Chemical Kinetics

Module 9.1: Concept of reaction rates, rate law, units of rate and rate constant

Introduction:

Chemistry, by its nature, is concerned with change. Substances with well defined properties are converted by chemical reactions into other substances with different properties. For any chemical reaction, chemists try to find out
(a) The feasibility of a chemical reaction which can be predicted by thermodynamics (A reaction with $\Delta G < 0$, at constant temperature and pressure is feasible);
(b) Extent to which a reaction will proceed can be determined from chemical equilibrium;
(c) Speed of a reaction i.e. time taken by a reaction to reach equilibrium.

Along with feasibility and extent, it is equally important to know the rate and the factors controlling the rate of a chemical reaction for its complete understanding. For example, which parameters determine as to how rapidly food gets spoiled? How to design a rapidly setting material for dental filling? Or what controls the rate at which fuel burns in an auto engine? All these questions can be answered by the branch of chemistry, which deals with the study of reaction rates and their mechanisms, called **chemical kinetics**.

The first chemical reaction whose rate was quantitatively studied was the hydrolysis of sucrose. It was studied by L.Wilhemly in 1850. Since then many advances have been made in this field, which enable chemists to study very fast reactions (reactions that occur within less than a second). This has enabled the chemists to discover intermediates in many elementary reactions and thereby propose mechanisms of complex reactions. Chemical kinetics is vast and complex. Here, in this chapter basic aspects of chemical kinetics relating to rates of reactions and their mechanisms are discussed.

Rate of Reaction:

The rate of a reaction is the speed with which the reactants are converted into products.

(or)

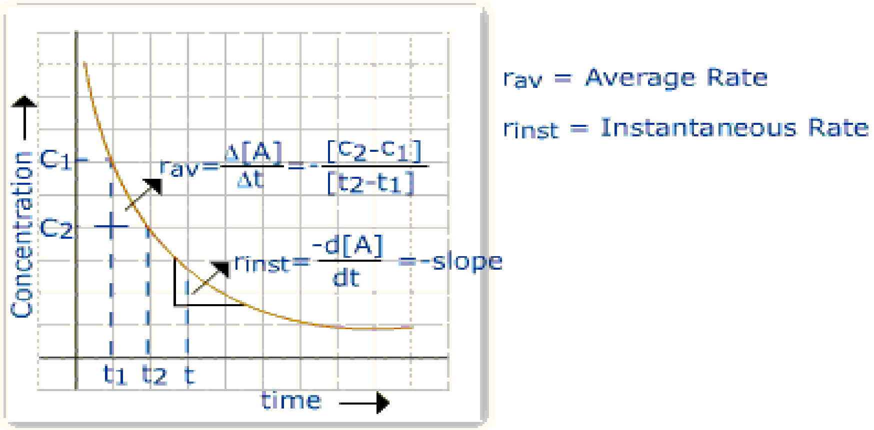
The rate of reaction is defined as the rate of change of concentration of the reactant or product per unit time. The rate of reaction 'r' at any given instant, will be replaced by the following expression

$$r = \frac{dx}{dt} = \frac{-dC_A}{dt} = kC_A$$

Where dC_A denotes the infinitesimally small decrease in the concentration of A in an infinitesimally small internal of time dt, C_A denotes the concentration of reactant A at the given instant and k is known as the rate constant of a reaction.

Explanation:

For a hypothetical reaction, $A \longrightarrow B$, as the reaction proceeds the concentration of the reactant (A) decreases with time while the concentration of the product (B) increases as shown in the figure



Change in concentration of reactant with time

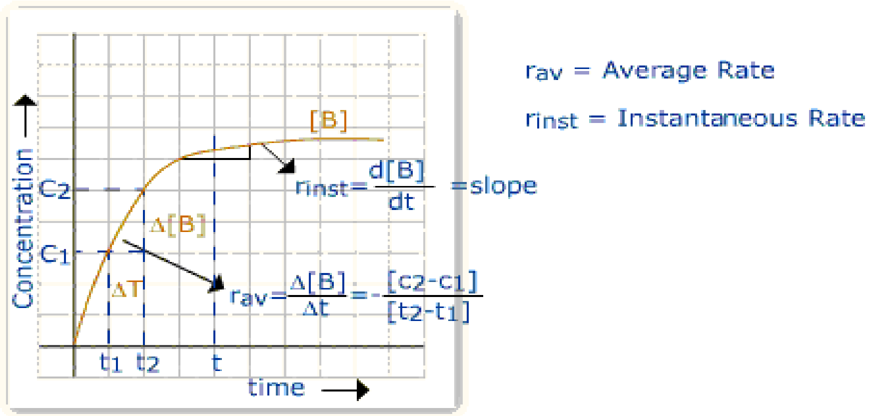
If the concentration of the reactant (A) is monitored at different times, say t_1 and t_2 then the rate of the reaction is given by

$$\text{rate } (r) = \frac{[A]_2 - [A]_1}{t_2 - t_1} \quad \ldots\ldots(1)$$

Where $[A]_2$ is the concentration of A at time t_2 while $[A]_1$ is the concentration A at a time t_1. Equation 1 can be written as,

$$r = -\frac{\Delta [A]}{\Delta t}, \quad \ldots\ldots\ldots(2)$$

Where $[A_2] - [A_1] = \Delta[\Delta]$ and $(t_2 - t_1) = \Delta t$



Change in concentration of Product with time

If the product [B] is monitored then the rate of the reaction is given by

$$(r) = +\frac{[B]_2 - [B]_1}{t_2 - t_1} \quad \ldots\ldots\ldots\ldots(3)$$

$$= +\frac{\Delta[B]}{\Delta t} \quad \ldots\ldots\ldots\ldots(4)$$

Equations (2) and equation (4) represent the average rate of a reaction.

$$\therefore r = -\frac{\Delta [A]}{\Delta t} = +\frac{\Delta [B],}{\Delta t} \quad \ldots\ldots\ldots\ldots(5)$$

The rate measured over a long time interval is called average rate and the rate measured for an infinitesimally small time interval is called instantaneous rate.

In a chemical change, reactants and products are involved. As the chemical reaction proceeds, the concentration of the reactants decreases, i.e., products is produced. The rate of reaction (average rate) is defined as the change of concentration of any one of its reactants (or products) per unit time.

Average rate of reaction,

r_{av} = (Change of concentration one of the reactants or products)/(Time taken for the change)

Consider a common hypothetical reaction,

$$A \rightarrow B$$

The average rate of reaction may be expressed either in terms of decrease in concentration of A (reactants) or in terms of increase in concentration of B (product).

or Average rate of reaction= (Decrease in concentration of A)/(Time taken)

Average rate of reaction= (Increase in concentration of B)/(Time taken)

The average rate of a reaction is a positive quantity; therefore a negative sign precedes in the term in the equation of the rate of reaction when it is expressed in terms of concentrations of the reactants. Average rate of a reaction does not represent the actual rate of a reaction at any instant of time. From the above figures, it is clear that the rate of reaction actually decreases with time. This is because the rate of reaction depends on the concentration of the reactants.

Units of rate of reaction:

$$\text{Rate of reaction} = \frac{\text{Change in concentration}}{\text{Time taken}}$$

Units of concentration (in solutions) is moles per litre

Unit of time is seconds, minutes etc.

$$\therefore \text{ Unit of rate of reaction} = \frac{\text{moles/litre}}{\text{second}} = \text{mol } L^{-1}s^{-1}$$

However, in gaseous reactions, when the concentration of gases is expressed in terms of their

Partial pressures, then the units of the rate equation will be atm s^{-1}.

The units of rate of reaction may be expressed as:

mole/litre sec (mol L^{-1} s^{-1})

or mole/litre min (mol L^{-1} min^{-1})

or mole/litre hour (mol L^{-1} h^{-1})

or mole/litre day (mol L^{-1} d^{-1})

or mole/litre year ($mol^{-1}y^{-1}$)

Expressions for Rates of a Reaction:

The amounts of reactants and products in a chemical reaction are related by stiochiometry. Therefore, the concentration of any reactant or product can be used to express the rate of a reaction. Take for e.g., in the reaction

$$A + B \rightarrow C$$

For every molecule of A consumed, a molecule of B is also consumed and thereby a molecule of C, the product, is formed. Hence, the rate of a reaction can be expressed as

$$r = -\frac{d\,[A]}{d\,t} = -\frac{d[B],}{dt} = +\frac{d[C]}{dt}$$

Consider the following reaction between CO and NO_2

$$CO + NO_2 \rightarrow CO_2 + NO$$

The equation shows that when one mole of CO reacts with one mole of NO_2, one mole each of CO_2 and NO are formed. The average rate of reaction can be expressed either by decrease of concentration of any one of the reactants (CO or NO_2) or by the increase in concentration of any one of the products (CO_2 or NO).

Thus, $-d[CO]/dt = -d[NO_2]/dt = d[CO_2]/dt = d[NO]/dt$

However, for the below reaction,

$$2H_2O_2 \rightarrow 2H_2O + O_2$$

it is observed that when 2 moles of H_2O_2 decompose, one mole of O_2 is formed in the same time interval. The rate of increase in the concentration of O_2, therefore, is half that of the disappearance of the concentration of H_2O_2 in the same time interval;

So $d[O_2]/dt = -1/2\ d[H_2O_2]/dt$

In general, for a reaction,

$$n_1A + n_2B \rightarrow m_1C + m_2D$$

The rate expression may be expressed as

$$(-1/n_1)\ d[A]/dt = (-1/n_2)d[B]/dt = (1/m_1)d[C]/dt = (1/m_2)d[D]/dt$$

Thus, for the reaction,

$$H_2 + I_2 \leftrightarrow 2HI$$

the rate may be expressed as

$$-\ d[H_2]/dt = d[I_2]/dt = 1/2\ d[HI]/dt$$

Similarly, for the decomposition of N_2O_5 in CCl_4 medium, the rate may be expressed as

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

$$-\ 1/2\ d[N_2O_5]/dt = 1/4\ d[NO_2]/dt = d[O_2]/dt$$

Rate Equation or Rate Law:

The rate of a chemical reaction at a given temperature may depend on the concentration of one or more reactants and products. The representation of rate of reaction in terms of concentration of the reactants is known as **rate law**. It is also called as rate equation or rate expression.

Expression for rate law and Rate Constant:

Experimentally, it is found that the rate of a reaction is proportional to the concentrations of the reactants raised to some power, provided that other factors, which also affect the rate of the reaction are kept constant.

Rate law is the expression in which reaction rate is given in terms of molar concentration of reactants with each term raised to some power, which may or may not be same as the stoichiometric coefficient of the reacting species in a balanced chemical equation.

Example: for the hypothetical reaction,

$$2A + B \longrightarrow C + D$$

The rate of reaction might depend on the concentrations of A and B in the following manners.

$$rate \ \propto [A]^2[B]$$

$$rate\ (r) = \ k[A]^2[B]$$

Here k is the rate coefficient or specific rate constant of the reaction.

Note:

This constant is independent of concentration but is dependent on temperature.

Theoretically, there are many possibilities to rate law expression of a reaction. However, only one expression will fit the experimentally determined rate data.

In general, for any hypothetical reaction,

$$aA + bB \longrightarrow cC + dD$$

The rate law expression can be written as

$$\text{Rate (r)} = k\,[A]^a\,[B]^b$$

Rate law expression serves three purposes:

1. If the composition of the reaction mixture and the rate constant are known, then the rate of the reaction can be predicted.
2. It is useful in postulating the mechanism of a reaction.
3. It is useful in classifying the reactions into various orders

Units of Rate Constant:

The rate constant (k) or velocity constant of reaction may be defined as equal to the rate of reaction when the concentration of each of the reactant is unity.

The rate(r) and the rate constant (k) are related by the equation.

$$r = k[reactants]^n$$

$$k = \frac{r}{[reactants]^n}$$

Where, k = rate constant

[Reactants] = concentration of reactants

n = sum of the powers of concentrations terms in the rate equation.

Depending on the nature of the reaction, the value of ‘n’ varies. It can be zero or any integer or a fraction.

For a general reaction,

$$aA + bB \rightarrow cC + dD$$

$$Rate = k\,[A]^x\,[B]^y$$

$$k = \frac{Rate}{[A]^x[B]^y}$$

Where, (x+y) = n = order of reaction.

Taking SI units of concentration (mol L^{-1}) and units of time (seconds), the units of k for different reaction order are listed in below table.

Reaction	**Order**	**Units of rate constant** $\frac{(units\ of\ Rate)}{(concentration)^n}$
Zero order reaction	0	$\frac{mol\ L^{-1}}{s} \times \frac{1}{(mol\ L^{-1})^0} = mol\ L^{-1}s^{-1}$
First order reaction	1	$\frac{mol\ L^{-1}}{s} \times \frac{1}{(mol\ L^{-1})^1} = s^{-1}$
Second order reaction	2	$\frac{mol\ L^{-1}}{s} \times \frac{1}{(mol\ L^{-1})^2} = mol^{-1}Ls^{-1}$

SAQs:

1. The branch of chemistry which deals with the reaction rates and reaction mechanism is called
   a. Thermo Chemistry
   b. Photo Chemistry
   c. Analytical Chemistry
   d. Chemical Kinetics

Solution: d)

2. Rate expression is the expression that gives relation between rate of reaction and
   a. Temperature
   b. Catalyst
   c. Concentration of products
   d. Concentration of reactants

Solution: d)

3. The rate constant of a reaction is 0.2 min^{-1}. The order of the reaction
   a. 0
   b. 1
   c. 2
   d. 3

Solution: b)

4. The unit of rate of a reaction
    a. $Time^{-1}$
    b. Mole lit^{-1}
    c. Lit $mole^{-1}$
    d. Mole lit^{-1} sec^{-1}

Solution: d)

LAQs:

1. Define rate of reaction

Solution:

Rate of Reaction:

The rate of a reaction is the speed with which the reactants are converted into products.

(Or)

The rate of reaction is defined as the rate of change of concentration of the reactant or product per unit time. The rate of reaction 'r' at any given instant, will be replaced by the following expression

$$r = \frac{dx}{dt} = \frac{-dC_A}{dt} = kC_A$$

Where dC_A denotes the infinitesimally small decrease in the concentration of A in an infinitesimally small internal of time dt, C_A denotes the concentration of reactant A at the given instant and k is known as the rate constant of a reaction.

2. What is rate law?

Solution:

Rate Equation or Rate Law:

The equation that describes mathematically the dependence of the rate of a reaction on the concentration terms of the reactants is known as the rate equation or rate law.

3. Define rate constant of reaction

Solution:

Units of Rate Constant:

The rate constant (k) or velocity constant of reaction may be defined as equal to the rate of reaction when the concentration of each of the reactant is unity

The rate(r) and the rate constant (k) are related by the equation

$$r = k[reactants]^n$$

$$k = \frac{r}{[reactants]^n}$$

Where, k = rate constant

[Reactants] = concentration of reactants

n = sum of the powers of concentrations terms in the rate equation.

Depending on the nature of the reaction, the value of ‘n’ varies. It can be zero or any integer or a fraction.

Problem Set:

1. The rate of chemical reaction ______ as the reaction proceeds
   a. Increases
   b. Decreases
   c. May increase or decrease
   d. Remains constant

Solution: b)

2. For the reaction A + 2B $\longrightarrow$ C, any given instance the correct relation is represented by
   a. $+\frac{d[A]}{dt} = +\frac{1}{2}\frac{d[B]}{dt} = +\frac{d[C]}{dt}$
   b. $+\frac{d[A]}{dt} = +\frac{1}{2}\frac{d[B]}{dt} = -\frac{d[C]}{dt}$
   c. $-\frac{d[A]}{dt} = -\frac{1}{2}\frac{d[B]}{dt} = +\frac{d[C]}{dt}$
   d. $+\frac{1}{2}\frac{d[A]}{dt} = +\frac{1}{2}\frac{d[B]}{dt} = +\frac{d[C]}{dt}$

Solution: c)

3. The units of rate constant is
   a. $\text{Litre}^{(1-n)}\ \text{mole}^{(1-n)}\ \text{sec}^{-1}$
   b. $\text{Litre}^{(n-1)}\ \text{mole}^{(n-1)}\ \text{sec}^{-1}$
   c. $\text{Mol}^{(1-n)}\ \text{litre}^{(n-1)}\ \text{sec}^{-1}$
   d. $\text{Mol}^{(n-1)}\ \text{litre}^{(1-n)}\ \text{sec}^{-1}$

Solution: c)

4. Consider the chemical reaction,

$$N_{2(g)} + 3H_{2(g)} \longrightarrow 2NH_{3(g)}$$

   The rate of this reaction can be expressed in terms of time, derivatives of concentration of $N_{2\,(g)}$, $H_{2\,(g)}$ or $NH_{3\,(g)}$. Identify the correct relationship amongst the rate expression
   a. Rate $= -\frac{d[N_2]}{dt} = -\frac{1}{3}\frac{d[H_2]}{dt} = \frac{1}{2}\frac{d[NH_3]}{dt}$
   b. Rate $= -\frac{d[N_2]}{dt} = -3\frac{d[H_2]}{dt} = 2\frac{d[NH_3]}{dt}$
   c. Rate $= \frac{d[N_2]}{dt} = \frac{1}{3}\frac{d[H_2]}{dt} = \frac{1}{2}\frac{d[NH_3]}{dt}$
   d. Rate $= -\frac{d[N_2]}{dt} = -\frac{d[H_2]}{dt} = \frac{d[NH_3]}{dt}$

Solution: a)

5. Identify the reaction order of the reaction from each of the following rate constants

a. $k = 2.3 \times 10^{-5}$ L $mol^{-1}s^{-1}$
b. $k = 3 \times 10^{-4}$ s^{-1}

Solution:

a. Second order reaction
b. First order reaction

6. Consider the following reaction:

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

If the rate of loss of hydrogen is 0.03 mol L^{-1} S^{-1}, what is the rate of production of ammonia?

Solution:

From the balanced equation we see that there are 2 moles of ammonia produced for every 3 moles of H_2 used. Thus rate of NH_3 production is

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

3 moles of hydrogen ⟶ 2 moles of ammonia

0.03 moles of hydrogen ⟶ ?

$$= \frac{2}{3} \times 0.03$$

$$= 0.02 \text{ mol.L}^{-1}.\text{s}^{-1}$$

7. Derive the units of rate constant. For the following reactions
   a. $2A + B \longrightarrow$ p; products
   b. $3A \longrightarrow$ p; products
   c. $A + B + C \longrightarrow$ p; products

Solution:

a. $2A + B \rightarrow$ products

$$r = k\,[A]^2\,[B]$$

$$k = \frac{r}{[A]^2[B]}$$

$$= \frac{\text{conc}}{\text{time}} \times \frac{1}{(\text{conc})^3}$$

$$= sec^{-1} \times \frac{1}{(mol/lit)^2}$$

Units of k = mol^{-3} lit^{3} sec^{-1}

b. 3 A → P; products

r = k $[A]^3$

$$\text{k} = \frac{\text{r}}{[\text{A}]^3}$$

$$= \frac{\text{conc}}{\text{time}} \times \frac{1}{(\text{conc})^3}$$

$$= sec^{-1} \times \frac{1}{(mol/lit)^2}$$

Unit of k = mol^{-2} lit^{2} sec^{-1}

c. A + B + C $\longrightarrow$ p; products

r = k [A][B][C]

$$\text{k} = \frac{r}{[A][B][C]}$$

$$= \frac{cocentrated}{time} \times \frac{1}{conc.conc.conc}$$

$$= \frac{conc}{time} \times \frac{1}{conc^3}$$

$$= \text{sec}^{-1} \times \frac{1}{(\frac{mol}{lit})^2}$$

mol^{-2} lit^{2} sec-1

Exercise Questions:

1. Rate constant of a reaction is equal to rate of a reaction, when the concentrations of the each reactants
   a. Do not change with time
   b. Is equal to concentration of products
   c. At time t = 0
   d. Is equal to unity
2. For the reaction

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

   Rate of reaction with respect to hydrogen may be expressed as $-\frac{d[H_2]}{dt}$. In this expression $\frac{d[H_2]}{dt}$ represents
   a. A negative rate of reaction
   b. Amount of hydrogen left unreacted
   c. Decreases in the rate of change in concentration of hydrogen
   d. Decrease in concentration of H_2 in unit time

3. Following mechanism has been proposed for a reaction.

$$2A + B \rightarrow D + E$$
$$A + B \rightarrow C + D \text{ (slow)}$$
$$A + C \rightarrow E \text{ (fast)}$$

   The rate law expression for the reaction is
   a. $R = K [A]^2 [B]$
   b. $R = K [A] [B]$
   c. $R = K [A]^2$
   d. $R = K [A] [C]$

4. For the given reaction A +B → products
   Following data are given.

Initial conc (m / L) A	**Initial conc (m / L) B**	**Initial rate ($m\ L^{-1}\ S^{-1}$)**
0.1	0.1	0.05

0.2	0.1	0.1
0.1	0.2	0.05

a. Write the rate equation
b. Calculate the rate constant

5. In the following decomposition rection

$$2\,N_2O_5 \xrightarrow{\quad\quad} 4\,NO_2 + O_2$$

Oxygen is produced at the average rate of 9.1×10^{-4} mol L^{-1} S^{-1} over the same period, what is average rate of the following

a. The production of nitrogen dioxide
b. The loss of nitrogen pentoxide

Solution to exercise questions:

1. d
2. d
3. b
4. (a) Rate is independent of [B] because on doubling the initial concentration of B alone, the initial rate remains unaffected, while it is doubled when initial concentration of A is doubled

Let the order with respect to A and B be ‘m’ and ‘n’ respectively

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

Now for A

$$0.05 = k\,[0.1]^m\,[0.1]^n \text{ ------ } 1$$

$$0.1 = k\,[0.2]^m\,[0.1]^n \text{ ------- } 2$$

From 1 and 2

$$2 = [2]^m$$

$$\Rightarrow m = 1$$

Secondly for B

$$0.05 = k\,[0.1]^m\,[0.1]^n \text{ ------ } 3$$

$$0.05 = k\,[0.1]^m\,[0.2]^n \text{ ------ } 4$$

Now comparing 1 and 2 we get

$$1 = [2]^n$$

$=> n = 0$

Rate equation of a reaction is

$$\text{Rate} = k\,[A]^1\,[B]^0$$

$$0.1 = k\,[0.2]^1\,[0.1]^0$$

$$K = 0.1/0.2 = 0.5\ s^{-1}$$

5. From the equation we see that every 1 mole of oxygen formed, four moles of nitrogen dioxide are produced. Thus, the rate of production of nitrogen dioxide is four times that of oxygen

   Rate of NO_2 production $= 4 \times (9.1 \times 10^{-4})$

   $= 3.6 \times 10^{-3}$ mol $L^{-1}\ s^{-1}$

   Nitrogen pentoxide is consumed at twice the rate of formation of oxygen

   Rate loss of $N_2O_5 = 2 \times 9.1 \times 10^{-4}$

   $= 1.82 \times 10^{-3}$ mol $L^{-1}\ s^{-1}$

CAT questions:

1. The rate constant for the reaction,

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

   is 3.0×10^{-5} sec^{-1}. If the rate of dissociation of N_2O_5 is 2.40×10^{-5} mol lit^{-1} sec then the concentration of N_2O_5 (in mol/L) is
   a. 1.4
   b. 1.2
   c. 0.04
   d. 0.8

Solution: d)

2. If the rate for chemical reaction is expressed as rate = $k\,[A]^n[B]^0$ then order of reaction is
   a. One
   b. n
   c. n+1
   d. n-1

Solution: c)

Chemical Kinetics

Module 9.2: Factors Affecting the Rate of a Reaction, Law of mass action

The rate of reaction depends on the following factors:

- Concentration of the reactants
- Nature of the reactants
- Temperature
- Catalyst
- Light

1. Effect of Concentration of the reactants:

The rate of a reaction generally increases with increase in concentration of the reactants. This fact was proposed by Guldberg and Waage in the form of a law. This is known as law of mass action.

