CHEMICAL KINETICS

BY

Dr. SIDDHARTH SHARMA

Slow reactions

Fast reactions

Very fast reactions: These reactions proceed at a very fast speed; the rate of such reactions can be measured by using special methods. Examples are ionic reactions/acid base reactions, organic substitution reactions, biochemical reactions and combustion reactions etc.

Very slow reactions: These reactions proceed at a very low speed, which cannot be estimated. $2H_2 + O_2 \longrightarrow 2H_2O$

Moderate speed reactions: Some reactions proceed at moderate speed such as inversion of cane sugar and decomposition of nitrogen pentaoxide. The rate of moderate speed reactions can be estimated easily.

Chemical Kinetics

Chemical kinetics is defined as the branch of chemistry which deals with the study of the rate of chemical reactions and their mechanism.

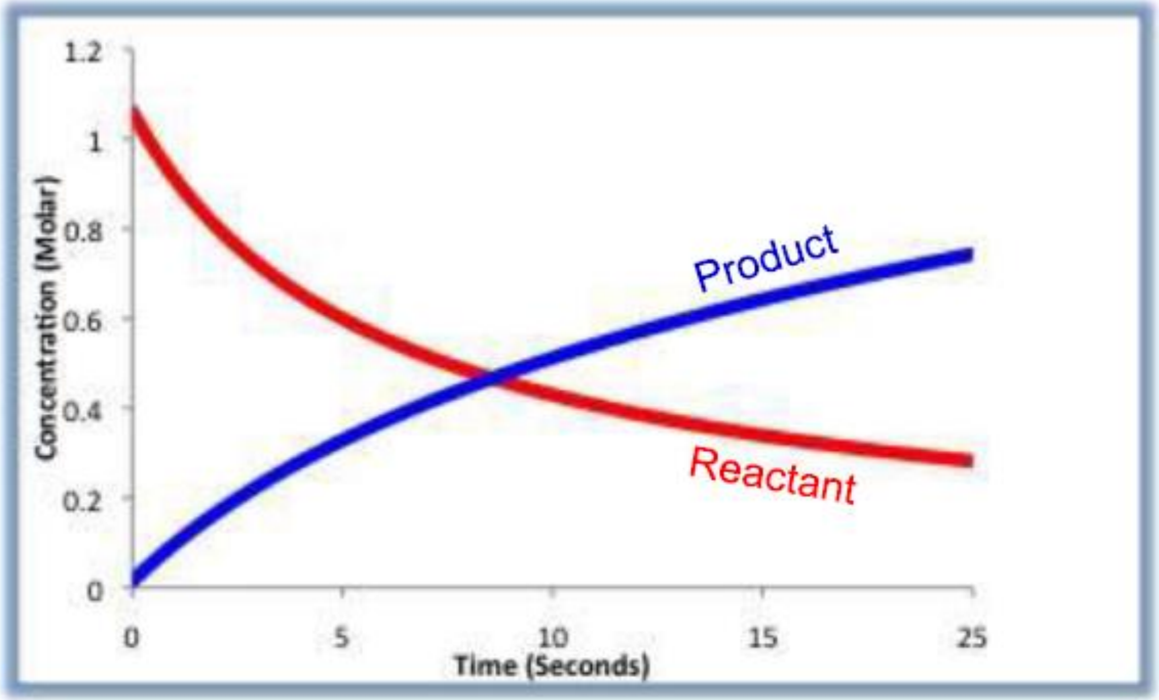
- **Studies the rate of a chemical reactions & rate laws**
  - a) Shows time needed for a given amount of the product
  - b) Shows amount of product in a given amount of time
  - c) Shows how to control the reaction
  - d) Guide towards the mechanism of a reaction

- **Factors affecting the rate of a reaction**
  (Temperature, pressure, concentration and catalyst)

- **Studies the mechanism of a chemical reaction**
  - a) Predict products of similar reactions
  - b) Better understand the reaction
  - c) Accurately manipulate the reaction for a desired result
  - d) Organize and simplify the study of chemistry

Rate of Reaction

$$A \longrightarrow B$$



"The rate of reactions is defined as the change in concentration of any of reactant or products per unit time"

Rate of Reaction

$$\xcancel{\textit{Rate} \text{ of reaction (r)} = \frac{\text{Amount of A consumed}}{\text{Time taken}}}$$

$$\xcancel{\textit{Rate} \text{ of reaction (r)} = \frac{\text{Amount of B produced}}{\text{Time taken}}}$$

$$\textit{Rate} \text{ of reaction (r)} = \frac{dx}{dt}$$

Rate of Reaction

$$A \xrightarrow{\hspace{3em}} B$$

Rate of Reaction (r) = Rate of disappearance of A

$$= \frac{-d[A]}{dt} = \frac{-\Delta[A]}{dt}$$

= Rate of appearance of B

$$= \frac{+d[B]}{dt} = \frac{+\Delta[B]}{dt}$$

Unit of Rate

Concentration/Time (Mole/litre)/sec $\text{mol l}^{-1}\ \text{s}^{-1}$

Rate of Reaction

$$A + B \longrightarrow C + D$$

Rate of Reaction (r) = Rate of disappearance of A = $\dfrac{-\mathrm{d}[A]}{dt}$

= Rate of disappearance of B = $\dfrac{-\mathrm{d}[B]}{dt}$

= Rate of appearance of C = $\dfrac{+d[C]}{dt}$

= Rate of appearance of D = $\dfrac{+d[D]}{dt}$

Rate of Reaction & Stoichiometry

$$n\mathbf{A} + m\mathbf{B} \longrightarrow p\mathbf{C} + q\mathbf{D}$$

Rate of Reaction (r) = Rate of disappearance of A = $\frac{-1}{n}\frac{\mathrm{d}[A]}{dt}$

= Rate of disappearance of B = $\frac{-1}{m}\frac{\mathrm{d}[B]}{dt}$

= Rate of appearance of C = $\frac{+1}{p}\frac{d[C]}{dt}$

= Rate of appearance of C = $\frac{+1}{q}\frac{d[D]}{dt}$

A more complicated example considering stoichiometry:

$$2\ NO(g) + O_2(g) \rightarrow 2\ NO_2(g).$$

The rate of reaction at any given time will depend upon the concentration of the reactants at that time. As the reaction progresses, the concentration of reactants keeps on falling with time. We can specify the rate of this reaction by telling the rate of change of the partial pressures of one of gases. However, it is convenient to convert these pressures into concentrations, so we will write our rates and rate equations in terms of concentrations. So the rate of reaction will be

$$\text{Rate} = -\frac{d[O_2]}{dt} = \frac{d[NO_2]}{dt} = -\frac{1}{2}\frac{d[NO]}{dt} \qquad \text{……. (8.1)}$$

This is unambiguous. The negative sign tells us that that species is being consumed and the fractions take care of the stoichiometry. Any one of the three derivatives can be used to define the rate of the reaction.

