

## CHEMICAL KINETICS

PREPARED BY A K SAMAL, PGT(CHEM.) ,KV NO-2, CRPF, BHUBANESWAR)PH.NO-738188460

### CHAPTER - 4

#### CHEMICAL KINETICS

**1. Rate of reaction:** it is defined as the decrease in concentration of any one of the reactants or increase in concentration of any one of the products per unit time.



$$\text{Rate} = -\Delta[R]/\Delta t = +\Delta[P]/\Delta t$$

**2. Unit of rate:** mole  $L^{-1} \text{Sec}^{-1}$  or atm  $\text{sec}^{-1}$

**3. Unit of rate constant (K) =** mole<sup>1-n</sup> litre<sup>n-1</sup> sec<sup>-1</sup>, For zero order = mole  $L^{-1} \text{Sec}^{-1}$  or atm  $\text{sec}^{-1}$

**For first order =**Sec<sup>-1</sup>, for second order = L mole<sup>-1</sup> Sec<sup>-1</sup>

**3. Rate constant:** Rate constant is defined as rate of a chemical reaction when the molar concentration of reacting species is unity.

4.

Order of reaction	Molecularity
It is defined as sum of powers of the concentration of the reactants in the rate law expression i	it is defined as the no. Of reacting species (atoms, ions or molecules) taking part in an elementary reaction, which must collide simultaneously in order to bring about a chemical reaction
It is determined experimentally	it is determined the theoretically
It may be 0,1,2.3 & fraction	it is always a whole number molecularity= 1 – Unimolecular, 2- Bimolecular, 3- Termolecular

#### 5. Elementary reaction

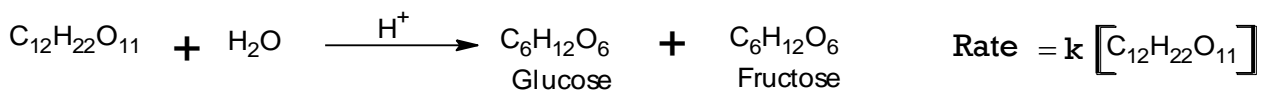
The reaction taking place in one step is called elementary reaction. From elementary reaction one can determine the molecularity and order of reaction.

6. **Pseudo first order reaction** In this type of reaction, the rate of reaction depends upon only the concentration of one species, whereas the concentration of other species remains almost constant.



$$\text{Rate} = K[\text{ester}]$$

### Inversion of cane sugar:



**7. Activation energy:** It is defined as the excess amount of energy required by reactant molecules to form **activated complex**.

$$E_{\text{act}} = (\text{threshold energy} - \text{average energies of reacting species}) = E_{\text{th}} - E_r$$

**8. Threshold energy:** It is defined as the minimum amount of energy required by reacting species to form **activated complex**.

### 9. Half life of reaction ( $t_{\frac{1}{2}}$ )

Half life is the time in which the concentration of reactant is reduced to half of its initial

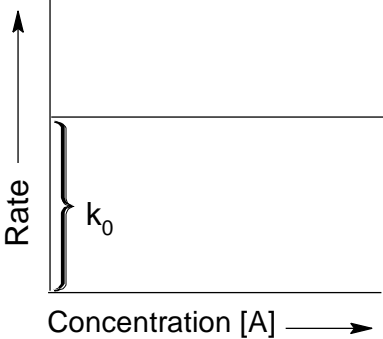
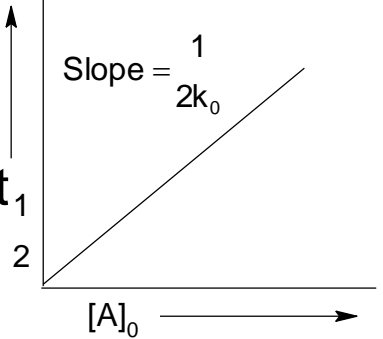
concentration. When  $t = t_{\frac{1}{2}}$   $[A] = \frac{[A]_0}{2}$

Zero order	First order
$k_0 = \frac{[A]_0 - [A]}{t} \Rightarrow k_0 = \frac{[A]_0 - \frac{[A]_0}{2}}{t_{\frac{1}{2}}}$ $t_{\frac{1}{2}} = \frac{[A]_0}{2k_0}$ <p>The half-life period is directly proportional to initial concentration of the reactant.</p>	$k_1 = \frac{2.303}{t} \log \frac{[A]_0}{[A]} = \frac{2.303}{t_{\frac{1}{2}}} \log \frac{[A]_0}{\frac{[A]_0}{2}} = \frac{2.303}{k_1} \log 2 = \frac{2.303 \times 0.3010}{k_1}$ $t_{\frac{1}{2}} = \frac{0.693}{k_1}$ <p>The half-life period is independent of initial concentration of the reactant.</p>

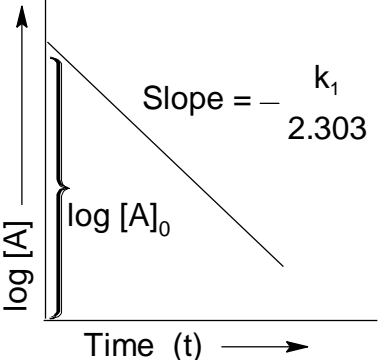
It is found that half-life of  $n^{\text{th}}$  order reaction  $t_{\frac{1}{2}} \propto \frac{1}{(\text{Concentration of reactant})^{n-1}}$

