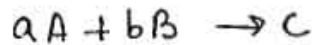


### Order of rxn

The order of the rxn refers to the powers to which the concn are raised in the kinetic rate law.

- It is an experimental qty.
- It can be zero, fractional value or -ve
- It can be whole number,



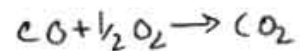
$$-r_A = k [A]^{\alpha} [B]^{\beta}$$

$$\boxed{n = \alpha + \beta}$$

### Zero order rxn :-

$$n = 0$$

Photosynthesis rxn,



$$r \propto \frac{1}{CO}$$

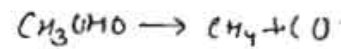
$$r \propto CO^{-1}$$

$$\boxed{n = -1}$$

### First order rxn :-

$$n = 1$$

Radioactive decomposition



$$r \propto C_{CH_3OH}^{3/2}$$

$$n = 3/2$$

Q → What will be the over all order of rxn.

$$r = k [A]^{0.3} [B]^{1.5}$$

$$n = 0.3 + 1.5 = 1.8$$

⊗  $A + 2B \rightarrow 3R + S$ , rate of rxn is define as.  $r = k [A] [B]^2$ ,

then what will be the rate of rxn  $2A + 4B \rightarrow 6R + 2S$

$$r = k [A] [B]^2$$

### Relative rate of rxns :-



$$-r_A =$$

$$-r_B = \frac{b}{a} (-r_A)$$

(7)

### Arrhenius theory:-

$$k \propto \exp(-E/RT)$$

$k_0$  has same unit as  $k$

$$k = k_0 e^{-E/RT}$$

$k_0 \rightarrow$  Pre exponential factor.  
 $\rightarrow$  frequency factor

$$k_0 \neq f(T)$$

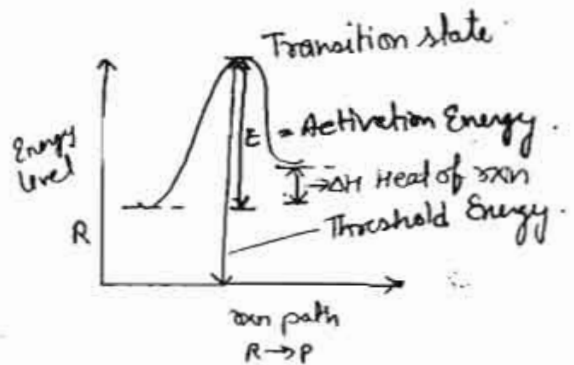
$E =$  Activation Energy, J/mol

$R =$  Universal gas constant, J/mol.K

$T \Rightarrow$  Absolute temp, K

Threshold energy is, actually

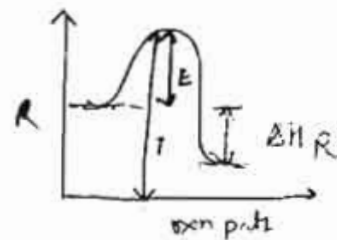
Required energy	addition energy	Energy of molecules
Threshold Energy	Activation Energy	+



$$\Delta H_R = \sum H_{\text{prod}} - \sum H_{\text{react}}$$

$\Delta H_R > 0 \Rightarrow$  Endothermic rxn

$\Delta H_R < 0$  Exothermic



$$k_1 = k_0 e^{-E/RT_1}$$

$$k_2 = k_0 e^{-E/RT_2}$$

Assumption

Activation energy is constant for temp range.

$$r_C = \frac{1}{a} (-r_A)$$

$$r_D = \frac{d}{a} (-r_A)$$

$$\boxed{-\frac{r_A}{a} = -\frac{r_B}{b} = \frac{r_C}{c} = \frac{r_D}{d}}$$

Q) for the rxn  $3A + 4B \rightarrow 2C + 5D$

$$\boxed{-\frac{r_A}{3} = -\frac{r_B}{4} = \frac{r_C}{2} = \frac{r_D}{5}}$$

Rate Constant :- (k) sp. rxn rate.

