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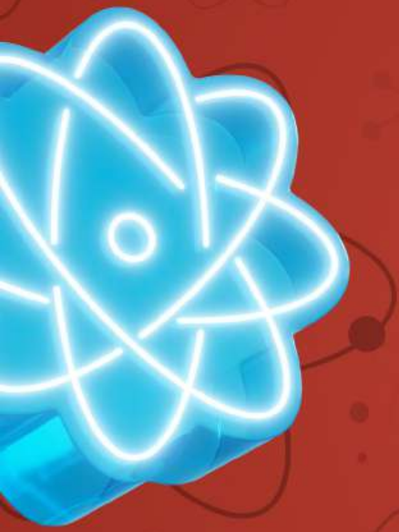
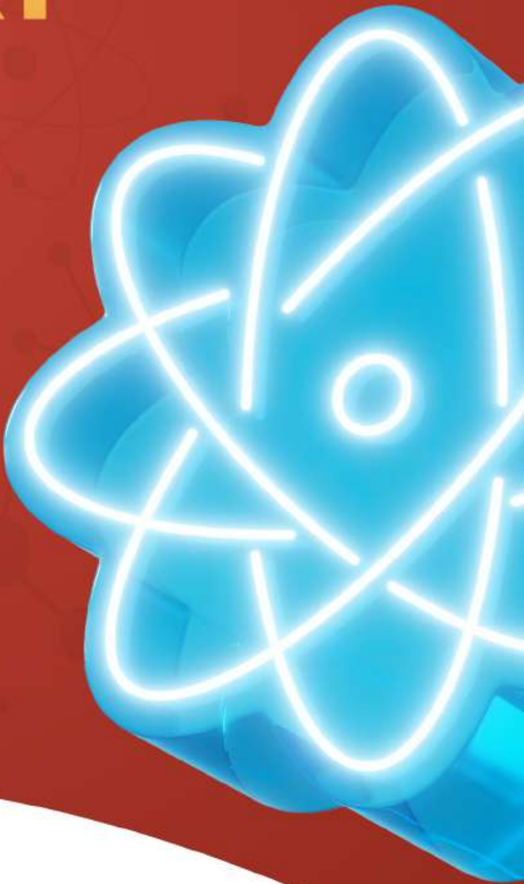


PHYSICAL CHEMISTRY

BOOK 3



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UNIT - V

PHYSICAL
CHEMISTRY

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SYLLABUS

Chemical kinetics:
Empirical rate laws and temperature dependence, Rate of reaction, order of a reaction, examples and rate equations for zero order, first order, second order and third order reaction. Molecularity of a reaction – unimolecular and bimolecular reaction, half-life period. Theories of reaction rates – collision theory, kinetics of collision theory, failure of collision theory, modification of collision theory, Lindeman theory, Hinshelwood theory and transition state theory/absolute reaction rate theory (ARRT). Potential energy surfaces and reaction coordinates. Study of complex reactions – kinetics of reversible, parallel, consecutive and chain reactions, photochemical reactions (H_2–Br_2), steady-state approximation, Stern–Volmer equation. Reactions in solutions – cage effect, primary and secondary salt effects, kinetic isotropic effect, linear free energy relationships, Hammett and Taft equation. Kinetic methods of analysis – flow techniques, stopped-flow and continuous-flow techniques, pulse methods, flash photolysis and pulse radiolysis. Relaxation theory and relaxation technique – kinetic of relaxation methods (T-jump and P-jump). Ionic liquids and its applications. Catalysis – homogeneous catalysis, acid-base catalysis, protolytic and prototropic mechanism, acidity function. enzyme catalysis – Michaelis-Menten kinetics, types of inhibitor in enzyme catalysis.

Electrochemistry:
Faraday's laws of electrolysis; specific, equivalent, and molar conductance, measurement of conductance. Variation of conductance with dilution for strong and weak electrolytes. Kohlrausch's law and its applications. Ostwald's dilution law, transport number and its determination by Hittorf method and moving boundary method. Debye-Huckel theory. Electrochemical cells – types of cells, galvanic cells, reversible and irreversible cells, electrode potential, oxidation potential, reduction potential, Nernst equation, redox systems.

Ion-ion interaction and activity coefficient – concept of ionic atmosphere, derivation of Debye-Huckel limiting law, verification and experimental validity. Ion transport in solution – electrolytic conductance, derivation of Debye-Huckel-Onsager equation and experimental validity, first and second Wien effect. Ion association – Bjerrum treatment of ion association, factors influencing ion association, effect of ion association on conductivity and activity coefficient of electrolytes in solution and triple ion formation.
Electrodics – electrode-electrolyte interface, electrical double layer – Helmholtz-Perrin, Gouy-Chapman and stern models and its comparison. Electrocapillary phenomena and electrocapillary curves, Lippmann equation, electrocapillary maximum, electrokinetic phenomena, Zeta potential and its applications. Electrode kinetics Bulter-Volmer equation for one-step electron transfer, high field approximation, Tafel equation, high and low over potential limits, ionic equilibria, conductometric and potentiometric titrations. Electrochemical energy systems – primary and secondary cells, fuel cells, types of fuel cells, batteries – primary and secondary batteries, lead acid storage battery, liquid lithium-ion batteries, solid-state sodium-ion batteries.

Solid state: Classification of solids, isotropic and anisotropic crystals, unit cell and space lattice, Miller indices for lattice planes, crystal structures, diffraction of X-rays by crystals, Bragg's law and its applications. Defects of crystals and band structure of solids.

Polymer chemistry: Polymerization – types of polymerization, mechanism of free radical, anionic and cationic polymerization. Polymers molecular weigh determination. Preparation, properties, uses of thermoplastic and thermosetting polymers. Elastomers, vulcanization and molding methods of polymers.

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1. 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 is the concentration of a reactant at any time t is, the rate is dC/dt or if the concentration of a product be x at any time t, the rate would be 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.

The Rate Law and the Rate Constant

The rate of the reaction A→ Products, is experimentally found to be given by

$$r = kc_{\mathrm{A}}$$

where k is the rate constant or the velocity constant of the reaction at the given temperature. If concentration of A is unity, i.e., $c_{\mathrm{A}} = 1$, then, evidently, $r = k$. For a general reaction of the type:

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

the rate of the reaction is given by the rate-law expression

$$r = kc_{\mathrm{A}}^{a} c_{\mathrm{B}}^{b} c_{\mathrm{C}}^{c}$$

If $c_{\mathrm{A}} = c_{\mathrm{B}} = c_{\mathrm{C}} = 1$, then $k = r$. Thus, the rate constant of a reaction, in general "k" is defined as the rate of the reaction when the concentration of each reactant is unity.

The Order of a Reaction.

In the study of chemical kinetics, reactions are generally classified in terms of their 'order'. We may define the order of a reaction as the sum of the powers to which the concentration (or pressure) terms are raised in the rate-law expression.

Thus, a reaction is said to be of the

first order if its rate is given by the expression of the type : $r = k_1 c_{\mathrm{A}}$;

second order if the rate is given by the expression of the type : $r = k_2 c_A^2$ or $r = k_2 c_A c_{\mathrm{B}}$;

third order if the rate is given by the expression of the type: $r = k_3 c_{\mathrm{A}}^3$ or $r = k_3 c_{\mathrm{A}}^2 c_{\mathrm{B}}$ or $r = k_3 c_{\mathrm{A}} c_{\mathrm{B}}^2$ or $r = k_3 c_{\mathrm{A}} c_{\mathrm{B}} c_{\mathrm{C}}$ and so on.

For a zero-order reaction, the rate equation is written as $r = k_0$. It is to be noted that the order of a reaction is essentially an experimental quantity. Thus, the order of the general reaction given above may or may not be numerically equal to $a + b + c$.

The concentrations of the various species involved in a reaction such as $c_{\mathrm{A}}, c_{\mathrm{B}}, c_{\mathrm{L}}, c_{\mathrm{M}}$ etc., can, also be expressed as [A], [B], [L], [M], etc.

The units of the rate constant for the n th-order reaction are given by $(\mathrm{dm}^3)^{\mathrm{n}-1}\ \mathrm{mol}^{1-n}\ \mathrm{s}^{-1}$.

(i) $n = 0$, the units are $\mathrm{dm}^{-3}\ \mathrm{mol\,s}^{-1}$

(ii) $n = 1/2$, the units are $(\mathrm{dm}^3)^{-1/2}\ \mathrm{mol}^{1/2}\ \mathrm{s}^{-1}$

(iii) $n = 1$, the units are s^{-1}

(iv) $n = 3/2$, the units are $(\mathrm{dm}^3)^{1/2}\ \mathrm{mol}^{-1/2}\ \mathrm{s}^{-1}$

(v) $n = 2$, the units are $\mathrm{dm}^3\ \mathrm{mol}^{-1}\ \mathrm{s}^{-1}$

(vi) $n = 5/2$, the units are $(\mathrm{dm}^3)^{3/2}\ \mathrm{mol}^{-3/2}\ \mathrm{s}^{-1}$

(vii) $n = 3$, the units are $\mathrm{dm}^6\ \mathrm{mol}^{-2}\ \mathrm{s}^{-1}$

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.

$H_2 + Cl_2 \xrightarrow{hv} 2\ HCl + 188\ kJ$

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.

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

$$\text{Rate } = KC_{HI}^2$$

$$\text{Rate } = KC_{HI}^2$$

and the hydrogen - iodine reaction

$$H_2 + I_2 \longrightarrow 2HI$$

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

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 $A, B, C, \ldots$….etc are involved and it is observed experimentally that the rate of the process is given by,

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

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

The reaction is said to be αth order with respect to A, βth 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

$$-\frac{d[H_2]}{dt} = KC_{H_2}^{3/2}$$

Molecularity of a Reaction

The molecularity of a reaction should not be confused with its order. Molecularity of a reaction is defined as the number of molecules involved in the step leading to the chemical 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. If only one molecule is involved, the reaction is said to be unimolecular. The example is the dissociation of nitrogen pentoxide : .

$$N_2O_5(g) \longrightarrow N_2O_4(g) + (1/2)O_2(g)$$

If two molecules are involved, the reaction is said to be bimolecular.

$$2HL(g) \longrightarrow H_2(g) + I_2(g)$$

Similarly, if three molecules are involved, the reaction is said to be trimolecular. The example is the oxidation of nitric oxide :

$$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$$

Order and Molecularity of Simple Reactions

From a study of the kinetics of a number of simple reactions, we conclude that their order is the same as their molecularity. Thus, the order of the reaction involving the decomposition of nitrogen pentoxide is 1 , that of the reaction involving the dissociation of hydrogen iodide is 2 and that of the reaction involving combination of nitric oxide and oxygen is 3 .

But, this is not always the case. In several reactions, the order is different from molecularity. This is particularly so when one of the reactants is present in large excess. The examples are hydrolysis of ethyl acetate and inversion of cane sugar in aqueous solutions:

$$\underset{\text{(large excess)}}{CH_3COOC_2H_5 + H_2O} \xrightarrow{H^+} CH_3COOH + C_2H_5OH$$

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + \underset{\text{(large excess)}}{H_2O} \xrightarrow{H^+} \underset{\text{Gulcose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

The molecularity of each reaction is 2 . The order of each reaction, however, is 1 since we know from experiment that the rate of the reaction varies directly as the concentration of ethyl acetate in the first case and that of sucrose in the second case. The reason is that water is present in such a large excess that its concentration (i.e., the number of moles per litre) remains almost constant in the course of the reaction in each case. The rate of the reaction, therefore, varies only with the concentration of the ester in the first case and that of sucrose in the second case. Such reactions are known as pseudo-monomolecular reactions.

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.

