# Reaction of First Order

A reaction is said to be of the first order if the rate of the reaction depends upon only on concentration term only. Thus we may have

For the reaction : $A \longrightarrow$ Products
Rate of reaction $\propto [A]$.
For the reaction : $2A \longrightarrow$ Products
Rate of reaction $\propto [A]$ only.
For the reaction : $A + B \longrightarrow$ Products
Rate of reaction $\propto [A]$ or $[B]$ only.

Let us consider the simplest case viz.

$$A \longrightarrow \text{Products}$$

Suppose we start with 'a' moles per litre of the reactant A. After time t, suppose x moles per litre of it, have decomposed. Therefore, the concentration of A after time $t = (a - x)$ moles per litre. Then according to Law of Mass Action.

Rate of reaction $\propto (a - x)$

i.e., $$\frac{dx}{dt} \propto (a - x)$$

or $$\frac{dx}{dt} = k\,(a - x) \qquad \text{..... (1)}$$

where k is called the rate constant or the specific reaction rate for the reaction of the first order. The expression for the rate constant k may be derived as follows :

Equation (1) may be rewritten in the form

$$\frac{dx}{a - x} = kdt \qquad \text{.....(2)}$$

Integrating equation (2), we get $\int \frac{dx}{a - x} = \int kdt$

or $$k = \frac{1}{t} \ln \frac{a}{a - x} \qquad \text{.....(3)}$$

or $$k = \frac{2.303}{t} \log \frac{a}{a - x} \qquad \text{.....(4)}$$

Equation (4) is sometimes written in another form which is obtained as follows :

If the initial concentration is $[A]_0$ and the concentration after time t is $[A]$, then putting $a = [A]_0$ and $(a - x) = [A]$ equation (iv) becomes

$$k = \frac{2.303}{t} \log \frac{[A]_0}{[A]} \qquad \text{..... (5)}$$

Further, putting $a = [A]_0$ and $(a - x) = [A]$ in eqn. (3), we get

$$kt = \ln \frac{[A]_0}{[A]}$$

which can be written in the exponential form as

$$\frac{[A]_0}{[A]} = e^{kt} \quad \text{or} \quad \frac{[A]}{[A]_0} = e^{-kt}$$

or $$[A] = [A]_0\, e^{-kt} \qquad \text{..... (6)}$$

***Example 11 :***

***It was found that cane sugar solution in water was hydrolysed to the extent of 25 per cent in one hour. Calculate the time that will be taken for the sugar to be hydrolysed to the extent of 50 %, assuming that the reaction is of the first order.***

***Solution :***

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

Where $\frac{x}{a} = f$

$$t_f = \frac{2.303}{k_1}\log\frac{1}{(1-f)} = -\frac{2.303}{k_1}\log(1-f) \qquad .....(1)$$

Putting f = 0.25 at $t_{0.25}$ = 1 hour from the data

$$t_{0.25} = 1\text{ hr} = \frac{2.303}{k_1}\log(1-0.25) = \frac{2.303}{k_1}\log 4/3 \qquad .....(2)$$

$$\text{Similarly } t_{0.5} = -\frac{2.303}{k_1}\log(1-0.5) = \frac{2.303}{k}\log 2 \qquad .....(3)$$

Dividing (iii) by (ii) $\frac{t_{0.5}}{1\text{hr}} = \frac{\log 2}{\log 4/3} = 2.4$ hours

Hence time required for 50% hydrolysis = 2.4 hours.

***Example 12 :***

***The half time of first order decomposition of nitramide is 2.1 hour at 15°C.***

$$NH_2NO_2(s) \longrightarrow N_2O(g) + H_2O(l)$$

***If 6.2 g of $NH_2NO_2$ is allowed to decompose, calculate***

***(a) time taken for $NH_2NO_2$ to decompose 99% and***

***(b) volume of dry $N_2O$ produced at this point measured at STP.***

***Solution :***

For a first-order reaction, rate constant expression is $k = \frac{2.303}{t}\log\frac{[A]_0}{[A]_t}$

$$\text{Initial moles of nitramide} = \frac{6.2}{62} = 0.1$$

$$t = \frac{2.303\times 2.1}{0.693}\log\frac{0.1}{0.001} = 13.95\text{ hours}$$

Since, the decomposition is 99 %, so 99 % of the initial moles of $NH_2NO_2$ would be converted to $N_2O$.

$$\text{Moles of } N_2O = \frac{0.1\times 99}{100}$$

$$\text{Volume of } N_2O \text{ at STP} = \frac{0.1\times 99\times 22.4}{100} = 2.217\text{ litre}.$$

*Example 13 :*

***A drug becomes ineffective after 30 % decomposition. The original concentration of a sample was 5mg/mL which becomes 4.2 mg/mL during 20 months. Assuming the decomposition of first order, calculate the expiry time of the drug in months. What is the half life of the product?***

