CHEMICAL KINETICS
INTEGRATED RATE EQUATIONS

❖ Rate constants & its characteristics:

Rate Constants

Rearranging the rate equation, the value of the rate constant 'k' is given by:

$$k = Rate/[A]^x[B]^y$$

Hence, the units of k (assuming concentration is denoted in mol L^{-1} or M and time is denoted in seconds) can be determined using the following equation.

$$k = (M\ s^{-1})*(M^{-n}) = M^{(1-n)}\ s^{-1}$$

The units of the rate constants for zero, first, second, and nth-order reactions are tabulated below.

Reaction Order	Units of Rate Constant
0	$M\ s^{-1}$ (or) $mol\ L^{-1}.s^{-1}$
1	s^{-1}
2	$M^{-1}\ s^{-1}$ (or) $L\ mol^{-1}\ s^{-1}$
N	$M^{1-n}\ s^{-1}$ (or) $L^{(-1+n)}\ mol^{(1-n)}.s^{-1}$

Differential Rate Equations

Differential rate laws are employed to articulate the rate of a reaction by considering the change in the concentration of reactants (d[R]) over a brief time interval (dt). Consequently, the differential expression of the rate from the preceding subsection is expressed as:

$$-d[R]/dt = k[A]^x[B]^y$$

Differential rate equations can be applied to compute the instantaneous rate of a reaction, representing the reaction rate within an extremely small-time interval. It's important to recognize that the ordinary rate law functions as a differential rate equation as it provides information about the instantaneous rate of the reaction.

Integrated Rate Equations

Integrated rate equations articulate the concentration of reactants in a chemical reaction as a time-dependent function. Consequently, these rate equations are useful for determining the duration required for a specific percentage of reactants to undergo consumption in a chemical reaction. It's crucial to recognize that reactions of various orders are associated with distinct integrated rate equations.

Integrated Rate Equation for Zero-Order Reactions

The integrated rate equation for a zero-order reaction is given by:

$$kt = [R_0] – [R] \text{ (or) } k = ([R_0] – [R])/t$$

Where,
$[R_0]$ is the initial concentration of the reactant (when t = 0)
$[R]$ is the concentration of the reactant at time 't'
k is the rate constant

Integrated Rate Equation for First-Order Reactions

The integrated rate law for first-order reactions is:

$$kt = 2.303 \log([R_0]/[R]) \text{ (or) } k = (2.303/t) \log([R_0]/[R])$$

Integrated Rate Equation for Second-Order Reactions

For second-order reactions, the integrated rate equation is:

$$kt = (1/[R]) - (1/[R_0])$$

Solved Examples on the Rate Law

Ex For the reaction given by $2NO + O_2 \rightarrow 2NO_2$,
The rate equation is:

$$\text{Rate} = k[NO]^2[O_2]$$

Find the overall order of the reaction and the units of the rate constant.

Sol. The overall order of the reaction = sum of exponents of reactants in the rate equation

$$= 2+1 = 3$$

The reaction is a third-order reaction. Units of rate constant for 'nth' order reaction

$$= M^{(1-n)}\, s^{-1}$$

Therefore, units of rate constant for the third-order reaction

$$= M^{(1-3)}\, s^{-1} = M^{-2}\, s^{-1} = L^2\, mol^{-2}\, s^{-1}$$

Ex For the first-order reaction given by $2N_2O_5 \rightarrow 4NO_2 + O_2$ the initial concentration of N_2O_5 was 0.1M (at a constant temperature of 300K). After 10 minutes, the concentration of N_2O_5 was found to be 0.01M.
Find the rate constant of this reaction (at 300K).

Sol From the integral rate equation of first-order reactions:

$$k = (2.303/t)\log([R_0]/[R])$$

Given, $t = 10 \text{ mins} = 600 \text{ s}$
Initial concentration, $[R_0] = 0.1M$
Final concentration, $[R] = 0.01M$

Therefore, rate constant, $k = (2.303/600s)\log(0.1M/0.01M) = 0.0038\ s^{-1}$

The rate constant of this equation is $0.0038\ s^{-1}$

Characteristic of rate constant: -

The rate constant serves as an indicator of the reaction rate.

LARGER THE VALUE OF K →→ FAST REACTION
SMALLER THE VALUE OF K →→→→ SLOW REACTION

Different reactions have different value of k.