1.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

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

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

or, $dx = Kdt$

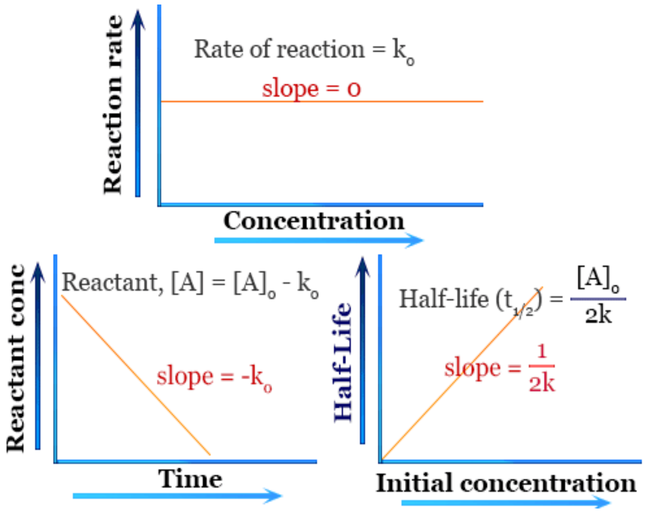
On integration, $\int dx = K \int dt$

or, $x = Kt + Z$ (Integration Constant).

When $t = 0, x = 0$ hence $Z = 0$ So, $x = Kt$

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 .



(Plot of concentration against t for a reaction)

$H_2 + Cl_2 \xrightarrow{hv} 2\,HCl$; The rate of this reaction does not depend on concentration.

2. First Order Kinetics

A reaction of the first order is represented as

$$X \longrightarrow Y$$

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

$$-\frac{dc}{dt} = KC$$

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.

$$\text{Thus } -\frac{dc}{C} = Kdt$$

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. $C=C_0$ 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

$$C = C_o e^{-Kt}$$

The concentration C therefore diminishes exponentially with time. We may also write

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

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

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

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

$$\frac{dx}{a-x} = Kdt$$

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

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

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

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

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

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

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

The fractional extent of the reaction at any time t is

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

When the initial concentration ais 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 timet t_1 and t_2, the corresponding concentrations of reactants would be $(a - x_1)$ and $(a - x_2)$. So

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

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

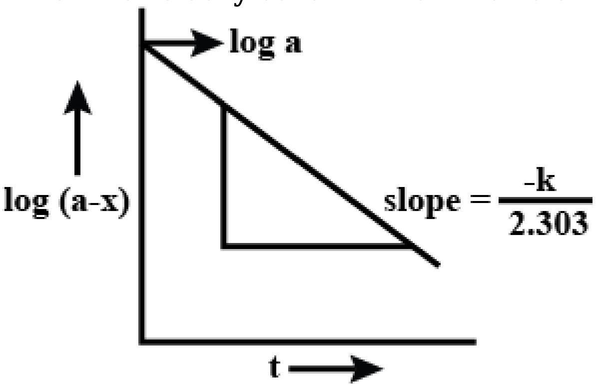
Characteristics

1 In a first order reaction $C = C_o e^{-KI}$, the reaction can not be complete because C would become zero at infinite time. The quantity $\frac{a}{(a-x)}$ or $\left(\frac{C_o}{C}\right)$ 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} :

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

$$\log(a-x) = -(K/2.303)t + \log a$$

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 $-\frac{K}{2.305}$ from which the velocity constant K can be determined.



(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 $x = \frac{a}{z}$. 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

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

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

3. 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 → 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

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

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

On integration,

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

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

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

Substituting the value of Z

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

Thus the velocity constant

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

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

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

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

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

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

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

On integration,

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

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

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

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

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

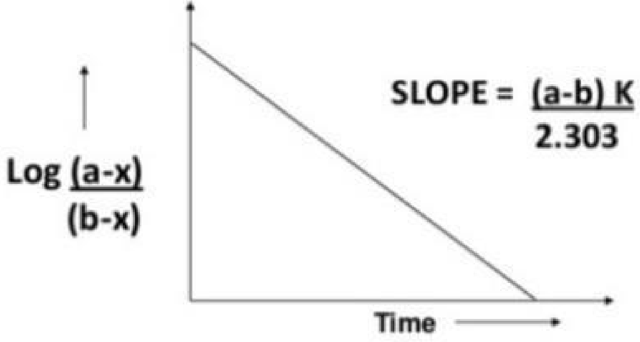
$$K = \frac{1}{t(a-b)} \ln \frac{b(a-x)}{a(b-x)}$$

It may also be written as

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

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.

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



(Plot of log b(a-x)/ a(b-x) against t for a reaction)

4. Third Order Reaction

Rate of change in concentration is proportional to three concentration terms However such reactions are there and their analysis is complex reaction of even higher order is unlikely to occur.

Rate equation of third order reaction is as follows:

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

Integration of Rate Expression for Third-Order Reactions

Let us consider a third-order reaction of the type

$$3\,\mathrm{A} \longrightarrow \mathrm{P}$$

Let a be the initial concentration of A and x the amount of A that has reacted at time t so that the amount of A remaining at time t is $a - x$. The differential rate equation is

$$r = \frac{dx}{dt} = k_3(a-x)^3$$

where k_3 is the third-order rate constant. Separatiag the variables and integrating, we get

$$\because \quad \therefore \int \frac{dx}{(a-\dot{x})^3} = \int k_3 dt = k_3 \int dt$$

or

$$\frac{1}{2(a-x)^2} = k_3 t + C$$

To determine the integration constant, C, we know that at $t = 0, x = 0$ so that $C = 1/2a^2$. Substituting in above equation, transposing and solving for k_3, we get

$$k_3 = \frac{1}{2t}\left[\frac{1}{(a-x)^2} - \frac{1}{a^2}\right] = \frac{1}{2t}\left[\frac{x(2a-x)}{a^2(a-x)^2}\right]$$

For the third-order reaction $2\,\mathrm{A} + \mathrm{B} \longrightarrow \mathbf{P}$, the differential rate equation is

$dx/dt = k_0(a-2x)^2(b-x)$.

Integrate this rate equation.

Solution :

$$\frac{dx}{dt} = k_3(a-2x)^2(b-x)$$

where a and b are the initial molar concentrations of A and B, respectively and x is the concentration of the product formed at time t so that at time t, the concentrations of A and B are $(a-2x)$ and $(a-x)$, respectively. Separating the variables in Eq. (i) and integrating, we get

$$\int \frac{d}{(a-2x)^2(b-x)} = k_3 \int dt = k_9 t + C$$

where C is the constant of imegration,

Resolving into partial fractions, we have

$$\frac{1}{(a-2x)^2(b-x)} = -\frac{2}{(2b-a)^2(a-2x)} + \frac{2}{(2b-a)(a-2x)^2} + \frac{1}{(2b-a)^2(b-x)}$$

Carrying out the integration of Eq. (iii), making use of the above partial fractions, we obtain

$$\begin{aligned}
\int \frac{dx}{(a-2x)^2(b-x)} &= -\frac{2}{(2b-a)^2}\int \frac{dx}{a-2x} + \frac{2}{(2b-a)}\int \frac{dx}{(a-2x)^2} + \frac{1}{(2b-a)^2}\int \frac{dx}{b-x} \\
&= -\frac{2}{(2b-a)^2}\left[-\frac{1}{2}\right]\ln(a-2x) - \frac{1}{(2b-a)^2}\ln(b-x) + \frac{2}{(2b-a)}\int \frac{1}{a-2x}\Bigg]\left[\frac{1}{2}\right] \\
&= \frac{1}{(2b-a)^2}\ln(a-2x) - \frac{1}{(2b-a)^2}\ln(b-x) + \frac{1}{(2b-a)}\left[\frac{1}{a-2x}\right] \\
&= \frac{1}{(2b-a)^2}\ln\left[\frac{a-2x}{b-x}\right] + \frac{1}{(2b-a)(a-2x)} = k_3 t + C
\end{aligned}$$

At $t = 0, x = 0$, so that from Eq. (iv),

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$$C = \frac{1}{(2b-a)^2}\ln(a/b) + \frac{1}{(2b-a)a}$$

Substituting for C in Eq. (iv) and transposing, we have

$$\frac{1}{(2b-a)^2}\left\{\ln\left[\frac{(a-2x))(b-x)}{a/b}\right] + (2b-a)\left[\frac{a-(a-2x)}{a(a-x)}\right]\right\} = k_3 t \quad (or)$$

$$\therefore\ \frac{1}{(2b-a)^2}\left[\ln\frac{b(a-2x)}{a(b-x)} + \frac{(2b-a)(2x)}{a(a-2x)}\right] = k_3 t$$

This is the desired integrated rate equation:

5.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.

$$C_{12}H_{22}0_{11} + H_20 = 2C_6H_{12}0_6$$

$$CH_3COOC_2H_5 + H_2O = CH_3COOH + C_2H_5OH$$

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. 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 reduces to

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

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.

$$-\frac{dc}{dt} = KC_{\text{sugar}}\,C_{H_20} = K^{/}C_{\text{sugar}}$$

Thus these reactions follow first order kinetics. This type of reaction is known as pseudo unimolecular reaction. Specific reaction rate First order reaction $K = \left(-\frac{dc}{dt}\right)\Big|\ C$. Hence dimension of K is $\frac{\text{molespor lìreper sec}}{\text{moles per lüre}} = \sec^{-1}$

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

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

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

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

6.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

$$S + C \underset{K_2}{\overset{K_1}{\rightleftharpoons}} \times \xrightarrow{K_3} P + C$$

Kinetics

The rate of reaction = rate of formation of the product

$$\frac{dC_p}{dt} = K_3 C_X$$

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

$$C_X = \frac{K_1 C_S C_C}{K_2 + K_3}$$

Substituting the value of C_X in equation

$$\frac{dC_P}{dt} = \frac{K_3 K_1 C_s C_C}{(K_2 + K_3)}$$

$$= K_C C_S C_C$$

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.

Effect of Temperature on Reaction Rates

It is a common experience that increase of temperature has a marked effect on the rate of a chemical reaction. Temperature has a profound influence on the reaction velocity. The ratio of the rate constants of a reaction at two temperatures differing by 10°C is known as the temperature coefficient of the-reaction. In homogenous thermal reactions, for every ten degree rise in temperature, the velocity of reaction is doubled or trebled.

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

The temperatures usually selected for this purpose are 25° and 35°C. Thus,

$$\text{Temperature coefficient } = \frac{\text{Rate constant at } 35°\text{C}}{\text{Rate constant at } 25°\text{C}}$$

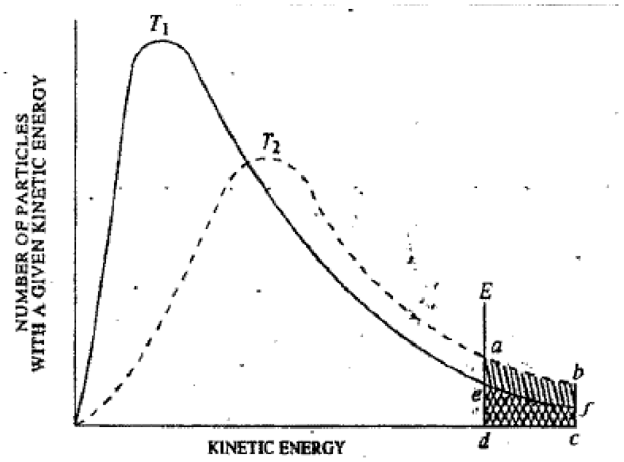
$$= \frac{k_{35}}{k_{25}}$$

The value of the temperature coefficient for most of the reactions is close to 2 and in some cases it approaches even 3.

Why such a small rise of temperature speeds up a reaction to such a large extent can be explained on the basis of the collision theory. According to this theory, for chemical reactions to occur, there must be collisions between the reactant molecules. However, most of the colisisons taking place between the molecules are ineffective. The important postulate of the collision theory is.

Arrhenius used the Maxwell's distribution of molecular energies to explain the temperature dependence of reaction rates.

