



Government Engineering College Valsad



PHYSICAL AND INORGANIC CHEMISTRY (2140501) **CHEMICAL KINETICS**

Guidance By
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Submitted By: Group 4

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Introduction

- **Kinetics** (Ancient Greek: "kinesis", movement or to move)
- **Chemical Kinetics** : The branch of physical chemistry, which deals with the rate of reactions and there is called chemical Kinetics.
- The feasibility of a chemical reaction is predicted on the basis of three factors like :composition of reactants & environmental condition of reaction temperature & pressure.
- Chemical Kinetics is the study of the rates of chemical reactions.
- A spontaneous reaction may be slow or it may be fast or very fast or very slow.
- Example NaCl & AgNO_3 is a fast reaction .

Rusting of iron is a slow reaction that occurs over the years.

Reaction rate

- Simple reaction $A \rightarrow B$
- For the give reaction the rate of reaction may be equal to rate of disappearance of a which is equal to the rate of appearance of B.
- Thus, Rate of reaction = Rate of disappearance of reactant (A) = $- d[A]/dt$
- Also, Rate of reaction = Rate of appearance of product (B) = $+d[B]/dt$

Rate of a Reaction

Rate is defined as $R = \frac{\text{change in concentration } (\Delta C)}{\text{time } (\Delta t)}$

$$\text{Rate} = \frac{\pm d[\text{concentration}]}{dt}$$

- Where [] represent the concentration in moles per liter whereas 'd' represents infinity small change in concentration
- Negative sign shows the concentration of reactant A whereas the positive sign indicates the increase in concentration of the product B with time.