***Solution :*** $k = \frac{2.303}{t} \log \left[\frac{a}{a-x}\right]$

$$= \frac{2.303}{20} \log_{10}\left(\frac{5}{4.2}\right)$$

$$= 0.00872 \text{ min}^{-1}$$

Expiry time 't' may be calculated as

$k = \frac{2.303}{t} \log_{10} \frac{a}{a-x}$  $0.00872 = \frac{2.303}{t} \log_{10} \frac{100}{70}$

$t = 40.9 \approx 41$ months  $t_{1/2} = \frac{0.693}{0.00872} = 79.4$ months

*Example 14 :*

***A first order reaction is 20 % completed in 10 minutes. Calculate the time taken for the reaction to go to 80 % completion.***

**Solution :**

Applying first order equation,

$$k = \frac{2.303}{t} \log_{10} \frac{100}{(100-20)} = \frac{2.303}{10} \log_{10} \frac{100}{80} = 0.0223 \text{ min}^{-1}$$

Again applying first order equation,

$$t = \frac{2.303}{k} \log_{10} \frac{100}{(100-80)} = \frac{2.303}{0.0223} \log_{10} \frac{100}{20} = 72.18$$

## Some Important Characteristics of First Order Reactions :

**(i)** Any reaction of the first order must obey equation (5) or (6). This may be tested in any one of the following ways :

**(a)** ***Substitution method :*** Starting with a known concentration 'a' or $[A]_0$, the concentration of the reactant (a – x) or [A] at different intervals of time may be noted. For every value of t, the corresponding value of (a – x) i.e. [A] may be substituted in equation (vi) or (vii). If the values of k thus obtained are nearly constant (within the experimental error), the reaction is of the first order.

**(b)** ***Graphical method :*** Equation (6) may be written as

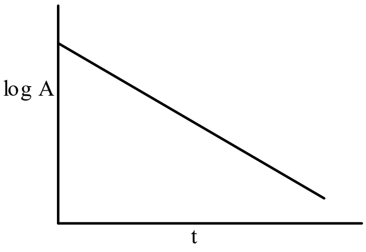
$$\frac{k}{2.303} t = \log \frac{[A]_0}{[A]} = \log[A]_0 - \log[A]$$

$$\text{or} \quad \log[A] = -\frac{k}{2.303} t + \log[A]_0 \qquad ..... (7)$$

This is the equation of a straight line (y = mx + c). Thus if log [A] or log (a – x) values are plotted against time 't', the graph obtained should be a straight line if the reaction is of the first order.

The intercept made on the y-axis would be 'log $[A]_0$' and the slope of the line would be equal to $\left(-\frac{k}{2.303}\right)$ i.e., slope $= -\frac{k}{2.303}$

From this, the value of k can be calculated.



**(ii)** ***Half-life Period :*** The time taken for any fraction of the reaction to be completed is independent of the initial concentration. For example, let us test the truth of this statement for half of the reaction to be completed. Equation (5) may be written as

$$t = \frac{2.303}{k} \log \frac{a}{a - x} \qquad \text{..... (8)}$$

When half of the reaction is completed, x = a/2. Representing the time taken for half of the reaction to be completed by $t_{1/2}$ equation (8) becomes

$$t_{1/2} = \frac{2.303}{k} \log \frac{a}{a - \frac{a}{2}} = \frac{2.303}{k} \log 2 = \frac{0.693}{k} \qquad \text{i.e,} \qquad t_{1/2} = \frac{0.693}{k}$$

Thus 'a' does not appear in this equation so that $t_{1/2}$ is independent of a. Similarly, it can be seen that $t_{1/2}$, $t_{2/3}$ etc. will also be independent of the initial concentration.

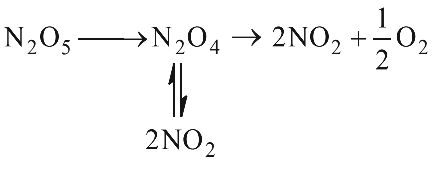
The time taken for half of the reaction to be completed i.e., the time in which the concentration of a reactant is reduced to half of its original value is called Half-life period of the reaction.

The above result can also be used to test a reaction of the first order. The method is called fractional life method.

**(iii)** The units of k are independent of the units in which the concentrations are expressed. This is obvious from equation (5) because in this equation k depends upon the ratio of two concentrations viz. $\frac{a}{a-x}$ and the time t. Thus so long as both a and (a – x) are expressed in the same concentration units, the value of k is not affected. The units of k, therefore, depend only upon the units of time 't'. Depending upon whether t is expressed in second, minutes or hours, k would be in $sec^{-1}$, $min^{-1}$ or $hr^{-1}$ respectively.

## Examples of the Reactions of First Order

**1.** ***Decomposition of Nitrogen Pentoxide :*** The compound, nitrogen pentoxide, is a volatile solid which decomposes in the gaseous state as well as in the form of its solution in an inert solvent like carbon tetrachloride, chloroform etc. according to the equation.



