Chemical Kinetics

❖ Rate of Reaction:

The quantity of a reactant species consumed or the quantity of a product species formed in unit time in a chemical reaction is called the rate of the reaction.

Consider a reaction, $A \rightarrow B$

$$Rate = -\frac{d[A]}{dt} = +\frac{d[B]}{dt}$$

$-ve$ sign indicates that with progress of time concentration of A will decrease.

❖ Rate Laws & Rate Constant:

Let us consider a general reaction,

$$A + B \rightarrow Product$$

According to rate law,

$$Rate \propto [A][B]$$
$$Or, Rate = K[A][B]$$

This is known as rate law & $'K'$ is called rate constant which is independent of concentration but depend on temperature.

➢ Mention the factors affect the rate of a chemical reaction.

Factors affecting the rate of a chemical reaction are following –

i.   Nature of reactants
ii.   Concentration of reactants
iii.   Effect of temperature
iv.   Surface area of reactants
v.   Presence of catalyst
vi.   Presence of light

❖ Order of a Reaction:

Order of a reaction is defined as the sum of the powers or exponents to which the molar concentrations are raised in the rate law or rate equation.

Let us consider a general reaction,

$$lA + mB \rightarrow Product$$
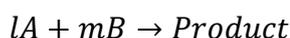
According to rate law,

$$R = K[A]^a[B]^b$$

where a & b may or may not be equal to l & m respectively. Here the overall order of the reaction is $(a + b)$.

- ✓ Order of a reaction is purely experimental quantity.
- ✓ Order of reaction may be fraction, zero or even negative. As for example, thermal decomposition of acetaldehyde,

$$CH_3CHO \rightarrow CH_4 + CO$$
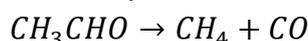
has order equal to $3/2$.

❖ Example of Reactions having Different Order:

I. <u>Zero order reaction</u>: Dissociation of ammonia on tungsten or dissociation of HI on gold surface.

II. <u>First order reaction</u>: Conversion of cyclopropane to propylene, substitution reaction of tertiary alkyl halide by nucleophile.

III. <u>Second order reaction</u>: $H_2 + I_2 \rightarrow 2HI$, substitution reaction of primary alkyl halide by nucleophile.

IV. <u>Fractional order reaction</u>: Thermal decomposition of acetaldehyde,
$$CH_3CHO \rightarrow CH_4 + CO$$
has order equal to $3/2$.
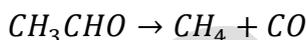
❖ Elementary Reaction:

A chemical reaction that takes place in one & only one step, i.e., all that occurs in a single step is called elementary reaction. For example –
$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$
$$2HI \rightleftharpoons H_2 + I_2$$
Molecularity of an elementary reaction is the number of the reactant particles that are involved in each individual chemical event.
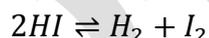
❖ Molecularity of Elementary Reaction:

It is defined as the number of reactant particles (atoms, molecules, free radicals or ions) that are involved in each individual chemical event.

If a reaction takes place in a number of steps then slowest step is usually the rate determining step. Molecularity of the rate determining step is said to be the molecularity of the reaction.

✓ Molecularity of a reaction is purely theoretical concept.

✓ Molecularity of a reaction is necessarily a positive integer.

➢ Elementary reactions with molecularity greater than three generally do not occur – justify.

The reactants are activated as a result of molecular collisions. But the collisions generally require high amount of energy because of inter – nuclear & inter – electronic repulsions. For a collision minimum two molecules are must. If the molecularity of an elementary step is 3, then three molecules must collide requiring high amount of energy. For a four – body collision, energy required will be still higher & therefore unknown. It is far easier to have two – body collisions & that will take place easily. Therefore, elementary reaction of molecularity 4 or greater is unknown. If molecularity becomes greater than 3, then such reaction involve two or more steps, such that each step has its own molecularity not greater than 3.