As the temperature increases from T_1 to T_2, the energy distribution undergoes a change. There is a general shift in the distribution of energies as shown in the figure. Now there are more molecules on the high side of kinetic energy. The number of molecules whose energies are equal to or greater than the threshold energy E at temperature T_1 is represented by the shaded area efcd and at temperature T_2 by the shaded area $abcd$. As can be seen, the shaded area $abcd$ is nearly twice the shaded area efcd. This means that the number of molecules having energy equal to or greater than the threshold energy (whose collisions result in chemical reaction) becomes nearly double even with a small increase of temperature from T_1 to T_2. Consequently, the rate of reaction which depends upon the number of effective collisions, becomes almost double with a small increase of temperature.

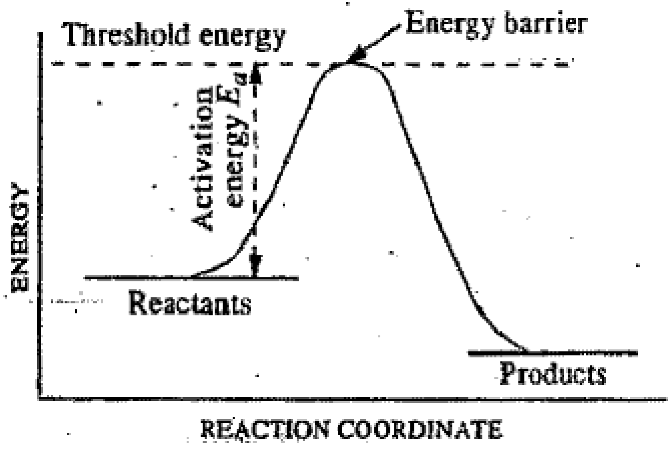


(Energy distribution in molecules at two different temperatures)

As discussed above, there is a certain minimum energy (threshold energy) which the colliding molecules must acquire before they are capable of reacting. Most of the molecules, however, have much less kinetic energy than the threshold energy. The excess energy that the reactant molecules having energy less than the threshold energy must acquire in order to react to yield products is known as activation energy. Thus,

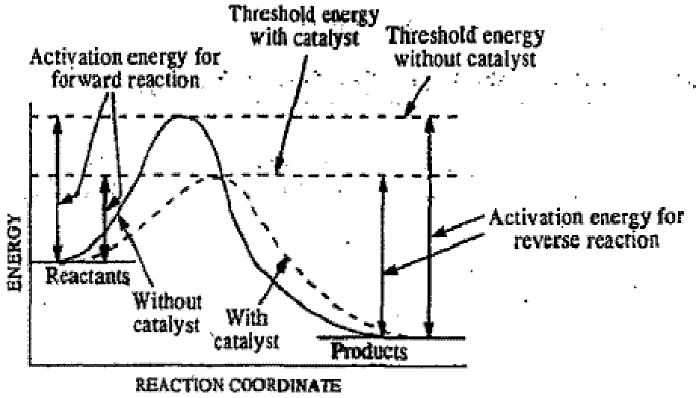
Activation Energy = Threshold energy - Energy actually possessed by molecules

It follows from the above discussion that there is an energy barrier placed between reactants and products. This barrier has to be crossed before reactants can yield products. This barrier determines the magnitude of threshold energy which reactant molecules must acquire before they can yield products.



Effect of a Catalyst.

A catalyst is a substance that can increase the rate of a reaction but which itself remains unchanged in amount and chemical composition at the end of the reaction. When a catalyst is added, a new. reaction path with a lower energy barrier is provided (cf. dotted curve). Since the energy barrier is reduced in magnitude, a larger number of molecules of the reactants can get over it. This increases the rate of the reaction.



A catalyst does not alter the position of equilibrium in a reversible reaction. It simply fastens the approach of the equilibrium by speeding up both the forward and the backward reactions.

Arrhenius Equation.

Arrhenius proposed the following empirical equation for calculating the energy of activation of a reaction having rate constant k at temperature T:

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

where E_a is called the Arrhenius activation energy and A is called the Arrhenius pre-exponential factor. Since the exponential factor is dimensionless, the pre-exponential factor A has the same units as the rate constant k. The units of k for a first-order reaction are s^{-1}, which is the unit of frequency. Hence, A is also called the frequency factor. E_a and A are called the Arrhenius parameters.

Taking logs of equation, we have

$$\ln k = -E_a(RT) + \ln A$$

From this, it is evident that a plot of ln k versus the reciprocal of absolute temperature ($1/\bar{T}$) gives a straight line with slope $= -E_a/R^r$ and intercept = ln A.

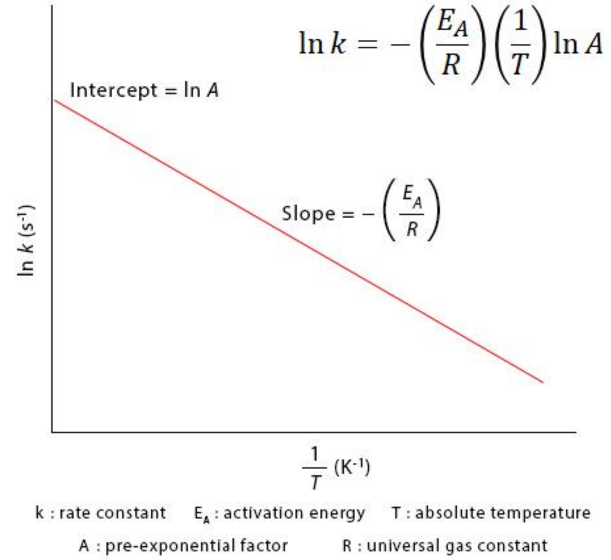
Differentiating Eq. with respect to temperature, we

$$d\ln k/dT = E_a/RT^2$$

Integrating it between temperatures T_1 and T_2 when the corresponding rate constants are k_1 and k_2, respectively and assuming that E_a is constant over this temperature range, we obtain

$$\ln\frac{k_2}{k_1}=\frac{E_a}{R}\left[\frac{T_2-T_1}{T_1T_2}\right]$$

This is the integrated Arrhenius equation. Thus, knowing the rate constants at two different temperatures, the energy of activation E_a can be readily determined.

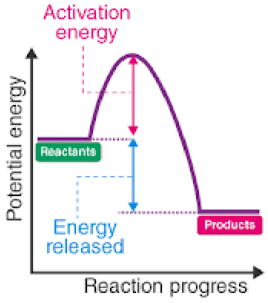


Activation energy of a reaction: its significance

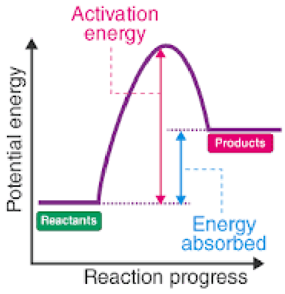
The average energy of the reactant is represented by E_A and that of the resultant by E_B. But if E_A is greater than E_B the reactant A will not be straight way transformed to the product B. There is a minimum energy level for the reaction denoted by E_x to which the reactant molecule must be raised 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 undergo transformation is the activation energy E_1.

Molecules, having energy EX 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, where as if $E_2 < E_1$, the reaction is endothermic.



Exothermic Reaction



Endothermic Reaction

Half-Life Time of a Reaction

In order to characterize the rate at which a chemical reaction may proceed, it is customary to introduce a convenient parameter called the half-life time of the reaction. It is defined as the time required for the reaction to be half completed and is denoted by the symbol, $t_{1/2}$. It can be related to the corresponding rate constant.

1. $t_{1/2}$ for a First-Order Reaction. It follows that at $x=a/2, t=t_{1/2}$. Hence,

$$k_1=\frac{1}{t_{1/2}}\ln\frac{a}{a-(a/2)}=\frac{1}{t_{1/2}}\ln\ 2=\frac{0.693}{t_{1/2}}$$

Thus,

$$t_{1/2}=0.693/k_1$$

2. $t_{1/2}$ for a Second-Order Reaction. From Eq. 25, we see that at $x=a/2, t=t_{12}$. Hence,

$$k_2=\frac{1}{t_{1/2}}\left[\frac{a/2}{a(a-a/2)}\right]=\frac{1}{t_{1/2}}\times\frac{a/2}{a(a/2)}=\frac{1}{at_{1/2}}$$

Thus,

$$t_{1/2}=1/(k_2a)$$

The $t_{1/2}$ of a second-order reaction is inversely proportional to the initial concentration of the reactant and this, it does not remain constant as the reaction proceeds.

3. $t_{1/2}$ for an n th-Order Reaction.

In general, for an n th-order reaction,

n A ⟶ Products,

$$r=d[\mathrm{A}]/dt=k_n[\mathrm{A}]^n,$$

It has been shown in Example 26, that

$$t_{1/2}=\frac{2^{n-1}-1}{k_n(n-1)a_0^{n-1}}$$

where a_0 is the initial concentration of A and k_n is the n th-order rate constant.

From equation, $t_{1/2}\propto 1/a_0^{n-1}$

For a first-order reaction $(n = 1), t_{1/2}$ is independent of a_0, for a second-order reaction $(n = 2), t_{1/2} \propto 1/a_0$, for a third-order reaction $(n = 3), t_{1/2} \propto 1/(a_0)^2$, and so on.

4.Expression for the half-life of an nth-order reaction where $n \geq 2$.

An nth-order reaction may be represented as

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

The differential rate equation is

$$-\alpha[A]'dt = k_n[A]^n$$

where k_n is the ath-order rate constant. Separating the variables and integrating, we obtain

$$\int -\frac{d[A]}{[A]^*} = k_n \int dt$$

or

$$t = \frac{1}{k_n(n-1)(A)^{n-1}} + C$$

where C is the constant of integration which we bave to determine. Let $[A] = a$ and $[A]_0 = a_0$, the initial concenuraion. Then, Equation can be written as

$$t = \frac{1}{k_n(n-1)n^{n-1}} + c$$

At $t = 0, a = a_0$, so that $C = \frac{1}{k_\pi(n-\eta)a_0^{n-1}}$

Substituting for C in equation, we get

$$t = \frac{1}{k_n(n-1)}\left[\frac{1}{a^{n-1}} - \frac{1}{a_0^{n-1}}\right]$$

When $t = t_{1/2}, a = a_0/2$ so that from equation,

$$t_{12} = \frac{1}{k_n(n-1)}\left[\frac{1}{(a_0/2)^{n-1}} - \frac{1}{a_0^{n-1}}\right]$$

or

$$\left(1/2 = \frac{2^{n-1} - 1}{k_n(n-1)k_0^{n-1}}\right)$$

which is the desired expression. This expression shows that for an nth-order reaction,

$t_1/\propto (1/a_0)^{n-1}$ where n ≥ 2.

Theories of Reaction Rates

Absolute Reaction Rate Theory (ARRT) of Bimolecular Reactions

Absolute Reaction Rate Theory (ARRT) provides an approach to explain the temperature and concentration dependence of the rate law. The colliding molecules must have sufficient energy to overcome a potential energy barrier to react.

Principles

There is a thermodynamic equilibrium between the transition state and the state of reactants at the top of energy barrier/activation energy barrier. The rate of chemical reaction is proportional to the concentration of the particles in a high-energy. transition state leading to the formation of activated complex. So this theory is also called as Transition state theory or Activated -complex theory. It takes enormous amount of free energy (G) to achieve the transition state, so the state is a high energy substance. The energy difference between the reactants and the potential energy maximum is referred to as activation energy

The bimolecular reaction

$$A + B \xrightarrow{k} C$$

$$v = \frac{d(C)}{dt} = k \cdot [A][B]$$

is considered by 'transition state theory'.

According to the transition state model, the reactants are getting over into an unsteady intermediate state on the reaction pathway.

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} AB^\ddagger \xrightarrow{k_2} C$$

Reaction Coordinates

There is an- 'energy barrier' on the pathway between the reactants (A, B) and the product (C). The barrier determines a 'threshold energy' or minimum of energy necessary to permit the reaction to occur.

