

## Chemical Kinetics

- \* ROR - Change in the conc. of reactants/products per unit time.  $R \rightarrow P$ .  
Unit =  $\text{mol L}^{-1} \text{time}^{-1} / \text{atm time}^{-1}$ , Eg:  $\alpha A + \beta B \rightarrow \gamma C + \delta D$ .

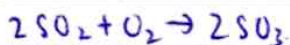
$$\text{ROR} = -\frac{\Delta[A]}{\Delta t} = -\frac{\Delta[B]}{\beta \Delta t} = +\frac{\Delta[C]}{\gamma \Delta t} = +\frac{\Delta[D]}{\delta \Delta t}$$

Graphs of Reactants & Products

No. of coefficients in ROR, R.O disappearance of A =  $-\frac{\Delta[A]}{\Delta t}$ , B =  $-\frac{\Delta[B]}{\Delta t}$

R.O appearance/formation of C =  $+\frac{\Delta[C]}{\Delta t}$ , Instantaneous ROR:  $-\frac{dA}{dt} = \frac{dC}{dt} = \dots$

- Q If ROR of  $\text{SO}_2$  is  $2 \times 10^{-3} \text{ M sec}^{-1}$ . Find ROA.



$$2 \times 10^{-3} = -\frac{\Delta \text{SO}_2}{\Delta t} = \frac{\Delta \text{SO}_3}{\Delta t}, \text{ROA of SO}_3 = 2 \times 10^{-3} \text{ M sec}^{-1}$$

- \* Factors affecting ROR.

- 1) Nature of Reactants :-  $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$  Fast.  
 $2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2$  Slow.
- 2) Conc. of reactants :-  $\uparrow$ , rate  $\uparrow$
- 3) Temp  $\uparrow$ , ROR  $\uparrow$
- 4) Catalyst :- Speeds up the reaction.
- 5) Surface area of reactants :-  $\downarrow$  particle size,  $\uparrow$  reaction. Greater is surface.

- \* Rate Law and Rate Constant.

Rate Law :- Rate  $\propto$  conc. of reactants.

Rate law is a mathematical equation that describes relationship between reaction rate and the concentration of reactions.



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

$k$  = Rate constant

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

- $\alpha = x, \beta = y$  for elementary rxns, 1 step rxns, Rate determining step  
 $\rightarrow$  Order  $= x + y$

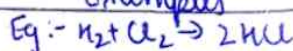
Order

Unit of  $k$

Examples

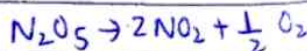
0

$$\frac{\text{mol}}{\text{L s}} \times \left(\frac{1}{\text{mol}}\right)^0 = \text{mol L}^{-1} \text{s}^{-1}$$



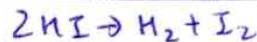
1

$$\frac{\text{mol L}^{-1}}{\text{s}} \times \left(\frac{1}{\text{mol L}^{-1}}\right)^1 = \text{s}^{-1}$$



2

$$\frac{\text{mol L}^{-1}}{\text{s}} \times \left(\frac{1}{\text{mol L}^{-1}}\right)^2 = \text{mol}^{-1} \text{L s}^{-1}$$





$k$  is defined as the rate of rxn when the molar conc. of each reactant is unity.

Page No.

Date:

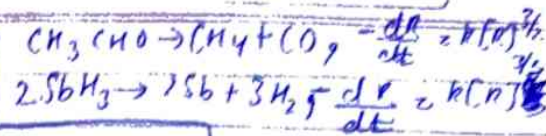
### Fractional Order



$$\text{Rate} = k [\text{CHCl}_3] [\text{Cl}_2]^{1/2}$$

$$\text{Order} = \frac{3}{2}$$

Eg:- nitration of phenol



- Complex Rxns:- Rxns take more than 1 step. Slowest step is rate determining step. Order is for both elementary & complex rxns but molecularity is for elementary rxns. Order is given by slowest step in complex and molecularity of slowest step is same as order. Order = Experimental, Molecularity = Theoretical (unimolecular, bimolecular, etc.)

