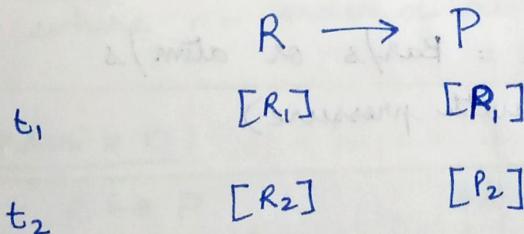


## Chapter - 4 : Chemical Kinetics

- It is the branch of chemistry that deals with study of reactions and their mechanism.
- Feasibility of a reaction can be predicted by thermodynamic factors.  
e.g. Diamond  $\rightarrow$  graphite : Thermodynamically feasible.  
But it won't occur since reaction rate is very slow.
- Usefulness : fixes the conditions by which reaction can be altered to get the desired product.
- Factors that affect the rate of reaction:
  - Concentration
  - Temperature
  - Pressure
  - Catalyst
- Macroscopic - Speed  
Microscopic - Mechanism
- How to determine the rate of rxn?

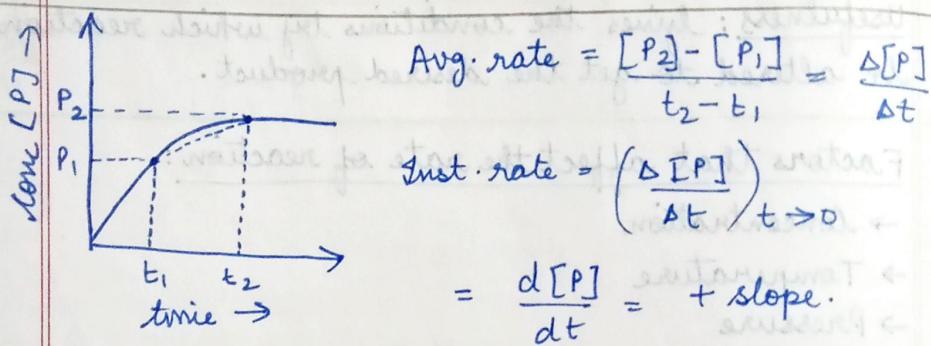
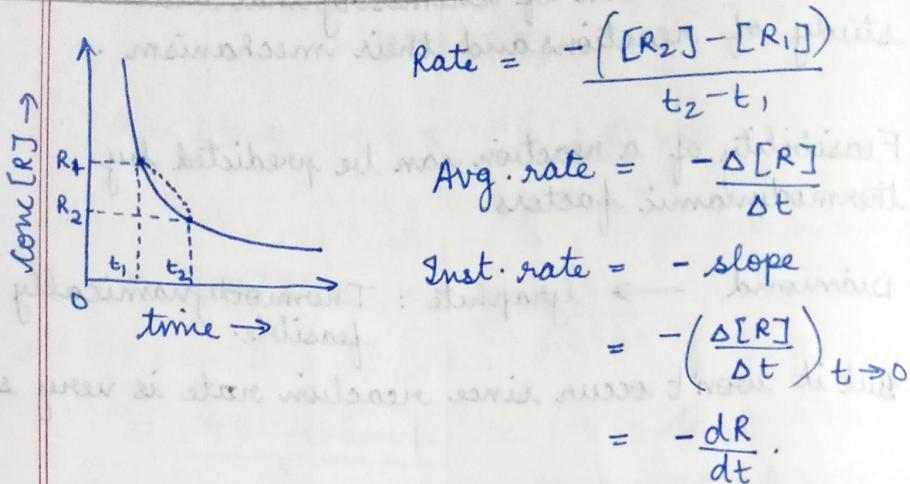


Change in conc. w.r.t. time = Rate of rxn.

$$\text{Rate} = -\frac{[R_2] - [R_1]}{t_2 - t_1} = \frac{[P_2] - [P_1]}{t_2 - t_1}$$

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

Rate of rxn = Rate of disappearance of reactants  
= Rate of appearance of products.



