



UNIVERSITY  
OF  
JOHANNESBURG

Department of Applied  
Chemistry

# *CHEMICAL KINETICS*

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# PRESENTATION FLOW

Slide 2

★ *Kinetics – Background*

★ *Rate Of Reaction*

★ *Factors Affecting the Rate*

★ *Concentration & Rate – Rate Laws, Order*

★ *Reaction Mechanism – Molecularity*

★ *Temperature & Rate – Arrhenius equation*

★ *Pseudo Order Reactions - Brief Overview*

★ *Adsorption Kinetic Models – Types*

★ *Adsorption Reaction Models*

★ *Adsorption Diffusion Model*

★ *Kinetic Best Fit Model Interpretation*

# KINETICS - BACKGROUND

Slide 3

- To understand & predict behaviour of a chemical system one must consider both Thermodynamics & Kinetics

**Thermodynamics** : does a reaction takes place ???

**Kinetics** : how fast does a reaction proceed ???

- Factors to be considered when predicting whether or not a change will take place

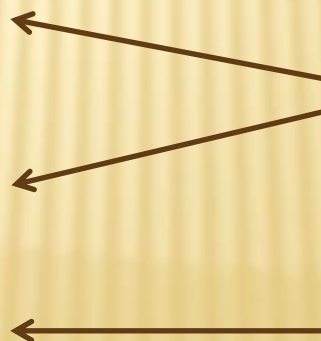
1. Gibbs Free Energy  $\Delta G$

2. Entropy Change  $\Delta S$

3. The **RATE** of the change

**Thermodynamics**

**Kinetics**





# RATE OF REACTION

Slide 4

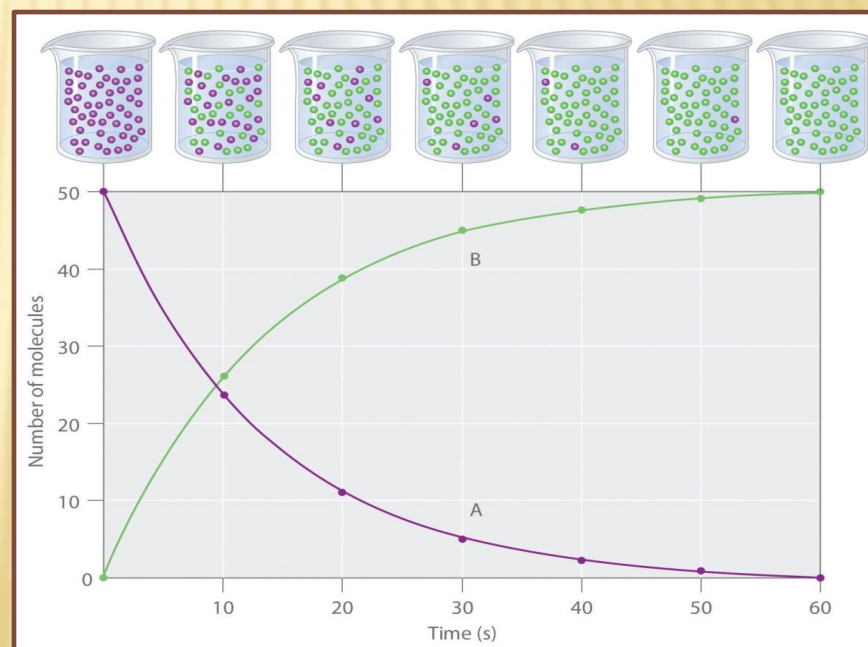
## Rate Of Reaction

*Change in the concentrations of reactants or products per unit time*

*Progress of a simple reaction,*



- Concentration of Reactant A (**purple**) decreases with time
- Concentration of Product B (**Green**) increases with time
- Concentrations of A & B are measured at time  $t_1$  &  $t_2$  respectively  $A_1$ ,  $A_2$  &  $B_1$ ,  $B_2$



*The graph shows the change in the number of A and B molecules in the reaction as a function of time over a 1 min period (bottom)*



# CONTINUED .....

Slide 5

Rate with respect to **A**

$$\text{Rate} = \frac{\text{Change in concentration of A}}{\text{change in time}} = - \frac{\text{Conc. } A_2 - \text{Conc. } A_1}{t_2 - t_1} = - \frac{\Delta[A]}{\Delta t}$$

Rate with respect to **B**

$$\text{Rate} = \frac{\text{Change in concentration of B}}{\text{change in time}} = \frac{\text{Conc. } B_2 - \text{Conc. } B_1}{t_2 - t_1} = \frac{\Delta[B]}{\Delta t}$$

$$\text{Rate} = \frac{\Delta[A]}{\Delta t} = \frac{\Delta[B]}{\Delta t} \dots\dots\dots \text{for simpler reactions}$$

The ( - ve ) sign is used because the concentration of A is decreasing.

# CONTINUED .....

Slide 6

## For complex Reactions



where  $a, b, c, \dots, e, f, g, \dots$  are **stoichiometric coefficients** in the balanced Chemical equation &  $A, B, C, \dots, E, F, G, \dots$  are **Chemical Species**

At const.  $V \dots$

$$\text{Rate} = - \frac{1}{a} \frac{\Delta[A]}{\Delta t} = - \frac{1}{b} \frac{\Delta[B]}{\Delta t} = \frac{1}{e} \frac{\Delta[E]}{\Delta t} = \frac{1}{f} \frac{\Delta[F]}{\Delta t}$$

Unit Of Rate

**$\text{mol L}^{-1} \text{s}^{-1}$**  for gaseous reactants & products ,  
conc. is usually expressed as partial pressures ,  
so  **$R$**  is  **$\text{atm s}^{-1}$**



# CONTINUED .....

Slide 7

*Average Rate Of Reaction decreases with time as concentration of reactants decreases*

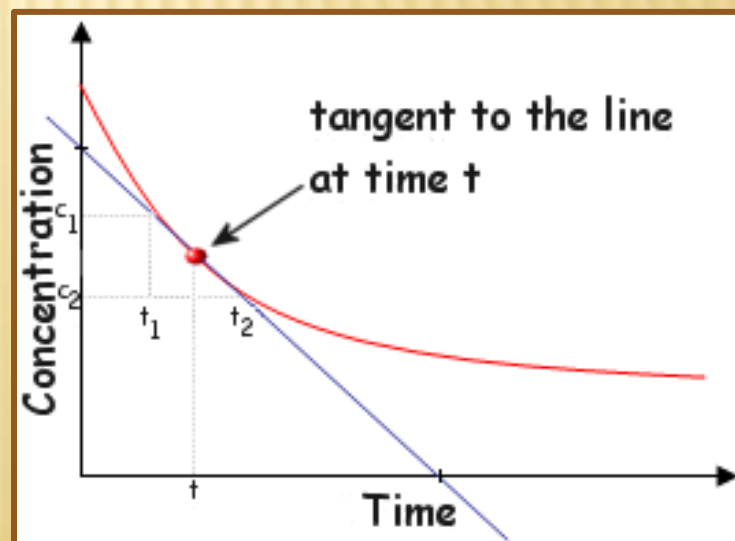
**Instantaneous Rate**

*Change in the concentration of reactants or products at a given instant of time*

*slope of a tangent line to the curve of a conc. versus time plot*

$$\text{Slope} = \frac{C_2 - C_1}{t_2 - t_1}$$

$$\text{Instantaneous Rate} = \lim_{t \rightarrow 0} \frac{\Delta x}{\Delta t} = dx/dt$$



**Concentration Versus Time Plot**

# FACTORS AFFECTING THE RATE

Slide 8

FACTORS

Nature Of Reactants

Surface Area Of Reactants

Concentration Of Reactants

Temperature

Catalyst

Nature Of Reactants

- Rate of “**Homogeneous Reactions**” is higher than the “**Heterogeneous Reactions**”
- Rate depends on the physical state of reactants , e.g. liquid /gaseous/solid
- Rate depends on the number of collisions or encounters between the reacting species

Surface Area Of Reactants

- **Heterogeneous** reaction occurs at interface of two phases of reactants
- If one reactant is **Solid** , rate increases with increase in surface area of solid phase reactant
- Surface area increases , area of contact between reactants increases - rate of encounter between reactants increases - **Rate** increases
- Surface area of a solid can be increased by **Sub-division** i.e. dividing the bigger particles in smaller