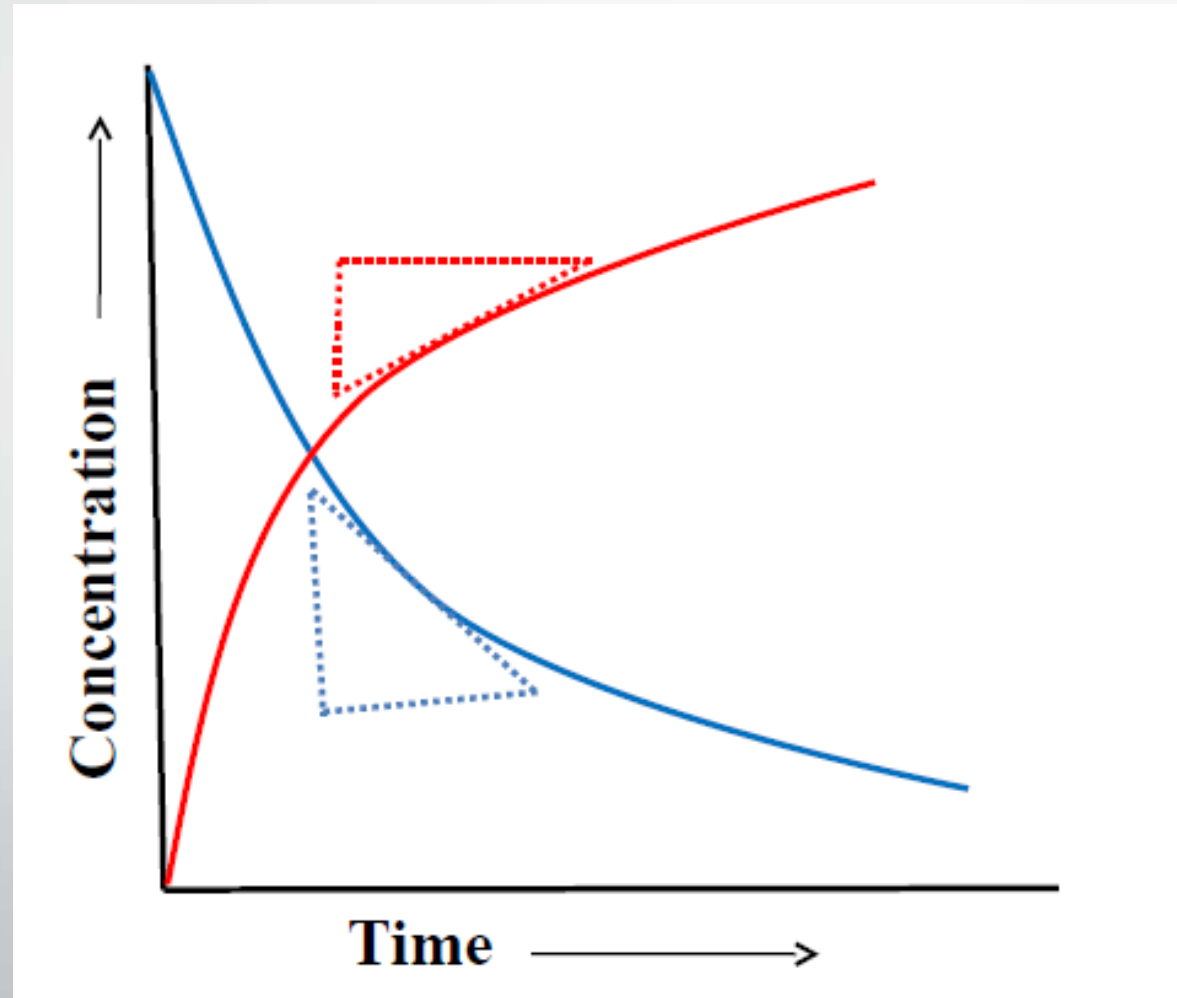
Units of Rate

- The rate of reaction is concentration of reactant or product divided by time. The unit of concentration is mol liter^{-1} and time is generally expressed by second. so, reaction rate has units of $\text{moles litre}^{-1} \text{ second}^{-1}$. But time may be given in any convenient unit second (s), minutes(min),hours(h),day(d) or possible years. Therefore, the units of reaction rates may be
- mole/liter sec or $\text{mol l}^{-1} \text{ sec}^{-1}$
- mole/liter min or $\text{mol l}^{-1} \text{ min}^{-1}$
- mole/ liter hour or $\text{mol l}^{-1} \text{ h}^{-1}$

Rate Laws

- The rate law or rate equation or rate expression is a mathematical explanation of the variation of the rate of a chemical reaction at a function of time.
- The reaction rate is depends on concentration of reactants at a fixed temperature.
- The rate of a reaction is directly proportional to the reactant concentrations, each concentration bring raised to some power.
- **Rate of reaction $\propto [A]^m$**
or, Rate of reaction = $k[A]^m$
- 'k' is the proportionality constant known as rate constant
- It is independent of concentrations and time
- Has a specific value at a given temperature

The concentration is increasing with time e.g. a product
The concentration is falling with time e.g. a reactant.



Order of a reaction

- Sum of the power of concentration.

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

- The order of such a reaction is (m + n).
- Order of reaction:- positive, negative, zero and fractional.
- Example:



$$\text{reaction order} = 1 + 1 = 2$$

- Reaction order is determined by experiment.

Rate law	Reaction order
$\text{rate} = k[\text{N}_2\text{O}_5]$	1
$\text{rate} = k[\text{H}_2][\text{NO}]^2$	$1 + 2 = 3$
$\text{rate} = k[\text{CHCl}_3][\text{Cl}_2]^{1/2}$	$1 + 1/2 = 3/2$

Zero Order Reaction

- A Reactant whose concentration does not affect reactions rate is not included in there in effects, the concentration of such a reactant has the power 0.
- Zero order reactions is One rate is independent of concentration.
- The common rate of reaction