### Units of Rate of Reaction :

$$[\text{conc}] = \text{mol/L}$$

$$\text{time} = \text{s}$$

$$\text{Rate} = \text{mol/L s} \text{ or } \text{mol L}^{-1} \text{s}^{-1}$$

For gases : Rate = Bar/s or atm/s  
(Replace conc. with pressure)

$$\frac{[A] - [A_0]}{t - t_0} = \frac{([A] - [A_0])}{t - t_0} = \text{rate}$$

## RATE LAW

(or Rate equation or Rate expression)

Representation of Rate of Reaction in terms of concentrations of Reactants and Products.



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

$x$  = order w.r.t.  $[A]$

$y$  = order w.r.t.  $[B]$

$x+y$  = overall order.

$x$  and  $y$  need not always be equal to  $a$  and  $b$  respectively.

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

where  $k$  = rate constant / specific reaction rate.

When  $[A] = 1$ ,  $[B] = 1$ ,

$$\text{Rate} = k [1]^x [1]^y$$

$$\text{Rate} = k.$$

$k$  is defined as the rate of a reaction when the concentration of reactants is taken as unity.

In general, units for rate constant

$$= (\text{mol L}^{-1})^{1-n} \text{s}^{-1}$$

where  $n$  = order of rxn (overall order)

order = 0 :

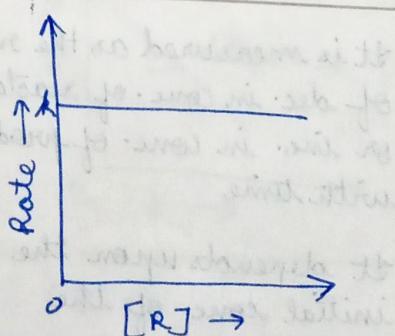


$$\text{Rate} = k [R]^0$$

$$y = m.$$

$$\text{Rate} = k$$

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



order = 1 :

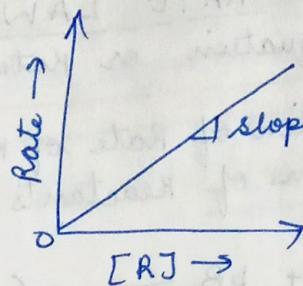


$$\text{Rate} = k[R]$$

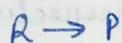
$$y = mx$$

$$k = \frac{\text{Rate}}{[R]}$$

$$\text{units} = \text{s}^{-1}$$



Order = 2 :



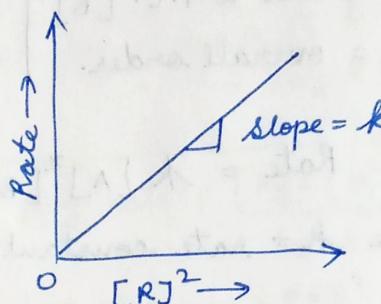
$$\text{Rate} = k[R]^2$$

$$y = mx$$

$$(x = [R]^2)$$

$$k = \frac{\text{Rate}}{[R]^2}$$

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



(Trick to determine order of reaction from rate constant's unit:  
Add +1 to the power of L)

### Rate of Reaction

- It is the speed with which the reactants are converted into products
- It is measured as the rate of dec. in conc. of reactants or inc. in conc. of products with time
- It depends upon the initial conc. of the reactants

### Rate constant (k)

- It is a proportionality constant.
- It is equal to rate of rxn where conc. of each of the reactant is unity.

- It is independent of initial conc. of reactants
- It has a const. value at a fixed temp.

