4. CHEMICAL KINETICS

Differences between Order and Molecularity of a reaction

|	Order	Molecularity
1.	It is the sum of the powers of the concentration terms in the rate law expression	It is the total number of reactant species collide simultaneously in a chemical rk$^{\underline{n}}$
2.	It is an experimental quantity	It is a theoretical quantity
3.	It can be zero or fractional	It cannot be zero or fractional
4.	It is applicable to both elementary and complex rk$^{\underline{n}}$	It is applicable only to elementary rk$^{\underline{n}}$

Elementary and complex reactions

A reaction that takes place in a single step is called elementary reaction. While a reaction that occurs in more than one step is called a complex reaction. In a complex reaction one of the steps is slower than the other steps and this step is called the Rate determining step. The overall rate of the reaction is controlled by this slowest step. The sequence of steps by which a chemical reaction occurs is called the mechanism of the reaction.

Consider the decomposition of hydrogen peroxide which is catalyzed by iodide ion in alkaline medium.

$$2H_2O_2 \xrightarrow[\text{Alkaline Medium}]{I^-} 2H_2O + O_2$$

The rate equation for this reaction is found to be $r = -\dfrac{d[H_2O_2]}{dt}$

This reaction is first order with respect to both H_2O_2 and I^-. This reaction takes place in two steps

(1) $\quad H_2O_2 + I^- \longrightarrow H_2O + IO^-$

(2) $\quad H_2O_2 + IO^- \longrightarrow H_2O + I^- + O_2$
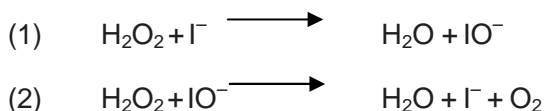
Here the first step is slower than the second. So it is the rate determining step (rds).

Unit of Rate constant

Different ordered reactions have different units for k.

For an nth order reaction $nA \longrightarrow$ products, rate= $k[A]^n$

Therefore, $k = \dfrac{\text{rate}}{[\text{Concentration}]^n}$

$$= \dfrac{mol/L/sec}{(mol/L)^n}$$

Unit of $k = (mol/L)^{1-n} s^{-1}$

The units of rate constant for different ordered reactions are:

Reaction	Order	Unit of rate constant
Zero order reaction	0	Mol $L^{-1}s^{-1}$
First order reaction	1	s^{-1}
Second order reaction	2	$Mol^{-1}L\ s^{-1}$

Integrated Rate law Equations

These are equations relating the rate of a reaction and concentration of reactants. Different ordered reactions have different integrated rate law equations.

1. Integrated Rate law Equation for a Zero Order Reaction

Zero order reactions are reactions in which the rate of reaction is independent of concentration of the reactants. Consider a zero order, $R \rightarrow P$

The rate expression for the above reaction is $r = -\dfrac{d[R]}{dt}$ …………(1)

Rate law for the above reaction is $r = k[R]^0 = k$

From equations (1) & (2), we can write $-\dfrac{d[R]}{dt} = k$

The above equation is known as *differential rate equation for a zero order reaction*.

Or, $d[R] = -k.dt$

On integrating the above equation we get, $[R] = -kt + C$ …………..(3)

Where C is the constant of integration. To evaluate the value of C, consider the initial conditions.

i.e., when $t = 0$, $[R] = [R]_0$

Substitute these values in eqn. (3)
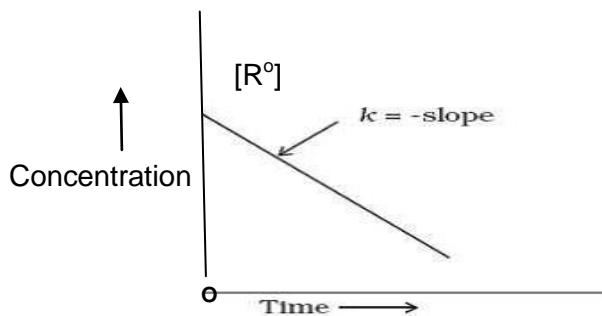
$[R]_0 = -k \times 0 + C$

Or, $C = -[R]_0$

Substituting in equation (3), we get $[R] = -kt - [R]_0$ ………………(4)
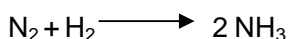
Or, $[R]_0 - [R] = kt$

Or, $k = \dfrac{[R]_0 - [R]}{t}$ ……………… (5)

This equation is of the form of a straight line, $y = mx + c$. So if we plot $[R]$ against t, we get a straight line with

slope $= -k$ and intercept equal to $[R]_0$.

