

1) Sampling, Quenching and Titration Method

Common Example: Acid Catalysed Reaction of Propanone with Iodine

- $\text{CH}_3\text{COCH}_3 (\text{aq}) + \text{I}_2 (\text{aq}) \rightarrow \text{CH}_2\text{ICOCH}_3 (\text{aq}) + \text{HI} (\text{aq}) + \text{I}_2 (\text{aq})$ (unreacted)
- Rate of reaction is determine by measuring the amount of **unreacted iodine** in the reaction mixture at regular time interval by **titration with sodium thiosulfate (VI) solution**.
- $2\text{S}_2\text{O}_3^{2-} (\text{aq}) + \text{I}_2 (\text{aq}) \rightarrow \text{S}_4\text{O}_6^{2-} (\text{aq}) + 2\text{I}^- (\text{aq})$
- Quenching is performed by adding NaHCO_3 solution into the pipetted reaction which reacts with the H^+
- By plotting a graph of "volume of $\text{S}_2\text{O}_3^{2-}$ used" against "time", order of reaction w.r.t I_2 can be determined.

Note: Quenching can be performed using large amount of distilled water – it lower the kinetic energy of reactant particles and lower the concentration of reactant particles, leading to fewer number of effective collisions hence stopping the reaction.

Note: Sources of error could be that the ice-cold distilled water slowly gained heat from the surroundings as the reaction proceeded leading to temperature fluctuations, especially for the last few reactants that were being quenched.

Note: The volume of sodium thiosulfate should be measured precisely, using a burette, in each of the experiments as the volume of thiosulfate determines the amount of iodine unreacted in the previous experiment which should be accurate for comparison of the rates.

2) Measurement of Physical Properties Method

- **Colour** intensity / Absorbance
- Electrical Conductivity: must have change in [ions]
- Pressure
- Volume of Gas Produced

Common Example: Decomposition of H_2O_2

- $2\text{H}_2\text{O}_2 (\text{aq}) \rightarrow 2\text{H}_2\text{O} (\text{l}) + \text{O}_2 (\text{g})$
- Rate of reaction is determine by measuring the volume of **oxygen gas produced** at regular time interval.
- By plotting a graph of "volume of O_2 produced" against "time", order of reaction w.r.t H_2O_2 can be determined.

Note: Cannot be used for reversible reactions

Note: A graph of " $V_\infty - V_t$ " against "time" can also be plotted

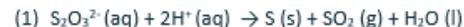
Note: Reasons for difference between theoretical maximum volume of gas obtained and experimental volume could be that some of the gases dissolved in water OR obstruction to airflow as rubber tubing is narrow.

Note: Improvement to experimental design is to use a lubricated gas syringe for gas collection

Non-Continuous Rate Method (Initial Rate Method)

This method uses different starting concentrations of reactants by performing separate sets of the same experiment:

Common Example: Clock Method, which determine the rate of reaction by measuring the time taken for a prescribed visual change to occur.



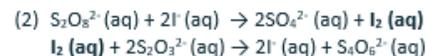
- Rate of reaction is determine by measuring the **time taken for a fixed amount of sulfur (yellow precipitate)** to form over a **printed X**.
- Involves making a simple "dilution" table with different volumes of $\text{Na}_2\text{S}_2\text{O}_3$ (FA1) and HCl (FA2) added:
- $\text{Rate} \propto \frac{1}{\text{time}}$

| Exp. | Volume of FA1 / cm^3 | Volume of FA2 / cm^3 | Volume of water / cm^3 | Time / s |
|------|-------------------------------|-------------------------------|---------------------------------|----------|
| 1 | 50.0 | 5.0 | 0.0 | ? |
| 2 | 40.0 | 5.0 | 10.0 | ? |
| 3 | 30.0 | 5.0 | 20.0 | ? |
| 4 | 20.0 | 5.0 | 30.0 | ? |

Note: Water is used to ensure total volume of reaction mixture is kept constant.

