Chemical kinetic

* what is rate of reaction? state the rate laws.

⇒ The rate of reaction is defined as the change in concentration of any of reactants or products per unit time.

Let us consider a reaction –

$A \longrightarrow B$

For the given reaction the rate of reaction may be equal to the rate of di-sappearance of A which is equal to the rate of appearance of B.

$$\therefore \text{rate} = -\frac{d[A]}{dt} = +\frac{d[B]}{dt}$$

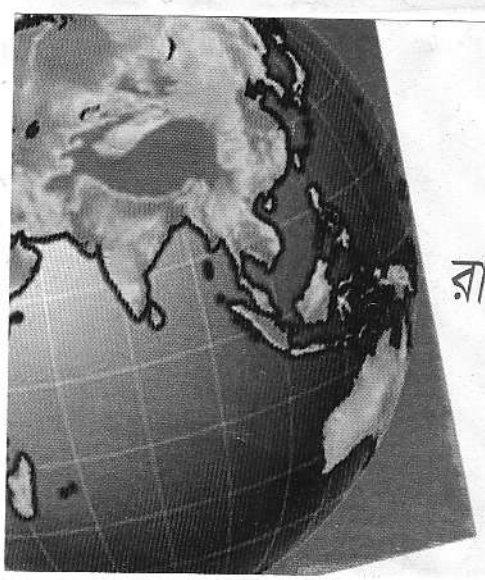
$$\Rightarrow \text{rate} = -\frac{dc}{dt} = \frac{dx}{dt} \quad (m/L)$$

⇒ The rate of reaction is directly proportional to the reactant concentrations, each concentration being raised to some power.

. Thus for a substance A undergoing reaction,

$$\text{rate} \propto [A]^n$$

$$\Rightarrow \text{rate} = K[A]^n$$



ইসলাম একটি বিপ্লব
কুরআন সেই বিপ্লবের মূলমন্ত্র
রাসূল (সা) সেই বিপ্লবের সিপাহসালার
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বাংলাদেশ ইসলামী ছাত্রশিবির
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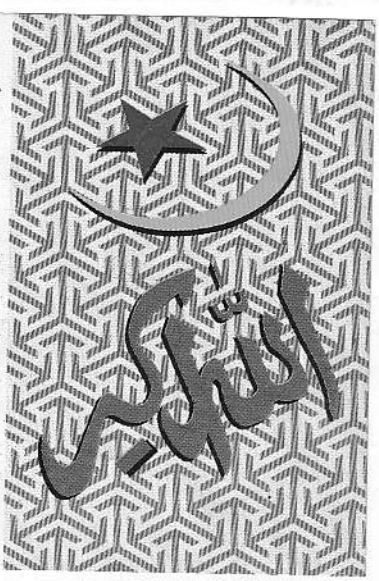

* Define molecularity and order of reaction.

⇒ The molecularity of a reaction is defined as the number of atoms or molecules of all the species participating in the reaction.

For example:

Reaction	molecularity
$PCl_5 \longrightarrow PCl_3 + Cl_2$	1
$2FeCl_3 + SnCl_2 \longrightarrow 2FeCl_2 + SnCl_4$	3

⇒ The order of reaction is defined as the number of atoms or molecule whose concentrations determine the rate of reaction.

For example -

Reaction	order
$2N_2O_5(g) \longrightarrow 4NO_2(g) + N_2(g)$	1
$H_2 + I_2 \longrightarrow 2HI$	2

* Disguise between order and molecularity.

⇒

order	molecularity
i) Defination	i) Defination
ii) It is an experimental concept.	ii) It is a theoritical concept.
iii) It can have fractional value	iii) It's value always be whole number.
iv) It can assume zero value.	v) It can not have zero value.

* Define zero order reaction. Show that in a zero-order reaction, rate is independent of the concentration of the reactants.

⇒ A zero-order reaction is one whose rate is independent of concentration of reactant means the reaction moves at a constant rate.

⇒ Let us consider a zero-order reaction-

$A \longrightarrow$ product

Let, a mole/L be the initial concentration of A and x mole/L is converted to product after t second and final concentration be (a-x) mole/L.