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

(i) When the reaction is carried out in the solution, $N_2O_4$ and $NO_2$ remain in the solution and the volume of oxygen gas collected is noted at different intervals of time. It is obvious that Volume of oxygen gas collected at any time $(V_t)$ $x \propto V_t$.Amount of

$N_2O_5$ decomposed (x) i.e.,

$$x \propto V_t$$

(ii) Volume of oxygen gas collected at infinite time ($V_\infty$) (which is done by heating the reaction vessel) $\Big\}$ $\propto$ Amount of $N_2O_5$ initially taken (a)

$$a \propto V_\infty$$

i.e., Substituting these values in the first order equation viz.

$$k = \frac{2.303}{t}\log\frac{a}{a-x} \qquad \text{We get} \qquad k = \frac{2.303}{t}\log\frac{V_\infty}{V_\infty - V_t}$$

The constancy in the value of k proves the reaction to be of the first order.

***Example 15 :***

***For decomposition of $N_2O_5$ in $CCl_4$ solution at 320 K***

$$2N_2O_5 \longrightarrow 4NO_2 + O_2$$

***show that the reaction is of first order and also calculate the rate constant:***

| ***Time in minutes*** | ***10*** | ***15*** | ***20*** | ***25*** | ***$\infty$*** |
|---|---|---|---|---|---|
| ***Volume of $O_2$ evolved (in ml)*** | ***6.30*** | ***8.95*** | ***11.40*** | ***13.50*** | ***34.75*** |

***Solution :***

If the reaction is of first order, it must obey the equation

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

In the above reaction, $NO_2$ remains in solution and oxygen is liberated and collected at different intervals of time.

Therefore , $V_t \propto x$ $\qquad$ $V_\infty \propto a$

Substituting these values in the first order equation

$$k = \frac{2.303}{t}\log\frac{a}{a-x} = \frac{2.303}{t}\log\frac{V_\infty}{V_\infty - V_t}$$

| Time | $V_t$ | $V_\infty - V_t$ | $k = \frac{2.303}{t}\log\frac{V_\infty}{V_\infty - V_t}$ |
|---|---|---|---|
| 10 | 6.30 | $34.75 - 6.30 = 28.45$ | $k = \frac{2.303}{10}\log\frac{34.75}{28.45} = 0.0198$ |
| 15 | 8.95 | $34.75 - 8.95 = 25.80$ | $k = \frac{2.303}{15}\log\frac{34.75}{25.80} = 0.0198$ |
| 20 | 11.40 | $34.75 - 11.40 = 23.35$ | $k = \frac{2.303}{200}\log\frac{34.75}{23.35} = 0.0198$ |
| 25 | 13.50 | $34.75 - 13.50 = 21.25$ | $k = \frac{2.303}{25}\log\frac{34.75}{21.25} = 0.0198$ |

Since the value of k comes out to be constant the reaction, therefore, is of first order. The average value of rate constant is 0.0198 $min^{-1}$.

**Decomposition of Hydrogen Peroxide :** The decomposition of hydrogen peroxide in aqueous solution (catalysed by the presence of finely divided platinum) takes place according to the equation

$$H_2O_2 \longrightarrow H_2O + \tfrac{1}{2}O_2$$

The kinetics of this reaction may be studied either by the same method as done earlier (i.e. collecting the oxygen gas produced and noting its volume at different intervals of time) or by making use of the fact that $H_2O_2$ solution can be titrated against $KMnO_4$ solution. Thus by withdrawing equal amounts of the solution (usually 5 cc) at regular intervals of time and titrating against the same $KMnO_4$ solution, the amount of $H_2O_2$ present can be found every time. It is obvious that for the same volume of the reaction solution withdrawn,

$$\left.\begin{matrix}\text{Volume of } KMnO_4 \text{ solution used}\\ \text{before the commencement of the}\\ \text{reaction i.e. at zero time } (V_0)\end{matrix}\right\} \propto \left\{\begin{matrix}\text{Initial concentartion}\\ \text{of } H_2O_2 \text{ (a)}\end{matrix}\right.$$

i.e., $a \propto V_0$

$$\left.\begin{matrix}\text{Volume of } KMnO_4 \text{ solution used}\\ \text{at any instant of time t } (V_t)\end{matrix}\right\} \propto \left\{\begin{matrix}\text{Amount of } H_2O_2\\ \text{present at that}\\ \text{instant i.e. (a - x)}\end{matrix}\right.$$

$$(a - x) \propto V_t$$

Substituting these values in the first order equation, we get

$$k = \frac{2.303}{t}\log\frac{a}{a-x} \qquad \text{or} \qquad k = \frac{2.303}{t}\log\frac{V_0}{V_t}$$

The decomposition of hydrogen peroxide, as tested by this equation, is found to be of the first order.

***Example 16 :***

***From the following data show that the decomposition of an aqueous solution of hydrogen peroxide is of first order :***

| ***Time (minutes)*** | ***0*** | ***10*** | ***20*** | ***30*** |
|---|---|---|---|---|
| ***V (ml)*** | ***46.1*** | ***29.8*** | ***19.6*** | ***12.3*** |

***where V is the volume of potassium permanganate solution in ml required to decompose a definite volume of the peroxide solution.***

***Solution :***

It is evident from the given data that at zero time, titre value is proportional to the original concentration of hydrogen peroxide, i.e., a. The titre value at any time t corresponds to undecomposed hydrogen peroxide, i.e., (a – x).

