

Half-life Period

$$k_0 = \frac{x}{t} \text{ or } t = \frac{x}{k_0}$$

Let $t_{1/2}$ be the half-life period.

i.e. when, $t = t_{1/2}, x = \frac{a}{2}$

$$\therefore t_{1/2} = \frac{a}{2k_0} \text{ or } t_{1/2} \propto a \left(\frac{1}{2k_0} \text{ is constant} \right)$$

Thus $t_{1/2}$ for zero order reaction is proportional to a .

4.2 First order reaction

The rate of reaction at any time t is given by the following first – order kinetics.

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

$$\frac{da}{dt} = 0 \quad \because a \text{ has a given value for a given expt.}$$

where k is the rate constant of the reaction.

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

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

$$\int \frac{dx}{a-x} = k \int dt \quad \text{or} \quad -\ln(a-x) = kt + C \quad \dots(1)$$

Where C is integration constant.

The constant C can be evaluated by applying the initial condition of the reaction i.e. 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

$$-\ln(a - x) = kt - \ln a \quad \text{or} \quad k = \frac{1}{t} \ln \frac{a}{a - x} = \frac{2.303}{t} \log \frac{a}{a - x} \quad \text{..(2)}$$

If $[A_0]$ and $[A]$ be the concentrations of reactant at zero time and time t , respectively then Eq. 2 may be put as

$$k = \frac{1}{t} \ln \frac{[A_0]}{[A]}$$

This is the integrated rate expression for first order reaction. Unit of the rate constant is s^{-1}

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

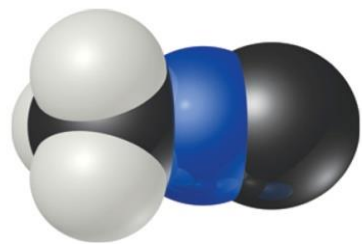
$$kt = \ln a - \ln(a - x)$$

$$a - x = ae^{-kt}$$

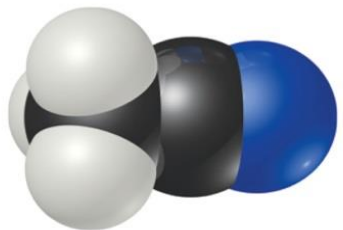
$$x = a(1 - e^{-kt})$$

First-Order Processes

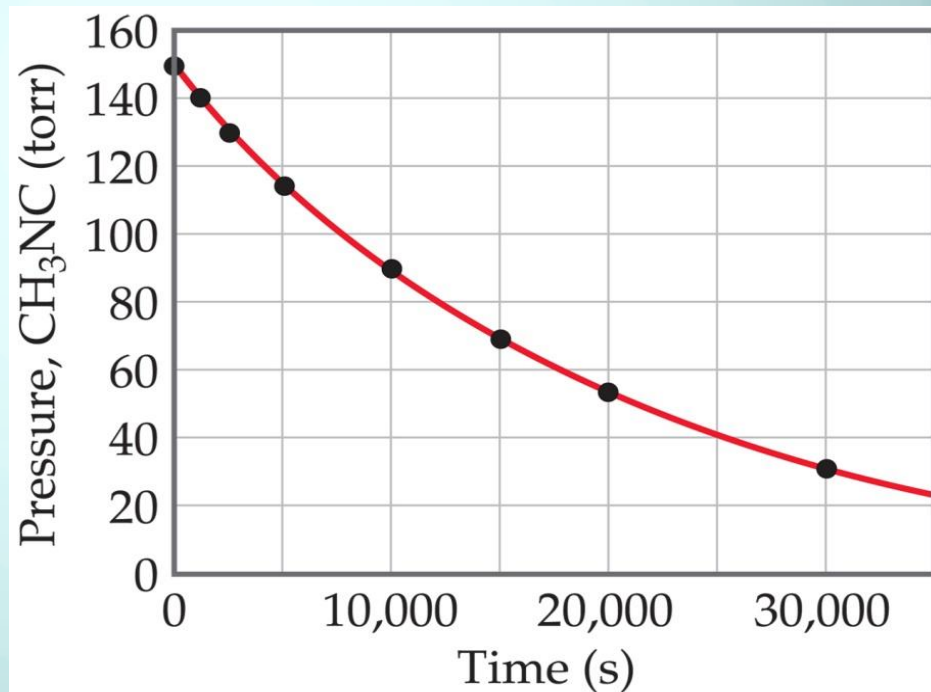
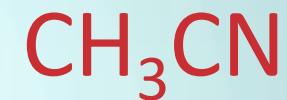
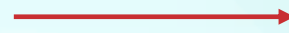
Consider the process in which methyl isonitrile is converted to acetonitrile.



Methyl isonitrile



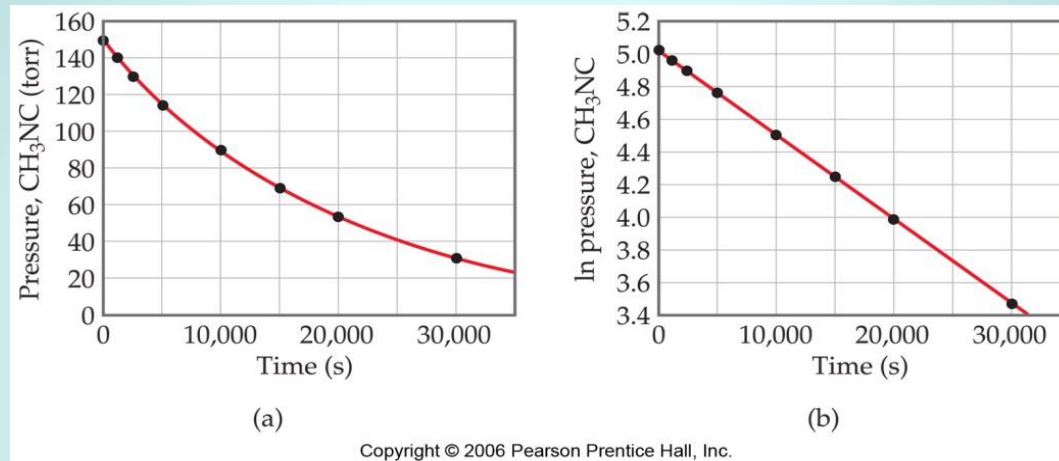
Acetonitrile



This data was collected for this reaction at 198.9°C.

First-Order Processes

$$\ln [A]_t = -kt + \ln [A]_0$$



When $\ln P$ is plotted as a function of time, a straight line results.
Therefore,

The process is first-order.

k is the negative slope: $5.1 \times 10^{-5} \text{ s}^{-1}$.

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

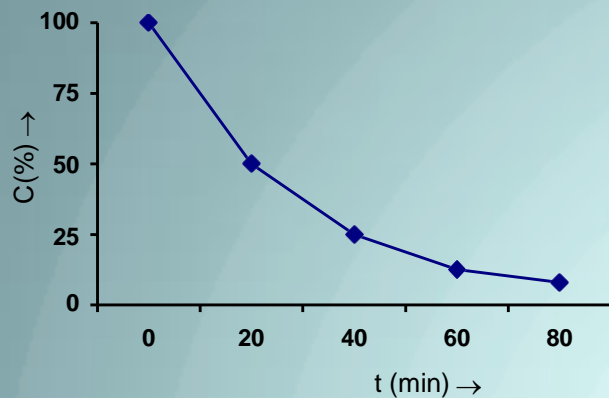
The half-time of a reaction is defined as the time required to reduce the concentration of the reactant to half of its initial value. It is denoted by the symbol $t_{1/2}$. Thus,

When $x = \frac{a}{2}$, $t = t_{1/2}$

Putting these in equation 2 mentioned above, we get

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

$$t_{1/2} = \frac{0.693}{k} \quad \dots(3)$$



In other words, if during 20 minute 50% of the reaction completes, then in 40 minute 75%, in 60 minute 87.5% of the reaction and on will complete as shown with following plot. Thus,

$$\text{Fraction left after } n \text{ half-lives} = \left(\frac{1}{2}\right)^n$$

$$\text{Concentration left after } n \text{ half lives } a_n = \left(\frac{1}{2}\right)^n a_0$$

It is also to be noted that
to calculate $t_{1/2}$ or k with the knowledge of k or $t_{1/2}$.
A general expression for $t_{1/2}$ is as follows

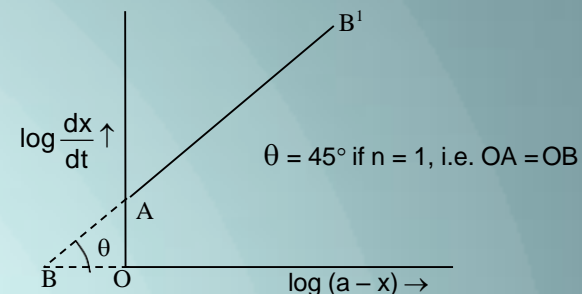
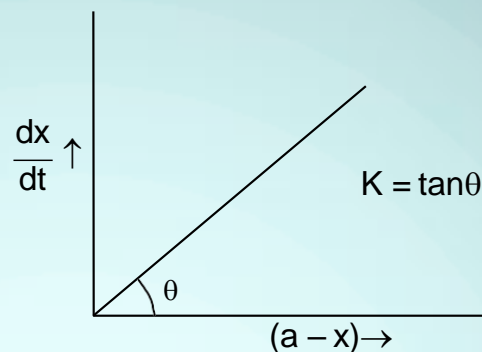
$$t_{1/2} \propto \frac{1}{a^{n-1}}$$

Where n = order of reaction.