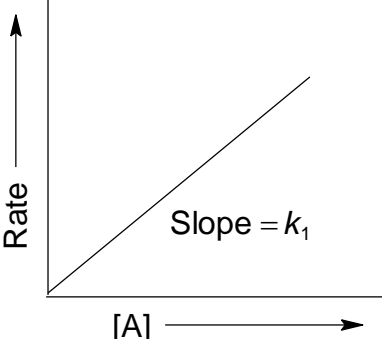
### Graphical representation of Zero order reaction

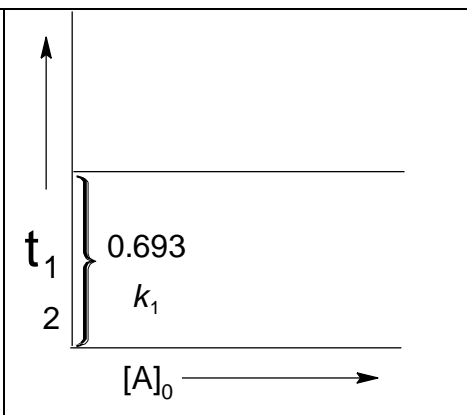
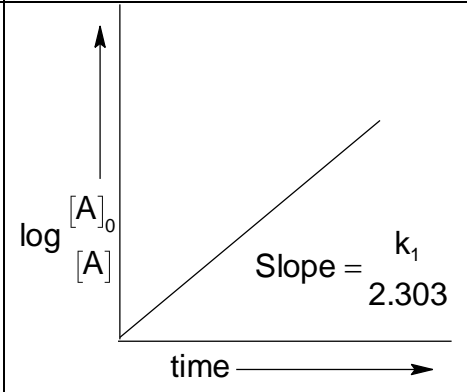
Versus	Derivation	Plot
Concentration & time	$k_0 = \frac{[A]_0 - [A]}{t} \Rightarrow k_0 t = [A]_0 - [A]$ $\Rightarrow [A] = (-k_0) t + [A]_0$ $y = m x + c$	

Rate & Concentration	$\text{Rate} = -\frac{d[A]}{dt} = k_0[A]^0 = k_0$	
Half-life & Initial concentration	$t_{\frac{1}{2}} = \frac{[A]_0}{2k_0}$ $t_{\frac{1}{2}} = \left(\frac{1}{2k_0}\right)[A]_0 + 0$ $y = m x + c$	

### Graphical representation of first order reaction

log [A] & time	$k_1 = \frac{2.303}{t} \log \frac{[A]_0}{[A]} \Rightarrow \frac{k_1 t}{2.303} = \log[A]_0 - \log[A]$ $\Rightarrow \log[A] = \left(-\frac{k_1}{2.303}\right)t + \log[A]_0$ $y = m x + c$	
----------------	---	---

Rate & Concentration	$\text{Rate} = \frac{d[A]}{dt} = k_1[A]$ $y = m x + c$	
----------------------	--	---

Half-life & Initial concentration	$t_{\frac{1}{2}} = \frac{0.693}{k_1}$	
$\log \frac{[A]_0}{[A]}$ & time	$k_1 = \frac{2.303}{t} \log \frac{[A]_0}{[A]}$ $\log \frac{[A]_0}{[A]} = \left( \frac{k_1}{2.303} \right) t$ $y = mx + c$	

### Arrhenius equation for Activation energy

The temperature dependence of the rate constant ( $k$ ) is directly proportional to the fraction of molecules having energy equal to or greater than the activation energy ( $E_a$ ).

$$k \propto e^{-\frac{E_a}{RT}} \quad \Rightarrow \quad k = Ae^{-\frac{E_a}{RT}}$$

A - Frequency factor, is a constant for a particular reaction.

R-  $8.314 \text{ JK}^{-1}\text{mol}^{-1}$

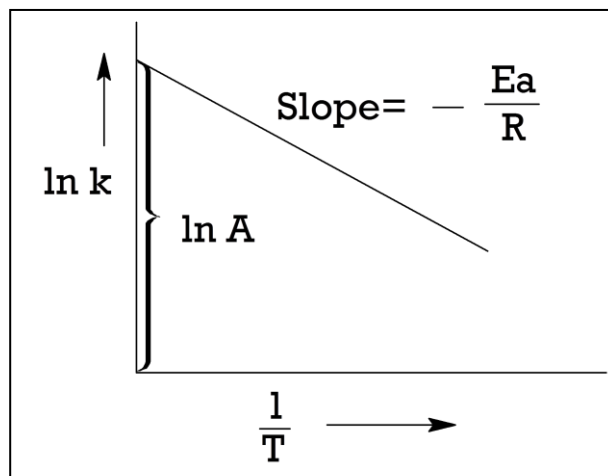
$E_a$  :- Activation energy  $\text{J mol}^{-1}$

A &  $E_a$  known as Arrhenius parameters

$$\ln k = \ln A - \frac{E_a}{RT}$$

$$\Rightarrow \ln k = \left( -\frac{E_a}{R} \right) \frac{1}{T} + \ln A$$

$$y = mx + c$$



If  $k_1$  and  $k_2$  are the values of rate constants at temperature  $T_1$  and  $T_2$ , then:

$$\ln k_1 = \ln A - \frac{E_a}{RT_1} \quad \text{----- (1)}$$

$$\ln k_2 = \ln A - \frac{E_a}{RT_2} \quad \text{----- (2)}$$

$$\ln k_2 - \ln k_1 = \frac{E_a}{RT_1} - \frac{E_a}{RT_2} = \frac{E_a}{R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right]$$

Subtracting equation (1) from (2), we get  $\Rightarrow \ln \frac{k_2}{k_1} = \frac{E_a}{R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right]$

$$\Rightarrow \log \frac{k_2}{k_1} = \frac{E_a}{2.303 R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right]$$