Integrated Rate laws

1.Zero order Reaction:

A reaction , whose rate is independent of concentration , is a zero order reaction. Thus for a zero order reaction

$$A \longrightarrow \text{Product} \quad \ldots\ldots\ldots\ldots\ldots\ldots(14)$$

$$\mathbf{-dC_A/dt = kC^0_A}$$

$$\mathbf{So,\ -dC_A/dt = k}$$

Where $\mathbf{C_A}$ is the concentration of the reactant A at time t . Thus

$$\mathbf{dC_A = -kdt} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(15)$$

Integrating, $\mathbf{C_A = a - kt}$ ………………………..(16)

Where a is the integration constant and equal to the concentration of the reactant at t=0 [i.e, the initial conc.]. Thus a plot of $\mathbf{C_A}$ vs t should be linear with –k as slope.

A zero order reaction will be complete at time t= a/k, , when $\mathbf{C_A=0}$**.** The half life period [time to complete half,i.e when half of the reactant is spent], $t_{1/2}$ is a/2k [when C_A =a/2]

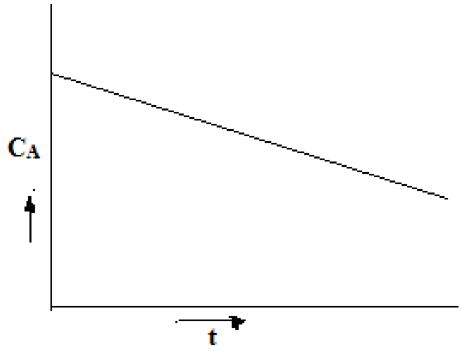


Fig2: Conc. vs time plot for zero order reaction

No known homogeneous gas reaction is of zero order. In solution, iodination of acetone in presence of acid catalyst is found to have zero order with respect to iodine. Many enzyme catalysed reactions are zero order with respect to the reactant. The decomposition of various gases on the surface of solid catalyst, such as the decomposition of HI on gold surface is of zero order.

2. First order reactions:

Consider a reaction , $A \longrightarrow \text{Products}$ ……………………………………………(17)

Let a mol dm^{-3} be the initial conc. of A. If after time t, x mol dm^{-3} of A decompose, the remaining concentration of A is (a-x). The rate of formation of the product at any instant is dx/dt. For a first order reaction, the rate is proportional to the instantaneous concentration of A, so that

$-dC_A/dt = -d(a-x)/dt = dx/dt \infty (a-x)$ ………………………….(18)

$dx/dt = k(a-x)$

$dx/(a-x) = k\,dt$……………………………….(19)

where k is the proportionality constant called the first order rate constant. Its unit is $time^{-1.}$

Now integration of equation (19)

i.e $\int dx/(a-x) = k\int dt$

$-\ln(a-x) = kt + I$ ……………………………………..(20)

Where I is the constant of integration and its value is obtained from the initial conditions of the reaction. Initially, when t=0,x=0 , putting these values in equation (20), we get

$I = -\ln a$

And hence eqn. (20) becomes,

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

$\mathbf{\ln(a/a-x) = kt}$ ……………………………….(21)

or $\mathbf{x = a(1-e^{-kt})}$

$[A]_t = [A]_0 e^{-kt}$…………………………….(22)

Where $[A]_0$ is the initial concentration of the reactants and $[A]_t$ its value after time t. It is clear from this expression that the quantity of reacting material falls off exponentially, and theoretically the reaction is complete, i.e, $[A]_t = 0$, only when t is infinity. In other words, the reaction is never 100% complete. The rate at which the curve (Fig1) approaches time axix depends on the value of k. If the value of k is large, the curve will approach the time axix in shorter time than for a smaller value of k.

Equation (21) can be rewritten as ,

$k = 1/t \ln(a/a-x)$

or, $k = 2.303/t \log(a/a-x)$ ……………………………….(23)

$k = 2.303/t \log [A]_0/[A]_t$ ……………………………………………….(24)

This equation is known as the integrated rate equation for reaction of the first order.

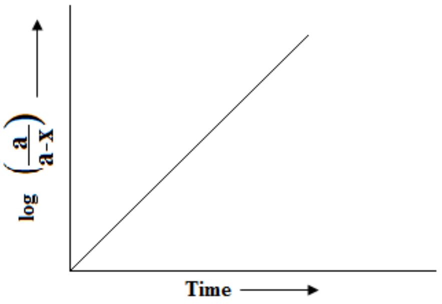


Fig3: Plot of log(a/a-x) vs t

If log(a/a-x) is plotted against t, a straight line passing through the origin is obtained; the slop of which is k/2.303 (Fig.3).

