

CHEMICAL KINETICS

Objectives

- Order and molecularity
- Kinetics of first and second order reaction
- Pseudo unimolecular reaction
- Arrhenius equation

1.1 Chemical Kinetics

Chemical kinetics is the branch of physical chemistry which deals with a study of the speed of chemical reactions. Such studies also enable us to understand the mechanism by which the reaction occurs. Thus, in chemical kinetics we can also determine the rate of chemical reaction.

From the kinetic stand point the reactions are classified into two groups:

a) homogeneous reactions which occur entirely in one phase b) heterogeneous reactions where the transformation takes place on the surface of a catalyst or the walls of a container.

1.2 Rate of reaction

The rate of reaction i.e. the velocity of a reaction is the amount of a chemical change occurring per unit time.

The rate is generally expressed as the decrease in concentration of a reactant or as the increase in concentration of the product. If C the concentration of a reactant at any time t is, the rate is $-\frac{dC}{dt}$ or if the concentration of a product be x at any time t , the rate would be $\frac{dx}{dt}$.

The time is usually expressed in seconds. The rate will have units of concentration divided by time.

The concentrations are taken in gm-moles/litre, hence rate is moles/litre/second.

Factors influencing the rate of reaction

Rate of a chemical reaction is influenced by the following factors

(i) Temperature (ii) Concentration of the reactants (iii) Nature of reactants (iv) Catalysts (v) Radiation

(i) Temperature

In most cases, the rate of a reaction in a homogeneous reaction is approximately doubled or tripled by an increase in temperature of only 100 C. In some cases the rise in reaction rates are even higher.

(ii) Concentration of the reactants

At a fixed temperature and in the absence of catalyst, the rate of given reaction increases with increased concentration of reactants. With increasing concentration of the reactant

the number of molecules per unit volume is increased, thus the collision frequency is increased, which ultimately causes increased reaction rate.

(iii) Nature of reactants

A chemical reaction involves the rearrangement of atoms between the reacting molecules to the product. Old bonds are broken and new bonds are formed. Consequently, the nature and the strength of the bonds in reactant molecules greatly influence the rate of its transformation into products. The reaction in which involve lesser bond rearrangement proceeds much faster than those which involve larger bond rearrangement.

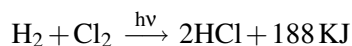
(iv) Catalysts

The rate of a chemical reaction is increased in presence of a catalyst which ultimately enhanced the speed of a chemical reaction.

(v) Radiation

The rate of a number of chemical reactions increases when radiations of specific wave length are absorbed by the reacting molecules. Such reactions are called photochemical reactions.

For example, chlorine may be mixed safely with hydrogen in dark, since the reaction between the two is very slow. However when the mixture is exposed to light, the reaction is explosive.



SKILL TEST

1. What do you mean by chemical kinetics?
2. What do you mean by rate of a reaction?
3. What is specific reaction rate or velocity constant (k)?
4. What are the factors that can change the value of K?

1.3 Order of reaction

The order is the number of concentration terms on which reaction rates depends. Thus, if the rate of a reaction depends on the first power of the concentration of reactant, i.e.

$$\text{Rate} = KC^1$$

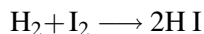
Thus the reaction is said to be of the **first order**. When the rate is proportional to the product of two reactant concentrations or the square of the concentration of a reactant, the reaction is of the **second order**.

For example, the decomposition of hydroiodic acid

$$\text{Rate} = K C_{HI}^2$$

$$\text{Rate} = K C_{HI}^2$$

and the hydrogen - iodine reaction



$$\text{Rate} = KC_{H_2}C_{I_2}$$

Here both are **second order** reactions.

If the reaction rate is experimentally found to be represented by

$$-\frac{dC}{dt} = KC^n$$

The order of the reaction is n .

If several reactants A, B, C,etc are involved and it is observed experimentally that the rate of the process is given by,

$$-\frac{dc}{dt} = KC_A^\alpha C_B^\beta C_C^\gamma \dots\dots$$

Then the order of the reaction would be $n = \alpha + \beta + \gamma + \dots\dots$

The reaction is said to be α th order with respect to A, β th order with respect to B etc.

But there are reactions in which the order is fractional i.e. $n = \frac{1}{2}, \frac{3}{2}$ etc.. For example,

the ortho - para hydrogen conversion, its rate is expressed by $-\frac{d[H_2]}{dt} = K C_{H_2}^{3/2}$

1.4 Molecularity of a reaction

The molecularity of a reaction is defined as the number of molecules or atoms which take part in the process of a chemical change.

The reaction is said to be **unimolecular**, **bimolecular**, **termolecular** according to one, two, or three molecules are involved in the process of a chemical change.

The term unimolecular was used for all first order reactions, the term bimolecular for 2nd order reactions etc.

SKILL TEST

1. What do you mean by the order of a reaction?
2. What is the molecularity of a reaction?
3. Can order of a reaction be fractional?
4. Is it possible for a reaction to have identical values for molecularity and order?

1.5 Zero Order Kinetics

A chemical reaction whose rate does not depend on concentration of reactants is called a zero order chemical reaction.

The rate of the reaction can be written as

$$\frac{dx}{dt} = \text{Constant}$$

$$\Rightarrow \frac{dx}{dt} = K$$

$$\text{or, } dx = K dt$$

$$\text{On integration, } \int dx = K \int dt$$

$$\text{or, } x = Kt + Z \text{ (Integration Constant).}$$

$$\text{When } t = 0, x = 0 \text{ hence } Z = 0$$

$$\text{So, } x = Kt$$

$$\text{Or, } K = \frac{x}{t}$$

A plot of x versus t should give a straight line passing through the origin as shown in the figure and the slope of this straight line is K .