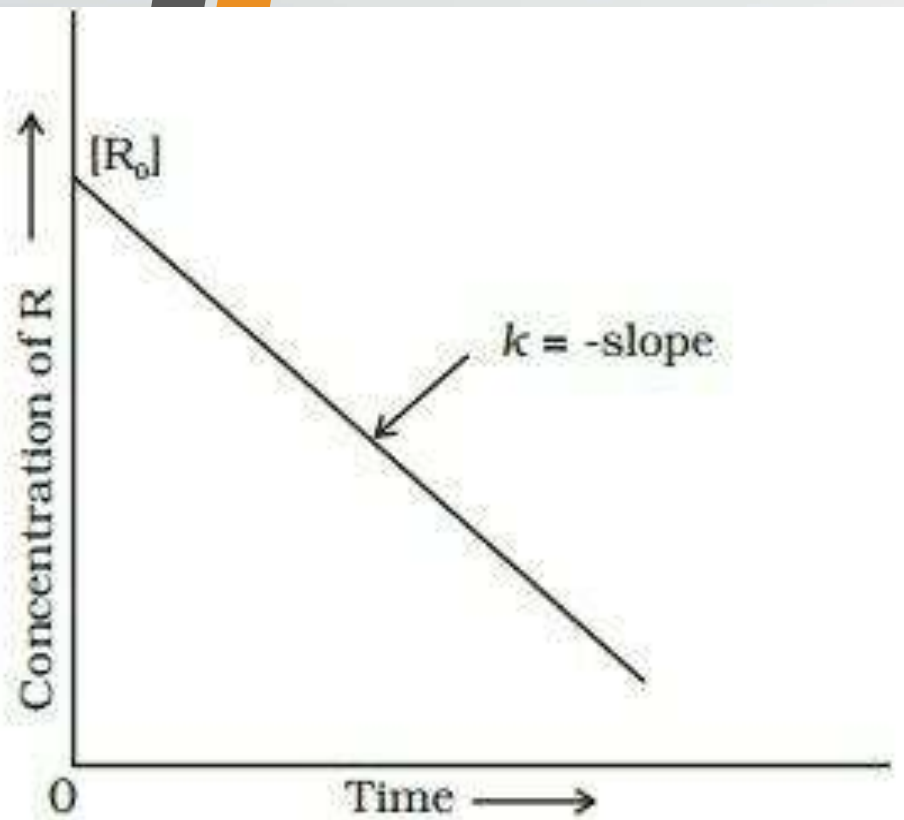
$$\frac{d[x]}{dt} = k_0$$

- For the zero-order reaction the rate of reaction is written as

$$k_0 = \frac{x}{t}$$

- The half-life period of a zero order reactions is directly proportional to the initial concentrate of the reactant and is referred as

$$t_{1/2} = \frac{a}{2k_0}$$

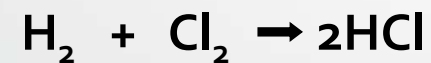


- The half-life period of a zero order reactions is directly proportional to the initial concentrate of the reactant and is referred as

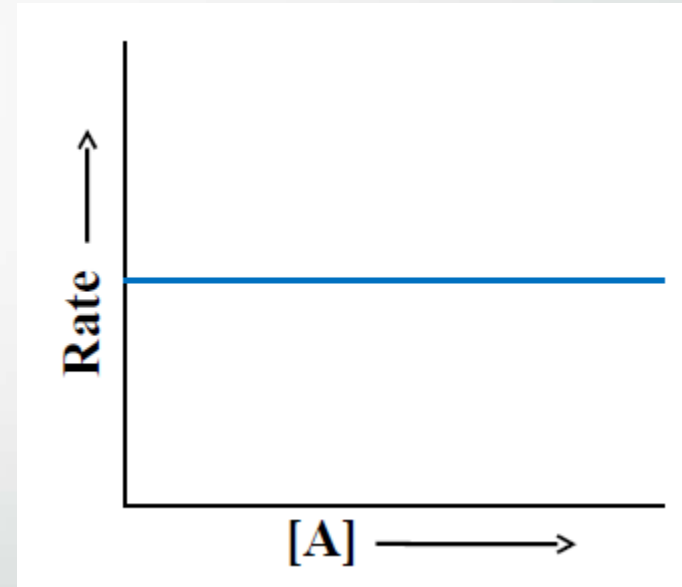
$$t_{1/2} = \frac{a}{2k_0}$$

For example,

- Photochemical reaction between Hydrogen and Chlorine,



- Another reaction of zero-order reaction is decomposition of hydrogen iodide in Gold enzyme catalysed reactions at higher substrate concentration.



