BRUSH UP YOUR CONCEPTS

Class XII

This specially designed column will help you to brush up your concepts by practicing questions. You can mail us your queries and doubts related to this topic at editor@mtg.in. The queries will be entertained by the author.*

CHEMICAL KINETICS

- The change in molarity of a reactant or a product in unit time is called rate of reaction.

  For $aA \longrightarrow bB$,

  $$\text{Average rate of consumption of } A = -\frac{\Delta[A]}{\Delta t}$$

  $$\text{Average rate of production of } B = +\frac{\Delta[B]}{\Delta t}$$

  $$\text{Average rate of reaction } = -\frac{1}{a}\cdot\frac{\Delta[A]}{\Delta t} = +\frac{1}{b}\cdot\frac{\Delta[B]}{\Delta t}$$

  Instant rate of consumption of A

  $$= -\lim_{\Delta t\to 0}\frac{\Delta[A]}{\Delta t} = -\frac{d[A]}{dt}$$

  Instant rate of production of B

  $$= +\lim_{\Delta t\to 0}\frac{\Delta[B]}{\Delta t} = +\frac{d[B]}{dt}$$

  $$\text{Instant rate of reaction} = -\frac{1}{a}\cdot\frac{d[A]}{dt} = +\frac{1}{b}\cdot\frac{d[B]}{dt}$$

- Rate of a reaction is affected by the nature of reactants, their concentration or pressure, surface area, temperature, catalyst and effect of light.
- For the reaction, $aA + bB \rightarrow$ Products.

  Experimentally, rate $(r) = k[A]^x\,[B]^y$ [Rate law]

(a) If x and y are equal to a and b respectively, the reaction is a single step (elementary reaction) otherwise it has some mechanism.

(b) x and y are orders of reaction w.r.t. A and B and $x + y$ is the net order of the reaction.

(c) k is the rate constant and has a fixed value at a given temperature. Increase in temperature increases the value of k. Faster reactions have higher value of k.

(d) Order can be +ve, –ve, whole number or a fraction.

- **Zero order reactions :**

(a) Reaction of $H_{2(g)}$ and $Cl_{2(g)}$ in diffused sunlight.

(b) Decomposition of $NH_{3(g)}$ over Pt, W, Au, etc. at high pressure.

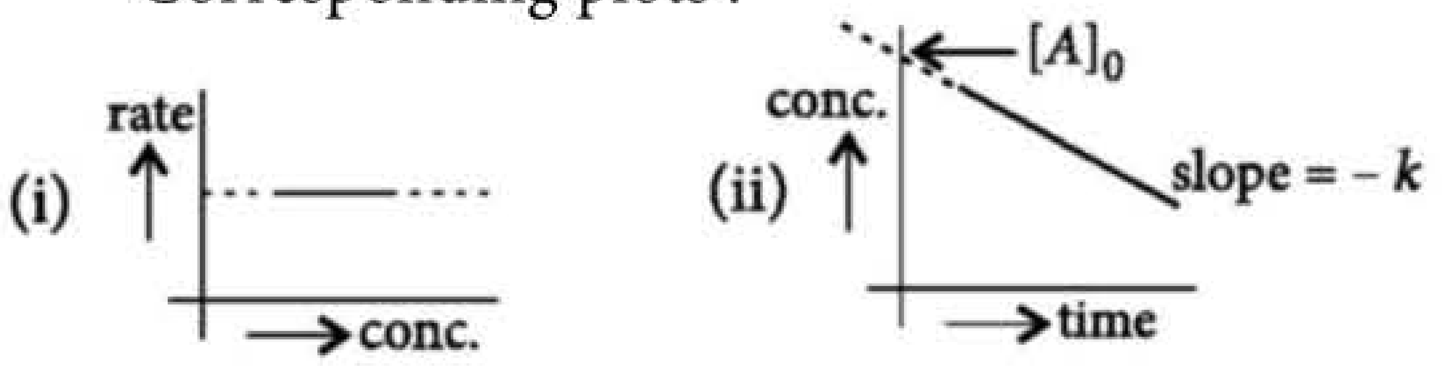
(c) One free radical reacts with another.