Note: $\frac{1}{\text{time}}$ is a measure of the rate constant k as the amount of thiosulfate ions are small and constant and [reactants] are kept approximately constant ($\text{rate} = k[\text{A}][\text{B}]$) hence $\text{rate} \propto 1/t$

Note: It is necessary to rapidly add FA1 to FA2 during the reaction as the rate of formation of S (s) is very rapid. The use of a burette to add FA1 directly into FA2 is not recommended as if a burette, which releases FA1 slowly, is used, more time than expected will be taken to form the S (s).



- Rate of reaction is determine by measuring the **time taken for starch to turn blue-black** by reacting with the excess I_2 .

Practice Questions

Question: The concentration of sugar during fermentation is found to decrease from the initial concentration of 10 mol dm^{-3} to 5 mol dm^{-3} in the first 5 hours and to 2.5 mol dm^{-3} in the next 5 hours. Determine the order of reaction and the value of rate constant and the time taken for the initial concentration to drop to $0.15625 \text{ mol dm}^{-3}$.

Answer: Reaction is 1st order w.r.t [sugar], $k = 0.139 \text{ h}^{-1}$ (3 sf), time taken = 30 hours

Question: The decomposition of hydrogen peroxide is a 1st order reaction with a half-life of 10 days. Find the time taken for it to decrease from $0.100 \text{ mol dm}^{-3}$ to $0.0293 \text{ mol dm}^{-3}$?

Answer: 17.7 days (3 sf)

Practice Questions

Question: The following results were obtained for the hydrolysis of sucrose:

- (a) Find the order of reaction with respect to both HCl and sucrose and hence the rate constant.
(b) The half-life of sucrose in experiment 1 was 5 seconds. Predict the half-life of sucrose in Experiment 2 and 3.

| Experiment Number | Initial [HCl] / mol dm ⁻³ | Initial [sucrose] / mol dm ⁻³ | Initial rate / mol dm ⁻³ s ⁻¹ |
|-------------------|--------------------------------------|------------------------------------------|-----------------------------------------------------|
| 1 | 0.100 | 0.100 | 0.024 |
| 2 | 0.100 | 0.150 | 0.036 |
| 3 | 0.200 | 0.100 | 0.048 |

Answer:

(a) HCl = 1st order

Sucrose = 1st order

$k = 2.4 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$

(b) Experiment 2 = 5 seconds

Experiment 3 = 2.5 seconds

Practice Questions

Question: The following results were obtained for the reaction between P and Q.

Plot these data on suitable axes and use your graphs to

- Find the order of reaction with respect to [P]
- Find the order of reaction with respect to [Q]
- Construct a rate equation for the reaction and find a value for the rate constant

Answer:

(a) $[P] = 1^{\text{st}}$ order

(b) $[Q] = 1^{\text{st}}$ order

(c) Rate = $[P][Q]$; $k = 5.95 \times 10^{-2} \text{ mol}^{-1} \text{ dm}^3 \text{ min}^{-1}$

| Time / min | [P] / mol dm ⁻³ when [Q] = 0.1 mol dm ⁻³ | [P] / mol dm ⁻³ when [Q] = 0.15 mol dm ⁻³ |
|------------|-------------------------------------------------------------------|--------------------------------------------------------------------|
| 0 | 0.0100 | 0.0100 |
| 40 | 0.0079 | 0.0070 |
| 80 | 0.0062 | 0.0049 |
| 120 | 0.0049 | 0.0034 |
| 160 | 0.0038 | 0.0024 |
| 200 | 0.0030 | 0.0017 |
| 240 | 0.0024 | 0.0012 |

Practice Questions

Question: Rate = $k[\text{NO}][\text{F}_2]$ for the reaction between nitrogen monoxide and fluorine: $2\text{NO} + \text{F}_2 \rightarrow 2\text{ONF}$

Proposed a reaction mechanism of two steps whereby one of these step produces ONF and $\text{F}\cdot$ in equimolar amounts.