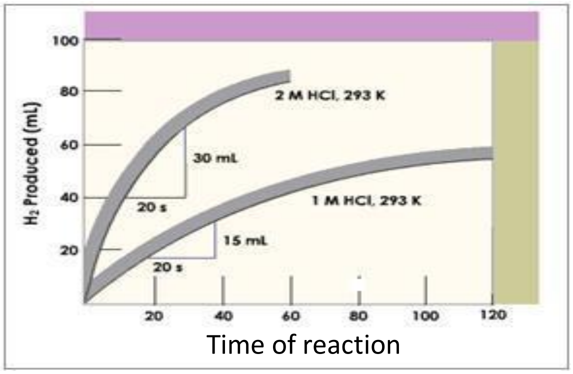
"The rate of a reaction at any instant is directly proportional to the product of the concentrations (active masses) of the reactants taking part in the reaction at that instant."

Different reactants can affect the rate of a particular reaction to different extents.

10 mL of 1 M HCl, 10 mL of 2 M HCl, A graduated syringe and a boiling tube.

The syringe is attached to the boiling tube and the reaction is carried out with 3g of zinc and 5 mL of 1 M HCl and next with 3g of zinc and 5 mL of 2 M HCl.

The volume of the gas at time intervals of 20s, 40s and 60s is recorded and the results are plotted.

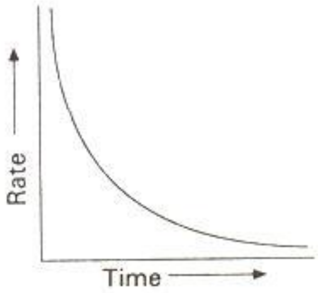


Data Plot Demonstrating Concentration Effects at 1 M and 2 M HCl, at constant Temperature

From the above experiment, we can say that, as the concentration increases reaction rate increases

Let us consider the reaction:

$A + B \rightarrow C + D$; Rate = $k[A][B]$



Rate of the above reaction decreases with the passage of time because the concentration of reactants A and B will decrease as time pass on.

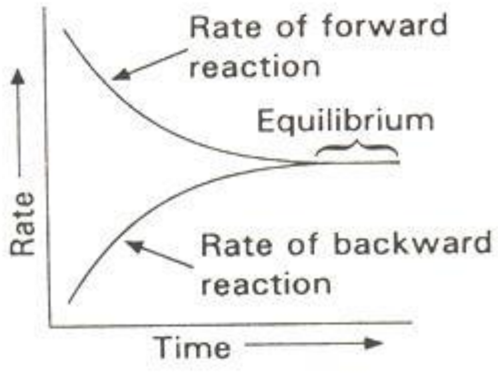
Let us consider the following reversible reaction:

$A + B \leftrightarrow C + D$

Rate of forward reaction = $k_f[A][B]$

Rate of backward reaction = $k_b[C][D]$

We found that, rate of forward reaction decreases and that of backward reaction increases with passage of time. At equilibrium both the rates become equal.



2. Effect of nature of the reactants:

(a) Physical state of reactants:

This has considerable effect over rate of reaction.

(Gaseous state>Liquid state>Solid state): (Decreasing rate of reaction)

Similarly in a heterogeneous system collision is not as effective as in homogenous system. Thus, reactions in liquid phase or solution phase will be faster in comparison to heterogeneous conditions when same concentrations of the reactants are taken.

(b) Physical size of the reactants

Among the solids, rate increases with decrease in particle size. In powdered state rate of reaction is maximum because in powdered state, surface area is maximum.

The rate of the reaction increases as the surface area of the reactants increases. It is a common observation that saw dust burns more rapidly while logs of wood burn slowly. For example, magnesium powder reacts with dilute sulphuric acid more rapidly than magnesium ribbons. Thus smaller the size of reacting particles, the greater is the total surface area exposed for reaction and consequently greater is the rate of the reaction.

(c) Chemical nature of reactants:

Consider the following two reactions:

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

$CH_2(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O$ ..... (ii)

The first reaction is faster than the second because in the first reaction only $N \equiv O$ bond is to be broken where as in the second reaction four (C-H) bonds are to be broken.

Similarly consider another example of two similar reactions:

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

$2CO(g) + 2O_2(g) \rightarrow 2CO_2(g)$ ...... (iv)

No bond is weaker than CO bond, hence broken easily. Thus reaction (iii) is faster than (iv).

Rates of chemical reaction depend on the inherent characteristics or nature of the reactants. That is the reason, why some reactions are fast while others are slow.

Example:

i. The reaction between NaCl and $AgNO_3$ (both ionic compounds) in solution to give AgCl precipitate and $NaNO_3$ occurs very fast (instantaneously)

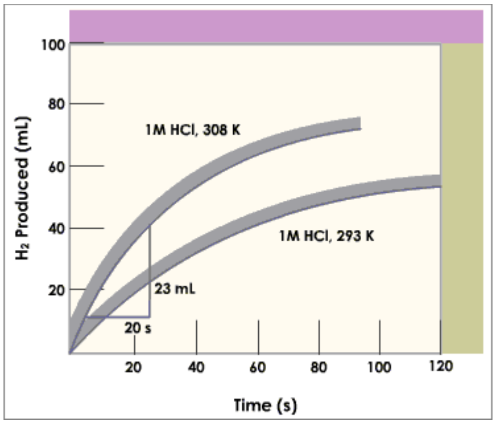
ii. The reaction between ethyl alcohol and acetic acid (both covalent compounds) to form ethyl acetate and water in presence of an acid occurs slowly

The reactions taking place between covalent compounds involve breaking of the covalent bonds existing between the atoms of the reactants and forming of the new covalent bonds. Hence these reactions generally are slow. In ionic reactions however no such breaking and forming of bonds is necessary. Hence these reactions are faster than the covalent reactions.

3. Effect of temperature:

Most of the chemical reactions are accelerated by increase in temperature. For example, in decomposition of N_2O_5, the time taken for half of the original amount of material to decompose is 12 min at 50^0c, 5 h at 25^0c and 10 days at 0^0c. You also know that in a reaction of potassium permanganate ($KMnO_4$) with oxalic acid

($H_2C_2O_4$), potassium permanganate gets decolourised faster at a higher temperature than that at a lower temperature.



The reaction between zinc and hydrochloric acid can be performed at two different temperatures: 293 k and 308 k

It will be found that the volume of hydrogen formed during the same interval of time will be more at 308 k then at 298 k

It has been found that for a chemical reaction with rise in temperature by 10°, the rate constant is nearly doubled. The temperature dependence of the rate of a chemical reaction can be accurately explained by Arrhenius equation. It was first proposed by Dutch chemist, J.H. Van't Hoff but Swedish chemist,
Arrhenius provided its physical justification and interpretation.

$$k = Ae^{-Ea/RT} --- (1)$$

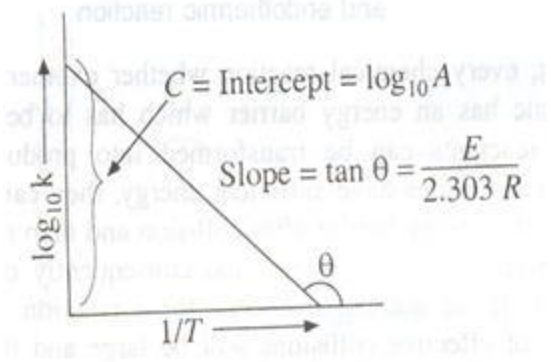
Here A is the Arrhenius factor or the frequency factor. It is also called pre-exponential factor. It is a constant specific for a particular reaction. *R* is gas constant and E_a is activation energy measured in energy units. In SI system we use joule/mole. In the Arrhenius equation the factor $e^{-Ea/RT}$ corresponds to the fraction of molecules that have kinetic energy greater than E_a.
Taking natural logarithm on both sides of equation

$$In\ k = -\frac{E_a}{RT} + In\ A$$

$$Iog\ k = -\frac{E_a}{2.303RT} + Iog\ A$$

The plot of log k vs 1/T gives a straight line according to the above equation

Thus, it has been found from Arrhenius equation that increasing the temperature or decreasing the activation energy will result in an increase in the rate of the reaction and an exponential increase in the rate constant.



A plot between logk and 1/T

In above figure, slope = – E_a/*2.303R* and intercept = log A. So we can calculate E_a and A using these values.

At temperature T_1, Arrhenius equation is

$$Iog\ k_1 = -\frac{E_a}{2.303RT_1} + Iog\ A$$

At temperature T_2, Arrhenius equation is

$$Iog\ k_2 = -\frac{E_a}{2.303RT_2} + Iog\ A$$

Solving the above equations, we obtain

$$Iog\ k_2 - Iog\ k_1 = -\frac{E_a}{2.303RT_2} + Iog\ A + \frac{E_a}{2.303RT_1} - Iog\ A$$

$$Iog\ (k_2 - k_1) = -\frac{E_a}{2.303RT_2} + \frac{E_a}{2.303RT_1}$$

$$log\ \frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$$log\ \frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

A is constant for a given reaction. k_1 and k_2 are the values of rate constants at temperatures T_1 and T_2 respectively.

Logarithmic Arrhenius equation is:

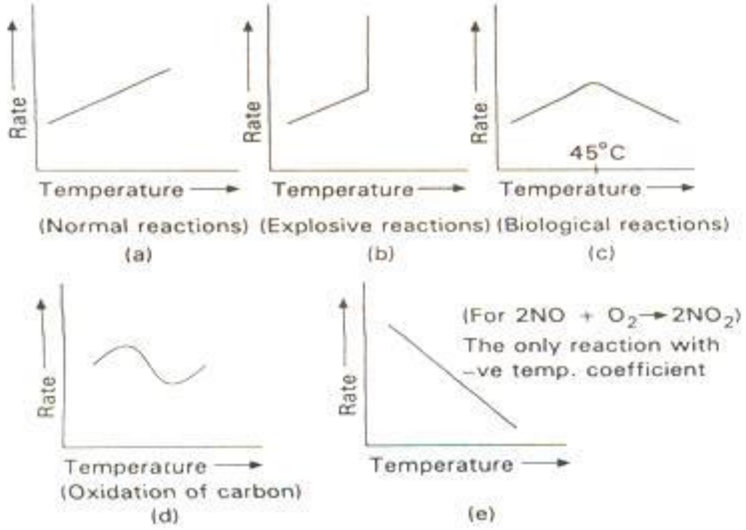
$\log_{10} k = \log_{10} A - E_a/(2.303\ R)(T)$

$Y = C + M X$

It is the equation of straight line with negative slope. On plotting $\log_{10} k$ against [1/T] we get a straight line. The graph gives two kinetic parameters.

The slope gives activation energy and intercept gives frequency factor.

Reactions on the basis of influence of temperature are classified into five types. There are shown in the graphs.



4. Effect of Catalyst:

Catalysts are substances, which alter the rate of chemical reactions without themselves undergoing any overall chemical change.

In the manufacture of ammonia, iron is used as a catalyst and it enhances the rate of this reaction.

$$\longrightarrow$$

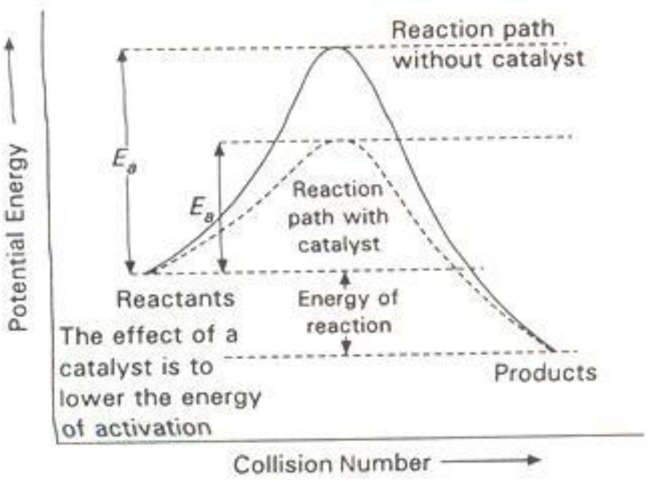
Sometimes catalysts are used to retard or slow down the rates of reaction. For example, glycerol is used to slow down the decomposition of hydrogen peroxide. Such catalysts are known as negative catalysts or inhibitors.

Many industrial processes like the manufacture of polythene and polystyrene require catalysts.

In the living bodies, a large number of complex chemical reactions occur which are catalyzed by complex organic molecules called enzymes. For example, enzyme amylase presents in saliva catalyses the decomposition of starch into maltose.

Presence of a positive catalyst:

The function of a positive is to lower down the activation energy. The greater the decrease in the activation energy caused by the catalyst, higher will be the reaction rate. In the presence of a catalyst, the reaction follows a path of lower activation energy. Under this condition, a large number of reacting molecules are able to cross over the energy barrier and thus the rate of reaction increases. Fig . 8.10. shows how the activation energy is lowered in presence of a catalyst.

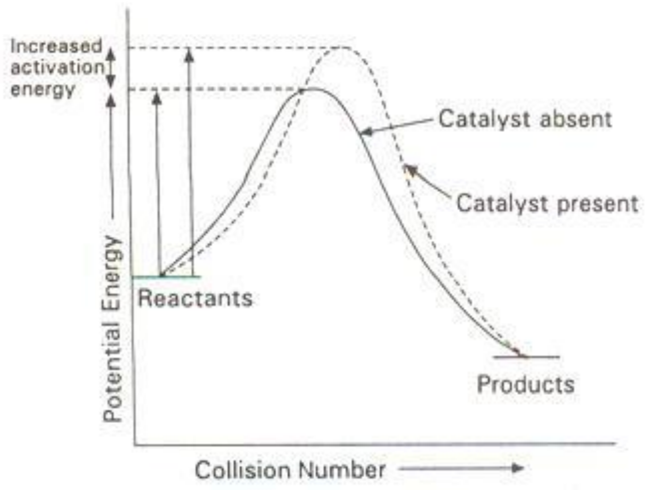


A catalyst changes the reaction path (positive catalyst)

Presence of a negative catalyst:

A negative catalyst increases the activation energy of reaction by forming a new intermediate of high energy, i.e., by changing the reaction mechanism.

Due to increased activation energy, some active molecules become inactive, therefore, rate of reaction decreases.



A catalyst changes the reaction path (Negative catalyst)

Let 'p' denote presence of catalyst and 'a' denote absence of catalyst.

$k_p = Ae^{-E_p/RT}$ .... (i)

$k_a = Ae^{-E_a/RT}$ ... (ii)

Dividing (1) by (2), we get

$k_p/k_a = e^{(E_a - E_p)/RT} = e^{\Delta E/RT}$

$k_p/k_a = \text{Antilog}[\Delta E/(2.303\ RT)]$

5. Effect of Light:

There are many reactions, which are influenced by light. Examples are photosynthesis and photography. Such reactions are known as photochemical reactions.

Other examples are:

$\xrightarrow{\text{Sunlight}}$

$\xrightarrow{\text{light}}$

(Used in photography)

$\longrightarrow$ **Phosgene**

$\longrightarrow$ **Sulphuryl chloride**

Light supplies the necessary energy for the reaction to take place. Photographic films which are normally coated with silver bromide (and a very small amount of silver iodide) undergo photo chemical decomposition when exposed to sunlight. This basic reaction is used in photography.

Law of mass action: (Goldberg and Waage, 1864)

This law relates rate of reaction with active mass or molar concentration of reactants.

At a given temperature, the rate of a reaction at a particular instant raised to powers which are numerically equal to the numbers of their respective molecules in the stoichiometric equation describing the reaction."

Active mass = molar concentration of the substance

= (number of gram moles at the substance)/(volume in litres)

= $(w/M)/V=n/V$

Where w = mass of substance and 'M' is the molecular mass in grams. 'n' is the number of g moles and V is volume in litres.

Example: 4 g of hydrogen and 128 g of hydrogen iodide are present in a 2 litre flask. What are their active masses?

Solution: Mass of hydrogen = 4 g

Mol. mass of hydrogen = 2

Volume of the flask = 2 litres

Active mass of hydrogen = 4/2(2) = 1 mol L^{-1}

Mass of HI = 128 g

Mol. mass of HI = 128 g

Volume of the flask = 2 litre

Active mass of hydrogen iodide = 128/128(2) = 0.5 mol L^{-1}

SAQs:

1. The rate of a chemical reaction depends upon
   a. Catalyst
   b. Temperature
   c. Concentration of the reactants
   d. All the above

Solution: d)

2. Rate of reaction
   a. Increases with increase in temperature
   b. Decreases with increase in temperature
   c. Does not depend on temperature
   d. Does not depend on concentration of the reactants

Solution: a)

3. Under a given set of experimental conditions an increase in concentration of the reactants the rate of chemical reaction
   a. Increases
   b. Decreases
   c. Does not alter
   d. Increases first and then decreases

Solution: a)

4. Mention the factors that effect the rate of a reaction

Solution:

The rate of reaction depends on the following factors:

- Concentration of the reactants
- Nature of the reactants
- Surface area of the reactants
- Temperature
- Catalyst
- Light

LAQs:

1. Calculate the rate constant of a reaction at 293 K when the energy of activation is 103 kJ mol^{-1} and the rate constant at 273 K is 7.87×10^{-7} s^{-1} (R = 8.314×10^{-3} kJ mol^{-1} K^{-1}).

Solution:

The Arrhenius equation is

$\log_{10} k_2/k_1 = E_a/2.303R[(T_2-T_1)/T_1T_2]$

Given: $k_1 = 7.87 \times 10^{-7}$ s^{-1}; $E^a = 103$ kJ mol^{-1}

R = 8.314×10^{-3} kJ mol^{-1} K^{-1}

$T_1 = 273$ K and $T_2 = 293$ K

Substituting the values in Arrhenius equation

$\log_{10} = k_2/(7.87\times10^{-7}) = (10.3\times20)/(2.303\times8.314\times10^{-2}\times293\times273)$

= 1.345

$k_2 = 1.74 \times 10^{-5}$ s^{-1}

2. At 407 K, the rate constant of a chemical reaction is 9.5×10^{-5} s^{-1} and at 420 K, the rate constant is 1.9×10^{-4} s^{-1}. Calculate the frequency factor of the reaction.

Solution:

The Arrhenius equation is,

$\mathrm{Log}_{10} = k_2/k_1 = E_a/(2.303\times R)\ [(T_2-T_1)/(T_1\ T_2\ )]$

Given: $k_1 = 9.5 \times 10^{-5}\ s^{-1}$; $k_2 = 1.9 \times 1.4\ s^{-1}$.

$R = 8.314\ J\ mol^{-1}\ K^{-1}$

$T_1 = 407$ K and $T_2 = 420$ K

Substituting the values in Arrhenius equation

$\log_{10}(1.9\times10^{-4})/(9.5\times10^{-5}) = E_a/(2.303\times8.314)\ [(420-407)/(420\times407)]$

$E_a = 75782.3\ J\ mol^{-1}$

Applying now $\log k_1 = \log A - E_a/(2.303\ RT_1)$

$\log 9.5 \times 10^{-5} = \log A - 75782.3/(2.303\times8.314\times407)$

or $\log A/(9.5\times10^{-5}\ ) = 75782.3/(2.303\times8.314\times407) = 9.7246$

$A = 5.04 \times 10^5\ s^{-1}$

3. The energy of activation for a reaction is 100 kJ mol^{-1}. Presence of a catalyst lowers the energy of activation by 75%. What will be effect on rate of reaction at 20^{o}C, other things being equal?

Solution : The Arrhenius equation is

$k = Ae^{-E_a/RT}$

In absence of catalyst, $k_1 = Ae^{-100/RT}$

In presence of catalyst, $k_2 = Ae^{-25/RT}$

So $k_2/k_1 = e^{75/RT}$ or $2.303 \log k_2/k_1 = 75/RT$

or $2.303 \log k_2/k_1 = 75/(8.314 \times 10^{-3}\times 293)$

or $\log k_2/k_1 = 75/(8.314\times10^{-3} \times 293 \times 2.303)$

or $k_2/k_1 = 2.34\times10^{13}$

As the things being equal in presence or absence of a catalyst.

k_2/k_1 must be = (rate of presence of catalyst)/(rate in absence of catalyst)

i.e., $r_2/r_1 = k_2/k_1 = 2.34\times10^{13}$

4. What is the effect of temperature on the rate of a reaction?

Solution:

It has been found that for a chemical reaction with rise in temperature by 10°, the rate constant is nearly doubled. The temperature dependence of the rate of a chemical reaction can be accurately explained by Arrhenius equation. It was first proposed by Dutch chemist, J.H. Van't Hoff but Swedish chemist,
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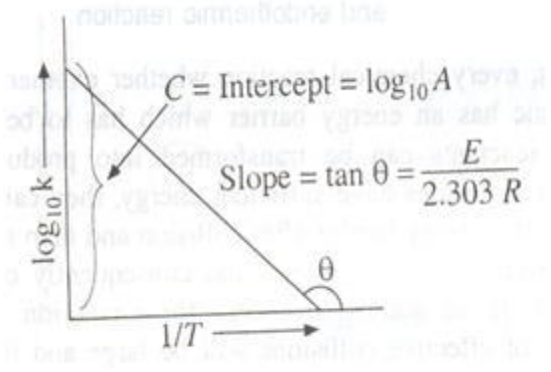

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At temperature T_1, Arrhenius equation is

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At temperature T_2, Arrhenius equation is

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Solving the above equations, we obtain

$$Iog\ k_2 - Iog\ k_1 = -\frac{E_a}{2.303RT_2} + Iog\ A + \frac{E_a}{2.303RT_1} - Iog\ A$$

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A is constant for a given reaction.k_1 and k_2 are the values of rate constants at temperatures T_1 and T_2 respectively.