Example 1:

Write the rate expressions for the following reactions in terms of the disappearance of the reactants and the appearance of the products:

(a) $I_2(aq) + OCl_2(aq) \longrightarrow Cl_2(aq) + OI_2(aq)$

(b) $4NH_3(g) + 5O_2(g) \longrightarrow 4NO(g) + 6H_2O(g)$

(a) Because each of the stoichiometric coefficients equals 1,

$$-\frac{d[I]}{dt} = -\frac{d[OCl^-]}{dt} = \frac{d[Cl^-]}{dt} = \frac{d[OI^-]}{dt}$$

(b) Here the coefficients are 4, 5, 4, and 6, so

$$-\frac{1}{4}\frac{d[NH_3]}{dt} = -\frac{1}{5}\frac{d[O_2]}{dt} = \frac{1}{4}\frac{d[NO]}{dt} = \frac{1}{6}\frac{d[H_2O]}{dt}$$

Determination of Rate

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$$

$$\boxed{rate = -\frac{d[Zn]}{dt} = -\frac{d[H_2SO_4]}{dt} = \frac{d[ZnSO_4]}{dt} = \frac{d[H_2]}{dt}}$$

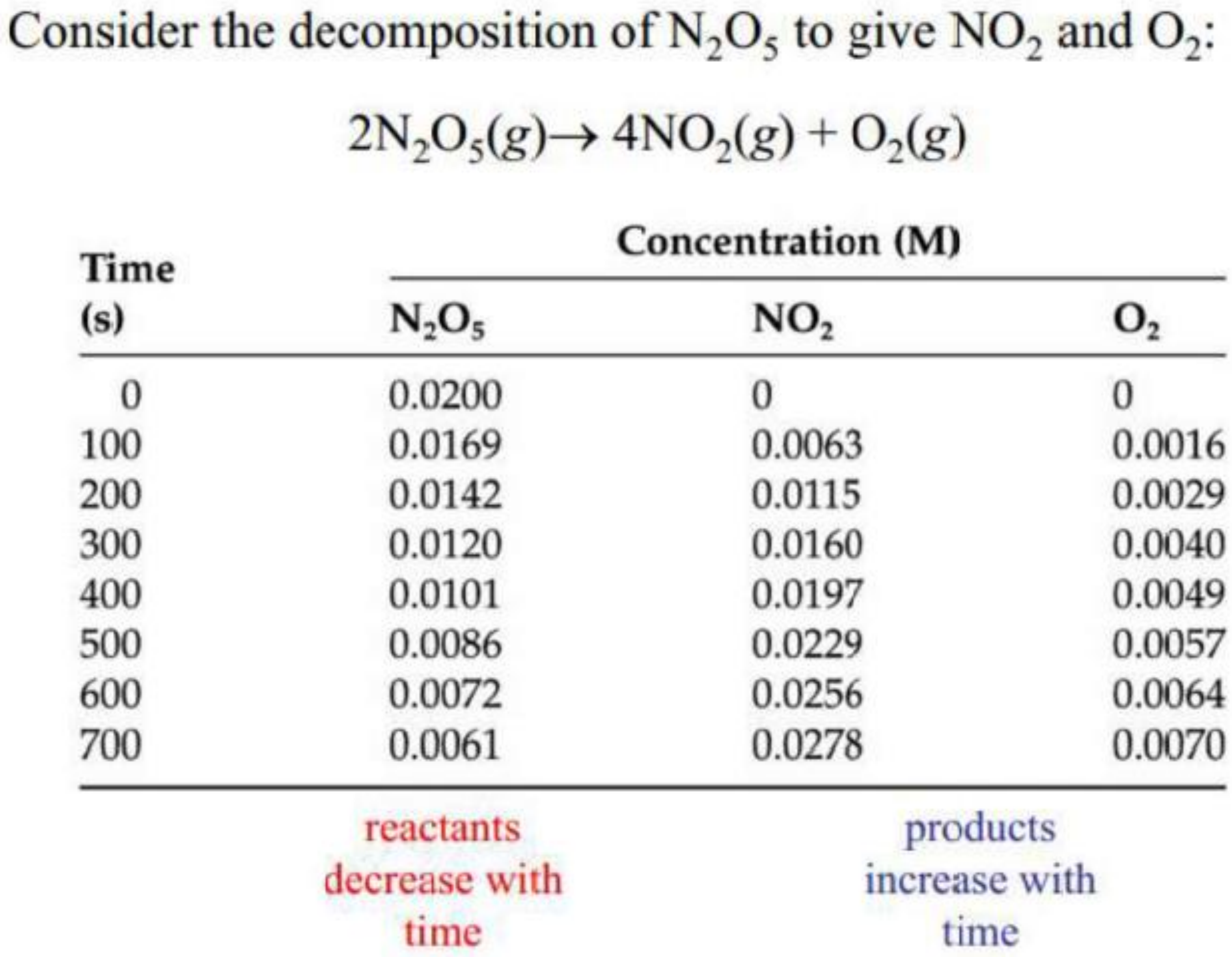
$$N_2 + 3H_2 \longrightarrow 2NH_3$$

$$\boxed{rate = -\frac{d[N_2]}{dt} = -\frac{1}{3}\frac{d[H_2]}{dt} = \frac{1}{2}\frac{d[NH_3]}{dt}}$$

$$H_2 + I_2 \longrightarrow 2HI$$

$$\boxed{rate = -\frac{d[H_2]}{dt} = -\frac{d[I_2]}{dt} = \frac{1}{2}\frac{d[HI]}{dt}}$$

An Example



Consider the decomposition of N_2O_5 to give NO_2 and O_2:

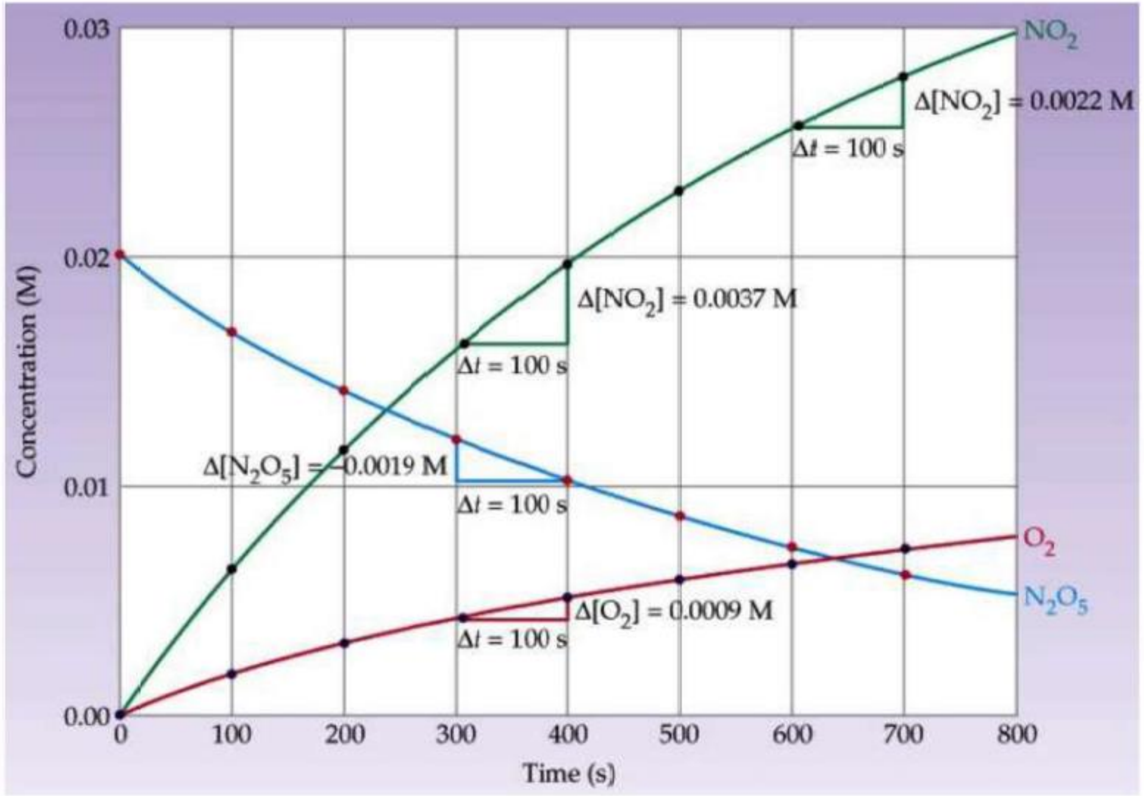
$$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$$