❖Difference Between Molecularity & Order:

The main differences are –

I. Order is an experimental quantity whereas molecularity of a reaction is a purely theoretical concept.

II. Order of a reaction is not necessarily integer. It may be fraction, zero or even negative. Whereas molecularity of a reaction is necessarily a positive integer.

III. Order may change with physical condition, such as pressure, solvent etc whereas molecularity is an invariant number for a given chemical reaction.

➤ Give an example of a chemical reaction where molecularity & order is different.

$$CH_3CHO \rightleftharpoons CH_4 + C0$$
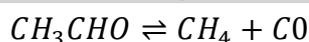
So, rate $= k[CH_3CHO]^{3/2}$. Here the order of the eaction is 1.5 but molecularity is 1. Hence order & molecularity is different.

❖Integrated Rate Laws:

1. **Zero Order Reaction**: A reaction whose rate is independent of concentration is called a zero order reaction. Thus for a zero order reaction –

$$A \rightarrow pdt.$$
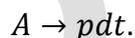
$$So, rate = -\frac{d[A]}{dt} = k[A]^0 = k$$

$$where\ [A]\ is\ the\ concentration\ of\ the\ reactant\ A\ at\ time\ t, thus -$$

$$\int_a^{[A[} d[A] = -k \int_0^t dt$$

$$Or, [A] - a = -kt$$

$$Or, [A] = a - kt$$

A zero order reaction will be completed when $[A] = 0, so,$

$$a - kt_{completion} = 0$$

$$Or, \boldsymbol{t_{completion}} = \left(\frac{\boldsymbol{a}}{\boldsymbol{k}}\right)$$

Graphical Representation: If we plot $[A]\ vs\ t$, we get a straight line with slope $= -k$.
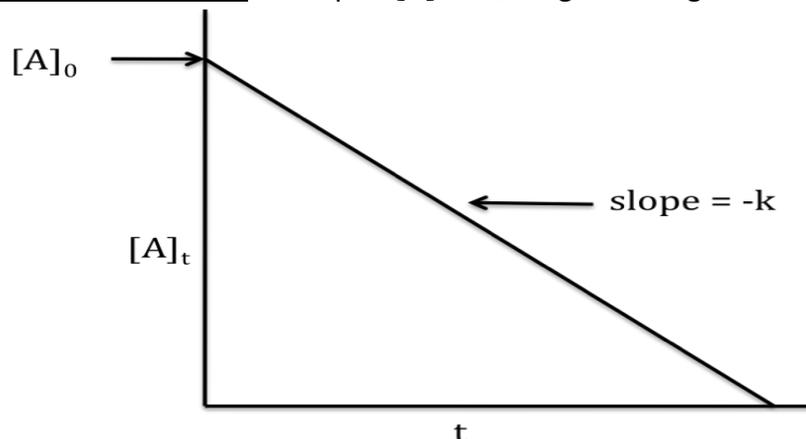
<u>Half – life period</u>: $When\ t = t_{\frac{1}{2}}, then, [A] = {}^{a}/_{2}, now -$

$$\frac{a}{2} = a - kt_{\frac{1}{2}}$$

$$Or, t_{\frac{1}{2}} = \left(\frac{a}{2k}\right), i.e.,\ t_{1/2} \propto a$$

<u>Unit of rate constant</u>: $mol.L^{-1}sec^{-1}$

<u>Characteristics</u>:

  I.   Rate is independent of instantaneous concentration of the reactant.
  II.   Unit of rate & rate constant are the same.
  III.   Zero order reaction must be multistep in nature.
  IV.   Zero order reaction can be completed in a finite time.
  V.   Half – life period is directly proportional to initial concentration of reactant.

➢ Write down the unit of the rate constant of a zero order reaction.

$$mol.L^{-1}sec^{-1}$$

➢ What do you mean by half-life period of a reaction?

The half-life of a reaction, $t_{1/2}$, is the amount of time needed for a reactant concentration to decrease by half compared to its initial concentration.

➢ Zero order reaction is multistep —Explain.

