

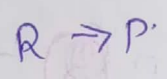
Further simplifying equation - (3)
we get rate constant, k as -

$$k = \frac{[R]_0 - [R]}{t}$$

Zero order reactions are relatively uncommon.
The decomposition of gaseous ammonia on a hot platinum surface is a zero order rxn at high pressure.

First Order Rxn:-

In this class of reactions, the rate of reaction is proportional to the first power of concentration of reactant R. For eg:-



$$\text{Rate} = -\frac{d[R]}{dt} = k[R]$$

$$\text{or } \frac{d[R]}{[R]} = -k \cdot dt$$

Integrating this eqn, we get:-

$$\ln [R] = -kt + I \text{ --- (1)}$$

Again I is the constant of integration and its value can be determined easily:-
when $t = 0$, $R = [R]_0$, where $[R]_0$ is the initial concn of reactant.

Therefore eqn - ① can be written as: - ①

$$\ln [R]_0 = -k \times 0 + I$$

$$\ln [R]_0 = I \quad \text{--- ②}$$

Substitute ② in ①, the value of I in eqn ① -

$$\ln [R] = -kt + \ln [R]_0 \quad \text{--- ③}$$

Rearrange eqn ③ -

$$kt = \ln [R]_0 - \ln [R]$$

~~$$\ln \frac{[R]}{[R]_0} = -kt$$~~

~~$$kt = \ln \frac{[R]_0}{[R]} \quad k = \frac{1}{t} \ln \frac{[R]_0}{[R]}$$~~

$$\text{or } k = \frac{1}{t} \ln \frac{[R]_0}{[R]} \quad \text{--- ④}$$

At time t_1 , from eqn ③ -

$$\ln [R]_1 = -kt_1 + \ln [R]_0 \quad \text{--- ⑤}$$

At time t_2 -

$$\ln [R]_2 = -kt_2 + \ln [R]_0 \quad \text{--- ⑥}$$

where $[R]_1$ and $[R]_2$ are the concentrations of reactants at time t_1 and t_2 .

Substn of (6) form (5) - (7)

$$\ln [R]_1 - \ln [R]_2 = -kt_1 - (-kt_2)$$

$$\ln \frac{[R]_1}{[R]_2} = k(t_2 - t_1)$$

$$k = \frac{1}{(t_2 - t_1)} \ln \frac{[R]_1}{[R]_2} \quad \text{--- (7)}$$

Equation (3) can also be written as: -

$$\ln \frac{[R]}{[R]_0} = -kt$$

Taking antilog of both sides: -

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

Comparing eqn (3) with $y = mx + c$, if we plot $\ln [R]$ against t , we get a straight line with slope = $-k$ and intercept equal to $\ln [R]_0$.

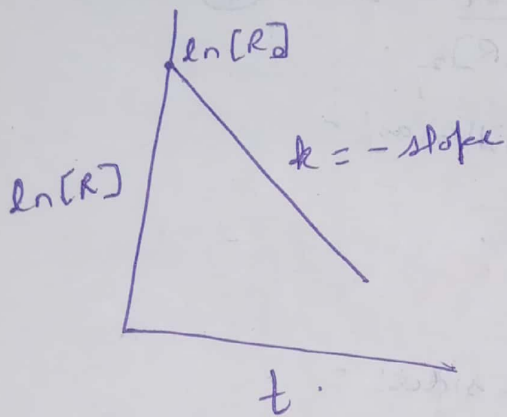
The first order rate equation (4) can also be written in the form of: -

$$k = \frac{2.303}{t} \cdot \log \frac{[R]_0}{[R]}$$

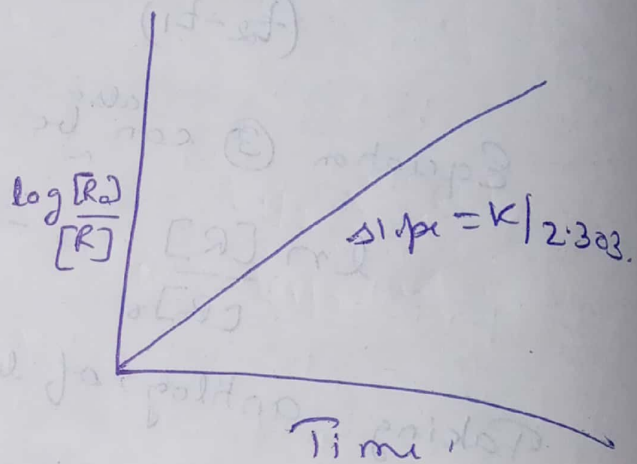
$$\log \frac{[R]_0}{[R]} = \frac{kt}{2.303}$$

If we plot a graph between $\log [R]_0/[R]$ vs t ,
 the slope = $k/2.303$.

eg. Hydrogenation ethene is an example
 of first order rxn.



Plot of $\ln [R]$ and t .



Plot of $\log [R]_0/R$ vs
 time

Half life of Reaction:-

The half life of the reaction is the time in
 which the concentration of a reactant is reduced
 to one half of its initial concentration. It is
 represented as $t_{1/2}$.

For a zero order reaction, rate constant
 is given by:-

$$R = \frac{[R]_0 - [R]}{t}$$

$$\text{At } t = t_{1/2}, [R] = \frac{1}{2} [R]_0$$

The rate constant at $t_{1/2}$ becomes -

$$k = \frac{[R]_0 - \frac{1}{2} [R]_0}{t_{1/2}}$$

$$t_{1/2} = \frac{[R]_0}{2k}$$

It is clear that $t_{1/2}$ for a zero order reaction is directly proportional to the initial concentration of the reactants and inversely proportional to the rate constant.

For first order rxn: -

$$k = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$$

$$\text{at } t_{1/2} = [R] = \frac{[R]_0}{2}$$

So the above eqn becomes! -

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

$$\text{or } t_{1/2} = \frac{2.303 \log 2}{k}$$