5. How does the catalyst effect the rate of reaction

Solution:

Effect of Catalyst:

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$$\longrightarrow$$

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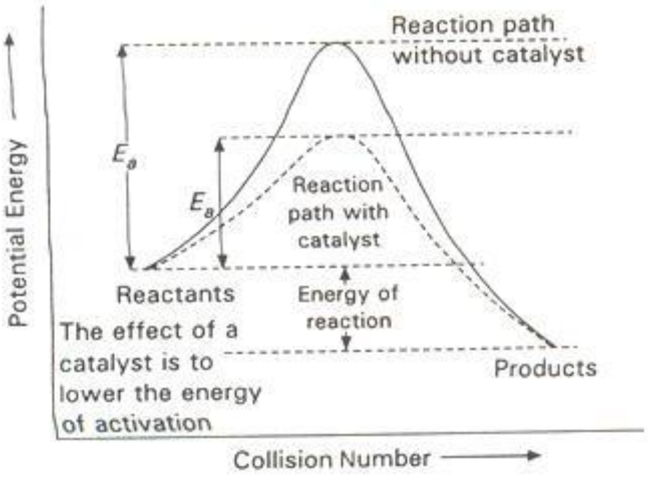

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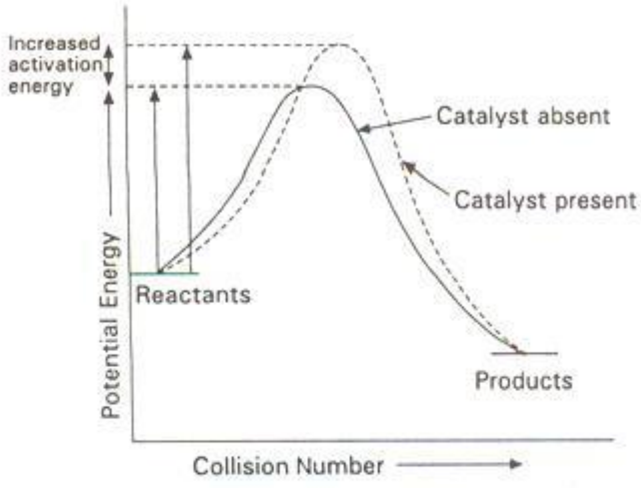


A catalyst changes the reaction path (Negative catalyst)

Problem Set:

1. The rate of reaction between two substances A and B is expressed as rate = k $[A][B]^2$. On doubling the concentration of both the reactants A and B the reaction rate increases by ___ times

a. 4
b. 6
c. 8
d. 10

Solution: c)

2. According to Arrhenius equation, k = $A\ e^{-E_a/RT}$ when graph is plotted between log k and $\frac{1}{T}$ the slope of the graph is equal to ___
   a. $\frac{-E_a}{2.303R}$
   b. $\frac{-E_a}{4.576}$ (cal)
   c. – 0.2183 E_a (cal)
   d. All the above

Solution: d)

3. The rate of a reaction, that does not involve gases, does not depend upon
   a. Pressure
   b. Temperature
   c. Concentration
   d. Catalyst

Solution: a)

4. The activation energy of a reaction is 90 k cal/ mol. Then what will be its rate constant when the temperature is increased from 298 K to 308 K?

Solution:

T_1 = 298

T_2 = 308

E_a = 90 k cal / mol

$$\log\frac{k_2}{k_1} = \frac{90}{2.303 \times 0.002}\ [\frac{10}{308 \times 298}]$$

$$\log\frac{k_2}{k_1} = 0.2129$$

$$\frac{k_2}{k_1} = 1.63$$

The increase in rate constant is $(1.63\ K_1 - k_1) = 0.63\ k_1$

5. For a reaction, $E_a = 0$ and rate constant k at 300 K is $4.2 \times 10^5\ sec^{-1}$. What is the value of k at 310 K

Solution:

When $E_a = 0$
Then

$$log\ \frac{k_2}{k_1} = \frac{E_a}{R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

$$log\ k_2 - \ log k_1 = 0$$

$$\frac{k_2}{k_1} = 1$$

$$k_1 = \ k_2$$

Therefore $k = 4.2 \times 10^5\ sec^{-1}$

Exercise Questions:

1. Which of the following would decrease the amount of time of a glow stick to stay bright?
   a. Increase the temperature of the reactants
   b. Decrease the concentration of one of the reactants
   c. Decrease the temperature of the reactants
   d. Increase the size of the glow stick

2. Why food materials are stored in refrigerators?
   a. The lower temperatures do not spoil food materials
   b. Refrigerators often contain enzymes that act as inhibitors to the spoiling of food
   c. The concentration of the food materials decreases
   d. Bacteria does not grow well at low temperatures

3. Enzymes are an important component in the human body. Without enzymes, many chemical reactions do not occur, or take place much too slowly to be useful. What functions do the enzymes do? They are the

   a. Catalysts
   b. Molecules used to increase concentration
   c. Chemicals that increase surface area
   d. Simple chemicals that protect biochemicals

4. The process of rusting is actually the oxidation of iron, that produces iron oxide why does a coating of oil slow the oxidation of iron?
   a. The oil stops oxygen from reaching the iron, and therefore decreases the concentration of oxygen in the rusting reaction
   b. The oil cools the chain so that the rusting reaction occurs much slower
   c. The oil's surface decreases the surface area of iron, slowing the rusting reaction
   d. The oil is an "anti-catalyst", which actually causes the opposite reaction to occur.

5. Which one of the following reactions would you expect to be fastest at room temperature and why?
   a. lead salt solution + HCl → white precipitate of $PbCl_2$
   b. lead metal heated in Cl_2 gas to give $PbCl_2$

6. Consider the following reactions. Which do you predict will occur most rapidly at atmospheric conditions and which one will be the slowest
   a. $C_2H_{6\,(g)} + O_{2\,(g)} \rightarrow 2\ CO_{2\,(g)} + 3\ H_2O_{(g)}$
   b. $Fe_{(s)} + O_{2\,(g)} \rightarrow Fe_2O_{3\,(s)}$
   c. $H_2O_{(l)} + CO_{2\,(g)} \rightarrow H_2CO_{3\,(g)}$
   d. $2\ Fe^{3+}_{(aq)} + Sn^{2+}_{(aq)} \rightarrow 2\ Fe^{2+}_{(aq)} + Sn^{4+}_{(aq)}$

7. Phosgene, $COCl_2$, one of the poisonous gases used during World War I, is formed from chlorine and carbon monoxide. The mechanism is thought to proceed by:

   a. Write the overall equation for the reaction. $CO + Cl_2 \rightarrow COCl_2$
   b. Identify the reaction intermediates.

8. Consider the following reaction that occurs between hydrochloric acid, HCl, and zinc metal:

$HCl_{(aq)} + Zn_{(s)} \rightarrow H_{2\,(g)} + ZnCl_{2\,(aq)}$

Will this reaction occur faster with 6 M solution of HCl or with 0.5 M solution of HCl? Explain

9. Consider the reaction between hydrochloric acid and zinc. How will the increase in the temperature affect the rate of the reaction? Explain.

Solutions to exercise questions:

1. a
2. a
3. a
4. a
5. a. Fastest - ions in aqueous solution react very quickly; all are in the same phase
   b. slower - one of the reactants is a solid

6. Slow due to covalent bonding (unless the reaction is highly exothermic)
   Slowest - solid reactant (Fe); this reaction describes the rusting of iron
   Slow due to covalent bonding
   Fastest - ions in solution react very quickly

7. The overall reaction:
   a. $CO + Cl_2 \longrightarrow COCl_2$
   b. The reaction intermediate is COCl - it is produced during the first step but immediately used up in the second step.
8. The reaction will occur faster with 6 M HCl, because it is more concentrated than the 0.5 M solution. In the more concentrated solution there are more moles of HCl present - with a higher concentration of reacting substances, collisions will occur more frequently, leading to a faster rate of reaction.

9. Increasing the temperature will increase the rate of the reaction.

CAT:

1. The rate of reaction is doubled for every 10^0c rise in temperature. the increase in the rate as a result of increase in temperature from 10^0c to 100^0c is
   a. 112
   b. 512
   c. 400

d. 256

Solution: b)

2. The effect of temperature on the rate constant of reaction is expressed as
    a. $k = E_a/RT$
    b. $k = A.e^{-E_a/RT}$
    c. $k = log\ e^{-E_a/RT}$
    d. $k = e^{-E_a/RT}$

Solution: b)

Match the following:

List – I	**List – II**
(a) first order reaction	1) $\propto \frac{1}{a^{n-1}}$
(b) zero order reaction	2) Radio active decay
(c) tri molecular reaction	3) Photo chemical reactions
(d) Half – life period of nth order	4) $2CO + O_2 \longrightarrow 2CO_2$

a. A – 1, B – 2, C – 3, D – 4
b. A – 2, B – 3, C – 4, D – 1
c. A – 3, B – 4, C – 2, D – 1
d. A – 4, B – 3, C – 2, D – 1

The correct matching is [ ]

Solution: b)

Chemical Kinetics

Module 9.3: Order and Molecularity of a reaction, integrate rate equations and half life

Molecularity:

It is the sum of the number of molecules of various reactants that take part in a chemical reaction as represented by a balanced chemical equation.

The molecularity of a reaction must always be a whole number. Molecularity gives no information about the rate of a reaction. The molecularity of a reaction is the number of reactant molecules taking part in a single step of the reaction.

For example:

$PCl_5 \longrightarrow PCl_3 + Cl_2$ (unimolecular)

$2HI \longrightarrow H_2 + I_2$ (bi molecular)

$2\ FeCl_3 + SnCl_2 \longrightarrow 2FeCl_2 + SnCl_4$ (trimolecular reaction).

$2SO_2 + O_2 \longrightarrow 2SO_3$ (trimolecular)

$NO + O_3 \longrightarrow NO_2 + O_2$ (bimolecular)

$2CO + O_2 \longrightarrow 2CO_2$ (trimolecular)

$2FeCl_3 + SnCl_2 \longrightarrow SnCl_2 + 2FeCl_2$ (trimolecular)

The minimum number of reacting particles (molecules, atoms or ions) that come together or collide in a rate determining step to form product or products is called the molecularity of a reaction.

For example, decomposition of H_2O_2 takes place in the following two steps:

$H_2O_2 \rightarrow H_2O + 1/2O_2$ (overall reaction)

Step 1: $H_2O_2 \rightarrow H_2O + [O]$ (Slow)

Step 2: $[O] + [O] \rightarrow O_2$ (fast)

The slowest step is rate-determining. Thus from step 1, reaction appears to be unimolecular.

Note:

(i) Molecularity is a theoretical concept.

(ii) Molecularity cannot be zero, -ve, fractional, infinite and imaginary.

(iii) Molecularity cannot be greater than three because more than three molecules may not mutually collide with each other.

There are some chemical reactions whose molecularity appears to be more than three from stoichiometric equations, e.g. in

$$4HBr + O_2 \rightarrow 2H_2O + 2Br_2$$

$$2MNI_4^- + 16H^+ + 5C_2O_4^{2-} \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

In the first reaction molecularity seems to be '5' and in the second reaction molecularity seems to be '23'. Such reactions involve two or more steps; each step has its own molecularity not greater than three, e.g., in first reaction.

$$HBr + O_2 \rightarrow HOOBr$$

$$HOOBr + HBr \rightarrow 2HOBr$$

$$[HOBr + HBr \rightarrow H_2O + Br_2] \times 2$$

$$4HBr + O_2 \rightarrow 2H_2O + Br_2$$

Molecularity of each of the above steps is 2.

(a)Reaction between Br^- and H_2O_2 in acidic medium:

The overall reaction is

$2Br^- + H_2O_2 + 2H^+ \rightarrow Br^2 + 2H_2O$

The proposed mechanism is

$2Br^- + H_2O_2 + H^+ \rightarrow HOBr + H_2O$ (slow)

$HOBr + H^+ + Br^- \rightarrow Br^2 + H_2O$ (fast)

The reaction is trimolecular

(b) Reaction between NO_2 and F_2:

The overall reaction is

$2NO_2 + F_2 \rightarrow 2NO_2F$

The proposed mechanism is

$NO_2 + F_2 \rightarrow NO_2 + F$ (slow)

$NO_2 + F \rightarrow NO_2F$ (fast)

The reaction is bimolecular.

(c) Decomposition of H_2O_2:

The overall reaction is

$H_2O_2 \rightarrow H_2O + O$ (slow)

$H_2O_2 + O \rightarrow H_2O + O_2$ (fast)

Rate = $k[H_2O_2]$

The reaction is unimolecular

Order of the reaction:

An equation which relates the rate of a reaction to the concentrations of the reactants is called the rate law or rate equation.

The order of reaction may be defined as the number of molecules whose concentration alters as a result of chemical change. It determines the rate and kinetics of the reaction. (Or) The order of reaction is given by the total number of molecules or atoms whose concentrations determine the rate of the reaction.

$$xA + yB + \text{........} \longrightarrow \text{products}$$

The rate of such reaction $\propto [A]^x \ [B]^y$ ....

$$r = K [A]^x \ [B]^y \ .....$$

Then the order of such a reaction = $x + y + ...$

Therefore the order of the reaction may be defined as

"The sum of powers of which the concentration or pressure terms are raised in order to determine the rate of the reaction" is known as order of the reaction.

For example, decomposition of N_2O_5 gas

$$N_2O_5 \longrightarrow 2NO_2 + \frac{1}{2} O_2 \text{ is a first order reaction}$$

$$\text{Rate} = \frac{-\,d.\,[N_2O_5]}{dt} \ \alpha \ [N_2O_5]$$

The order of the reaction is not always a whole number. It may also be fractional.

For example the order of the following reaction is $\frac{3}{2}$

$$H_2\,(g) + Br_2\,(g) \longrightarrow 2HBr\,(g)$$

Examples:

(i) $2H_2O_2 \rightarrow 2H_2O + O_2$

(Observed from law of mass action)

Step 1: $H_2O_2 \rightarrow H_2O + [O]$ [slow]

Step 2: $[O] + [O] \rightarrow O_2$ (fast)

Actual rate $-dx/dt = k[H_2 O_2]$

Thus, order of reactions in unity

(ii) $2NO_2 + F_2 \rightarrow 2NO_2F$

Rate law from law of mass action:

$-dx/dt = k[NO_2][F_2]$

Experimentally observed rate law:

$-dx/dt = k[NO_2][F_2]$

Slowest step is $NO_2 + F_2 \rightarrow NO_2F + [F]$

Thus, order of reaction = 1 + 1 = 2

(iii) $CH_3CHO \rightarrow CH_4 + CO$

The rate equation derived from experimental data is found to be

$-dx/dt = k[CH_3CHO]^{1.5}$

The order of reaction is 1.5

From the study of the kinetics of many simple reactions, it is observed that for a large number of reactions, the molecularity and order are same. Some examples are given below to justify this point.

1. Dissociation of N_2O_5.

$N_2O_5 \rightarrow N_2O_4 + O_2$

Order = 1, Molecularity = 1

2. Dissociation of H_2O_2.

$H_2O_2 \rightarrow H_2O + 1/2O_2$

Order = 1, Molecularity = 1

3. Dissociation of HI,

$2HI \rightarrow H_2 + I_2$

Order = 2, Molecularity = 1

4. Formation of NO_2.

$2NO + O_2 \rightarrow 2NO_2$

Order = 3, Moelcularity =3

PSEUDO-ORDER REACTION

Reactions whose actual order is different from that expected using rate law expression are called pseudo-order reactions; e.g.,

(i) $RCl + H_2O \rightarrow ROH + HCl$

Expected rate law:

Rate = $k[RCl]\,[H_2O]$ Expected order = 1+1 =2

Actual rate law:

Rate = $k'[RCl]$; Actual order = 1

Water is taken in excess; therefore, its concentration may be taken constant. The reaction is, therefore, pseudo first order. Similarly, the acid catalysed hydrolysis of ester, viz.,

$RCOR' + H_2O \leftrightarrow RCOOH + R'OH$

follow first order kinetics:

Rate = k[RCOOR']

It is also a pseudo-first order reaction.

Differences between Molecularity and Order of a Reaction

Molecularity	Order
It is the number of reacting species undergoing simultaneous collision	It is the sum of the powers of the concentration terms in the rate law expression
It is a theoretical concept	It is experimentally determined
It has integral values only	It can have fractional values also
It cannot be zero	It can be zero
It provides no information on reaction mechanism	The slowest step in the reaction can be judged by the order of the reaction and this gives further information about the mechanism.

Integrated Rate equations and half life for zero and first order reactions

Zero order reactions

A reaction in which the rate of reaction is independent of the concentration of the reacting substances is called "zero order" reactions.

$$-\frac{dc}{dt} = \frac{dx}{dt} = kc^0$$

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

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

x = kt

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

x = kt for zero order

Examples: Decomposition of NH_3 on metal surfaces such as gold and molybdenum. The metals act as catalysts.

Characteristics of zero order reactions:

a. Units of zero order rate constant, *k*. According to the zero order rate equation.

$$x = kt$$

Or

$$k = \frac{x}{t} = \frac{\text{moles / litre}}{\text{time}}$$

$$= \text{mole litre}^{-1}\ \text{time}^{-1}$$

Since concentration term is involved in the unit of *k*, the numerical value of the rate constant k depends on the unit in which concentration is expressed.

b. Half – life (fractional) period of a zero order reaction. The expression for the **half – life period** (i.e. time taken for converting the original concentration of the reactants to one half) may be obtained as follows.

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

Where a is the initial amount i.e. when t = 0, and *x* is the amount reacted at time *t* which is $t_{1/2}$ in case of half – life period.

Substituting the value of *x* and *t* in the zero order reaction,

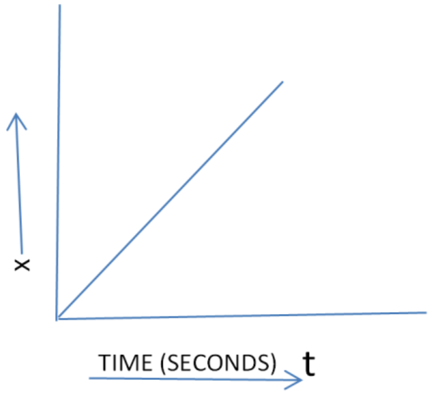
$$x = kt$$

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

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

c. Evaluation of k. A plot of x against t will yield a straight line passing through the origin. The slope of this straight line is *k*.

Examples of zero order reactions are photochemical reactions.



Photochemical reactions are those reactions which take place in the presence of light *(photons)*. Combination of hydrogen and chlorine in presence of light to form hydrogen chloride is a typical example.

$$H_2(g) + Cl_2(g) \xrightarrow{\text{light}} 2HCl(g)$$

However, note that the above reaction is of zero order only when HCl formed is removed spontaneously by dissolving in water. In case, HCl so formed is not removed spontaneously, concentrations of the reactants (H_2 and Cl_2) change with time as a result of which the rate of reaction will not remain constant and hence the reaction will not conform to zero order.

First order reaction

Let the reaction be represented as R ⟶ P. Let 'a' moles dm^{-3} be the initial concentration of R. let the concentration of A remaining at time't' be (a – x) moles dm^{-3}

x = amount of A decomposed in time't' seconds.

The rate $\left(-\frac{dc}{dt}\right)$ or $\left(\frac{dx}{dt}\right)$ at time'tʼ seconds is proportional to the concentration of 'R' at time'tʼ seconds. Since it is first order

$$\frac{dx}{dt}\ \alpha\ (a - x)$$

$$\frac{dx}{dt} = k_1(a - x)$$

$$\frac{dx}{(a - x)} = k_1\ dt. \qquad [k_1 = \text{specific rate of the reaction}]$$

On integration

$$\int \frac{dx}{(a - x)} = \int k_1\ dt$$

$- \ln (a - x) = k_1 t. + C$; where C = constant of intergrations. When $t = 0$, $x = 0$

$\therefore\ - \ln (a - 0) = k_1 \times 0 + C$

$\therefore\ - \ln a = C$

Hence $- \ln (a - x) = k_1 t - \ln a$

or $k_1 t = \ln \left[\frac{a}{(a - x)}\right]$

$k_1 = \frac{1}{t} \ln \left[\frac{a}{(a - x)}\right]$ or

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

$k = \frac{2.303}{t} \log\left[\frac{a}{(a-x)}\right]$ for 1^{st} order reaction. This is the integral form of the first order equation.

Characteristics of first order reactions

a. Units of first order rate constant (k):

According to first order rate equation

$$k_1 = \frac{2.303}{t} \log\left[\frac{a}{(a-x)}\right]$$

The fraction $\frac{a}{a-x}$ is a ratio of two concentrations; the value of velocity constant is independent of the actual concentration units used. The rate constant, therefore, has the units $\frac{1}{time}$, and is usually expressed in $second^{-1}$

$$k_1 = \frac{2.303}{time} \log \frac{(moles/litre)}{(moles/litre)}$$

$$k_1 = time^{-1}$$

Thus if time is expressed in seconds,

$$k_1 = second^{-1}$$

Examples of first order reactions

1. Decomposition of H_2O_2 in aqueous solution

$$H_2O_2 \rightarrow H_2O + 1/2\ O_2$$

2. Hydrolysis of methyl acetate in presence of mineral acids.

$$CH_3COOCH_3 + H_2O \xrightarrow{Acid} CH_3COOH + CH_3OH$$

3. Inversion of cane sugar in presence of mineral acids.

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

4. Decomposition of ammonium nitrite in aqueous solution.

$$NH_4NO_2 \rightarrow N_2 + 2H_2O$$

5. Hydrolysis of diazo derivatives.

$$C_5H_5N = NCl + H_2O \rightarrow C_6H_5OH + N_2 + HCl$$

b. Half – life (fractional) period of a first order reaction:

In general, half – life period of a reaction is the time required to convert the concentration (a) of the reactants to exactly half (a/2); By substituting the value $\frac{a}{2}$ in place of x in 1st order equation, the half – life of the reaction can be ascertained.

$t = t_{1/2}$, when $x = a/2$

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

$$t = \frac{2.303}{k_1} \log \frac{a}{(a - x)} \text{ or } \quad t_{\frac{1}{2}} = \frac{2.303}{k_1} \log \left[\frac{a}{(a - a/2)}\right]$$

$$t_{\frac{1}{2}} = \frac{2.303}{k_1} \log \frac{a}{(a/2)} = \frac{2.303}{k_1} \log(2)$$

$$t_{1/2} = \frac{2.303}{k_1} \times \log(2)$$

$$= \frac{2.303 \times 0.3020}{k_1} = \frac{0.693}{k_1}$$

$$\boxed{t_{1/2} = \frac{0.693}{k_1}}$$

$t_{1/2} = \frac{0.693}{k}$ for 1st order reaction.