If zero order reaction is single step then the reaction would be an elementary reaction & in that case order of the reaction would be same as molecularity. But molecularity of a reaction cannot be zero. So zero order reaction must be a multistep reaction. The reactant with respect to which the order becomes zero is involved in a step which is not the rate determining step (r.d.s.).

➢ Does a zero order reaction go to completion?

Rate equation for a zero order reaction —

$$-\frac{dc}{dt} = kC^{0}$$

$Or, \int dc = - \int kdt$

$Or, C = -kt + IC$

$at\ t = 0, C = C_{0}, then\ IC = C_{0}$

$So, C = C_{0} - kt$

Hence, a zero order reaction will go to completion & time duration is $\frac{C_{0}}{k}$.

➢ For a reaction the plot of log $t_{1/2}$ versus log a turns out to be a straight line with positive slope and intercept, which makes an angle of 45^{0} with the log a axis. What is the order of the reaction?

We know half – life period of a nth order reaction is given as –

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

$$Or, \log t_{1/2} = \log k + (1 - n)\log a$$

Slope of $\log t_{1/2}$ $vs \log a = (1 - n)$.

So we can write –

$$(1 - n) = tan45^0 = 1$$
$$Or, n = 0$$

Hence the given reaction is a zero order reaction.

2. **First Order Reaction**: A first order reaction is one whose rate is linearly proportional to the instantaneous concentration of the reactant. Let us consider a first order reaction –

$$A \rightarrow B$$

Let initial concentration of reactant is $[A]_0 = a$ & $at\ an\ arbitrary\ time\ t$ it is $[A] = a - x$. Then the differential rate law is given as –

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

$$Or, \left(\frac{dx}{dt}\right) = k(a - x)$$

$$Or, \int_0^x \frac{dx}{(a - x)} = k \int_0^t dt$$

$$Or, \ln\left(\frac{a}{a - x}\right) = kt$$

$$Or, \log\left(\frac{a}{a - x}\right) = \frac{k}{2.303}t$$

$$Or, \boldsymbol{t = \frac{2.303}{k}\log\left(\frac{a}{a - x}\right)}$$

Graphical Representation: If we plot $\ln(^a/_{a} - x)\ vs\ t$, we get a straight line passing through the origin & slope $= k$.

Slope = k/2.303

$\log \dfrac{[A]_o}{[A]}$

Time →
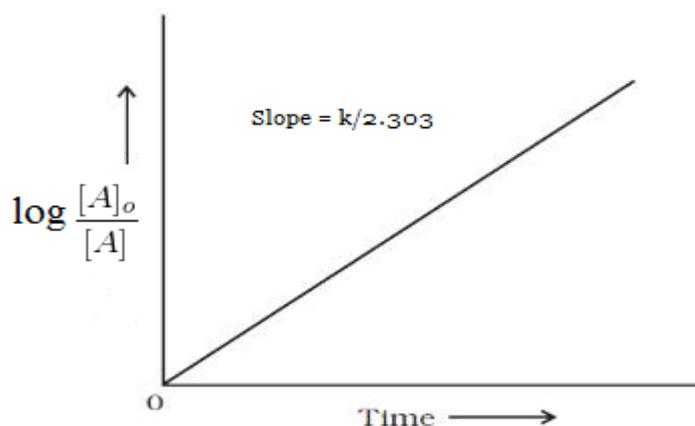
Half – life period: $When\ t = t_{\frac{1}{2}}, then, x = ^a/_2\ , from\ above\ equation$ –

$$t_{\frac{1}{2}} = \frac{2.303}{k}\log\left(\frac{a}{a - \frac{a}{2}}\right) = \frac{1}{k}\ln 2 = \frac{\boldsymbol{0.693}}{\boldsymbol{k}}$$

So, half – life period is independent of initial concentration of reactant.

Unit of rate constant: sec^{-1}

Characteristics:

    I.   First order reaction never goes to completion.

    II.   Half – life period is independent of initial concentration of reactant.

➤ First order reaction never proceeds to completion – justify or criticize.