The same mass of Steel wool bursts into flame



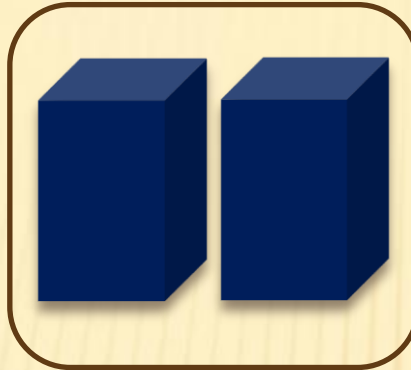
A Hot Steel nail glows feebly when placed in oxygen



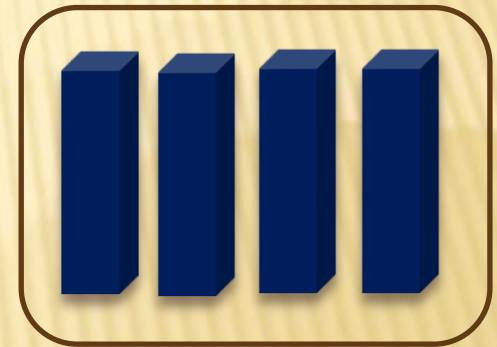
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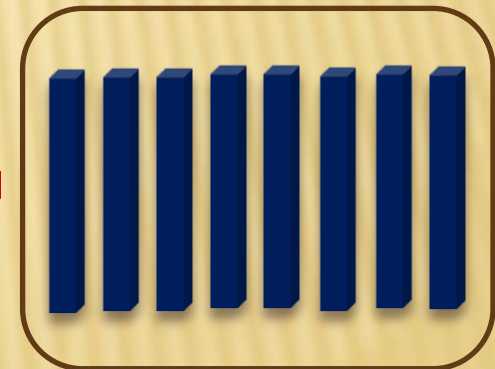
$$V = 1 \text{ m}^3$$
$$A = 6 \text{ m}^2$$



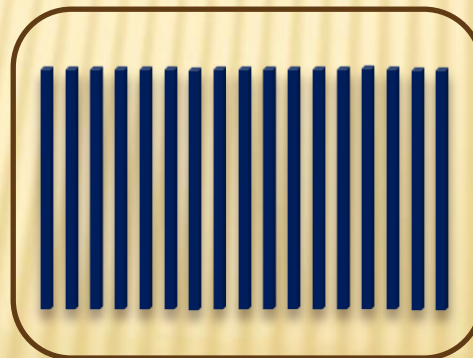
$$V = 1 \text{ m}^3$$
$$A = 8 \text{ m}^2$$



$$V = 1 \text{ m}^3$$
$$A = 12 \text{ m}^2$$



$$V = 1 \text{ m}^3$$
$$A = 20 \text{ m}^2$$



$$V = 1 \text{ m}^3$$
$$A = 36 \text{ m}^2$$



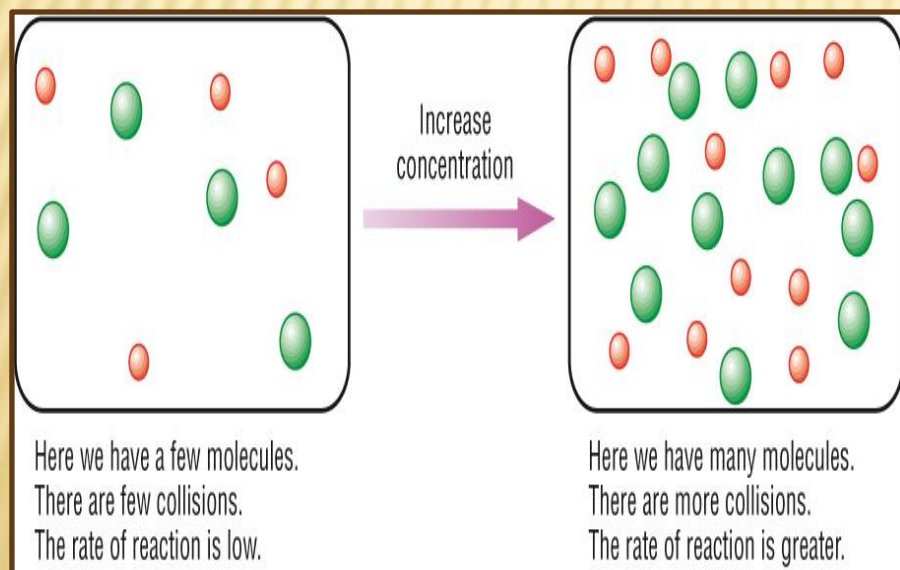
$$V = 1 \text{ m}^3$$
$$A = \text{?????}$$

# CONCENTRATION & TEMPERATURE

Slide 10

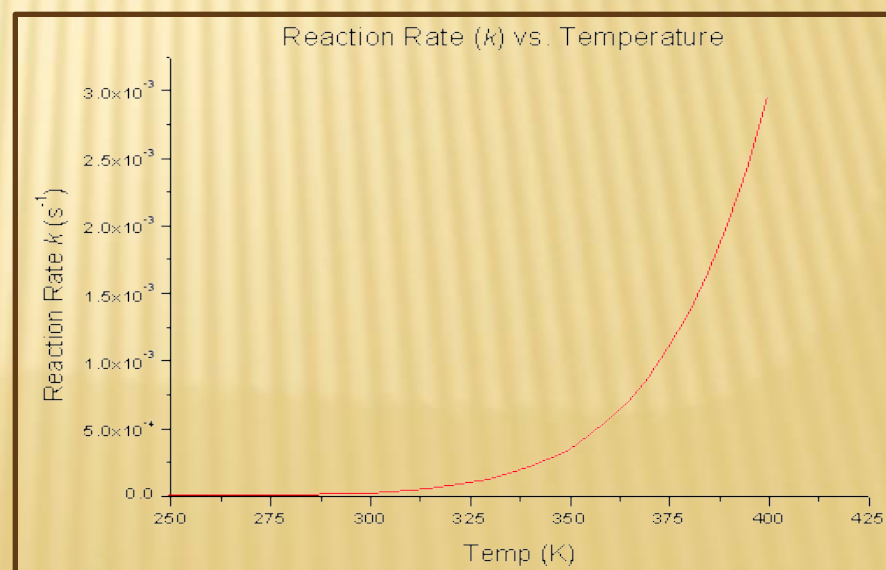
## Concentration

- Reacting molecules must **Collide** with proper **Orientation** & sufficient **Energy**
- Above factors increases as conc. increases & hence **Rate** increases



## Temperature

- As **T** increases avg **K.E** increases
- As avg. K.E increases, the particles move faster & **Collision energy** & **Collision frequency** increases & hence **Rate** increases







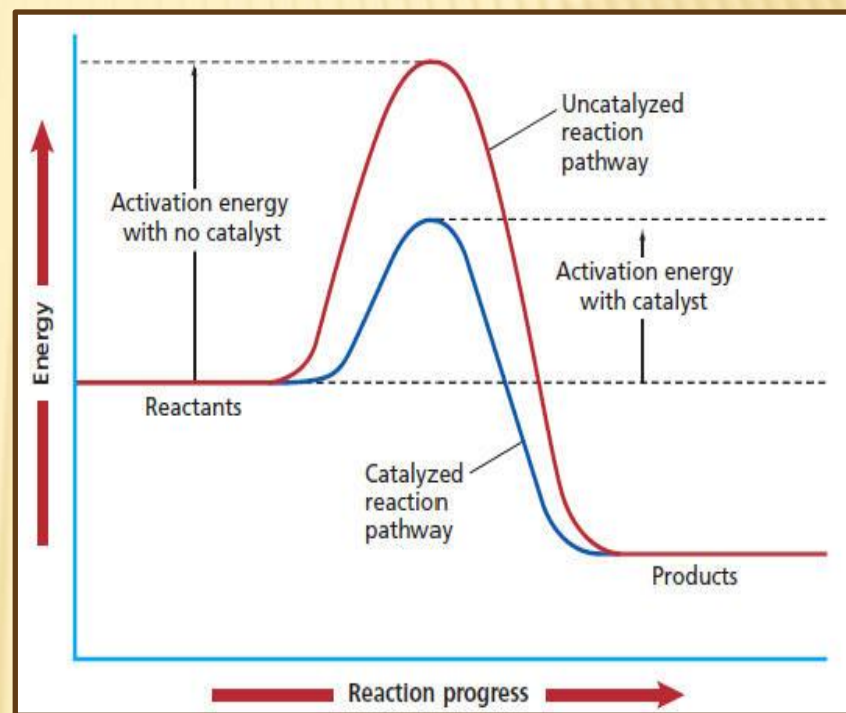
# PRESENCE OR ABSENCE OF CATALYST

Slide 11

## Catalyst

- *A substance that increases the reaction rate without undergoing a chemical change itself*
- *Provides an alternate reaction mechanism faster than mechanism in absence of catalyst*
- *Lowers the activation energy for a chemical reaction*
- *Simple Catalyzed Reaction Scheme :*

