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:

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

Therefore, the units of k (assuming that concentration is represented in mol L^{-1} or M and time is represented in seconds) can be calculated via 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 used to express the rate of a reaction in terms of change in the concentration of reactants (d[R]) over a small interval of time (dt). Therefore, the differential form of the rate expression provided in the previous subsection is given by:

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

Differential rate equations can be used to calculate the instantaneous rate of a reaction, which is the reaction rate under a very small-time interval. It can be noted that the ordinary rate law is a differential rate equation since it offers insight into the instantaneous rate of the reaction.

Integrated Rate Equations

Integrated rate equations express the concentration of the reactants in a chemical reaction as a function of time. Therefore, such rate equations can be employed to check how long it would take for a given percentage of the reactants to be consumed in a chemical reaction. It is important to note that reactions of different orders have different integrated rate equations.

Integrated Rate Equation for Zero-Order Reactions

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

$kt = [R_0] - [R]$ (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:

$kt = 2.303 \log([R_0]/[R])$ (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 mins = 600 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: -

Rate constant is a measure of the rate of the reaction.

LARGER THE VALUE OF K →→ FAST REACTION

SMALLER THE VALUE OF K →→→→ SLOW REACTION

Different reactions have different value of k.

The value of k changes with change in temperature and catalyst.

The rate constant is independent on concentration of reactants zero order reactions.

Integrated rate equations (part i):-

The concentration dependence of rate is called differential rate equation. Integrated rate equation gives a relation between directly measured experimental quantities i.e. concentrations at different times. The integrated rate equations are different for reactions of different orders.

The instantaneous rate of a reaction is given by differential rate law equations.

For example: For a general reaction

aA +bB —–> 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:

$k = molL^{-1}sec^{-1}$Unit of rate of reaction = 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 $t = t_{1/2}$; $x = \frac{a}{2}$

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

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

Integrated rate equations (part ii):-

First order reaction

When the rate of reaction depends only on one concentration term of reactant.

A first order reaction is one whose rate varies as first power of the concentration of the reactant, i.e. the rate increases as number of times as the concentration of reactant is increased.

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

A → 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.

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

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

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,

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

This is the integrated rate expression for first order reaction

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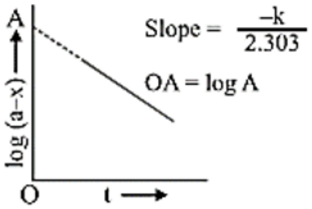


$$\text{As, } k = \frac{1}{t}\ln\frac{a}{a-x} \Rightarrow \log(a-x) = \log(a) - \frac{kt}{2.303}$$

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

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

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

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:

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

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

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

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

For zero order reaction, n = 0 and hence,

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

For first order reaction, n = 1 and hence,

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

For second order reaction, n = 2 and hence,

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

The rate constant of a first order reaction has only time in its unit. It has no concentration term in the unit. This means the numerical value of k for a first order reaction is independent of the unit in which concentration is expressed. If concentration unit is changed, the numerical value of k for a first order reaction will not change. However, it would change with change in time. Say, k is 6.0×10^{-3} min then it may also be written as 1×10^{-4} s^{-1}, i.e., numerical value of k will decrease 60 times if time unit is changed from hour to minute or from minute to second.

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

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

$(\because \log 2 = 0.30103)$

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

Since k is a constant for a given reaction at a given temperature and the expression lacks any concentration term so from Eq. **(3)** it is evident that independent of initial concentration of reactant.

This means if we start with 4 moles L^{-1} of a reactant reacting by first order kinetics, then after 20 minutes it is reduced to 2 moles L^{-1}. That is, after 20 minutes from the start of reaction reactant will be 2 moles L^{1}after 40 minutes from the start of reaction, the concentration is 1 mole L^{-1}. After 60 minutes from the start of reaction, the concentration of the reactant will be reduced to 0.5 mol L^{-1}. In other words, if during 20 minutes 50% of the reaction completes, then in 40 minutes 75%, in 60 minutes 85.5% of the reaction and so on, will complete as shown 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 ® Product

2NO $2N_2 + O_2$

$2Cl_2O_7$ ® $2Cl_2 + 7O_2$

(A) Unit of rate constant of first order reaction

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

(B) Velocity constant for first order reaction

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

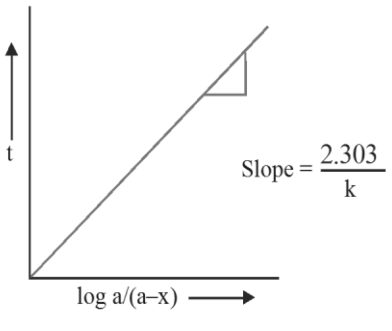
where t = time, a = initial concentration at t = 0

(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,

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

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

Also,

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

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

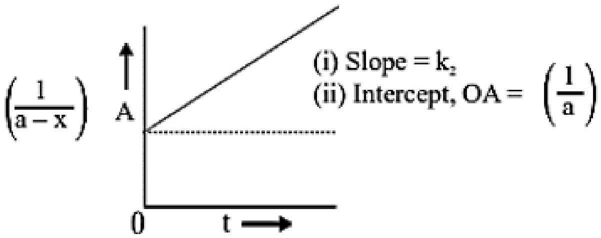
$$k_2 = \frac{2.303}{t \times a}\log_{10}\frac{b}{a - x}$$

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

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

$$\frac{a}{(a - x)} = k_2 t + \frac{1}{a}$$

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

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

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

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