Time (s)	**Concentration (M)**		
	N_2O_5	**NO_2**	**O_2**
0	0.0200	0	0
100	0.0169	0.0063	0.0016
200	0.0142	0.0115	0.0029
300	0.0120	0.0160	0.0040
400	0.0101	0.0197	0.0049
500	0.0086	0.0229	0.0057
600	0.0072	0.0256	0.0064
700	0.0061	0.0278	0.0070

reactants decrease with time

products increase with time

Determination of Rate



$$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$$

Determination of Rate

From the graph looking at t = 300 to 400 s

$$\text{Rate } O_2 = \frac{0.0009\text{M}}{100\text{s}} = 9 \times 10^{-6}\,\text{Ms}^{-1}$$

$$\text{Rate } NO_2 = \frac{0.0037\text{M}}{100\text{s}} = 3.7 \times 10^{-5}\,\text{Ms}^{-1}$$

$$\text{Rate } N_2O_5 = \frac{0.0019\text{M}}{100\text{s}} = 1.9 \times 10^{-5}\,\text{Ms}^{-1}$$

Average Rate & Instantaneous Rate

$$CO(g) + \mathrm{NO}_2(g) \rightarrow \mathrm{CO}_2 + \mathrm{NO(g)}$$

$$\text{Average rate} = \frac{-\Delta[\mathrm{CO}]}{\Delta \mathrm{t}} = \frac{-d[\mathrm{CO}]}{d\mathrm{t}}$$

[CO] (mol/liter)	0.100	0.067	0.050	0.040	0.033
Time (sec)	0	10	20	30	40

Factors influencing the rate of reaction

- **Nature of reactants & products**
  e.g., solution *vs* gas phase
- **Concentration**
  Usually increase as reactant increases.
- **Temperature**
  Usually faster at higher temperature
- **Pressure**
  Increases as pressure increases
- **Solvent**

- **Light**

- **Catalyst**
  Speed chemical reactions

Nature of the reactants

Rate of reaction depends on the type of reacting substances. Acid/base reactions or the reaction between ionic molecules occur almost instantaneously. When covalent bond formation takes place between the molecules and when large molecules are formed, the reactions tend to be very slow. Nature and strength of bonds in reactant molecules greatly influence the rate of its transformation into products.

Physical state of reactants

The physical stateof a reactant is also influence the rate of change. When reactants are in the same phase, as in aqueoussolution, rate of reaction become faster, but when they are in different phases, the reaction is limited to the interface between the reactants. Reaction can occur only at their area of contact; so the surface area of reactants affects the rate of reaction. Higher the surface area of the reactants higher will be the rate of reaction. This means that the more finely divided a solid or liquid reactant the greater its surface area per unit volume and the more contact it makes with the other reactant, thus the faster the reaction.

Concentration

The reactions are due to collisions of reactant species. The rate of a chemical reaction is influenced by the number of collision per second between the reactant molecules. Thus, an increase in the concentrations of the reactants will result in increased number of collisions, the corresponding increase in the reaction rate, while a decrease in the concentrations will have a reverse effect.

Temperature

Temperature has a major effect on the rate of a chemical reaction. The rate of reaction is generally increased with increasing temperature. This is due to the fact that at high temperature the proportion of reacting molecules is significantly higher

so that the collision frequency is increased. Thermal energy of molecules is also high. Generally the rate of reaction is almost doubled by increase of 10 °C in temperature.

$$\frac{\text{Rate of reaction at } 35^{0}\text{C}}{\text{Rate of reaction at } 25^{0}\text{C}} = \frac{K_{35}}{K_{25}} = 2 \text{ to } 3$$

Catalysts

A catalyst is a substance that decrease or increase the rate of a chemical reaction but remains chemically unchanged afterwards. The catalyst increases rate reaction by providing a different reaction pathway with lower activation energy (Figure 2).

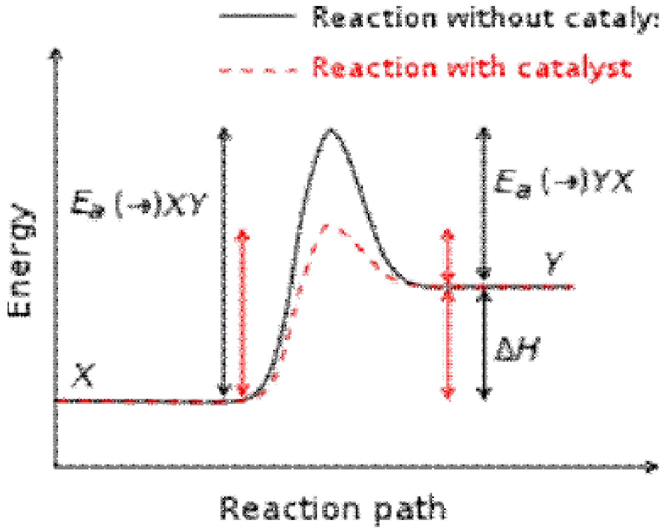


Figure 8.2: Effect of catalyst on rate of reaction.

The plot shows that the presence of the catalyst opens a different reaction pathway (shown in dated line) with lower activation energy. The final result and the overall thermodynamics are the same.

Pressure

Increasing the pressure in a gaseous reaction will increase the number of collisions between reactants, increasing the rate of reaction. This is because the activity of a gas is directly proportional to the partial pressure of the gas. This is similar to the effect of increasing the concentration of a solution.

Law Mass Action & Rate of Reaction

Law of mass action, first proposed by Guldberg & Waage in 1867 and states that the rate at which a substance reacts is proportional to its active mass, i.e., molar concentration and the rate of a chemical reaction is directly proportional to the product of the active masses or molar concentrations of the reactants.