Example: Photochemical combination of H_2 and Cl_2 to form HCl .

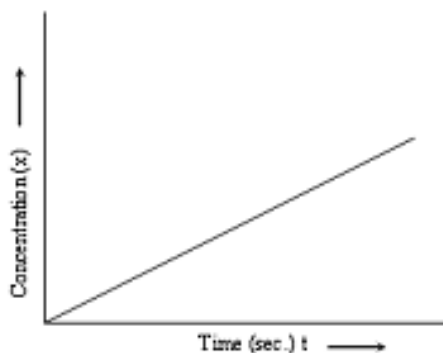
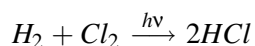


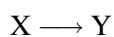
Figure 1.1: Plot of concentration against t for a reaction



The rate of this reaction does not depend on concentration.

1.6 First Order Kinetics

A reaction of the first order is represented as



where X is the reactant and Y the product. The rate of the reaction will be directly proportional to the concentration i.e.,

$$(1.1) \quad -\frac{dc}{dt} = KC$$

in which C is the concentration of the reactant at any time t and K is a constant, called the velocity constant or specific reaction rate.

$$\text{Thus } -\frac{dc}{C} = K dt$$

On integration $-\int \frac{dc}{C} = K \int dt$

$-\ln c = kt + Z$ (Integration Constant).

If at the start of the reaction the initial concentration of the reactant is C_o then we have at $t = 0$, $C = C_o$

Substituting $-\ln C_o = Z$

$$-\ln C = Kt - \ln C_o$$

$$\ln \frac{C_o}{C} = Kt$$

Or $\frac{C}{C_o} = e^{-Kt}$ Or

$$(1.2) \quad C = C_o e^{-Kt}$$

The concentration C therefore diminishes exponentially with time.

We may also write

$$(1.3) \quad C_o - C = C_o(1 - e^{-Kt})$$

The rate equation may also be conveniently expressed in an alternative form, by expressing the rate in terms of the product. When x moles per unit volume of product Y is formed from the reactant, the concentration of the reactant is $(a - x)$, where a is the initial concentration of the reactants. So

$$-\frac{d}{dt}(a - x) = K(a - x)$$

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

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

On integration $\int \frac{dx}{a-x} = K \int dt$

or, $-\ln(a - x) = Kt + Z'$ (Integration Constant)

When $t = 0, x = 0$, hence $-\ln a = Z'$

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

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

$$(1.4) \quad K = \frac{1}{t} \ln \frac{a}{(a-x)}$$

$$(1.5) \quad x = a(1 - e^{-Kt})$$

The fractional extent of the reaction at any time t is

$$(1.6) \quad \frac{x}{a} = (1 - e^{-Kt})$$

When the initial concentration a is not known but the concentrations at two intervals t_1 and t_2 are known, the rate equation can be derived. If x_1 and x_2 are the concentrations of product at time t_1 and t_2 , the corresponding concentrations of reactants would be $(a - x_1)$ and $(a - x_2)$. So

$$Kt_1 = \ln \frac{a}{a-x_1} \text{ and } Kt_2 = \ln \frac{a}{a-x_2}$$

$$(1.7) \quad K(t_2 - t_1) = \ln \frac{a-x_1}{a-x_2}$$

Characteristics

1) In a first order reaction $C = C_0 e^{-Kt}$, the reaction can not be complete because C would become zero at infinite time.

2) The quantity $\frac{a}{(a-x)}$ or $\left(\frac{C_0}{C}\right)$ is a ratio of concentrations, so, its value will be the same what ever units are employed to express the concentrations e.g. moles/litre, gms/c.c etc. It shows that the velocity constant $K \left(= \frac{1}{t} \ln \frac{a}{a-x}\right)$ will have the dimension of reciprocal time, Sec^{-1} :

3) The equation is $\ln(a - x) = -Kt + \ln a$

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

If $\log(a - x)$ is plotted graphically against time, it would give a straight line. So when a plot constructed from experimental values of $\log(a - x)$ and t is found to be linear, the reaction is of the first order. The slope of the line is $-\frac{K}{2.303}$ from which the velocity constant K can be determined.

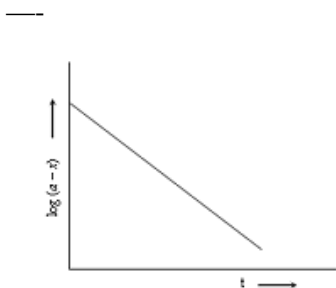


Figure 1.2: Plot of $\log(a - x)$ against t for a reaction

4) The time required for half the reactant to change can be easily evaluated. Let $t_{1/2}$ be the time required when $x = \frac{a}{2}$.

$$\text{Then } t_{1/2} = \frac{1}{K} \ln \frac{a}{a - a/2}$$

$$= \frac{1}{K} \ln \frac{a}{a/2} = \frac{2.303 \log 2}{K} = \frac{0.693}{K}$$

The period of half decomposition is thus constant for a given reaction and is independent of initial concentration. The time required is called half value period or half life in case of radioactive changes.

The time necessary to complete any definite fraction (ϕ) of the reaction is independent of the initial concentration in first order kinetics, for

$$t_{\phi} = \frac{2.303}{K} \log \frac{a}{a - a\phi}$$

$$= \frac{2.303}{K} \log \frac{1}{1 - \phi} = \text{constant.}$$

1.7 Second Order Kinetics

A reaction will be of the second order when the reaction rate would depend upon the product of two concentrations.