Answer: The proposed reaction mechanism is

Step 1: $\text{NO} + \text{F}_2 \rightarrow \text{ONF} + \text{F}\cdot$ (slow)

Step 2: $\text{NO} + \text{F}\cdot \rightarrow \text{ONF}$ (fast)

Question: Write out the reaction mechanism for the following reaction: $\text{A} + 2\text{B} \rightarrow \text{AB}_2$; Rate = $k[\text{A}][\text{B}]$

Answer: The proposed reaction mechanism is

Step 1: $\text{A} + \text{B} \rightarrow \text{AB}$ (slow)

Step 2: $\text{AB} + \text{B} \rightarrow \text{AB}_2$ (fast)

Practice Questions

Question: Find the half-life for the hydrolysis of an ester in the presence of 100 mol dm^{-3} NaOH with a rate constant of $0.5 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$.

Answer: $t_{1/2} = 0.0139 \text{ seconds (3 sf)}$

Question: Consider the following equation: $\text{Zn} + \text{CuSO}_4 \rightarrow \text{ZnSO}_4 + \text{Cu}$

- (a) Write the rate equation
- (b) State the order of reaction with respect to the reactants
- (c) Calculate the overall order of reaction (d) Determine the units of k

Answer:

(a) $\text{Rate} = k[\text{Zn}][\text{CuSO}_4]$

(b) Zn = 1st order

CuSO₄ = 1st order

(c) 2nd order

(d) $\text{mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$

Test yourself!

- (a) explain and use the terms: *rate of reaction*; *rate equation*; *order of reaction*; *rate constant*; *half-life of a reaction*; *rate-determining step*; *activation energy*; *catalysis*
- (b) construct and use rate equations of the form $\text{rate} = k[\text{A}]^m[\text{B}]^n$ (limited to simple cases of single-step reactions and of multi-step processes with a rate-determining step, for which m and n are 0, 1 or 2), including:
- (i) deducing the order of a reaction by the initial rates method
 - (ii) justifying, for zero- and first-order reactions, the order of reaction from concentration-time graphs
 - (iii) verifying that a suggested reaction mechanism is consistent with the observed kinetics
 - (iv) predicting the order that would result from a given reaction mechanism
 - (v) calculating an initial rate using concentration data
[integrated forms of rate equations are **not** required]
- (c) understanding of half-life
- (i) show understanding that the half-life of a first-order reaction is independent of concentration
 - (ii) use the half-life of a first-order reaction in calculations

Test yourself!

- (d) calculate a rate constant using the initial rates method
- (e) devise a suitable experimental technique for studying the rate of a reaction, from given information
- (f) explain qualitatively, in terms of frequency of collisions, the effect of concentration changes on the rate of a reaction
- (g) show understanding, including reference to the Boltzmann distribution, of what is meant by the term *activation energy*
- (h) explain qualitatively, in terms both of the Boltzmann distribution and of collision frequency, the effect of temperature change on a rate constant (and hence, on the rate) of a reaction

Test yourself!

- (i) understanding catalyst
- (i) explain that, in the presence of a catalyst, a reaction has a different mechanism, i.e. one of lower activation energy, giving a larger rate constant
- (ii) interpret this catalytic effect on a rate constant in terms of the Boltzmann distribution

- (j) outline the different modes of action of homogeneous and heterogeneous catalysis, including:
 - (i) the Haber process
 - (ii) the catalytic removal of oxides of nitrogen in the exhaust gases from car engines
 - (iii) the catalytic role of atmospheric oxides of nitrogen in the oxidation of atmospheric sulfur dioxide
 - (iv) catalytic role of Fe^{2+} in the $\text{I}^-/\text{S}_2\text{O}_8^{2-}$ reaction

- (k) describe enzymes as biological catalysts which may have specific activity

- (l) explain the relationship between substrate concentration and the rate of an enzyme-catalysed reaction in biochemical systems

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