## ZERO ORDER REACTION



$$-\frac{d[R]}{dt} = k [R]^0$$

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

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

$$\int d[R] = - \int k dt$$

$$[R] = -kt + c \quad \text{--- (1)}$$

when  $t=0$ ,  $[R]= [R_0]$ .

$$[R_0] = -k(0) + c$$

$$[R_0] = c \quad \text{--- (2)}$$

sub. (2) in (1),

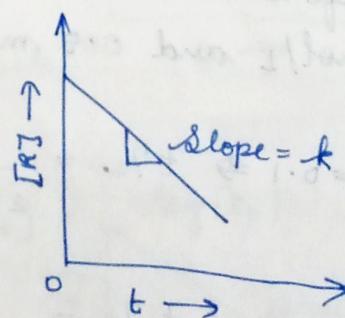
$$[R] = -kt + [R_0] \quad \text{--- (3)}$$

$$y = mx + c$$

(3) is rearranged and written as:

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

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



Half life of a reaction: ( $t_{1/2}$ )

Time taken for initial conc. to reduce to half

$$t \frac{1}{2} = \frac{[R_0] - [R]}{k}$$

(for  $t^{1/2}$ ,  $[R] = [R_0/2]$ )



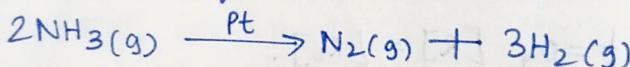
$$t^{1/2} = \frac{[R_0] - [R_0/2]}{k}$$

$$t^{1/2} = \frac{[R_0]}{2k} \rightarrow y = mx.$$

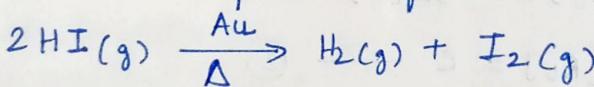
$t^{1/2} \propto [R_0]$  for zero order rxn.

Examples of zero order reactions:

- Decomposition of  $\text{NH}_4$  ion on Pt surface:



- Thermal decomposition of  $\text{HI}$  on Au surface



- Q) Decomposition of  $\text{NH}_4$  on platinum surface has  $k = 2.5 \times 10^{-4} \text{ mol/L s}$ . Calculate the half life when initial conc. of ammonia is  $0.1 \text{ mol/L}$  and  $0.5 \text{ mol/L}$  respectively.

$$\text{When } [R_0] = 0.1 \Rightarrow t^{1/2} = \frac{0.1}{2 \times 2.5 \times 10^{-4}} = 200 \text{ s}$$

$$\text{When } [R_0] = 0.5 \Rightarrow t^{1/2} = \frac{0.5}{2 \times 2.5 \times 10^{-4}} = 1000 \text{ s}$$

# FIRST ORDER REACTION



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

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

$$\left[ \frac{dx}{x} = \ln x \right] = \int + \frac{d[R]}{[R]} = -k \int dt.$$

$$= \ln [R] = -kt + c \quad \text{--- (1)}$$

when  $t=0$ ,  $[R]= [R_0]$ .

$$\ln [R_0] = k(0) + c$$

$$c = \ln [R_0] \quad \text{--- (2)}$$

sub. (2) in (1)

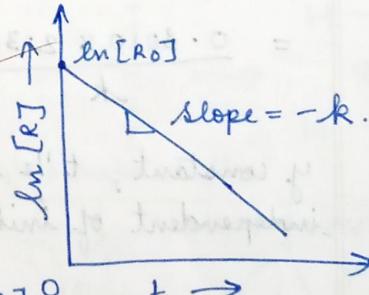
$$\ln [R] = -kt + \ln [R_0]$$

$$y = mx + c$$

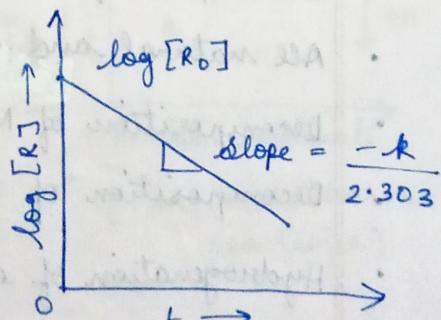
$$2.303 \log [R]$$

$$= -kt + 2.303 \log [R_0]$$

$$(\div 2.303)$$



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



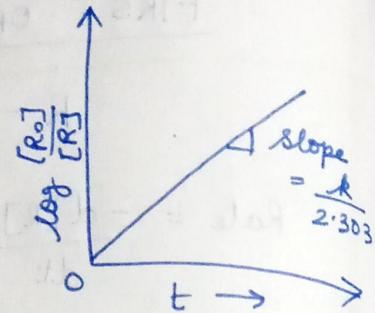
$$\log [R] - \log [R_0] = \frac{-kt}{2.303}$$