Second order reactions are of two types

(i) The rate is proportional to the square of the same reactant concentration

(ii) The rate is proportional to the product of the two reactant concentration

(i) The rate is proportional to the square of the same reactant concentration

Let say, $2A \longrightarrow \text{Products}$

$$(a - x)$$

If the two substances have the same initial concentration(a) and if x denotes the concentration of the reactants which disappears in time t , then the rate will be

$$\frac{dx}{dt} = K(a - x)^2$$

$$\frac{dx}{(a - x)^2} = K dt$$

On integration,

$$\int \frac{dx}{(a - x)^2} = K \int dt$$

$$\frac{1}{(a - x)} = Kt + Z(\text{Integration constant})$$

$$\text{When } t = 0, x = 0 \therefore \frac{1}{a} = Z$$

Substituting the value of Z

$$(1.8) \quad \frac{1}{(a - x)} - \frac{1}{a} = Kt$$

Thus the velocity constant

$$(1.9) \quad K = \frac{x}{at(a - x)}$$

Hence at any time t , the fractional extent of the reaction would be

$$\frac{x}{a} = 1 - \frac{1}{1 + Kta}$$

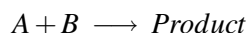
In a second order reaction, where the two initial concentrations are the same then from 1.9 the half value period is given by

$$t_{1/2} = \frac{x}{ak(a - a/2)} = \frac{a/2}{a \cdot k \cdot a/2} = \frac{1}{ak}$$

i.e. the time required for half the amount of reactant to undergo the change is inversely proportional to initial concentration a , where as in first order reaction $t_{1/2}$ is constant.

(ii) *The rate is proportional to the product of the two reactant concentration*

Let say another type of reaction



$$(a - x) (b - x)$$

When the initial concentrations of the two substances participating are different, say a and b , then the rate is given by,

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

where x is the amount of any reactant transformed in time t

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

$$\frac{1}{(a - b)} \left[\frac{1}{(b - x)} - \frac{1}{(a - x)} \right] dx = K dt$$

On integration,

$$\frac{1}{(a - b)} \int \frac{dx}{(b - x)} - \frac{1}{(a - b)} \int \frac{dx}{(a - x)} = K \int dt$$

$$\frac{1}{(a - b)} [-\ln(b - x) + \ln(a - x)] = Kt + Z (\text{Integration constant})$$

$$\text{or } \frac{1}{(a-b)} \ln \frac{(a-x)}{(b-x)} = Kt + Z$$

when $t = 0, x = 0$ therefore $\frac{1}{(a-b)} \ln \frac{a}{b} = Z$

$$\text{Substituting } \frac{1}{(a-b)} \ln \frac{(a-x)}{(b-x)} - \frac{1}{(a-b)} \ln \frac{a}{b} = Kt$$

$$K = \frac{1}{t(a-b)} \ln \frac{b(a-x)}{a(b-x)}$$

It may also be written as

$$(1.10) \quad t = \frac{2.303}{K(a-b)} \log \frac{b(a-x)}{a(b-x)}$$

The plot of $\log \frac{b(a-x)}{a(b-x)}$ against t for such a reaction would be linear. The straight line would pass through the origin and from its slope $\frac{2.303}{K(a-b)}$, the velocity constant would be obtained.

$$\log \frac{b(a-x)}{a(b-x)} \log \frac{b(a-x)}{a(b-x)}$$

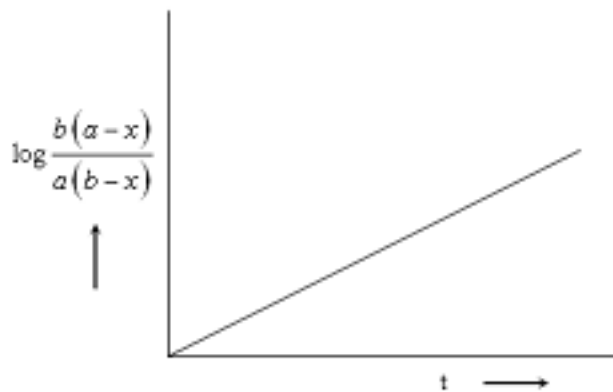
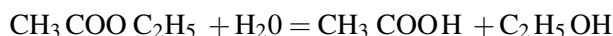
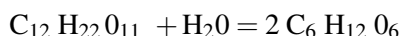


Figure 1.3: Plot of $\log \frac{b(a-x)}{a(b-x)}$ against t for a reaction

1.8 Pseudo unimolecular Reactions

There are a number of reactions, which follow the first order kinetics though more than one kind of reactants is involved in the reaction. Common examples are the inversion of cane sugar or the hydrolysis of an ester in an acid medium.



These are truly second order reactions. Two substances water and cane sugar, or water and ester participate, but the rate of reaction is experimentally observed to depend only on the concentration of cane sugar or ester.

A second order reaction is governed by the equation (3). If the concentration of one of the participants is very large compared to that of the other, say $b \gg a$, then $b - x \approx b$ and $a - b \approx -b$, which is practically constant.

Hence, equation (3) reduces to

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

$$\text{Or } K' = \frac{1}{t} \ln \frac{a}{(a-x)}$$

That is, under these circumstances, the reaction will follow first order kinetics.

In these reactions water is present in such large excess, that even if the reaction is complete, the concentration of water would virtually remain unaltered.

$$-\frac{dc}{dt} = K C_{sugar} C_{H_2O} = K' C_{sugar}$$

Thus these reactions follow first order kinetics. This type of reaction is known as pseudo unimolecular reaction.