∴ rate of reaction, $\frac{dx}{dt} \propto (a-x)^0$

$\Rightarrow \frac{dx}{dt} = K_0(a-x)^0$ | K_0 = constant ——— (i)

$\Rightarrow \frac{dx}{(a-x)^0} = K_0 dt$

By integrating we get,

$\int dx = \int K_0 dt$ | $\because (a-x)^0 = 1$

$\Rightarrow x = K_0 t + C$ ——— (ii)

From initial condition ($t=0$; $x=0$;)

$C = 0$

$\therefore x = K_0 t$ | K_0 = rate constant of a zero-order reaction ——— (iii)

From equation (i) we can say, in a zero-order reaction rate is independent of reactants concentration.

The equation (iii) be the equation of zero-order reaction.

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By integrating we get;

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* What is first-order reaction? Derive a 1st order rate constant equation of the following equation:
$A \longrightarrow$ product.

⇒ The first order reaction is defined as the reaction rate is determined by only one variable's concentration.

Reaction: $A \longrightarrow$ product

a mol/L	0
(a−x) mol/L	x

According to law of mass-action,

$$\frac{dx}{dt} \propto (a-x)$$

$$\Rightarrow \frac{dx}{dt} = k(a-x) \quad \text{---------- (1)}$$

where k = the rate constant of first-order reaction

By integrating, $\int \frac{dx}{a-x} = \int k\,dt$

$\Rightarrow -\ln(a-x) = kt + c$ | c = proper/integrating constant

when $t=0$ and $x=0$, then

$-\ln a = c$

$\therefore -\ln(a-x) = kt - \ln a$

$\Rightarrow kt = \ln a - \ln(a-x) = \ln \frac{a}{a-x}$

$\therefore k = \frac{1}{t} \ln \frac{a}{a-x}$

This is the equation of rate constant of first-order reaction.

* What is half life of reaction? Show that half life of a first order reaction is independent of initial concentration or, it is inversely proportional to k.

⇒ The half life of a reaction is defined as the time required for the concentration of a reactant to decrease to half its initial value. It is noted by $t_{1/2}$.

⇒ We know that, the rate constant of first order reaction –

$$k = \frac{1}{t} \ln \frac{a}{a-x} \quad \text{---------- (i)}$$

Let $t_{1/2}$ be the time required when $x = a/2$.

So, $t = t_{1/2}$

From equation (i)

$$k = \frac{1}{t_{1/2}} \ln \frac{a}{a - a/2}$$

$$\Rightarrow k = \frac{1}{t_{1/2}} \ln 2$$

$$\Rightarrow t_{1/2} = \frac{\ln 2}{k}$$

$$\therefore t_{1/2} \propto \frac{1}{k} \quad \text{[where } \ln 2 = \text{constant]}$$

So, the half life of a reaction which is first order is independent of initial concentration or, it is inversely proportionate to k.

* Mention the properties of first order reaction.

⇒ The properties of first order reaction are given below-

i) First order reaction is never completed.

ii) The time taking for the completion half of a given reaction is independent of initial concentration of reactant.

iii) A change in concentration unit with not alter the rate constant.

* Show that the first order reaction is completed by infinite time.

we know,

The equation of rate constant of first order reaction

$$K = \frac{1}{t} \ln \frac{a}{a-x} \quad \text{---------- (i)}$$

Let $a = c_0$ and $a - x = c$

$\therefore \ln \frac{c_0}{c} = Kt$

$\Rightarrow \frac{c_0}{c} = e^{Kt}$ ---------- (ii)

when the reaction completes, $c = 0$.

$\therefore \frac{c_0}{0} = e^{Kt}$

$\Rightarrow e^{Kt} = \infty$

Since $K \neq 0$ and $K \neq c_0$

$t = \infty$.

Thus 1st order reaction gets completed in infinite time.

* What is second-order reaction? Derive a equation of rate constant of second order reaction when two reactants are same.

⇒ A reaction is said to be of second order when its rate depends upon two concentrations terms which may or may not same.