*C* is catalyst , *R<sub>1</sub>* & *R<sub>2</sub>* reactants , *P<sub>1</sub>* & *P<sub>2</sub>* products , *I* is intermediate



# CONCENTRATION & RATE

Slide 12

- A General reaction occurring at a const  $T$



- Acc. to the Law Of Mass Action  $\longrightarrow$  Rate Of Reaction  $\propto [A]^a [B]^b$

**Rate Law** : expresses the relation between rate of reaction & concentration of reactants

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

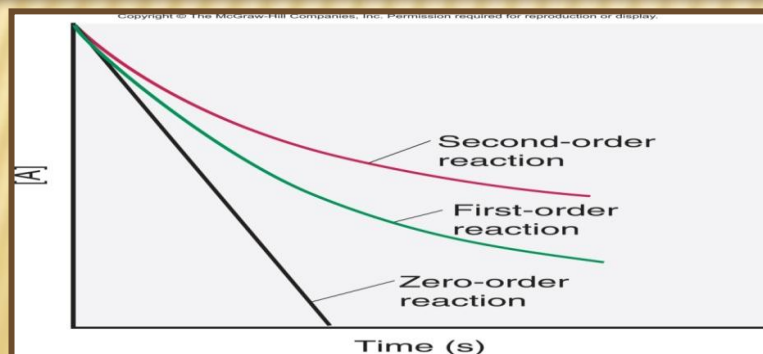
- $k$  is Rate Constant & is a function of  $T$  &  $P$  (  $P$  dependence is small & usually ignored )
- Reaction has an individual **Order** with respect to each reactant
- Reaction **order wrt A = m** & **wrt B = n** ; **Overall Order** of the reaction = **m + n**



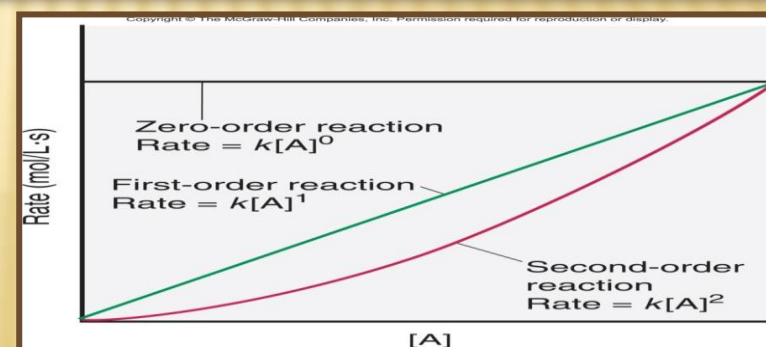
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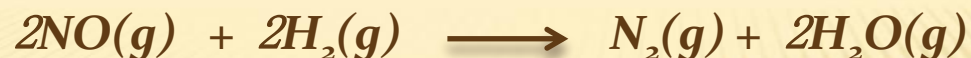
Reaction Order "n"	Rate variation with Conc.	Differential Rate Law	Integrated Rate Law
1	Rate doubles when [A] doubles	$\text{Rate} = k [A]^1$	$\ln [A]_t / [A]_o = -kt$
2	Rate quadruples as [A] doubles	$\text{Rate} = k [A]^2$	$1/[A]_t = kt + 1/[A]_o$
0	Rate does not change with [A]	$\text{Rate} = k [A]^0$	$[A]_t - [A]_o = -kt$



[A] versus Time plot for 0, 1<sup>st</sup> & 2<sup>nd</sup> order rxns



Rate versus [A] plot for 0, 1<sup>st</sup>, 2<sup>nd</sup> order rxns



**Rate Law** :  $k[\text{NO}]^2[\text{H}_2]$

**Order of reaction** = 3

**1<sup>st</sup> Order** wrt  $[\text{H}_2]$   
**2<sup>nd</sup> Order** wrt  $[\text{NO}]$

**Stoichiometric coefficient** of  $[\text{H}_2] = 2$   
**Order** with respect to  $[\text{H}_2] = 1$



*Reaction orders must be determined from experimental data and cannot be deduced from the balanced equation*

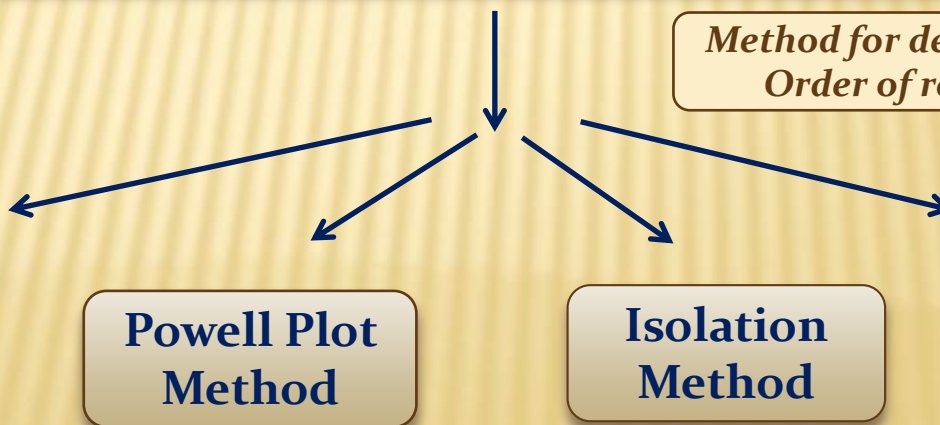
*Method for determining  
Order of reaction*

**Half Life  
Method**

**Powell Plot  
Method**

**Isolation  
Method**

**Initial Rate  
Method**



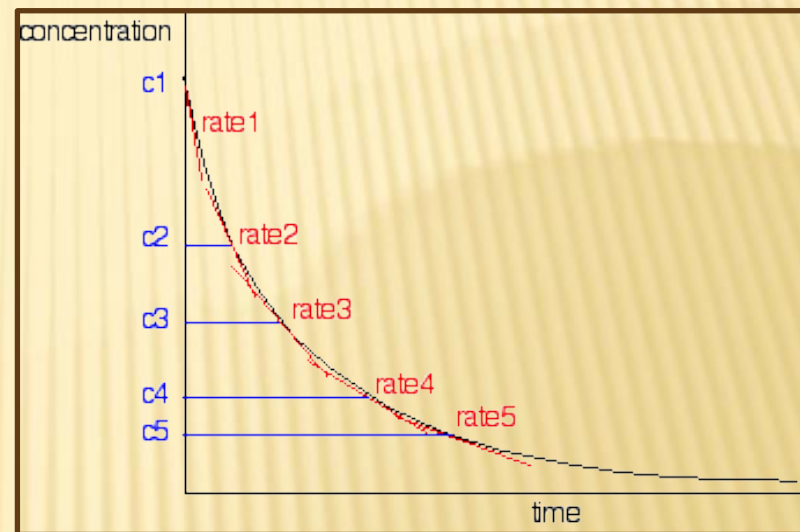


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Slide 15

## Initial Rate Method

- A series of experiments wherein the concn of one reactant at a time is varied, initial rate  $R_0$  at time  $t_0$  of the rxn is measured.
- By comparing the concn. change to the Rate change, Order wrt each reactant can be determined