Specific reaction rate

$$\text{First order reaction } K = \left(-\frac{dc}{dt}\right) | C$$

$$\text{Hence dimension of K is } \frac{\text{moles per litre per sec}}{\text{moles per litre}} = \text{sec}^{-1}$$

$$\text{For second order reaction } K = \left(-\frac{dc}{dt}\right) | C^2$$

$$\text{Hence dimension of K is litre } \text{mole}^{-1} \text{sec}^{-1}$$



In general, the units of K for a reaction of nth order would be given by,

$$\frac{\text{moles/litre/sec}}{(\text{moles/litre})^n} = \text{litre}^{n-1} \text{ moles}^{1-n} \text{ sec}^{-1}$$

SKILL TEST

1. What is first order reaction? Give examples of first order reaction.
2. What is a second order reaction?
3. Comment on half life of a first order and second order reaction.
4. Is a first order or a second order reaction completed?
5. For a first order reaction one hour is needed for a change of concentration C to $\frac{C}{2}$.
What is the time for the change from $\frac{C}{2}$ to $\frac{C}{4}$?
6. What is the special characteristic of a zero order reaction?

1.9 Catalytic Reactions

Definition

Catalysis is the process of enhancing the rate of the reaction by means of a foreign substance which remains unchanged in mass and chemical composition.

Classification

i) **Homogeneous Catalysis**

Homogeneous Catalysis is where the catalyst and the reactant constitute a single phase.

ii) **Heterogeneous Catalysis**

Heterogeneous Catalysis is where the catalyst and the reactant constitute separate phase.

Homogeneous Catalysis

Example

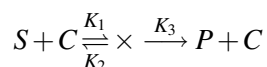
- i) Nitric Oxide in the oxidation of carbon monoxide to carbon dioxide.
- ii) H^+ ion acts as a catalyst in the hydrolysis of ester or sugar.

Mechanism

Theory (Intermediate compound formation theory)

Substrate (S) reacts with the catalyst (C) producing an intermediate compound(X). The intermediate compound then reacts to produce the product (P) along with the catalyst (C). Moreover the intermediate compound also decomposes to produce the substrate along with the catalyst.

Scheme



Kinetics

The rate of reaction = rate of formation of the product

$$(1.11) \quad \frac{dC_p}{dt} = K_3 C_X$$

For the intermediate X, if we invoke the steady state postulate,

$$\frac{dC_X}{dt} = K_1 C_S C_C - K_2 C_X - K_3 C_X = 0$$

$$\text{Or } (K_2 + K_3) C_X = K_1 C_S C_C$$

Or

$$(1.12) \quad C_X = \frac{K_1 C_S C_C}{K_2 + K_3}$$

Substituting the value of C_X in equation 1.11

$$\frac{dC_p}{dt} = \frac{K_3 K_1 C_S C_C}{(K_2 + K_3)}$$

$$(1.13) \quad = K_C C_S C_C$$

Comments

i) It is clearly shown that the rate is dependent on catalyst concentration(C_C). For a

given concentration of catalyst

$\frac{dC_p}{dt} = K' C_S$ where $K' = K_C C_C$ i.e. K' is proportional to C_C .

ii) The constant K_C is known as the “catalytic co-efficient” for the catalyst.

Characteristics

- i) The catalyst remains unchanged in mass and in chemical composition at the end of the reaction.
- ii) A very minute quantity of a catalyst can produce an appreciable effect on the speed of a reaction.
- iii) A catalyst can not start a reaction but only increases its speed. The catalyst really provides an alternative path for the transformation in which the require activation energy is less. Lesser activation energy permits larger amounts of reaction in a given time.
- iv) The catalyst does not affect the final state of equilibrium.

SKILL TEST

1. What is catalysis?
2. What is a second order reaction?
3. Give an example of solution phase homogeneous catalysis.
4. How does the catalyst influence the rate of the reaction?

1.10 Temperature and Reaction Rates

The Arrhenius Equation

Temperature has a profound influence on the reaction velocity. In homogenous thermal reactions, for every ten degree rise in temperature, the velocity of reaction is doubled or trebled. The ratio is called **temperature coefficient**.

$$\frac{K_{t+10}}{K_t} \approx 2 \text{ or } 3$$

Arrhenius (1889) showed that the velocity constant (**K**) of a chemical process increases exponentially with temperature for a large number of reactions. It was observed that the plot of $\log K$ against $\frac{1}{T}$ gives a linear relation.

He, therefore, suggested empirically the relation as

$$\frac{d \ln K}{dT} = \frac{E}{RT^2}$$

or $K = Ae^{-E/RT}$ ($A = \text{constant}$)

A is called the frequency factor or pre exponential factor.

E is called the activation energy of the reaction.

These two quantities have definite values for any given reaction. By measuring the velocity constant K and K' at two temperatures T and T' respectively, we have,

$$\log K = -\frac{E}{2.303R} \times \frac{1}{T} + \log A$$

$$\log K' = -\frac{E}{2.303R} \times \frac{1}{T'} + \log A$$

$$\log \frac{K}{K'} = -\frac{E}{2.303R} \left[\frac{T' - T}{T T'} \right]$$

Hence the activation energy E is easily obtained.

Alternatively, a plot of $\log K$ against $\frac{1}{T}$ gives a straight line. The slope of such line gives the value of $\frac{E}{2.303R}$ from which E is evaluated. The intercept of the line would also enable one to find out the value of the frequency factor A .