Half-Life Period Of The First Order Reaction

The time required when half of the reactant is converted into the products is called half life period of a reaction. It is denoted by $t_{1/2}$

Mathematically, when

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

Putting these values in eqn.(23), we get

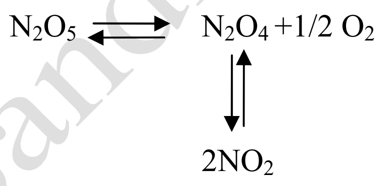
$$k= 2.303/\ t_{1/2} \log (a-a/2)$$

$$t_{1/2}=0.0693/k \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\ (25)$$

The result shows that for a first order reaction the half –life period is independent of the initial concentration of the reactant. This means that for a given first order reaction, half-life period is the same, whatever be the initial concentration. This simple relation represented by eqn. (25) makes the half –life a useful quantity for first order reactions.

Some Examples of The First Order Reaction

i) The thermal decomposition of nitrogen pentoxide in gaseous phase is a first order reaction and the product are oxygen, nitrogen dioxide and nitrogen tetroxide. The overall reaction is represented as



$$\begin{tikzcd} N_2O_5 \arrow[r, shift left] & N_2O_4 + 1/2\ O_2 \arrow[l, shift left] \arrow[d, shift right] \\ & 2NO_2 \arrow[u, shift right] \end{tikzcd}$$

ii) Hydrolysis of an ester in the presences of mineral acid: The hydrolysis of an ester is usually catalysed by an acid. The reaction is represented as

$$CH_3COOC_2H_5 + H_2O \xrightarrow{H_3O^+} CH_3COOH + C_2H_5OH$$

The rate of this reaction is determined only by the concentration of ester as water is present in large excess and its concentration is assumed to be constant. Hence this is a first order reaction. The kinetics of the reaction is studied in the laboratory by titrating a known volume of ester containing HCl against standard alkali. The amount of alkali used is equivalent to the amount of acetic acid obtained by the ester hydrolysis and the total amount of HCl added. When t=0, i.e., at the start of the reaction, volume of alkali used is equivalent to the HCl added. Let it be V_0. If V_t be the volume of alkali used after time t, then $(V_t - V_0)$ is the volume required to neutralize acetic acid formed by the hydrolysis of ester in time t. This quantity $(V_t - V_0)$ is thus proportional to x in the rate equation for first order reaction. When the reaction is complete,i.e, at t=∞, let V_∞ be the volume of the alkali used. This corresponds to the amount of acetic acid obtained by complete hydrolysis of the ester and the amount of the HCl initially added. Thus, $(V_\infty - V_0)$ is proportional to a, the initial concentration of the ester. Since the concentration of the ester at any time t is proportional to (a-x) and this can be obtained as

$$(a-x) \infty (V_\infty - V_0) - (V_t - V_0)$$

$$= V_\infty - V_t$$

Hence the equation for the first order reaction becomes

$$\mathbf{k = 2.303/t \log \{(V_\infty - V_0)/(V_\infty - V_t)\}} \quad \ldots\ldots\ldots\ldots\ldots\ldots (26)$$

Hence a plot of the ln $[\mathbf{V_\infty - V_t}]$ versus t will be linear with k as slope. Now, $\mathbf{V_0}$ may be eliminated if we use Δt:

$$\mathbf{t_1 = 2.303/k \log \{(V_\infty - V_0)/(V_\infty - V_{t1})\}}$$

$$\mathbf{t_2 = 2.303/k \log \{(V_\infty - V_0)/(V_\infty - V_{t2})\}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\mathbf{(27)}$$

Here obviously, Rate $=kC_{\mathbf{CH3COOC2H5}}$ ………………………………**(28)**

The solvent H_2O participates in the reaction and the rate law have been

$$r = \mathbf{k^{/}}\, C^{v1}_{\mathbf{CH3COOC2H5}}\, \mathbf{C^{v2}}_{H2O.} \quad \ldots\ldots\ldots\ldots(29)$$

However, H_2O is always present in the greater excesses, and thus its concentration remain nearly constant during a given run and from one run to another.

Thus $\mathbf{k^{/}\, C^{v2}}_{H2O}$ is another constant k. The reaction is pseudo 1st order since ν1=1

iii)The inversion of cane sugar in the presence of dilute mineral acids is a first order reaction and is presented as

$$C_{12}H_{22}O_{11} \xrightarrow{H_3O^+} C_6H_{12}O_6 + C_6H_{12}O_6$$

The progress of this reaction has been followed by measuring the change in the angle of rotation at various intervals of time . Let α_0, α_t and α_∞ represent the angles of rotation when t=0 (at the start of the reaction), after time t and at the completion of the reaction respectively. Then evidently, $a \infty (\alpha_0 - \alpha_\infty)$ and $(a-x) \infty (\alpha_t - \alpha_\infty)$. Hence the rate equation becomes

$$\mathbf{k = 2.303/t \log \{(\alpha_0 - \alpha_\infty)/(\alpha_t - \alpha_\infty)\}} \quad \ldots\ldots\ldots\ldots\ldots\ldots \mathbf{(30)}$$

And a plot of $\mathbf{ln(\alpha_t - \alpha_\infty)}$ versus t will be linear.