## Information sequence to determine the Kinetic parameters of a Reaction

Series of Plot of  
Concentration  
versus time



Initial rates  
determination by  
drawing tangent to  
the plot of Conc vs T



Calculation of  
Reaction order



Rate Constant  
 $k$  & actual rate  
law



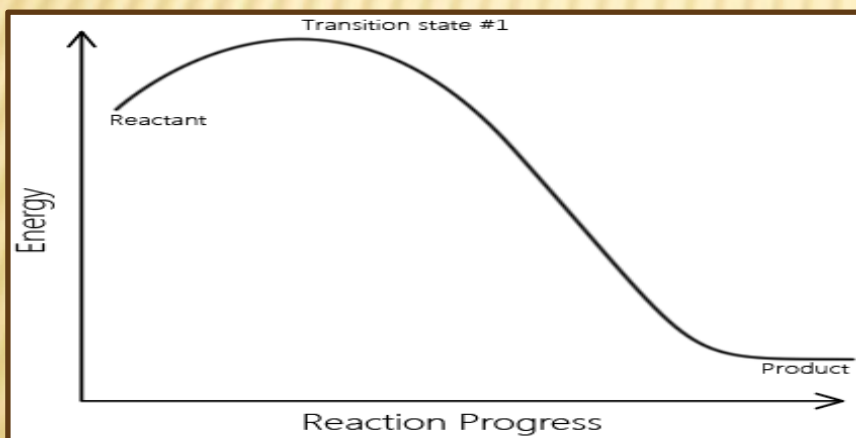
# REACTION MECHANISM

Slide 16

Reactions can be divided on the basis of Reaction mechanism

## Elementary Reactions

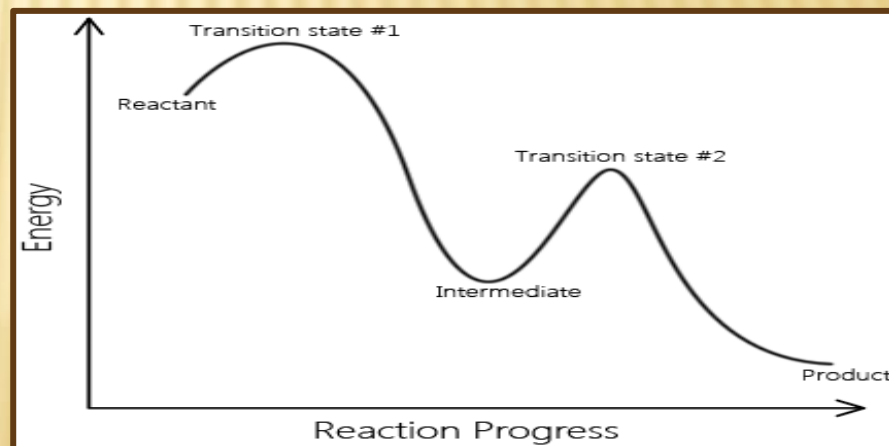
- Only one step reactions
- No **Intermediate**
- Only One **Transition state**
- Further divided in **Unimolecular**, **Bimolecular** & **Termolecular rxn** based on Molecularity



**Elementary Reaction**

## Complex Reactions

- Two or more steps
- With **Intermediate** formation
- Multiple **Transition states**
- Rate of over all complex rxn is the rate of slowest rxn step (**Rate determining Step**)



**Complex Reaction**

# MOLECULARITY

Slide 17

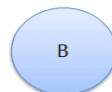
## Molecularity

Number of colliding molecular entities that are involved in a single reaction step

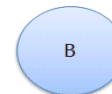
### Unimolecular



### Bimolecular



### Termolecular



Molecularity	Elementary Step	Rate law	Examples
Unimolecular	$A \longrightarrow \text{Products}$	$\text{rate} = k[A]$	$N_2O_4(g) \longrightarrow 2NO_2(g)$
Bimolecular	$A + A \longrightarrow \text{Products}$ $A + B \longrightarrow \text{Products}$	$\text{rate} = k[A]^2$ $\text{rate} = k[A][B]$	$2NOCl \longrightarrow 2NO(g) + CO_2(g)$ $CO(g) + NO_3(g) \longrightarrow NO_2(g) + CO_2(g)$
Termolecular	$A + A + A \longrightarrow \text{Products}$ $A + A + B \longrightarrow \text{Products}$ $A + B + C \longrightarrow \text{Products}$	$\text{rate} = k[A]^3$ $\text{rate} = k[A]^2[B]$ $\text{rate} = k[A][B][C]$	$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$ $H + O_2(g) + M \longrightarrow HO_2(g) + M$



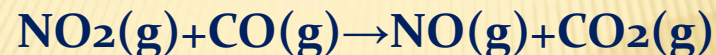
Molecularity	Order
<ul style="list-style-type: none"><li>• Number of reacting species which collide to result in reaction</li><li>• Only positive integral values e.g 1,2,3 &amp; never -ve</li><li>• Theoretical concept &amp; value is derived from mechanism of reaction</li></ul>	<ul style="list-style-type: none"><li>• Sum of powers to which concentrations are raised in the rate law expression</li><li>• Zero, fractional or even be -ve</li><li>• Experimental fact &amp; derived from rate law</li></ul>

Rate  
Determining  
Step



Slowest step of a  
chemical reaction  
that determines the  
speed (rate) at  
which the overall  
reaction proceeds

Eg : A complex reaction



occur in two elementary steps :



$$\text{Rate} = k_1 [\text{NO}_2][\text{NO}_2] = k_1 [\text{NO}_2]^2$$



# TEMPERATURE & RATE

Slide 19

## Collision Model

- Rxns occur when molecules undergo **Collisions**
- All Collisions are not **Effective**
- Collisions of molecules with **Sufficient Energy** are only Effective

## Orientation Barrier

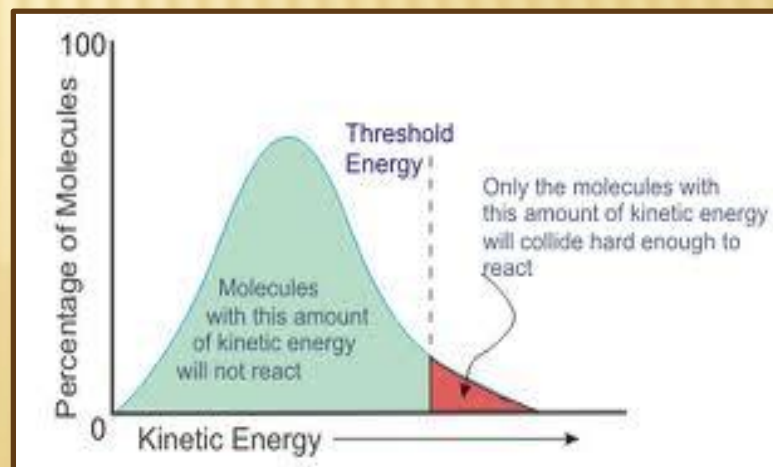
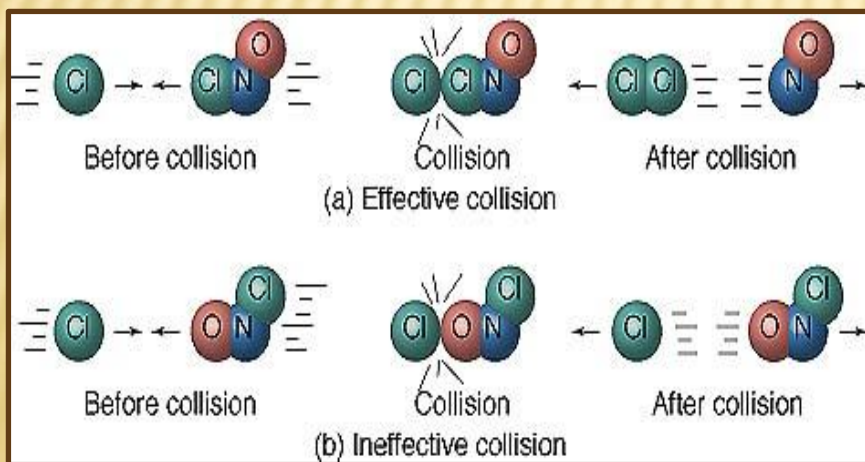
Reactants must collide in favourable orientation to make & break bonds  
E.g.  $\text{Cl} + \text{NOCl} \rightarrow \text{NO} + \text{Cl}_2$