Suppose K_1 and K_2 are the velocity constants in the two opposite directions of a reversible process at temperature T .



$$\ln K_1 = -\frac{E_1}{RT} + \ln A_1 \text{ (Constant)}$$

and $\ln K_2 = -\frac{E_2}{RT} + \ln A_2 \text{ (Constant)}$

Subtracting, $\ln \frac{K_1}{K_2} = \frac{(E_2 - E_1)}{RT} + \ln \frac{A_1}{A_2}$

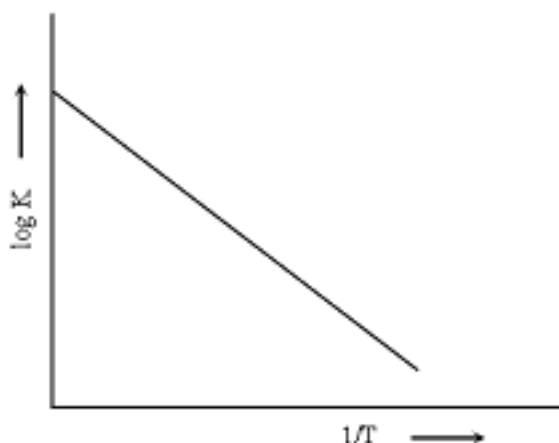


Figure 1.4: Plot of log K against 1/T for a reaction

But $\frac{K_1}{K_2} = K$, equilibrium constant of the reaction.

$$\text{Hence } \ln K = \frac{E_2 - E_1}{RT} + \ln \frac{A_1}{A_2}$$

where E_1 and E_2 are the activation energies of the two opposite processes.

$$\text{Hence } \frac{d \ln K}{dT} = -\frac{(E_2 - E_1)}{RT^2}$$

$$= \frac{E_1 - E_2}{RT^2}$$

But from Vant Hoff equation $\frac{d \ln K}{dT} = \frac{\Delta H}{RT^2}$

where ΔH is the heat change of the chemical process. Comparing the two expressions we get, $\Delta H = E_1 - E_2$

Activation energy of a reaction: its significance

The average energy of the reactant is represented by E_A and that of the resultant by E_B . But if E_A is greater than E_B the reactant A will not be straight way transformed to the product B. There is a minimum energy level for the reaction denoted by E_X to which the reactant molecule must be raised in order to enable it to undergo the chemical change.

The excess or additional energy ($E_X - E_A$) which the reactant must acquire in order to

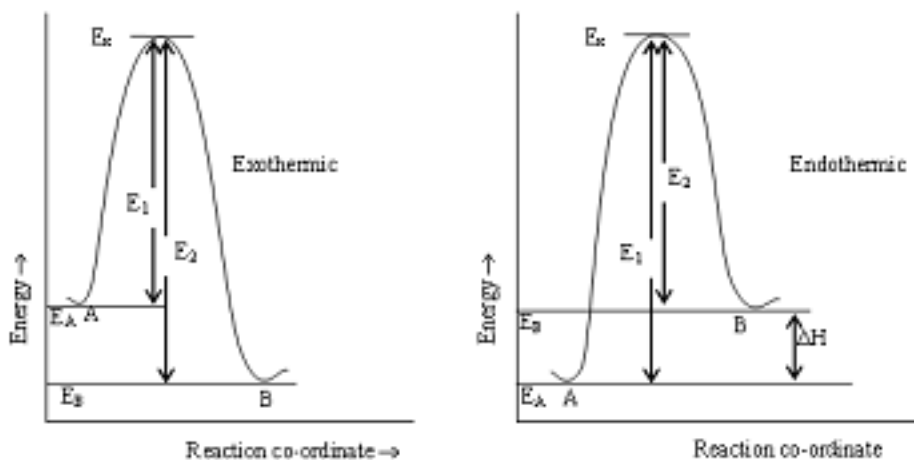


Figure 1.5: Potential energy profile of exothermic and endothermic reaction

undergo transformation is the activation energy E_1 .

Molecules, having energy E_X or above are said to be in **activated state** and such molecules only are fit for chemical reaction.

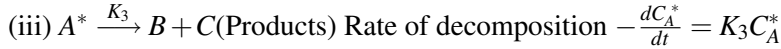
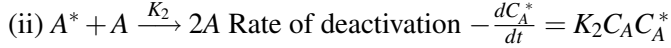
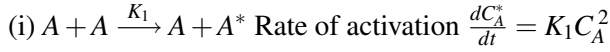
If $E_2 > E_1$, the reaction is evidently exothermic, whereas if $E_2 < E_1$, the reaction is endothermic.

1.11 Collision Theory

The collision theory explains the mechanism of bimolecular reactions, but with unimolecular reactions the theory apparently fails. In the unimolecular reactions which are also of the first order, only one molecule takes part in the reaction.

According to Lindemann hypothesis the molecules acquire activation energy through collisions, but the activated molecules decompose only after some time has elapsed after the collision. That is, there is a time lag between the moment of activation and the moment of decomposition. When this time lag is relatively large, there is every possibility for most of the activated molecules being deactivated by subsequent collisions to ordinary molecules. As a result, the rate of decomposition will not be proportional to all the activated molecules but only to a fraction which survives the time lag. The ac-

tivated molecules therefore disappears through two parallel processes, namely through deactivation and through decomposition.



where A represents ordinary and A^* activated molecules.

The rate of reaction of A is the rate at which products are formed

$$-\frac{dC_A}{dt} = \frac{dC_B}{dt} = K_3 C_A^*$$

Now, activated molecules are short lived and have a small concentration at any time during the process. So from the steady state principle, the rate of formation of A^* molecules and the rate of their disappearance would be the same

$$K_1 C_A^2 = K_2 C_A C_A^* + K_3 C_A^*$$

$$C_A^* = \frac{K_1 C_A^2}{K_2 C_A + K_3}$$

\therefore Rate of reaction, $-\frac{dC_A}{dt} = K_3 C_A^* = \frac{K_1 K_3 C_A^2}{(K_2 C_A + K_3)}$

Case 1: When rate of deactivation is very large compared with that of decomposition i.e. when $K_2 C_A \gg K_3$

$$-\frac{dC_A}{dt} = \frac{K_1 K_3}{K_2} C_A$$

$$-\frac{dC_A}{dt} = K' C_A$$

which is the expression for first order kinetics.