Graphical Representation

Since for nth order reaction

$$\frac{dx}{dt} = k(a - x)^n, \quad \text{or} \quad -\frac{dx}{dt} = k.c^n$$



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

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

Thus, a plot of $\log (a - x)$ vs. t will be straight line with slope equal to $-\frac{k}{2.303}$ and intercept equal to $\log a$, if the reaction is of first order.

Example8:

The reaction $N_2O_5 \rightarrow N_2O_4 + \frac{1}{2}O_2$ obeys the rate law: $\text{rate} = k[N_2O_5]^x$, in which the specific rate constant is 0.00840 s^{-1} at a certain temperature. If 2.50 moles of N_2O_5 were placed in a 5 L container at that temperature, how many moles of N_2O_5 would remain after 1.00 min?

Solution

The reaction is of first order as its specific rate constant has unit s^{-1}

Given, $k = 0.00840 \text{ s}^{-1}$, $t = 60.0 \text{ s}$,

$$a = [N_2O_5]_0 = 2.5 \text{ mol}$$

$$k = \frac{2.303}{t} \log \frac{[N_2O_5]_0}{[N_2O_5]_t}$$

$$k = 0.0084 = \frac{2.303}{60} \log \frac{2.5}{[N_2O_5]_t}$$

$$\therefore [N_2O_5]_t = 1.51 \text{ mol}$$

Example9:

Radioactive decay is a first order process. Radioactive carbon in wood sample decays with a half-life of 5770 year. What is the rate constant (in year^{-1}) for the decay? What fraction would remain after 11540 years?

Solution: disintegration constant, $\lambda = \frac{0.6932}{t_{1/2}}$

(or rate constant)

$$k = \frac{0.6932}{5770} = 0.00012 \text{ yr}^{-1}.$$

Again, for the radioactive disintegration process says,

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

$$\log \frac{a}{(a-x)} = \frac{0.00012 \times 11540}{2.303} = 0.6013 \quad (a)$$

Taking antilog,

$$\frac{a}{(a-x)} = 3.993$$

$$\therefore \text{fraction of A remained} = \frac{(a-x)}{a} = \frac{1}{3.993} \approx \frac{1}{4}$$

4.3 Second order reaction

Type I:



Initial concentration a 0

Concentration after time t (a-x) x

Differential rate law:

$$-\frac{d(a-x)}{dt} = +\frac{dx}{dt} = k_2(a-x)^2$$

Integrated rate law (on integration of above equation):

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

Second-Order Processes

The decomposition of NO_2 at 300°C is described by the equation:



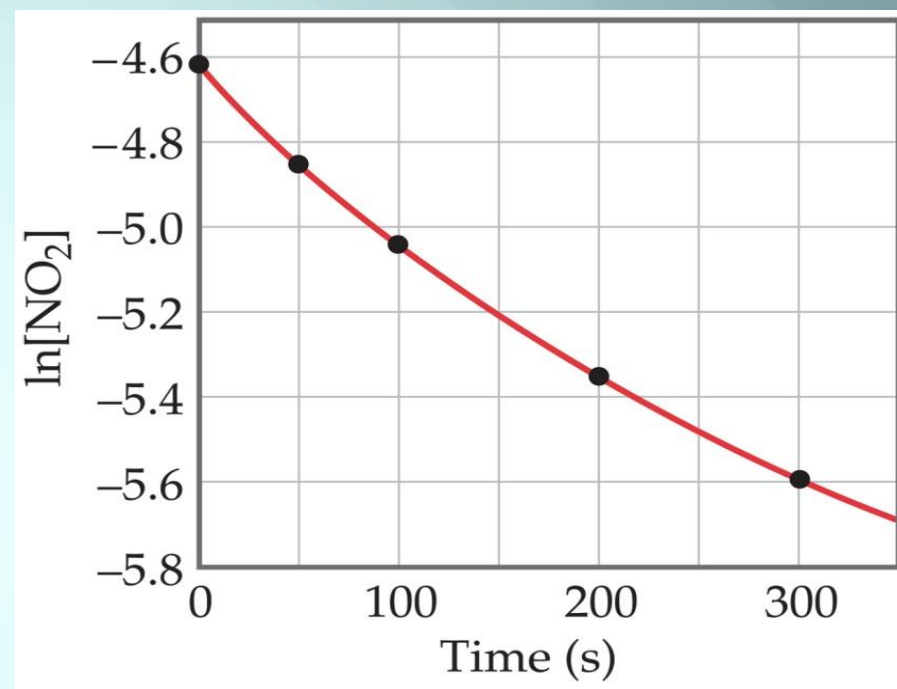
and yields data comparable to this:

Time (s)	$[\text{NO}_2]$, M
0.0	0.01000
50.0	0.00787
100.0	0.00649
200.0	0.00481
300.0	0.00380

Second-Order Processes

- Graphing $\ln [\text{NO}_2]$ vs. t yields:
- The plot is *not* a straight line, so the process is *not* first-order in $[\text{A}]$.

Time (s)	$[\text{NO}_2]$, M	$\ln [\text{NO}_2]$
0.0	0.01000	-4.610
50.0	0.00787	-4.845
100.0	0.00649	-5.038
200.0	0.00481	-5.337
300.0	0.00380	-5.573



Read only

Type II:

(i) Reactants A and B have the same initial concentration

	A	+	B	→	Products
Initial concentration	a		a		0
Concentration after time, t	(a-x)		(a-x)		x

Differential Rate Law:

$$-\frac{d(a-x)}{dt} = +\frac{dx}{dt} = k_2(a-x)(a-x) = k_2(a-x)^2$$

Integrated Rate Law:

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

(Same as for A → products)

(ii) Reactants A and B have different initial concentrations.

	A	+	B	→	products
Initial concentration	a		b		0
Concentration after time, t	(a-x)		(b-x)		x

Differential Rate Law:

$$-\frac{d(a-x)}{dt} = -\frac{d(b-x)}{dt} = +\frac{dx}{dt} = k_2(a-x)(b-x)$$

Integrated Rate Law:

$$\text{When } a > b: k_2 = \frac{2.303}{t(a-b)} \log \frac{b(a-x)}{a(b-x)}$$

$$\text{When } b > a: k_2 = \frac{2.303}{t(b-a)} \log \frac{a(b-x)}{b(a-x)}$$

The unit of the rate constant, k_2 is concentration $^{-1}$ time $^{-1}$.

Pseudo-first-order reaction

Measuring a second-order reaction rate with reactants A and B can be problematic: The concentrations of the two reactants must be followed simultaneously, which is more difficult than to measure one of them and calculate the other as a difference, which is less precise. A common solution for that problem is the **pseudo-first-order approximation**

$$r = k[A][B] = k'[A]$$

Where $k' = k[B]_0$ (k' or k_{obs} with units s^{-1}) and an expression is obtained identical to the first order expression above.

One way to obtain a pseudo-first-order reaction is to use a large excess of one of the reactants ($[B] \gg [A]$) so that, as the reaction progresses, only a small amount of the reactant is consumed, and its concentration can be considered to stay constant.

Example 10:

Compounds A and B react to form C and D in a reaction that was found to be second –order overall and second-order in A. The rate constant at 30°C is $0.622 \text{ L mol}^{-1} \text{ min}^{-1}$. What is the half-life of A when

$4.10 \times 10^{-2} \text{ M}$ of A is mixed with excess B?