For a zero order reaction, $A \rightarrow$ Products

$$-\frac{d[A]}{dt} = k[A]^0 \qquad \text{...(i)}$$

$$[A] = -kt + [A]_0 \qquad \text{...(ii)}$$

Corresponding plots :



$$k = \frac{[A]_0 - [A]}{t} = \frac{x\,(\text{consumption, mol L}^{-1})}{t\ (\text{time})} \qquad \text{...(iii)}$$

$$t_{1/2} = \frac{[A]_0}{2k} \qquad \text{...(iv)}$$

For $t_{100\%}$, $[A] = 0$; $t_{100\%} = \dfrac{[A]_0}{k} = 2t_{1/2}$

- **First order reactions :**

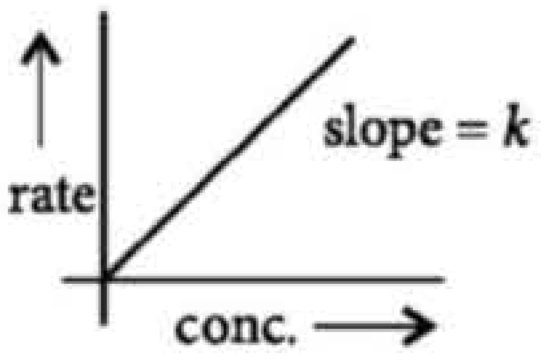
(a) All nuclear disintegrations

(b) Thermal decomposition of $N_2O_{5(g)}$, $H_2O_{2(l)}$ and $NH_4NO_{2(s)}$

(c) Growth of population if rate of birth and rate of death do not change.

For a first order reaction,

$A \rightarrow$ Products



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

$$kt = \ln\frac{[A]_0}{[A]};\ [A] = [A]_0\,e^{-kt};$$

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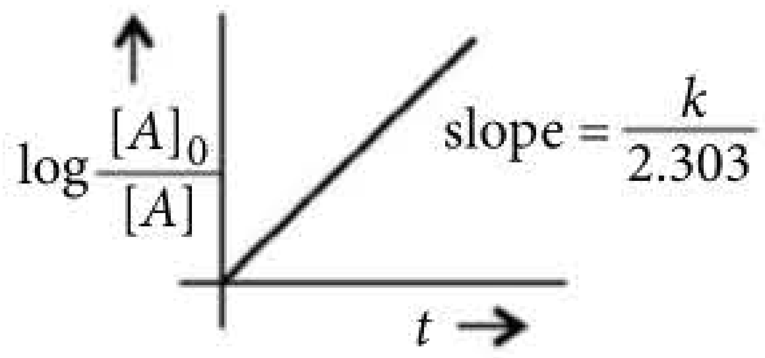
*By **R.C. Grover**, having 45+ years of experience in teaching chemistry.

$$kt = 2.303 \log \frac{[A]_0}{[A]}$$



$$[A] = [A]_0 \times 10^{-\frac{kt}{2.303}}$$

$$t_{1/2} = \frac{2.303}{k} \log \frac{[A]_0}{[A]_0/2} = \frac{2.303 \log 2}{k} = \frac{0.693}{k}$$

$t_{1/2}$ is independent of initial concentration.

- $t_{1/2}$ is always proportional to $[A]_0^{1-n}$.
- **Pseudo first order reaction :** If the molecularity of balanced equation of reaction is not one but the rate law has first order with respect to any one reactant while other reactants do not appear in the rate law, the reaction is pseudo first order reaction. *e.g.*, hydrolysis of ester, inversion of cane sugar, etc.
- For determination of order of reaction, integrated rate law, simple rate law (Ostwald isolation method) or initial concentration method can be applied.
- The number of molecules of reacting species that collide simultaneously to bring about a chemical reaction is called its molecularity.

