CHEMICAL KINETICS

I. If $aA + bB \rightarrow cC$

Then instanteneous rate of reaction

$$= -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = \frac{1}{c}\frac{d[C]}{dt}$$

II. If rate of reaction = $k\,[A]^{l}\,[B]^{m}\,[C]^{n}$

Then overall order of reaction = $l + m + n$

III. Units of rate constant (k) for

Zero order reaction = mol L^{-1} s^{-1}

First order reaction = s^{-1}

Second order reaction L mol^{-1} s^{-1}

Third order reaction = L^{2} mol^{-2} s^{-1}

Third order reaction = $L^2\ mol^{-2}\ s^{-1}$
n^{th} order reaction = $(mol\ L^{-1})^{1-n}\ s^{-1}$

IV. $K_1 = \frac{2.303}{t} \log \frac{[A_0]}{[A]} = \frac{2.303}{t} \log \frac{a}{a-x}$

V. $t_{1/2} = \frac{0.693}{k_1}$

VI. $k = Ae^{-Ea/Rt}$ (Arrhenius equation)

VII. Rate of reaction is always a positive quantity.

VIII. Rate law is the experimentally determined expression that represents the relation between reaction rate and concentration of the reactants.

IX. Instantaneous rate of reaction at any time can be determined by the slope of the tangent at a point on concentration vs. time curve corresponding to that time.

X. If time interval is very small, then average rate of reaction equals instantaneous rate of reaction.

XI. Units of rate constant for gaseous reactions are:
For first order reaction = s^{-1}.
For second oreder reaction = $atm^{-1} s^{-1}$.
For third order reaction = $atm^{-2} s^{-1}$.

XII. Unit of rate constant for nth order reaction are,

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

XIII. Collision frequency is the number of collisions that take place per second per unit volume of the reaction mixture.

XIV. Boltzamann factor = $e^{-Ea/RT}$.

XV. The catalyst does not change the heat or energy of reaction.

XVI. Einstein's law of photochemical equivalence states that absorption of one photon of light activates 1 atom. or 1 molecule.

XVII. Smaller the particle size, greater is the rate of reaction.

XVIII. First order reaction has a constant half-

XIX. The rate constant is a measure of the number of activated molecules per unit volume per second.

Law of Mass Action

1. For a reversible reaction : $A + B \rightleftharpoons C + D$,

$$K_C = \frac{[C][D]}{[A][B]}$$

2. For a general reversible reaction : $aA + bB \rightleftharpoons cC + dD$

$$K_C = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b} \text{ and } K_P = \frac{P_C^c \times P_D^d}{P_A^a \times P_B^b}$$

3. $K_P = K_C(RT)^{\Delta n}$
where, Δn = Change in no. of moles = No. of moles of product – No. of moles of reactants

If $\Delta n > 0$, $K_P > K_C$.$[PCl_5 \rightleftharpoons PCl_3 + Cl_2]$

If $\Delta n < 0$, $K_P < K_C$.$[N_2 + 3H_2 \rightleftharpoons 2NH_3]$

If $\Delta n = 0$, $K_P = K_C$.$[2HI \rightleftharpoons H_2 + I_2]$

where, K_C = concentration equilibrium constant

and K_P = Partial pressure equilibrium const.

- Rate of decay $\left(\frac{dN}{dt}\right) = -\lambda N$; where λ is called decay constant or disintegration constant. – ve sign indicates that N decrease with lapse of time.
- $T_A = \frac{1}{\lambda}$; where T_A is mean life or average life.
- $T_{1/2} = 0.693 \times T_A = 69.3\%$ of T_A; where $T_{1/2}$ is half life
- $T_{1/2} = \frac{0.693}{\lambda} = \frac{\log_e 2}{\lambda}$
- $\frac{N}{N_o} = \left(\frac{1}{2}\right)^n$

where, N_o = Original number or amount of nuclei, N = Number of undisintegrated nuclei after lapse of time t

N = Number of half lives passed and $n = t/T_{1/2}$.

- % Radioactivity = $\left(\frac{1}{2}\right)^n \times 100$
- **Remember :** Full life > Average life > Half life
- **Unit of Radioactivity**

(a) Curie : It is the quantity of a radioactive substance which gives 3.7×10^{10} disintegrations /sec.

1 Curie = 3.7×10^{10} disintegrations/sec

1 Milli Curie (10^{-3} Curie) = 3.7×10^{7} disintegrations/sec

(b) Rutherford : It is the quantity of a radioactive material which gives 10^{6} disintegrations/sec.

1 Rutherford = 10^{6} disintegrations/sec

1 Milli Rutherford = 10^{3} disintegrations/sec

1 Micro Rutherford = 1 (one) disintegrations/ sec

(c) **Becquerel :** It is the quantity of a radioactive element which gives 1 (one) disintegration per second.

- **Photo-electric effect :** The phenomenon of emission of electrons from the surface of metals when light radiations of suitable frequency fall on them, is called photo-electric effect.

Laws of Photo-electric Effect

(*i*) For a given metal, there exists a certain minimum frequency of the incident light radiations (called as threshold frequency) below which no emission of photo-electrons takes place.

