CHEMICAL KINETICS

Paper : IA Physical Chemistry

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Units of Second Order Rate Constant :-

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

$$= \frac{1}{time} \times \frac{concentration}{concentration \times concentration}$$

$$= \frac{1}{time} \times \frac{1}{concentration}$$

$$= \frac{1}{second} \times \frac{1}{moles/litre}$$

$$= litre/mole/second$$

∴ Units of $k \Rightarrow L \cdot mol^{-1} s^{-1}$
for second order
reaction

Half - life of a Second Order Reaction :-

for a simple second order reaction of the type $2A \rightarrow Products$, the integrated rate equation is

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

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

By definition, if $t = t_{1/2}$, $x = \frac{a}{2}$

On putting these values in the above equation we get

$$t_{1/2} = \frac{1}{k} \cdot \frac{a/2}{a(a - a/2)}$$

$$= \frac{1}{k} \cdot \frac{1}{a}$$

$$\alpha \quad t_{1/2} = \frac{1}{ka}$$

From this equation, we say that half-life period of a second order reaction is inversely proportional to the initial concentration of reactants.

In general, half-life of any reaction of nth order varies inversely as $(n-1)$ power of the initial concentration of reactants, i.e. for the reaction $nA \longrightarrow$ Products

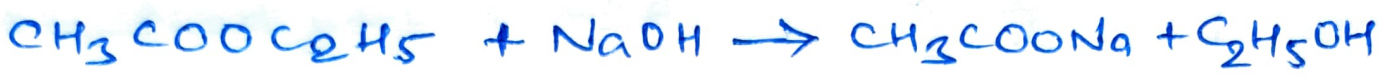$$t_{1/2} = \frac{1}{k} \times \frac{1}{a^{n-1}} = \text{constant} \times \frac{1}{a^{n-1}}$$

$$\boxed{\text{or,} \quad t_{1/2} \propto \frac{1}{a^{n-1}} \quad \text{or,} \quad t_{1/2} \propto a^{1-n}}$$

Here the magnitude of the constant depends on the order of a reaction.

Examples of Second Order Reactions :—

A typical example of the second order reaction is the hydrolysis (or saponification) of an ester (e.g. ethyl acetate) with

a strong base (e.g. NaOH). The reaction takes place as

$$CH_3COOC_2H_5 + NaOH \rightarrow CH_3COONa + C_2H_5OH$$

The reaction mixture is prepared by mixing a known amount (generally equimolar) of ethyl acetate with a known amount of NaOH. Let 'a' and 'b' be the initial concentrations of ester and base respectively. The course of the reaction is followed by removing a definite quantity of the reaction mixture from time to time and titrating with standard acid to know the concentration of NaOH left behind. As we see from reaction, the concentration of NaOH will decrease with time. If x is the decrease in concentration of NaOH at any time t, then $(b-x)$ is the amount of unreacted NaOH left behind. Similarly $(a-x)$ will be the amount of unreacted ester at time t. The specific rate constant, k then be calculated using equation

$$k = \frac{2.303}{t(a-b)} \log \frac{b(a-x)}{a(b-x)}$$

Determination of Order of Reactions :—

The following methods are commonly used for determining the order of a reaction.

1. Intigrated Rate Equation Method :—

It is also known as "Hit and Trial Method".
This method can be used either analytically or
graphically.

a. Analytical Method :

In this method, experiments are made
with different initial concentrations and concen-
trations at different intervals of time. By using
integrated rate laws for different orders of
reactions, value of k is calculated and the
equation from which constant value of k is
obtained gives the order of reaction. The
different integrated rate laws one

$$k = \frac{2.303}{t} \log \frac{a}{(a-x)} \qquad \text{(First Order Reaction)}$$

$$k = \frac{1}{t} \cdot \frac{x}{a(a-x)} \qquad \text{(Second Order Reaction)}$$

More simply the experimental values of a,
(a-x) and t are substituted into the integrated
rate equations for the first and second order
reactions. The rate equation which yields a
constant value of k corresponds to the correct
order of the reaction.

b. Graphical Method :

In this method, we can determine

the order of reaction by seeing whether a graph of the data fits one of the integrated rate equations.

__In case of First-Order :__ The first order equation is given by

$$k = \frac{2.303}{t} \cdot \log \frac{a}{(a-x)}$$

On simplifying it, we get-

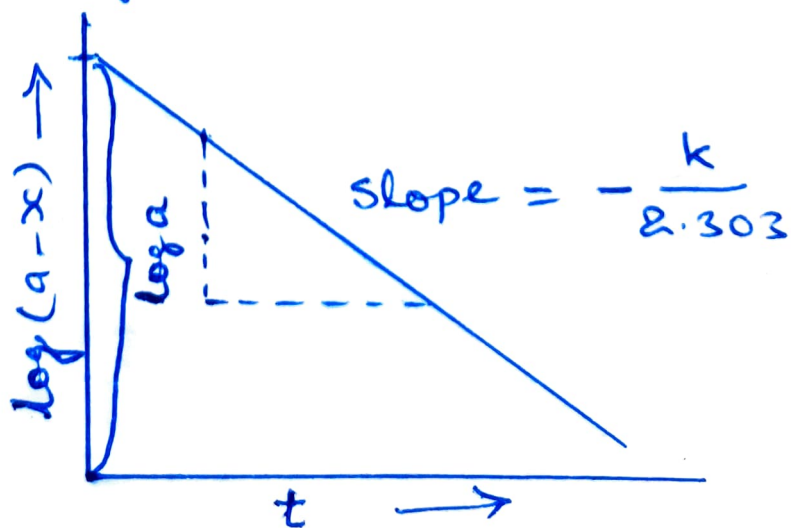$$\log(a-x) = \left(-\frac{k}{2.303}\right)t + \log a$$

Comparing this equation with the classical equation of a straight line, $y = mx + c$, the two variables are

$$y \Rightarrow \log(a-x) \quad \text{and}$$
$$x \Rightarrow t$$

And a plot of $\log(a-x)$ versus t for a first-order reaction should be a straight-line with a slope equal to $-\frac{k}{2.303}$ and intercept on the y-axis equal to $\log a$.

However, if a curve is obtained the reaction is not of the first-order.

Slope $= -\frac{k}{2.303}$

The rate constant k can thus be calculated from measuring the slope

$$slope = - \frac{k}{2.303}$$

or, $k = 2.303 \times slope$

.... to be continued