

(6)

Characteristics of 1st order reaction :-

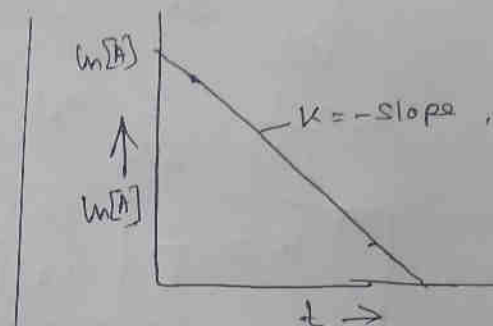
- (i) Unit of rate constant k is time^{-1} ,
(ii) The eqnⁿ $\ln[A] = -k_1 t + \ln[A]_0$ is of the form $y = mx + c$.
Therefore the plot of $\ln[A]$ vs t will be a straight line with (-)ve slope.

- (iii) A first order reaction never completes, since

$$\ln[A] = -kt + \ln[A]_0$$

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

It is called Wilhelmium's reaction. From this equation it is seen that $\text{the reaction is completed when } [A] = 0, \text{ when } t = \infty.$



Plot of $\ln[A]$ vs t for a first order reaction.

- (iv) The half life period of a 1st order reaction is constant.

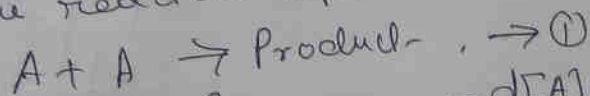
$$\begin{aligned} t_{1/2} &= \frac{2.303}{k_1} \log \frac{[A]_0}{[A]_{0/2}} \\ &= \frac{2.303}{k} \log 2 \\ &= \frac{2.303 \times 0.3010}{k} = \frac{0.693}{k} \end{aligned}$$

2nd order reaction :- The 2nd order reactions are

of two types, (1) When the reactant species are same.

(2) When the reactant species are different.

type (1) When the reactant species are same,



$$\frac{-d[A]}{dt} = k[A]^2, \text{ or } \frac{-d[A]}{[A]^2} = k dt \rightarrow (2)$$

(7)

On integration between the limits $[A]_0$ at $t=0$ and $[A]$ at $t=t$, we have.

$$-\int_{[A]_0}^{[A]} \frac{d[A]}{[A]^2} = \int_0^t k dt$$
$$= \frac{1}{[A]} - \frac{1}{[A]_0} = k t$$

$$\text{on } k = \frac{1}{t} \left[\frac{[A]_0 - [A]}{[A][A]_0} \right] \Rightarrow (3)$$

It is the ~~exp~~ expression for the rate constant of a 2nd order reaction.

Characteristics of 2nd order reaction:

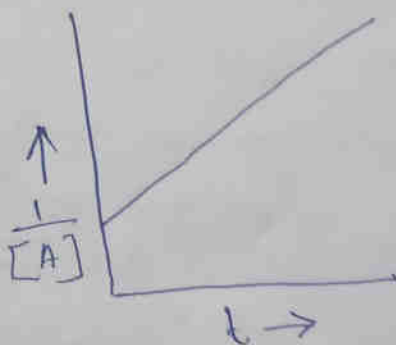
- (i) Unit of k is $\text{L mol}^{-1} \text{sec}^{-1}$
- (ii) Half life period of 2nd order reaction is inversely proportional to the initial concentration of the reactant.

A half life period $t_{1/2}$, $[A] = [A]_0/2$

From eqn (3) $k = \frac{1}{t_{1/2}} \Rightarrow t_{1/2} = \frac{1}{k} \frac{[A]_0/2}{[A]_0/2 [A]_0}$

$$t_{1/2} = \frac{1}{k [A]_0} \rightarrow (4)$$

- (iii) A plot of $1/[A]$ vs t , is a straight line with slope k .



$1/[A]$ vs t plot for 2nd order reaction.

(2)

Type (2), when the reactants are different:



The rate equation for the reaction:

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

Let x mols of A reacts with time t , then the concentration of A at time $t = [A]_0 - x$.

Concentration of B " " " " = $[B]_0 - x$.

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

Now the rate $\frac{dx}{dt} = k([A]_0 - x)[B]_0 - x$.