## Effective Collisions

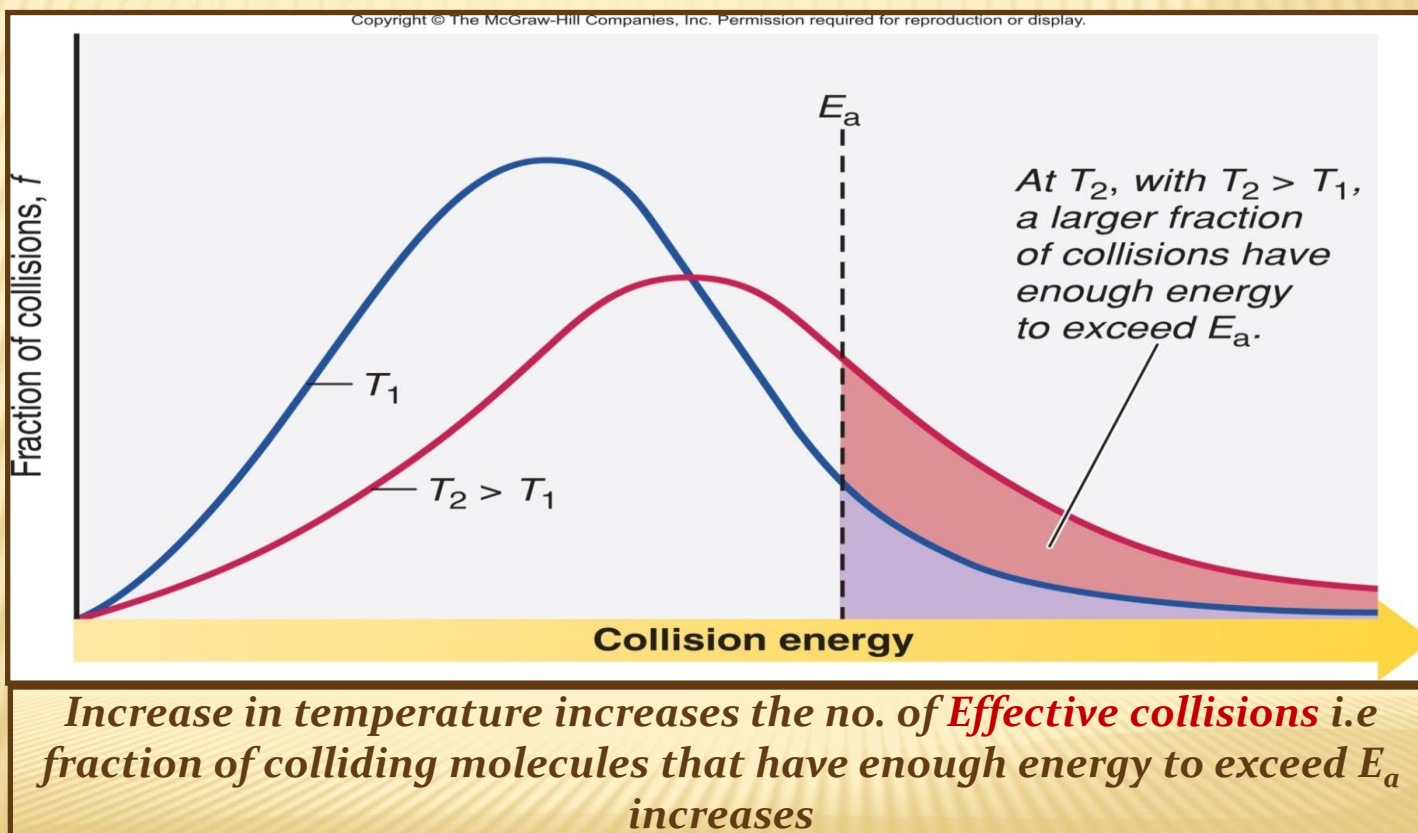
- Collisions** which lead to product formation
- Governed by 2 factors :

## Energy Barrier

Molecules having energy greater than or equal to threshold energy will only form Product



*Explanation for increase in Rate of reaction with temperature by  
: **Energy- distribution Curve** at two temperatures  $T_2$  &  $T_1$*

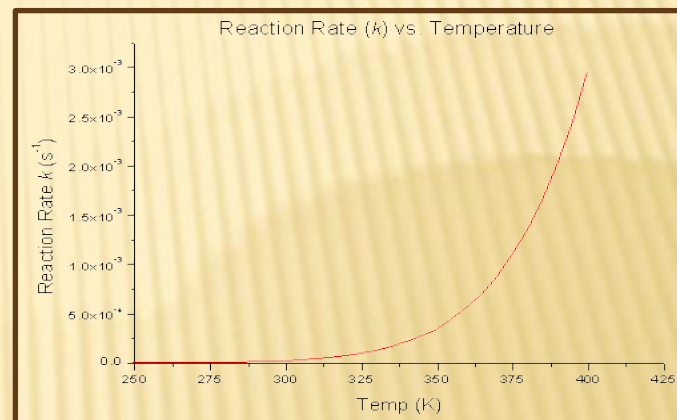




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Slide 21

- *Temperature dependence is expressed by - Arrhenius Equation*
- *Rate increases non linearly with temperature as shown in graph,  $k$  increases exponentially as  $T$  increases :*



**Arrhenius Equation**

$$k = Ae^{-E_a/RT}$$

$k$  = rate constant  
 $A$  = frequency factor  
 $E_a$  = activation energy

Taking log

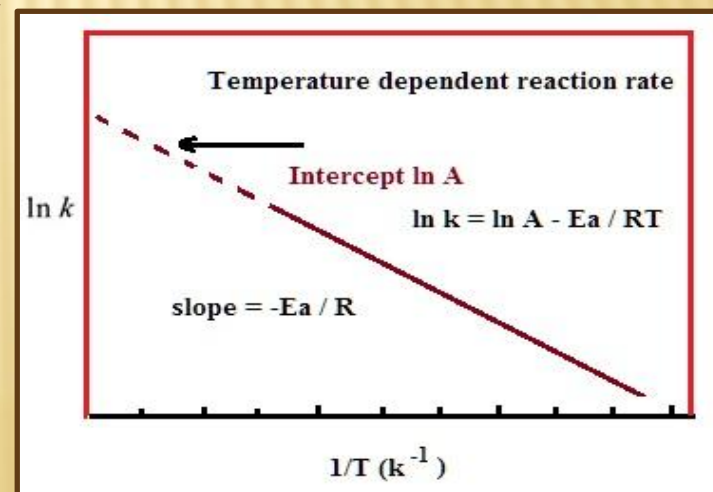
$$\ln k = \ln A - E_a / RT$$

**Activation Energy**

Minimum energy required to initiate a chemical reaction

Higher  $T \longrightarrow$  Larger  $k \longrightarrow$  Increases Rate

Smaller  $E_a \longrightarrow$  Larger  $k \longrightarrow$  Increases Rate



**Arrhenius Plot**



# PSEUDO ORDER REACTIONS

Slide 22

## Pseudo Order Reactions

An order of a chemical reaction that appears to be less than the true order due to experimental conditions ; when one reactant is in large excess

### Pseudo First Order Reactions

**2<sup>nd</sup> Order kinetics** can be approximated as **1<sup>st</sup> Order** under certain experimental condition

**Pseudo first order kinetics**

**2<sup>nd</sup> order rate law** =  $k [A] [B]$

- Reduces to Pseudo first order if either  $[A]$  or  $[B]$  is in large excess
- Pseudo first order rate law =  $k' [B]$  where  $k' = k [A]$  ..... Pseudo first order rate constant