Substituting the value in the equation

$$k_1 = \frac{2.303}{t}\log\frac{a}{a-x}, \text{ we get}$$

(i) $$k_1 = \frac{2.303}{10}\log\frac{46.1}{29.8} = 4.364\times10^{-2}$$

(ii) $$k_1 = \frac{2.303}{20}\log\frac{46.1}{19.6} = 4.276\times10^{-2}$$

(iii) $k_1 = \frac{2.303}{30}\log\frac{46.1}{12.3} = 4.404\times10^{-2}$

Since $k_1$ comes out to be constant in the two cases, the reaction is a first order one with the average value of three.

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## Pseudo Unimolecular Reaction

Consider the following acid-catalysed reactions:

**(i)** Hydrolysis of ethyl acetate

$$\underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + H_2O \xrightarrow{H^+} \underset{\text{Acetic acid}}{CH_3COOH} + \underset{\text{Ethyl alcohol}}{C_2H_5OH}$$

**(ii)** Inversion of cane-sugar

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{Glu cos e}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

Both the above reactions are bimolecular but are found to be of the first order, as experimentally it is observed that

For the first reaction, Rate of reaction $\propto$ $[CH_3COOC_2H_5]$ only

and for the second reaction, Rate of reaction $\propto$ $[C_{12}H_{22}O_{11}]$ only.

The reason for such a behaviour is obvious from the fact that water is present in such a large excess that is concentration remains almost constant during the reaction.

Such reactions which are not truly of the first order but under certain conditions become reactions of the first order are called pseudo-unimolecular reactions.

**The kinetics of the above reactions have been studied as follows :**

### (a) Hydrolysis of Ethyl acetate

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

In this reaction acetic acid is one of the products, the amount of which can be found by titration against standard NaOH solution. But being an acid-catalysed reaction, the acid present originally as catalyst, also reacts with NaOH solution. Hence a little careful though reveals that for the same volume of reaction mixture withdrawn at different times.

$$\left.\begin{matrix}\text{Volume of NaOH solution used in}\\ \text{the beginning i.e. at zero time } (V_0)\end{matrix}\right\} \propto \left\{\begin{matrix}\text{Amount of acid present only as catalyst}\\ \text{(as no } CH_3COOH \text{ is produced at } t=0)\end{matrix}\right. \quad \text{..... (i)}$$

$$\left.\begin{matrix}\text{Volume of NaOH solution used}\\ \text{at any instant of time t } (V_t)\end{matrix}\right\} \propto \left\{\begin{matrix}\text{Amount of acid present as catalyst}\\ +\text{ amount of } CH_3COOH \text{ produced}\end{matrix}\right. \quad \text{..... (ii)}$$

Combining results (i) and (ii), we find that

$$\left.\begin{matrix}\text{Amount of } CH_3COOH \text{ produced}\\ \text{at any instant of time}\end{matrix}\right\} \propto (V_t - V_0) \quad \text{..... (iii)}$$

$$\left.\begin{matrix}\text{But amount of } CH_3COOH \text{ produced}\\ \text{at any instant of time}\end{matrix}\right\} \propto \left\{\begin{matrix}\text{Amount of } CH_3COOC_2H_5\\ \text{that has reacted (x)}\end{matrix}\right.$$

Hence $x \propto (V_t - V_0)$ ..... (iv)

Further

$$\left.\begin{array}{l}\text{Volume of NaOH solution used after the reaction}\\ \text{has taken place for a long time, say 24 hours or so,}\\ \text{called infinite time } (V_\infty)\end{array}\right\} \propto \left\{\begin{array}{l}\text{Amount of acid present as}\\ \text{catalyst + Max. amount}\\ \text{of CH}_3\text{COOHproduced}\end{array}\right. \quad .....(v)$$

Combining results (i) and (v), we find that

Max. amount of $CH_3COOH$ produced $\propto (V_\infty - V_0)$

But Max. amount of $CH_3COOH$ produced

$$\propto \text{ Initial concentration of } CH_3COOC_2H_5 \qquad .....\text{(vi)}$$

Hence, $a \propto (V_\infty - V_0)$

From equations (iv) and vi), we have

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

or $$(a - x) \propto (V_\infty - V_t) \qquad .....\text{(vii)}$$

Substituting the values of a and (a – x) from equations (vi) and (vii) in the first order equation, we get

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

or $$k = \frac{2.303}{t} \log \frac{V_\infty - V_0}{V_\infty - V_t}$$

***Example 17 :***

***In an experiment to study hydrolysis of an ester 0.5 M HCl at 300 K was used. 5 cm$^3$ of the reaction mixture was withdrawn after definite intervals and titrated against 0.2 M NaOH solution. Calculate the rate constant at 300K from the following data.***

| ***t (sec)*** | ***0*** | ***600*** | ***1200*** | ***1800*** | ***∞*** |
|---|---|---|---|---|---|
| ***v (cm$^3$ of NaOH used)*** | ***11.5*** | ***12.0*** | ***12.5*** | ***13.0*** | ***25.5*** |