An 'activated complex 'AB' or 'transition state' is formed at the potential energy maximum. The high-energy complex represents an unstable molecular arrangement, in which bonds break and form to generate the product C or to degenerate back to the reactants A and B. Once the energy barrier is surmounted, the reaction proceeds downhill to the product.

There is a thermodynamic equilibrium between the transition state and the state of reactants at the top of the energy barrier. The rate of chemical reaction is proportional to the concentration of the reactants in the high energy transition state. The reaction process can be divided into two stages:

(i) A direct step downhill from the transition state to the product.

(ii) The equilibrium between the reactants and the transition state.

The change in the concentration of the complex $AB^\ddagger$. over time can be described by the following equation,

$$\frac{d[AB^\ddagger]}{dt} = k_1[A][B] - k_{-1}[AB^\ddagger] - k_2[AB^\ddagger]$$

Due to the equilibrium between the 'activated complex' AB ' and the reactants A and B, the components $k_1[A][B]$ and $\mathrm{k}_1[AB^\ddagger])$ cancel out. Thus the rate of the direct reaction is proportional to the concentration of AB :

$$\frac{d(C)}{dt} = -\frac{d[AB^\ddagger]}{dt} = \mathrm{k}^2.[AB^\ddagger]$$

k_2 is given by statistical mechanics:

$$k_2 = \frac{k_BT}{h}$$

k_B = Boltzmann's constant $[1.381 \times 10^{-23}\ \mathrm{J\ K^{-1}}]$

T = Absolute temperature in degrees Kelvin (K)

h = Plank constant $[6.626 \times 10^{-34}$ Js]

$\mathbf{k}_2$ is called 'universal constant for a transition state' ($\sim 6 \times 10^{-12}\mathrm{sec}^{-1}$ at room temperature).

Additionally, $[\mathrm{AB}^\dagger]$ can be derived from the quasi stationary equilibrium between AB‡ and A, B by applying the mass action law.

$$[\mathrm{AB}^\ddagger] = K^\ddagger[A][B]$$

$K^\ddagger$ = Thermodynamic equilibrium constaint

Due to the equilibrium that will be reached rapidly, the reactants and the activated complex decrease at the same rate. Then

$$-\frac{d[AB^\ddagger]}{dt} = \frac{k_BT}{h}K^\ddagger[A][B]$$

Comparing the derived rate law and the expression yields for the rate constant of the overall reaction

$$k = \frac{k_BT}{h}K^\ddagger$$

Additionally, thermodynamics gives a further description of the equilibrium constant:

$$\Delta G^\ddagger = -RT\ln\ K^\ddagger$$

Furthermore ΔG^t is given by

$$\Delta G^\ddagger = \Delta H^\ddagger - \mathrm{T}\cdot\Delta\ \mathrm{S}^\ddagger$$

R = Universal Gas Constant $= 8.3145\ \mathrm{J/mol}K$

$\Delta G^\ddagger$ = free activation enthalpy $[\mathrm{kJ\ mol^{-1}}]$

$\Delta S^\ddagger$ = activation entropy $[\mathrm{J\ mol^{-1}\ K^{-1}}]$

$\Delta H^\ddagger$ = activation enthalpy $[\mathrm{kJ\ mol^{-1}}]$

$\Delta H^\ddagger$ is the enthalpy difference between the transition state of a reaction and the ground state of the reactants. It is called activation enthalpy. S is for the entropy, the extent of randomness or disorder in a system. The difference between the entropy of the transition state and the sum of the entropies of the reactants is called activation entropy $\Delta S^\ddagger$.

$\Delta G^\ddagger$ is the free activation enthalpy (Gibb's free energy). According to equation given above $\Delta G^\ddagger$ is equal to the change in enthalpy $\Delta\mathrm{H}^\ddagger$ minus the product of temperature T (which is in Kelvin) and the change in entropy $\Delta\mathrm{S}^\ddagger$ of the system $\Delta G^\ddagger$ represents the determining driving power for a reaction. The sign of ΔG determmes if a reaction is spontaneous or not.

The higher the amount of negative activation entropy is, the higher the free enthalpy of activation. Combining the above equations and solving for ln k yields:

$$\ln\ \mathrm{K}^\ddagger = \frac{\Delta H^\ddagger}{RT} + \frac{\Delta S^\ddagger}{R}$$

The Eyring equation is

$$k = \frac{k_BT}{h} \times e^{-\frac{\Delta H^\ddagger}{RT}} \times e^{\frac{\Delta s^\ddagger}{R}}$$

The Hard-Sphere and Simple Collision Theory

This is the earliest theory of reaction rates. Since the reaction between two species takes place only when they are in contact, it is reasonable to suppose that the reaction species must colloid before they react. The simplest model of a bimolecular reaction is one in which the two molecules are pictured as hard spheres that do not interact at all until they collide. When they collide, if they have sufficient energy (either kinetic energy along the line of centers, or total energy, or energy in certain degrees of freedom, depending on the exact flavor of theory being used) they are assumed to react. If they have less energy, they do not react. So, we will calculate the reaction rate as

Rate = (collision rate) × (Fraction of collisions with sufficient energy to react)

The non-reactive collisions are assumed to be elastic - that is, both the total momentum and total kinetic energy are unchanged in the collision. An elastic collision is what we observe when macroscopic hard spheres (billiard balls or bocce balls or bowling balls or marbles) collide. In an inelastic collision (which could be reactive or non-reactive) the total kinetic energy changes during the collision.

Momentum is conserved in any isolated collision.

A simplified derivation of the collision frequency is as follows:

From the kinetic theory of gases, the number of bimolecular collisions per sec per cm^{-3}. Among molecules of one species is given by

From the kinetic theory of gases, the number of bimolecular collisions per sec per cm^{-3}. Among molecules of one species is given by

$$\mathbf{Z = 2n^2\ d^2(8\Delta kT/\mu)^{1/2}}$$

For reactions involving two different gases A and B, the rate of bimolecular reactions between unlike molecules is given by

$$Z_{AB} = n_A n_B (d_{an})^2 (8\Delta kT/\mu)^{1/2}$$

Where, n_A and n_B are numbers of A and B molecules, respectively, d_{av} is average collision diameter defined as $(dA + dB/2)$ and μ is the reduced mass defined as

$\mu = (m_A\ m_B)/(m_A + m_B)$.

The collision number Z_{AB} is given, in terms of molar masses M_A and M_B of the two gases, the expression

$$Z_{AB} = n_A n_B (d_{av})^2 \left[\frac{M_A + M_B)8\prod\ RT}{M_A M_B}\right]^{1/2}$$

The activation energy E_a in the Arrhenius equation is thus identified with the- relative kinetic energy E along the line of centres of two colhdmg molecues which is required to cause the reaction between them.

The collision theory is applicable to simple gaseous reaction. For reactions between complicated molecules, the observed rate is found to be much smaller than the theoretically predicted rate, some tunes by a factor of 10^5 for reactions involving fairly complicated molecules. The discrepancy is explained by the fact that the colliding molecules are treated as a hard sphere having no internal energy.

Again, the spherical model ignores the dependence of the effectiveness of collisions on the relative orientation of the colliding molecules. Also, the activation energy has been treated as though it were related entirely to translational motion, ignoring the effect of rotational and vibrational motion. For this reason, the collision theory is applicable to only to reactions between very simple gaseous molecules. The collision theory can be generalized by introducing so called steric factor, p, into the equation for the bimolecular rate constant in order to take account for the orientational requirement. Accordingly,

$$\mathrm{k}_2 = \mathrm{p}A_e{}^{-\mathrm{Ea/RT}}$$

The steric factor is supposed to be equal to the fraction of molecular collisions in which the molecules A and B posses the relative orientation necessary for the reaction. However, the steric factor cannot be reliably calculated. Perhaps its introduction oversimplifies the actual situation.

Using collision theory, the Arrhenius pre-exponential factor for unlike molecules is given by

$$A = (2.75 \times 10^{29})p(d_{av})^2 \left[\frac{T(M_A + M_B)}{M_A M_B}\right]^{1/2}$$

and for like molecules it is given by

$$A = (3.89 \times 1029)pd^2 \left(\frac{T}{M}\right)^{1/2}$$

In these equations, the molar mass is in units of gram/mole and the units of A are dm^3/mole/sec.

Application of ARRT to Unimolecular Reactions

Lindemann/Lindemann-Hinshelwood Theory

This is the simplest theory of unimolecular reaction rates, and was the first to successfully explain the observed first-order kinetics of many unimolecular reactions. The proposed mechanism actually consists of a second order bimolecular collisional activation stop, followed by a rate-determining unimolecular step.

$$A + M \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A^* + M$$

$$A^* \overset{k_2}{\rightarrow} P$$

Applying the steady-state approximation to the concentration of A* gives

$$[A^*] = \frac{k_1[A][M]}{k_{-1}[M] + k_2}$$

$$\frac{d[P]}{dT} = k_2[A^*] = \frac{k_1 k_2[A][M]}{k_{-1}[M] + k_2}$$

This is often written as

$$\frac{d[P]}{dT} = k_{eff}[A]$$

where

$$k_{eff} = \frac{k_1 k_2[M]}{k_{-1}[M] + k_2}$$

is an effective first-order rate constant, k_{off} is, of course, a function of pressure. At high pressures, collisional deactivation of A^* is more likely than unimolecular reaction, k_{cff} reduces to $k_1 k_2 / k_{-1}$ and the reaction is truly first order in A. At low pressures, bimolecular excitation is the rate determining step; once formed A* is more likely to react than be collisionally deactivted. The rate constant reduces to $k_{eff} = k_1[\text{M}]$ and the reaction is second order.

Lindemann Theory Breaks Down for Two Main Reasons

(i) The bimolecular step takes no account of the energy dependence of activation; the internal degrees of freedom of the molecule are completely neglected, and the theory consequently underestimates the rate of activation.

(ii) The unimolecular step fails to take into account that a unimolecular reaction specifically involves one particular form of molecular motion (e.g. rotation around a double bond for cis-trans isomerization).

Subsequent theories of unimolecular reactions have attempted to address these problems. Hinshelwood theory offers a solution to problem.

Hinshelwood Theory

Hinshelwood modelled the internal modes of A by a hypothetical molecule having s equivalent simple harmonic oscillators of frequency n and using statistical methods to determine the probability of the molecule being collisionally activated to a reactive state. The number of ways of distributing a given number of quanta, v, among the s oscillators (i.e. the number of degenerate states of the system at an energy (v + ½)h) is

$$g_v = \frac{(v + s - 1)!}{v!\,(s - 1)!}$$

a handwavy explanation of where this comes from is that $(v + s - 1)$! is the number of permutations of all the quanta and all the harmonic oscillators. This has to be divided by the number of ways in which the quanta can be pennuted amongst themselves, $v!$, and the number of ways the oscillators can be permuted amongst themselves, ($s - 1$)! The fraction of molecules in state v is given by the Boltzmann distribution.

$$\frac{n_v}{N} = \frac{gve^{-vin/kT}}{q} \text{ where } q = \left(\frac{1}{1 - e^{-hu/kT}}\right)^3$$

Hinshelwood now made the strong collision assumption. He assumed that the probability of deactivation of A^* in any given collision is unity, so that the rate constant $k - 1$ of the Lindemann mechanism is equal to the collision frequency Z. Because the collisions promote equilibrium, the probability of forming a state v in a collision is given by the Boltzmann distribution. The rate constant for activation to state v is therefore given by

$$k_1^v = Z\frac{gv^{E^{-vin/kT}}}{q}$$

The overall rate of activation (i.e. rate of formation of collisionally excited A^* with enough energy to react) is found by summing the $\text{k}_1{}^{v}$ over all the energy levels which can dissociate i.e. all levels with an energy greater than the critical energy E_0 which the molecule needs to react. If the vibrational quantum number of the state with energy E_0 is m, we have

$$k_1 = \sum_{m}^{\infty} Z\frac{gv^{-kmv/kT}}{q}$$

The energies involved are usually large, with $E_0 \gg$ hn. Hinshelwood developed equations for the case in which the energy levels can be assumed to be continuous ($kT \gg hn$). The expression then becomes

$$dk_1 = Z\frac{N(E)e^{-E/k\tau}dE}{q}$$

where $N(E)$ is the density of states; $N(E)dE$ is therefore the number of energy levels with energy between E and $E + dE$, and dk_1 is the rate constant for activation into this energy range. The total rate of activation is found by integrating dk_1 over all energies greater than the critical energy.

$$k_1 = \frac{X}{(s-1)!}\left(\frac{E_0}{kT}\right)^{s-1} \exp\left(-E_d/kT\right)$$

This differs from the simple collision theory rate constant, $k_2 = Z\exp\left(-E_0\right) kT$, by a factor of

$$\frac{1}{(s-1)!}\left(\frac{E_0}{kT}\right)^{s-1}$$

leading to an increased theoretical value of k_1. The increase is more pronounced for large molecules, which have more oscillators, and is exactly what is required to overcome the first failure of the Lindemann theory.