This concentration of acid catalyst H^+ is constant during a given run, and water is taken in excess. The above reaction is a pseudo 1st order reaction. However, the rate study indicates that it is 1st order in H^+ and 6th order in water concentration[explained by a mechanism involving hexahydrate of sucrose] and

Rate= $\mathbf{k}^{/}$ C $C_{12}H_{22}O_{11}\mathbf{C}^{6}{}_{H2O}$ …………………… (31)

During a given run, the order of inversion of sucrose was initially shown to be 1st order by L.Wilhelmy in 1850. The above reaction are also referred to as pseudo unimolecular reactions.

3. Second Order Reactions

The reaction

A+A→ Product (s)

Follows a second order kinetics if the rate is proportional to the square of the concentration of A i.e,

$-d[A]/dt=k[A]^2$ ……………………………………..(32)

However, if the reaction is , A+B→ Product (s)

the rate is proportional to the product of the concentration of each reactant

$-d[A]/dt=-d[B]/dt =\mathbf{dx}/dt=\mathbf{k}[A][B]$ …………………………………..(33)

where **dx**/dt is the rate of disappearance of A or B or appearance of the products. From eq. (32), $\mathbf{dx}/dt=k(a-x)^2$ ………………………………………..(34)

From eq. (33), $\mathbf{dx}/dt=k(a-x)(b-x)$ ………………………………………..(35)

In these equations a and b are the initial concentration of A and B in mol dm^{-3} respectively. In Eq.(35) if a=b, i.e, when the concentration of two reacting species are same, then the rate is given by eqn (34). Integrating this eqn we get

$$\int \mathbf{dx}/(a-x)^2=k\int dt$$

$$1/(a-x)=kt+I \;\text{…………………..(36)}$$

Where I is the constant of integration and its value can be obtained by applying the initial conditions, i.e., when t=0, x=0

$$I = 1/\mathbf{a}$$

Putting the of integration constant in Eq.(36), we get

$$1/(a-x) = kt + 1/\mathbf{a}$$

$$\textbf{or,}\quad \mathbf{k = x/at(a-x)} \quad \ldots\ldots\ldots\ldots\ldots(37)$$

From eq.(37), it is clear that k has units of $(\text{time})^{-1}(\text{concentration})^{-1}$.

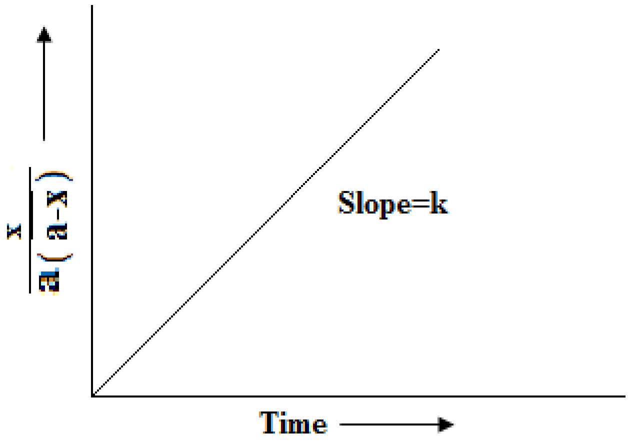


Figure 4: Plot of x/a(a-x) verses t

A plot of x/a(a-x) verses t should be a straight line passing through the origin with slop equal to k (**Fig 4**).

When the concentration of the reacting species are different, i.e.,a≠b, then the rate is given by Eq.(35),

$$\mathbf{dx}/dt = k(a-x)\,(b-x)$$

separating the variable, we get

$$\mathbf{dx}/(a-x)\,(b-x) = k\,dt \quad \ldots\ldots\ldots\ldots\ldots\ldots (38)$$

The expression $\mathbf{1}/(a-x)\,(b-x)$ can be resolved into partial fraction as

$$\mathbf{1}/(a-x)\,(b-x) = \mathbf{A}/(a-x) + \mathbf{B}/\,(b-x)$$

$$\mathbf{1}/(a-x)\,(b-x) = \{A(b-x)+B(a-x)\}\{(a-x)(b-x)\}$$

$$\mathbf{1 = A}(b-x) + B(a-x)$$

$1=Ab+Ba$

And $-A-B=0$

From this we get $A=1/(b-a)$

And $B= 1/(a-b)$

Hence, $\mathbf{1}/(a-x)(b-x)=1/(b-a)(a-x)+1/(a-b)(b-x)$

$=1/(a-b)[1/(b-x)-1/(a-x)]$

Eq(38) becomes

$1/(a-b)[1/(b-x)-1/(a-x)]dx=kdt$

On integrating this equation, we get

$1/(a-b)[\int dx/(b-x)-\int dx/(a-x)]dx=k\int dt$

or, $1/(a-b)[-\ln(b-x)+\ln(a-x)]dx=kt+I$ ……………………………. (39)