***Solution :***

From the given data, $V_0 = 11.5$ cm$^3$; $V_\infty = 25.5$ cm$^3$

$\therefore \quad a \alpha V_\infty - V_0 = 25.5 - 11.5 = 14.0$ and $(a - x) \alpha V_\infty - V_t$

Putting the values of $V_t = 12.0$ at 600 sec.; 12.5 at 1200 sec. and 13.0 at 1800 seconds in the equation

$$k_1 = \frac{2.303}{t} \log \frac{V_\infty - V_0}{V_\infty - V_t}, \text{we get}$$

**(i)** $$k_1 = \frac{2.303}{600} \log \frac{14.0}{(25.5 - 12.0)} = \frac{2.303}{600} \log \frac{14.0}{13.5} = 6.061 \times 10^{-5} s^{-1}$$

**(ii)** $$k_1 = \frac{2.303}{1200} \log \frac{14.0}{(25.5 - 12.0)} = \frac{2.303}{1200} \log \frac{14.0}{13.0} = 6.176 \times 10^{-5} s^{-1}$$

**(iii)** $$k_1 = \frac{2.303}{1800} \log \frac{14.0}{(25.5 - 12.0)} = \frac{2.303}{1800} \log \frac{14.0}{12.5} = 6.296 \times 10^{-5} s^{-1}$$

The average value of rate constant $k_1 = 6.177 \times 10^{-5}$ s$^{-1}$

## (b) Optical Rotation Method

### Inversion of Cane Sugar (Sucrose)

$$\underset{\substack{((+);66.5^\circ)\\ \text{dextro-rotatory}}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underbrace{\underset{\substack{\text{glucose}\\((+);52.5^\circ)}}{C_6H_{12}O_6} + \underset{\substack{\text{fructose}\\((-);-92^\circ)}}{C_6H_{12}O_6}}_{\text{laevo-rotatory}}$$

In this reaction by the hydrolysis of dextro-rotatory sucrose produces a mixture of glucose (dextro-rotatory) and fructose (laevo rotatory). As laevo rotation of fructose is more therefore the resulting mixture is laevo rotatory.

The kinetics of above reaction is studied by noting the angle of rotation at different intervals of time using polarimeter.

Say angle of rotation at the start of experiment = $r_0$

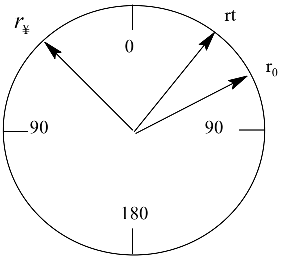
Angle of rotation at any time t = $r_t$

Angle of rotation at ∞ time = $r_\infty$

Now , Angle of rotation at any instant of time = $(r_0 - r_t) \propto$ amount of sucrose hydrolysed

or $x \propto (r_0 - r_t)$

Similarly, angle of rotation at ∞ time



$= (r_0 - r_\infty) \propto$ initial conc. of sucrose (a)

or $a \propto (r_0 - r_t)$

Thus, $(a - x) \propto (r_0 - r_\infty) - (r_0 - r_t)$

$\propto (r_t - r_\infty)$

Hence, $k = 2.303 \log \frac{r_0 - r_\infty}{r_t - r_\infty}$

***Example 18 :***

***The optical rotation of sucrose in 0.5 N-hydrochloric acid at 308 K and at various time intervals are given below. Find out the rate constant for the first order hydrolysis of sucrose.***

| ***Time (minutes)*** | ***0*** | ***10*** | ***20*** | ***30*** | ***60*** | ***∞*** |
|---|---|---|---|---|---|---|
| ***Rotation (degrees)*** | ***+32*** | ***25.5*** | ***20.0*** | ***15.5*** | ***5.0*** | ***-10.50*** |

***Solution :***

Here a , the initial concentration $\propto (r_0 - r_\infty)$

x, the change in time t $\alpha$ $(r_0 - r_t)$

$\therefore$ $(a - x) \propto (r_t - r_\infty)$

Substituting these values for different (a – x) values corresponding to time t from the data in the equation for first order reaction

$$k = \frac{2.303}{t}\log\frac{a}{a-x} = \frac{2.303}{t}\log\frac{r_0 - r_\infty}{r_t - r_\infty},\ \text{we get}$$

**(i)** $$k_1 = \frac{2.303}{10}\log\frac{32-(-10.5)}{25.5-(-10.5)} = \frac{2.303}{10}\log\frac{42.5}{36.0} = 0.0166\ \text{min}^{-1}$$

**(ii)** $k_1 = \frac{2.303}{20}\log\frac{32-(-10.5)}{20.0-(-10.5)} = \frac{2.303}{20}\log\frac{42.5}{30.0} = 0.0166\ \text{min}^{-1}$

**(iii)** $k_1 = \frac{2.303}{30}\log\frac{32-(-10.5)}{15.5-(-10.5)} = \frac{2.303}{30}\log\frac{42.5}{26.0} = 0.0164\ \text{min}^{-1}$