→ k is strongly temp<sup>r</sup> dependent term.

$$\boxed{\text{Units of } k = (\text{time})^{-1} (\text{concn})^{1-n}}$$

! n = order of rxn

for first order rxn

$$\text{unit of } k = s^{-1}$$

for second order rxn

$$\text{unit of } k = s^{-1} (\text{mol/L})^{-1} = L/\text{smol}$$

Q) for the rxn  $A + 3B \rightarrow 2C$

$$-r_A = k [A] [B]^3$$

$$\text{unit} = s^{-1} (\text{mol/L})^{-3} = s^{-1} \frac{L^3}{\text{mol}^3}$$

Q) for a rxn, rate constant is given as  $k = 3 \frac{\text{mol}^2}{\text{mol}^3 \cdot \text{s}}$  . n = ?

n = 4

$$s^{-1} \frac{\text{mol}^2}{\text{L}^3}$$

(9)

$$k \propto T^{1/2} \cdot e^{-E/RT}$$

$$k = k_0 T^{1/2} e^{-E/RT}$$

### Transition State Theory:-

→ Based on Statistical Mechanics.

$$k \propto T \cdot e^{-E/RT}$$

$$k = k_0 T e^{-E/RT}$$

\*\*\*

$$k \propto T^n \cdot e^{-E/RT}$$

$$\Rightarrow n=0 \quad \text{for AT}$$

$$\Rightarrow n=1/2 \quad \text{for C.T}$$

$$\Rightarrow n=1 \quad \text{for TST}$$

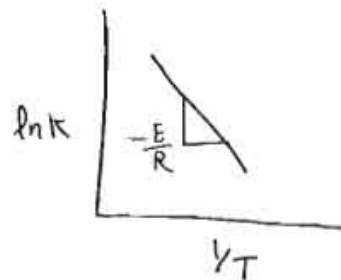
### \* Effect of temp<sup>r</sup>

#### Arrhenius Theory-

$$k = k_0 e^{-E/RT}$$

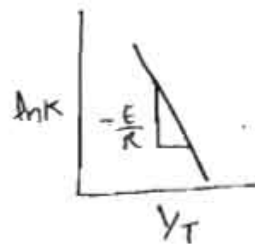
$$\ln k = \ln k_0 - \frac{E}{RT}$$

$$y = c + mx$$



→ for higher value of Activation Energy

Temp<sup>s</sup> Sensitive rxn.



$$k \propto e^{-E/RT}$$

$$T \uparrow \quad k \uparrow$$

$$T \downarrow \quad k \downarrow$$

$$e^{-\infty} \rightarrow 0$$

$$e^0 \rightarrow 1$$

E. = ~

$$\ln k_1 = \ln k_0 - E/RT_1 \quad \text{---(1)}$$

$$\ln k_2 = \ln k_0 - E/RT_2 \quad \text{---(2)}$$

eqn (2) - (1)

$$\boxed{\ln(k_2/k_1) = E/R \left( \frac{1}{T_1} - \frac{1}{T_2} \right)}$$

\* Collision Theory -

→ Based on kinetic theory of gases.

Sep 16, 14 collision

Q. > at 500K, the rxn rate was 10 times faster than that of at 400K,

for gaseous rxn we use collision theory.