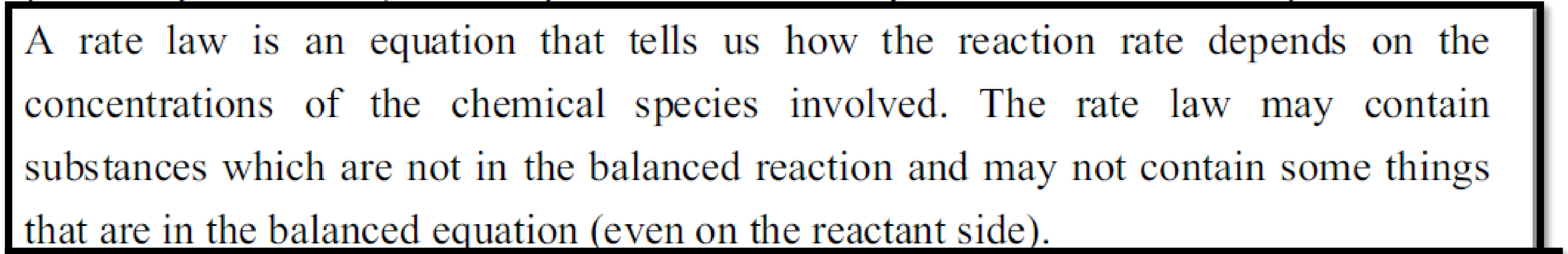
$$nA + mB \longrightarrow \text{Product}$$

$$\text{Rate} \propto [A]^n\ [B]^m$$

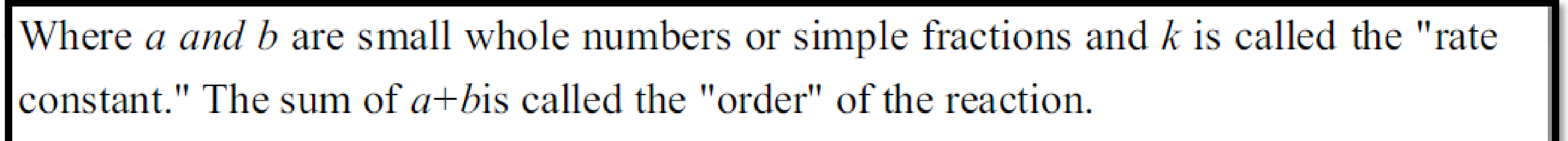
$$\boxed{\text{Rate} = k\ [A]^{n}\ [B]^{m}}$$

K is the rate constant

(Velocity constant, Velocity co-efficient or Specific reaction rate)



A rate law is an equation that tells us how the reaction rate depends on the concentrations of the chemical species involved. The rate law may contain substances which are not in the balanced reaction and may not contain some things that are in the balanced equation (even on the reactant side).



Where *a and b* are small whole numbers or simple fractions and *k* is called the "rate constant." The sum of $a+b$is called the "order" of the reaction.

Rate Laws/Rate Equation

It is an expression showing the relationship between the reaction rate and the concentrations of reactants

$$nA + mB \longrightarrow \text{Product}$$

$$\text{Rate} \propto [A]^n\ [B]^m$$

$$\boxed{\text{Rate} = k\,[A]^n\ [B]^m}$$

K is the rate constant
(Velocity constant, Velocity co-efficient or Specific reaction rate)

Rate Constant

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

$$\text{Rate} \propto [A]\,[B]$$

$$\boxed{\text{Rate} = k\,[A]\,[B]}$$

If $[A] = [B] = 1$, then

$$\text{Rate} = k \times 1 \times 1 = k$$

Thus, rate constant of a reaction may be defind as the rate of reaction when the concentration of each of the reactants is unity at a given temperature

Characteristics of k

- Different value for different reactions.
- A measure of rate of reaction.
- Independent of reactant concentration.
- Varies with change in temperature.

Order of a Reaction

The sum of the powers of concentrations in the rate law

$$nA + mB \longrightarrow \text{Product}$$

$$\text{Rate} \propto [A]^m\ [B]^n$$

$$\boxed{\text{Rate} = k\,[A]^{m}\ [B]^{n}}$$

Order of the reaction = m + n

m + n = 0, a zero order reaction
m + n = 1, a first order reaction
m + n = 2, a second order reaction
m + n = 3, a third order reaction

Molecularity of a Reaction

The number of reactant molecules involved in a reaction

Unimolecular reactions $A \longrightarrow \text{Product}$

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

Termolecular reactions $A + B + C \longrightarrow \text{Product}$

The decomposition of N_2O_5

$$\begin{array}{lcll} N_2O_5 & \longrightarrow & NO_2 + NO_3 & \textit{(Slow)} \\ N_2O_5 + NO_3 & \longrightarrow & 3NO_2 + O_2 & \textit{(Fast)} \\ \hline 2N_2O_5 & \longrightarrow & 4NO_2 + O_2 & \end{array}$$

The total number of reactant particles involved in the overall reaction, is called as molecularity of a reaction

Thus in the reaction -

$N_2O_5\,(g) \longrightarrow 2NO_2\,(g) + 1/2O_2(g)$ it is unimolecular

$2HI\,(g) \longrightarrow H_2(g) + I_2(g)$ it is bimolecular

and $2NO\,(g) + O_2(g) \longrightarrow 2NO_2$ it is trimolecular

Why high molecularity reaction are rare

Most of the reactions involve one, two or at the most three molecules. The reactions involving four or more molecules are rare. This can be explained on kinetic molecular theory. According to this theory, the rate of a chemical reaction is proportional to the number of collisions taking place between the reacting molecules. The chances of simultaneous collision of reacting molecules will go on decreasing will increase in number of molecules. Thus the possibility of three molecules colliding is much less than in case of bimolecular collision. For a reaction of molecularity 4, the four molecules must come closer and collide will one another at the same time.

The possibility of their doing so is much less than even in the case of termolecular reactions. Hence the reactions involving many molecules proceed through a series of steps, each involving two, three or less number

Order of a reaction	**Molecularity of a reaction**
Sum of the power of the concentration terms in the rate low.	Number of reacting species involved in a simple reaction.
Experimentally determined.	A theoretical concept
Can have fractional value.	Always a whole number
Can have zero value.	Do not have zero value
Can be changed with reaction conditions.	Can not be changed with reaction conditions.
For a complex reaction, the slowest step gives the order of the reaction	For a complex reaction, each step has its own molecularity.

$2 \quad dt \quad 2$

Problem 3 For an elementary reaction, $2\,A + B \longrightarrow 3\,C$, the rate of appearance of C at time 't' is $1{\cdot}3 \times 10^{-4}$ mol L^{-1} s^{-1}. Calculate at this time

(i) rate of the reaction (ii) rate of disappearance of A.