RRK Theory

A minimum amount of energy must be localised in specific modes of molecular motion in order for the unimolecular step to take place. A new step is added to the Lindemann mechanism, in which the generally excited molecule A* is converted into the specifically excited 'activated complex' $A^{\ddagger}$.

$$A^* \overset{k_{2a}}{\rightarrow} A^{\ddagger} \overset{k^{\ddagger}}{\rightarrow} P$$

k^* is of the order of a vibrational frequency, and k_{22} is generally much smaller. This means that conversion of A^* to $A^{\dagger}$ is rate determining, and k_{2a} is the overall rate coefficient for conversion of A* to products. Because $k_{2a} \ll k^*, (A^{\dagger}]$ is very small and we can use the steady state approximation to find k_{2a}, giving

$$k_{2a} = k^{\ddagger}\frac{[A^{\ddagger}]}{[A^*]}$$

RRK theory assumes that energy can flow freely from one vibrational mode to another within the molecule (this is a fairly reasonable assumption, since molecular vibrations are highly anharmonic at chemical energies and are therefore coupled). As before in the discussion of the Hinshelwood theory, for a molecule with s equivalent oscillators, the degeneracy of the 5th vibrational level is

$$\frac{(v+s-1)!}{v!\,(s-1)!}$$

If we have to locate at least m quanta in one particular mode for dissociation to occur (i.e., $E_0 = mh$?), this simply reduces our choice of quanta to $(v-m)$, and the total number of ways of arranging these is

$$\frac{(v-m+s-1)!}{(v-m)!\,(s-1)!}$$

The probability $P_m v$ of locating at least m quanta out of v in the dissociation mode is the ratio of these two quantities.

$$= \frac{(v-m+s-1)!}{(v-m)!\,(s-1)!}\frac{v!\,(s-1)!}{(v+s-1)!}$$

$$= \frac{(v-m+s-1)!\,v!}{(v-m)!\,(v+s-1)!}$$

Because the quantum numbers involved are very large (i.e., v and m are $\gg$s) we have

$$\frac{(v-m+s-1)!}{(v-m)!}$$

$$\rightarrow (v-m)s-1 \text{ and } \frac{v!}{(v+s-1)!}$$

$$\rightarrow v-(s-1)$$

So that

$$Pm^v = (v-m)s - 1\mathrm{v}^{-(s-1)}\left(\frac{v-m}{v}\right)^{s-1}$$

$$= (1-m/v)s-1$$

Since $E = vhf$ and $E_0 = mhf$, this expression can be rewritten in terms of energies.

$$P_{E_0}^{E} = (1-E_0/E)^{s-1}$$

$P_{E_0}^{E}$ is the probability of locating a minimum amount of energy E_0 out of the total energy E in the dissociation mode. If energy randomization takes place rapidly enough for the vibrational energy to be distributed statistically, then

$$\frac{[A^{\ddagger}]E}{[A^*]E} = P_{E_0}^{E}, \text{ and the rate constant is } k_2(E)$$

$$= k^{\ddagger}(1-E_0/E)^{s-1}$$

k_2 increases with energy, since the probability of localising a given amount of energy E_0 in one particular mode increases as E increases. The localisation probability decreases as a increases since there are more modes to spread the energy across. Consequently, k_2 becomes smaller as the molecule becomes more complex, in contrast to the behaviour of the rate constant for activation k_1.

RRKM Theory

Based on the results of Hinshelwood and RRK theory, the reaction mechanism can be rewritten to take account of the fact that the rates of collisional activation and unimolecular dissociation are energy dependent.

$$A + M \frac{dk_1(E)}{k_{-1}} A^*(E) + M$$

$$A^*(E) \overset{k_2(E)}{\rightarrow} P$$

Applying the steady state approximation to $[A^*(E)]$ leads to the rate expresion

$$\frac{d[P(E)]}{dt} = \frac{k_2(E)dk_1(E)[A][M]}{k_{-1}[M] + k_2(E)}$$

from which we can identify the unimolecular rate coefficient for the energy range from E to $E + dE$ as

$$k(E) = \frac{k_2(E)dk_1(E)[M]}{k_{-1}[M] + k_2(E)}$$

The thermal rate coefficient is obtained by integrating over E from E_0 to a

$$k = \int_{E_0}^{\alpha} \frac{k_2(E)dk_1(E)(M)}{k_1[M] + k_2(E)}$$

$$= \int_{E_0}^{\alpha} \frac{k_2(E)dk_1(E)[M]}{k_{-1}(1 + k_2(E)/k_{-1}[M]}$$

In RRKM theory, the energy of the molecule is partitioned into fixed and non-fixed components. Only the nonfixed component E^*, which can flow freely around the various modes of motion of the molecule, can contribute to reaction. The various terms of the rate expression are now evaluated using statistical mechanics.

(i) $dk_1(E^*)/k_{-1}$ is the equilibrium constant for energization of the A molecules into the energy rante E^* to $E^* + dE^*$, and can be calculated from the partition function ratio

$$QA^*(E^*)/QA$$

(ii) $k_2(E^*)$ is obtained by applying the steady state treatment to the activated complex $A^\ddagger$ as in RRK theory, with the modification that the overall reaction is broken down into energy, contributions from translation and from rotation/vibration. The rate constant $k^\ddagger$ and ratio of concentrations $[A^\ddagger]/[A^*]$ are evaluated using partition functions ($k^\ddagger$ is treated as a translation along the reaction coordinate).

In the high pressure limit, RRKM theory reduces to transition state theory. In the general case, RRKM theory admits equilibrium between A^* and $A^\ddagger$, but not between A^* and A . However, at high pressures A^* and A are also in equilibrium. Transition state theory assumes that the activated complex $A^\ddagger$ is in thermal equilibrium with the rectants. This is equivalent to assuming that the thermal Boltzmann distribution is maintained at all energies, which is true at sufficiently high pressures ⇒ at high pressures the RRKM model becomes the same as the transition state theory model, and the results of the two theories coincide.

Slater Theory

As opposed to statistical theories with energy flow between the vibrations, Slater proposed a dynamic theory without energy flow. Vibrations are required to be simple harmonic, which does not allow energy flow between modes, but when different modes come in to phase, the vibrational amplitude is changed. For suitable phase relationships the vibrational amplitude may be extending beyond the critical length corresponding to the reaction.

Slater provided a classical treatment in 1939 and later a quantum mechanical derivation. The mathematical treatment is again complex but the variation of K_{uni} with [A] can be calculated. The number of vibrational modes that may contribute to the critical reaction coordinate is selected to give the best fit with the experimental data, and the result is approximately half the maximum possible modes of vibration.

Under high pressure conditions, the rate constant Ka may be expressed as

$$k_{\propto\kappa} = \nu\exp(-\epsilon^*/\kappa T)$$

Kinetics of Third Order Reactions

A chemical reaction said to be third order if its rate depends on three concentration terms. In general, a third order reaction may be represented as,

I. 3A → Products

II. 2 A + B → Products

III. A + B + C → Products

Type-1: Now consider a Type I in which initial concentration of all three reacting molecules is the same

3A → Products

Suppose a is the initial concentration of each reactant in gram mole/I. Suppose x is the concentration change of the time t. Then, the concentration of A at time t is $(a-x)$ gram moles/I. According to the law of mass action, the rate of such reactions at time t given by

$$\frac{dx}{dt}\alpha(a-x)(a-x)(a-x) \text{ or } \frac{dx}{dt}=k_2(a-x)^2$$

In integrating Equation, we obtain

$$\frac{1}{2(a-x)^2}=k_3+t+\mathrm{I}_3$$

Where I_3 is know as constant of integration. Its value is determined from the initital conditions of the experiment i.e., when $t=0, x=0$; Equation takes the form

$$I_3=\frac{1}{2a^2}$$

Substituting the value of I_3 in the Equation, we obtain

$$\frac{1}{2(a-x)^2} = k_3t\frac{1}{2a^2}$$

$$k_3 = \frac{1}{2t}\left[\frac{1}{(a-x)_2}-\frac{1}{a^2}\right]$$

The above equation is known as the **kinetic equation of the third order reaction** when the concentration of the three reactant is the same. Equation can be simplified as

$$k_3=\frac{1}{2t}\left(\frac{x(2a-x)}{a^2(a-x)^2}\right)$$

Type II: We will now consider Type II in which two reactants are equal and the third one is different.

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

Suppose a and b are the initial concentration of A and B respectively. Suppose x is the change of concentration after the time t from the commencement. Then the rate of the reaction is given be

$$\frac{dx}{dt}=k_3(a-2x)^2(b-x)$$

Where the amount of A decomposed at any instant in is $2x$ which is twice that of B i.e., on separating the variables and integrating the Equation, we obtain

$$k_3=\frac{1}{t(a-2b)^2}\left(\frac{2x(2b-a)}{a(a-2x)}+1n\frac{b(a-2x)}{a(b-x)}\right)$$

Again, Equation is known as the **kinetic equation for a third order reaction.**

Type III: The last case, is

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

Suppose, a, b and c are the initial concretions of A, B and C respectively. Suppose, x is the concentration change after time t from the commencement. Then, the rate of the reaction is given by

$$\frac{dx}{dt} = k_3(a-x)(b-x)(c-x)$$

$$\frac{dx}{(a-x)(b-x)(c-x)} = k_3dt$$

Integrating it, we obtain

$$k_3=\frac{1}{t}\frac{(b-c)\ln\frac{a-x}{a}+(c-a)\ln\frac{b-x}{b}+(a-b)\ln\frac{c-x}{c}}{(b-c)(a-b)(c-a)}$$

Examples of Third Order Reaction

1 **Gaseous Reactions**: There only five gaseous reactions of the third order. Each of these reactions involves the nitric oxide as one of the reactants. These reactions are

2 (a) $2NO + Cl_2 \rightarrow 2NOCl$

(b) $2NO + Br_2 \rightarrow 2NOBr$

(c) $2NO + O_2 \rightarrow 2NO_2$

(d) $2NO + H_2 \rightarrow N_2O + H_2O$

(e) $2NO + D_2 \rightarrow N_2O + D_2O$

3 **Reaction in Solution**: Noise and Cottle showed that the reduction of $FeCl_3$ by $SnCl_2$ was of the third order.

$$2FeCl_3 + SnCl_2 \rightarrow 2FeCl_2 + SnCl_4$$

They studied this reaction by mixing equal quantities of $SnCl_2$ and $FeCJ_3$ solution in flask which was kept in a thermostat. They with drew equal volumes of reaction mixture at regular intervals of time. The excess of $SnCl_2$ was removed by adding $HgCl_2$ to it and the $FeCl_2$ was estimated by titrating it against $K_2Cr_2O_7$ solution. It has been now proved that the reaction is of the second order only.