Note that half – life period of a first order reaction is independent of the initial concentration, a characteristic of the first order reaction.

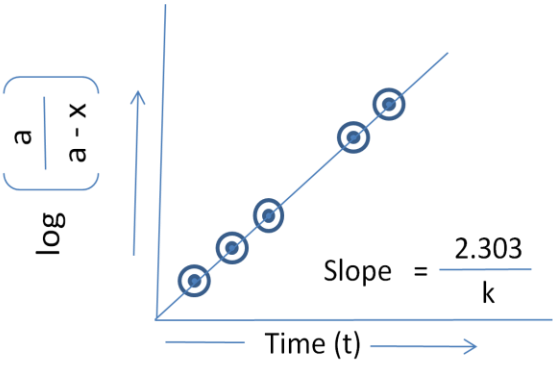
c. Evaluation of ***k_1*****:**

The first order rate constant can be evaluated by two methods, viz.

a. By means of first order reaction
b. By graphical method.

a. Since the initial concentration with which reaction is started is known, by determining the concentration of the reactant at different time intervals (t), k_1 can be easily calculated by putting these values in first order reaction. The calculated value of k_1 at different times remains the same; (an average value is taken for the final calculation of k_1).

b. In the graphical method $\log\left[\frac{a}{a-x}\right]$ is plotted against the corresponding time intervals (t) when a straight line passing through the origin will be obtained. The slope of the straight line will be equal to $\frac{2.303}{k_1}$. Thus from the slope, the value of *k* can be calculated.



Hydrogenation of ethane is an example of first order reaction.

$$C_2H_4 + H_2 \longrightarrow C_2H_6$$

$$\text{Rate} = k\,[C_2H_4]$$

All natural and artificial radio active decay of unstable nuclei take place by first order kinetics

Ex:

$$^{226}_{88}\text{Ra} \longrightarrow {}^{4}_{2}\text{He} + {}^{222}_{86}\text{Rn}$$

$$\text{Rate} = k_1\,[\text{Ra}]$$

Decomposition of nitrogen pentoxide, ethyl acetate in acid solution is some more examples of first order reactions.

Note:
For zero order reaction $t_{1/2}$ is proportional to initial concentration of reactant. For first order reaction $t_{1/2}$ is independent of initial concentration of reactant.

Second order reactions:

A reaction is said to be of second order if its reaction rate is determined by the variation of two concentration terms.

The kinetics of second order reactions are given as follows:

(i) When concentration of both reactants are equal or two molecules of the same reactant are involved in the change, i.e.,

$A + B \rightarrow$ products

or $2A \rightarrow$ products

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

On solving this equation by integration we get,

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

where a = initial concentration of the reactant or reactants and

x = concentration of the reactant changed in time t. $k = \frac{2.303}{t(a-x)} \log \frac{b(a-x)}{a(b-x)}$

(ii) When the initial concentrations of the two reactants are different, i.e.,

A + B → products

Initial conc. a b

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

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

The above equation on integration, we get;

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

(a - x) and (b - x) are the concentrations of A and B after time interval, t.

Characteristics of the second order reactions

(i) The value of k(velocity constant) depends on the unit of concentration. The unit of k is expressed as $(\text{mol/litre})^{-1}$ time^{-1} or litre mol^{-1} time^{-1}.

(ii) Half life period for second order decomposition can be calculated by putting x=a/2 when t= $t_{1/2}$ in the equation, $k = \frac{x}{t[a(a-x)]}$

$$t_{1/2} = \frac{1}{k} \frac{a/2}{a(a-a/2)} = \frac{1}{ka}$$

Thus, half life is inversely proportional to initial concentration.

(iii) Second order reaction conforms to the first order when one of the reactants is present in large excess.

Taking $k = \frac{2.303}{t(a-x)} \log \frac{b(a-x)}{a(b-x)}$; if a>>> b then (a-x) = a

Hence,, $k = \frac{2.303}{ta} \log \frac{ba}{a(b-x)}$

$$ka = k^{'} = \frac{2.303}{t} \log \frac{b}{(b-x)}$$

(Since 'a' being very large, may be treated as constant after the change). Thus the reaction follows first order kinetics with respect to the reactant taken relatively in small amount.

Examples of second order reactions

1. Hydrolysis of ester by an alkali (saponification).

   $CH_3COOC_2H_5 + NaOH \rightarrow CH_3COONa + C_2H_5OH$

2. The decomposition of NO_2 into NO and O_2.

3. Conversion of ozone into oxygen at 100°C

   $2NO_2 \rightarrow 2NO + O_2$

4. Thermal decomposition of chlorine monoxide.

   $2Cl_2O \rightarrow 2Cl_2 + O_2$

<u>Third order reactions</u>:

A reaction is said to be of third order if its rate is determined by the variation of three concentration terms.

When the concentration of all the three reactants is same or three molecules of the same reactant are involved, the rate expression is given as

3A → products

A + B + C → products

$dx/dt = k(a-x)^3$

On solving this equation by integration we get;

$$k = \frac{1}{2t}\left[\frac{1}{(a-x)^2} - \frac{1}{a^2}\right]$$

Characteristic of third order reaction

1. Half life period is calculated as;

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

$$t_{1/2} = \frac{3}{2k\,a^2}$$

Thus, half life is inversely proportional to the square of initial concentration.

2. The change in the unit of concentration changes the numerical value of k.

3. The unit of k is expressed as $(mol/litre)^{-2}$ $time^{-1}$ or $litre^2$ mol^{-2} $litre^{-1}$.

Examples of third order reacting

1. Reacting between nitric oxide and oxygen

   $2NO + O_2 \rightarrow 2NO_2$

2. Reaction between nitric oxide and chlorine.

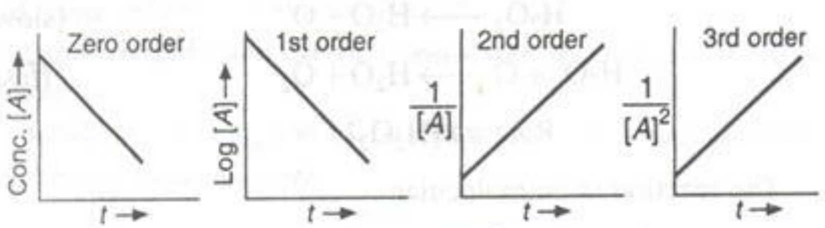
   $2NO + Cl_2 \rightarrow 2NOCl$

3. Reduction of $FeCl_3$ by $SnCl_2$

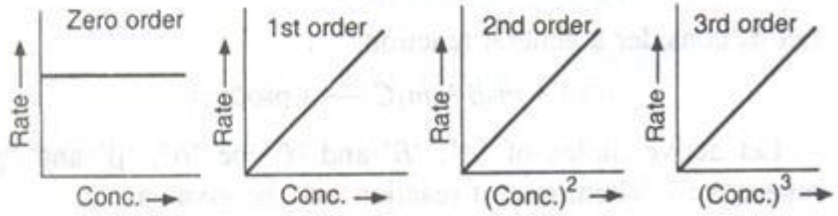
$2F_2Cl_3 + SnCl_2 \rightarrow SnCl_4 + 2FeCl_2$

Some typical linear plots for the reactions of different orders:

Plots rate vs concentrations [Rate = $k(\text{conc.})^n$]



(b) Plots from integrated rate equations:



SAQs:

1. Order of a reaction
   a. Can be written from the balanced chemical equation.
   b. Depends on the stoichiometric coefficients of reactants and products
   c. Can have a fractional value
   d. Depends on the stoichiometric co efficient of products only

   Solution: c)

2. For the elementary step

   $(CH_3)_3\ CBr \longrightarrow (CH_3)_3\ C^+ + Br^-$ The molecularity is

   a. Zero
   b. One
   c. Two
   d. Three

Solution: b)

3. Equation for the half – life period of a first order reaction is;
    a. $t_{\frac{1}{2}} = \frac{0.602}{k}$
    b. $t_{\frac{1}{2}} = \frac{0.693}{k}$
    c. $t_{\frac{1}{2}} = \frac{k}{0.693}$
    d. $t_{\frac{1}{2}} = \frac{k}{0.602}$

Solution: b)

4. The acid catalysed hydrolysis of the methyl acetate ester is ___________ order reaction
    a. Zero
    b. First
    c. Second
    d. Third

Solution: b)

5. Define “order” and “molecularity” of a reaction

Solution:

“The sum of powers of which the concentration or pressure terms are raised in order to determine the rate of the reaction”.

It is the sum of the number of molecules of various reactants that take part in chemical reactions as represented by a balanced chemical equation.

LAQs:

1. Derive the relation for the rate constant (k) of a first order reaction.

Solution:

First order reaction

Let the reaction be represented as R $\longrightarrow$ P. Let 'a' moles dm^{-3} be the initial concentration of R. let the concentration of A remaining at time't' be (a – X) moles dm^{-3}

X = amount of A decomposed in time't' seconds.

The rate $\left(-\frac{dc}{dt}\right)$ or $\left(\frac{dx}{dt}\right)$ at time't' seconds is proportional to the concentration of 'R' at time't' seconds. Since it is first order

$$\frac{dx}{dt} \alpha \left(a - x\right)$$

$$\frac{dx}{dt} = k_1\left(a - x\right)$$

$$\frac{dx}{\left(a - x\right)} = k_1 \ dt. \qquad [k_1 = \text{ specific rate of the reaction}]$$

On integration

$$\int \frac{dx}{\left(a - x\right)} = \int k_1 \ dt$$

– ln (a – X) = k_1 t. + C; where C = constant of intergrations. When t = 0, X = 0

$\therefore$ – ln (a – 0) = k_1 x 0 + C

$\therefore$ – ln a = c

Hence – ln (a – X) = k_1t – ln a

or $k_1t = \ln\left[\frac{a}{\left(a - x\right)}\right]$

$$k_1 = \frac{1}{t} \ln \left[\frac{a}{(a - x)} \right]$$ or

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

$$k = \frac{2.303}{t} \log \left[\frac{a}{(a - x)} \right]$$ for 1st order reaction. This is the integral form of the first order equation.

2. Derive the relation for the rate constant (k) of second and third order reactions, and also write down the characteristics of them.

Solution:

Second order reactions:

A reaction is said to be of second order if its reaction rate is determined by the variation of two concentration terms.

The kinetics of second order reactions are given as follows:

(i) When concentration of both reactants are equal or two molecules of the same reactant are involved in the change, i.e.,

A + B → products

or 2A → products

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

On solving this equation by integration we get,

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

where a = initial concentration of the reactant or reactants and

x = concentration of the reactant changed in time t. $k = \frac{2.303}{t(a-x)} \log \frac{b(a-x)}{a(b-x)}$

(ii) When the initial concentrations of the two reactants are different, i.e.,

A + B → products

Initial conc. a b

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

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

The above equation on integration, we get;

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

(a - x) and (b - x) are the concentrations of A and B after time interval, t.

Characteristics of the second order reactions

(i) The value of k(velocity constant) depends on the unit of concentration. The unit of k is expressed as $(\text{mol/litre})^{-1}$ time^{-1} or litre mol^{-1} time^{-1}.

(ii) Half life period for second order decomposition can be calculated by putting x=a/2 when t= $t_{1/2}$ in the equation, $k = \frac{x}{t[a(a-x)]}$

$$t_{1/2} = \frac{1}{k} \frac{a/2}{a(a-a/2)} = \frac{1}{ka}$$

Thus, half life is inversely proportional to initial concentration.

(iii) Second order reaction conforms to the first order when one of the reactants is present in large excess.

Taking $k = \frac{2.303}{t(a-x)} \log \frac{b(a-x)}{a(b-x)}$; if a>>> b then (a-x) = a

Hence,, $k = \frac{2.303}{ta} \log \frac{ba}{a(b-x)}$

$$ka = k^{'} = \frac{2.303}{t} \log \frac{b}{(b-x)}$$

(Since 'a' being very large, may be treated as constant after the change). Thus the reaction follows first order kinetics with respect to the reactant taken relatively in small amount.

Third order reactions:

A reaction is said to be of third order if its rate is determined by the variation of three concentration terms.

When the concentration of all the three reactants is same or three molecules of the same reactant are involved, the rate expression is given as

3A → products

A + B + C → products

$dx/dt = k(a-x)^3$

On solving this equation by integration we get;

$$k = \frac{1}{2t} \left[\frac{1}{(a-x)^2} - \frac{1}{a^2} \right]$$

Characteristic of third order reaction

1. Half life period is calculated as;

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

$$t_{1/2} = \frac{3}{2k\,a^2}$$

Thus, half life is inversely proportional to the square of initial concentration.

2. The change in the unit of concentration changes the numerical value of k.
3. The unit of k is expressed as $(\text{mol/litre})^{-2}$ time^{-1} or litre^2 mol^{-2} litre^{-1}.

3. Give any two first order reactions you know.

Solution:

1. Inversion of cane sugar in presence of mineral acids.

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

2. Decomposition of ammonium nitrite in aqueous solution.

$$NH_4NO_2 \rightarrow N_2 + 2H_2O$$

3. Hydrolysis of diazo derivatives.

$$C_5H_5N = NCl + H_2O \rightarrow C_6H_5OH + N_2 + HCl$$

Problem Set:

1. In a first order reaction the time required to complete half of the reaction was found to be 11 minutes and 33 seconds. Then rate constant would be ________sec^{-1}.
   a. 1×10^{-4} min^{-1}
   b. 1×10^{-3} sec^{-1}
   c. 2×10^{-4} sec^{-1}
   d. 1×10^{-3} min^{-1}

Solution: b)

2. Which of the following cannot be determined experimentally?
   a. Order of a reaction
   b. Rate of a reaction
   c. Rate constant
   d. Molecularity of the reaction

   Solution: d)

3. What fraction of a reactant in a first order reaction remains after 40 minutes, if $t_{\frac{1}{2}}$ is 20minutes?
   a. $\frac{1}{4}$
   b. $\frac{1}{2}$
   c. $\frac{1}{8}$
   d. $\frac{1}{6}$

   Solution: a)

4. Distinguish between “order” and “molecularity” of a reaction.

Solution:

Molecularity	Order
It is the number of reacting species undergoing simultaneous collision	It is the sum of the powers of the concentration terms in the rate law expression
It is a theoretical concept	It is experimentally determined
It has integral values only	It can have fractional values also
It cannot be zero	It can be zero

It provides no information on reaction mechanism	The slowest step in the reaction can be judged by the order of the reaction and this gives further information about the mechanism.

5. Derive the rate equation for the half - life first order reaction?

Solution:

Half – life (fractional) period of a first order reaction:

In general, half – life period of a reaction is the time required to convert the concentration (a) of the reactants to exactly half (a/2); By substituting the value $\frac{a}{2}$ in place of x in 1st order equation, the half – life of the reaction can be ascertained.

$t = t_{1/2}$, when $x = a/2$

$$\therefore k_1 \frac{2.303}{t} \log \frac{a}{(a - x)}$$

$$t = \frac{2.303}{k_1} \log \frac{a}{(a - x)} \text{ or } \quad t_{\frac{1}{2}} = \frac{2.303}{k_1} \log \left[\frac{a}{(a - a/2)} \right]$$

$$t_{\frac{1}{2}} = \frac{2.303}{k_1} \log \frac{a}{(a/2)} = \frac{2.303}{k_1} \log(2)$$

$$t_{1/2} = \frac{2.303}{k_1} \times \log(2)$$

$$= \frac{2.303 \times 0.3020}{k_1} = \frac{0.693}{k_1}$$

$$\boxed{t_{1/2} = \frac{0.693}{k_1}}$$

$$t_{1/2} = \frac{0.693}{k} \text{ for } 1^{st} \text{order reaction.}$$

Note that half – life period of a first order reaction is independent of the initial concentration, a characteristic of the first order reaction.

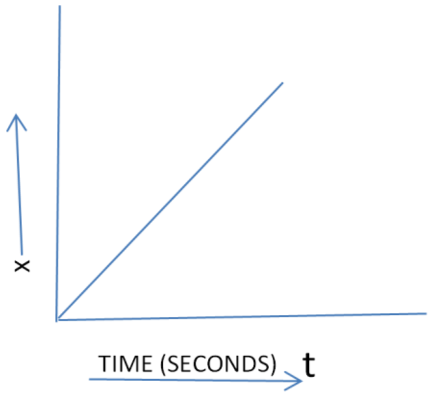
6. Write about zero order reaction giving suitable examples.

Solution:

Evaluation of *k*. A plot of X against t will yield a straight line passing through the origin. The slope of this straight line is *k*.

Examples of zero order reactions.

Photochemical reactions.



Photochemical reactions are those reactions which take place in the presence of light *(photons)*. Combination of hydrogen and chlorine in presence of light to form hydrogen chloride is a typical example.

$$H_2(g) + Cl_2(g) \xrightarrow{\text{light}} 2HCl(g)$$

However, note that the above reaction is of zero order only when HCl formed is removed spontaneously by dissolving in water. In case, HCl so formed is not removed spontaneously, concentrations of the reactants (H_2 and Cl_2) change with time as a result of which the rate of reaction will not remain constant and hence the reaction will not conform to zero order.

Exercise questions:

1. The experimental data of the reaction A + B ⟶ C + D is given below

Experiment	[A]	[B]	Rate of formation of D [mol lit^{-1} min^{-1}]
1	0.1	0.1	5×10^{-3}
2	0.2	0.1	2×10^{-2}
3	0.2	0.3	6×10^{-2}

What is the order?

i. With respect to A
ii. With respect to B
   a. 2, 2
   b. 1, 2
   c. 2, 1
   d. 1, 1

2. If the concentration of a reactant in a first order reaction is increased by m times, then the rate constant will be.
   a. k_1 m
   b. (k_1 + m)
   c. k_1/m
   d. k_1

3. The time required for the completion of 99.9% of a first order reaction is equal to how many times that of its half – life?
   a. 5
   b. 2
   c. 10
   d. 4
4. A first order reaction is 20% completed in 10 minutes. Calculate
   i. The rate constant of the reaction, and
   ii. The time taken for the reaction to go to 75% completion.

5. A first order reaction has $k_1 = 1.5 \times 10^{-6}$ per second at 200 ^{0}C. If the reaction is allowed to run for 10 hours, what percentage of initial concentration would have changed in the product? What is the half life of this reaction

Solutions to Exercise Questions

1. c
2. d
3. c
4.

i. $k_1 = \frac{2.303}{t} \log \left[\frac{a}{a-x}\right]$

k_1 = specific reaction rate.

Let initial conc. (a) = 100g, t = 10min.

$(a - x)$ = 80g [∵ reaction is 20% complete]

$K_1 = \frac{2.303}{10} \log \frac{100}{80}$

0.0223 min^{-1}

ii. $t = \frac{2.303}{k_1} \log \left[\frac{a}{a-x}\right]$

a = 100g and $(a - x)$ = 25g [∵ reaction is 75% complete]

t = 0.0223 min^{-1}

$t = \frac{2.303}{0.0223} \log \frac{100}{25}$

= 62.18 min

5.

a. Given that k = 1.5 x 10^{-6} s^{-1}

$$\therefore\ t_{\frac{1}{2}} = \frac{0.693}{k_1}$$

$$= \frac{0.693}{1.5 \times 10^{-6}}$$

= 462000 s

= 128.33 hr

b. Let initial con be 100 moles. t = 10hr = 3600sec

x = ?

$$k_1 = \frac{2.303}{t} \log \left[\frac{a}{a-x}\right]$$

$$\left[1.5 \times 10^{-6}\right] = \frac{2.303}{t} \log \left[\frac{a}{a-x}\right]$$

$$1.5 \text{ x } 10^{-6} = \frac{2.303}{3600} \log \frac{100}{100-x} \text{ on calculating}$$

$$x = 5.2$$

Thus initial concentration changed into product is 5.2%

CAT

1. If a reaction with $t_{\frac{1}{2}}$ = 69.3 seconds has a rate constant 10^{-2} second, the order is
   a. Zero
   b. One
   c. Two
   d. Three

Solution: b)

2. A first order reaction is carried out with an initial concentration of 10 moles per litre and 80% of the reactant changes into the product in a certain time. Now if the same reaction is carried out with an initial concentration of 5 mole per litre the percentage of the reactant changing to the product in the same duration of time is
    a. 40
    b. 80
    c. 160
    d. 320

    Solution: b)

3. For a chemical reaction n $[\mathrm{n}\ x \rightarrow \mathrm{y}]$, it is found that the rate of reaction increases 2.25 times when the concentration of "x" is increased by 1.5 times. What is the order of the reaction?

Solution:

Rate = $[X]^n$

$[1.5\ X]^n = 2.25$ (rate)

$\Rightarrow (1.5)^n = 2.25$

i.e., $n = 2$

But $\sqrt{2.25} = 1.5$

$$\therefore n = 2$$

Match the following set:

List I	**List II**
a. Zero order reaction	1. $\mathrm{Mol^{-1}\ Lit\ Sec^{-1}}$
b. First order reaction	2. $\mathrm{Mole^{-2}\ Lit^{2}\ Sec^{-1}}$
c. Second order reaction	3. $\mathrm{Mole\ Lit^{-1}\ Sec^{-1}}$

d. Third order reaction 4. Sec^{-1}

a. A – 1, B – 2, C – 3, D – 4
b. A – 3, B – 4, C – 1, D - 2
c. A – 1, B – 2, C – 4, D - 3
d. A – 2, B – 1, C – 3, D – 4

Solution: b)

Chemical Kinetics

Module 9.4: Methods of Determination of the Order of a Reaction

Methods to Determine Order of a Reaction:

For the determination of the order of a reaction, following methods are usually employed.

1. Integration method (or) Hit and Trial method
2. Half Life method
3. Graphical Method
4. Initial Rate Method
5. van't Hoff differential method
6. Ostwald's Method of Isolation

1. Integration method (or) Hit and Trial method:

The values of a, the initial concentration, and of a – x, the concentration after t, are determined for a number of values of t. these values are then substituted into the different integrated rate equations. The order of reaction is given by the equation which gives a constant value of the velocity constant, k.