Solution:

– Since B is taken in excess, only the concentration of A affect the rate. The reaction is second order in A and second –order overall, hence,

$$\frac{dx}{dt} = k[A]^x[B]^y = k[A]^2 \quad \text{If } a = \text{initial concentration of A then, at } t = T_{50}, \text{ concentration of A after}$$

$$T_{50} = \frac{a}{2}$$

$$\therefore (a - x) = \frac{a}{2}$$

$$\therefore k = \frac{1}{t} \left[\frac{1}{a - x} - \frac{1}{a} \right]$$

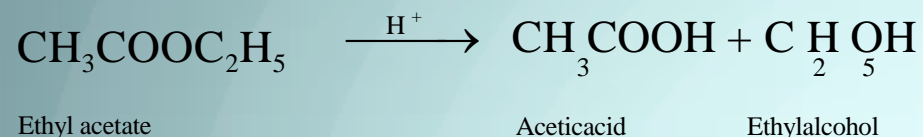
$$T_{50} = \frac{1}{k} \left[\frac{1}{a/2} - \frac{1}{a} \right]$$

$$T_{50} = \frac{1}{ka} = \frac{1}{0.622 \times 4.10 \times 10^{-2}} = 39.2$$

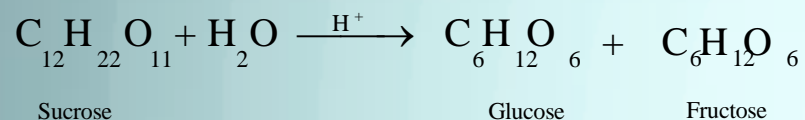
Example11:

Consider the following acid- catalyzed reactions:

(i) Hydrolysis of ethyl acetate



(ii) Inversion of cane-sugar



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

For the first reaction, Rate of reaction $\propto [\text{CH}_3\text{COOC}_2\text{H}_5]$ only

and for the second reaction, Rate of reaction $\propto [\text{C}_{12}\text{H}_{22}\text{O}_{11}]$ only.

The reason for such a behavior is obvious from the fact that water is present in such a large excess that its 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.

Half life for Second-Order Reaction:

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

for t to be $t_{1/2}$, $x = \frac{a}{2}$

$$t_{1/2} = \frac{1}{k_2} \times \frac{1}{a}$$

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

Thus $t_{1/2}$ for a second-order reaction is inversely proportional to $\frac{1}{a}$.

Note that in reactions with more than one reactant, $t_{1/2}$ of the reaction is calculated from the limiting reactant.

4.4 n^{th} Order reaction

Assume $A \rightarrow \text{Product}$
Is a n^{th} order reaction

Rate law is $\frac{dx}{dt} = k[A]^n = k(a-x)^n$

On integration, $\int \frac{dx}{(a-x)^n} = k_n \int dt$

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

But $n > 1$

Half – Life of a nth Order Reaction

Let us venture on to find out the $t_{1/2}$ for a nth order reaction where $n \neq 1$.

$$\begin{aligned}
 \therefore \quad \frac{d[A]}{dt} &= k[A]^n \Rightarrow \frac{d[A]}{[A]^n} = k dt \Rightarrow - \int_{[A]_0}^{[A]_0/2} \frac{d[A]}{[A]^n} = k \int_0^{t_{1/2}} dt \\
 \int_{[A]_0/2}^{[A]_0} [A]^{-n} d[A] &= kt_{1/2} \Rightarrow \left[\frac{[A]^{1-n}}{1-n} \right]_{[A]_0/2}^{[A]_0} = kt_{1/2} \Rightarrow \frac{1}{1-n} \left([A]_0^{1-n} - \left[\frac{[A]_0}{2} \right]^{1-n} \right) = kt_{1/2} \\
 \Rightarrow \frac{[A]_0^{1-n}}{1-n} \left[1 - \left(\frac{1}{2} \right)^{1-n} \right] &= kt_{1/2} \Rightarrow \frac{1}{(1-n)[A]_0^{n-1}} [1 - 2^{n-1}] = kt_{1/2} \\
 \Rightarrow \frac{(2^{n-1} - 1)}{(n-1)[A]_0^{n-1}} &= kt_{1/2} \text{ (order } n \neq 1)
 \end{aligned}$$

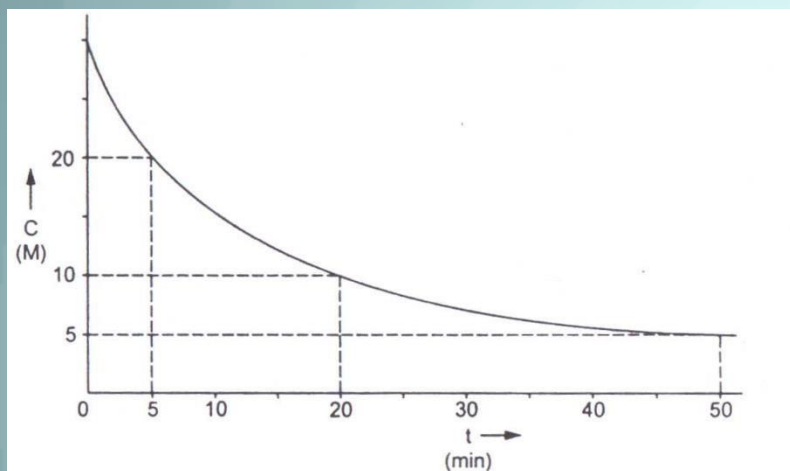
Therefore for a nth order reaction, the half life is inversely related to the initial concentration raised to the power of (n-1). i.e.

$$t_{1/2} \propto \frac{1}{[A]_0^{n-1}}$$

Note : It can be noted that for a zero order reaction $t_{1/2} = \frac{[A]_0}{2k}$.

Example12:

For a reaction, the concentration of the reactant C varies with time t as shown by the following graph:



What do you conclude about the order of their reaction?

Solution: The change in concentration of the reactant from 20M to 10M takes 15 minutes and when it changes from 10M to 5M, it takes 30 minutes. So, for the given reaction, $t_{1/2}$ is inversely proportional to the initial concentration of the reactant suggesting that the reaction is of second order.

5.METHOD TO FIND ORDER OF REACTION

5.1 Initial rate method

Example 13:

For the reaction, $2\text{NO} + \text{Cl}_2 \rightarrow 2\text{NOCl}$
at 300K following data are obtained

Expt. No.	Initial Concentration		Initial rate
	[NO]	[Cl ₂]	
1.	0.010	0.010	1.2×10^{-4}
2.	0.010	0.020	2.4×10^{-4}
3.	0.020	0.020	9.6×10^{-4}

Write rate law for the reaction. What is the order of the reaction? Also calculate the specific rate constant.

Solution:

Let the rate law for the reaction be

$$\text{Rate} = k[\text{NO}]^x[\text{Cl}_2]^y$$

$$\text{From Expt. (1) , } 1.2 \times 10^{-4} = k[0.010]^x[0.010]^y \quad \dots\dots\text{(i)}$$

$$\text{From Expt. (2), } 2.4 \times 10^{-4} = k [0.010]^x[0.020]^y \quad \dots \text{ (ii)}$$

$$\text{From Expt. (3), } 9.6 \times 10^{-4} = k [0.020]^x[0.020]^y \quad \dots \text{ (iii)}$$

$$\text{Order of reaction} = x + y = 2 + 1 = 3$$

$$\text{Rate law for the reaction is, Rate} = K [\text{NO}]^2[\text{Cl}_2]$$

$$\text{Considering Eq. (i) } 1.2 \times 10^{-4} = k[0.010]^2[0.010]$$

$$k = \frac{1.2 \times 10^{-4}}{[0.010]^3} = 1.2 \times 10^2 \text{ mol}^{-2} \text{ litre}^2 \text{ sec}^{-1}$$

5.2 Integrated rate law method

the reaction has the rate law $\text{rate} = k [\text{H}_2\text{O}_2]^2$.

$[\text{H}_2\text{O}_2]$	$t(\text{min})$
0.300M	0
0.221M	1
0.107M	5
0.065M	10
0.047M	15
0.037M	20

This data fit to a straight line only for 2nd order reaction in integrated rate law.