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

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

$y = mx.$

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



$[R_0]$  = Initial conc.

$[R]$  = conc. at time 't'.

$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$

where  $a$  = initial conc.

$x$  = no. of moles reacted

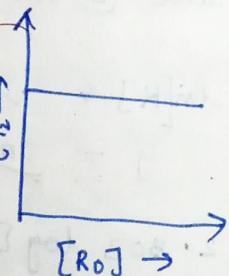
$a-x$  = conc. at time  $t$ .

### Half life period:

$$t^{1/2} = \frac{2.303}{k} \log \frac{[R_0]}{[R_{1/2}]} = \frac{2.303}{k} \log 2$$

$$= \frac{0.3010 \times 2.303}{k} = \frac{0.693}{k}$$

$y$  constant,  $t^{1/2}$  is independent of initial conc.



### Examples of first order rxn:

- All natural and artificial radioactive reactions
- Decomposition of  $N_2O_5$
- Decomposition of  $N_2O$
- Hydrogenation of ethene ( $C_2H_4 + H_2 \rightarrow C_2H_6$ )

## Temperature dependence on the rate of reaction

For every  $10^{\circ}$  rise in temperature, the rate constant is nearly doubled

The temperature dependence of a rate of a chemical reaction is given by Arrhenius equation:

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

$k$  = rate constant

$A$  = Arrhenius factor or

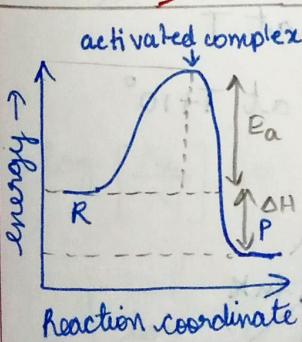
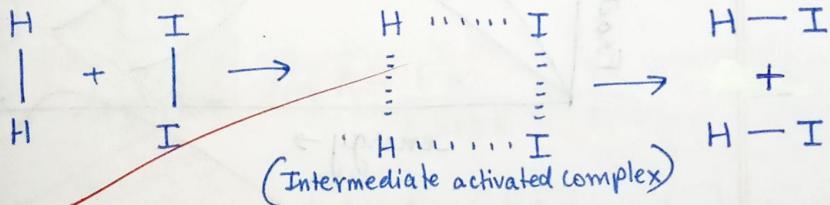
Frequency factor or

Pre exponential factor

$R$  = gas constant

$T$  = Temperature

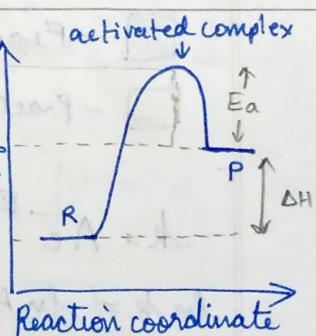
$E_a$  = Activation energy.