(*ii*) The number of photo-electrons emitted per second (i.e., photo-electric current) is directly proportional to the intensity of the incident light and is independent of its frequency.

(*iii*) The emission of photo-electrons is an instantaneous process, i.e., it starts immediately as the light falls on the surface of the metal.

Factors Influencing Rate of Chemical Reactions

Following factors are influencing the rate of chemical reactions:

(*a*) *Concentration of the reactants:* Reaction rate increases with the increase of concentration of the reactatns.

(*b*) *Nature of reactants*

(*c*) *Temperature:* Reaction rate increase with the rise of temperature of the reactants.

(*d*) *Surface area:* The larger the surface area, the faster is the reaction rate.

(*e*) *Presence of a catalyst*: Catalyst increases the rate of reaction.

(*f*) *Exposure to radiation:* Generally, exposure to radiation increases the rate of reaction.

Concentration of the Reactants

Rate of chemical reaction increases with the increase of concentration of the reactants.

According to law of mass action, at the given temperture the rate of a chemical reaction is directly proporational to the product of the molar concentration of the reactants.

Consider the following general equation,

$$aA + bB \rightarrow \text{products}$$

According to the law of mass action (theoretical concept),

Rate of reaction = k $[A]^a$ $[B]^b$.

But the rate of reaction depends upon the experimentally determined value 'l' concentration term of A and 'm' concentration term of B.

But experimentally, the rate of reaction is given by the rate law as:

Rate of reaction = k $[A]^l$ $[B]^m$

Where, k = rate-constant

l and m = order of reaction with respect of A and B respectively.

Differences Between Rate of Reaction and Rate-constant

Rate of reaction	Rate-constant
I. Rate of reaction is the rate of disappearance of a reactant or rate of appearance of a product.	I. Rate constant is a proportionality constant in the rate law and is equal to rate of reaction when the concentration of reactant is unity.
II. It is dependent upon the concentration of the reactants.	II. It is independent of the initial concentration of the reactants.
III. Its unit is mol L^{-1} s^{-1}.	III. The unit of rate constant depends upon the order of the

Order of Reaction

Order of reaction is defined as the sum of powers of the concentration terms in the experimentally determined rate equation.

The order of above reaction = $l + m$

Depending upon whether $l + m$ is 0, 1, 2 or 3 the reaction is said to be zero order, Ist order, 2nd order or 3rd order.

I. **Zero order reaction:** When the reaction-rate is independent of the concentration of the reacting species, the reaction is known to be zero order reaction.

Here, $2\,HI\,(g) \rightarrow H_2\,(g) + I_2\,(g)$

Unit of rate constant (k) for zero order reaction:

$$\text{Rate} = k\,[A]^\circ = k$$

So, $k = \text{mol L}^{-1}\,\text{s}^{-1}$

II. **First order reaction:** When the reaction-rate is dependent upon the one concentration term of the reacting species, the reaction is known to be a first order reaction. Now.

$$A \rightarrow \text{Product}$$

$$\text{Rate} = k\,[A]$$

Here, $2N_2O_5\,(g) \rightarrow 4NO_2\,(g) + O_2\,(g)$

$$\text{Rate} = k\,[N_2O_5]$$

Unit of rate constant (k) for first order reaction:

$$\text{Rate} = k\,[A]$$

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

$$k = \text{s}^{-1}.$$

III. **Second order reaction:** When the reaction rate is dependent upon the two concentration terms of the reacting species, the reaction is said to be a second order reaction. Now,

$$A + A \rightarrow \text{product}$$

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

Here, $2NO_2\,(g) + F_2\,(g) \rightarrow 2NO_2F\,(g)$.

$$\text{Rate of reaction} = k\,[NO_2]\,[F_2]$$

The order of raction = 1 + 1 = 2.

Unit of rate constant (k) for second order reaction:

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

$$\text{mol L}^{-1}\,\text{s}^{-1} = k\,[\text{mol L}^{-1}]^2$$

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

IV. **Third order reaction:** When the reaction rate is dependent upon the three concentration terms of the reacting species, the reaction is said to be a third order reaction. Now,

$$A + A + A \rightarrow \text{product}$$

$$\text{Rate} = k\,[A]^3$$

Here, $2NO\ (g) + O_2\ (g) \rightarrow 2NO_2\ (g)$

$$\text{Rate of reaction} = k\,[NO]^2\,[O_2]^1.$$

The order of reaction = 2 + 1 = 3.

Unit of rate constant (k) for third order reaction :

$$\text{Rate} = k\,[A]^3$$

$$\text{mol L}^{-1}\,\text{s}^{-1} = k\,[\text{mol L}^{-1}]^3$$

$$k = \text{L}^2\,\text{mol}^{-2}\,\text{s}^{-1}.$$

V. **Fractional order of reaction:** As the rate of reaction is dependant upon the experimentally determined concentration terms of reacting species and not on the stoichiometric coefficients in the balanced equation, so order of reaction can be fractional also.

e.g., $CH_3CHO(g) \xrightarrow{723\,K} CH_4(g) + CO\ (g)$

$\text{Rate} = k\,[CH_3CHO]^{3/2}$