5.3 Graphical method:

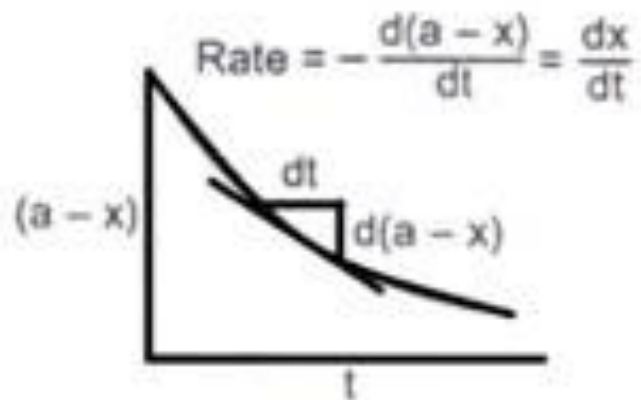


Fig. 1

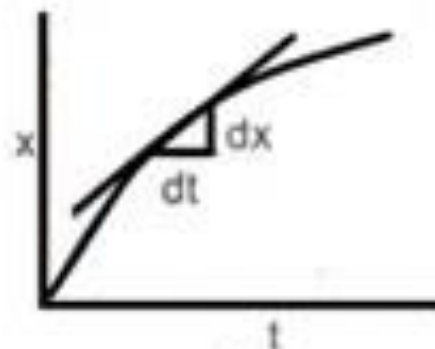


Fig. 2

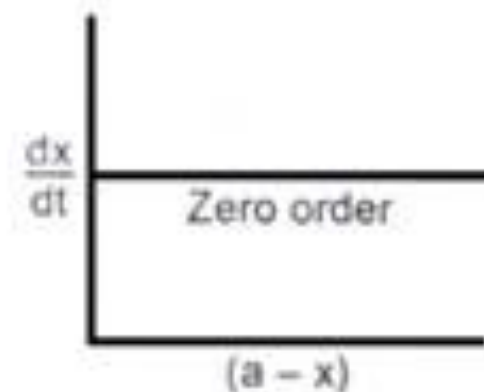


Fig. 3

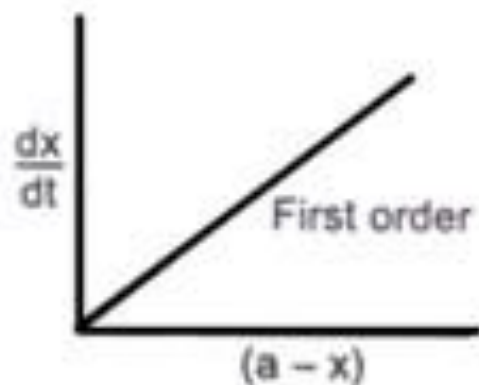


Fig. 4

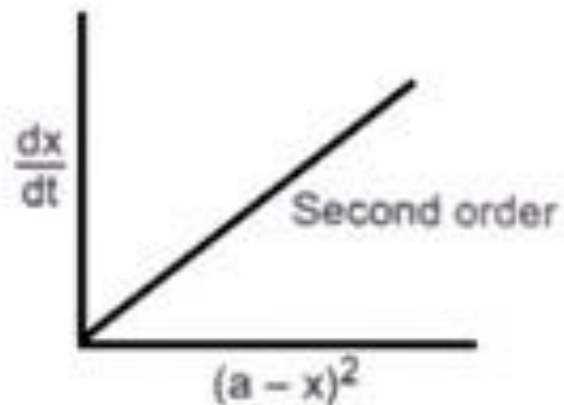


Fig. 5

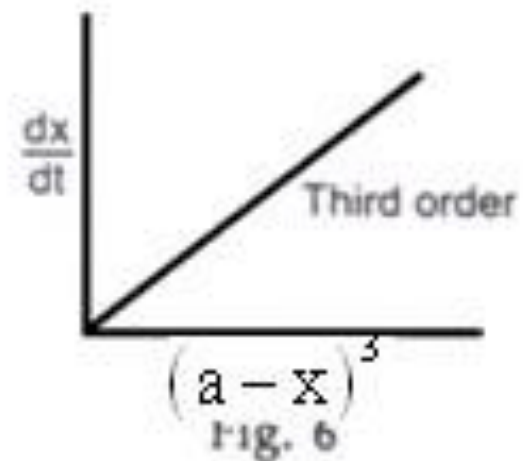
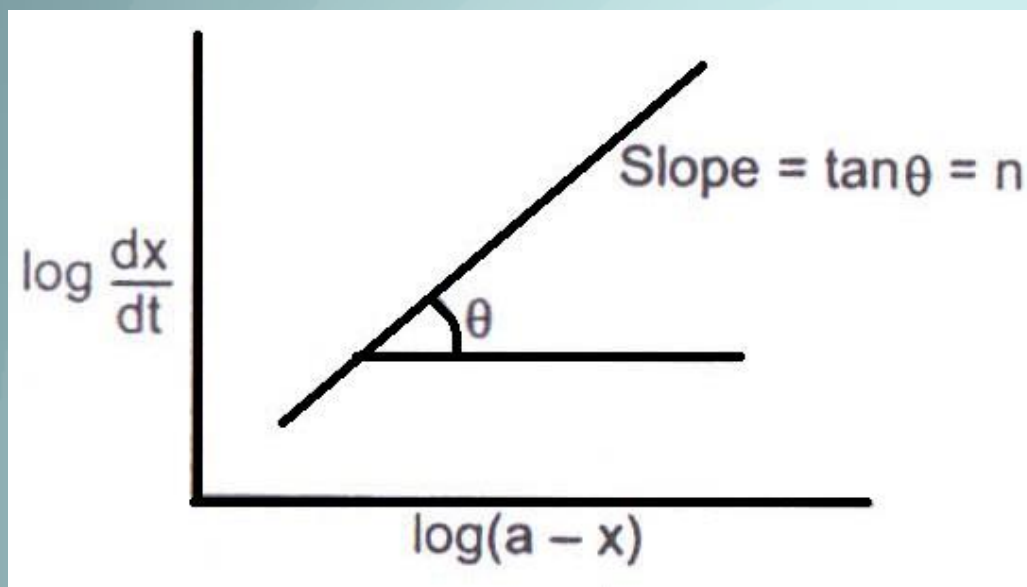


Fig. 6

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

$$\log \left(\frac{dx}{dt} \right) = \log k + n \log (a - x)$$



For zero-order reaction, $t_{1/2} \propto a$

i.e, $t_{1/2} \propto \frac{1}{a^{-1}}$

For first-order reaction, $t_{1/2}$ is independent of a

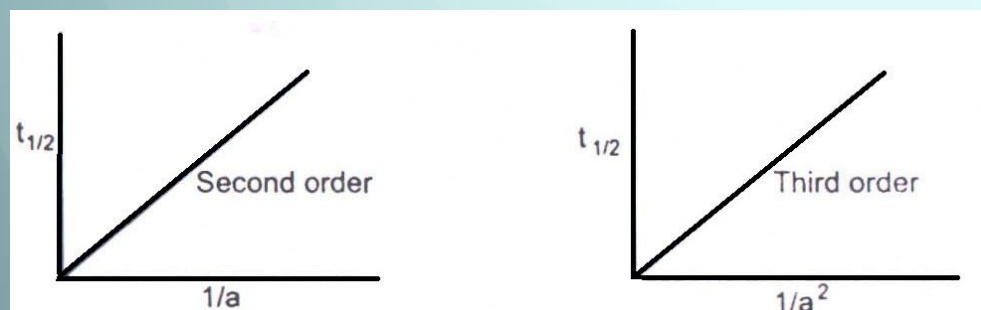
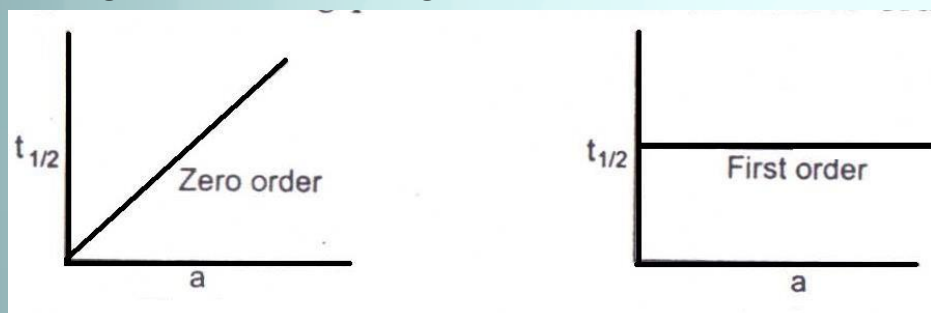
i.e., $t_{1/2} \propto \frac{1}{a^0}$