- Order of a reaction:- Sum of powers to which the molar conc. in the rate law equation are raised.
- Molecularity:- The no. of atoms, ions or molecules that must collide with one another simultaneously to result into a chemical rxn. Eg:-  $2\text{HI} \rightarrow \text{H}_2 + \text{I}_2$ , Molecularity - 2  
 $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$ , Molecularity - 3

- Integrated rate Law:- These are studied by integrating the above differential equations in order to predict the conc. at any time and to determine the order of rxn accurately.

→ Zero order:- ROR & zero power of conc of reactants

$$[R] = k[R]^0$$

$$-\frac{d[R]}{dt} = k, d[R] = -k dt$$

Integrating both sides.

$$\int d[R] = -\int k dt, [R] = -kt + c$$

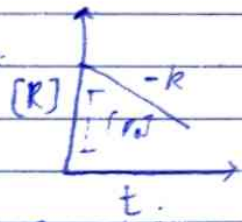
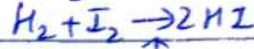
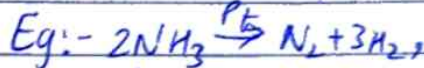
$$\text{At } t=0, [R] = [R_0]$$

i.e. when

$$c = [R_0]$$

$$[R] = -kt + [R_0]$$

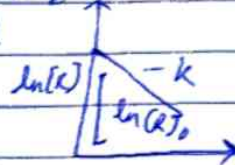
$$y = mx + c$$



→ First order:-  $[R] = k[R]^1, -\frac{d[R]}{dt} = k[R]$

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

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

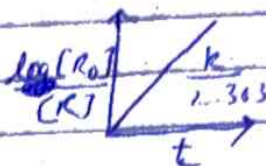


Ex:  $^{226}_{88}\text{Ra} \rightarrow ^4_2\text{He} + ^{222}_{86}\text{Rn}$  and all radioactive decay  
 $(\text{H}_2 + \text{H}_2 \rightarrow \text{C}, \text{H}_2)$

$$kt = \ln[R_0] - \ln[R]$$

$$kt = \ln \frac{[R_0]}{[R]}$$

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



\*  $t_{1/2}$ : Time in which ROR is reduced to half of its initial conc.  
 → Zero order:-

$$k = \frac{[R]_0 - [R]}{t}$$

$$t = t_{1/2}, [R] = \frac{[R_0]}{2}$$

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

$$\boxed{t_{1/2} \propto [R_0]}$$

→ First order:-

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

$$t = t_{1/2}, [R] = \frac{[R_0]}{2}$$

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

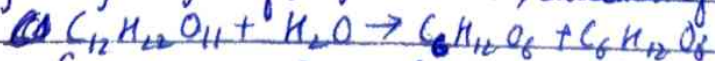
$t_{1/2}$  not proportional to  $[R]$ .

\*  $n^{\text{th}}$  order reaction.

$$kt = \frac{R_0^{1-n} - C^{1-n}}{1-n} \quad t_{1/2} \propto R_0^{1-n}$$

\* Pseudo 1st order:- Second order made to behave like 1st order by conditions.

Ex:- Hydrolysis of Ethyl acetate, Inversion of Cane Sugar



Sucrose

Glucose Fructose

Rate  $\propto k[\text{C}_{12}\text{H}_{22}\text{O}_{11}]$  as in soln, amount of water is excessively high as compared to sugar, so  $[\text{H}_2\text{O}]$  is constant.



→ Second Order

$$\frac{1}{Rt} = kt + \frac{1}{R_0}$$

$$t_{1/2} = \frac{1}{kR_0}$$

Page No.

Date:

\* Effect of temperature on reaction rates (Arrhenius Equation)  
 → Chemical rxns faster at ↑ temp. As temp ↑, molecules move faster and collide more vigorously enabling bond cleavages & rearrangements.