⇒ For same reactants, consider a second order reaction –

$$2A \longrightarrow \text{product}$$

t=0	a	0
t=t	a-x	x

Suppose, the initial concentration of A is a mole/L and after t time, x moles of A have reacted, the concentration of A is (a-x)

Thus,

$$-\frac{dx}{dt} \propto (a-x)^2$$

$$\Rightarrow \frac{dx}{dt} = K(a-x)^2$$

$$\Rightarrow \frac{dx}{(a-x)^2} = K dt$$

Integrating, $\frac{1}{a-x} = Kt + I$ ——— (1)

At the initial position,
t = 0 and x = 0

$\therefore \frac{1}{a} = I$

Now, $\frac{1}{a-x} = Kt + \frac{1}{a}$

$\Rightarrow K = \frac{1}{t} \frac{x}{a(a-x)}$ ——— (2)

This is the required equation.

* Deduce an expression for the rate constant of the following types of reaction— $A+B \longrightarrow$ product.

⇒ The given reaction—

	A + B	⟶	product
t = 0	a	b	0
t = t	(a−x)	(b−x)	x

Let a mole/L and b mole/L are the initial concentration of A and B respectively and x mole/L is the amount of each that has been reacted at time t.

Therefore,

$$\frac{dx}{dt} = k(a-x)(b-x)$$

$$\Rightarrow \frac{dx}{(a-x)(b-x)} = k\,dt \quad \Rightarrow \frac{1}{a-b}\left\{\frac{1}{b-x} - \frac{1}{a-x}\right\}dx = k\,dt$$

Integrating,

$$\frac{1}{a-b}\ln\frac{a-x}{b-x} = kt + I \qquad \text{---------- (i)}$$

When $t=0$, $x=0$

we get from (i)

$$I = \frac{1}{a-b}\ln\frac{a}{b}$$

$$\therefore \frac{1}{a-b}\ln\frac{a-x}{b-x} = kt + \frac{1}{a-b}\ln\frac{a}{b}$$

$$\Rightarrow \frac{1}{a-b}\ln\frac{b(a-x)}{a(b-x)} = kt$$

$$\therefore \text{Ans } K = \frac{1}{t(a-b)}\ln\frac{b(a-x)}{a(b-x)} \qquad \text{---------- (ii)}$$

This is the required equation.

* Show that the half life of 2nd order reaction is inversely proportional to rate / initial concentration.

⇒ We know,

The equation of 2nd order reaction:

$$K = \frac{1}{t} \frac{x}{a(a-x)}$$

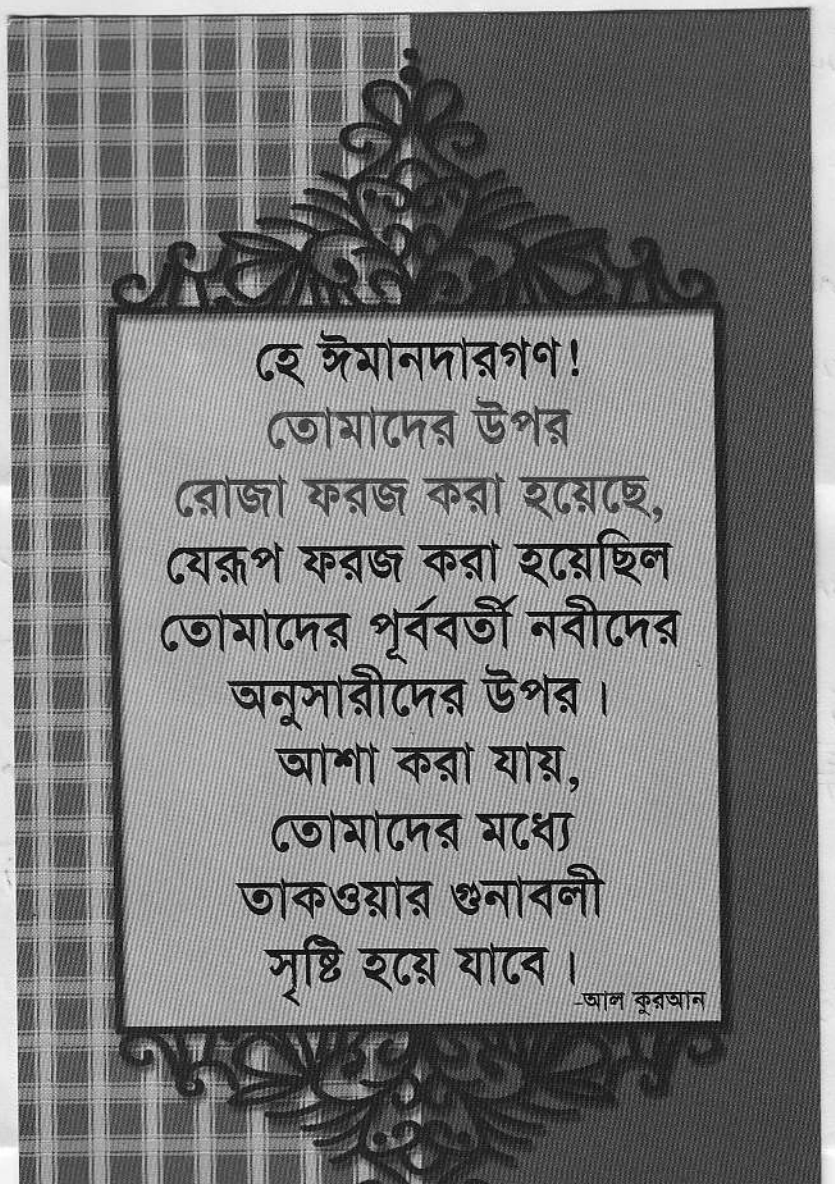
$$\Rightarrow t = \frac{1}{K} \cdot \frac{x}{a(a-x)}$$

Let half life $= t_{1/2}$ which is calculated when $x = a/2$

$$\therefore t_{1/2} = \frac{1}{K} \frac{a/2}{a(a-a/2)}$$

$$\Rightarrow t_{1/2} = \frac{1}{K} \cdot \frac{1}{a}$$

$$\therefore t_{1/2} \propto \frac{1}{K}$$



* How does the rate constant for a reaction vary with temperature.

Or, Temperature dependence of reaction rate and Arrhenius equation.

According to vant-Hoff's equation -

$$\frac{d\ln K}{dt} = \frac{\Delta E_a}{RT^2}$$

K = equilibrium constant
K_1 = rate constant of forward
K_2 = rate constant of backward

$$\Rightarrow \frac{d\ln\left(\frac{K_1}{K_2}\right)}{dt} = \frac{\Delta E}{RT^2}$$

$\Delta E = E_1 - E_2$

$$\Rightarrow \frac{d\ln K_1}{dT} - \frac{d\ln K_2}{dT} = \frac{\Delta E}{RT^2} = \frac{E_1 - E_2}{RT^2} \quad \text{(I)}$$

The equation can be devided into two equation

$$\frac{d\ln K_1}{dT} = \frac{E_1}{RT^2} + \text{const} \quad \text{(II)}$$

and $$\frac{d\ln K_2}{dT} = \frac{E_2}{RT^2} + \text{const} \quad \text{(III)}$$

Taken the value of constant is zero.

The equation may be expressed in general -

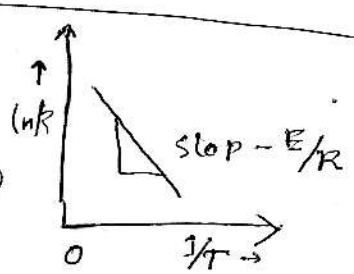
$$\frac{d\ln k}{dT} = \frac{d\ln E}{RT^2}$$

Here k = rate constant
E = activation energy

$$\therefore \ln k = -\frac{E}{RT} + \text{Const} \quad \text{(IV)}$$

From (I), $\ln K_1 = -\frac{E}{RT_1} + \text{const}$ (V)

and $\ln K_2 = -\frac{E}{RT_2} + \text{const}$ (VI)



From (V) and (VI)

$$\ln \frac{K_2}{K_1} = \frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\log \frac{K_2}{K_1} = \frac{E}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) = \frac{E}{2.303R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$$