Difference between order and molecularity of reaction

Order of reaction	Molecularity of reaction
<ol style="list-style-type: none">1.) It is sum of powers of concentration of reactant, with respect to rate of reaction.2.) It is determine experimentally.3.) It may be fractional value.4.) Sometime, its value is zero.5.) Order of reaction can be change with the parameters like, pressure, temperature, concentration.6.) Order of reaction gives information about the slowest step and hence explain the mechanism of reaction.7.) Order of reaction is based on the overall reaction.	<ol style="list-style-type: none">1.) It is sum of reacting atom or molecule undergoing the chemical reaction to form product.2.) It is a theoretical concept.3.) It is always whole number.4.) It cannot have zero value.5.) Molecularity is not changes with external parameters.6.) It does not give details about the mechanism of reaction.7.) The overall molecularity of a complex reaction has no significance.

Pseudo order reaction

- An order of a chemical reaction that appears to be Less than the true order due to experimental conditions ; when a one reactant is in large excess.
- There are two types of reaction
 1. Pseudo first order reaction
 2. Pseudo second order reaction

First order reaction	Second order reaction
<ul style="list-style-type: none">• Pseudo first order kinetics 2nd order rate law = $k [A][B]$• Reduce to first Pseudo first order if either [A] or [B] in large excess.• Pseudo first order rate law = $k' [B]$, Where $k' = k [A]$ Pseudo first order reaction.	<ul style="list-style-type: none">• Pseudo second order kinetic 3rd order rate law = $k[A]^2 [B]$• Reduce 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.