**(iv)** $k_1 = \frac{2.303}{60}\log\frac{32-(-10.5)}{5.0-(-10.5)} = \frac{2.303}{60}\log\frac{42.5}{15.5} = 0.0168\ \text{min}^{-1}$

Average value of $k_1 = 0.0166\ \text{min}^{-1}$

## Half Life of nth order reaction

$$\begin{array}{lcc} & A \longrightarrow & \text{Product} \\ t = 0 & a & 0 \\ t = t & a - x & x \end{array}$$

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

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

$$\int_0^{a/2} \frac{dx}{(a-x)^n} = \int_0^{t_{1/2}} Kdt$$

Let $a - x = z$

$-dx = dz$, when $x = 0$, $z = a$

When $x = a/2$, $z = a/2$

$$\int_a^{a/2} \frac{-dz}{z^n} = \int_0^{t_{1/2}} Kdt > \left[\frac{Z^{-n+1}}{-n+1}\right]_a^{a/2} = kt_{1/2}$$

$$\frac{1}{n-1}\left[\left(\frac{a}{2}\right)^{1-n} - a^{1-n}\right] = kt_{1/2}$$

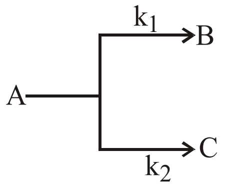
$$\frac{1}{a^{n-1}(n-1)}[2^{n-1}-1] = kt_{1/2},\ (a^{n-1}).t_{1/2} = \left(\frac{1}{K(n-1)}(2^{n-1}-1)\right) = k$$

Therefore for a nth order reaction, half life period in inversely related to initial amount

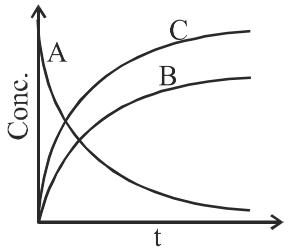
$$t_{\frac{1}{2}}a^{n-1} = \text{constant}$$

## Reaction involving Two First Order Parallel Reactions Or Concurrent Reaction:

These are reactions in which a reacting substance do not follow a particular path to give a particular set of products. It follows one or more paths to give different products. For example,



The reactant A follows two different paths to form B and C. (The change in concentration of A, B and C is given in figure below)



Change in conc. of A, B and C

Let initial conc. of A = a mol $L^{-1}$ and say the amount transformed in time t = x mol $L^{-1}$.
If y and z be amounts of B and C formed at time t, then

$$\frac{dx_A}{dt} = \frac{dy_B}{dt} + \frac{dz_C}{dt}$$

Now if the reaction is unimolecular and $k_1$ and $k_2$ are rate constants for formation of B and C from A then

rate of formation of y, $\frac{dy_B}{dt} = k_1(a - x);$

and rate of formation of z, $\frac{dz_C}{dt} = k_2(a - x)$

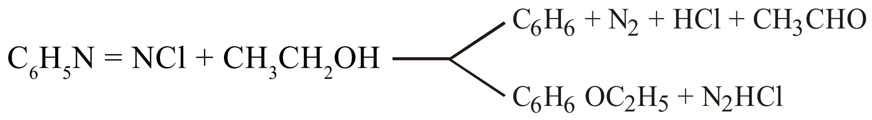
Thus, $\frac{dx_A}{dt} = k_1(a - x) + k_2(a - x) = (k_1 + k_2)(a - x)$

If $k_1 + k_2 = k$, Then $\frac{dx_A}{dt} = k(a - x)$ (Here $r_f B \neq r_f C$)

or the rate of reaction will be $k(a - x)$

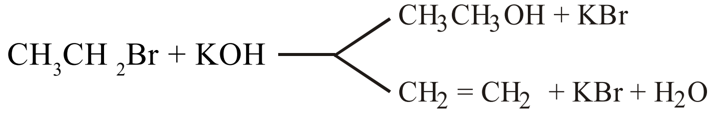
## Some examples of side reactions

**(i)**



$$C_6H_5N = NCl + CH_3CH_2OH \longrightarrow \begin{cases} C_6H_6 + N_2 + HCl + CH_3CHO \\ C_6H_6\ OC_2H_5 + N_2HCl \end{cases}$$

**(ii)**



$$CH_3CH\ _2Br + KOH \longrightarrow \begin{cases} CH_3CH_3OH + KBr \\ CH_2 = CH_2\ + KBr + H_2O \end{cases}$$

### Reactions involving opposing or reversible reactions :

Such reactions results in equilibrium. In other words the reactant changes to product and vice versa.

Say we have an opposing reaction in which both forward and backward reactions are first order, viz.,

($k_1$ and $k_2$ are rate constant of forward and backward reaction)

Say initial conc. of A and B are a and b mol $L^{-1}$ respectively.

If after time t, x moles/L of A change into B, then conc. of A and B will be (a – x) and (b + x) respectively.