Solution. Rate $= -\frac{1}{2}\frac{d[A]}{dt} = -\frac{d[B]}{dt} = +\frac{1}{3}\frac{d[C]}{dt}$. Given : $\frac{d[C]}{dt} = 1{\cdot}3 \times 10^{-4}\ \text{mol}\,L^{-1}\,s^{-1}$

$$\therefore \text{Rate of reaction} = \frac{1}{3}\frac{d[C]}{dt} = \frac{1}{3} \times 1{\cdot}3 \times 10^{-4}\ \text{mol}\,L^{-1}\,s^{-1} = \mathbf{4{\cdot}33 \times 10^{-5}\ mol\ L^{-1}\ s^{-1}}$$

$$\text{Rate of disappearance of A} = -\frac{d[A]}{dt} = \frac{2}{3}\frac{d[C]}{dt} = \frac{2}{3} \times 1{\cdot}3 \times 10^{-4}\ \text{mol}\,L^{-1}\,s^{-1} = \mathbf{8{\cdot}66 \times 10^{-5}\ mol\ L^{-1}\ s^{-1}}$$

Alternatively, $\frac{1}{6}\frac{d[H_2O]}{dt} = \frac{1}{4}\frac{d}{dt} \Rightarrow$

Problem 2 **The reaction, $2\,N_2O_5\,(g) \rightleftharpoons 4\,NO_2\,(g) + O_2\,(g)$ was studied in a closed vessel. It was found that the concentration of NO_2 increases by $2{\cdot}0 \times 10^{-2}$ mol L^{-1} in five seconds. Calculate (i) the rate of reaction (ii) the rate of change of concentration of N_2O_5.**

Solution. (*i*) Rate of reaction $= \frac{1}{4}\frac{d[NO_2]}{dt}$. But $\frac{d[NO_2]}{dt} = \frac{2.0\times10^{-2}\,\text{mol}\,L^{-1}}{5\,s} = 4\times10^{-3}\,\text{mol}\,L^{-1}\,s^{-1}$

$$\therefore \quad \text{Rate of reaction} = \frac{1}{4}\times4\times10^{-3} = \mathbf{10^{-3}\,mol\,L^{-1}\,s^{-1}}$$

(*ii*) Rate of change of conc. of $N_2O_5 = -\frac{d[N_2O_5]}{dt} = -\frac{1}{2}\times$ Rate of formation of NO_2

$$= -\frac{1}{2}\frac{d[NO_2]}{dt} = -\frac{1}{2}\times(4\times10^{-3}\,\text{mol}\,L^{-1}\,s^{-1}) = \mathbf{2\times10^{-3}\,mol\,L^{-1}\,s^{-1}}$$

Common types of Rate Laws

(i)First Order Reactions: In a first order reaction

$$A \longrightarrow B$$

the rate is proportional to the concentration of one of the reactants. That is,

$$\text{rate} = k[A], \qquad \ldots\ldots\ (8.4)$$

where A is a reactant. If we have a reaction which is known to be first order in A, we would write the rate law as,

$$-\frac{d[A]}{dt} = k[A] \qquad \ldots..(8.5)$$

The constant *k*, in this rate equation is the first order rate constant.

Common types of Rate Laws

Second Order Reactions

In a second order reaction the rate is proportional to concentration squared. For example, possible second order rate laws might be written as

$$\text{Rate} = k[\text{A}]^2 \qquad \ldots\ldots(8.6)$$

or as

$$\text{Rate} = k[\text{A}][\text{B}]. \qquad \ldots\ldots(8.7)$$

That is, the rate might be proportional to the square of the concentration of one of the reactants, or it might be proportional to the product of two different concentrations.

Common types of Rate Laws

(iii) Third Order Reactions

There are several different ways to write a rate law for a third order reaction. One might have cases where

$$\text{Rate} = k[\text{A}]^3, \qquad \text{..... (8.8)}$$

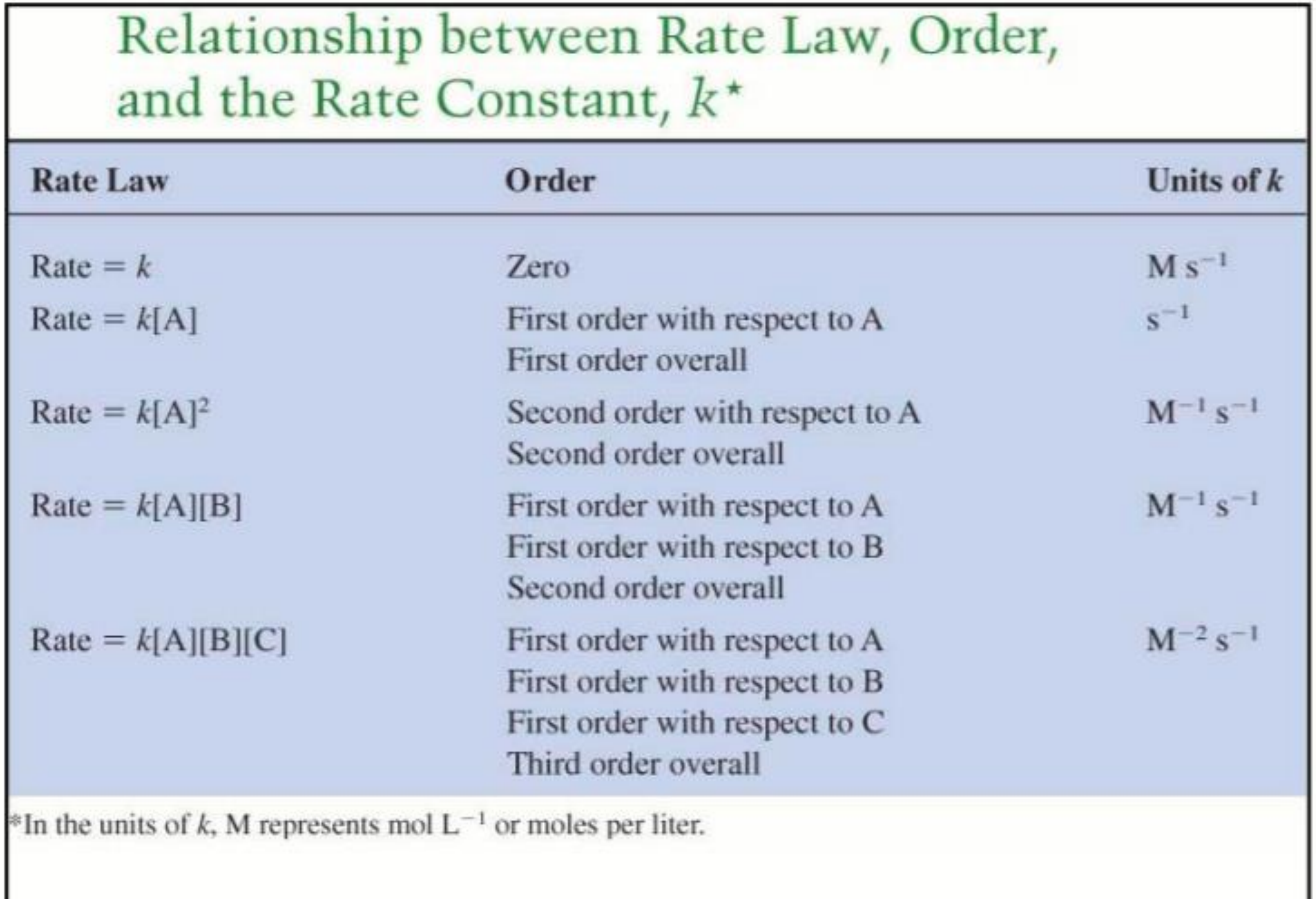
or

$$\text{Rate} = k[\text{A}]^2[\text{B}], \qquad \text{..... (8.9)}$$

or

$$\text{Rate} = k[\text{A}][\text{B}][\text{C}], \qquad \text{.....(8.10)}$$

and so on.