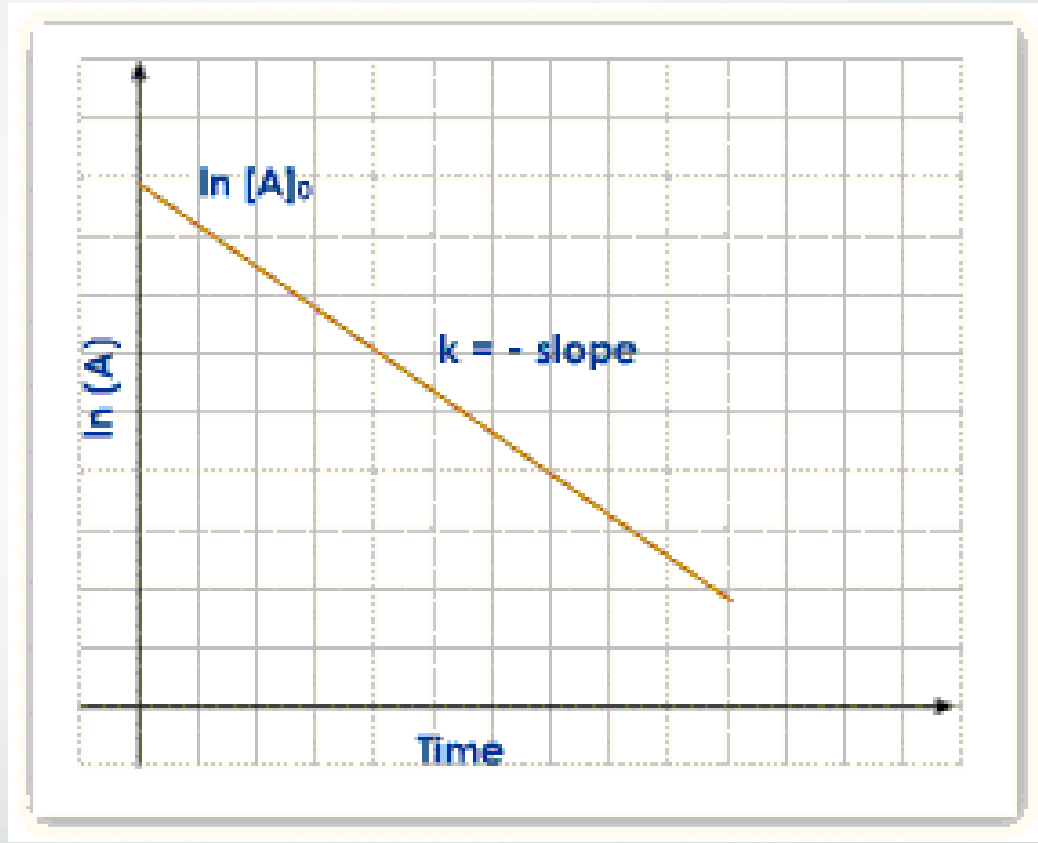
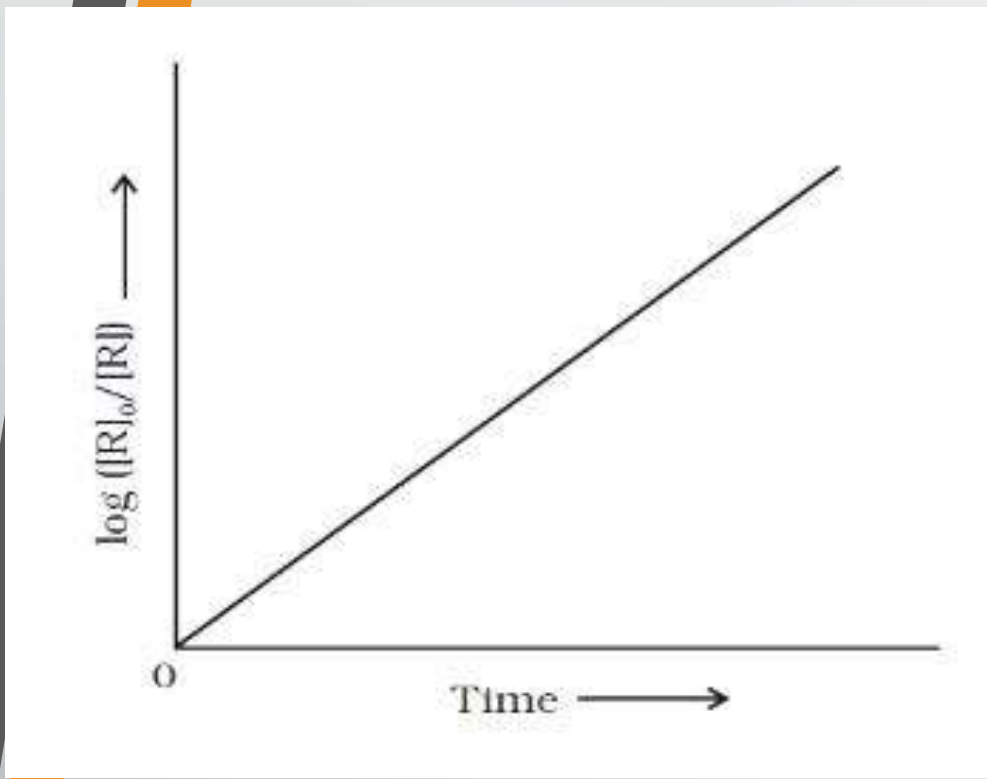
First order reaction

- By definition, the reaction whose rate of reaction is determined by only single then, these reaction is called First order reaction. The differential equation describing first-order kinetics is given below:

$$\text{Rate} = -\frac{d[A]}{dt} = k[A]$$

- The rate constant of first order reaction is $\therefore k = \frac{2.303}{t} \log_{10} \frac{C_0}{C}$
- This is the equation for the first-order reaction, in which C_0 is the initial concentration of reactant and C is concentration of reactant at time t . The rate constant is also determined by plotting the graph of (C_0/C) versus time t , we get straight having slope of $2.303/k$.
- **Half-life period of reaction is**

$$\therefore t_{1/2} = \frac{0.693}{k}$$



First Order Reaction Graph

Second Order Reaction

- A chemical reaction in which the rate of reaction is proportional to the concentration of each of two reacting molecules is the order of a reaction.
- According to the Rate Law Equation