### Pseudo Second Order Reactions

**3<sup>rd</sup> Order kinetics** can be approximated as **2<sup>nd</sup> Order** under certain experimental condition

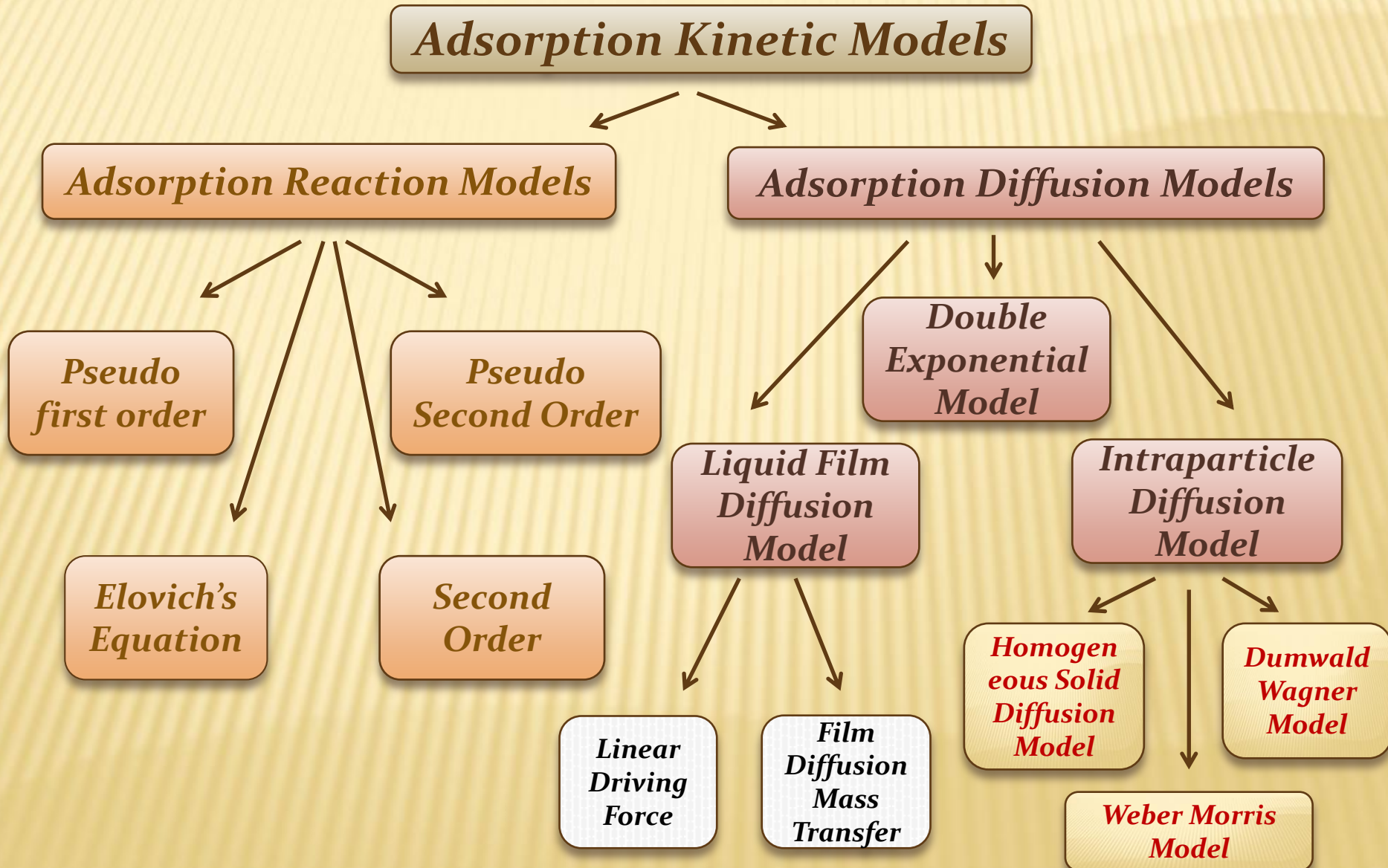
**Pseudo Second order kinetics**

**3<sup>rd</sup> order rate law** =  $k [A]^2 [B]$

- Reduces to Pseudo first order , if  $[A]$  is in excess Pseudo second order if  $[B]$  is in excess
- Pseudo Second order rate law =  $k' [A]^2$  where  $k' = k [B]$  ..... Pseudo second order rate constant

# ADSORPTION KINETICS MODELS

Slide 23



# ADSORPTION REACTION MODELS

Slide 24

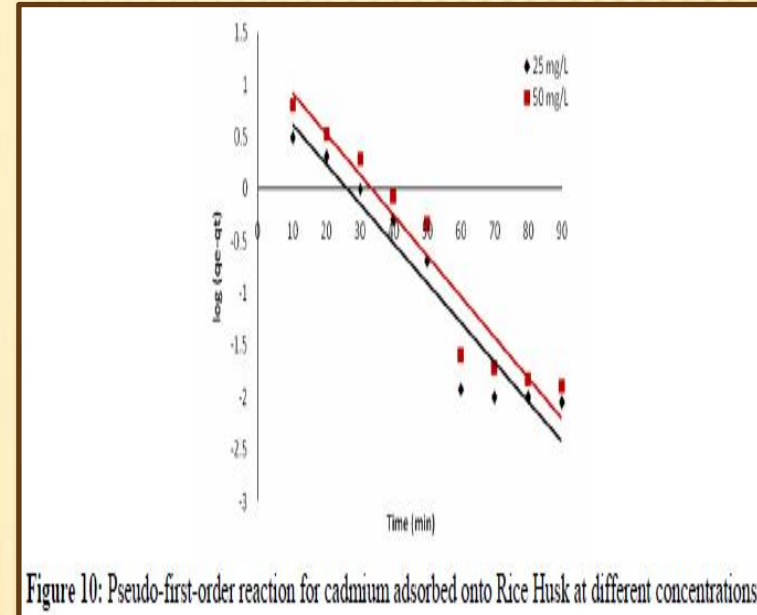
## Pseudo First Order

- **Earliest Model** ; Proposed by **Lagergren** (1898) to describe kinetic process of Liq-sol phase adsorption
- **Recent uses** : kinetic study of adsorption of pollutants from waste water

## Rate Equation

$$dq_t / dt = k_{p1} (q_e - q_t)$$

- Integrated form of rate eq.  $\log (q_e - q_t) = \log q_e - k_{p1} t / 2.303$
- Plot of  $\log (q_e - q_t) \sim t$  should give a linear relationship **Lagergren Plot** ;  $k_{p1}$  &  $q_e$  can be determined from slope & intercept of Lagergren Plot
- **Fig 1** : **Lagergren Plot** for Cadmium adsorption on Rice husk



**Fig 1**



# ADSORPTION REACTION MODELS

Slide 25

## Pseudo Second Order

- Proposed by **Ho** (1995)
- To describe kinetic process of adsorption of divalent metal ions on Peat
- Recent Uses** : Kinetic study of adsorption process of divalent metal ions, dyes , organic substances from aq. solns

### Rate Equation

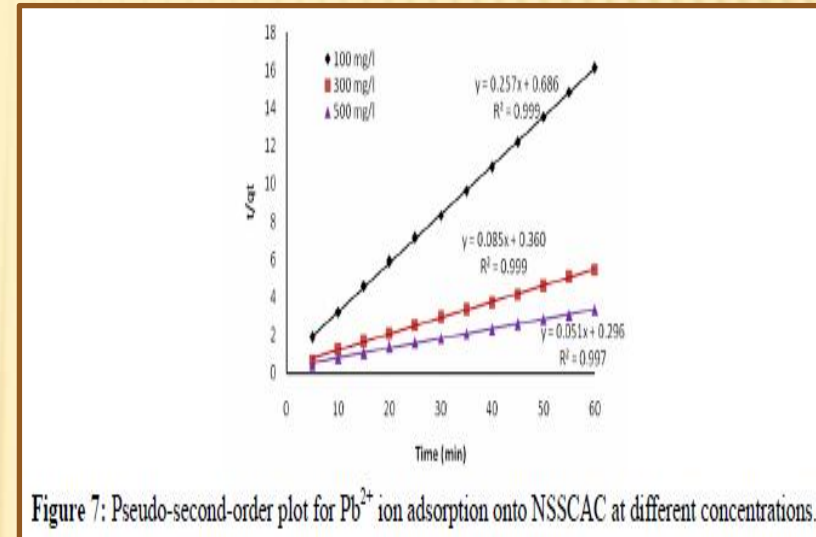
$$\frac{d(P)_t}{dt} = k_{p2} [(P)_o - (P)_t]^2$$

- Integrated form of rate eq.

$$t/q_t = 1/k_{p2} q_e^2 + 1/q_e t$$

- Plot of  $t/q_t \sim t$  should give a linear relationship with a slope of  $1/q_e$  & intercept of  $1/k_{p2} q_e^2$

- Fig 2** : Pseudo second order plot for  $Pb^{2+}$  ions onto NSSCAC at diff concs.