Common molecularities are 1, 2 or 3. Higher molecularity is rarely available, *e.g.*, 12 for $5Br^-_{(aq)} + BrO_3^-{}_{(aq)} + 6H^+_{(aq)} \rightarrow 3Br_{2(aq)} + 3H_2O_{(l)}$

- Units of rate constant : $mol^{1-n}\ L^{n-1}\ s^{-1}$
- **Effect of temperature on rate of reaction :**

Arrhenius theory,

Temperature coefficient, $\mu = \frac{k_{(T+10)}}{k_T} = 2$ (generally)

$$\frac{\text{new rate}}{\text{old rate}} = (\mu)^{\frac{\Delta T}{10}}$$

Fraction of molecules $\left(\frac{n}{N}\right)$ having received energy equal to or more than E_a(activation energy) at temperature T (kelvin) was given by Arrhenius. Here, A is Arrhenius factor.

$$\frac{n}{N} = \frac{k}{A} = e^{-\frac{E_a}{RT}} \Rightarrow k = A\,e^{-\frac{E_a}{RT}}$$

$e^{-\frac{E_a}{RT}}$ or $\frac{n}{N}$ is called Boltzmann factor .

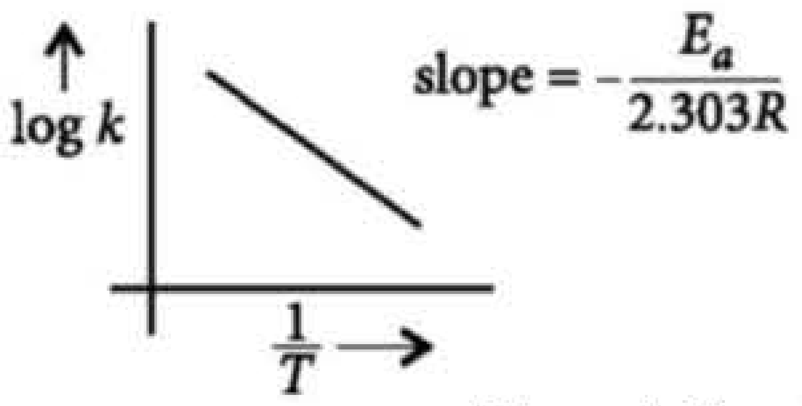
(a) T cannot be extremely high, that will give $k = A$, *i.e.*, all collisions produce products, which is not possible.

(b) E_a cannot be zero. It will again give $k = A$ as in (a).

(c) E_a cannot be less than zero. It will give $k >> A$ which is impossible.

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

Also, $\log k = -\frac{E_a}{2.303RT} + \log A$



At two different temperatures T_1 and T_2 where $T_2 > T_1$ and $\frac{k_2}{k_1} = \frac{r_2}{r_1}$

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$E_a = \frac{2.303R\,T_2T_1}{T_2 - T_1} \log \frac{k_2}{k_1}$$

- **Effect of catalyst :** $\frac{k_{\text{cat.}}}{k} = (e)^{(E-E_c)/RT} = (e)^{\Delta E/RT}$

$$\Delta E = 2.303RT \log \frac{k_c}{k}$$

- **Collision theory :** $\text{Rate} = PZ\,e^{-\frac{E_a}{RT}}$

P is probability for effective collisions.

Z is collision frequency (number of collisions per unit volume per second).

MULTIPLE CHOICE QUESTIONS

1. For the reaction, $A + B \rightarrow$ Products, it was found that 75% consumption of A needs double the time for 50% consumption. Regarding B, the time for 100% consumption is double that of its half life. The net order of reaction is

(a) 1.0 (b) 1.5 (c) 2.0 (d) 2.5

2. For a reaction, instantaneous rate of reaction is $-\lim_{\Delta t \to 0} \frac{\Delta[A]}{\Delta t}$. What does the negative sign show?

(a) Increase in concentration of substance A.
(b) Decrease in concentration of substance A.
(c) Concentration of substance does not change.
(d) The approach of Δt to zero is extremely slow.

3. Which of the following is not compulsorily increasing the rate of reaction?

(a) Increase in concentration of reactant
(b) Increase in surface area of reactant
(c) Increase in temperature of the reaction mixture
(d) Increase in wavelength of light falling on the mixture

4. Which of the following is not correct for rate constant?

(a) It has a fixed value for a given temperature.
(b) Higher the initial concentration, higher is the rate constant.
(c) Higher is the value of rate constant, faster is the reaction.
(d) Units of rate constant depend upon units of time and concentration and the order of reaction.