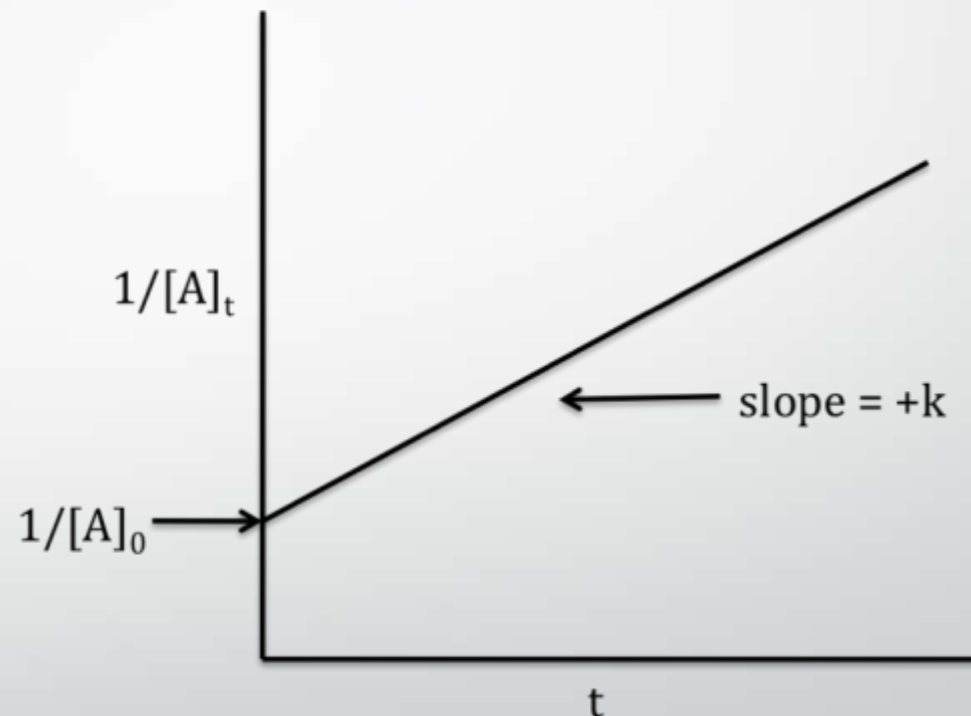
$$-\frac{d[A]}{dt} = k[A]^2$$

- The Rate Constant for one reactant is

$$k = \frac{1}{t} \left(\frac{1}{C} - \frac{1}{C_0} \right)$$

The Rate Constant for two reactant is

$$k = \frac{1}{t} \left[\frac{2.303}{a-b} \log_{10} \frac{b(a-x)}{a(b-x)} \right]$$



Third Order Reaction

- Reaction whose rate of reaction is calculated by the variation three concentration is known as third order reaction.
- According to the Rate Law Equation

$$-\frac{d[A]}{dt} = k[A]^3$$

- The Rate Constant for Third Order Reaction is

$$k = \frac{1}{2t} \left(\frac{x(2a - x)}{a^2(a - x)^2} \right)$$

- The Half-Life Third Order Reaction is

$$t_{1/2} = \frac{3}{2K(C_0)^2}$$

Order of Reaction	Rate Law	Characteristic Kinetic Plot	Slope Kinetic Plot	Half-Life	Rate Constant
Zero order Rate constant	$-\frac{d[x]}{dt} = k_0$	[A] vs t	-K	$t_{1/2} = \frac{a}{2k_0}$	<i>mole litre⁻¹time⁻¹</i>
First order Rate constant	$-\frac{d[A]}{dt} = k[A]$	ln [A] vs t	-K	$t_{1/2} = \frac{0.693}{k}$	<i>time⁻¹</i>
Second order Rate constant	$-\frac{d[A]}{dt} = k[A]^2$	1/[A] vs t	K	$t_{1/2} = \frac{1}{k C_0}$	<i>litre mole⁻¹time⁻¹</i>
Third order Rate constant	$-\frac{d[A]}{dt} = k[A]^3$	1/[A-x] ² vs t	1/2K	$t_{1/2} = \frac{3}{2K(C_0)^2}$	<i>litre mole⁻²time⁻¹</i>

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