

## Chemical Kinetics

### 1. Rate of Rxn:

Change in concentration of reactant (or) product in unit time

$$\text{Rate} = \frac{-\Delta R}{\Delta t} = \frac{\Delta P}{\Delta t}$$

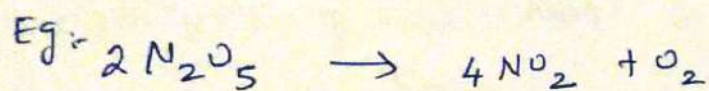
Unit  $\rightarrow$  concn  $\text{time}^{-1}$

$$\text{mol L}^{-1} \text{s}^{-1}$$

Gas

$\downarrow$

$$\text{bar s}^{-1} \text{ (or) } \text{atm s}^{-1}$$



$$\text{Average rate} = -\frac{1}{2} \left[ \frac{\Delta \text{N}_2\text{O}_5}{\Delta t} \right] = \frac{1}{4} \left[ \frac{\Delta \text{NO}_2}{\Delta t} \right] = \left[ \frac{\Delta \text{O}_2}{\Delta t} \right]$$

### Rate expression:-



$$\text{Rate} \propto [A]^x [B]^y \rightarrow \text{Experimental quantity}$$

$k \rightarrow$  Rate constant

$$-\frac{dR}{dt} = k [A]^x [B]^y$$

### Order of a reaction.

$$\text{Order} = x + y$$

$$\text{Order of Reactant A} = x$$

$$\text{Order of Reactant B} = y$$

Order = 0, 1, 2, and even fraction.

#### 4. Unit of rate constants



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

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

$$\text{Unit of } k = \frac{\text{Concn}}{\text{time}} \times \frac{1}{(\text{Concn})^n} \quad n = \text{order of Rm.}$$

$$\text{Unit of } k \text{ zero order} \rightarrow \text{mol L}^{-1} \text{s}^{-1}$$

$$\text{First order} \rightarrow \text{s}^{-1}$$

$$\text{Second order} \rightarrow \text{mol}^{-1} \text{L s}^{-1}$$

#### 5. Molecularity:

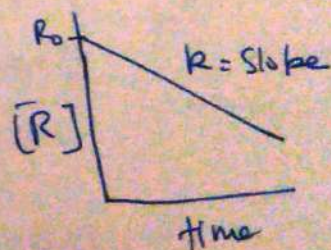
In rate determining step  $\rightarrow$  Unimolecular  $\rightarrow$  1<sup>st</sup> order  
Bimolecular  $\rightarrow$  2<sup>nd</sup> order  
Trimolecular  $\rightarrow$  3<sup>rd</sup> order.

For complex rxn, order given by exps.

#### Integrated Rate equation

1) Zero order rxn

$$kt = [R]_0 - [R]$$



## 7. Half life of a Reaction

(i)  $t_{1/2}$  for zero order reaction:-

$$t_{1/2} = \frac{R_0}{2k}$$

$t_{1/2} \propto R_0$   
Inv Prop  $k$

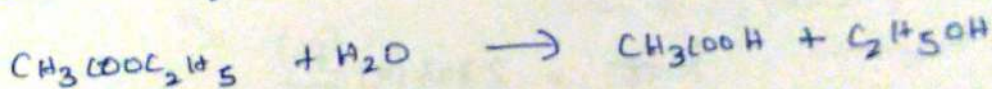
(ii)  $t_{1/2}$  for first order rxn:-

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

$t_{1/2}$  independent of  $[R]_0$

• pseudo first order rxn.

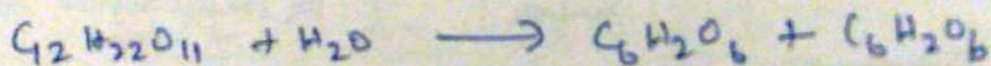
Hydrolysis of ester:-



$$\text{Rate} = k' [\text{CH}_3\text{COOC}_2\text{H}_5] [\text{H}_2\text{O}]$$

$$k = k' [\text{H}_2\text{O}]$$

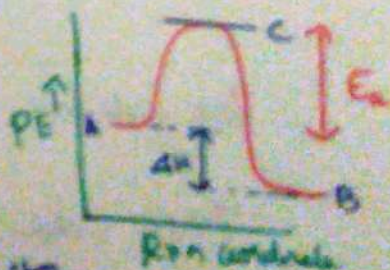
Inversion of cane sugar.