3. The reaction between potassium oxalate and mercuric chloride is of 3rd order:

$2HgCl_2 + K_2C_2O_4 \rightarrow 2KCl + 2CO_2 + Hg_2Cl_2$

3 Potential Energy Surfaces (Hyper Surfaces)

Much of the microscopic theory of chemical kinetics depends on the idea of a potential energy surface (often called a potential energy hyper surface, because it usually involves more than 3 dimensions). These are based on the Born-Oppenheimer approximation of quantum mechanics. This approximation states that, because the atomic nuclei are thousands of times heavier than the electrons, we can separate the motion of the electrons from that of the nuclei. The nuclear motion is much, much slower then the motion of the electrons, so we can assume that the electron cloud responds instantaneously to any changes in the nuclear position. For now, we will consider only the ground electronic state of a molecule - the one in which the electrons occupy the orbitals of lowest energy.

An assembly of N atomic nuclei has 3N degrees of freedom - each of the N molecules can move in 3 dimensions. We could describe the system using 3 Cartesian coordinates for each atom. However, if 'the state of the system only depends on the arrangement of the atoms relative to each other, then 6 of these degrees of freedom can be eliminated (5 for a linear molecule). That is because three degrees of freedom correspond to overall translation of the whole system (in 3 dimensions) and three degrees of freedom (2 for a linear molecule) correspond to overall rotation of the whole system. Translating or rotating the whole molecule does not change the relative positions of the atoms (the distance between any pair of atoms).

In the absence of any imposed fields (magnetic, electrical, etc.) the position and orientation of a molecule will not affect its energy.

4 Simple Interatomic Potentials

The potential energy surface for a molecule or a reaction is a description of the total ei1ergy of the atoms involved (all of the nuclei and all of the electrons) as a function of the positions of. the nuclei. A chemical reaction can be described in detail as motion of the atoms on this potential energy surface. We Saddle point will begin by considering the potential energy surface for a system of 2 atoms (a diatomic molecule if they form a chemical bond). The energy of this system depends on (3N–5) = 1 degree of freedom - the distance between the atoms.

The potential energy is denoted as V (or V(r), where r is the distance between the atoms) then the force acting on atom.

For some types of interaction, particularly electrostatic interactions among only two particles, we know what the interaction potential looks like: Ion-ion interaction: Ion-dipole interaction: And others for all the various combinations that we can think of - dipole-dipole, dipole-induced dipole, etc. The interaction potentials listed above (except for the interaction between charged particles of the same sign) are attractive potentials. For these, the potential keeps decreasing with decreasing r all the way until r = 0, where V = –8. Of course, this cannot really be the case, or everything around us would collapse into a single, very dense point. So, any realistic interaction potential must include a repulsive term (V increasing with decreasing r for sufficiently small r), and this term must doh1inate at very si1ort interparticle distances. For molecules, this term results from the Pauli exclusion principle that you learned about in chemistry. It says that multiple electrons cannot occupy the same region of space - doing so is quantum mechanically forbidden (there is a 'strictly enforced' maximum of two electrons per orbital). Of course, the electrons also repel each other through electrostatic interactions, but that is a smaller effect.

5 Kinetic Isotopic Effect

The term kinetic isotopic effect relates to changes in the rate of reaction. Isotopic effects are small if the isotopic substitution is far from the seat tab reaction. If the bond involving the substituted ~tom is broken or formed during the reaction the effects are much greater. The effect of changing the atom connected by the bond is referred as primary kinetic isotopic effect. Otherwise it is described as secondary effect. Isotopic effects being influenced solely by the atomic masses or greatest when there is a large relative change in the masses. The effects are usually large when an ordinary hydrogen atom (H) is replaced by deuterium (D) or Tritium (T),

the relative masses then approximately 1:2:3. Replacement of C^{12} and C^{13} is a much small effect. Since, the ratio is only 12: 13. The kinetic isotope effects are dealt by Bigeleisen on the basis of conventional transition state theory.

When an atom is replaced by an isotope there is no change in classical potential energy surfaces, but, there are changes in vibrational frequencies and therefore, in zero point energies. At relatively low temperatures H_2 and D_2 molecules are largely at their zero point levels. Thus, as far as the initial state of reaction is concern a hydrogen molecule having 7.6k J $mole^{-1}$ more zero point energy, will tend to react more rapidly and its reaction will tend to have a higher equilibrium constants. In general and simplified semi classical discussion of kinetic isotopic effect in hydrogen atom transfers processes is given. Consider the abstraction reaction

$$\mathrm{R-H+R' \rightarrow (R \ldots . H \ldots R)^{\ddagger} \rightarrow R+H-R'}$$

$$\mathrm{R-D+R' \rightarrow (R \ldots . D \ldots . R)^{\ddagger} \rightarrow R+D-R'}$$

The situation is particularly simple Rand R ' much heavier than either H or D. The partition functions are for $\mathrm{R-H}$ and $\mathrm{R-D}$ and the practically the same, as or the partition functions for the activated complexes $\mathrm{(R \ldots . . H \ldots . . R')^{\ddagger}}$ & $\mathrm{(R\ldots\ D\ldots\ R')^{\ddagger}}$. Also, the relevant vibration frequencies in the activated complexes are almost same for the two atoms.

The asymmetric vibration frequencies are different for the two isotopic forms. The zero point energies are therefore much the same for H and D . Since, the partition function for the two isotopic forms are practically the same, is semi classical ratio $\mathrm{K_h^S/K_d^S}$ is determined almost entirely zero point energy difference in the initial state. Thus, it is given by

$$\mathrm{K_h^S/K_d^S = e^{-4.5}}k\ \mathrm{J\ mole\ -1/KRT}$$

The main assumptions made in the Urey-Bigeleisen --Meyer treatment are as follows:

1 Conventional transition state theory is valid

2 All vibrations are purely harmonic

3 Use can be made of the limiting high temperature expression for the transitional and rotational partition functions

4 The partition function for types of motion not appreciably affected by the isotopic substitution can be taken to cancel out entirely in the rate expression

5 Quantum mechanical tunnelling is neglected; i.e., the treatment is semi classical.

THEORIES OF REACTION RATES

There are two important theories of reaction rates. These are the collision theory developed by Arrhenius and van't Hoff and the modern transition state theory, also called the activated complex theory developed by Eyring, Polanyi and Evans in 1935.

Collision Theory of Bimolecular Gaseous Reactions

This is the earliest theory of reaction rates. Since reaction between two species takes place only when they are in contact, it is reasonable to suppose that the reactant species must collide before they react. Since our knowledge of molecular collisions is more complete for the gaseous phase than for the liquid phase (in the latter case we speak of encounters rather than collisions); we wilf restrict our discussion to bimolecular reactions in the gaseous phase.

From the kinetic theory of gases, the number of bimolecular collisions per second per cm^{-3} among. molecules of one species is given by

$$Z = 2n^2 d^2 (8\pi kT/\mu)^{12})$$

For a reaction involving two different gases A and B , the rate of bimolecular collisions between unlike molecules is given by .

$$Z_{AB} = n_A n_B (d_{2v})^2 \left(8\pi k I_\mu\right)^{1/2}$$

where n_A and n_B are numbers of A and B molecules, respectively, d_{av} is the average collision diameter defined as $(d_{\mathrm{A}}+d_{\mathrm{B}})/2$ and μ is the reduced mass defined as $\mu=(m_{\mathrm{A}}m_{\mathrm{B}})/(m_{\dot{A}}+m_{\mathrm{B}})$. The collision number Z_{AB} is given, in terms of molar masses M_{A} and M_{B} of the two gases, by the expression

$$Z_{\mathrm{AB}}=n_{\mathrm{A}}n_{\mathrm{B}}(d_{\mathrm{dv}})^{2}\left[\frac{(M_{\mathrm{A}}+M_{\mathrm{B}})8\pi RT}{M_{\mathrm{A}}M_{\mathrm{B}}}\right]^{1/2}$$

Let us calculate Z_{AB}. for the reaction between H_2 and I_2 at 700 K and 1 atm pressure, the quantities of the two gases being 1 mole each. Accordingly, $n_{\mathrm{H}_2}=n_{\mathrm{H}_2}\approx 10^{19}$ molecules cm^{-3}; $d_{\mathrm{H}_2}=2.2\text{Å}, d_{\mathrm{I}_2}=4.6\text{Å}$ so that $d_{\mathrm{av}}=3.4\text{Å}$. Hence, according to Eq. 47 ,

$$\begin{aligned} Z_{AB} &= (10^{19})^2(3.4\times10^{18})^2\left[\frac{(2+254)8\times3.14\times8.314\times10^{7}\times700}{2\times254}\right]^{1/2} \\ &= 10^{38}\times1\cdot16\times10^{-15}\times8.58\times10^{5}\approx10^{29}\text{ collisions s}^{-1}\text{ cm}^{-3} \end{aligned}$$

Since there are approximately 10^{29} collisions s^{-1} for 10^{19} molecules of each species, each molecule makes about 10^{10} collisions s^{-1} with the molecules of the other species. If each collision were to lead to a chemical reaction, then the whole reaction would have been completed in abouit $10^{-\ \ 10}$ s. However, this predicted rate of the reaction is in complete disagreement with the experimental rate. Hence, we conclude that all collisions do not result in chemical reaction.

In order for a reaction to occur, the energy of collision must equal or exceed the threshold energy. The effective energy is, of course, not the total kinetic energy of the two colliding molecules but is, instead, the kinetic energy corresponding to the component of the relative velocity of the two molecules along the line of their centres at the moment of collision. It is this energy with which the two molecules are pressed together.

The detailed analysis of the dynamics of bimolecular collisions leads to the result that the line of centres is greater than the threshold's energy is given by

$$Z_{AB}'=Z_{AB}e^{-E}/_{RT}$$

Assuming that Z_{AB}' gives the rate of relative collisions between A and B, we can write

$$\begin{aligned} -dn_{\mathrm{A}}/dt &= Z_{\mathrm{AB}}' \\ &= n_{\mathrm{A}}n_{\mathrm{B}}(d_{\mathrm{av}})^2\cdot\left[\frac{(M_{\mathrm{A}}+M_{\mathrm{B}})8\pi RT}{M_{\mathrm{A}}M_{\mathrm{B}}}\right]^{1/2}\mathrm{e}^{-E/RT}\text{ mol cm}^{-3}\cdot\ \mathrm{s}^{-1} \end{aligned}$$

Let us now proceed to obtain the theoretical expression for the rate constant. If the concentration is expressed in mol dm^{-3}, then

$$[\mathrm{A}]=10^3 n_{\mathrm{A}}/N_{\mathrm{A}} \text{ and } [\mathrm{B}]=10^3 n_{\mathrm{B}}/N_{\mathrm{A}}$$

where N_{A} is Avogadro's number. Hence, the rate law expression

$$-a[\mathrm{~A}]/dt=k_2[\mathrm{~A}][\mathrm{B}]$$

can be written as

$$-\frac{10^3 dn_{\mathrm{A}}}{N_{\mathrm{A}}^{dt}}=k_2\frac{10^6}{(N_{\mathrm{A}})^2}n_{\mathrm{A}}n_{\mathrm{B}}$$

Hence,

$$k_2=-\frac{N_{\mathrm{A}}}{10^3 n_{\mathrm{A}}n_{\mathrm{B}}}\times\frac{dn_{\mathrm{A}}}{dt}$$

Using equation for $-dn_{\mathrm{A}}/dt$, we have

$$k_2=\frac{N_{\mathrm{A}}(d_{3\mathrm{~V}})^2}{10^3}\left[\frac{(M_{\mathrm{A}}+M_{\mathrm{B}})8\pi RT_{\mathrm{A}}}{M_{\mathrm{A}}M_{\mathrm{B}}}\right]^{1/2}\cdot\mathrm{e}^{-E/RT}$$

Comparing equation with the Arrhenius equation $k_2=A\mathrm{e}^{-E_a/RT}$, we find that the Arrhenius pre-exponential factor is given by

$$A=\frac{N_{\mathrm{A}}(d_{\mathrm{av}})^2}{10^3}\left[\frac{(M_{\mathrm{A}}+M_{\mathrm{B}})8\pi RT}{M_{\mathrm{A}}M_{\mathrm{B}}}\right]^{1/2}$$

The activation energy E_a in the Arrhenius equation is thus identified with the relative kinetic energy E along the line of centres of the two colliding molecules which is required to cause a reaction between them.