Relationship between Rate Law, Order, and the Rate Constant, k*

Rate Law	Order	Units of k
Rate = k	Zero	$\mathrm{M\ s^{-1}}$
Rate = $k[\mathrm{A}]$	First order with respect to A First order overall	$\mathrm{s^{-1}}$
Rate = $k[\mathrm{A}]^2$	Second order with respect to A Second order overall	$\mathrm{M^{-1}\ s^{-1}}$
Rate = $k[\mathrm{A}][\mathrm{B}]$	First order with respect to A First order with respect to B Second order overall	$\mathrm{M^{-1}\ s^{-1}}$
Rate = $k[\mathrm{A}][\mathrm{B}][\mathrm{C}]$	First order with respect to A First order with respect to B First order with respect to C Third order overall	$\mathrm{M^{-2}\ s^{-1}}$

*In the units of k, M represents $\mathrm{mol\ L^{-1}}$ or moles per liter.

Units for the rate constant:

The units of a rate constant will change depending upon the overall order.

The units of rate are always M/s or Ms^{-1}

To find the units of a rate constant for a particular rate law, simply divide the units of rate by the units of molarity in the concentration term of the rate law.

$$\text{Rate } (Ms^{-1}) = k[A] \quad 1^{st} \text{ order}$$

$$k(\text{units}) = \frac{Ms^{-1}}{M} = s^{-1}$$

Zero Order Reaction

The rate is independent of reactant concentrations.

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

Initial conc.	a	0
Final conc.	a-x	x

$$Rate = \frac{-\mathrm{d}[A]}{dt} = k[A]^0$$

$$\frac{dx}{dt} = \frac{-\mathrm{d}(a-x)}{dt} = k(a-x)^0 = k$$

$$\int dx = \int k dt$$

x = kt or $k = \frac{x}{t}$

Unit of k = concentration per unit time

Examples of Zero Order Reaction

Photochemical reactions:

$$H_2(g) + \mathrm{Cl}_2(g) \xrightarrow{\textit{Sunlight}} \mathrm{2HCl(g)}$$

Heterogeneous reactions:

$$2HI \xrightarrow{\mathrm{Au}} \mathrm{H}_2 + \mathrm{I}_2$$

$$2NH_3 \xrightarrow{\mathrm{Pt}} \mathrm{N}_2 + 3\mathrm{H}_2$$

$$N_2O \xrightarrow{\mathrm{Pt}} \mathrm{N}_2 + \frac{1}{2}O_2$$

First Order Reaction

Rate is determined by the change of only one concentration term

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

Initial conc.	a	0
Final conc.	a-x	x

$$Rate = \frac{-\mathrm{d}[A]}{dt} = k[A]$$

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

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

First Order Reaction

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

-ln (a-x) = kt + I, the constant of integration

If t = 0 and x = 0
I = -ln a

$$\ln \frac{a}{a-x} = kt$$

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

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

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

ln(a) – ln (a-x) = kt

ln (a/a-x) = kt

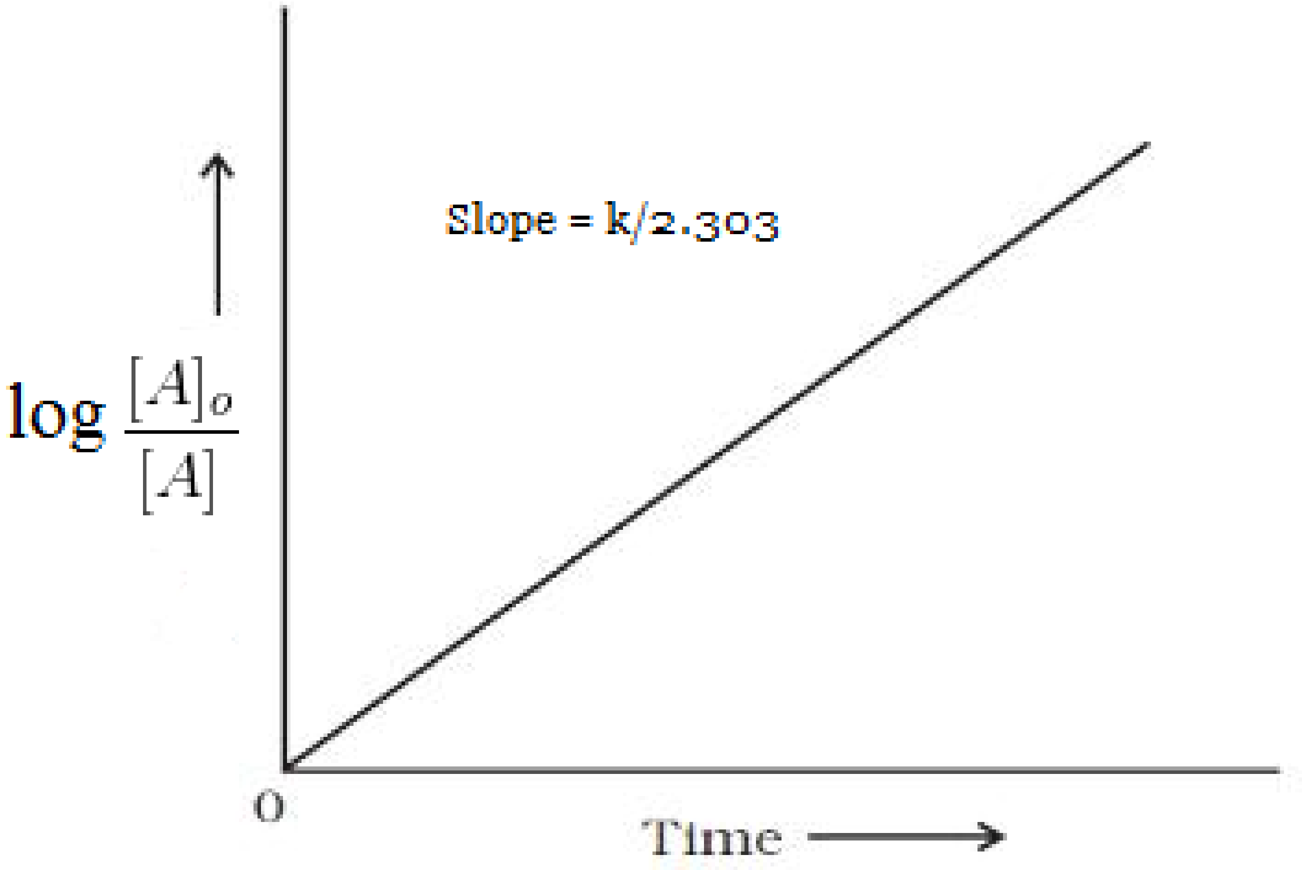
Unit of k = $(\text{time})^{-1}$

Units of rate constant

- For **first order**
- $k = 2.303/t \ . \log a/(a-x)$
- $k = 2.303/t \ . \log [A]_0/[A]_t$
- $k = 1/\text{time}$
- **$k = \text{time}^{-1}$**