For Second-order reaction, $t_{1/2} \propto \frac{1}{a}$

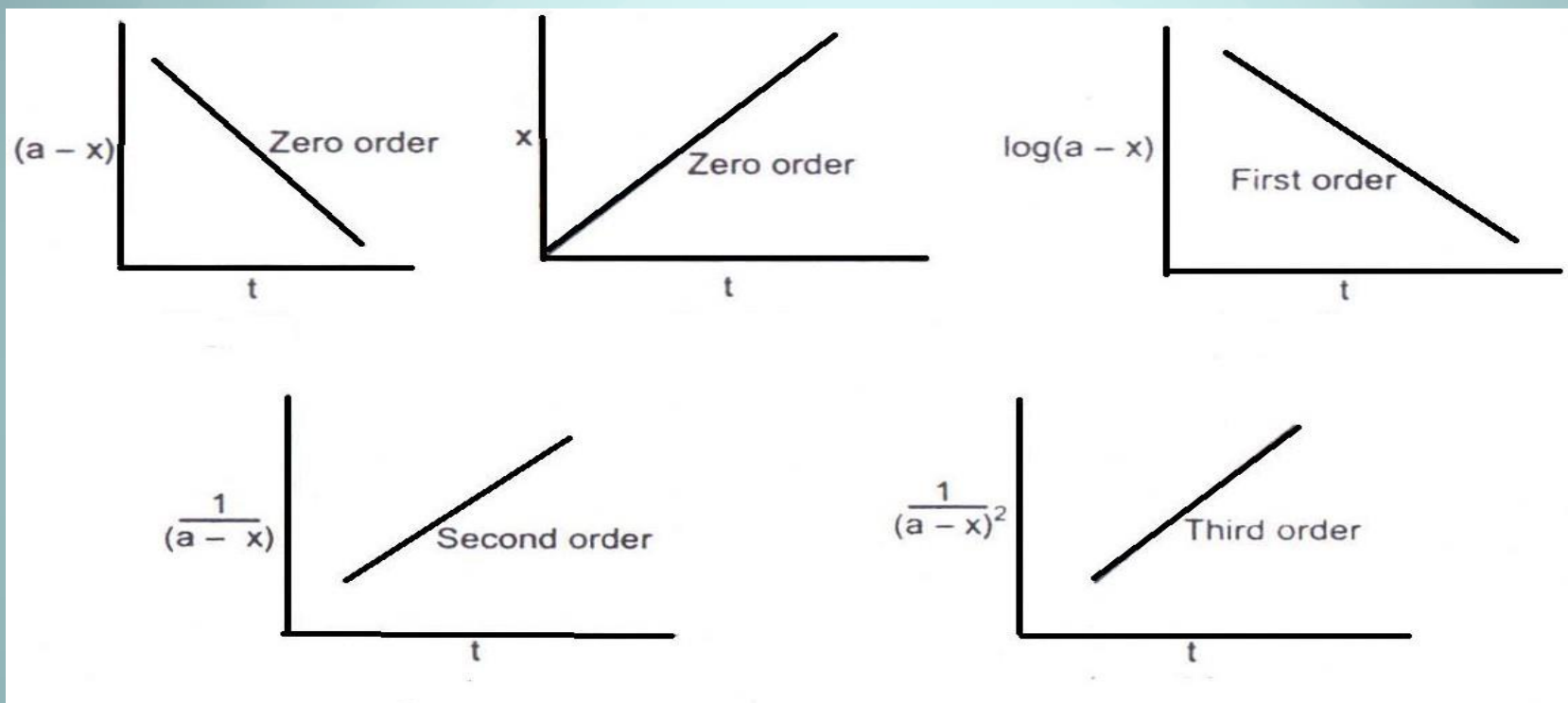
For third-order reaction, $t_{1/2} \propto \frac{1}{a^2}$

for n th – order reaction , $t_{1/2} \propto \frac{1}{a^{(n-1)}}$

Thus we get the following plots for reactions of various orders :



From integrated rate law equations of various reactions of different orders, we may have the following plots.

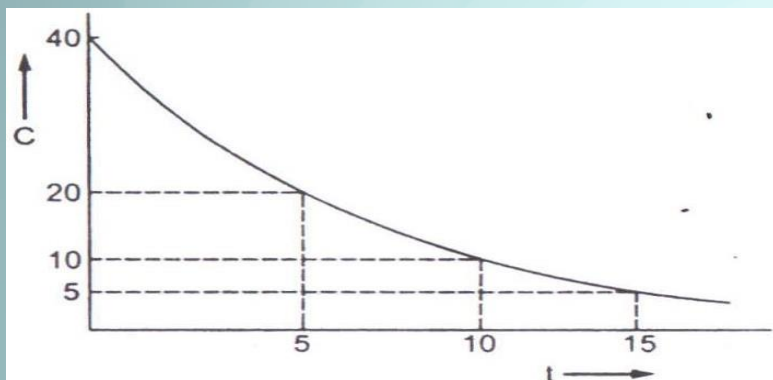


In case of gaseous reactions, concentration may be replaced by pressure.

Example14:

For a reaction, a graph was plotted between reaction concentration C and time t as shown in the figure. Identify the order of reaction?

Can concentration of the reactant be theoretically zero after infinite time?



Solution:

From the graph we see that the concentration reduces from 40 to 20 in 5 minutes, reduces from 20 to 10 in 5 minutes, and reduces from 10 to 5 in again 5 minutes, which shows that half-life period is independent of concentration which is the characteristic of a first order reaction. In a first order reaction the concentration of the reactant can never be theoretically zero.

5.4 Half life method

As we know that

$t_{1/2} \propto \left(\frac{1}{a}\right)^{n-1}$ where n is the order

We may have the following relation

$$\frac{\left(\frac{t_{1/2}}{2}\right)_1}{\left(\frac{t_{1/2}}{2}\right)_2} = \left\{\frac{a_2}{a_1}\right\}^{n-1}$$

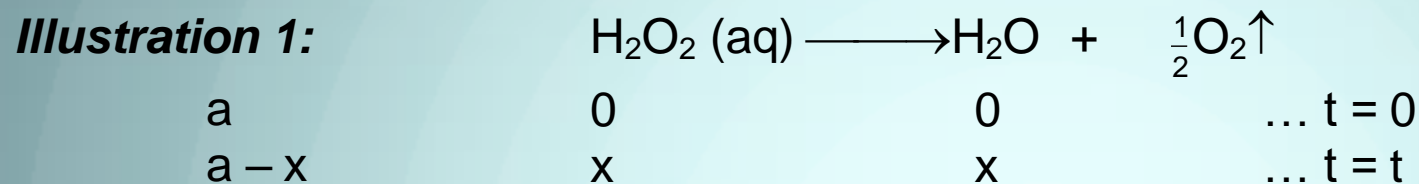
$$n = 1 + \frac{\log \left(\frac{\left(t_{1/2}\right)_1}{\left(t_{1/2}\right)_2} \right)}{\log \left(\frac{a_2}{a_1} \right)}$$

Where, $\left(\frac{t_{1/2}}{2}\right)_1$ and $\left(\frac{t_{1/2}}{2}\right)_2$ are the half-life periods, or time for a definite fractional change of a reaction when the respective initial concentrations of the reactants are a_1 and a_2 .

Taking log we have,

6. CONCENTRATION TERMS REPLACED BY OTHER TERMS IN 1ST ORDER KINETICS

6.1 Concentration terms replaced by titer reading



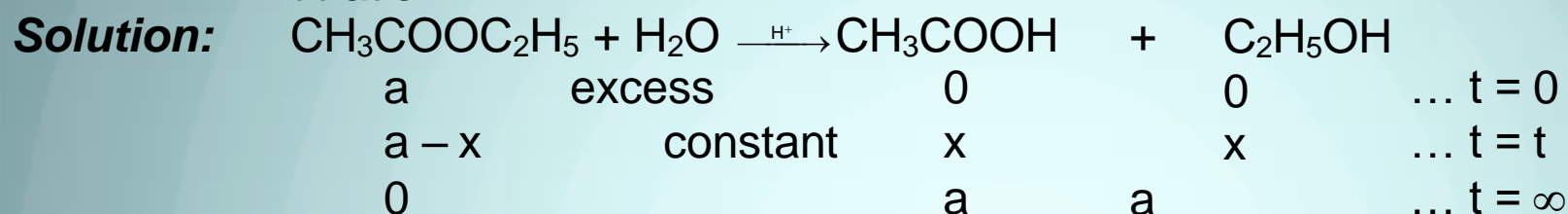
Since H_2O_2 acts as a reducing agent towards KMnO_4 , so concentrations of H_2O_2 at various time intervals may be determined by the titration of the reaction mixture against standard KMnO_4 solution. The titre value will go on decreasing with time.