Case 2: When concentration C_A is lowered considerably, the chances of deactivation by collision decrease largely, then $K_3 \gg K_2 C_A$, hence we have,

$$-\frac{dC_A}{dt} = K_1 C_A^2$$

Thus at low concentration the process would follow second order kinetics.

1.12 Transition state theory

According to this theory, the two reactants say, AB and C first form a transition complex $A\text{---}B\text{---}C$ which then decomposes into A and BC.

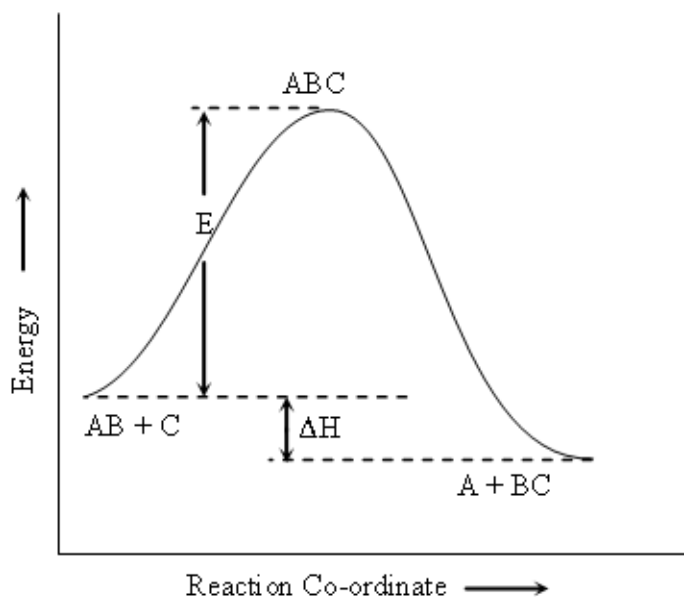


Figure 1.6: Potential energy profile of an exothermic reaction

The basic idea is that, we must somehow force C to come so close to B that B becomes undecided as to which atoms it now belongs to. This state of indecision as to B, being simultaneously attached both to A and C, though somehow loosely than before, is the transition state, also called the activated complex. The energy necessary to push C to approach B to form this transition state or activated complex is the energy of activation. The observed rate of reaction would be equal to the net rate of formation of the activated complex.

SKILL TEST

1. What is activation energy?
2. What is threshold energy?
3. Draw the energy profile diagram of an exothermic reaction and label the activation energy for the forward and reverse direction and enthalpy of the forward and reverse reaction.
4. How does such a curve change with the addition of a catalyst?

Review Questions

1. What is rate of a reaction? What is its unit?

Answer:

The rate of reaction i.e. the velocity of a reaction is the amount of a chemical change occurring per unit time.

The rate is generally expressed as the decrease in concentration of a reactant or as the increase in concentration of the product. If C is the concentration of a reactant at any time t , the rate is $-\frac{dC}{dt}$ or if the concentration of a product be x at any time t , the rate would be $\frac{dx}{dt}$.

The unit of reaction rate is moles/litre/second.

2. What is rate constant? What is the unit of rate constant for n th order reaction?

Answer:

Let us consider a reaction,



where X is the reactant and Y the product. The rate of the reaction will be directly proportional to the concentration i.e.,

$$(1.14) \quad \frac{dc}{dt} = KC$$

in which C is the concentration of the reactant at any time t and K is a constant, called the velocity constant or specific reaction rate.

In general, the units of K for a reaction of n th order would be given by,

$$\frac{\text{moles/litre/sec}}{(\text{moles/litre})^n} = \text{litre}^{n-1} \text{ moles}^{1-n} \text{ sec}^{-1}$$

3. What is order of a reaction? Give an example of fractional order reaction.

Answer:

The order is the number of concentration terms on which reaction rates depends. If several reactants A, B, C,etc are involved and it is observed experimentally that the rate of the process is given by,

$$-\frac{dc}{dt} = KC_A^\alpha C_B^\beta C_C^\gamma \dots\dots$$

Then the order of the reaction would be $n = \alpha + \beta + \gamma + \dots\dots$

The reaction is said to be α th order with respect to A, β th order with respect to B etc.

Order is experimentally determined quantity. It may have whole number, zero and even fractional value.

The example of fractional order reaction is ortho – para hydrogen conversion, its rate is expressed by $-\frac{d[H_2]}{dt} = K C_{H_2}^{3/2}$.

4. What is molecularity of a reaction?

Answer:

The molecularity of a reaction is defined as the number of molecules or atoms which take part in the process of a chemical change.

The reaction is said to be **unimolecular**, **bimolecular**, **termolecular** according to one, two, or three molecules are involved in the process of a chemical change.

5. What is the difference between order and molecularity of a chemical reaction?

Answer:

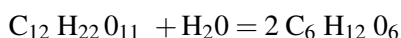
Order of reaction	Molecularity of reaction
1. It is experimentally determined quantity.	1. It is theoretical concept.
2. It is obtained from the rate of the overall reaction.	2. It is calculated on the basis of the rate determining step.
3. It may have whole number, zero and even fractional value.	3. It is always a whole number.
4. It can not be obtained from balanced or stoichiometric equation.	4. It can be obtained from balanced equation of single reaction.
5. It is equal to the sum of the exponents of the molar concentration of the reactants in the rate equation.	5. It is equal to the minimum number of species (molecule, atom or ions) taking part in a single rate determining step of chemical reaction.
6. It does not give any information about the reaction mechanism, though it can give some suggestion.	6. It reveals some fundamental facts about the reaction mechanism.