First Order Reaction

$\log a/a-x = k/2.303 * t + 0$



$k = 2.303/t \log_{10} a/(a-x)$ ……………………………(6)

Examples of First Order Reaction

Decomposition of N_2O_5 in CCl_4 solution:

$$N_2O_5 \rightarrow 2NO_2 + \tfrac{1}{2}O_2$$

$$k = \frac{2.303}{t}\log_{10}\frac{V_\infty}{V_\infty - V_t}$$

Problem:

From the following data for the decomposition of N_2O_5 in CCl_4 solution at 48 °C, show that it is a first order reaction.

t (mins)	10	15	20	25	∞
V_{CO_2}	6.30	8.95	11.40	13.5	34.75

Examples of First Order Reaction

Decomposition of H_2O_2 in aqueous solution:

$$H_2O_2 \xrightarrow{\text{Pt}} \mathrm{H_2O + O}$$

$$\mathrm{k} = \frac{2.303}{\mathrm{t}} \log_{10} \frac{a}{a-x}$$

Problem:

The catalysed decomposition of H_2O_2 in aqueous solution is followed by titrating equal volume of sample solutions with $KMnO_4$ solution at different time interval give the following results. Show that the reaction is a first order reaction.

t (mins)	0	5	15	25	45
V_{KMnO_4}	37	29.8	19.6	12.3	5.0

Second Order Reaction

Reaction	**A-->**	**Product**
Initial conc	a	0
Final conc	a-x	x

- For second order reaction rate of reaction is proportional to square of concentration of reactants

- $dx/dt = k\ (a-x)^2$

Second Order Reaction

- $dx/dt = k\,(a-x)^2$
- $dx/(a-x)^2 = k\,dt$
- On integration $\int dx/(a-x)^2 = \int k\,dt$
- $1/(a-x) = kt + I$
- At $t=0$, $x=0$…. $I = 1/a$

Second Order Reaction

- Substituting value of I in above equation
- $1/(a-x) = kt + 1/a$
- $kt = 1/(a-x) - 1/a$

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

Second Order Reaction

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

Initial conc.	a	b	0
Final conc.	a-x	b-x	x

$$-\frac{d[A]}{dt} = -\frac{d[B]}{dt} = \frac{dx}{dt} = k[A][B]$$

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

$$\Rightarrow \frac{dx}{(a-x)(b-x)} = kdt$$

Integrating,

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

Units of rate constant

- For **second order reaction**
- k= 1/t . x/a(a-x)
- k= 1/t . $x/[A]_0([A]_0-x)$
- k= 1/time . concentration/concentration^2
- k= 1/time . 1/concentration
- k= 1/time . 1/(mol/lit)
- k= **mol^{-1} lit time^{-1}**

Pseudo order reaction

- Experimental order of reaction which is not actual is known as pseudo order
- Reaction **A+B --> Product**
- If **B is in excesses,** its concentration will practically constant and only concentration of A will affect rate of reaction hence rate law will be..
- **Rate = k' [A]...**

Pseudo order reaction (Example)

- Ethyle acetate+ Water (excesses) --> Acetic acid + EtOH

Pseudo-Order Reaction

Acid Hydrolysis of a Ester:

$$CH_3COOC_2H_5 + H_2O \xrightarrow{\text{Acid}} CH_3COOH + C_2H_5OH$$

Inversion of Cane sugar:

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{Acid}} C_6H_{12}O_6 + C_6H_{12}O_6$$

The experimental order which is not the actual one observed.

$$A + B_{(excess)} \longrightarrow \text{Product}$$

$$Rate = k[A][B]$$

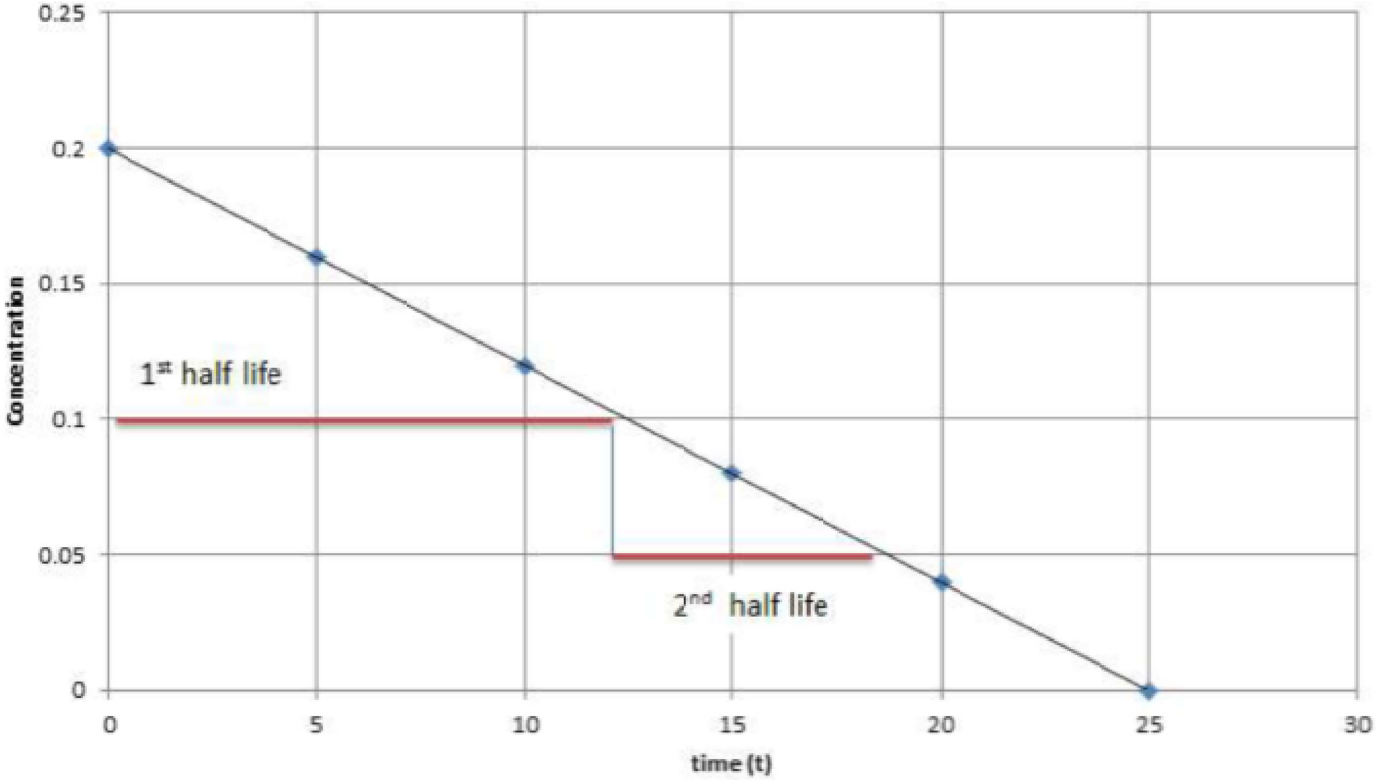
$$Rate = k'[A] \qquad Where, k' = k[B]$$