Sol<sup>n</sup>

$$k = k_0 T^{1/2} e^{-E/RT}$$

$$\ln k = \ln k_0 + \frac{1}{2} \ln T - \frac{E}{RT}$$

$$\ln \left( \frac{k_2}{k_1} \right) = \frac{1}{2} \ln \left( \frac{T_2}{T_1} \right) + \frac{E}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

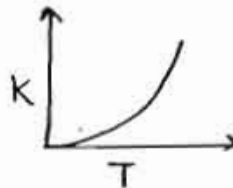
$$\ln(10) = \frac{1}{2} \ln \left( \frac{500}{400} \right) + \frac{E}{R} \left( \frac{1}{400} - \frac{1}{500} \right)$$

$$R = 1987 \text{ cal/mol}\cdot\text{K}$$

$$\boxed{E = 8707.08 \text{ cal/mol}}$$

$$k = k_0 e^{-\dots}$$

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{E}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$



$$\gamma \propto k$$

$$\ln\left(\frac{\gamma_2}{\gamma_1}\right) = \frac{E}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Q-7 The  $E_a$  of a bimolecular rxn is abt 9150 cal/mol. How much faster will this rxn takes place at 500 K than at 400 K.

$$R = 1.987 \frac{\text{cal}}{\text{mole K}} \quad \ln\left(\frac{k_2}{k_1}\right) = \frac{9150}{R} \left(\frac{1}{400} - \frac{1}{500}\right)$$
$$= \frac{4.575 \times 4.18}{8.314}$$

$$\ln\left(\frac{k_2}{k_1}\right) = 2.302$$

$$\frac{k_2}{k_1} = 9.998$$

$$k_2 \approx 10k_1$$



Kinetics

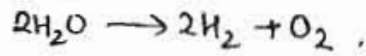
Reaction:-

When a component loses its identity to form a new identity.

Chemical rxn can be of following type.

1) Decomposition rxn:- When a big molecule breaks into smaller molecules.

eg -> Electrolysis of water



2) Synthesis rxn:- When two or more smaller molecules combined together to form a big molecule.

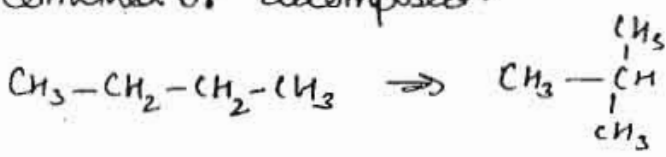
eg ->  $A+B \rightarrow AB$

$C+O_2 \rightarrow CO_2$

} when two smaller molecules combine in such a way that third comp is not formed.

Isomerization Rxn:-

When molecular structure of the molecule is changed w/o being combined or decomposed.



Rate of rxn

Based on unit volume of rxn mixture,

for homogeneous rxn system

$$r_i = \frac{1}{V} \frac{dN_i}{dt}, \frac{mol}{m^3.s}$$

- Rxn mixture contains
- Reactants, pds, inerts.

Based on unit interfacial area of two fluid system,

for heterogeneous system

$$r_i'' = \frac{1}{S} \frac{dN_i}{dt}, \frac{mol}{m^2.s}$$

S = interfacial surface area

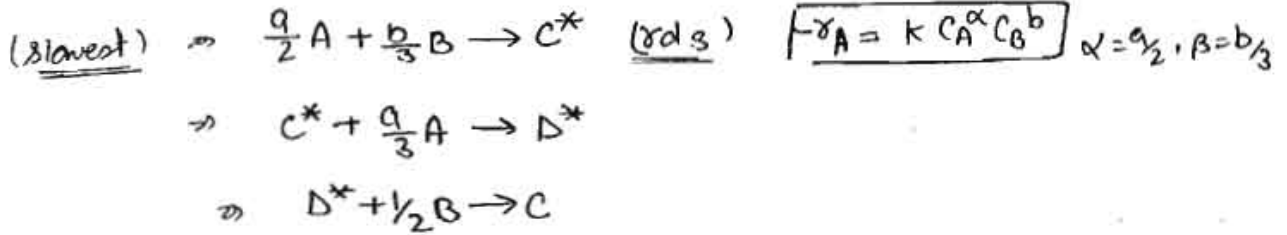
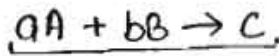
Based on unit weight of solid in fluid-solid system,

for heterogeneous system

$$r_i' = \frac{1}{W} \frac{dN_i}{dt}, \frac{mol}{kg.s}$$

Non-Elementary rxn :-

which proceeds in more than one rxn.