6. What is pseudo unimolecular reaction? Show that the specific reaction rate of a pseudo unimolecular reaction follows first order kinetics.

Answer:

There are a number of reactions, which follow the first order kinetics though more than one kind of reactants are involved in the reaction. These types of reactions are called pseudo unimolecular reaction.

The example of pseudo unimolecular reaction is the inversion of cane sugar.



A second order reaction, in which two reactants are different, is governed by the equation:

$$K = \frac{1}{t(a-b)} \ln \frac{b(a-x)}{a(b-x)}$$

If the concentration of one of the participants is very large compared to that of the other, say $b \gg a$, then $b-x \approx b$ and $a-b \approx -b$, which is practically constant.

Hence, the equation reduces to

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

$$\text{Or } K' = \frac{1}{t} \ln \frac{a}{(a-x)}$$

That is, under these circumstances, the reaction will follow first order kinetics.

7. A reaction is found to be zero order. Will its molecularity be zero?

Answer:

No, Molecularity of a reaction can not be zero.

8. Write down the Arrhenius equation. Explain the each term.

Answer:

Arrhenius (1889) showed that the velocity constant (K) of a chemical process increases exponentially with temperature for a large number of reactions. It was observed that the plot of $\log K$ against $\frac{1}{T}$ gives a linear relation.

He, therefore, suggested empirically the relation as

$$\frac{d \ln K}{dT} = \frac{E}{RT^2}$$

or $K = Ae^{-E/RT}$ (A = constant)

Where, K = the velocity constant or specific reaction rate.

E = the activation energy of the reaction.

A = the frequency factor or pre exponential factor.

T = the absolute temperature.

R = the universal gas constant.

Arrhenius equation may also be represented in logarithmic form as,

$$\log K = -\frac{E}{2.303R} \times \frac{1}{T} + \log A$$

9. Is a first order or a second order reaction completed?

Answer:

In a first order reaction $C = C_0 e^{-Kt}$, the reaction can not be complete because C would become zero at infinite time.

The rate equation of a second order reaction is $K = \frac{x}{at(a-x)}$ when $x = a, t = \infty$.

So a second order reaction also is not completed.

10. What is the special characteristic of a zero order reaction?

Answer:

The rate equation of a zero order reaction is $K = \frac{C_0 - C}{t}$, where C_0 is the initial concentration and C is the concentration at any time t .

When, $C = 0; t = \frac{C_0}{K}$, which is a finite quantity.

So, the zero order reaction will be completed and rate of the reaction is independent of the concentrations of the reactants.

Worked –Out Examples

- 1. At 25°C the half-life period for the decomposition of N_2O_5 is 5.7 hr. and is independent of the initial pressure of N_2O_5 . Calculate (a) the specific rate constant (b) the time required to go to 90% completion.**

Answer:

As half-life period is independent of initial i.e., concentration, so it is a first order reaction, whose half-life period

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

$$\text{or, } K = \frac{0.693}{t_{1/2}} = \frac{0.693}{5.7} \text{ hr}^{-1} = 0.1216 \text{ hr}^{-1}$$

$$\text{Here } K = \frac{1}{t} \ln \frac{a}{a-x}$$

When 90% completed $X = 0.9a$

$$\text{So } 0.1216 = \frac{1}{t} \ln \frac{a}{a-0.9a}$$

or, $t = 18.94 \text{ hr.}$

2. The catalytic decomposition of H_2O_2 is followed by removing equal volume samples at various time intervals and titrating them with KMnO_4 . The results are

Time (min)	0	5	10	20
MI. of	46.2	37.1	29.8	19.6
KMnO₄				

Find out the order and determine the half-life.

Answer:

Let us first see whether it is first order or not. For first order reaction

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

Since it is the reactant (H₂O₂) that reacts with KMnO₄, so volume of KMnO₄ required at any time is proportional to concentration of H₂O₂ present.

So initial volume $V_o \propto a$

and volume required at time 't' $V_t \propto (a - x)$

So, $K = \frac{1}{t} \ln \frac{V_o}{V_t}$; Here $V_o = 46.2$ ml.

Putting t = 5 mins.	Vt = 37.1 ml	K = 0.043 min ⁻¹
Putting t = 10 mins.	Vt = 29.1 ml	K = 0.046 min ⁻¹
Putting t = 20 mins.	Vt = 19.6 ml	K = 0.043 min ⁻¹

Since constant values are coming, given data fit well in the first order rate equation. Hence, the reaction is of first order with average rate constant = 0.044 min⁻¹

Hence $t_{1/2} = \frac{0.693}{0.044} = 15.75$ min.

- 3. At 25°C the specific rate constant for the hydrolysis of ethyl acetate by NaOH is 6.36 litre mole⁻¹ min⁻¹. Starting with concentrations of base and ester of 0.02 moles/litre, what proportion of ester will be hydrolysed in 10 min.**

Answer:

$K = 6.36 \text{ litre mole}^{-1} \text{ min}^{-1}$. Unit of K indicates that the reaction is second order. So

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

Given $6.36 = \frac{1}{10} \cdot \frac{x}{0.02(0.02-x)}$ or $X = 0.011 \text{ moles/litre}$

80% of ester hydrolyzed $\frac{0.011}{0.02} \times 100 = 55\%$.