**Fig 2**

# ADSORPTION REACTION MODELS

Slide 26

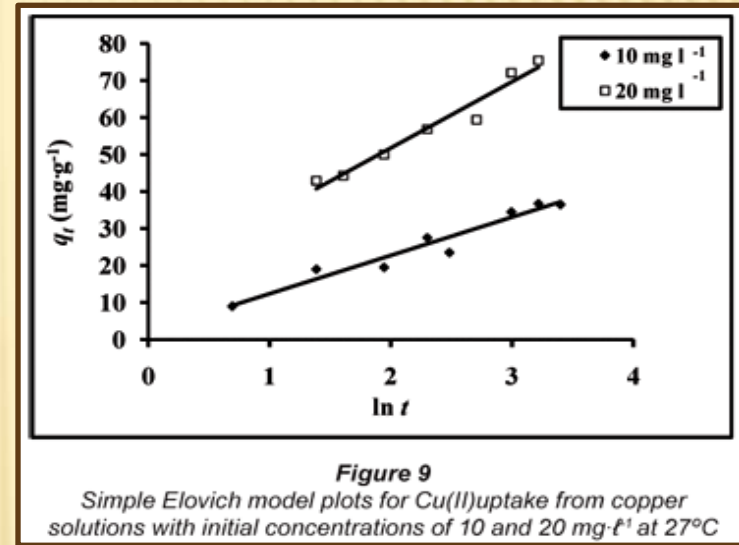
## Elovich's Model

- Proposed by **Zeldowitsch** (1934) to study kinetics of Chemisorption of gases onto heterogeneous solids
- Recent Uses** : kinetics study of removal of pollutants from aq. solns

## Elovich Equation

$$dq / dt = ae^{-\alpha q}$$

- Integrated form of rate eq. 
$$q = \alpha \ln(a\alpha) + \alpha \ln t$$
- Plot of  $q \sim \ln t$  should be linear **Elovich Plot** ; slope gives  $\alpha$  & intercept gives  $a$
- Fig 3 : Elovich Plot** for uptake of Cu(II) from copper solns at two concs 10mg/L & 100mg/L



**Fig 3**

# LIQUID FILM DIFFUSION MODEL

Slide 27

## Liquid Film Diffusion Model

2 Rate laws of  
this model

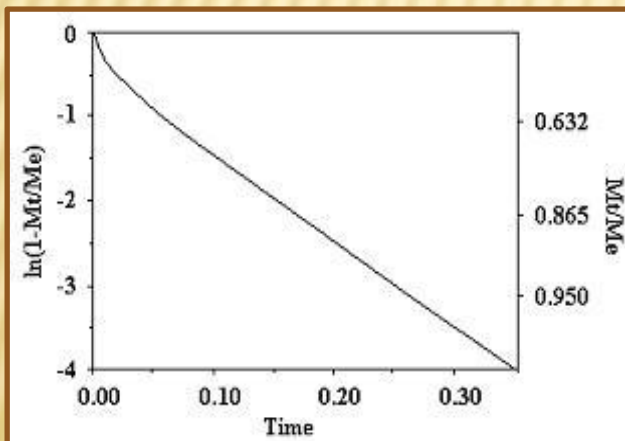
Linear driving force rate law

$$\delta q / \delta t = k_f S_o (C - C_i)$$

Film Diffusion Mass  
transfer rate law

$$\ln (1 - q_t/q_e) = - 3D_e^1 t / r_o \Delta r_o k'$$

• Applied to describe mass transfer  
through liquid film

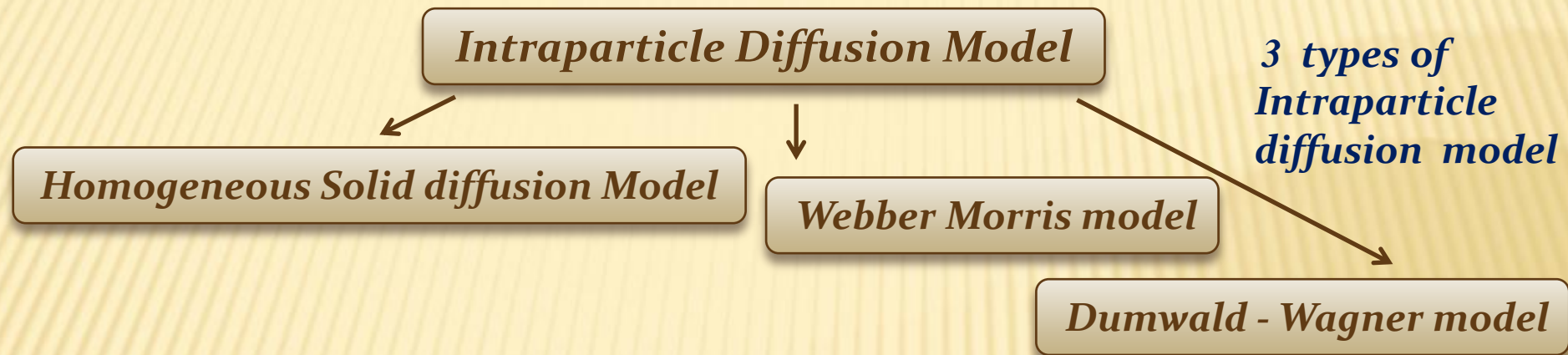


- Plot of  $\ln (1 - q_t/q_e) \sim t$  straight line with a slope of  $3D_e^1 / r_o \Delta r_o k'$  if the film diffusion is the rate limiting step
- **Recent Uses :** Applied to model several liquid / solid adsorption cases e.g. Phenol adsorption by a polymeric adsorbent NDA – 100
- **Fig 4 :** Liquid film diffusion model plot

**Fig 4**



# INTRAPARTICLE DIFFUSION MODEL



## Homogeneous Solid diffusion Model

- Describes mass transfer in an amorphous & homogeneous sphere
- **Recent Uses** : Kinetic study of adsorption of salicylic acid & 5-sulfosalicylic acid from aq. solns by hypercrosslinked polymeric adsorbent NDA-99 & NDA - 101

## HSDM Equation

$$\delta q / \delta t = D_s / r^2 \delta / \delta r (r^2 \delta q / \delta r)$$

$D_s$  = intraparticle diffusion coefficient

$r$  = radial position

$q$  = adsorption quantity of solute in the solid varying with radial position at time  $t$

# CONTINUED.....

Slide 29

## Webber Morris model

- Acc to this model : solute uptake varies proportionally with  $t^{1/2}$  rather than with contact time  $t$

## Webber Morris Equation

$$q_t = k_{int} t^{1/2} + C_i$$

$k_{int}$  = intraparticle diffusion  
rate constant

$t^{1/2}$  = half life time

$C_i$  = the intercept of the stage i  
associated with the thickness  
of the boundary layer.

- Plot of  $q_t \sim t^{1/2}$  should be straight line with a slope of  $k_{int}$  & intercept  $C_i = 0$  when *Intraparticle diffusion* is the rate limiting step
- Rate Equation modifies to .....

$$q_t = k_{int} t^{1/2}$$

- Intercept of above plot gives an idea of thickness of boundary layer i.e. larger the intercept , the greater **Boundary effect**

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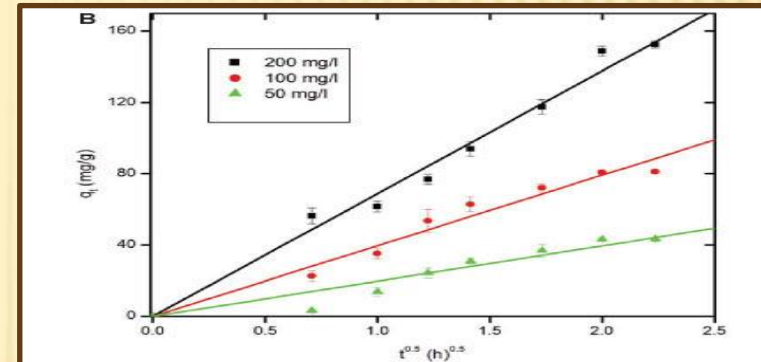
- **Fig 1a** : Rate controlling step in  $Pb^{2+}$  adsorption by heat treated ( in air ) composites : **Intraparticle diffusion**
- **Fig 1b** : Plot shows **Multilinearity**, there are three different linear regions.