Zero order $x = kt \text{ or } k = \frac{x}{t}$

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

For second order, $$k = \frac{1}{t}\left[\frac{1}{(a-x)} - \frac{1}{a}\right]$$

For third order, $$k = \frac{1}{2t}\left[\frac{1}{(a-x)^2} - \frac{1}{a^2}\right]$$

This is illustrated by the following example

Example:

The following results were obtained for the dissociation of H_2O_2

t (minutes)	0	5	10	20	30
N(ml) (a – x)	46.5	37.0	29.8	19.5	12.5

Solution:

The initial concentration, a = 46.5

t (minutes)	**a – x**	$\boldsymbol{k = \frac{2.303}{t} \times \log \frac{a}{a-x} min^{-1}}$
5	37	$k = \frac{2.303}{5} \times \log \frac{46.5}{37} = \frac{2.303}{5} \times 0.0993 = 0.04572$
10	29.8	$k = \frac{2.303}{10} \times \log \frac{46.5}{29.8} = \frac{2.303}{10} \times 0.1933 = 0.0445$
20	19.5	$k = \frac{2.303}{20} \times \log \frac{46.5}{19.5} = \frac{2.303}{20} \times 0.3775 = 0.04248$
30	12.5	$k = \frac{2.303}{30} \times \log \frac{46.5}{12.5} = \frac{2.303}{30} \times 0.5706 = 0.0438$

The values of **k** are constant. Hence the reaction is first order

2. Half Life Method:

Half life of a reaction is defined as the time required for reducing the concentration of a reactant to half its initial value. It is denoted as $t_{1/2}$.

As discussed before, the $t_{1/2}$ of a zero order reaction is given as

$$t_{\frac{1}{2}} = \frac{[A_0]}{2k_0}\ (zero\ order) \qquad where\ [A_0] = \ initial\ concentration$$

While for the first order reaction it is given as

$$t_{\frac{1}{2}} = \frac{0.693}{k_1}\ (first\ order)$$

In general, for a reaction of order n, $t_{1/2}$ is proportional to initial concentration of A raised to power n - 1, that is,

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

Only for the first order reaction $t_{1/2}$ is independent of the initial concentration of the reactant. This relation can be used to determine the order of a reaction.

A reaction is carried out at two different initial concentrations of a reactant [A], that is $[A]_{0,1}$ and $[A]_{0,2}$ and the respective $t_{1/2}$ values $(t_{1/2})$ and $(t_{1/2})_2$ are obtained. The order of the reaction can be calculated as follows

$(t_{\frac{1}{2}})_1 \propto \frac{1}{[A]_1{}^{n-1}}$ and $(t_{\frac{1}{2}})_2 \propto \frac{1}{[A]_2{}^{n-1}}$

$$\frac{(t_{\frac{1}{2}})_1}{(t_{\frac{1}{2}})_2} = \frac{[A]_2{}^{n-1}}{[A]_1{}^{n-1}}$$

$$(n-1)\log\left\{\frac{[A]_2}{[A]_1}\right\} = \log\left\{\frac{(t_{\frac{1}{2}})_1}{(t_{\frac{1}{2}})_2}\right\}$$

$$n-1 = \frac{\log(t_{\frac{1}{2}})_1 - log(t_{\frac{1}{2}})_2}{log\,[A]_2 - \,log\,[A]_1}$$

$$\boldsymbol{n = \frac{\log(t_{\frac{1}{2}})_1 - log(t_{\frac{1}{2}})_2}{log\,[A]_2 - \,log\,[A]_1} + \,1}$$

Example:

Half life of a particular reaction is 50 minutes when the concentration is doubled. The half life becomes 100 times minutes. Find the order.

Solution:

We know that $\frac{t_1}{t_2} = \left(\frac{a_2}{a_1}\right)^{n-1}$

Here, let us assume that $a_1 = x$

Half life of the reaction $t_1 = 50$ minutes

When the concentration is doubled, $a_2 = 2x$

Half life of this reaction $t_2 = 100$ times

Therefore $\frac{50}{100} = \left(\frac{2x}{x}\right)^{n-1}$

$\frac{1}{2} = 2^{n-1}$

i.e., $2^{-1} = 2^{n-1}$

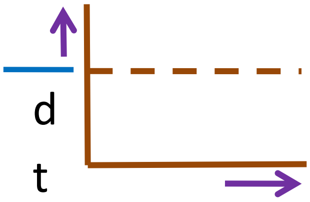
i.e., $-1 = n - 1$

Therefore $n = 0$, it is zero order reaction

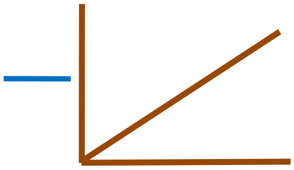
3. Graphical Method:

The concentrations of the reactants are determined at different intervals of time. Then, a graph is plotted between concentration and time. From the resulting plot, the instantaneous rates are determined by drawing tangents to curve and then calculating their slopes. The reaction rates so obtained are plotted against concentrations raised to various powers. That is rates are plotted against $[C]^1$, $[C]^2$ and $[C]^3$… $[C]^n$, n (n need not be integral numbers). From the nature of the plots, the order of the reaction can be judged.

For a zero order reaction, the rate will not vary with concentration and the plot will be a line parallel to the time axis.



If the reaction displays any other order, then the plot of rate against concentration raised to the appropriate order will be linear which obeys the relation, y = mx. The slope m gives the rate constant k of the reaction.



4. Initial Rate Method:

This method is used for reactions where more than one reactant species are involved. Initial rates of the reaction are determined by varying the concentration of only one reactant while keeping the concentrations of other reactants constant. Initial rate of reaction corresponds to the rate at the start of the reaction. The rate is calculated over the first smallest possible time interval. This calculation is done by numerically.

- The sum total of the individual orders with respect to each reactant gives the order of the reaction.

Illustration

The method is illustrated by taking hypothetical reaction :

$$2\,A + 2\,B \rightarrow \text{Products.}$$

The experimental data for this reaction is given below:

Experiment	[A]	[B]	Rate of reaction
1	0.01	0.01	0.005
2	0.02	0.01	0.020
3	0.02	0.03	0.060

The general form of the rate law may be written as :

$$\text{Rate} = k\,[A]^p\,[B]^q$$

Then, the expression for initial rate is :

$$(\text{Rate})_o = k\,[A]_o^p\,[B]_o^q$$

where subscript zero denotes initial values. The problem involves the determination of p and q.

Consider the experiments I and II and substituting the values we get,

$$(\text{Rate})_1 = k\,(0.01)^p\,(0.01)^q = 0.005 \text{ …….(1)}$$

$$(\text{Rate})_2 = k\,(0.02)^p\,(0.01)^q = 0.020 \text{ ……..(2)}$$

Dividing Eq(2) by Eq.(1) :

$$\frac{(0.020)^p}{(0.01)^p} = \frac{(0.02)}{(0.005)}$$

On solving $p = 2$

Similarly, comparing experiments 2 and 3,

$$(\text{Rate})_2 = k\,(\,0.02)^p\,(0.01)^q = 0.020 \text{ ………(3)}$$

$$(\text{Rate})_3 = k\,(0.02)^p\,(0.03)^q = 0.060 \text{ ………(4)}$$

Dividing equation (4) by (3), we get :

$$\frac{(0.03)^q}{(0.01)^q} = \frac{(0.060)}{(0.020)}$$

On solving q = 1

Therefore , the order with respect to A is 2 and the order with respect to B is 1. Thus, the rate law may be written as:

$$\text{Rate} = k\,[A]^2\,[B]$$

5. Van't Hoff differential method:

As we know that, the rate of a reaction varies as the nth power of the concentration of the reactant where 'n' is the order of the reaction. Thus, for two different initial concentrations C_1 and C_2, equations can be written in the form

$$-(dC_1)/dt = kC_1^n \quad \text{and} \quad -(dC_2)/dt = kC_2^n$$

Taking logarithms,

$$\log_{10}(-(dC_1)/dt) = \log_{10}k + n\log^{10} C_1 \qquad \text{.... (i)}$$

$$\text{and } \log_{10}(-(dC_2)/dt) = \log_{10}k + n\log^{10} C_2 \qquad \text{.....(ii)}$$

Subtracting Eq. (ii) from (i),

$$\log_{10}(-(dC_1)/dt) - \log_{10}((-dC_2)/dt) = n(\log_{10} C_1 - \log_{10} C_2)$$

The rate $-\frac{dC}{dt}$ for a reaction of nth order is given by the equation,

$$n = \frac{log\left(-\frac{dC_1}{dt}\right) - log\left(-\frac{dC_2}{dt}\right)}{(\log C_1 - \log C_2)}$$

For two different initial concentrations Cc_1 and C_2, the rates are determined at any given time from C – t graph. These are substituted in the above equation and 'n' is calculated

6. Ostwald's isolation method:

This method was introduced by Ostwald in 1902 and is used to find the order of a reaction with respect to one reactant at a time. The total order of the reaction is equal to the sum of the orders of reaction for individual reactants. This method is based on the principle that if the concentrations of all but one reactant are taken in excess, then during the course of the reaction, the concentration of those reactants taken in excess will remain almost constant and hence variation in rate will correspond to the concentration of that reactant whose concentration is small. This process is repeated with other reactants and order with respect to each reactant is determined. The overall order will be the sum of all these orders. For example, consider the general reaction :

a A + b B + c C → Products

Suppose we isolate A by taking B and C in large excess and get the order of the reaction with respect to A (say p) . Similarly, we isolate B by taking A and C in excess and isolate C by taking A and B in excess and get order with respect to B and (say q) and C (say r) respectively.

Overall order of the reaction n = p + q + r

SAQs:

1. Which order reaction obeys the relation $t_{\frac{1}{2}} = \frac{0.693}{k}$
   a. First
   b. Second
   c. Third
   d. Zero

Solution: a)

2. The following equation for the rate constant indicates that the reaction is of $k = \frac{2.303}{t} log \frac{a}{a-x}$
   a. First
   b. Zero
   c. Third
   d. Second

Solution: a)

3. Order of reaction can be deduced from
   a. Chemical equation
   b. Experiments
   c. Rate constant
   d. Thermo chemical equation

Solution: b)

4. Name any 4 methods for the determination of the order of a reaction

Solution:

Methods to Determine Order of a Reaction:

For the determination of the order of a reaction, following methods are usually employed.

a. Integration method (or) Trial method
b. Half Life method
c. Graphical Method
d. Initial Rate Method
e. Van't Hoff differential method
f. Ostwald Method of Isolation

LAQs:

1. How is half – life method useful in the determination of the order of a reaction?

Solution:

Half Life Method:

Half life of a reaction is defined as the time required for reducing the concentration of a reactant to half its initial value. It is denoted as $t_{1/2}$.

As discussed before, the $t_{1/2}$ of a zero order reaction is given as

$$t_{\frac{1}{2}} = \frac{[A_0]}{2k_0}\ (zero\ order) \quad where\ [A_0] = \ initial\ concentration$$

While for the first order reaction it is given as

$$t_{\frac{1}{2}} = \frac{0.693}{k_1}\ (first\ order)$$

In general, for a reaction of order n, $t_{1/2}$ is proportional to initial concentration of A raised to power n - 1, that is,

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

Only for the first order reaction $t_{1/2}$ is independent of the initial concentration of the reactant. This relation can be used to determine the order of a react

A reaction is carried out at two different initial concentrations of a reactant [A], that is $[A]_{0,1}$ and $[A]_{0,2}$ and the respective $t_{1/2}$ values $(t_{1/2})$ and $(t_{1/2})_2$ are obtained. The order of the reaction can be calculated as follows

$(t_{\frac{1}{2}})_1 \propto \frac{1}{[A]_1{}^{n-1}}$ and $(t_{\frac{1}{2}})_2 \propto \frac{1}{[A]_2{}^{n-1}}$

$$\frac{(t_{\frac{1}{2}})_1}{(t_{\frac{1}{2}})_2} = \frac{[A]_2{}^{n-1}}{[A]_1{}^{n-1}}$$

$$(n-1)\log\left\{\frac{[A]_2}{[A]_1}\right\} = \log\left\{\frac{(t_{\frac{1}{2}})_1}{(t_{\frac{1}{2}})_2}\right\}$$

$$n-1 = \frac{\log(t_{\frac{1}{2}})_1 - log(t_{\frac{1}{2}})_2}{log\,[A]_2 - \,log\,[A]_1}$$

$$n = \frac{\log(t_{\frac{1}{2}})_1 - log(t_{\frac{1}{2}})_2}{log\,[A]_2 - \,log\,[A]_1} + 1$$

2. Write a short note on Initial rate method and Ostwald's isolation method to determine the order of a reaction

Solution:

Initial rate method:

This method is used for reactions where more than one reactant species are involved. Initial rates of the reaction are determined by varying the concentration of only one reactant while keeping the concentrations of other reactants constant. Initial rate of reaction corresponds to the rate at the start of the reaction. The rate is calculated over the first smallest possible time interval. This calculation is done by numerically.

- The sum total of the individual orders with respect to each reactant gives the order of the reaction.

Illustration

The method is illustrated by taking hypothetical reaction :

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The general form of the rate law may be written as :

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Then, the expression for initial rate is :

$$(\text{Rate})_o = k\,[A]_o^p\,[B]_o^q$$

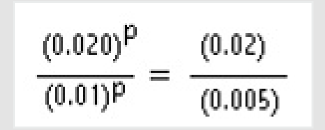
where subscript zero denotes initial values. The problem involves the determination of p and q.

Consider the experiments I and II and substituting the values we get,

$$(\text{Rate})_1 = k\,(0.01)^p\,(0.01)^q = 0.005\ \ldots\ldots.(1)$$

$$(\text{Rate})_2 = k\,(0.02)^p\,(0.01)^q = 0.020\ \ldots\ldots..(2)$$

Dividing Eq(2) by Eq.(1) :



$$\frac{(0.020)^p}{(0.01)^p} = \frac{(0.02)}{(0.005)}$$

On solving p = 2

Similarly, comparing experiments 2 and 3,

$(\text{Rate})_2 = k\,(0.02)^p\,(0.01)^q = 0.020$ ………(3)

$(\text{Rate})_3 = k\,(0.02)^p\,(0.03)^q = 0.060$ ………(4)

Dividing equation (4) by (3), we get :

$$\frac{(0.03)^q}{(0.01)^q} = \frac{(0.060)}{(0.020)}$$

On solving q = 1

Therefore , the order with respect to A is 2 and the order with respect to B is 1. Thus, the rate law may be written as:

$$\text{Rate} = k\,[A]^2\,[B]$$

Ostwald’s isolation method:

This method was introduced by Ostwald in 1902 and is used to find the order of a reaction with respect to one reactant at a time. The total order of the reaction is equal to the sum of the orders of reaction for individual reactants. This method is based on the principle that if the concentrations of all but one reactant are taken in excess, then during the course of the reaction, the concentration of those reactants taken in excess will remain almost constant and hence variation in rate will correspond to the concentration of that reactant whose concentration is small. This process is repeated with other reactants and order with respect to each reactant is determined. The overall order will be the sum of all these orders. For example, consider the general reaction :

$$a\,A + b\,B + c\,C \rightarrow \text{Products}$$

Suppose we isolate A by taking B and C in large excess and get the order of the reaction with respect to A (say p) . Similarly, we isolate B by taking A and C in excess and isolate C by taking A and B in excess and get order with respect to B and (say q) and C (say r) respectively.

Overall order of the reaction n = p + q + r

Problem Set:

1. The first order rate constant for a certain reaction is $6.93 \times 10^{-3}\ s^{-1}$, therefore its half life in seconds is
   a. 10
   b. 100
   c. 1000

   d. 1

Solution: b)

2. What is the half – life of a first order reaction for an active substance, if 75% of any given amount of the substance disintegrates in 60 minutes
   a. 2 hours
   b. 30 minutes
   c. 45 minutes
   d. 20 minutes

Solution: b)

3. Which of the following method is used to determine the order with respect to each reactant of a reaction separately
   a. Van't Hoff differential method
   b. Ostwald's isolation method
   c. Graphical method
   d. Half life method

Solution: b)

4. The half – life of a chemical reaction at a particular concentration is 50 minutes when the concentration is doubled, the half life becomes 100 min. find the order of the reaction

Solution:

$$\left[\frac{t_{\frac{1}{2}}}{t^{1}_{\frac{1}{2}}}\right] = \left(\frac{a_1}{a}\right)^{n-1}$$

$$\frac{50}{100} = \left(\frac{2a}{a}\right)^{n-1}$$

$$\frac{1}{2} = 2^{n-1}$$

Therefore n = 0

5. The following data is given for the decomposition of phosphine. Find the order of the reaction

Initial pressure (mm of Hg)	707	500	79	37.5

Half life $\left(\frac{min}{sec}\right)$	84	83.8	84	83.5

Solution:

$$\frac{t_{\frac{1}{2}}}{t^{1}_{\frac{1}{2}}} = \left(\frac{a^{1}}{a}\right)^{n-1}$$

$$\left(\frac{84}{83.8}\right) = \left(\frac{500}{707}\right)^{n-1}$$

By considering, we get n = 1

6. 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 first order and also calculate the rate constant

Time (minutes)	10	15	20	25	α
Volume of O_2 evolved (ml)	6.30	8.95	11.40	13.50	34.75

Solution:

Where v_t = volume of reactant at time‘t’

v_∞ = volume of the reactant at infinite time

Time	**V_t**	$v_\infty = v_t$	$k = \frac{2.303}{t} \log \frac{v_\infty}{v_\infty - v_t}$
10	6.30	28.45	$k = \frac{2.303}{10} \log \frac{34.75}{28.45} = 0.0198$
15	8.95	25.80	$k = \frac{2.303}{10} \log \frac{34.75}{25.80} = 0.0198$

20	11.40	23.35	$k = \frac{2.303}{10} \log \frac{34.75}{23.35} = 0.0198$
25	13.50	21.25	$k = \frac{2.303}{10} \log \frac{34.75}{21.25} = 0.0198$

Since the value of k comes out to be constant, the reaction is of first order

The average value of rate constant is 0.0198 min^{-1}

Exercise Questions:

1. The kinetic data's for the reaction

   $$2A + B_2 \longrightarrow 2AB$$

   are as given below:

[A] mol. L^{-1}	[B]mol L^{-1}	Rate (mol L^{-1} min^{-1})
0.5	1.0	2.5×10^{-3}
1.0	1.0	5.0×10^{-3}
0.5	2.0	1×10^{-2}

   Hence the order of reaction w.r.t A and B_2 are respectively
   a. 1 and 2
   b. 2 and 1
   c. 1 and 1
   d. 2 and 2

2. Thermal decomposition of a compound is first order. If 50% of a sample of the compound is decomposed in 120 minutes, how long will it take for 90% of the compound to decompose
   a. 399 min
   b. 410 min
   c. 250 min
   d. 120 min

3. At a certain temperature the half change period for the catalytic decomposition of ammonia were found as follows:

Pressure (pascals) (a):	6667	13333	26666
Half life period in hours $\left(t_{\frac{1}{2}}\right)$ **:**	3.52	1.92	1.00

Calculate the order of the reaction

4. Nitric oxide NO reacts with chlorine Cl_2 to form NOCl initial rates were measured at two different initial concentrations of nitric oxide and chlorine data obtained is given below.

Experiment	$\frac{[\mathrm{NO}]}{\mathrm{M}}$	$\frac{[Cl_2]}{M}$	**Rate (initial) Ms^{-1}**
1	0.38	0.38	5.0×10^{-3}
2	0.76	0.76	4.0×10^{-2}
3	0.38	0.76	1.0×10^{-2}

5. An initial study of kinetics of the reaction

I

H

3

2

C

+

+

C

H

3

C

C

C

H

3

+

H

2

C

I

C

H

2

.

C

C

C

H

→

at 298 K yielded the following data

S.no	[CH_3COCH_3]	[H_3O^+]	[I_2]	d [$CH_2I.\ COCH_3$]/dt
1	1.00	0.150	0.025	4.20×10^{-6}
2	1.00	0.200	0.025	5.60×10^{-6}
3	2.00	0.200	0.025	11.20×10^{-6}
4	2.00	0.150	0.010	8.4×10^{-6}

Find the rate law for the reaction and calculate the rate constant

6. Two substances A and B are present such that [A_1] = 4[B_0] and half life of A is 5 minutes and that of B is 15 minutes. If they start decaying at the same time following first order kinetics how much time later will the concentration of both of them would be same

7. The half – life of a substance is 50 minutes at a certain concentration. When the initial concentration of the substance is reduced to one – half of initial concentration, the half – life period is 25 minutes. Calculate the order of the reaction

Solutions to Exercise Questions:

1. a
2. a
3. $\dfrac{\left(t_{\frac{1}{2}}\right)_1}{\left(t_{\frac{1}{2}}\right)_2} = \left(\dfrac{a_2}{a_1}\right)^{n-1} \quad \Rightarrow \quad \dfrac{\log\left(t_{\frac{1}{2}}\right)_1 - \log\left(t_{\frac{1}{2}}\right)_2}{\log\,(a)_2 - \log\,(a)_1}$

From the given data

$$(i)\left(\frac{3.52}{1.92}\right) = \left(\frac{13333}{6667}\right)^{n-1} = 2^{n-1}$$

$$(ii)\left(\frac{3.52}{1.00}\right) = \left(\frac{26666}{6667}\right)^{n-1} = 4^{n-1}$$

$$(iii)\left(\frac{1.92}{1.00}\right) = \left(\frac{26666}{13333}\right)^{n-1} = 2^{n-1}$$

Taking logarithms on both sides

(i) log 3.52 – log 1.92 = (n – 1) log 2

0.5465 – 0.2833 = (n – 1) (0.3010)

$$(n-1) = \frac{0.2632}{0.3010}$$

(n – 1) = 0.874

n = 1.874 ≈ 2

Hence from (ii) we got n = 1.908 ≈ 2

Hence from (iii) we got n = 1.941 ≈ 2

Therefore the order of the reaction = 2

4. The order of the reaction with respect to Cl_2 is determined by using the rates obtained in experiment 1 and 3.

   Let the rate law be rate = k $[NO]^m$ $[Cl_2]^n$

   $Rate_1 = 5.0 \times 10^{-3} = k\,[0.38]^m\,[0.38]^n$

   $Rate_3 = 1.0 \times 10^{-2} = k\,[0.38]^m\,[0.76]^n$

   $$\frac{rate_1}{rate_3} = \frac{5.0 \times 10^{-3}}{1.0 \times 10^{-2}} = \frac{[0.38]^n}{[0.76]^n}$$

   $$\left[\frac{1}{2}\right]^n = \frac{1}{2}$$

   n = 1

   The value of m is now determined by taking the ratio of the rates from experiments 2 and 3.

   $$\frac{rate_2}{rate_3} = \frac{4.0 \times 10^{-2}}{1.0 \times 10^{-2}}$$

   $$\left[\frac{0.76}{0.38}\right]^m$$

   $$\frac{rate_2}{rate_3} = 4 = 2^m$$

$m = 2$

Therefore the probable rate law for the reaction is

Rate = k $[NO_2]^2$ $[Cl_2]^1$

Hence, overall order of the reaction is 3.

