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CHEMICAL KINETICS

* Catalyst ⇒ give new path to the rxns. ☆ ΔH remains same.

Speed or rate of the reactions.

RATE OF RXNS :-

Change in conc^n or pressure of the reactants or products per unit time.

$$\text{Rate} = \frac{\text{change in Conc}^n \text{ or Pressure}}{\text{Time taken}}$$

UNITS OF RXN

$\frac{\text{molarity}}{\text{time}}$ = mol L^{-1} sec^{-1} or mol L^{-1} min^{-1}

$\frac{\text{Pressure}}{\text{time}}$ = atm sec^{-1} or bar sec^{-1}

AVERAGE RATE OF RXN

$R \longrightarrow P$

defined over an interval of time.

Change in concentration = ΔC $= C_2 - C_1$

Time taken = $t_2 - t_1$

$$\text{Rate} = \frac{-C_2 - C_1}{t_2 - t_1} = \frac{-\Delta C}{\Delta t}$$

Note; Rate can never be negative

INSTANTANEOUS RATE

→ defined at an instant of time.

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

Eg = $A + B \longrightarrow C + D$

$$\text{Rate} = -\frac{d[A]}{dt} = -\frac{d[B]}{dt} = \frac{d[C]}{dt} = \frac{d[D]}{dt}$$

Rate is defined for one mole.

Rate of disapearence :-

Reactant, A & B

$-\frac{d[A]}{dt}$, $-\frac{d[B]}{dt}$

Rate of appearence :-

Products, C & D

$\frac{d[C]}{dt}$, $\frac{d[D]}{dt}$

RATE LAW :-

Rate of a Rxn is proportional to the product of molar concentration of reactant which each term raised to the power that has been found experimentaly.

$aA + bB \longrightarrow$ Products

Rate $\propto [A]^x [B]^y$

Rate = $K[A]^x [B]^y$

ORDER:

$aA + bB \longrightarrow$ Products

Rate = $K[A]^x[B]^y$

Order = $x + y$

NOTE; order can be +ve, -ve and even zero.

UNIT OF RATE CONST K:

→ $k = \left(\frac{mol}{L}\right)^{1-n} sec^{-1}$ n = order

zero order = $n = 0$ K = mol L^{-1} sec^{-1}

1st order = $n = 1$ K = sec^{-1}

In terms of pressure;

↳ $\{K = atm^{1-n}\ sec^{-1}\}$

ELEMENTARY REACTION

→ which completes in one single step.

→ order = Stoichiometric Coeff^n

Eg – $2A + 3B \longrightarrow$ Product

Rate = $K[A]^2[B]^3$

NOTE; Zero order Rxn can never be an elimentary reactions.

COMPLEX REATIONS :-

→ completed in multiple steps.

→ Slowest step = Rate determining step. (RDS)

$A + B \longrightarrow$ Product

$A + B \longrightarrow$ C (slow) RDS

$C \longrightarrow$ Product (fast)

'C' is Rxn intermediate

MOLECULARITY

→ No of reacting species participating in an elementary reaction.

elementary; $2H_2 + O_2 \longrightarrow 2H_2O$

molecularity = 2 + 1 = 3

Rarely goes above 3.

ZERO ORDER RXN :-

$R \longrightarrow P$

Rate = $K[R]^n \Rightarrow K[R]^0 = k$

$A \longrightarrow B$

t=0	A_0
⋮	
t=t	A_t

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

$A_t = A_0 - kt$ → integrated Rate law.

Half life ⇒ $t_{1/2} = \frac{A_0}{2k}$

FIRST ORDER RXNS :-

→ $n = 1$

$A \longrightarrow$ Product

Rate = $K[A]^n = K[A]^1$

t=0	A_0
⋮	
t=t	A_t

$\text{Rate} = -\frac{d[A]}{dt} = K[A]^1$

$A_t = A_0 e^{-kt}$

$k = \frac{2.303}{t} \log \frac{A_0}{A_t}$

Half life ⇒ $t_{1/2} = \frac{\ln 2}{K}$ ($\ln 2 = 0.693$)

↳ indipendent of conc^n

PSEUDO FIRST ORDER

→ Bimolecular Reaction

→ Appears to be of 2nd order but acctually is 1st order.

→ One of the reactant in excess.

Eg – hydrolysis of ester ($CH_3COOC_2H_5$)

order = 1.

COLLISION THEORY

→ Effective Collision :-

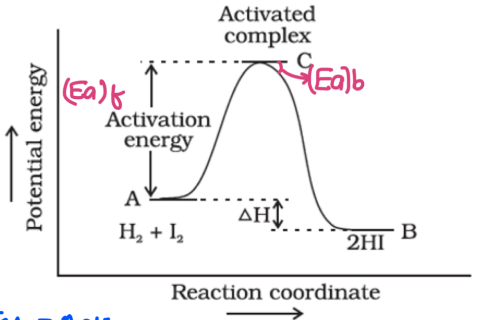
100 collisions → 2-3 only are effective.

→ Energy criteria; $R \longrightarrow P$

ΔH +ve (endothermic) $H_P > H_R$

ΔH -ve (exothermic) $H_P < H_R$

$\{\Delta H = H_P - H_R\}$



Eaf = Activation energy of forward reaction

Eab = Activation energy of backward reaction.

HOW RATE DEPENDS ON TEM

→ Arrhenius = $K = Ae^{-Ea/RT}$

A = Arrhenius constant

R = universal gas constant

T ↑ = K ↑↑ ⇒ Rate ↑↑

Temperature coefficient(μ):-

→ on increasing the temp by 10°C the rate increases by 2 times

$\mu = \frac{K_T + 10}{K_T}$

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