The rate constant (k) varies with alterations in temperature and the presence of a catalyst. For zero-order reactions, the rate constant remains unaffected by changes in the concentration of reactants.

Integrated rate equations (part i):

The relationship between concentration and rate is referred to as the differential rate equation, while the integrated rate equation establishes a connection between experimentally measured quantities, such as concentrations at different times. Integrated rate equations vary for reactions of distinct orders, and the instantaneous rate of a reaction is described by differential rate law equations.

For example: For a general reaction

$$aA + bB \longrightarrow \text{Products}$$

the differential rate law equation is:

$$dx/dt = k[A]^a [B]^b$$

The differential form of rate law is transformed to integrated form of rate law by simple mathematics (calculus).

Zero order reaction

Reaction whose rate is not affected by concentration said to be of zero order reaction.

Ex.: Reaction between Acetone and Bromine

Dissociation of HI on gold surface

Unit of Rate Constant:

$$k = \text{molL}^{-1}\text{sec}^{-1} \text{Unit of rate of reaction} = \text{Unit of rate constant.}$$

Rate Constant of Zero Order Reaction:

$$x = kt$$

The rate of reaction is independent of the concentration of the reaction substance.

Determination of Half-life Period of Zero Order Reaction:

At $t = t_{1/2}$; $x = \frac{a}{2}$

$$t_{1/2} = \frac{a}{2k} \quad \text{or} \quad t_{1/2} \propto a$$

The half-life period is directly proportional to the initial concentration of the reactants.

Integrated rate equations (part ii):

First order reaction

In a situation where the rate of reaction is influenced solely by one concentration term of the reactant, it is termed a first-order reaction. A first-order reaction exhibits a rate that changes in direct proportion to the concentration of the reactant, meaning the rate increases by the same factor as the concentration of the reactant is increased.

Let us, consider a unimolecular first order reaction represented by the general equation,

$A \rightarrow$ Product A Product

At $t = 0$ a 0

At $t = t$ $a - x$ x

The initial concentration of A is a mole L^{-1} and its concentration after time t is (a – x) mole L^{-1}. This means during the time interval t, x mole L^{-1} of A has reacted.
The rate of reaction at any time t is given by the following first order kinetics.

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

$$\frac{D(x)}{dt} \propto (a-x)$$

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

where k is the rate constant of the reaction.

$$\frac{dx}{a-x} = kdt$$

This is differential rate equation and can be solved by integration.

$$\int \frac{dx}{a-x} = k\int dt$$

$$-\ln(a-x) = k \cdot t + C \qquad \text{.... (1)}$$

where C is integration constant.
The constant C can be evaluated by applying the initial condition of the reaction i.c.
when $t = 0, x = 0$. Putting these in equation (1), we get

$$C = -\ln\ a$$

Putting the value of C in equation (1), we get

$$-\ln(a-x) = k \cdot t - \ln\ a$$

Or

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

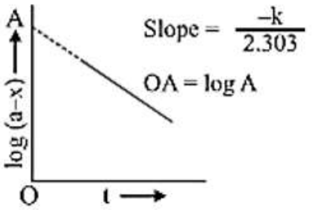
Also,

$$k = \frac{2.303}{(t_2 - t_1)}\log\frac{(a-x_1)}{(a-x_2)}$$

and

$$k = \frac{2.303}{(t_2 - t_1)}\log\frac{R_1}{R_2}$$

where $(a - x_1)$ is concentration at time t_1 and $(a - x_2)$ is concentration after time t_2 and R_1 is rate at time t_1 and R_2 is rate at time t_2



If $[A]_0$ and t respectively, then Eq. (2) may be put[A] be the concentrations of reactant at zero time as

$$k = \frac{1}{t}\ln\frac{[A]_0}{[A]}$$

Also,

$$[A] = [A]_0 c^{-k}$$

This is the integrated rate expression for first order reaction

This is the integrated rate expression for first order reaction.