Half life reaction

- It is defined as the time required as for the decrease in concentration of reactant to half of its initial value.
- When $x=a/2$, then $t=t_{1/2}$
- We can substitute this value in equation of reaction

Half-Life of a Reaction ($t_{1/2}$ or $t_{0.5}$)

Half-life is another expression for reaction rate and is defined as the time required for the concentration of a reactant to decrease to half its initial value



Using Half life method

- Seperate experiments should be performed using different initial concentration
- Half life for *n*th order reaction is

- $\mathbf{t_{1/2}} = 1/\,[A]^{n-1}$

Half-Life of a First-Order Reaction

As, [A] at $t_{1/2}$ is one-half of the original [A],

$[A]_t = 0.5\,[A]_0$.

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

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

$$k = \frac{2.303}{t_{1/2}}\log\frac{[A]_0}{0.5[A]_0}$$

$$k = \frac{2.303}{t_{1/2}}\log 2$$

$$t_{1/2} = \frac{2.303}{k}\log 2 = \frac{2.303}{k}\times 0.3010$$

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

NOTE: For a first-order process, the half-life does not depend on $[A]_0$ and is inversely proportional to k .

It is clear from the above discussion that

(i) Half life of a first order reaction is independent of the initial concentration.

(ii) Half life is inversely proportional to k.

Half-Life of a Zero-Order Reaction

As, [A] at $t_{1/2}$ is one-half of the original [A],

$[A]_t = 0.5\ [A]_0$.

$$k = \frac{x}{t}$$

$$\Rightarrow t = \frac{x}{k} = \frac{[A]_0 - [A]_t}{k}$$

$$\Rightarrow t_{0.5} = \frac{[A]_0 - 0.5[A]_0}{k_0}$$

$$\Rightarrow t_{0.5} = \frac{[A]_0}{2k}$$

Half-Life of a Second-Order Reaction

As, [A] at $t_{1/2}$ is one-half of the original [A],
$[A]_t = 0.5\,[A]_0$.

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

$$kt = \frac{x}{a(a-x)} = \frac{[A]_0 - [A]}{[A]_0[A]} = \frac{1}{[A]} - \frac{1}{[A]_0}$$

$$kt_{1/2} = \frac{1}{0.5[A]_0} - \frac{1}{[A]_0} = \frac{2}{[A]_0} - \frac{1}{[A]_0}$$

$$t_{1/2} = \frac{1}{k[A]_0}$$

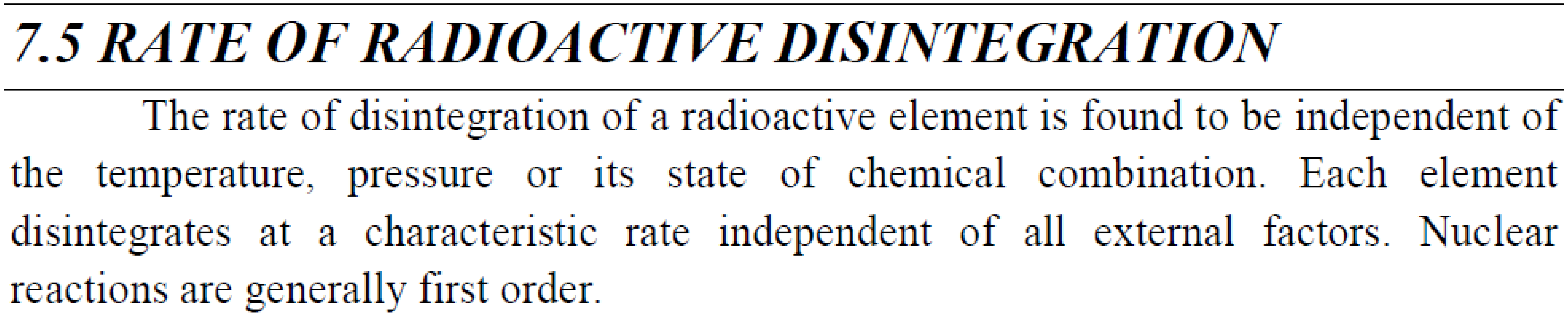
NOTE: For a second-order process, the half-life is inversely proportional to both k and $[A]_0$.

Summarising the all……….

At Time = 0, Concentration of reactant = $[A]_0$ or a
At Time = t, Concentration of reactant = [A] or (a-x)

$$nA \rightarrow \text{Product}$$
$$\text{rate} = k[A]^n$$

Order	Rate Law	Integrated Rate Law	Half-Life	Straight line Plot
0	$r = k[A]^0$	$[A] = -kt + [A]_0$ $(a-x) = -kt + a$	$t_{0.5} = \frac{[A]_0}{2k}$ $t_{0.5} = \frac{a}{2k}$	$[A]$ vs t $(a-x)$ vs t
1	$r = k[A]^1$	$\ln[A] = -kt + \ln[A]_0$ $\ln(a-x) = -kt + \ln a$	$t_{0.5} = \frac{0.693}{k}$	$\ln[A]$ vs t $\ln(a-x)$ vs t
2	$r = k[A]^2$	$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$ $\frac{1}{(a-x)} = kt + \frac{1}{a}$	$t_{0.5} = \frac{1}{k[A]_0}$ $t_{0.5} = \frac{1}{ka}$	$\frac{1}{[A]}$ vs t $\frac{1}{(a-x)}$ vs t



7.5 RATE OF RADIOACTIVE DISINTEGRATION

The rate of disintegration of a radioactive element is found to be independent of the temperature, pressure or its state of chemical combination. Each element disintegrates at a characteristic rate independent of all external factors. Nuclear reactions are generally first order.

The statement that half life period of say radium is 1600 years means after 1600 years any given quantity of radium will disintegrate to half of it.

Average life

The reciprocal of the disintegration constant k gives the average life of the disintegrating atom.

Hence $\lambda = 1/k = T/0.693$

$= 1.44T$

Using Half life method

- **Zero order**: Half life is **directly** proportional to initial concentration of the reactants
- **First order**: Half life is **independent** of the initial concentration of reactants
- **Second order**: Half life is **inversly proportional** to initial cincentration of reactants