Let us calculate A and k_2 for the $\mathrm{H}_2-\mathrm{I}_2$, reaction at 700 K. E_a has been found to be $167.4\mathrm{kJmol}^{-1}$. Substituting the various values in equation, A comes out to be $=6.0\times10^{11}\mathrm{dm}^3\ \mathrm{mol}^{-1}\mathrm{s}^{-1}$. Hence, from Arrhenius equation,

$$\begin{aligned} k_2 &= 6.0\times10^{11}\mathrm{dm}^3\ \mathrm{mol}^{-1}\ \mathrm{s}^{-1}\exp\left(-167400\ \mathrm{J\ mol}^{-1}\right. \\ &\qquad \left./8.314\ \mathrm{J\ K}^{-1}\ \mathrm{mol}^{-1}\times700\ \mathrm{K}\right) \\ &= 0.22\mathrm{dm}^3\ \mathrm{mol}^{-1}\ \mathrm{s}^{-1} \end{aligned}$$

which compares favourably with the experimental value of $0.064\mathrm{dm}^3\ \mathrm{mol}^{-1}\ \mathrm{s}^{-1}$, keeping in view the uncertainty in the values of the activation energy and the average collision diameter.

The collision theory is applicable to simple gaseous reactions. For reactions between complicated molecules, the observed rate is found to be much smaller than the theoretically predicted rate, sometimes by a factor of 10^3 for reactions involving fairly complicated molecules.

The discrepancy is explained by the fact that the colliding molecule is treated as a hard sphere having no internal energy. Again, the spherical model ignores the dependence of the effectiveness of a collision on the relative orientation of the colliding molecules. Also, the activation energy has been treated as though it were related entirely to translational motion, ignoring the effect of rotational and vibrational motion. For these reasons the collision theory is applicable only to reactions between very simple gaseous molecules.

The collision theory can be generalized by introducing the so-called steric factor, p, into the equation for the bimolecular rate constant in order to take account of the orientational requirement. Accordingly,

$$k_2 = pA\mathrm{e}^{-E_a/RT}$$

The steric factor is supposed to be equal to the fraction of molecular collisions in which the molecules A and B possess the relative orientations necessary for the reaction. However, the steric factor cannot be reliably calculated. Perhaps its introduction oversimplifies the actual situation.

Using collision theory, the Arrhenius pre-exponential factor for unlike molecules including the steric factor p is given by

$$A = (2.753 \times 10^{29})p(d_{\mathrm{av}})^2 \left[\frac{T(M_{\mathrm{A}} + M_{\mathrm{B}})}{M_{\mathrm{A}}M_{\mathrm{B}}}\right]^{1/2}$$

and for like molecules it is given by

$$A = (3.893 \times 10^{29})pd_{\mathrm{av}}^2 \left(\frac{T}{M}\right)^{1/2}$$

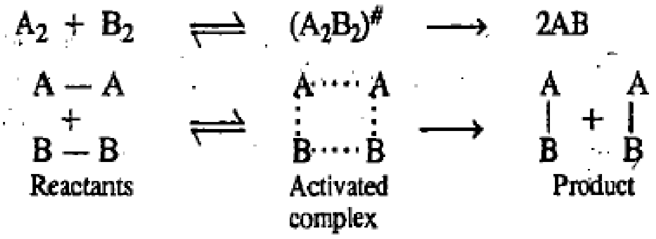
In these equations, the molar mass is in units of $\mathrm{g\,mol^{-1}}$ and the units of A are $\mathrm{dm^3\ mol^{-1}\ s^{-1}}$.

Activated Complex Theory (ACT) of Bimolecular Reactions

As a result of the development of quantum mechanics, another theoretical approach to chemical

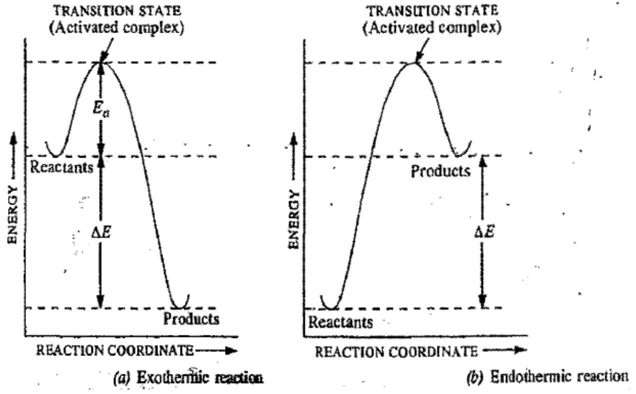
reaction· rates has been-developed which gives a deeper understanding of the reaction process. It is known as the absolute reaction rate theory (ARRT) or the transition state theory (TST) or, more commonly, as the activated complex theory (ACT), developed by Eyring, Polanyi and Evans in 1935.

According to ACT, the bimolecular reaction between two molecules A_2 and B_2 progresses through the formation of the so-called activated complex which then decomposes to yield the product AB, as illustrated below:



$$A_2 + B_2 \rightleftharpoons (A_2B_2)^{\#} \longrightarrow 2AB$$

The activated complex can be treated as a distinct chemical species in equilibrium with the reactants which then decompose into products. It is amenable to thermodynamic treatment, like any ordinary molecule. It is, however, a special molecule in which one vibrational degree of freedom has been converted to a translational degree of freedom along the reaction coordinate. The reaction coordinate shown as the abscissa in figure could be the bond length which charges in going from the reactants to the products. In other words, the reaction coordinate is. a measure of the progress of a reaction. It must be remembered that the activated complex is not merely an intermediate in the process of breaking or forming of chemical bonds. It is unstable because it is situated at the maximum of the potential energy barrier separating the products from the reactants. The difference between the energy of the activated complex and the energy of the reactants is the activation energy, E_a.



(a) Exothermic reaction (b) Endothermic reaction

For the thermodynamic formulation of the activated complex theory, consider a simple bimolecular reaction,

$$\mathrm{A}+\dot{\mathrm{B}} \overset{\kappa^{\#}}{\rightleftharpoons} (\mathrm{AB})^{\#} \overset{k_2}{\rightarrow} \text{ Products}$$

where $(AB)^{\#}$ is the activated complex and $K^{\#}$ is the equilibrium constant between the reactants and activated complex: As said above, in $(AB)^{\#}$ one of the vibrational degrees of freedom has become a translational degree of freedom. From classical mechanics, the energy of vibration is given by RT/N_{A} (or $k_{\mathrm{B}}T$ where k_{B} is the Boltzmann constant) whereas from quantum mechanics, it is given by $h\nu$ so that $h\nu = RT/N_{\mathrm{A}}$ or $\nu = RT/N_{\mathrm{A}}h = k_{\mathrm{B}}T/h$. The vibrational frequency ν is the rate at which the activated complex molecules move across the energy barrier. Thus, the rate constant k_2 can be identified with ν.

The reaction rate is given by

$$-d[\mathrm{A}]/dt = \kappa k_{[}[(\mathrm{AB})^{\#}] = \kappa(k_{\mathrm{B}}T/h)[(\mathrm{AB})^{\#}]$$

where the factor called the transmission coefficient is a measure of the probability that a molecule, once it passes over the barrier, will keep on going ahead and not return. The value of κ is taken to be unity, it is thas omitted from thie rate expression. The concentration of the activated complex, (AB), can be obtained by the equilibrium expression

$$K^{\#} = [(AB)^{\#}][A][B]$$

where

$$[(AB)^{\#}] = K^{\#}[A][B]$$

Substituting in equation, we obtain

$$-d[\mathrm{A}]/dt = (k_{\mathrm{B}}T/h)K^{\mu}[\mathrm{A}][\mathrm{B}]$$

Thus, the rate constant k_2 may be expressed as

$$k_2 = (k_{\mathrm{B}}T/h)\mathrm{K}^{\#}$$

The equilibrium constant K^{*} can be expressed in terms of $\left(\Delta\dot{G}^{\circ}\right)^{\#}$, called the standard Gibbs free energy of activation. Since for the activated complex, we can write

$$(\Delta G^{\circ})^{\#} = -RT\ln K^{\#} \text{ and } (\Delta G^{\circ})^{\#}$$
$$= (\Delta H^{\circ})^{\#} - T(\Delta S^{\circ})^{\#}$$

we obtain

$$K^{\#} = e^{-(\Delta G^{\mathrm{o}})^{\#}/RT} = e^{(\Delta S^{\circ})^{\#}/R}e^{-(\Delta H^{\circ})^{\#}/RT}$$

Hence, substituting in equation given above, we get

$$k_2 = (k_{\mathrm{B}}T/h)\mathrm{e}^{(\Delta S^{\circ})^{1/R}}\mathrm{e}^{-(\Delta H^{\circ})^{\#}/RT}$$

This is the well known **Eyring equation.** Here $(\Delta S^{\circ})^{\#}$ is the standard entropy of activation and $(\Delta H^{\circ})^{\#}$ is the standard enthalpy of activation. Although the application of the activated complex theory (ACT) to reactions in solution is quite complicated because of the participation of the solvent in the activated complex, fortunately, the Eyring equation holds for reactions in solution, too. The American chemist Henry Eyring (1901-1981) was a brilliant kineticist; however, he was not awarded the Nobel Prize in chemistry.

Taking logs of both sides of Equation and differentiating with respect to T, we obtain

$$d\ln k_2/dT = (\Delta H^{\circ})^{\#}/RT^2 + 1/T$$
$$= \{(\Delta H^{\circ})^{\#} + RT\}/RT^2$$

Also, from the Arrhenius equation,

$$d\ln k_2/dT = E_a/RT^2$$

Comparing equations above, we obtain

$$E_a = (\Delta H^{\circ})^{\#} + RT \text{ or } (\Delta H^{\circ})^{\#} = E_a - RT$$

Comparing Equation with Equation, we have

$$pA\mathrm{e}^{-E_a/RT} = \frac{k_{\mathrm{B}}T}{h}\mathrm{e}^{(\Delta S^{\circ})^{\ell}/RT}\mathrm{e}^{-(\Delta H^{\circ})^{t}RT}$$

If $(\Delta H^{\circ})^{\#} \approx E_a$, we can equate the exponential factors in Equation, obtaining

$$pA = (x_B T h)e^{(\Delta S^{\circ})^{\#}/RT}$$

For a first-order gaseous reaction, $p = 1$ and $A = 10^{10}\ \mathrm{s}^{-1}$. Also, at room temperature, $k_{\mathrm{B}}T/h = 10^{13}\ \mathrm{s}^{-1}$. Hence,

$$\mathrm{e}^{(\Delta S^{o})'/R} = 10^{10}\ \mathrm{s}^{-1}/10^{13}\ \mathrm{s}^{-1} = 10^{-3}$$
$$(\Delta S^{\circ})^{7} = -57.4\ \mathrm{J\ K}\ \mathrm{K}^{-1}\ \mathrm{mol}^{-1}.$$

If $p < 1$ (as in the case of complex molecules), $(\Delta S^{\circ})^{*}$ is lower than this value. Qualitatively, a negative value of entropy of activation corresponds to an increase in molecular order and a loss of excited degrees of freedom in the activated complex relative to the reactant molecules. A large negative value of $(\Delta S^{\circ})^{\#}$ corresponds to a highly ordered activated complex and this implies a small value of the steric factor. Finally, it may be remarked that for reactions involving simple molecules, the collision theory and ACT give identical results.