If V_0 and V_t be the titre values at zero time and any time t
 then $V_0 \propto a$ and $V_t \propto a - x$

The above reaction being first-order, its rate constant may be expressed as

$$k = \frac{2.303}{t} \log \frac{V_0}{V_t}$$

Example 15: The progress of this reaction given below can be followed by measuring the concentration of acid (HCl acid used as catalyst plus acetic acid formed during the reaction) by means of alkali titration.



If V_0 , V_t and V_∞ are the volumes of NaOH solution needed for the end point of titration of the reaction mixture at zero time, time t and at infinity i.e. after completion of the reaction

$$V_0 \propto [\text{acid catalyst}]$$

$$V_t \propto [\text{acid catalyst}] + x$$

$$V_\infty \propto [\text{acid catalyst}] + a \quad \therefore V_\infty - V_t \propto a - x \quad V_\infty - V_0 \propto a$$

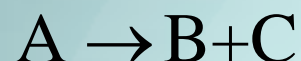
(since concentration of HCl acid acting as catalyst will remain constant).

The above reaction which is of first order (actually pseudo unimolecular) will, therefore,

obey following equation.

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

Illustration 2 Now let us assume that A,B and C are substances present in a solution. From a solution a certain amount of the solution (small amount) is taken and titrated with a suitable reagent that reacts with A. The volume of the reagent used is V_1 at $t = 0$ and V_2 at $t = t$.



Time	0	T
Volume of reagent	V_1	V_2

The reagent reacts only with A. Find k.

It can be understood that the volume of the reagent consumed is directly proportional to the concentration of A. Therefore the ratio of volume of the reagent consumed against A at $t=0$ and $t = t$ is equal to $[A]_0 / [A]_t$

$$\therefore k = \frac{1}{t} \ln \frac{[A]_0}{[A]} = \frac{1}{t} \ln \frac{V_1}{V_2}$$

Example 16: If $A \longrightarrow B + C$

Time	0	t
Volume of reagent	V_1	V_2

The reagent reacts with A,B and C. Find k.

Solution:

	A	\longrightarrow	B	+	C
At t = 0	V_1		0		0
At t = t	$V_1 - x$		x		x
At t = ∞	0		V_1		V_1

where x is the volume of the reagent for those moles of A which have been converted into B and C

$$\therefore V_1 + x = V_2 \Rightarrow x = V_2 - V_1 \Rightarrow V_1 - x = 2V_1 - V_2$$

$$\therefore k = \frac{1}{t} \ln \frac{[A]_0}{[A]} = \frac{1}{t} \ln \frac{V_1}{(2V_1 - V_2)}$$

- This result looks perfectly OK. The problem is that this is true only if we make an assumption in the beginning of this problem (which you may have thought about). The assumption is that the n'factor of A,B and C with the reagent is same.

Illustration 3: Now, we will consider a reaction $A \xrightarrow{D} B+C$ which is catalysed by D. We will assume in this problem that the concentration of the catalyst remains constant throughout. The data given to us is

Time	0	t	∞
Volume of reagent	V_1	V_2	V_3

The reagent reacts with all (A,B,C and D). Assume that n'factor of A,B and C are in the ratio of 1:1:1 and that of D is not known. Find k.

Let V_A be the volume of the reagent required by A initially and V_D be the volume required

by D. $\therefore V_1 = V_A + V_D$

$V_2 = (V_A - x) + x + x + V_D$ (x is the volume of the reagent required for those moles of A that have reacted to give B and C).

$$V_3 = 2V_A + V_D$$

We can see that, $V_3 - V_1 = V_A$ And $V_3 - V_2 = V_A - x$

$$\therefore k = \frac{1}{t} \ln \frac{[A]_0}{[A]} = \frac{1}{t} \ln \frac{(V_3 - V_1)}{(V_3 - V_2)}$$

6.2 Concentration terms replaced by Pressure change

Illustration 4: We are given a first order reaction

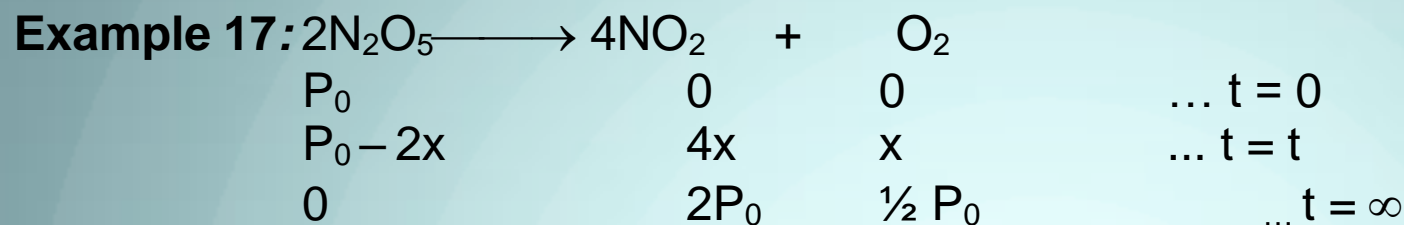
$A \rightarrow B + C$ where we assume that A, B and C are gases. The data given to us is

Time	0	t
Partial pressure of A	P_1	P_2

And we have to find the rate constant of the reaction.

Since A is a gas and assuming it to be ideal, we can state that $P_A = [A]RT$ [From $PV = nRT$]. \therefore at $t = 0$, $P_1 = [A]_0 RT$ and at $t = t$, $P_2 = [A]_t RT$. Thus the ratio of the concentration of A at two different time intervals is equal to the ratio of its partial pressure at those same time intervals.

$$\therefore \frac{[A]_0}{[A]_t} = \frac{P_1}{P_2} \qquad \therefore k = \frac{1}{t} \ln \frac{P_1}{P_2}$$



The progress of the reaction can be followed by measuring the pressure of the gaseous mixture in a closed vessel i.e. at constant volume. The expression for the rate constant in terms of pressure data will be as given below.

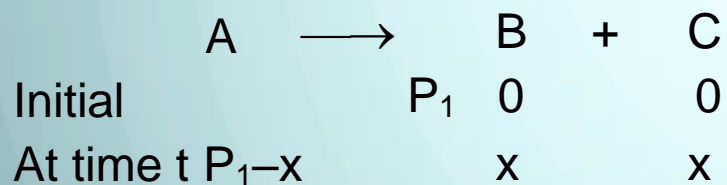
$$k = \frac{2.303}{t} \log \frac{P_0}{P_t}, \text{ when } P_t = P_0 - 2x$$

Total pressure after any time t and at ∞ was given then it is possible to find P_0 and x and hence k may be calculated.

Illustration 5: Now we consider the same reaction with different set of data $A \longrightarrow B + C$

Time	0	t
Total pressure of A +B+C	P_1	P_2

In this we are given total pressure of the system at these time intervals. The total pressure obviously includes the pressure of A, B and C. At $t = 0$, the system would only have A. Therefore the total pressure at $t = 0$ would be the initial pressure of A $\therefore P_1$ is the initial pressure of A. At time t let us assume that some moles of A decomposed to give B and C because of which its pressure is reduced by an amount x while that of B and C is increased by x each. That is



$$\therefore \text{total pressure at time } t = P_1 + x = P_2 \quad \Rightarrow x = P_2 - P_1$$

Now the pressure of A at time t would be $P_1 - x = P_1 - (P_2 - P_1) = 2P_1 - P_2$

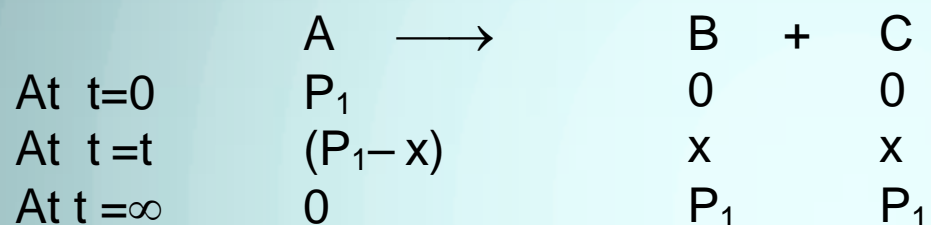
$$\therefore k = \ln \frac{[A]_0}{[A]} = \ln \frac{P_1}{(2P_1 - P_2)}$$

Illustration 6: Now let us move on to the next case. In this case we have $A \longrightarrow B + C$

Time	t	∞
Total pressure of A+B+C	P_2	P_3

Find k.