Again, when $t=0$, $x=0$, and therefore

$1/(a-b)[\ln(a/b)]=I$

Putting the value of I in eq (39), we obtain

$1/(a-b)[-\ln(b-x)+\ln(a-x)]dx=kt+1/(a-b)[\ln(a/b)]$

or, $kt=1/(a-b)\ln\{b(a-x)/a(b-x)\}$

$k= 2.303/(a-b)t\log\{b(a-x)/a(b-x)\}$ …………………………………. (40)

$t= 2.303/(a-b)k\log\{b(a-x)/a(b-x)\}$ …………………………………. ..(41)

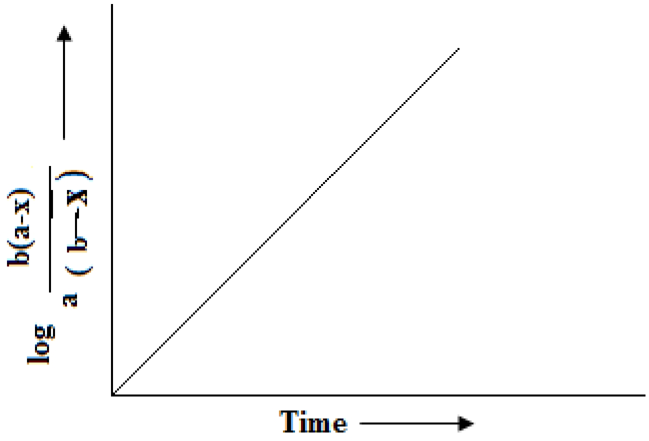


Fig 5: Plot of log {b(a-x)/a(b-x)} vs t

The eq (41) shows that the plot of log {b(a-x)/a(b-x)} versus t for such a reaction would be straight line passing through the origin and the slope of the line is equal to k(a-b)/2.303.

In the reaction A+B → Products, if the concentration of one of the reactants is taken in large excess, the reaction then becomes kinetically of first order. This can be shown as follows.

Let b be the excess concentration, i.e., b>>a or x, so that a-b≈-b and b-x≈b

Therefore eq (40) reduces to

k= -2.303/btlog b(a-x)/ab

=-2.303/btlog (a-x)/a

=2.303/btlog a/(a-x)

Since B is the reactant present in excess, so its concentration b may be taken as almost constant and hence the above equation is equivalent to that for a first order reaction (23)

Half-Life Period for a Second Order Reaction

The half -life period for a second order reaction in which the reactants are identical or different but have equal initial concentration can be calculated using Eq.(37). However, the half-life period cannot be calculated for reactions where concentrations of A and B are different as both A and B will have different times for half conversion.

Thus in equation,

$k=x/at(a-x)$

when $t=t_{1/2}$, $x=a/2$, we get $k=(a\backslash 2)/\ t_{1/2}.\ a.\ (a-a/2)$

$t_{1/2}=1/ka$ ………………. ……..……..(42a)

$t_{1/2}\infty 1/a$ ………………. ……..……..(42b)

The half-life period ($t_{1/2}$) for a second order reactions is inversely proportional to the first power of the initial concentration for the reactant. Knowing $\mathbf{t_{1/2}}$ and a, k is readily calculated from Eq.(42).A practical consequence of second order reaction is that the species which decay by second order reactions may persist in low concentrations for long time because their half-lifes are long when their concentration are low.

Example of 2nd order Reactions:

(i) The saponification of an ester is an example of a second order reaction.

$CH_3COOC_2H_5+OH^- \rightarrow CH_3COO^- +C_2H_5OH$

(ii) Decomposition of HI

$2HI\rightarrow H_2+I_2$

General Expression for the Rate of a Reaction

Reactions in which one reactant is involved may be represented as

$nA\rightarrow Product(s)$

The rate equation of such reactions is given as, $dx/dt=k(a-x)^n$ ……….. (43)

Integration of eq (43) becomes,

$$\int_0^x dx/(a-x)^n = \int_0^t k.dt$$

$1/(n-1)[1(a-x)^{n-1}-1/a^{n-1}]=kt$ …………………………… (44)

This equation holds for all values of n except for n=1. When n=1, (n-1)=0, the equation becomes indeterminate.

The half-life period($t_{1/2}$) for a reaction of of nth order is given by

$t_{1/2} = (2^{n-1}-1)/\{(n-1)a^{n-1}.k\}$

or $t_{1/2} \propto 1/a^{n-1}$ **…………………………………………. (45)**