**Multilinearity : Kinetic mechanisms involved**

Initial linear region is attributed to the **film diffusion** ; governed by **boundary layer effect**

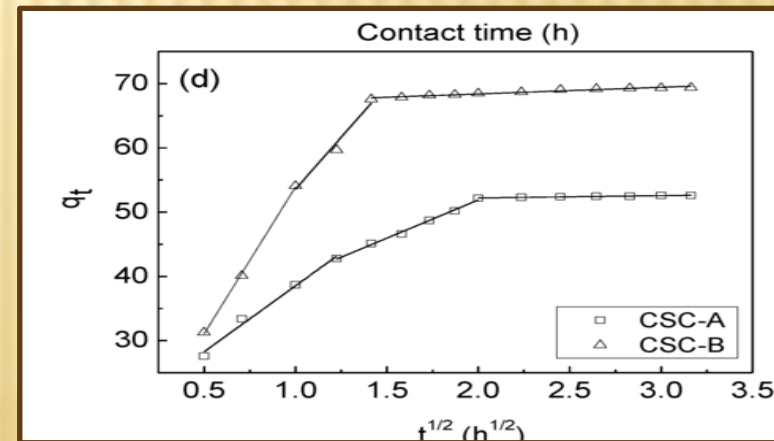
Second describes the **intraparticle diffusion stage**

Final gradual uptake is governed by the **pore-diffusion** mechanism.



**Figure 12**  
Transport models for the removal of  $Pb^{2+}$  with the heat-treated (in air) composite. A: liquid film diffusion; B: intraparticle diffusion

**Fig : 1a** : Webber Morris Intraparticle diffusion model plot of  $Pb^{2+}$  adsorption by heat treated ( in air ) composites



**Fig : 1b** : Webber Morris Intraparticle diffusion model plot of  $Pb^{2+}$  adsorption by coconut shell carbons



## *Dumwald - Wagner model*

### *Dumwald- Wagner Equation*

$$\log (1 - F^2) = - Kt/2.303$$

*Plot of  $\log (1 - F^2) \sim t$  should be linear*

### *Recent Uses*

*Kinetic study of adsorption systems e.g.  
p -toludine adsorption from aq. solns onto  
hypercrosslinked polymeric adsorbents*

# DOUBLE EXPONENTIAL MODEL

Slide 32

## Double Exponential Model

- Proposed by **Wilezak & Keinath** (1993)
- Kinetics of **Heavy metals adsorption** e.g Pb(II) & Cu(II) from aq. solns
- Two step mechanism :
  - A rapid phase involving external & internal diffusions followed by
  - A slow phase controlled by Intraparticle diffusion

## Double Exponential Equation

$$q_t = q_e - D_1/m_a \exp(-K_1 t) - D_2/m_a \exp(-K_2 t)$$

- If  $K_1 \gg K_2$  ; Rapid process can be assumed negligible on over all kinetics ; then simplified eq. :

$$q_t = q_e - D_2/m_a \exp(-K_2 t)$$

- DEM can also describe a process where adsorbent offers 2 different types of adsorption sites :
  - First type site – rapid adsorption**
  - Second site type – slow adsorption**

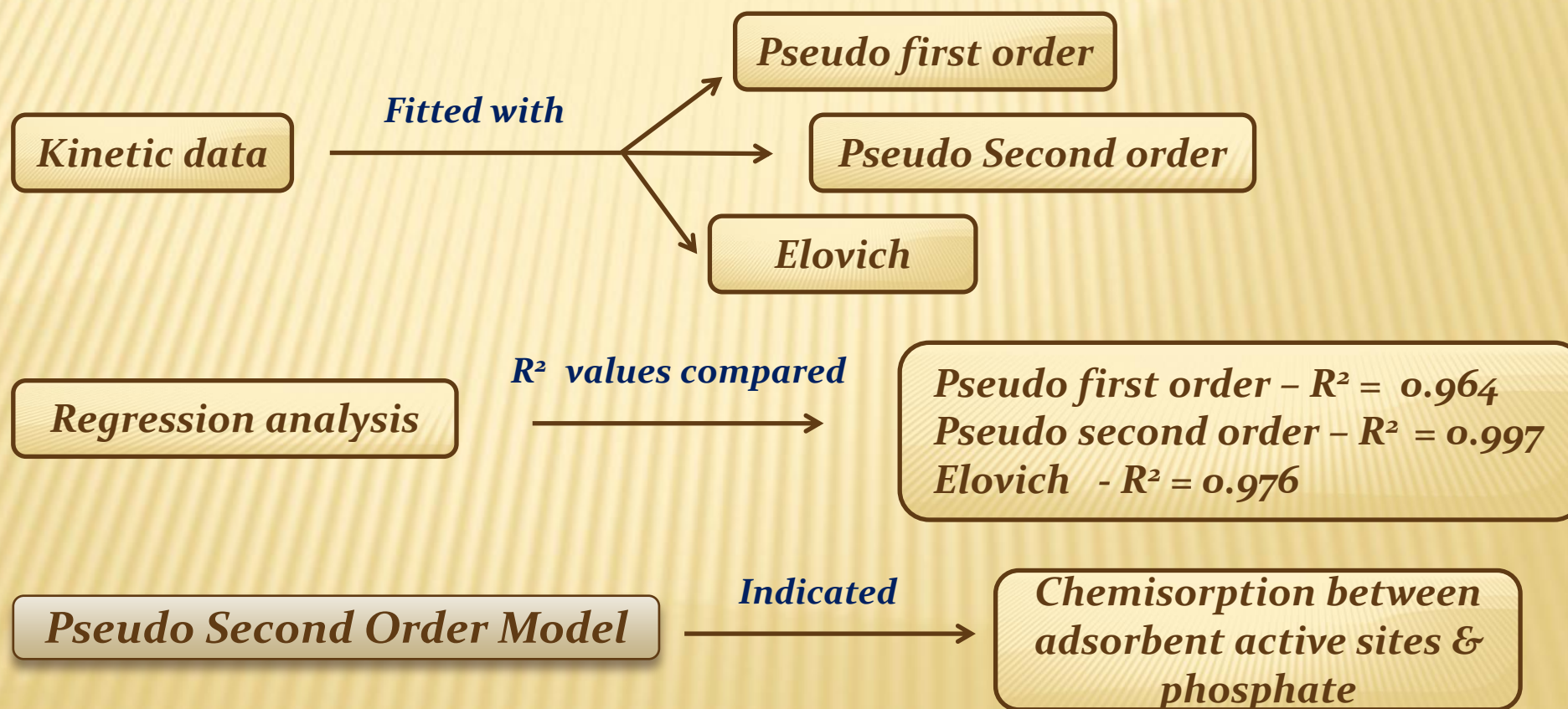


# KINETIC BEST FIT MODEL: INTERPRETATION

Slide 33

## Phosphate Sorption Kinetics

Phosphate Removal from aqueous solutions by a nanostructured Fe-Ti bimetal oxide sorbent ; Journal of Chemical Engineering Research & Design ; *Jianbo Lu<sup>a,b,\*</sup> et al*





# CONTINUED .....

Slide 34

## Elovich's Model

*Good correlation with experimental data*

*Indicated FTBMO -  
heterogeneous*

*Composite Fe-Ti bimetal oxide - Heterogeneous surface*

## Intraparticle diffusion model plot

*Non zero intercept*

*Indicated*

*Boundary layer diffusion- Rate limiting step*

## Correlation coefficient $R^2$

*measure of the linear correlation between two variables X and Y*

*Varies between -1 & +1*

*1 = positive correlation*

*0 = No correlation*

*-1 = Total negative correlation*

# *THANKS*