→ ROR doubles for a  $10^\circ$  ↑ in temp as proved by Arrhenius, he combined the concept of activation energy ( $E_a$ ) and Boltzmann distribution law.

$$k = A e^{-\frac{E_a}{RT}} \quad \text{--- (1)} \quad \left[ \begin{array}{l} \text{Keeping the conc constant, if} \\ \uparrow \text{ temp, ROR} \uparrow, k \uparrow \end{array} \right]$$

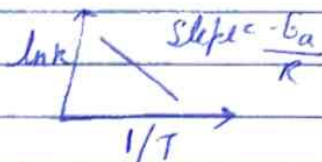
$k$  = rate constant,  $A$  = pre exponential factor,  $E_a$  = Activation energy,  $R$  = Gas constant,  $T$  = temp,  $RT$  = avg. Kinetic energy.

→ ↑ ( $A/R$  ratio, ↓ the rate (hence -ve sign)

→ ↑ temp & ↓  $E_a$  favors ↑  $k$  and speed up rxns

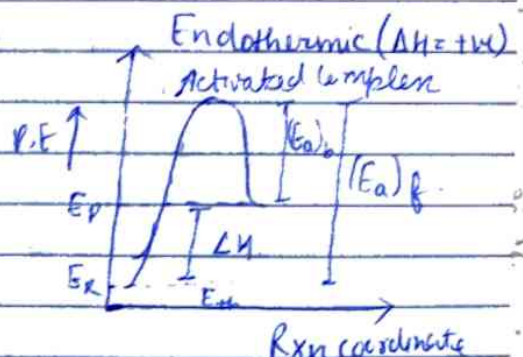
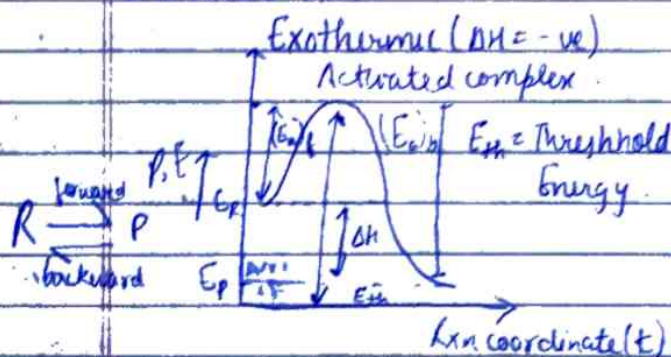
Taking log both sides of eq (1)

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



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

\*  $E_a$  (activation energy) :- Min. amount of energy that is required to activate atoms or molecules so that they can undergo a chemical rxn.



$$\Delta H = E_P - E_R = (E_a)_f - (E_a)_b$$

$$\Delta H = E_P - E_R = (E_a)_f - (E_a)_b$$

→ Activated complex is a short-lived state in which colliding particles are at the peak of P.E. curve



- \* Collision Theory - It explains why diff. reactions occur at diff. rates (particular for gases).
- It states that for a chemical reaction to occur, the reacting particles must collide with another.  $\therefore$  ROR depends on freq. of collisions.
  - A collision will be effective in producing chemical change only if the species brought together possess a certain min. amount of energy ( $E_a$ ).
  - Colliding particles must be oriented in a manner favorable to the necessary rearrangement of atoms.
  - Not all collisions are equal or bring about a chemical change.

When two gases A and B react, reaction becomes possible when A & B collide. So, no. of collisions per sec ( $Z$ ) in a given volume can be obtained from kinetic theory -

$$Z_{AB} = n_A n_B \sigma_{AB}^2 \left( \frac{8\pi RT}{\mu} \right)^{1/2}$$

$\sigma$  = collision diameter,  $\mu$  = reduced mass,  $R$  = Boltzmann constant.  
 $n_A$  &  $n_B$  - no. of molecules of A and B reacted in 1 sec, which can be obtained from rate constant ' $k$ '

- No. of molecules reacted is always less than no. of molecules collided, i.e. every collision does not yield a rxn.
- Arrhenius then proposed, molecules having  $E_a$  after collision will result in rxn.
- Acc. to Maxwell, at temp.  $T$ , ratio of total number of collisions and no. of collisions giving  $E_a$  to molecules is  $e^{-E_a/RT}$

$$Z' = Z e^{-E_a/RT}$$

$$-\frac{dn_A}{dt} = Z' \rightarrow \text{ideally}$$

$Z$  = total no. of collision,  $Z'$  = no. of collision giving  $E_a$  to molecules

$$\frac{N_A}{n_A n_B} \times Z e^{-E_a/RT} = k$$

$$k = \frac{p N_A}{n_A n_B}$$

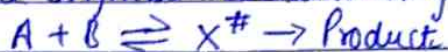
$$k = \frac{p N_A}{n_A n_B} \times Z e^{-E_a/RT}$$