5. Let the rate law be represented by

$$rate = \frac{-\,d\,[CH_3COCH_3]}{dt}$$

rate = k $[CH_3COCH_3]^x$ $[H_3O^+]^y$ $[I_2]^z$

From s.no 1 and from the above equation

rate = k $[1.0]^x$ $[0.15]^y$ $[0.025]^z$ = 4.2×10^{-6} ….. (i)

from s.no 2,

rate = k $[1.0]^x$ $[0.20]^y$ $[0.025]^z$ = 5.6×10^{-6} ….. (ii)

by dividing (i) and (ii) we get

$$\left(\frac{0.20}{0.15}\right)^y = \frac{5.6}{4.2}$$

or

$$\left(\frac{4}{3}\right)^1 = \frac{4}{3}$$

Therefore y = 1

Similarly solving data from s.no 3 and s.no 2, we get $\left(\frac{2.0}{1.0}\right)^x = \left[\frac{11.20 \times 10^{-6}}{5.60 \times 10^{-6}}\right]$

= 2

or x = 1

Therefore overall order = (1 + 1 + 0) = 2

Similarly from s.no 4 and s.no 1 we get z = 0

Substituting the values of x, y and z in (ii), we get

Put x = 1; y = 1 and z = 0

In ……… (ii) we get

$k\,(1)^1\,(0.2)^1\,(0.025)^0 = 5.6 \times 10^{-6}$

$\Rightarrow k\,(0.2) = 5.6 \times 10^{-6} = 2.8 \times 10^{-5}$

6. Amount of A in n_1 halves = $\left(\frac{1}{2}\right)^{n_1}[A_0]$

Amount of A in n_2 halves = $\left(\frac{1}{2}\right)^{n_2}[B_0]$

At the end, according to question

$$\frac{[A_0]}{2^{n_1}} = \frac{[B_0]}{2^{n_2}}$$

$$\frac{4}{2^{n_1}} = \frac{1}{2^{n_2}}$$

$$\frac{2^{n_1}}{2^{n_2}} = 4$$

$$2^{(n_1-n_2)} = 2^2$$

$$n_1 - n_2 = 2$$

$$n_2 = (n_1 - 2) \ldots..(1)$$

Let the concentration of both equal after time t_0

$$\frac{n_1 \times t_{\frac{1}{2}}(A)}{n_2 \times t_{\frac{1}{2}}(B)} = 1$$

$$\frac{n_1 \times 5}{n_2 \times 15} = 1$$

$$\frac{n_1}{n_2} = 3 \ldots..(2)$$

From 1 and 2

$n_1 = 3$, $n_2 = 1$

$t = n_1 \times t_{\frac{1}{2}}$

$= 3 \times 5$

= 15 minutes

7. Let initial concentration = a moles/ litre

For case when $t_{\frac{1}{2}}$ = 50 minutes

In second case $t^1{}_{\frac{1}{2}} = \left(\frac{a^1}{a}\right)^{n-1}$

$$\frac{50}{25} = \left(\frac{\frac{a}{2}}{a}\right)^{n-1}$$

$$2 = \left(\frac{1}{2}\right)^{n-1}$$

$$log^2 = (n-1)\,log^{\frac{1}{2}}$$

$$log^2 = -(n-1)\,log^2$$

Therefore n = 0

Hence the reaction is zero order

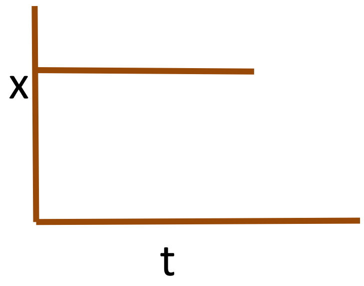
CAT:

1. The time required for the completion of 99.9% of a first order reaction is equal to how many times that of 90% completion of reaction
   a. 2
   b. 3
   c. 5
   d. 10

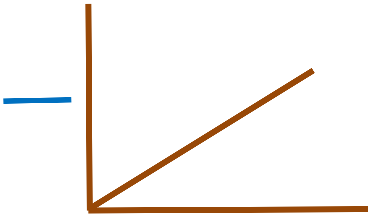
Solution: a)

2. Which one of the following graphs represents a 1st order reaction

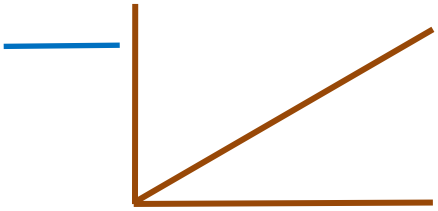
a.



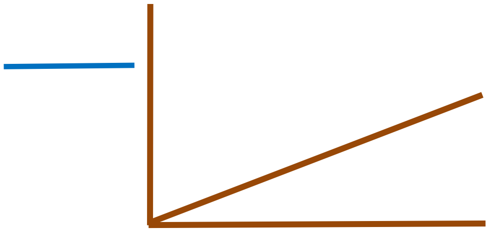
b.



c.



d.



Solution: b)

3. In an experiment the half – time is found to be same with different initial concentrations of the reactant. Then what is the order of the reaction?

Solution:

First

Chemical Kinetics

Module 9.5: Collision theory – Activation energy, Arrhenius equation

Though Arrhenius equation is applicable under a wide range of circumstances, collision theory, which was developed by Max Trautz and William Lewis in 1916 - 18, provides a greater insight into the energetic and mechanistic aspects of reactions. It is based on kinetic theory of gases. According to this theory, the reactant molecules are assumed to be hard spheres and reaction is postulated to occur when molecules collide with each other. **The number of collisions per second per unit volume of the reaction mixture is known as collision frequency (Z)**. Another factor which affects the rate of chemical reactions is activation energy (as we have already studied). For a bimolecular elementary reaction

$$A + B \rightarrow \text{Products}$$

Rate of reaction can be expressed as: Rate = $Z_{AB}\, e^{-Ea\, RT}$

Here Z_{AB} represents the collision frequency of reactants, A and B and $e^{-Ea\, RT}$ represents the fraction of molecules with energies equal to or greater than E_a. Comparing the above equation with Arrhenius equation, we can say that *A* is related to collision frequency.

According to this theory, a chemical reaction occurs only when reactant molecules collide with energy greater than some minimum value. Their collisions must occur with a proper orientation. These collisions give rise to the products of the reaction. The magnitude of the rate of a reaction can be explained based on the calculation of number of binary collisions that take place between the simple collision theories of reaction rates.

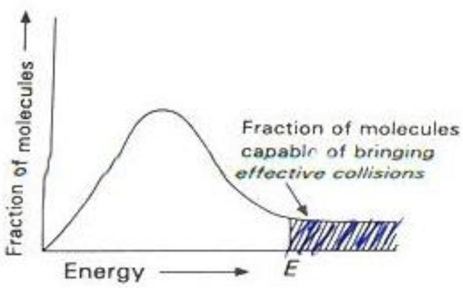
(1) A chemical reaction takes place due to collision among reactant molecules. The value of collision frequency is very high, of the order of 10^{25} to 10^{28} in case of binary collisions.

(2) Every collision does not bring a chemical change. The collisions that actually produce the products are effective collisions. The effective collisions which bring chemical change are few in comparison to the form a product are ineffective elastic collisions, i.e., molecules just collide and disperse in different directions with different velocities.

Postulates of simple collision theory of reaction rates:

1. A reaction occurs only when the atoms or molecules of the two substances collide with each other.
2. When collision occurs between molecules the old bonds are broken and new bonds are formed.
3. All the collisions do not lead to the formation of the products.
4. The rate of reaction at any given temperature is proportional to the total number of collisions taking place in unit time in unit volume at that temperature.

5. The minimum amount of energy which the colliding molecules must possess as to make the chemical reaction to occur is known as **threshold energy**.



6. The collisions which occur between the molecules having lower energies than threshold energy do not yield a product.
7. Collisions which yield the product are called **effective collisions** or **fruitful collisions** or **activated collisions.** In the above graph 'E' corresponds to minimum or threshold energy for effective collision in a hypothetical reaction.
8. The molecules having energy less than threshold energy are called **normal molecules.**

9. There is an energy barrier for each reaction. The reacting species must be provided with sufficient energy as to cross the energy barrier. The minimum amount of energy required by reactant molecules to participate in a reaction is called activation energy.

10. Greater the activation energy lower is the rate of the reaction.
11. The fraction of the activated collisions amongst the total collisions is very small.

$$\boxed{\text{Activation energy = [Threshold energy – Energy of normal colliding molecules]}}$$

Or

Activation energy = threshold energy - average kinetic energy of reacting molecules

Threshold energy = initial potential energy of reactant molecules + activation energy.

The above facts are represented schematically as follows

$$A + A \rightarrow A^* + A$$

$$A^* + A^* \rightarrow \text{products}$$

A = normal molecules

A* = activated molecules

12. "The number of collisions per second per unit volume of the reaction mixture is known as collision frequency (z)"

    The collision frequency is

    I.e. Number of binary collisions per unit time

$$Z = N^2 \sigma_{AB} \sqrt{\frac{8\,K_B T}{\pi \mu_{AB}}}$$

Where N = Avogadro's number

σ_{AB} = collision diameter or reaction cross section

μ_{AB} = reduced mass of reactant

k_B = Boltzmann's constant

13. The rate constant for a bimolecular reaction, as by predicted by Arrhenius collision theory is

$$k = Z\,\rho\, e^{\frac{-E_a}{RT}}$$

z = collision frequency

ρ = steric factor

E_a = activation energy

R = gas constant

Activated complex or transition state:

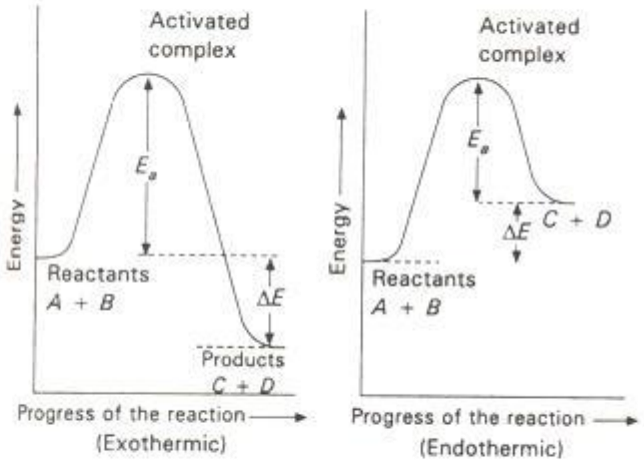
A chemical reaction involves the breaking of the old bonds and the formation of new bonds. The breaking of bonds involves absorption of energy while during the formation of bonds energy is released. A chemical reaction occurs only when the reactants possess sufficient activation energy to cross the energy barrier.

When two molecules having necessary energy of activation approach each other, they attain an intermediate configuration before they change into products. This configuration possesses a higher energy as compared to the sum of energies of reactants. The intermediate configuration corresponding to maximum potential energy of the system is called activated complex or *transition state.* The activated complex then changes into products and excess energy is released.

The formation of activated complex and the course of reaction can be understood by considering the following reaction:

$$\underset{\substack{\text{reactants}\\\text{(initial state)}}}{A + B-C} \rightarrow \underset{\text{activated complex}}{A \ldots B \ldots C} \rightarrow \underset{\substack{\text{products}\\\text{(final state)}}}{A-B + C}$$

A collision between high energy molecules overcomes the forces of repulsion and brings the formation of an unstable molecule cluster, called the activated complex. The life span of an activated complex is very small. Thus, the activated complex breaks either into reactants again or new substances, i.e., products. The activation energy (E_a) depends upon the nature of chemical bonds undergoing rupture and is independent of enthalpies of reactants and products. The energy changes during exothermic and endothermic reactions versus the progress of the reaction are shown in below figure.



Thus, every chemical reaction whether exothermic or endothermic has an energy barrier which has to be overcome before reactants can be transformed into products. If the reactant molecules have sufficient energy, they can reach the peak of the energy barrier after collision and then they can go to the right side of the slope and consequently change into products. If the activation energy for a reaction is low, the fraction of effective collisions will be large and the reaction will be fast. On the other hand, if the activation energy is high, then fraction of effective collisions will be small and the reaction will be slow. When temperature is increased, the number of active molecules increases, i.e., the number of effective collisions will increase and the rate of reaction will increase.

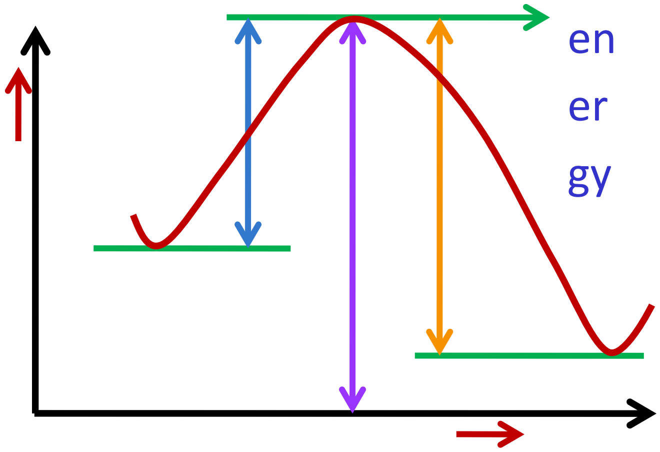
Activation energy $E_a = E_{(\text{activated complex})} - E_{(\text{ground state})}$

ΔH = activation energy of forward reaction - activation energy of background reactions

"The minimum extra energy over and above the average potential energy of the reactants (E_R), which must be supplied so that the reactants are able to cross over the energy barrier (i.e. threshold energy) E_T is called the activation energy (E_a)."

$$\boxed{\text{Activation energy} = \text{Threshold energy} - \text{Average energy of the reactants}}$$

$$\boxed{E_a = E_T - E_R}$$



E_R = energy of the reactant

E_P = energy of the product

E_T = Threshold energy

$E_a = E_T - E_R$ = activation energy of the forward reaction

$E_a^1 = E_T - E_P$ = activation energy of the backward reaction

Energy alone does not determine the effectiveness of the collision. The reacting molecules must collide in proper manner if the reaction is to occur. Rate of reaction is directly proportional to the number of effective collisions.

Rate = dx/dt = collision frequency × factor of effective collisions = $z \times f$

Example:

The threshold energy of a reacting molecule in a first order reaction is E_T.The activation-energy is E_a. What is the energy of the normal molecules?

Solution:

Energy of normal reacting molecule = [Threshold energy – Activation energy]

$$E_R = [E_T - E_a]$$

SAQs:

1. The Arrhenius equation expressing the effect of temperature on the rate constant of reaction is
   a. k = $\frac{E_a}{RT}$
   b. k = $Ae^{-E_a/RT}$
   c. k = $\log e^{E_a/RT}$
   d. k = $e^{-E_a/RT}$

Solution: b)

2. Collision theory satisfactorily explains
   a. First order reactions
   b. Zero order reactions
   c. Bimolecular reactions
   d. Any order reactions

Solution: c)

3. The minimum energy required for molecules to enter in to chemical reaction is called
   a. Kinetic energy
   b. Potential energy
   c. Threshold energy
   d. Activation energy

Solution: c)

4. Activation energy of a reaction is
   a. The energy released during the reaction
   b. The energy evolved when activated complex is formed
   c. Minimum amount of energy needed to overcome the potential barrier of reaction
   d. The energy needed to form one mole of the product

Solution: c)

5. Define threshold energy

Solution:

The minimum energy which must be associated with reactant molecules so that their mutual collision results in a chemical reaction is called **Threshold energy**

6. What is meant by fruitful collisions?

Solution:

Collisions which yield the product are called **effective collisions** or **fruitful collisions** or **activated collisions**

LAQs:

1. What is “activation energy” of a reaction?

Solution:

Concept of activation energy

For a reaction to occur, reactant molecules must collide with each other. Only those collisions result in product formation. This implies that there is an energy barrier between reactants and products which must be crossed before products can be formed. The energy required for crossing the energy barrier comes from the kinetic energy of reacting molecules

“The minimum extra energy over and above the average potential energy of the reactants (E_R), which must be supplied so that the reactants are able to cross over the energy barrier (i.e. threshold energy, E_T) is called the activation energy (E_a).”

$$\boxed{\text{Activation energy} = \text{Threshold energy} - \text{Average energy of the reactants}}$$

$$\boxed{E_a = E_T - E_R}$$

2. What are the main postulates of simple collision theory of reaction rates?

Solution:

a. A reaction occurs only when the atoms or molecules of the two substances collide with each other
b. When collision occurs between molecules the old bonds are broken and new bonds are formed
c. All the collisions do not lead to the formation of the products
d. If all collisions of the reactant molecules lead to the formation of products the rate of reaction at any given temperature is proportional to the number of collisions in unit time at that temperature
e. The minimum energy which must be associated with reactant molecules so that their mutual collision results in a chemical reaction is called **Threshold energy**
f. The collisions which occur between the molecules having lower energies than threshold energy do not yield a product
g. Collisions which yield the product are called **effective collisions** or **fruitful collisions** or **activated collisions**

Problem Set:

1. For A + B → C + D; ΔH = –20 kJ mol^{-1}. The activation energy for the forward reaction is 85 kJ mol^{-1}. The activation energy for backward reaction is ___ kJ mol^{-1}
   a. 65
   b. 105
   c. 85
   d. 40

Solution: b)

2. In Arrhenius equation k = $\rho\, z\, e^{\frac{-E_a}{RT}}$, the quantity, ρ is referred as
   a. Collision frequency
   b. Steric factor
   c. Activation factor
   d. Boltzmann factor

Solution: b)

3. What is the activation energy of a reaction whose rate quadruples when the temperature is raised from 293 K to 313 K?

Solution:

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$$\frac{k_2}{k_1} = 4, \qquad T_1 = 293\ K, \qquad T_2 = 313K$$

$$\log 4 = \frac{E_a}{2.303 \times 8.314}\left[\frac{1}{293} - \frac{1}{313}\right]$$

$$E_a = \frac{\log 4 \times 2.303 \times 8.314}{\left(\frac{1}{293} - \frac{1}{313}\right)}$$

= 52.85 kJ mol^{-1}

4. For a reaction with activation energy of 55 kJ mol^{-1}, by what factor will the rate constant go up with a rise in temperature from 300K to 310K?

Solution:

$$\log\frac{k_2}{k_1} = \frac{55000}{2.303 \times 8.314}\left[\frac{1}{300} - \frac{1}{310}\right]$$

= 0.30887

Where k_2 = rate constant at 310 K

k_1 = rate constant at 300 K

$$\Rightarrow \frac{k_2}{k_1} = 2.04$$

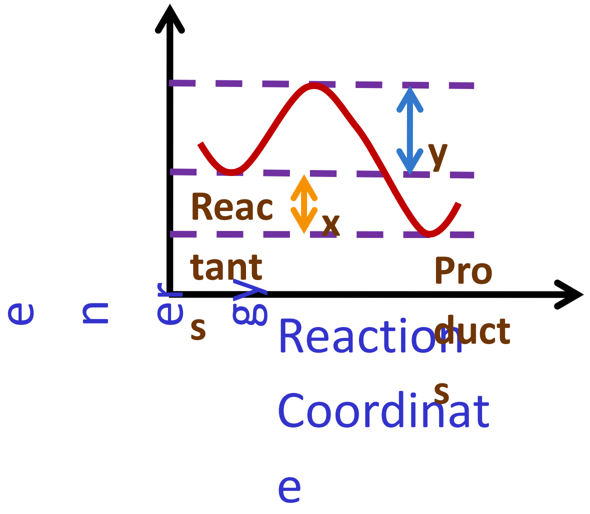
This example shows that for a 10 ^{0}C rise in temperature hear the room temperature results in doubling the rate of the reaction

Exercise Questions

1. For a slow reaction, the rate constant at 35 ^{0}Cis generally _____ times more than that at 25 ^{0}C
   a. 1
   b. 2
   c. 3
   d. 4

Solution: b)

2. The following figure denotes the energy diagram for a reaction



   Then the activation energy of the reverse reaction is

   a. 2x
   b. 2y
   c. (x + y)
   d. (y – x)

3. For an endothermic reaction where ΔH represents the enthalpy of the reaction, the minimum value for the energy of activation will be
   a. Less than ΔH
   b. Zero
   c. More than ΔH
   d. Equal to ΔH

4. In a chemical reaction when a catalyst is used, the energy of the reaction (ΔH) is
   a. Lowered
   b. Increased
   c. Remains constant
   d. Reduced to zero

5. The velocity constant of the decomposition of hydrogen iodide at 283 ^{0}C and 508 ^{0}C are 3.517×10^{-7} and 3.954×10^{-2} respectively. Calculate the frequency factor at 283 ^{0}C and activation energy of the reaction

6. For the decomposition of dimethyl ether, A in the Arrhenius equation $k = Ae^{-E_a/RT}$ has a value of 1.26×10^{13} and E_a value of 58.5 k cal. Calculate half life period for first order decomposition at 527 ^{0}C

7. Sketch a potential energy diagram for a general reaction $A + B \rightleftharpoons C + D$. Give that $\Delta H_{backward}$ = -10 kJ and E_a forward = + 40 kJ

Solutions to exercise questions:

1. c
2. c
3. c
4. c
5. $\log\frac{k_2}{k_1} = \frac{E_a}{R2.303}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$

$$E_a = \frac{2.303 \times R \times T_1 \times T_2}{(T_2 - T_1)} \log\frac{k_2}{k_1}$$

$$= \frac{2.303 \times R \times \ 556 \times 781}{(781 - 556)} \log\frac{3.954 \times 10^{-2}}{5.517 \times 10^{-7}}$$

$$= 44610\ Cal$$

$$we\ know\ k = \ A.e^{-E_a/RT}$$

$$3.517 \times 10^{-7} = A.e^{-44610/2 \times 556}$$

$$log 3.517 \times 10^{-7} = logA - \frac{44610}{2 \times 556}$$

log A = -6.4538 × 40.290

= 33.8372

A = 6.874×10^{33}

6. Taking logarithm of Arrhenius equation

$$k = A.e^{\frac{-E_a}{RT}} \ we\ get$$

$$logk = logA - \frac{E_a}{2.303\ RT}$$

$$logk = \log(1.26 \times 10^{13}) - \left[\frac{58.5 \times 10^2}{2.303 \times 1.987 \times 800}\right]$$

$$= 13.1003 - 15.9799$$

$$= -2.8796$$

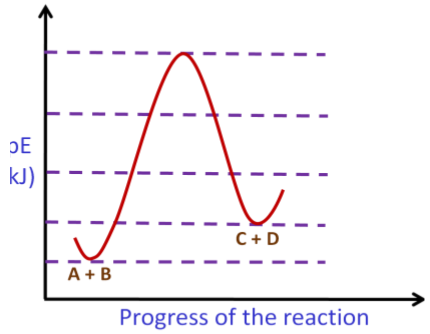
$$k = 1.3194 \times 10^{-3}\ time^{-1}$$

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

$$= \frac{0.693}{1.3194} \times 10^3$$

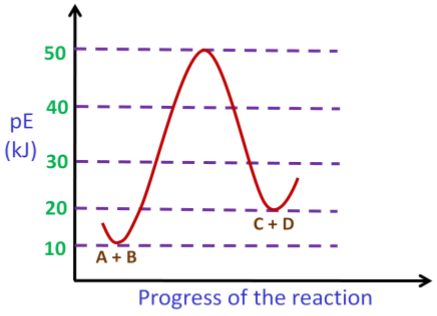
= 525

7. - Since $\Delta H_{backward}$ = -10 kJ you can determine that $\Delta H_{forward}$ = +10 kJ (same value, just change the sign). Since $\Delta H_{forward}$ is a positive you know that the forward direction of the reaction is endothermic.