For first order reaction –

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

When reaction will be completed then $[A]$ should be equal to zero & it will be possible only when $t = \infty$, so first order reaction never goes to completion.

➤ Show for a first order reaction, the time required for 99.9% completion of the reaction is almost 10 times the time for 50% completion.

For a first order reaction,

$$t = \frac{1}{k} ln \frac{a}{a-x} = \frac{2.303}{k} log \frac{a}{a - 0.999a}$$

$$Or, t = \frac{2.303}{k} log 10^3 = \frac{6.909}{k}$$

$$We\ know, t_{\frac{1}{2}} = \frac{0.693}{k}$$

$$So, \frac{t}{t_{\frac{1}{2}}} = \frac{6.909}{0.693} \cong 10.$$

$$Hence, t = 10 \times t_{1/2}\ (proved)$$

➤ Show that the time required for 75% completion of a first – order reaction is twice the time required for 50% completion of the reaction.

For a first order reaction,

$$t = \frac{1}{k} ln \frac{a}{a-x} = \frac{2.303}{k} log \frac{a}{a - 0.75a}$$

$$Or, t = \frac{2.303}{k} log 4 = \frac{1.3865}{k}$$

$$We\ know, t_{\frac{1}{2}} = \frac{0.693}{k}$$

$$So, \frac{t}{t_{\frac{1}{2}}} = \frac{1.3865}{0.693} \cong 2.$$

$$Hence, \qquad t = 2 \times t_{1/2}\ (proved)$$

3. **Second Order Reaction**: Consider a second order reaction involving only one reactant, i.e.
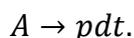
$$A \rightarrow pdt.$$

Let initial concentration of reactant is $[A]_0 = a$ & at an arbitrary time $t\ it\ is\ [A] = a - x$. Then the differential rate law is given as –

$$-\frac{d(a-x)}{dt} = k(a-x)^2$$

$$Or, \left(\frac{dx}{dt}\right) = k(a-x)^2$$

$$Or, \int_0^x \frac{dx}{(a-x)^2} = k \int_0^t k\, dt$$

$$Or, \left(\frac{1}{a-x}\right) - \frac{1}{a} = kt$$

$$Or, \frac{1}{a-x} = \frac{1}{a} + kt$$

$$Or, kt = \frac{x}{a(a-x)}$$

$$Or, t = \frac{1}{k} \times \frac{x}{a(a-x)}$$

Graphical Representation: If we plot $^1/(a-x)$ $vs\ t$, we get a straight line with intercept $= {^1/_a}$ & $slope = k$.
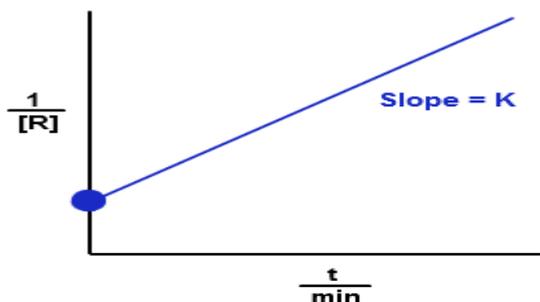
Half – life period: $When\ t = t_{\frac{1}{2}}, then, x = {^a/_2}$, $from\ above\ equation -$

$$t_{\frac{1}{2}} = \frac{1}{k} \times \frac{\frac{a}{2}}{a.\frac{a}{2}} = \frac{1}{ak}$$

Hence, half – life period is inversely proportional to initial concentration of reactant.

Unit of rate constant: $mol^{-1}lit.sec^{-1}$

Characteristics:

I. Second order reaction transfers to first order reaction when one of the reactant is present in large excess.

II. Half – life period of second order reaction is inversely proportional to initial concentration of reactant.

➢ Write down the unit of rate constant of a 2nd order reaction.

$$mol^{-1}lit.sec^{-1}$$

➢ Second order reaction never proceeds to completion – justify or criticize.