$p$  = probability factor



\* Activated Complex theory - (Also known as Transition State Theory)

- An activated complex is an unstable arrangement of atoms that is in between the reactants and products and exists momentarily at the peak of activation energy barrier.
- Because of its high energy, the activated complex exists for an extremely short period of time (about  $10^{-13}$  s).
- There is equal likelihood that the activated complex either reforms the original reactants or goes on to form products.



(Activated complex) AC

Here, ROK depends on 2 factors - ① Conc. of activated complex ② Freq. of decomposition of A.C.

Rate  $\propto$  (conc. of AC) (freq. of decomposition of AC) - ①

- ① Conc. of A.C. : Rxn is in equilibrium with A.C.

$$k^\ddagger \propto \frac{[X^\ddagger]}{[A][B]}, \quad [X^\ddagger] \propto k^\ddagger [A][B] \quad \text{--- (2)}$$

(Conc. of AC)

- ② Freq. of decomposition of A.C. :- Since, A.C. is in a process of decomposition so one of its vibration degree of freedom will change to translational dof. So,  $E_{vib}$  be the avg. vibrational energy which results in bond breaking.

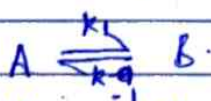
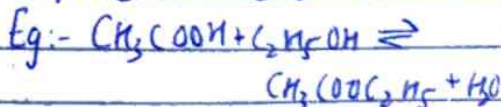
$$E_{vib} = hf, \quad E_{vib} \propto k_B T$$

$$k_2 \propto \left( \frac{k_B T}{h} \right) e^{(-\Delta H^\ddagger)/RT} e^{(\Delta S^\ddagger)/R}$$

$$E_a = (\Delta H^\ddagger) + RT$$

\* Complex reactions :- There will be intermediates in the rxn which should not appear in rate law.

\* Reversible Reaction :- A reaction in which conversion of reactants to products and conversion of products to reactants occur simultaneously.



At time  $t$ ,  $a-x$   $x$

At equilibrium,  $(a-x_0)$   $x_{eq}$

$$\text{Rate} = \frac{dx}{dt} = k_1[A] - k_{-1}[B]$$

$$= k_1(a-x) - k_{-1}(x) \quad \text{--- (2)}$$

At equilibrium,  $R_{eq} = \frac{x_{eq}}{a - x_{eq}}$  and rate  $= 0$ .

$$k_1(a - x_{eq}) = k_{-1}(x_{eq})$$

$$\frac{k_1}{k_{-1}} = \frac{x_{eq}}{a - x_{eq}} = R_{eq}$$

$$k_{-1} = k_1 \left( \frac{a - x_{eq}}{x_{eq}} \right) \quad \text{--- (2)}$$

From eq. (1) & (2).

$$\text{Rate} = \frac{dx}{dt} = k_1(a - x) - k_{-1}x \left( \frac{a - x_{eq}}{x_{eq}} \right)$$

$$\int \frac{dx}{x_{eq} - x} = \int \frac{a}{x_{eq}} k_1 dt$$

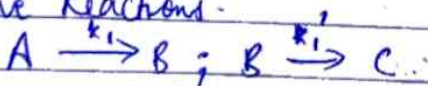
$$-\ln(x_{eq} - x) = \frac{a}{x_{eq}} [k_1 t + I]$$

at  $t = 0$ ,  $x = 0$ .

$$I = -\frac{x_{eq}}{a} \ln(x_{eq})$$

$$k_1 t = \frac{x_{eq}}{a} \ln \left( \frac{x_{eq}}{x_{eq} - x} \right)$$

### \* Consecutive Reactions.



$$-\frac{dA}{dt} = k_1[A]; \quad \frac{d[C]}{dt} = k'_1[B]$$

$$\frac{d[B]}{dt} = k_1[A] - k'_1[B]$$