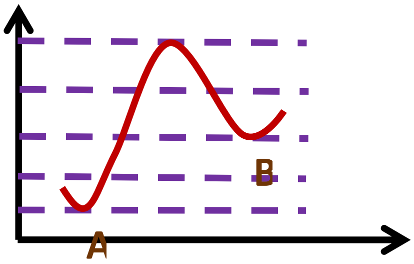
initial reactants (A+B) you need to go up 40 ener
units. Pick any value for a starting energy level, ar
then add 40 to find the peak of your graph.

Return to ΔH to determine the energy level of the products. Since $\Delta H_{forward}$ = +10 kJ, add 10 to o
starting value to determine energy level of tl



CAT:

1. Examine the plot given below and make conclusion about the numerical value of the activation energy of the conversion of A to B (kJ mol^{-1})



   a. +16
   b. +8
   c. 12
   d. +4

Solution: a)

2. For a reaction, $E_a = 0$ and rate constant k at 300 K is 4.2×10^5 sec^{-1}. The value of k at 310 K will be
   a. 8.4×10^5 sec^{-1}
   b. 8.4×10^6 sec^{-1}
   c. 4.2×10^5 sec^{-1}
   d. 8.4×10^5 mole lit^{-1} sec^{-1}

Solution: c)

3. If the activation energy of a forward reaction is 15 k cal mol^{-1} and for the backward reaction it is 25 k cal mol^{-1}. What is the change in internal energy of the reaction? Is the reaction exothermic or endothermic?

Solution:

$\Delta E = E_{a(forward)} - E_{a(backward)}$

$= 15 - 25$

$= -10$ k cal mol^{-1}

The reaction is exothermic

Match the following:

List I	**List II**
A. Collision frequency (z)	1) $\frac{\log\left(-\frac{dc_1}{dt}\right) - log\left(-\frac{dc_2}{dt}\right)}{(log\, c_1 - logc_2)}$
B. Specific rate (k)	2) $N^2 \sigma_{AB} \sqrt{\frac{8\,KT}{\pi \mu_{AB}}}$
C. Van't Hoff method for the order (n)	3) $Z\, \rho\, e^{\frac{-E_a}{RT}}$

The correct matching is [ ]

a. A – 1, B – 2, C – 3
b. A – 2, B – 3, C – 1
c. A – 3, B – 1, C – 2
d. A – 2, B – 1, C – 3

Solution: b)

Chemical Kinetics

Module 9.6: Problems

1. Calculate the ratio of rate constants at room temperature for two reactions that have the same A value but have E_a values that differ by 1 kcal mol^{-1}.
2. Calculate the activation energy of a reaction whose rate constant is tripled by a 10 ^{0}C rise in temperature in the vicinity of 27 ^{0}C.
3. Write the units of the rate constants for a
   i. Zero order reaction
   ii. Half order reaction
   iii. First order reaction
   iv. 3/2 order reaction
   v. Second order reaction
   vi. 5/2 order reaction
   vii. Third order reaction.
4. What is the half – life of a radioactive substance if 87.5 % of a given amount of the substance disintegrates in 40 minutes?
5. The half-life period ($t_{1/2}$) of a reaction is halved as the initial concentration of the reactant is doubled. What is the order of the reaction?
6. The half-life period of a reaction is 24 hours. If we start with 10 grams of the reactant, how many grams of it will remain after 96 hours?
7. The half – life period of a homogeneous gaseous reaction,
   $\mathbf{SO_2Cl_2 \rightarrow SO_2 + Cl_2}$,
   which obeys first order kinetics, is 8.0 minutes. How long will it take for the concentration of SO_2Cl_2 to be reduced to 1% of the initial value?
8. The activation energy of a non – catalyzed reaction at 37 ^{0}C is 83.68 kJ mol^{-1} and the activation energy of the same reaction catalyzed by an enzyme is 25.10 kJ mol^{-1}. Calculate the ratio of the rate constants of the enzyme catalyzed and the non – catalyzed reaction.
9. A first order gas reaction has $k = 1.5 \times 10^{-6}$ per second at 200 ^{0}C. If the reaction is allowed to run for 10 hours, what percentage of the initial concentration would have change into the product?

10. In the Arrhenius equation for a certain reaction, the value of A (Arrhenius constant) and E_a (activation energy) are 4×10^{13} sec^{-1}, and 98.6 kJ mol^{-1} respectively. If the reaction is of first order, at what temperature will its half – life period be 10 minutes?

11. The decomposition of N_2O_5 according to the equation,

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

Is a first order reaction. After 30 minutes from the start of the decomposition in a closed vessel, the total pressure developed is found to be 284.5 mm of Hg. On complete decomposition the total pressure is 584.5 mm of Hg. Calculate the rate constant of the reaction.

12. From the following data for the reaction between A and B:

[A], (mol / L)	[B], (mol / L)	Initial Rate (mol L^{-1} s^{-1} at)	
		300 K	320 K
2.5×10^{-4}	3.0×10^{-5}	5.0×10^{-4}	2.0×10^{-3}
5.0×10^{-4}	6.0×10^{-5}	4.0×10^{-3}	–
1.0×10^{-3}	6.0×10^{-5}	1.6×10^{-2}	–

Calculate

i. The order of the reaction with respect to A and with respect to B

ii. The rate constant at 300 K

iii. The energy of activation

iv. The pre-exponential factor using K and the order.

13. At 380 ^{0}C, the half – life period for the first order decomposition of H_2O_2 is 360 min. The energy of activation of the reaction is 200 kJ mol^{-1}. Calculate the time required for 75% decomposition at 450 ^{0}C.

14. A hydrogenation reaction is carried out at 500 K. If the same reaction is carried out in the presence of a catalyst at the same rate; the temperature required is 400 K. calculate the activation energy of the reaction if the catalyst lowers the activation barrier by 20 kJ mol^{-1}.

15. The rate of first order reaction is 0.04 mol L^{-1} s^{-1} at 10 minutes and 0.03 mol L^{-1} s^{-1} at 20 minutes from the start. Find the half – life of the reaction.

16. $2\,X\,(g) \rightarrow 3\,Y\,(g) + 2\,Z\,(g)$

Time (in min)	0	100	200
Partial pressure of X (in mm of Hg)	800	400	200

Assuming ideal gas condition. Calculate:

a. Order of reaction

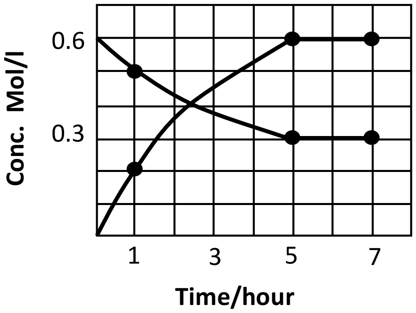
b. Rate constant

c. Time taken for 75% completion of reaction

d. Total pressure when $P_x = 700$ mm

17. The progress of the reaction $A \rightleftharpoons nB$ with time is presented in the figure. Determine:

(i) the value of n,
(ii) the equilibrium constant, K and
(iii) the initial rate of conversion of A.



18. The data given below are for the reaction of NO and Cl_2 to form NOCl at 295 K.

[Cl_2]	[NO]	Initial rate (mol litre^{-1} sec^{-1})
0.05	0.05	1×10^{-3}
0.15	0.05	3×10^{-3}
0.05	0.15	9×10^{-3}

(a) What is the order with respect to NO and Cl_2 in the reaction?
(b) Write the rate expression.
(c) Calculate the rate constant.
(d) Determine the reaction rate when conc. of Cl_2 and NO are 0.2 M and 0.4 M respectively.

19. Show that $t_{1/2} / t_{3/4}$ for nth order reaction is a function of 'n' alone. $t_{3/4}$ is the time required for concentration to become 1/4 of original concentration.

20. The gas phase decomposition of dimethyl ether follows first order kinetics.

$$CH_3 - O - CH_{3\,(g)} \rightarrow CH_{4\,(g)} + H_{2\,(g)} + CO_{(g)}$$

The reaction is carried out in a constant volume container at 500^0 C and has a half – life of 14.5 minutes. Initially only dimethyl ether is present at a pressure of 0.40 atmosphere. What is the total pressure of the system after 12 minutes? Assume ideal gas behavior.

21. The vapour- pressure of two miscible liquids A and B are 300 and 500 mm of Hg respectively. In a flask, 10 moles of A is mixed with 12 moles of B. However, as soon as B is added, A starts polymerizing into a completely insoluble solid. The polymerization follows first order kinetics. After 100 minutes, 0.525 moles of a solute is dissolved which arrests the polymerization completely. The final vapour – pressure of the solution is 400 mm of Hg. Estimate the rate constant of the polymerization reaction. Assume negligible volume change on mixing and polymerization and ideal behavior for the final solution.

Solutions:

1. The Arrhenius equation gives

$$\frac{k_1}{k_2} = \frac{A\,e^{-Ea_1/RT}}{A\,e^{-Ea_2/RT}}$$

$$= \exp \frac{E_{a_2} - E_{a_1}}{RT}$$

$$= \exp \frac{1 \text{ k cal mol}^{-1}}{1.987 \times 10^{-3} \text{ k cal mol}^{-1}\text{K}^{-1}(298 \text{ K})}$$

$$= 5.4$$

2. $T_1 = 27\ ^0C = 273 + 27 = 300$ K.
   In the vicinity of this temperature the two temperatures are evidently 295 and 305 K. according to Arrhenius activation equation.

   Given that, $\frac{k_{305}}{k_{295}} = 3$

   $$k = A\, e^{-E_a/RT}$$

   $$\frac{k_{305}}{k_{295}} = \frac{e^{-E_a/305\,R}}{e^{-E_a/295\,R}}$$

   $$3 = \frac{e^{-E_a/305\,R}}{e^{-E_a/295\,R}}$$

   Taking natural logarithm on both sides,

   $$\ln 3 = \frac{-E_a}{R}\left[\frac{1}{305} - \frac{1}{295}\right]$$

   $$\ln 3 = \frac{-E_a}{R}\left[\frac{10}{305 \times 295}\right]$$

   $$E_a = \frac{\ln 3 \times 8.314 \times 305 \times 295}{10}$$

   $$= 82182 \text{ J mol}^{-1}$$

   $$= 82.182 \text{ kJ mol}^{-1}$$

3. The units of the rate constant for the nth – order reaction are given by (litre)$^{n-1}$ (mol)$^{1-n}$ s^{-1}.
   i. n = 0, the units are litre^{-1} mol s^{-1}
   ii. n = ½, the units are litre$^{-1/2}$ mol$^{1/2}$ s^{-1}
   iii. n = 1, the units are s^{-1}
   iv. n = 3/2, the units are litre$^{1/2}$ mol$^{-1/2}$ s^{-1}
   v. n = 2, the units are litre mol^{-1} s^{-1}
   vi. n = 5/2, the units are litre$^{3/2}$ mol$^{-3/2}$ s^{-1}
   vii. n= 3, the units are litre^{2} mol^{-2} s^{-1}

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

   $$= \frac{2.303}{40} \log \frac{a}{a-0.875\,a}$$

   $$= \frac{2.303}{40} \log \frac{a}{0.125\,a}$$

$$= \frac{2.303}{40}\, log^{8}$$

$$= 0.051\, min^{-1}$$

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

$$= \frac{0.693}{0.051}$$

$$= 13.58\, min$$

5. $$t_{1/2} = \frac{1}{(a_0)^{n-1}}$$

where a_0 is the initial concentration, n is order of the reaction.

$$\frac{1}{2}\ t_{1/2} = \frac{1}{(2a_0)^{n-1}}$$

$$\frac{t_{1/2}}{\frac{1}{2}t_{1/2}} = \frac{1/(a_0)^{n-1}}{1/(2a_0)^{n-1}}$$

$2 = 2^{n-1}$

$1 = n - 1$

$n = 2$

6. $$a = \frac{a_0}{2^n} \text{ and } n = \frac{t}{t_{1/2}}$$

where $\mathbf{a_0}$ is the initial concentration of the reactant, **n** is the number of half-life periods, **a** is remaining part of the reactant.

$$n = \frac{96}{24} = 4$$

$$a = \frac{a_0}{2^n} = \frac{10}{2^4}$$

$$a = \frac{10}{16} = 0.625\, gms$$

7. $$k = \frac{o.693}{t_{1/2}}$$

$$= \frac{o.693}{8.0} = 0.087\, min^{-1}$$

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

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

$$= \frac{2.303}{0.087} \ln \left(\frac{100}{1}\right)$$

$$= 52.93\, min$$

8. According to the Arrhenius equation,

$$\mathrm{k} = \mathrm{Ae}^{-\mathrm{E_a/RT}}$$

Let k_e and k_n be the rate constants of the enzyme catalyzed and non-catalyzed reactions, respectively. Assuming that the Arrhenius pre-exponential factor A is the same in both cases, we have

$$\frac{k_e}{k_n} = \frac{\mathrm{e}^{-\mathrm{E_a/RT}}(\text{enzyme}-\text{catalyzed})}{\mathrm{e}^{-\mathrm{E_a/RT}}(\text{non}-\text{catalyzed})}$$

$$= \exp\left[\frac{83.68-25.10}{RT}\right]$$

$$= \exp \frac{(58.58\ \mathrm{k\,J\,mol^{-1}})}{8.314 \times 10^{-3}\ \mathrm{k\,J\,mol^{-1}k^{-1}} \times 310\ \mathrm{k}}$$

$$= e^{22.728}$$

$$\ln \frac{k_e}{k_n} = 22.78$$

$$\frac{k_e}{k_n} = 10^{10}$$

Thus, the enzyme-catalyzed reaction is about 10 billion times faster than the non-catalyzed reaction.

9. Given $k = 1.5 \times 10^{-6}\ s^{-1}$

Let initial conc. a = 100, t = 10 hr = 36000 sec, x = (?)

$$\mathrm{k} = \frac{2.3.03}{\mathrm{t}} \log \frac{\mathrm{a}}{(\mathrm{a}-\mathrm{x})}$$

$$1.5 \times 10^{-6} = \frac{2.303}{3.6 \times 10^{4}} log \frac{100}{(100-x)}$$

$$\therefore\ \mathrm{x} = 5.26$$

Thus initial concentration changed into product is, therefore, 5.2%

10. Given $A = 4 \times 10^{13}\ s^{-1}$

$E_a = 98.6 \times 10^3$ J mol^{-1},

$t_{1/2} = 10 \times 60$ s, k = [?]

$\therefore \ k_1 = Ae^{-E_a}/\,RT$

$\therefore \ k = 4 \times 10^{13}\, e^{-(98.6 \times 10^3 /\, 8.314 \times T)}$ ________ (1)

Now, for first order reaction:

$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{600}\, s^{-1}$ ________ (2)

From equation (1) and (2)

$$\frac{0.693}{600} = 4 \times 10^{13}\, e^{-(98.6 \times 10^3 /\, 8.314 \times T)}$$

$$or \quad log_e \frac{0.693}{600} = log_e[\ 4 \times 10^{13}] - \frac{98.6 \times 10^3}{8.314 \times T}$$

$$or \quad log_{10} \frac{0.693}{600} = log_{10}\ 4 \times 10^{13} - \left[\frac{98.6 \times 10^3}{8.314 \times 2.303 \times T}\right]$$

T = 311.35 K

11. $2\,N_2O_5\,(g) \rightarrow \ 4\,NO_2\,(g) + O_2\,(g)$

a	0	0	at, t = 0
(a-x)	2x	x/2	at, t = 30
0	2a	a/2	at, t = ∞

We know that:

(Pressure developed) ∞ (No. of moles)

at, t = 0, a ∞ P_0

at, t = 30 min, $a + \frac{3x}{2} \propto 284.5$

at, t = ∞, $\frac{5\,a}{2} \propto 584.5$

Thus, at, t = 0, $a \propto \frac{2 \times 584.5}{5} = 233.8\, mm\ og\ Hg$

at t = 30 min, x ∝ 33.8

[a – x] ∝ 200.0 mm of Hg

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

$\frac{2.303}{3o} \log \frac{233.8}{200}$

$= 5.206 \times 10^{-3}\ \text{min}^{-1}$.

12. Let the rate law equation for reaction between A and B be given by $\frac{dx}{dt} = k[A]^m[B]^n$

From data at 300 K

$$5 \times 10^{-4} = k[2.5 \times 10^{-4}]^m[3.0 \times 10^{-5}]^n \quad \text{....(i)}$$

$$4 \times 10^{-3} = k[5.0 \times 10^{-4}]^m[6.0 \times 10^{-5}]^n \quad ...(ii)$$

$$1.6 \times 10^{-2} = k[1.0 \times 10^{-3}]^m[6.0 \times 10^{-5}]^n ...(iii)$$

From equations (ii) and (iii)

$$\frac{1.6 \times 10^{-2}}{4 \times 10^{-3}} = \left[\frac{1.0 \times 10^{-3}}{5.0 \times 10^{-4}}\right]^m \times \left[\frac{6.0 \times 10^{-5}}{6.0 \times 10^{-5}}\right]^n$$

$4 = (2)^m$

$2^2 = 2^m$ or $m = 2$

From equation (i) and (ii)

$$\frac{4 \times 10^{-3}}{5 \times 10^{-4}} = \left[\frac{5.0 \times 10^{-4}}{2.5 \times 10^{-4}}\right]^m \times \left[\frac{6.0 \times 10^{-5}}{3.0 \times 10^{-5}}\right]^n$$

or $8 = 2^m \times 2^n$

or $8 = 2^2 \times 2^n$

or $2 = 2^n$

or $2^1 = 2^n$

$$\therefore n = 1$$

(i) Thus, order of reaction w.r.t. A and B are 2 and 1 respectively

(ii) Rate law equation is given as below:

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

From data at 300 K

$$5 \times 10^{-4} = k_{300}[2.5 \times 10^{-4}]^2[3.0 \times 10^{-5}]$$

$$\therefore k_{300} = 2.66 \times 10^8 L^2 mol^{-2} sec^{-1}$$

(iii) From data at 320 K

$$2 \times 10^{-3} = k_{320}[2.5 \times 10^{-4}]^2[3.0 \times 10^{-5}]$$

$$k_{320} = 1.07 \times 10^9 L^2 mol^{-2} sec^{-1}$$

As we know that

Activation energy (Ea) = $\frac{2.303R\ T_1T_2}{T_1 - T_2}\ log_{10} \frac{1.07 \times 10^9}{2.66 \times 10^8}$

= 55.34 × 103 J (because R is used in joule)

(iv) From Arrhenius equation

$k = Ae^{-E_a/RT}$

At 300 K

$2.66 \times 10^8 = Ae^{\frac{55.34 \times 10^3}{8.314 \times 300}}$

$or\ log_e 2.66 \times 10^8 = log_e A - \frac{55.34 \times 10^3}{8.314 \times 300}$

or $2.303 \times \log_{10} 2.66 \times 10^8 = 2.303\ log_{10} A - \frac{55.34 \times 10^3}{8.314 \times 300}$

By solving above equation, we get,

$A = 1.15 \times 10^{18} L^2 mol^{-2} sec^{-1}$

13. K[rate constant of first order reaction] = $\frac{0.693}{t_{\frac{1}{2}}}$

(where $t_{\frac{1}{2}}$ = half – life period = 360 minute)

$\therefore k = \frac{0.693}{360}\ min^{-1}\ at\ 380^0\text{C}$

Lower temperature (T_1) = 380 ^{0}C + 273 = 653 K

Higher temperature (T_2) = 450 ^{0}C + 273 = 723 K

Rate constant at t_1 (T_1) = $\frac{0.693}{360}$ = 1.925×10^{-3} min^{-1}

Rate constant at t_2 (k_2) =?

So, activation energy (E_a) = $\frac{2.303RT_1T_2}{T_2-T_1}\ log_{10}\frac{k_2}{k_1}$

$200\ kJ = \frac{2.303 \times 8.314 \times 10^{-3}\ kJ \times 653 \times 723}{(723-653)} \times log_{10}\frac{k_2}{1.925 \times 10^{-3}}$

On solving, we get $k_2 = 6.81 \times 10^{-2}$ min^{-1}

When 75% decomposition takes place at 723 K

$\therefore for\ first\ order\ reaction\ (k_2) = \frac{2.303}{t}\log\frac{N_0}{N_1}$

$\therefore 6.81 \times 10^{-2} = \frac{2.303}{t}\log\frac{100}{25}$

$\therefore t = 20.342\ minutes$

14. Rate of hydrogenation at 500 K for a reaction is equal to the rate of reaction in presence of catalyst at 400 K.

Let Ea and Ea' be the energy of activation in presence and absence of catalyst for hydrogenation reaction, then

$k = Ae^{-E_a/RT}$

In presence of catalyst: $k_1 = Ae^{-E_a/RT}$

In absence of catalyst: $k_2 = Ae^{-E_a'/RT}$

Given, the two rates are same, i.e., $r_1 = r_2$; (since $k_1 = k_2$)

Therefore $e^{-E_a/500\,R} = e^{-E_a'/400\,R}$

$$\frac{E_a}{500\,R} = \frac{E_a'}{400\,R}$$

$$\frac{E_a}{500} = \frac{E_a-20}{400} \qquad (E_a - E_a' = 20)$$

$E_a = 100$ kJ mol^{-1}

15. $$\left(\frac{-dc}{dt}\right)_{10} = 0.04\, mol\, L^{-1} sec^{-1}$$

$$\left(\frac{-dc}{dt}\right)_{20} = 0.03\, mol\, L^{-1} sec^{-1}$$

Rare of first order reaction is directly proportional to the concentration of its reactant.