(Rate is taken as formation of the product)

$$\frac{dx}{([A]_0 - x)([B]_0 - x)} = k dt \rightarrow (1)$$

We can write

$$\frac{1}{([A]_0 - x)([B]_0 - x)} = \frac{1}{[A]_0 - [B]_0} \left[\frac{1}{[B]_0 - x} - \frac{1}{[A]_0 - x} \right]$$

(Using partial fraction)

Substituting the value in (1) and integrating

$$\int \frac{dx}{([A]_0 - x)([B]_0 - x)} = \frac{1}{[A]_0 - [B]_0} \left[\int \frac{dx}{[B]_0 - x} - \int \frac{dx}{[A]_0 - x} \right] = k \int dt$$

$$= \frac{1}{[A]_0 - [B]_0} \left[-\ln([B]_0 - x) + \ln([A]_0 - x) \right] = kt + I$$

Integration

$$= \frac{1}{[A]_0 - [B]_0} \left[\ln \frac{[A]_0 - x}{[B]_0 - x} \right] = kt + I \rightarrow (2)$$

When $t = 0, x = 0$.

$$\frac{1}{[A]_0 - [B]_0} \ln \frac{[A]_0}{[B]_0} = C$$

Putting the value in (2)

$$\frac{1}{[A]_0 - [B]_0} \left[\ln \frac{[A]_0 - x}{[B]_0 - x} \right] = kt + \frac{1}{[A]_0 - [B]_0} \ln \frac{[A]_0}{[B]_0}$$

$$kt = \frac{1}{[A]_0 - [B]_0} \ln \frac{[A]_0 - x}{[B]_0 - x} - \frac{1}{[A]_0 [B]_0} \ln \frac{[A]_0}{[B]_0}$$

$$kt = \frac{1}{[A]_0 - [B]_0} \left\{ \ln \frac{[B]_0 ([A]_0 - x)}{[A]_0 ([B]_0 - x)} \right\}$$

$$\text{or } k = \frac{1}{([A]_0 - [B]_0)t} \ln \frac{[B]_0 ([A]_0 - x)}{[A]_0 ([B]_0 - x)}$$

This is the rate expression for 2nd order reaction when the reactants are different.

Effect of temperature on reaction rate (Arrhenius eqn)

An increase in temperature increases the reaction rate.

Generally for every 10°C rise in temperature, the rate of reaction increases by two to three times. This is represented by the temperature co-efficient.

$$\text{Temp}^{\vee} \text{ co-efficient} = \frac{k_{t+10}}{k_t} \approx 2 \text{ or } 3$$

The quantitative relationship between the rate constants and temperature is given by the following equation, called Arrhenius equation.

$$k = A e^{-E_a/RT} \quad \rightarrow (1)$$

Here A = frequency factor or preexponential factor.

E_a = Activation energy.

T = Absolute temperature

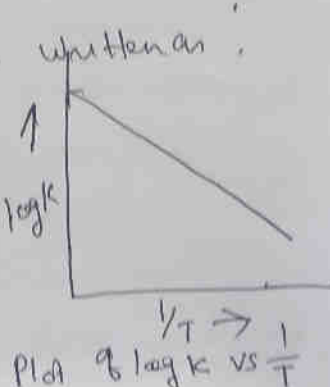
R = Gas constant

Taking logarithm eqn (1) can be written as:

$$\ln k = \ln A - E_a/RT$$

$$2.303 \log k = 2.303 \log A - E_a/RT$$

$$\log k = \log A - \frac{E_a}{2.303RT} \quad \rightarrow (2)$$



(10) When $\log k$ is plotted against $1/T$, we get a straight line. The intercept of the equation is $\log k$ and slope = $-E_a/2303R$.

The activation energy E_a and frequency factor (A) can be determined by measuring the rate constant at two different temperatures.

For a reaction, if k_1 is the rate constant at temperature T_1 and k_2 is the rate constant at temp T_2 , then,

$$\log k_1 = \log A - \frac{E_a}{2.303RT_1} \quad \text{and} \quad \log k_2 = \log A - \frac{E_a}{2.303RT_2} \quad \rightarrow (4)$$

Subtracting (3) from (4)

$$\log k_2 - \log k_1 = -\frac{E_a}{2.303RT_2} - \left(-\frac{E_a}{2.303RT_1}\right)$$

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

Activation Energy:-

~~The molecules of reactants in a chemical system have initial energy of their own E_0 (say)~~

According to Arrhenius theory, the reacting molecules must have a certain minimum amount of energy in order to undergo chemical transformation. The excess energy that one mole of reacting molecules must acquire to attain this minimum energy level (threshold energy) is called the activation energy.

Thus activation energy = Threshold Energy - average energy possessed by the molecule

Although the energy of the reactant is more than the energy of the product, Reactant A will not directly convert to B. For effective collision (the collision which are able to give product), it must acquire the activation energy.