Example for zero order reaction is the decomposition of gaseous ammonia on a hot platinum surface at high pressure.

$$N_2 + H_2 \longrightarrow 2\,NH_3$$

In this reaction, platinum metal acts as a catalyst. At high pressure, the metal surface gets saturated with gas molecules. So, a further change in reaction conditions does not change the rate of the reaction.

So it becomes a zero order reaction.

Another e.g. is the thermal decomposition of HI on gold surface.

2. Integrated Rate law Equation for a First order reaction

Here the rate of the reaction is proportional to the concentration of the reactant.

Consider a first order reaction, $R \longrightarrow P$

The rate expression for the above reaction is $r = -\dfrac{d[R]}{dt}$ .... (1)

Rate law for the above reaction is $r = k[R]$ .... (2)

From equations (1) & (2), we can write $-\dfrac{d[R]}{dt} = k[R]$ .... (3)

The above equation is known as *differential rate equation for a 1ˢᵗ order reaction*.

Or, $-\dfrac{d[R]}{[R]} = k.dt$

On integrating the above equation we get,

$$-\ln[R] = kt + C \quad\text{...................... (3)}$$

Where 'C' is the constant of integration. To evaluate the value of C, consider the initial conditions.

i.e., when $t = 0$, $[R] = [R]_0$

Substitute these values in eqn. (3)

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

Or, $C = -\ln[R]_0$

Substituting in equation (3), we get

$-\ln[R] = kt - \ln[R]_0$............ (4)

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

Or, $\ln[R]_0/[R] = kt$ .... (5)

$K = \dfrac{1}{t}\ln\dfrac{[R]_0}{[R]}$ .... (6)

On changing the base we get

$$k = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$$ .... (7)

This equation is known as *integrated rate equation for a first order reaction*.

From eqn. (4), $-\ln[R] = kt - \ln[R]_0$

On changing the sign we get $\ln[R] = -kt + \ln[R]_0$

This equation is of the form $y = mx + c$, equation for a straight line. So if we plot a graph between $\ln[R]$ against time, t we get straight line graph as follows:
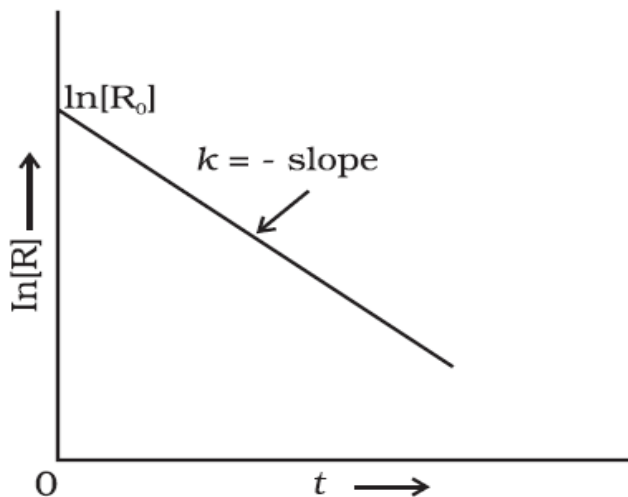
From the eqn. (5) $\ln[R]_0/[R] = kt$

Or, $2.303 \log[R]_0/[R] = kt$

Or, $\log[R]_0/[R] = kt/2.303$

So if we plot a graph between $\log[R]_0/[R]$ against 't', we get a straight line graph as shown above.

Examples for 1st order reactions are:

1. Hydrogenation of ethene: $C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$; $r = k[C_2H_4]$

2. All natural and artificial radioactive decay

Half life of a reaction ($t_{1/2}$)

The half-life of a reaction is the time taken for concentration of a reactant is reduced to one half of its initial concentration. Or, it is the time taken for half of a reaction to complete. It is represented as $t_{1/2}$.

1. Half life of a zero order reaction

For a zero order reaction, the integrated rate law is: $k = \dfrac{[R]_0 - [R]}{t}$

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

On substituting these values in the above equation,

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

or, $\boxed{t_{1/2} = \dfrac{[R]_0}{2k}}$

i.e. half life of a zero order reaction is directly proportional to the initial concentration of the reactants and inversely proportional to the rate constant.

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