So, $$\left(\frac{-dc}{dt}\right)_{10} \propto (C)_{10}$$

$$\left(\frac{-dc}{dt}\right)_{10} = k\, C_{10} \qquad \text{\_\_\_\_\_\_ (i)}$$

$$\left(\frac{-dc}{dt}\right)_{20} \propto (C)_{20}$$

$$\left(\frac{-dc}{dt}\right)_{20} = k\, C_{20} \qquad \text{\_\_\_\_\_\_ (ii)}$$

From equations (i) and (ii)

$$\frac{\left(\frac{-dc}{dt}\right)_{10}}{\left(\frac{-dc}{dt}\right)_{20}} = \frac{C_{10}}{C_{20}}$$

$$\frac{0.04}{0.03}\ or\ \frac{4}{3} = \frac{C_{10}}{C_{20}}$$

For first order reaction, when initial concentration is not given

$$\therefore \; k = \frac{2.303}{(t_{20}-t_{10})} \, log_{10} \frac{C_{10}}{C_{20}}$$

$$= \frac{2.303}{(20-10)} \, log_{10} \frac{4}{3}$$

$$= \frac{2.303}{10} \, (\log 4 - \log 3)$$

$$= \frac{2.303}{20-10} \, [2 \times 0.3010 - 0.4770]$$

$$\frac{2.303}{10} \times 0.1240 \, s^{-1}$$

$$= 2.855 \times 10^{-2} \, s^{-1}$$

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

$$t_{1/2} = \frac{0.693}{0.0285} = 24.31 \text{ min}$$

16. $2\,X\,(g) \rightarrow 3\,Y\,(g) + 2\,Z\,(g)$

At t = 0	800 mm	0	0	(partial pressure)
At time t	(800-2x) mm	3x mm	2x mm	
At t = 100 min	400 mm	600 mm	400 mm	
At = 200 min	200 mm	900 mm	600 mm	

Hence, for first order $k = \frac{2.303}{t} \, log_{10} \frac{p_0}{p_t}$

At $t = 100 \text{ min} \quad k_{100} = \frac{2.303}{100} \, log_{10} \frac{800}{400}$

$$= \frac{2.303}{100} log_{10} 2 = \frac{2.303 \times 0.3010}{100} min^{-1}$$

$$= 6.93 \times 10^{-3} \, \text{min}^{-1}$$

Thus, above reaction is first order reaction because

$k_{100} = k_{200}$

a. First order
b. Rate constant (k) = 6.93×10^{-3} min^{-1}
c. Suppose, t_1 minute is required for 75% completion of reaction

$$\therefore k = \frac{2.303}{t}\ log_{10}\frac{p_0}{p_t}$$

$$\because\ p_0 = 100\% p_{t_1} = 100 - 75 = 25\%$$

$$6.93\ \times 10^{-3} = \frac{2.303}{t_1}\ log_{10}\frac{100}{25}$$

$$t_1 = \frac{2.303}{6.93 \times 10^{-3}} \times 2\ \times 0.3010$$

$$=\ 2\ \times\ 10^{\ 2}\,\text{min} = \frac{200\ \text{min}}{60\,\text{min}\,\text{hr}^{-1}} = 3.3\ \text{hrs}$$

d.	$2\,X\,(g)$	$\rightarrow$	$3\,Y\,(g)$	+	$2\,Z\,(g)$
At t = 0	800		0		0
After some time	800-2x		3x		2x

$P_{total} = 800 - 2x + 3x + 2x = 800 + 3x$

Given that $800 - 2x = 700$

$x = 50$ mm

Hence, $P_{total} = 800 + 3 \times 50 = 950$

17. Loss in concentration of A in I^{st} hour = $\frac{0.6-0.5}{1} = 0.1$

Gain in concentration of B in I^{st} hour = $\frac{0.2-0}{1} = 0.2$

(i) $\because$ 0.1 mole of A changes to 0.2 mole of B in a given time and thus,

$n = 2$

(ii) Equilibrium constant, $K=\frac{[B]^n}{[A]}=\frac{[0.6]^2}{0.3}=1.2\ \text{mol litre}^{-1}$

($\because$ Equilibrium is attained after 5 hr, where *[B]* = 0.6 and *[A]* = 0.3)

(iii) Initial rate of conversion of *A* = changes in conc. of *A* during Ist hour

$$=\frac{0.1}{1}=0.1\ \text{mol litre}^{-1}\ \text{hour}^{-1}$$

18. For the reaction $2NO + Cl_2 \longrightarrow 2NOCl$

$$\text{Rate} = k[Cl_2]^m[NO]^n \qquad \text{---------}(1)$$

Where, *m* and *n* order of reaction with respect to Cl_2 and NO respectively.

From the given data:

$$1 \times 10^{-3} = k[0.05]^m[0.05]^n \qquad \text{---------}(2)$$

$$3 \times 10^{-3} = k[0.15]^m[0.05]^n \qquad \text{---------}(3)$$

$$9 \times 10^{-3} = k[0.05]^m[0.15]^n \qquad \text{---------}(4)$$

By eqs. (2) and (3), $m = 1$

By eqs. (2) and (4), $n = 2$

(a) $\therefore$ Order w.r.t. NO **is 2** and Cl_2 **is 1**.

(b) Also rate expression $\boldsymbol{r = K[Cl_2]^1[NO]^2}$

(c) And rate constant $k=\frac{r}{[Cl_2]^1[NO]^2}=\frac{1\times10^{-3}}{[0.05]^1[0.05]^1}=8\,L^2\,mol^{-2}\,sec^{-1}$

(d) Further, $r = K[Cl_2]^1[NO]^2$

$= 8[0.2]^1[0.4]^2$ **= 0.256 mol L^{-1} sec^{-1}**

19.

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

$$\therefore \quad \frac{-dC_A}{dt}=kC_A^n \qquad (\because \text{ order is } n)$$

On integrating $\frac{-\left(C_A\right)^{1-n}}{1-n}$ = kt + constant --------(1)

At t = 0, $C_A = C_0$ $\therefore$ constant $= \frac{C_0^{1-n}}{1-n}$ --------(2)

$$\therefore \text{ By Eqs.(1) and (2), } \quad -\frac{C_A^{1-n}}{1-n} = kt - \frac{C_0^{1-n}}{1-n}$$

or $$kt = \frac{1}{(1-n)}\left[C_A^{1-n} - C_0^{1-n}\right] \quad \text{--------(3)}$$

If $C_A = \frac{C_0}{2}$ at $t = t_{1/2}$ then by Eq.(3)

$$kt_{1/2} = \frac{1}{(n-1)}\left[\left(\frac{C_0}{2}\right)^{1-n} - \left(C_0\right)^{1-n}\right]$$

$$= \frac{1\left(C_0\right)^{1-n}}{(n-1)} \times \left[2^{n-1} - 1\right] \quad \text{--------(4)}$$

Similarly if C= $\frac{C_0}{4}$ at t = t3/4 , then by equation (3)

$$kt_{3/4} = \frac{C_0^{1-n}}{(n-1)}\left[4^{n-1} - 1\right] \quad \text{----------- (5)}$$

By equations (4) and (5),

$$\frac{t_{1/2}}{t_{3/4}} = \frac{2^{n-1} - 1}{4^{n-1} - 1}$$

Thus the ratio depends only on '**n**'

20. CH_3— O — CH_3 $_{(g)}$ $\rightarrow$ CH_4 $_{(g)}$ + H_2 $_{(g)}$ + CO $_{(g)}$

At t = 0 0.40 atm 0 0 0

After 12 min (0.40 – x) x atm x atm x atm

For first order reaction

$$k = \frac{2.303}{t}\log_{10}\frac{(P)_0}{(P)_t}$$

$$\frac{0.693}{14.5} = \frac{2.303}{12}\log_{10}\frac{0.40}{0.40 - x}$$

$$x = 0.175 \text{ atm}$$

Total pressure of closed container after 12 minutes

$= 0.40 – x + x + x + x = 0.4 + 2x$

$= 0.4 + 2 \times 0.175$

$= 0.75$ atm

21. On the basis of partial vapour pressure concept, $P_A + P_B = 400$ after polymerization

$\therefore$ Suppose n_A moles of A are polymerized out of its 10 moles

So, $$\frac{(10\text{-}n_A) \times 300}{(10\text{-}n_A) + (12+0.525)} + \frac{12 \times 500}{(10\text{-}n_A) + (12+0.525)} = 400$$

Here we have assumed that the solute added is non-volatile but miscible and the moles of B that vaporises upto equilibrium state is neglected.

or $$\frac{(10\text{-}n_A) \times 300 + 12 \times 500}{(10\text{-}n_A) + (12+0.525)} = 400$$

or $$\frac{(10\text{-}n_A)\, 3 + 12 \times 5}{(10\text{-}n_A) + (12+0.525)} = 4$$

or $90 – 3\, n_A = 90.10 – 4\, n_A$

$\therefore$ $n_A = 0.10$

This polymerization is an example of first order kinetics (because 0.1 mole is polymerized so remaining moles after 100 minutes)

So, $$k = \frac{2.303}{t}\log_{10}\frac{[A]_0}{[A]_t}$$

$$= \frac{2.303}{100} \log_{10} \frac{10}{(9.9)}$$

$$= 10 - 0.1 = 9.9$$

$\therefore \quad k = 1.013 \text{ X } 10^{-4} \text{ min}^{-1}$

Chemical Kinetics

Module 9.7: Catalysis

When oxygen is prepared by heating potassium chlorate the reaction needs strong heating and even then it is slow. On the other hand, if potassium chlorate is mixed with a small amount of manganese dioxide and then heated, oxygen starts evolving at a lower temperature and with a rapid speed. After the reaction, manganese dioxide is recovered in almost the same amount in which it is added. Such substance, like manganese dioxide in the present case, which increases (or sometimes decreases) the rate of a chemical reaction without itself being permanently changed is called a **catalyst** or a catalytic agent. The catalyst is written over the arrow in the chemical equation, e.g.

$$2KClO_3 \xrightarrow{MnO_2} 2KCl + 3O_2$$

"A catalyst is a substance that increases the rate of a reaction by providing an alternate path of lower activation energy".

"Catalysis is the process in which the rate of a chemical reaction is either increased or decreased by means of a chemical substance known as a catalyst".

Unlike other reactant that participates in the chemical reaction, a catalyst is not consumed by the reaction itself. Since catalysts are not consumed in a reaction, very small quantities of catalyst are required to enhance a reaction rate. The catalyst may participate in multiple stage chemical transformations.

Catalysts that slow down the reaction are called **negative catalysts or inhibitors**. Substances that increase the activity of catalysts are called **promoter**s and substances that deactivate catalysts are called **catalytic poisons**. For instance, in the reduction of ethyne to ethene, the catalyst is palladium (Pd) partly "poisoned" with lead (II) acetate [$Pb(CH_3COO)_2$]. If the deactivation of the catalyst is not done, the ethene produced will be further reduced to ethane.

Types of Catalysis:

Catalysis can be either **heterogeneous or homogeneous**, depending on whether a catalyst exists in the same phase as the substrate or not. Biocatalysts are often seen as a separate group.

Homogeneous Catalysts:

When a catalyst mixes homogenously with the reactants and forms a single phase it is called a homogenous catalyst. Most commonly, a homogeneous catalyst is dissolved in a solvent together with the reactants.

Some examples of homogeneous catalysis are given below

1) Oxidation of SO_2 in presence of NO catalyst

$$\longrightarrow$$

2) Catalytic decomposition of ozone by chlorine atoms

$$\longrightarrow$$

3) Hydrolysis of sugarcane solution in the presence of dilute sulphuric acid.

$$\xrightarrow{\text{dil.}H_2SO_4} \quad \text{Glucose} \quad \text{Fructose}$$

4) Formation of diethyl ether from ethyl alcohol using concentrated sulphuric acid as catalyst.

$$\xrightarrow{\text{Conc. } H_2SO_4}$$

5) Hydrolysis of esters in the presence of H_2SO_4 catalyst.

$$CH_3COOC_2H_5 + H_2O \xrightleftharpoons{H_2SO_4} CH_3COOH + C_2H_5OH$$

Heterogeneous Catalysts:

When a catalyst exists in a different phase from that of the reactants, it is called a heterogeneous catalyst. In heterogeneous catalysis, the catalyst is generally a solid while the reactants are gases. Sometimes solid catalysts with liquid reactants also are used. Heterogeneous catalysis is also called **surface catalysis** since the reaction starts from the surface of the solid catalyst. In heterogeneous catalysis, first, the chemical adsorption (chemisorption) of the reactants onto the surface of the catalyst takes place. The catalysts provide enormous surface areas (1 to 500 m^2/g) for contact.

Some examples of heterogeneous catalysis which are important industrial processes are listed below.

In Haber's Process for the manufacture of NH_3 from N_2 and H_2 using iron as catalyst, preparation of sulphuric acid by contact process where V_2O_5 is the solid catalyst and oxidation of NH_3 using Platinum as catalyst (Ostwald process).

Manufacture of methyl alcohol from CO and H_2 using ($ZnO + Cr_2O_3$) as catalyst

$$\xrightarrow[\text{heat}]{}$$

Oxidation of CO in automobile exhaust by platinum catalyst

$$\xrightarrow{Pt}$$

Addition of H_2 to C=C bonds of organic compounds to form C-C bonds (catalytic hydrogenation).

Catalytic hydrogenation is frequently used in petroleum, plastics and food industries. The conversion of vegetable oil into solid fat is an example of catalytic hydrogenation process. One of the simple hydrogenation processes is the conversion of ethylene to ethane in the presence of platinum catalyst. The mechanism of this hydrogenation reaction is illustrated in the figure.

Some Examples of Catalysts:

Catalyst	Examples	Function
Metals	Fe, Ni, Pt, Ag	Hydrogenation Dehydrogenation
Semiconducting oxides and sulphides	Mo, ZnO, MgO, Si_2O_3/MoO_3, MoS_2	Oxidation Desulphurization
Insulating oxides	Al_2O_3, SiO_2, MgO	Dehydration
Acids	SiO_2/Al_2O_3 zeolites	Cracking Polymerization Isomerization

The two important aspects of solid catalysts are (i) activity and (ii) selectivity.

i) Catalytic activity:

The catalytic activity of the catalyst depends on the strength of binding of the reactant on the surface of the catalyst. It is observed that the metals of group 7, 8 and 9 of the periodic table have maximum activity.

ii) Selectivity:

The catalyst is specific in its reactivity.

Example 1: The reaction of CO with H_2 yields different products when different catalysts are used i.e.

$$\longrightarrow$$

$$\longrightarrow$$

$$\longrightarrow$$

A catalyst of one reaction may not bring about the other reactions.

Example 2: The reaction of acetylene C_2H_2 with H_2 results in different products, ethane and ethylene, when different catalysts are used.

$$\longrightarrow$$

$$\longrightarrow$$

These two examples illustrate the point that a catalyst is highly selective, that is, a given catalyst can be active only in particular reactions and not in all reactions.

Zeolites (Shape-Selective Catalysis by Zeolites):

The catalytic reaction that depends upon the pore structure of the catalyst and the size of the reactant and product molecules is called shape-selective catalysis. Zeolites are good shape-selective catalysts because of their honeycomb-like structures. They are microporous aluminosilicates with three dimensional networks of silicates in which some silicon atoms are replaced by aluminum atoms giving Al – O – Si framework. The reactions taking place in zeolites depend upon the size and shape of reactant and product molecules as well as upon the pores and cavities of zeolites. They are found in nature as well as synthesized for catalytic selectivity

Enzyme Catalysis:

Enzymes are macromolecules, usually proteins, produced in living systems, which act as catalysts in physiological reactions. The striking characteristics of enzymes are their catalytic power and specificity. Enzymes have immense catalytic power;

they accelerate reactions by factors of at least a million. Most reactions in living systems do not occur at perceptible rates in the absence of enzymes. A simple reaction like hydration of CO_2 is catalyzed by the enzyme carbonic anhydrase. The transfer of CO_2 from tissues into the blood would be very slow in the absence of this enzyme. The enzyme can hydrate 10^5 molecules of CO_2 per second, which is 10^7 times faster than the uncatalysed one.

Enzymes are highly specific. An enzyme usually catalyses a single chemical reaction or a set of closely related reactions. For e.g., urease catalyses the hydrolysis of urea only.

$\xrightarrow{\text{Urease}}$

Other examples of enzyme catalyzed reactions are as follows:

Starch $\longrightarrow$ Maltose

$\xrightarrow{\text{Maltase}}$ Glucose

Glucose $\xrightarrow{\text{Zymase}}$

Catalysts in Industry:

The phenomenon of catalysis has made tremendous revolution in chemical industries. Some of the important industrial processes catalyzed by different catalysts are summarized below.

Important industrial process and their catalysts

S.No	Process	Catalyst
1.	Haber's process for synthesis of Ammonia	Iron; Mo(promoter)
2.	Contact process for manufacture of H_2SO_4	Pt, V_2O_5
3.	Ostwald process for manufacture of HNO_3	Pt gauze
4.	Deacon's process for manufacture of Cl_2	CuCl
5.	Manufacture of vegetable ghee	Ni
6.	Fischer – Tropsch process for synthesis of hydrocarbons	Co, ThO_2
7.	Synthetic petrol from coal (Bergius process)	Iron oxalate
8.	Manufacture of C_2H_5OH from sucrose	Invertase, zymase
9.	Manufacture of C_2H_5OH from starch	Diastase, maltose
10.	Preparation of O_2 from $KClO_3$	MnO_4
11.	Dehydration of alcohol to aldehyde	Copper

SAQs:

1. During hydrogenation of oils, the catalyst commonly used is _____.
   a. Pd or $CuCl_2$
   b. finely divided Ni
   c. Fe
   d. V_2O_5

Solution: b)

2. Which of the following kinds of catalysis can be explained by adsorption theory?
   a. Homogeneous
   b. Acid – base

   c. Heterogeneous
   d. Enzyme

Solution: c)

3. Substance which completely destroys the activity of catalyst is called
   a. Promoter
   b. Inhibitor
   c. Catalytic poison
   d. Auto catalyst

Solution: c)

4. A catalyst increases the rate of reaction because it
   a. Increases the activation energy
   b. Decreases the energy barrier for reaction
   c. Decreases the collision diameter
   d. Increases the temperature coefficient

Solution: b)

5. What is a catalyst?

Solution:

"A catalyst is a substance that increases the rate of a reaction by providing an alternate path of lower activation energy".

6. Define catalysis.

Solution:

"Catalysis is the process in which the rate of a chemical reaction is either increased or decreased by means of a chemical substance known as a catalyst".

7. What is homogeneous catalysis?

Solution:

Homogeneous Catalysts:

When a catalyst mixes homogenously with the reactants and forms a single phase it is called a homogenous catalyst.

8. What is heterogeneous catalysis?

Solution:

Heterogeneous Catalysts:

When a catalyst exists in a different phase from that of the reactants**,** it is called a heterogeneous catalyst.

Problem Set:

1. The inhibitors

   a. Retard the rate of chemical reaction
   b. Stop a chemical reaction immediately
   c. Are reducing agents
   d. Do not allow the reaction to proceed

Solution: a)

2. In which process a catalyst is not used

   a. Contact process
   b. Haber’s process
   c. Ostwald’s process
   d. Solvay’s process

Solution: d)

3. The effect of the catalyst on a chemical reaction is to change the

   a. Concentration of reactants
   b. Activation energy
   c. Heat of the reaction
   d. Final products

Solution: b)

4. What are the catalysts used in the following reactions.

$\longrightarrow$

$\longrightarrow$

Solution:

$\longrightarrow$

$\longrightarrow$

5. Write short notes on selective catalysis by zeolites.

Solution:

The catalytic reaction that depends upon the pore structure of the catalyst and the size of the reactant and product molecules is called shape – selective catalysis. Zeolites are good shape – selective catalysts because of their honeycomb-like structures. They are microporous aluminosilicates with three dimensional network of silicates in which some silicon atoms are replaced by aluminium atoms giving Al – O – Si framework. The reactions taking place in zeolites depend upon the size and shape of reactant and product molecules as well as upon the pores and cavities of zeolites. They are found in nature as well as synthesized for catalytic selectivity.

6. Write notes on

a. Catalytic activity
b. Selectivity
c. Enzyme catalysis

Solution:

i) Catalytic activity:

The catalytic activity of the catalyst depends on the strength of binding of the reactant on the surface of the catalyst. It is observed that the metals of group 7, 8 and 9 of the periodic table have maximum activity.

ii) Selectivity:

The catalyst is specific in its reactivity.

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Exercise Questions:

1. Select the correct catalyst?

$$\longrightarrow$$

$$\longrightarrow$$

$$\longrightarrow$$

$$\longrightarrow$$

2. Efficiency of catalyst depends on its

a. Particle size
b. Molecular weight
c. Solubility
d. All the above

3. Which is universally correct for a catalyst?
   a. Initiates reaction
   b. Does not initiate reactions
   c. Does not alter the nature of products
   d. Is not specific in nature

4. In Haber's process, hydrogen is obtained by reacting methane with steam in presence of NiO as catalyst. The process is known as steam reforming. CO is one of the products. Why is it necessary to remove CO when ammonia is obtained by Haber's process?

5. Why the ester hydrolysis is slow in the beginning and becomes faster after some time?
6. What is the role of desorption in the process of catalysis.
7. What is shape selective catalysis?

Solutions to Exercise Questions:

1. c
2. a
3. b
4. It is important to remove CO in the synthesis of ammonia as CO adversely affects the ability of the iron catalyst, used in Haber's process.

5. Ester hydrolysis can be represented as:

Ester + water → Acid + Alcohol

The acid produced in the reaction acts as a catalyst and makes the reaction faster. Substances that act as catalyst in the same reaction in which they are obtained as products are known as auto catalysts.

6. The role of desorption in the process of catalysis is to make the surface of the solid catalyst free for the fresh adsorption of the reactions on the surface.
7. A catalytic reaction which depends upon the pore structure of the catalyst and on the size of the reactant and the product molecules is called shape – selective catalysis.

   Ex: Zeolite is a shape-selective catalysis. The pore size present in the zeolite ranges from 260 – 740 pm. Thus, molecules having a pore size more than this cannot enter the zeolite and undergo the reaction.

CAT:

1. Which of the following is not involved in heterogeneous catalysis?
   a. Adsorption of reactants
   b. Diffusion of reactants along the surface
   c. Reaction at the active site to form adsorbed product
   d. Decomposition of the catalyst

Solution: d)

2. Which of the following statements about a catalyst is true
   a. It lowers the activation energy

b. The catalyst altered during the reaction is generated
c. It does not alter the equilibrium
d. All the above

Solution: d)

3. Distinguish between homogeneous catalysis and heterogeneous catalysis.

Solution:

Homogeneous Catalysts:

When a catalyst mixes homogenously with the reactants and forms a single phase it is called a homogenous catalyst.

Heterogeneous Catalysts:

When a catalyst exists in a different phase from that of the reactants, it is called a heterogeneous catalyst.

Match the following:

List I	**List II**
A) Haber's process	1) CuCl
B) Contact process	2) Iron; Mo
C) Deacon's process	3) Pt, V_2O_5

The correct matching is [   ]

a. A -1, B – 2, C – 3
b. A – 2, B – 3, C – 1
c. A – 3, B – 1, C – 2
d. A – 2, b – 1, c – 3

Solution: b)