Here ∞ means that the reaction is complete. Now we have



$$\therefore 2P_1 = P_3 \Rightarrow P_1 = \frac{P_3}{2}$$

$$\text{At time } t, \quad P_1 + x = P_2 \Rightarrow \frac{P_3}{2} + x = P_2 \Rightarrow x = P_2 - \frac{P_3}{2}$$

$$\Rightarrow P_1 - x = \frac{P_3}{2} - (P_2 - \frac{P_3}{2}) = P_3 - P_2 \quad \therefore$$

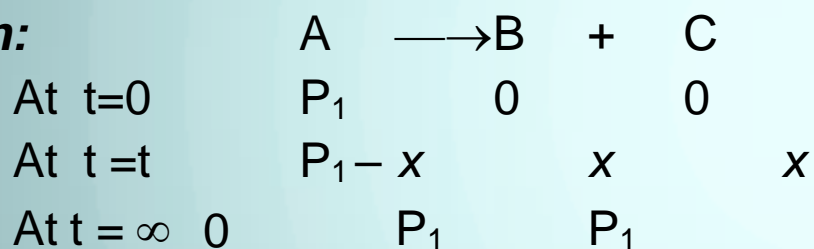
$$k = \frac{1}{t} \ln \frac{[A]_0}{[A]_t} = \frac{1}{t} \ln \frac{P_3/2}{(P_3 - P_2)} = \frac{1}{t} \ln \frac{P_3}{2(P_3 - P_2)}$$

Example 18: $A \longrightarrow B + C$

Time	t	∞
Total pressure of (B+C)	P_2	P_3

Find k .

Solution:



$$\therefore 2P_1 = P_3 \quad \Rightarrow P_1 = \frac{P_3}{2} \quad 2x = P_2 \Rightarrow x = \frac{P_2}{2}$$

$$\therefore P_1 - x = \frac{P_3}{2} - \frac{P_2}{2} = \frac{P_3 - P_2}{2} \quad \therefore k = \frac{1}{t} \ln \frac{[A]_0}{[A]_t} = \frac{1}{t} \ln \frac{P_3}{(P_3 - P_2)}$$

6.3 Concentration terms replaced by optical rotation terms

Now we shall see how to find the rate constant of a reaction using a very different set of data. There are some organic compounds which have a property of rotating a plane polarized light in a particular direction by a particular value. The compounds are called optically active compounds. One reaction in which an optically active substance converts to some other optically active substance is,



Sucrose, Glucose and Fructose are all optically active and while the first two compounds are dextro rotatory (rotating the plane polarized light in the right hand direction and the last is laevo rotatory (rotating the plane polarized light in the left hand direction). All the three compounds rotate the plane polarized light by different angles and their rotation is directly proportional to concentration.

Illustration 7: Now the problem is $S \longrightarrow G + F$ and the data is

Time	0	t
Rotation of sucrose	r_0	r_t

Find k.

Let the rotation of Sucrose be r_1° per mole and the initial moles of Sucrose be a.

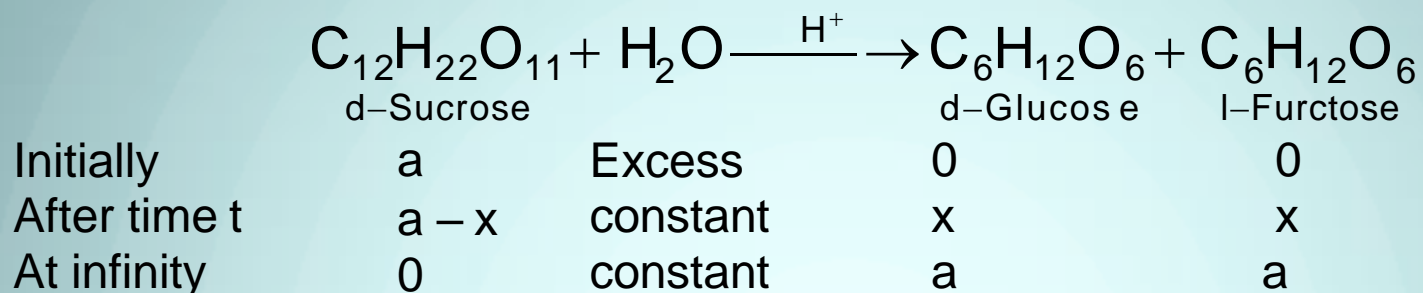
$$\therefore r_0 = ar_1^\circ$$

Let the moles of Sucrose that is converted to Glucose and Fructose be x.

$$\therefore r_t = (a-x) r_1^\circ \quad \therefore \frac{a}{a-x} = \frac{r_0}{r_t} \quad \therefore k = \frac{1}{t} \ln \frac{a}{a-x} = \frac{1}{t} \ln \frac{r_0}{r_t}$$

Illustration 8:

During the reaction angle of rotation goes on decreasing and after sometime there is reversal of the direction of rotation i.e. from dextro to laevo and hence the reaction is called “**inversion of cane sugar**” or inversion of sucrose.



If r_0 , r_t and r_∞ be the observed angle of rotations of the sample at zero time, time t and infinity respectively, and k_1 , k_2 and k_3 be the proportionately in terms of sucrose, glucose and fructose, respectively.

Then,

$$r_0 = k_1 a$$

$$r_t = k_1(a - x) + k_2 x + k_3 x$$

$$r_\infty = k_2 a + k_3 a$$

From these equations it can be shown that

$$\frac{a}{a-x} = \frac{r_0 - r_\infty}{r_t - r_\infty}$$

So, the expression for the rate constant of this reaction in terms of the optical rotational

data may be put as

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

Illustration 9: Now let us assume that the first order reaction is $A \longrightarrow B+C$ and this solution is taken in a tube. We radiate this solution with a monochromatic light of wavelength λ and we will assume that this radiation is absorbed only by A. Let the intensity of incident light be I_0 and that of the transmitted light be I_t . $\log \frac{I_t}{I_0}$ is called transmittance and it is inversely proportional to the concentration of A.

That is $\log \frac{I_t}{I_0} = \text{transmittance} \propto \frac{1}{[A]}$. The data given is

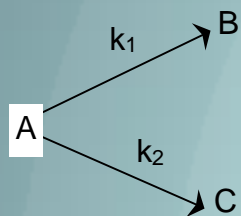
Time	0	t
$\log I_t / I_0$	x	y

Find k.

$$x \propto \frac{1}{[A]_0} \text{ and } y \propto \frac{1}{[A]_t} \quad \therefore k = \frac{1}{t} \ln \frac{[A]_0}{[A]_t} = \frac{1}{t} \ln \frac{y}{x}$$

7.SOME COMPLEX FIRST ORDER REACTIONS

7.1 Parallel Reactions



In such reactions (mostly organic) a single reactant gives two products B and C with different rate constants. If we assume that both of them are first order, we get.

$$\frac{-d[A]}{dt} = k_1[A] + k_2[A] = (k_1 + k_2)[A] \quad \dots(1)$$

$$\frac{d[B]}{dt} = k_1[A] \quad \dots(2)$$

And $\frac{d[C]}{dt} = k_2[A] \quad \dots(3)$

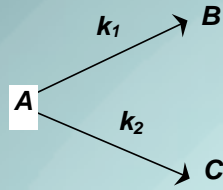
Let us assume that in a time interval, dt , x moles / lit of B was produced and y moles / lit of C was produced.

$$\therefore \frac{d[B]}{dt} = \frac{x}{dt} \text{ and } \frac{d[C]}{dt} = \frac{y}{dt} \therefore \frac{\frac{d[B]}{dt}}{\frac{d[C]}{dt}} = \frac{x}{y}.$$

We can also see that from (2) and (3), $\frac{\frac{d[B]}{dt}}{\frac{d[C]}{dt}} = \frac{k_1}{k_2}$

$\therefore \frac{x}{y} = \frac{k_1}{k_2}$. This means that irrespective of how much time is elapsed, the ratio of concentration of B to that of C from the start (assuming no B and C in the beginning) is a constant equal to k_1/k_2 .