The net rate of the reaction would be given as :

Rate = $k_1 (a - x) - k_2 (b + x)$ … (i) [$\because$ both processes occur simultaneously]

When equilibrium is reached, the net rate is zero

Thus, $k_1 (a - x_e) = k_2 (b + x_e)$ (e = equilibrium)

Hence, $(b + x_e) = \frac{k_1}{k_2} (a - x_e)$ or $b = \frac{k_1}{k_2} (a - x_e) - x_e$

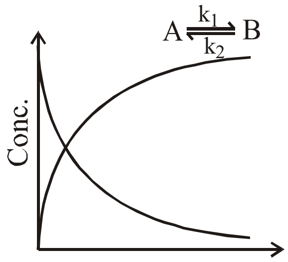
Substituting value of b in eqn. (i)

Rate of reaction, $\frac{dx}{dt} = k_1 (a - x) - k_2 \left[ \frac{k_1}{k_2} (a - x_e) - x_e + x \right]$

on solving, we get

Rate = $(k_1 + k_2) (x_e - x)$

After rearranging and integrating the equation, we get an equation similar to first order reaction as shown below.



or $\frac{dx}{x_e - x} = (k_1 + k_2) dt$ $\int_{x_0}^{x} \frac{dx}{x_e - x} = \int_0^t (k_1 + k_2) dt$

or $\log \frac{x_e - x_0}{x_e - x} = (k_1 + k_2) t$

or $(k_1 + k_2) = \frac{1}{t} \log \frac{x_e - x_0}{x_e - x}$

The equation is similar to first order reaction except that the measured rate constant is now the sum of the forward and the reverse rate constants.

# Exercise

## FIRST ORDER

Q.1 A first order reaction is 75% completed in 72 min.. How long time will it take for
(i) 50% completion (ii) 87.5% completion

Q.2 A first order reaction is 20% complete in 10 min. calculate (i) the specific rate constant , (ii) the time taken for the reactions to go to 75% completion.

Q.3 Show that in case of unimolecular reaction, the time required for 99.9% of the reaction to take place in ten times that required for half of the reaction.

Q.4 A first order reaction has a rate constant is $1.5 \times 10^{-3}$ $sec^{-1}$. How long will 5.0 g of this reactant take to reduce to 1.25 g.

Q.5 A drug is known to be ineffective after it has decomposed 30%. The original concentration of a sample was 500 units/ml. When analyzed 20 months later, the concentration was found to be 420 units/ml. Assuming that decomposition is of I order, what will be the expiry time of the drug?

Q.6 A viral preparation was inactivated in a chemical bath. The inactivation process was found to be first order in virus concentration. At the beginning of the experiment 2.0 % of the virus was found to be inactivated per minute . Evaluate k for inactivation process.

Q.7 If a reaction $A \longrightarrow$ Products, the concentrations of reactant A are $C_0$, $aC_0$, $a^2C_0$, $a^3C_0$, ............ after time interval 0, t, 2t, 3t, ............ where a is a constant. Given $0 < a < 1$. Show that the reaction is of first order. Also calculate the relation in k, a and t.

Q.8 The reaction $SO_2Cl_2(g) \longrightarrow SO_2(g) + Cl_2(g)$ is a first order gas reaction with $k = 2.2 \times 10^{-5}$ $sec^{-1}$ at 320°C. What % of $SO_2Cl_2$ is decomposed on heating this gas for 90 min.

## ORDER OF REACTION & RATE LAW

Q.9 At 800° C the rate of reaction

$$2\,NO + H_2 \longrightarrow N_2 + H_2O$$

Changes with the concentration of NO and $H_2$ are

| | [NO] in M | $[H_2]$ in M | $-\frac{1}{2}\frac{d[NO]}{dt}$ in M $sec^{-1}$ |
|---|---|---|---|
| (i) | $1.5 \times 10^{-4}$ | $4 \times 10^{-3}$ | $4.4 \times 10^{-4}$ |
| (ii) | $1.5 \times 10^{-4}$ | $2 \times 10^{-3}$ | $2.2 \times 10^{-4}$ |
| (iii) | $3.0 \times 10^{-4}$ | $2 \times 10^{-3}$ | $8.8 \times 10^{-4}$ |

(a) What is the order of this reaction?
(b) What is the rate equation for the reaction?
(c) What is the rate when
$[H_2] = 1.5 \times 10^{-3}$ M and $[NO] = 1.1 \times 10^{-3}$M?

Q.10 The data below are for the reaction if NO and $Cl_2$ to form NOCl at 295 K

| Concentration of $Cl_2$ [M] | Concentration of NO | Initial Rate (M $s^{-1}$) |
|---|---|---|
| 0.05 | 0.05 | $1 \times 10^{-3}$ |
| 0.15 | 0.05 | $3 \times 10^{-3}$ |
| 0.05 | 0.15 | $9 \times 10^{-3}$ |

(a) What is the order w.r.t NO and $Cl_2$ in the reaction.
(b) Write the rate expression
(c) Calculate the rate constant
(d) Determine the reaction rate when concentration of $Cl_2$ and NO are 0.2 M & 0.4 M respectively.