⇒ rxn rate

Calculated for rate determining step

⇒ rate determining step is the slowest step in the rxn mech.

$$-r_A = k C_A^\alpha C_B^\beta$$

$$\alpha = a, \beta = b$$

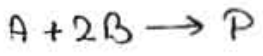
Molecularity :-

⇒ No. of molecules atoms, ions or moles, colliding in the rate determining step.

- ⇒ It is theoretical quantity.
- ⇒ It can not be zero or fractional value.
- ⇒ It is only, 1, 2 or 3.

molecules collide completely not in parts.

It is related to only elementary rxn,



Molecularity = 3

$$-r_A = k C_A C_B^2$$

$$n = 3$$

$$\text{Molecularity} = \text{Overall order of rxn} = \text{Sum of stoichiometry coeff}$$



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(11)

## Collision theory

Run only those molecules take part which have gone through a successful collision.

valid for only - molecularity greater than one.

It is failed for the unimolecular rxn.

$$k = k_0 T e^{-E/RT}$$

$$\ln\left(\frac{k_2}{k_1}\right) = \ln\left(\frac{T_2}{T_1}\right) + \frac{E}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Q) for the gaseous phase rxn. The rate exp is given as  $-\frac{dC_A}{dt} = k C_A^n$   
Then what will be rate exp in terms of partial pressure A.  
for the low pressure condition.

$$-\frac{dC_A}{dt} = k C_A^n$$

$$-\frac{dP_A}{dt} = ?$$

$$PV = nRT$$

$$\frac{P}{RT} = C$$

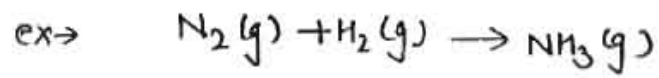
$$-\frac{d}{dt} \left( \frac{P_A}{RT} \right) = k \left( \frac{P_A}{RT} \right)^n$$

$$-\frac{dP_A}{dt} = \frac{k P_A^n}{(RT)^{n-1}} = k (RT)^{1-n} P_A^n$$

$$\left. \begin{aligned} PV &= nRT \\ P &= \frac{nRT}{V} \\ C &= \frac{P}{RT} \end{aligned} \right\} \text{for } P_A^n \text{ (RT)}$$

For homogeneous rxn system:-

where the rxn mixture contains only one phase.



$r_i = f(\text{temp}^x, \text{conc}^n)$

Reactant  $\rightarrow$  Product.



$(-r_A) \text{ or } (r_A^-) = -\frac{1}{V} \frac{dN_A}{dt}$

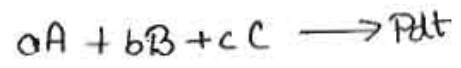
$dN_A = N_{Af} - N_{A0}$   
 $= -ve$

rate of formation of B  $r_B = \frac{1}{V} \frac{dN_B}{dt}$

or  
rate of rxn based on B

$dN_B = dN_{Bf} - N_{B0}$   
 $= +ve$

Power Law:-



$r_i = k C_A^x C_B^y C_C^z \dots$

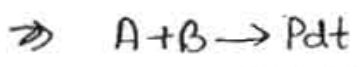
$r_i = k \prod C_i^{\alpha_i}$

overall order of rxn  
 $n = \sum \alpha_i$

$k$  = sp. rxn rate or rate constant.

$C_i$  = Conc<sup>n</sup> of 'i'

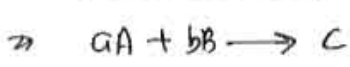
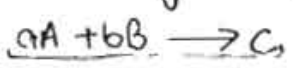
$\alpha_i$  = Apparent order of reactant



$-r_A = k C_A^x C_B^y = -\frac{1}{V} \frac{dN_A}{dt}$

Elementary rxns:-

which proceeds in single step



$-r_A = k C_A^x C_B^y$