Example19:



Let $k_1:k_2 = 1:10$. Calculate the ratio, $\frac{[C]}{[A]}$ at the end of one hour assuming that $k_1 = x \text{ hr}^{-1}$

Solution:
$$-\frac{d[A]}{dt} = (k_1 + k_2)[A] \quad \therefore \frac{-d[A]}{[A]} = (k_1 + k_2) dt$$

Integrating within the required limits, we get

$$\ln \frac{[A]_0}{[A]} = (k_1 + k_2)t \quad \therefore \ln \frac{[A] + [B] + [C]}{[A]} = (k_1 + k_2)t$$

Since $\frac{[B]}{[C]} = \frac{k_1}{k_2} = \frac{1}{10}$

$$\therefore \ln \frac{[A] + \frac{[C]}{10} + [C]}{[A]} = 11x$$

$$\frac{[C]}{[A]} = \frac{10}{11} (e^{11x} - 1)$$

7.2 Sequential Reactions

$A \xrightarrow{k_1} B \xrightarrow{k_2} C$. In this A decomposes to B which in turn decomposes to C.

$$\therefore \frac{-d[A]}{dt} = k_1 [A] \quad \dots(1)$$

$$\frac{d[B]}{dt} = k_1 [A] - k_2 [B] \quad \dots(2)$$

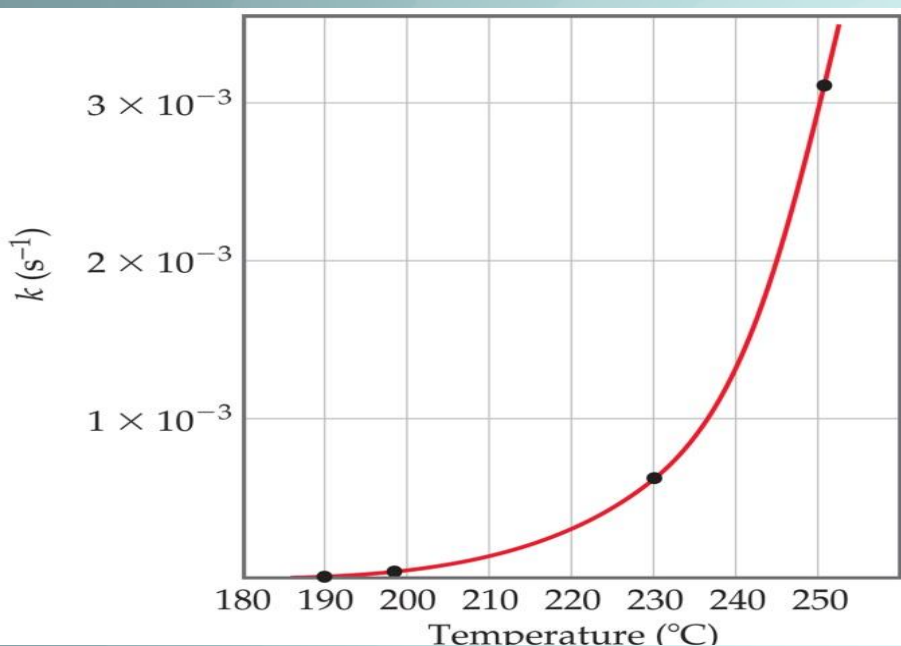
$$\frac{d[C]}{dt} = k_2 [B] \quad \dots(3)$$

$$[C] = \frac{[A]_0}{k_2 - k_1} \left[k_2 (1 - e^{-k_1 t}) - k_1 (1 - e^{-k_2 t}) \right]$$

B_{max}:

$$B_{\max} = [A]_0 \left[\frac{k_2}{k_1} \right]^{k_2/k_1 - k_2}$$

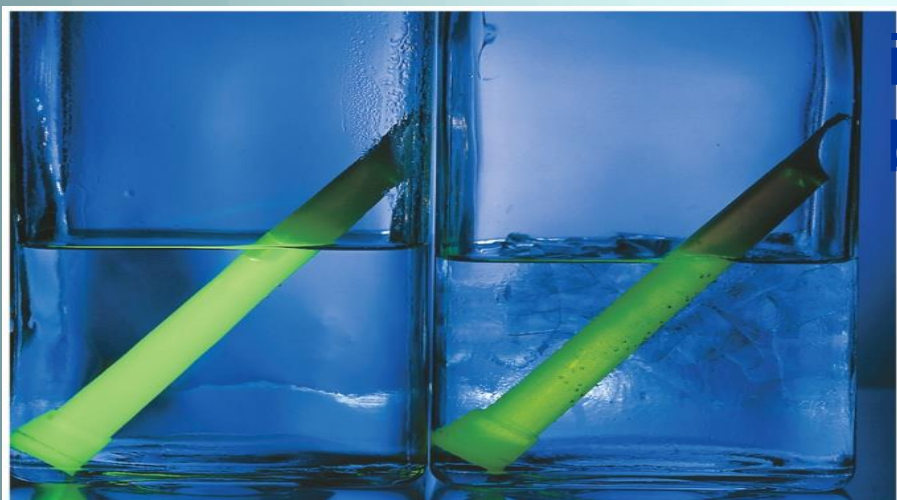
Temperature and Rate



➤ Generally, as temperature increases, so does the reaction rate.

➤ This is because k is temperature dependent. Most reactions speed up as temperature increases (E.g. food spoils when not refrigerated.)

➤ When two light sticks are placed in water: one at room temperature and one in ice, the one at room temperature is brighter than the one in ice.



Higher temperature

Lower temperature

Temperature and Rate

The Collision Model

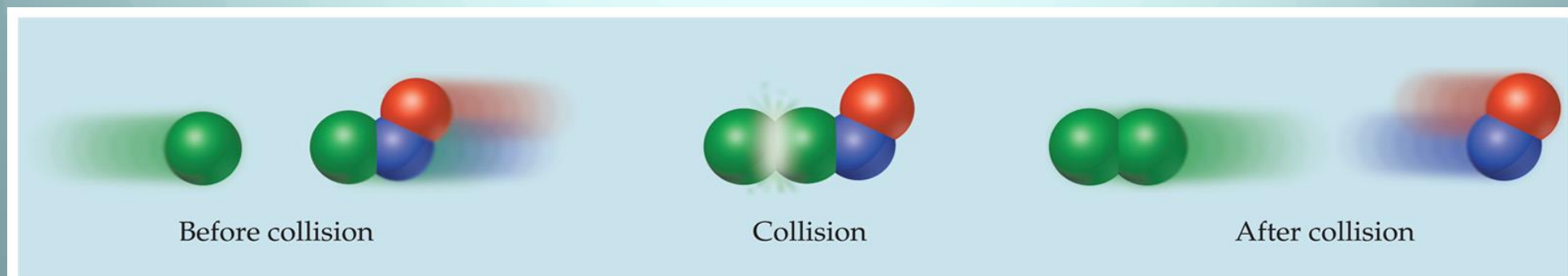
What is the collision model?



- It tries to explain why rates of reactions increase as concentration and temperature increases.
- The greater the number of collisions the faster the rate.
- The more molecules present, the greater the probability of collision and the faster the rate.

The Collision Model

- In a chemical reaction, bonds are broken and new bonds are formed.
- Furthermore, molecules must collide with the correct **orientation** and with enough **energy** to cause bond breakage and formation.



Temperature and Rate

The Collision Model

- The higher the temperature, the more energy available to the molecules and the faster the rate.
- Complication: not all collisions lead to products. In fact, only a small fraction of collisions lead to product.

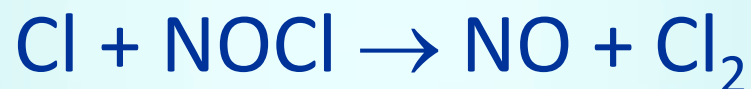
The Orientation Factor

- In order for reaction to occur the reactant molecules must collide in the correct orientation and with enough energy to form products.

Temperature and Rate

The Orientation Factor

➤ Consider:



➤ There are two possible ways that Cl atoms and NOCl molecules can collide; one is effective and one is not.

Temperature and Rate

The Orientation Factor



Before collision



Collision



After collision

(a) Effective collision



Before collision



Collision



After collision

(b) Ineffective collision

What is activation energy?

Just as a ball cannot get over a hill if it does not roll up the hill with enough energy, a reaction cannot occur unless the molecules possess sufficient energy to get over the activation energy barrier.