As, $$k = \frac{1}{t}\ln\frac{a}{a-x}$$

⇒ $$\log(a-x) = \log(a) - \frac{kt}{2.303}$$

$$kt = \ln a - \ln(a-x)$$

Also, $$(a-x) = ac^{-k}$$

$$x = a(1-c^{-li})$$

Degrec of dissociation

$$(\frac{x}{a}) = (1-c^{-kt})$$

Unit of Rate constant

The differential rate expression for n^{th} order reaction is as follows:

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

$$k = \frac{dx}{(a-x)^n dt} = \frac{(\text{concentration})}{(\text{concentration})^{\text{ntime}}} = (\text{conc.})^{1-n}\ \text{time}^{-1}$$

If concentration be expressed in mole L^{-1} and time in minutes, then

$$k = (\text{mole } L^{-1})^{1-n} \min^{-1}$$

For zero order reaction, n = 0 and hence,

$$k = \text{mole } L^{-1} \min^{-1}$$

For first order reaction, n = 1 and hence,

$$k = (\text{mole } L^{-1})\ 0 \min^{-1} = \min^{-1}$$

For second order reaction, n = 2 and hence,

$$k = (\text{mole } L^{-1})^{-1} \min^{-1} = \text{mole}^{-1} L \min^{-1}$$

The rate constant of a first-order reaction is exclusively expressed in terms of time and lacks a concentration term in its unit. Consequently, the numerical value of k for a first-order reaction remains unaffected by the unit in which concentration is measured. Altering the concentration unit does not cause a change in the numerical value of k for a first-order reaction. However, it does undergo variation with changes in time.

For instance, if k is 6.0×10^{-3} min, it can also be represented as 1×10^{-4} s^{-1}. In other words, the numerical value of k will decrease by 60 times if the time unit is shifted from hours to minutes or from minutes to seconds.

Half - time or half - life period of a first order reaction:

The half - time of a reaction is defined as the time required to reduce the concentration of the reactant to half of its initial value. It is denoted by the symbol $t_{1/2}$. Thus, When $x = \frac{a}{2}, t = t_{1/2}$

Putting these values in Eq. (2), we get

$$k = \frac{2.303}{t_{1/2}} \log \frac{a}{a-\frac{a}{2}} = \frac{2.303}{t_{1/2}} \log\ 2 = \frac{2.303}{t_{1/2}} \times 0.30103$$

$$(\because \log\ 2 = 0.30103)$$

$$t_{1/2} = \frac{0.693}{k}$$

Given that k remains constant for a specific reaction at a particular temperature and the expression lacks any concentration term, it is evident from Eq. (3) that the initial concentration of the reactant does not affect the reaction.

To illustrate, if we initiate a reaction with a reactant concentration of 4 moles L^{-1} undergoing first-order kinetics, after 20 minutes, the concentration decreases to 2 moles L^{-1}. Subsequently, after 40 minutes, it further reduces to 1 mole L^{-1}, and after 60 minutes, it reaches 0.5 mol L^{-1}. Essentially, if 50% of the reaction is completed in the first 20 minutes, then 75% is achieved in 40 minutes, 85.5% in 60 minutes, and so forth, as depicted in the figure above.

Thus, fraction left after n half-lives = $(\frac{1}{2})^n$

Concentration left after n half-lives, $[A] = (\frac{1}{2})^n\ [A]_0$

It is also to be noted that Eq. (3) helps to calculate $t_{1/2}$ or k.

A general expression for $t_{1/2}$ is as follows.

Half - life of a nth order reaction

Let us find out $t_{1/2}$ for n^{th} order reaction where n ^{1} 1.

$$\frac{-d[A]}{dt} = k_n[A]^n \Rightarrow \frac{-d[A]}{[A]^n} = kdt \Rightarrow -\int_{[A_b}^{AN_o/2} \frac{d[A]}{[A]^n} = k\int_0^{t_{1/2}} dt$$

$$\int_{[A_0/2}^{[Al_b} [A]^{-n} d[A] = k_n t_{1/2} [\frac{[A]^{1-n}}{1-n}]_{[A_l}^{[A_n} = k_n t_{1/2}$$

$$\frac{1}{1-n}([A]_0^{l-n} - [\frac{[A]_0}{2}]^{1-n}) = k_n t_{1/2} \Rightarrow \frac{[A]_0^{1-n}}{1-n}[1-(\frac{1}{2})^{1-n}] = k_n t_{1/2}$$

$$\frac{1}{(1-n)[A]_0^{n-1}}[1-2^{n-1}] = k_n t_{1/2} \Rightarrow \frac{(2^{n-1}-1)}{k_n(n-1)[A]_0} = t_{1/2}(\text{ order } n \neq 1)$$

Therefore, for n^{th} order reaction, the half-life is inversely related to the initial concentration raised to the power of (n – 1).$t_{1/2}$ μ

where n = order of reaction.