(for exothermic reactions)

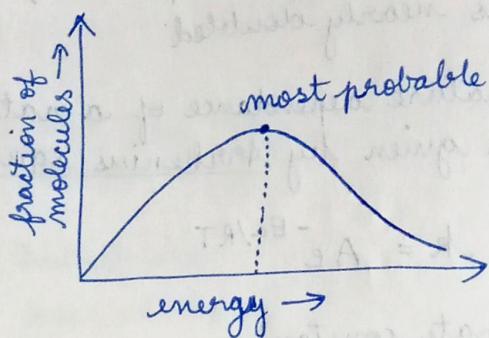
$E_a$  is the required energy by the reactants to form activated complex

(X)



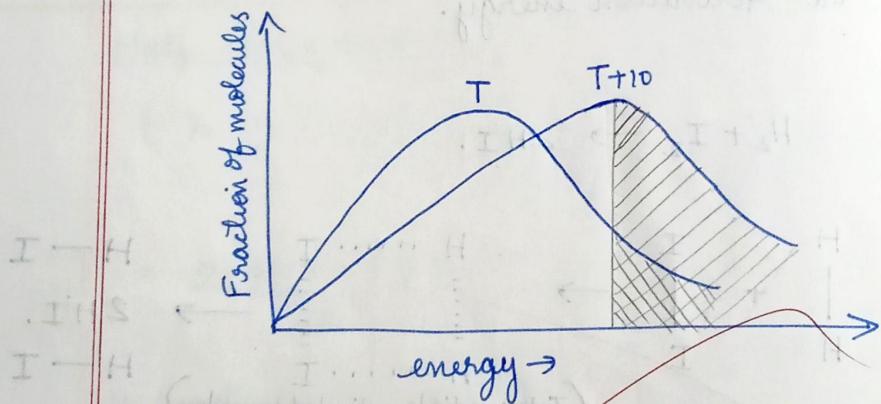
(for endothermic reactions)

# Maxwell Boltzmann's distribution curve



$$\text{Fraction of molecules} = \frac{N_E}{N_T}$$

$N_E$  = no. of molecules with energy E  
 $N_T$  = total no. of molecules.



■ - Fraction of molecules at T

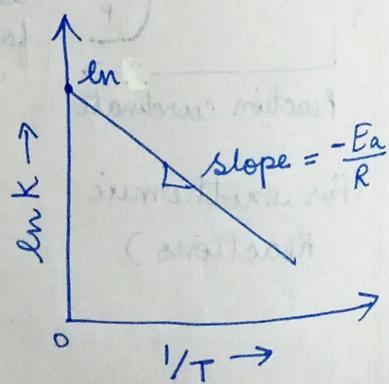
■ - Fraction of molecules at  $T+10^\circ$

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

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

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

$$y = \frac{\ln k}{C} + mx$$



$$2 \cdot 303 \log k = 2 \cdot 303 \log A - \frac{Ea}{RT}$$

$$(\div 2 \cdot 303)$$

$$\log k = \log A - \frac{Ea}{2 \cdot 303 RT}$$

$$\log k = \log A - \frac{Ea}{2 \cdot 303 R} \times \frac{1}{T}$$

$$y = c + m$$

When temp =  $T_1$ , rate const =  $k_1$ ,

$$\log k_1 = \log A - \frac{Ea}{2 \cdot 303 R} \times \frac{1}{T_1} \quad \text{①}$$

When temp =  $T_2$ , rate const =  $k_2$ .

$$\log k_2 = \log A - \frac{Ea}{2 \cdot 303 R} \times \frac{1}{T_2} \quad \text{②}$$

$$\text{②} - \text{①}$$

$$\log k_2 - \log k_1 = \log A - \frac{Ea}{2 \cdot 303 R} \times \frac{1}{T_1}$$

$$- \left[ \log A - \frac{Ea}{2 \cdot 303 R} \times \frac{1}{T_2} \right]$$

$$\Rightarrow \log \left[ \frac{k_2}{k_1} \right] = \frac{Ea}{2 \cdot 303 R} \left[ \frac{1}{T_2} - \frac{1}{T_1} \right]$$

$$= \boxed{\log \frac{k_2}{k_1} = \frac{Ea}{2 \cdot 303 R} \left( \frac{T_2 - T_1}{T_1 T_2} \right)}$$

$[X] P \times A \rightarrow [X] d \rightarrow (\text{atm})$

(arist P per constant) . (stat) F =