- 4. At 378.5°C. the half-life period for the first order thermal decomposition of ethylene oxide is 363 min and the energy of activation of the reaction is 52,000 cal/mole. From these data estimate the time required for ethylene oxide to be 75% decomposed at 450°C.**

Answer:

If K_1 is rate constant at 378.5°C then as the reaction is first order, so

$$363 = \frac{0.693}{K_1}$$

or, $K_1 = 1.91 \times 10^{-3} \text{ min}^{-1}$

From Arrhenius equation if K_2 is rate constant at 450°C then

$$\ln \frac{K_2}{K_1} = \frac{E}{R} \cdot \frac{T_2 - T_1}{T_1 T_2} \quad \begin{array}{l} T_1 = 651.5^\circ\text{A} \\ T_2 = 723^\circ\text{A} \end{array}$$

$$\text{So, } \ln \frac{K_2}{1.91 \times 10^{-3}} = \frac{52,000}{1.987} \times \frac{71.5}{651.5 \times 723}$$

or, $K_2 = 0.101 \text{ min}^{-1}$

If at 450°C 75% i.e. $\frac{3}{4}$ th of initial amount decomposes in time 't' then as $K = \frac{1}{t} \ln \frac{a}{a-x}$

So, $0.101 = \frac{1}{t} \cdot \ln \frac{a}{\frac{1}{4}a}$ or, $t = 13.7$ mins.

So, 13.7 mins. will be required for 75% decomposition at 450°C .

5. The specific rate constant for the second order neutralization of nitropropane by a base is given by

$$\log K = 11.899 - \frac{3169}{T}$$

Where concentration is in moles litre⁻¹ and time in minutes. Initial concentration of both reactant is 0.005M. Calculate E and $t_{1/2}$ at 25°C .

Answer:

$$\text{Arrhenius equation is } \ln K = \ln A - \frac{E}{RT}$$

$$\text{or, } \log K = \log A - \frac{E}{2.303RT}$$

$$\text{Comparing } \log K = 11.899 - \frac{3163}{T} \text{ with it we get } \frac{E}{2.303R} = 3163$$

$$\text{or, } E = 2.303 \times 1.987 \times 3163 = 14.5 \text{ Kcal}$$

$$\text{At } 25^\circ\text{C } \log K = 11.899 - \frac{3163}{298} \text{ or, } K = 19.2 \text{ litre mole}^{-1} \text{ min}^{-1}$$

$$\text{So } t_{1/2} = \frac{1}{Ka} = \frac{1}{19.2 \times 0.005} = 10.4 \text{ min.}$$

- 6. The activation energy of a gas reaction is 30 Kcal / mole in the temperature range 0° to 60°C . Calculate the approximate temperature co-efficient of the reaction.**

Answer:

The ratio $\frac{K_{35^\circ\text{C}}}{K_{25^\circ\text{C}}}$ is approximate temperature co-efficient.

$$\text{From Arrhenius equation } \ln \frac{K_{35^\circ\text{C}}}{K_{25^\circ\text{C}}} = \frac{30 \times 10^3}{1.987} \cdot \frac{308 - 298}{308 \times 298}$$

$$\text{So, } \frac{K_{35^\circ\text{C}}}{K_{25^\circ\text{C}}} = 5.18$$

- 7. A certain first order reaction is 20% complete in 15 minute at 20°C . How long will it take to complete 40% of the reaction at 40°C ? [The energy of activation = 23.03 K StateplaceCal / mole].**

Answer:

From the given data rate constant at 20°C is

$$K_{20^{\circ}\text{C}} = \frac{1}{15} \ln \frac{a}{a - 0.2a} = 0.015 \text{ min}^{-1}$$

From Arrhenius equation $\ln \frac{K_{40^{\circ}\text{C}}}{0.015} = \frac{23030}{1.987} \times \frac{20}{313 \times 293}$

or, $K_{40^{\circ}\text{C}} = 0.188 \text{ min}^{-1}$

If 't' is the time for 40% completion at 40°C then

$$0.188 = \frac{1}{t} \ln \frac{a}{a - 0.4a}$$

or, $t = 2.72 \text{ mins}$

8. The rate of decomposition of a gas was 7.25 in some unit when 5% had reacted and it was 5.14 in the same unit when 20% had undergone decomposition. Calculate the order.

Answer:

$$\text{Rate } r = K.C^n \quad [n = \text{order}]$$

If C_0 is initial concentration, then during 5% reaction $C = 0.95 C_0$ and during 20% reaction $C = 0.80 C_0$.

$$\text{Hence } 7.25 = K (0.95 C_0)^n$$

$$\text{and } 5.14 = K (0.80 C_0)^n$$

$$\text{or, } \frac{7.25}{5.14} = \left(\frac{0.95}{0.80}\right)^n$$

$$\text{or, } 1.4105 = (1.18)^n$$

$$\text{or, } n = \frac{\log 1.4105}{\log 1.18} = 2$$

Hence it is second order reaction.

Exercise

1. Deduce the expression for first order kinetics. Show that the time for half decomposition of a first order reaction is independent of the initial concentration of the reactant.
2. Deduce the expression for second order kinetics where the two reactants are same. Show that the time for half decomposition of a second order reaction is dependent on the initial concentration of the reactant.
3. What is pseudo unimolecular reaction? By taking an example show that the specific reaction rate of a pseudo unimolecular reaction follows first order kinetics.
4. What is homogeneous catalysis? Give an example of gas phase homogeneous catalyst. Show that for homogeneous catalysis the rate of reaction is dependent on catalyst concentration.
5. Write short notes on activation energy.
6. Deduce the expression for the rate of the bimolecular reaction by using collision theory. Under what condition the reaction will follow i) first order kinetics ii) second order kinetics.