Q.11 The catalytic decomposition of $N_2O$ by gold at 900°C and at an initial pressure of 200mm is 50% complete in 53 minutes and 73% complete in 100 minutes.

(i) What is the order of the reaction?

(ii) Calculate the velocity constant.

(iii) How much of $N_2O$ will decompose in 100 min. at the same temperature but at initial pressure of 600 mm?

Q.12 The following data are for the reaction $A + B \rightarrow$ products:

| **Conc. A** (M) | **Conc. B** (M) | **Initial Rate** (mol $L^{-1}$ $s^{-1}$) |
|---|---|---|
| 0.1 | 0.1 | $4.0 \times 10^{-4}$ |
| 0.2 | 0.2 | $1.6 \times 10^{-3}$ |
| 0.5 | 0.1 | $2.0 \times 10^{-3}$ |
| 0.5 | 0.5 | $1.0 \times 10^{-2}$ |

(i) What is the order with respect to A and B for the reaction?

(ii) Calculate the rate constant.

(iii) Determine the reaction rate when the concentrations of A and B are 0.2M and 0.35M, respectively.

Q.13 The pressure of a gas decomposing at the surface of a solid catalyst has been measured at different times and the results are given below

| t (sec) | 0 | 100 | 200 | 300 |
|---|---|---|---|---|
| Pr. (Pascal) | $4 \times 10^3$ | $3.5 \times 10^3$ | $3 \times 10^3$ | $2.5 \times 10^3$ |

Determine the order of reaction, its rate constant.

Q.14 The half life period of decomposition of a compound is 50 minutes. If the initial concentration is halved, the half life period is reduced to 25 minutes. What is the order of reaction?

Q.15 At 600°C, acetone ($CH_3COCH_3$) decomposes to ketene ($CH_2 = C = O$) and various hydrocarbons. Given the initial rate data in the table:

(a) What is the order?

(b) Write rate law

(c) Calculate rate constant

(d) Calculate the rate of decomposition when the acetone concentartion is $1.8 \times 10^{-3}$ M

| Experiment | Initial [$CH_3COCH_3$] | Rate M $s^{-1}$ |
|---|---|---|
| 1. | $6.0 \times 10^{-3}$ M | $5.2 \times 10^{-5}$ |
| 2. | $9.0 \times 10^{-3}$ M | $7.8 \times 10^{-5}$ |
| 3. | $1.8 \times 10^{-3}$ M | ? |

## ***HALF LIFE***

Q.16 The half life period of a first order reaction is 50 min. In what time will it go to 90% completion?

Q.17 A first order reaction has $k = 1.5 \times 10^{-6}$ per second at 200°C. If the reaction is allowed to run for 10 hrs., what percentage of the initial concentration would have changed into the product? What is the half life of this reaction?

Q.18 Show that in case of a first order reaction, the time required for 93.75% of the reaction to take place is four times that required for half of the reaction.

Q.19 The half time of the first order decomposition of nitramide is 2.1 hour at 15°C.

$$NH_2NO_2\ (aq.) \longrightarrow N_2O\ (g) + H_2O\ (l)$$

If 6.2 g of $NH_2NO_2$ is allowed to deompose, calculate (i) time taken for $NH_2NO_2$ to decompose 99%, and (ii) volume of dry $N_2O$ produced at this point, measured at STP.

# Answer Key

## FIRST ORDER

Q.1 (i) 36 min., (ii) 108 min. Q.2 (i) 0.0223 $\text{min}^{-1}$, (ii) 62.17 min Q.4 924.362 sec

Q.5 expiry time = 41 months Q.6 $3.3 \times 10^{-4}\text{s}^{-1}$ Q.7 $k = \frac{2.303}{t}\log\frac{1}{a}$ Q.8 11.2%

## ORDER OF REACTION & RATE LAW

Q.9 (a) Third order, (b) $r = k[NO]^2[H_2]$, (c) $8.85 \times 10^{-3}$ M $\text{sec}^{-1}$.

Q.10 (a) order w.r.t NO = 2 and w.r.t $Cl_2$ = 1, (b) $r = K[NO]^2[Cl_2]$, (c) K = 8 $L^2mol^{-2}s^{-1}$, (d) rate = 0.256 mole $L^{-1}s^{1}$]

Q.11 (i) first order (ii) $k = 1.308 \times 10^{-2}$ $\text{min}^{-1}$ (iii) 73%

Q.12 (i) rate=[A] [B] ; (ii) $k = 4\times10^{-2}M^{-1}s^{-1}$ ; (iii) rate = $2.8 \times 10^{-3}M\cdot s^{-1}$

Q.13 (i) Zero order, (ii) K = 5 Pa/s

Q.14 Zero order Q.15.(a) n =1, (b) $\frac{dx}{dt} = k[CH_3COCH_3]$, (c) $8.67 \times 10^{-3}$ $s^{-1}$, (d) $1.56 \times 10^{-5}$ M $s^{-1}$

## HALF LIFE

Q.16 166.6 min Q.17 $4.62 \times 10^5$ sec Q.18 (i) t = 13.96 hrs, (ii) 2.2176 litre