$For\ a\ 2nd\ order\ reaction,\ k = \frac{1}{t}\frac{x}{a(a-x)}$

$So, t = \frac{1}{k}\frac{x}{a(a-x)}$

$When \ t = t_{completion}, \qquad then \ a = 0,$

$So, t_{completion} = \dfrac{1}{k} \cdot \dfrac{x}{0} = \infty$

So, 2nd order reaction never goes to completion.

➢ For a second order reaction A —> products. Hence show that the time required for three – fourths of the reactant to decay ($t_{3/4}$) is equal to $3t_{1/2}$.

For a second order reaction —

$\dfrac{1}{a-x} = \dfrac{1}{a} + kt$

$Or, \dfrac{1}{a - \dfrac{3a}{4}} = \dfrac{1}{a} + kt_{\frac{3}{4}} \ \left(for \dfrac{3}{4} \ th \ of \ the \ reactant\right)$

$Or, \dfrac{1}{\dfrac{a}{4}} = \dfrac{1}{a} + kt_{\frac{3}{4}}$

$Or, kt_{\frac{3}{4}} = \dfrac{4}{a} - \dfrac{1}{a} = \dfrac{3}{a}$

$Or, t_{\frac{3}{4}} = 3 \times \dfrac{1}{ka} = 3t_{1/2} \ \left(we \ know \ for \ 2nd \ order \ reaction \ t_{\frac{1}{2}} = \dfrac{1}{ka}\right)$

$Or, t_{3/4} = 3 \times t_{1/2} \ (proved)$

➢ For a reaction A —> product, the plot of $\dfrac{1}{[A]}$ versus time is a straight line with a positive slope. What is the order of the reaction?

For a 2nd order reaction $\dfrac{1}{[A]_t} = \dfrac{1}{[A]_0} + kt$

Hence, now the plot of $\dfrac{1}{[A]_t} \ vs \ t -$

Graphical Representation:
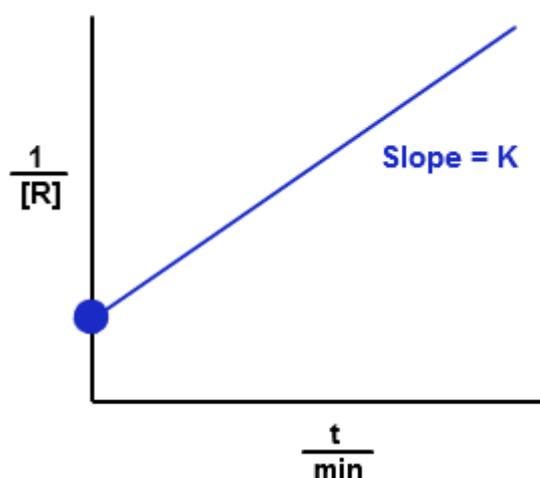
So, the order of the reaction is 2.

4. **n – th Order Reaction**: Let us consider a nth order reaction involving a single reactant. Its initial concentration is a. The rate law of such reaction is –

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

$$Or, \int_0^x \frac{dx}{(a - x)^n} = k \int_0^t dt$$

When $n \neq 1$, the integrated rate law is given as –

$$\frac{1}{n - 1}\left[\frac{1}{(a - x)^{n-1}} - \frac{1}{a^{n-1}}\right] = kt$$

$$Or, t = \frac{1}{k(n - 1)}\left[\frac{1}{(a - x)^{n-1}} - \frac{1}{a^{n-1}}\right]$$

<u>Half – life period</u>: $When\ t = t_{\frac{1}{2}}, then, x = {^a\!/_2},\ from\ above\ equation -$

$$t_{\frac{1}{2}} = \frac{1}{k(n - 1)}\left[\frac{1}{(a - \frac{a}{2})^{n-1}} - \frac{1}{a^{n-1}}\right]$$

$$= \frac{1}{k(n - 1)}\left(\frac{2^{n-1} - 1}{a^{n-1}}\right)$$

$$So, it\ implies\ that, \quad t_{\frac{1}{2}} \propto \frac{1}{a^{n-1}}$$