Ex. All radioactive reactions

$$A \rightarrow \text{Product}$$

$$2NO \rightarrow 2N_2 + O_2$$

$$2Cl_2O_7 \rightarrow 2Cl_2 + 7O_2$$

(A) Unit of rate constant of first order reaction

$$K = (\text{sec})^{-1} \quad Dn = 1$$

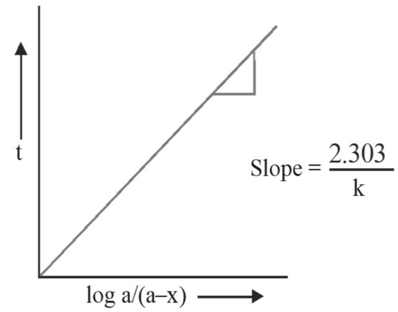
(B) Velocity constant for first order reaction

$$k_1 = \frac{2.303}{t}\log_{10}\frac{a}{(a-x)} \Rightarrow t = \frac{2.303}{k_1}\log_{10}\frac{a}{(a-x)}$$

where t = time, a = initial concentration at t = 0

(a – x) = concentration after time t

K = Rate constant



(C) Graphical Representation

Graph between t v/s log is a straight line

Second order reaction

$$A + A \longrightarrow \text{Product}$$

$$A + B \longrightarrow \text{Product}$$

At t = 0	a	a	0
At t = t	(a – x)	(a – x)	x
At t = t_1	(a – x_1)	(a – x_1)	x_1
At t = t_2	(a – x_2)	(a – x_2)	x_2

As per rate law,

$$\frac{dx}{dt} = k_2[A]^n = k_2[A]^2 = k_2[A][B]$$

$$(\frac{dx}{dt}) = k_2(a-x)^2 \;\; (k_2 = \text{ rate constant for second order reaction})$$

Also,

$$k_2 = \frac{1}{t}[\frac{1}{(a-x)} - \frac{1}{a}] = \frac{1}{t}\frac{a}{a(a-x)} \text{ or } k_2 = \frac{1}{(t_2-t_1)}[\frac{1}{(a-x_2)} - \frac{1}{(a-x_1)}]$$

Where $(a-x_1)$ and (a Where $(a-x_1)$ and $(a-x_2)$ are the concentration of the reactant A at time t_1 and t_2 respectively. If reactant A at B have different concentrations a and b, then

$$k_2=\frac{2.303}{t(a-b)}\log_{10}\frac{b(a-x)}{a(b-x)}$$

when $a>b$ then $(a-b)\approx a(a-x)\approx a$

Equation reduces to

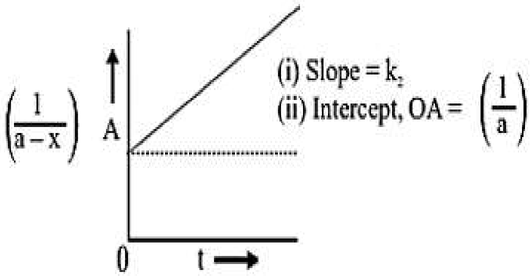
$$k_2=\frac{2.303}{t\times a}\log_{10}\frac{b}{a-x}$$

$$k_2'=k_2\times a=\frac{2.303}{t}\log_{10}\left(\frac{b}{b-x}\right)\text{ (equation for first order kinetics)}$$

This is an example of pseudo first order reaction. Equation for second order reaction can be rewritten as

$$\frac{a}{(a-x)}=k_2t+\frac{1}{a}$$

Graphical Representation



In general for nth order reaction

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

n general for nth order reaction

$$t_{1/2(n)}=\frac{2^{n-1}-1}{(n-1)k_n(a)^{n-1}}\,(n\geq 2)$$

$$t_{1/2(n)}\propto\frac{1}{a^{(n-1)}}$$

$$t_{1/2(n)}\propto a^{(1-n)}$$