$$\text{Rate} = k [\text{C}_{12}\text{H}_{22}\text{O}_{11}]$$

Arrhenius equation.

$$k = A e^{-E_a/RT}$$



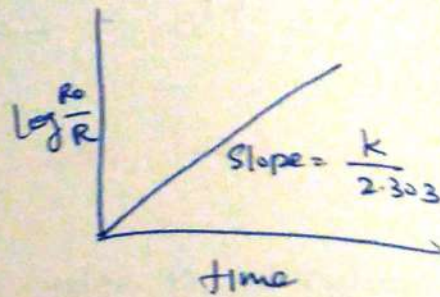
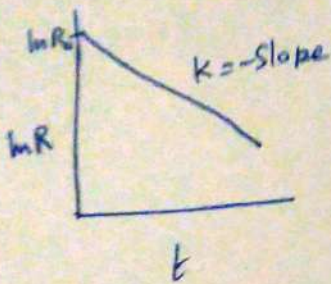
A → Arrhenius factor or frequency factor

$E_a$  → Activation energy Joules/mole ( $\text{J mol}^{-1}$ )

(B) First order reactions

$$\ln R = -kt + \ln R_0$$

$$kt = \frac{\ln[R_0]}{\ln[R]} \quad \begin{matrix} a \\ a-x \end{matrix}$$



$$kt = 2.303 \log \frac{[R_0]}{[R]}$$

Zero order Rxn

First order Rxn

Eg: 1. Enzyme catalyzed Rxn

Eg: Hydrogenation of ethene

2. Rxns which occur on metal surface

All Radioactive decay

Decomposition of  $\text{NH}_3$

Decomposition of  $\text{N}_2\text{O}_5$

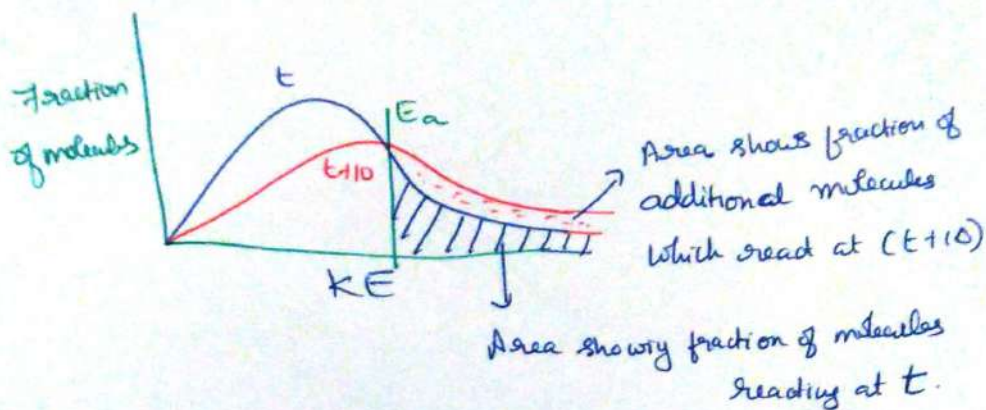
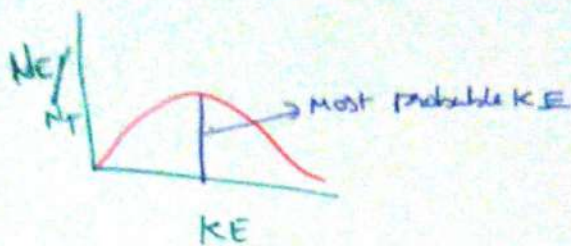
Normal Decomposition of HI on Au surface

For gaseous reactants

First order rate constant

$$k = \frac{2.303}{t} \log \frac{p_i}{2p_i - p_t}$$

## Maxwell Boltzmann distribution curve.

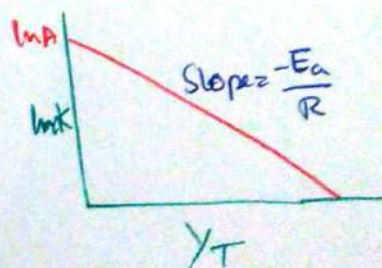


Temp.

## Log form of Arrhenius eqn:-

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

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



## Collision Theory:-

$$\text{Rate} = P Z_{AB} e^{-E_a/RT}$$

$P \rightarrow$  probability or steric factor

$Z_{AB} \rightarrow$  collision frequency of reactant A & B.