The first direct experimental evidence for the existence of the activated complex was obtained in 1989 by Ahmed Zewail (1946-) using femtosecond laser spectroscopy. A. Zewail, the Egyptian American chemist, was awarded the 1999 Chemistry Nobel Prize for his contributions to molecular reaction dynamics using femtosecond laser techniques.

Isotopic Effect: Introduction

A Potential Energy Surface (PES) describes the potential energy of a system, especially a collection of atoms, in terms of certain parameters, normally the positions of the atoms. The surface might define the energy as a function of one or more coordinates; if there is only one coordinate, the surface is called a potential energy curve or energy profile. It is helpful to use the analogy of a landscape: for a system with two degrees of freedom, for example, two bond lengths, the value of the energy is a function of two bond lengths. The Potential Energy Surface represents the concepts that each geometry, i.e., both external and internal of the atoms of the molecules in a chemical reaction is associated with it a unique potential energy. This creates a smooth energy landscape and chemistry can be viewed from a topology perspective, of particles evolving over valleys and passes. In physical organic chemistry, a Kinetic Isotope Effect (KIE) is the change in the reaction rate of a chemical reaction when one of the atoms in the reactants is replaced by one of its isotopes. Formally, it is the ratio of rate constants for the reactions involving the light (k_L) and the heavy (k_H) isotopically substituted reactants (isotopologues).

Potential Energy Surfaces

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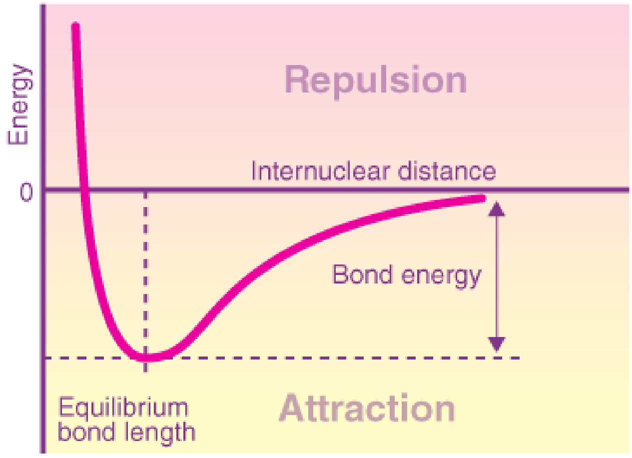
Potential Energy Curves (1-D Potential Energy Surfaces)

The PES is the energy of a molecule as a function of the positions of its nuclei r. This energy of a system of two atoms depends on the distance between them. At large distances the energy is zero, meaning no interaction. At distances of several atomic diameters attractive forces dominate, whereas at very close approaches the force is repulsive, causing the energy to rise. The attractive and repulsive effects are balanced at the minimum point in the curve. Plots that illustrate this relationship are quite useful in defining certain properties of a chemical bond.



(A Potential Energy Curve for a Covalent Bond)

The inter-nuclear distance at which the potential energy minimum occurs defines the bond length. This is more correctly known as the equilibrium bond length, because thermal motion causes the two atoms to vibrate about this distance. In general, the stronger the bond, the smaller will be the bond length. Attractive forces operate between all atoms, but unless the potential energy minimum is at least of the order of RT, the two atoms will not be able to withstand the disruptive influence of thermal energy long enough to result in an identifiable molecule. Thus we can say that a chemical bond exists between the two atoms in H_2. The weak attraction between argon atoms does not allow Ar_2 to exist as a molecule, but it does give rise to the van Der Waals force that holds argon atoms together in its liquid and solid forms.

Potential, Kinetic and Total Energy for a System

Potential energy and kinetic energy Quantum theory tells us that an electron in an atom possesses kinetic energy K as well as potential energy V, so the total energy E is always the sum of the two: $E=V+K$. The relation between them is surprisingly simple: $K=-0$. This means that when a chemical bond forms (an exothermic process with $\Delta E<0$), the decrease in potential energy is accompanied by an increase in the kinetic energy (embodied in the momentum of the bonding electrons), but the magnitude of the latter change is only half as much, so the change in potential energy always dominates. The bond energy ΔE has half the magnitude of the fall in potential energy.

The Dimensionality of a Potential Energy Surface

To define an atom's location in 3-dimensional space requires three coordinates (for example., x, y, and z or r, θ and ϕ in Cartesian and Spherical coordinates) or degrees of freedom. However, a reaction and hence the corresponding PESs do not depend of the absolute position of the reaction, only the relative positions (internal degrees). Hence both translation and rotation of the entire system can be removed (each with 3 degrees of freedom, assuming nonlinear geometries). So the dimensionality of a PES is $3N-6$(2.6.1) where N is the number of atoms involves in the reaction, i.e., the number of atoms in each reactants). The PES is a hyper surface with many degrees of freedom and typically only a few are plotted at any one time for understanding.

Application of Potential Energy Surfaces

A PES is a conceptual tool for aiding the analysis of molecular geometry and chemical reaction dynamics. Once the necessary points are evaluated on a PES, the points can be classified according to the first and second derivatives of the energy with respect to position, which respectively are the gradient and the curvature. Stationary points (or points with a zero gradient) have physical meaning: energy minima correspond to physically stable chemical species and saddle points correspond to transition states, the highest energy point on the reaction coordinate (which is the lowest energy pathway connecting a chemical reactant to a chemical product).

- PES do not show kinetic energy, only potential energy.
- At T = 0 K (no KE), species will want to be at the lowest possible potential energy, (i.e., at a minimum on the PES).
- Between any two minima (valley bottoms) the lowest energy path will pass through a maximum at a saddle point, which we call that saddle point a transition-state structure.

The PES concept finds application in fields such as chemistry and physics, especially in the theoretical sub-branches of these subjects. It can be used to theoretically explore properties of structures composed of atoms, for example, finding the minimum energy shape of a molecule or computing the rates of a chemical reaction.

KINETIC ISOTOPIC EFFECT

In physical organic chemistry, a Kinetic Isotope Effect (KIE) is the change in the reaction rate of a chemical reaction when one of the atoms in the reactants is replaced by one of its isotopes. Formally, it is the ratio of rate constants for the reactions involving the light (k_L) and the heavy (k_H) isotopically substituted reactants (isotopologues):

$$KIE = \frac{k_L}{k_H}$$

This change in reaction rate is a quantum mechanical effect that primarily results from heavier isotopologues having lower vibrational frequencies compared to their lighter counterparts. In most cases, this implies a greater energetic input needed for heavier isotopologues to reach the transition state (or, in rare cases, the dissociation limit), and consequently, a slower reaction rate. The study of kinetic isotope effects can help the elucidation of the reaction mechanism of certain chemical reactions and is occasionally exploited in drug development to improve unfavorable pharmacokinetics by protecting metabolically-vulnerable C-H bonds.

$$\mathrm{CN^- + {}^{12}CH_3 - Br \overset{k_{12}}{\rightarrow} {}^{12}CH_3 - CN + Br^-}$$

$$\mathrm{CN^- + {}^{13}CH_3 - Br \overset{k_{13}}{\rightarrow} {}^{13}CH_3 - CN + Br^-}$$

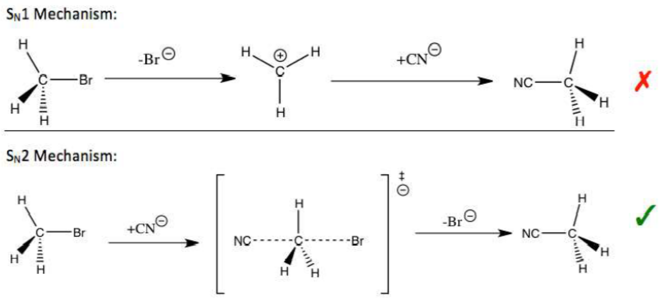
$$\mathrm{KIE} = \frac{k_{12}}{k_{13}} = 1.082 \pm 0.008$$

An example of the kinetic isotope effect, In the reaction of methyl bromide with cyanide, the kinetic isotope effect of the carbon in the methyl group was found to be 1.082 ± 0.008.

Background

The kinetic isotope effect is considered to be one of the most essential and sensitive tools for the study of reaction mechanisms, the knowledge of which allows the improvement of the desirable qualities of the corresponding reactions. For example, kinetic isotope effects can be used to reveal whether a nucleophilic substitution reaction follows a unimolecular (S_N1) or bimolecular (S_N2) pathway.

In the reaction of methyl bromide and cyanide, the observed methyl carbon kinetic isotope effect indicates an S_N2 mechanism. Depending on the pathway, different strategies may be used to stabilize the transition state of the rate determining step of the reaction and improve the reaction rate and selectivity, which are important for industrial applications.



Isotopic rate changes are most pronounced when the relative mass change is greatest, since the effect is related to vibrational frequencies of the affected bonds. For instance, changing a hydrogen atom (H) to its isotope deuterium (D) represents a 100% increase in mass, whereas in replacing carbon-12 with carbon- 13, the mass increases by only 8 percent. The rate of a reaction involving a C–H bond is typically 6–10 times faster than the corresponding C–D bond, whereas a ^{12}C reaction is only 4 percent faster than the corresponding ^{12}C reaction.

Isotopic substitution can modify the rate of reaction in a variety of ways. In many cases, the rate difference can be rationalized by noting that the mass of an atom affects the vibrational frequency of the chemical bond that it forms, even if the potential energy surface for the reaction is nearly identical. Heavier isotopes will (classically) lead to lower vibration frequencies, or, viewed quantum mechanically, will have lower zero-point energy. With a lower zero-point energy, more energy must be supplied to break the bond, resulting in a higher activation energy for bond cleavage, which in turn lowers the measured rate.

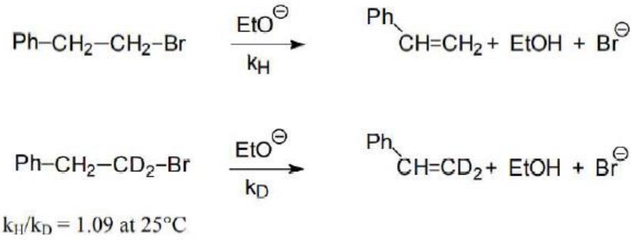
Classification

There are Several Different Classifications for KIEs Primary kinetic isotope effects. A primary kinetic isotope effect may be found when a bond to the isotopically labelled atom is being formed or broken. Depending on the way a kinetic isotope effect is probed (parallel measurement of rates vs. Intermolecular competition vs. intramolecular competition), the observation of a primary kinetic isotope effect is indicative of breaking/forming a bond to the isotope at the rate limiting step, or subsequent product-determining step(s).

For the previously mentioned nucleophilic substitution reactions, primary kinetic isotope effects have been investigated for both the leaving groups, the nucleophiles, and the α-carbon at which the substitution occurs. Interpretation of the leaving group kinetic isotope effects had been difficult at first due to significant contributions from temperature independent factors. Kinetic isotope effects at the α-carbon can be used to develop some understanding into the symmetry of the transition state in S_N2 reactions, although this kinetic isotope effect is less sensitive than what would be ideal, also due to contribution from non-vibrational factors.

Primary Kinetic Isotope Effect (Primary KIE or 1°KIE)

Contrast with:



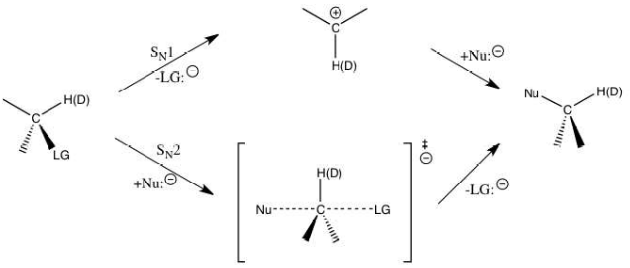
$k_H/k_D = 1.09$ at 25°C

In this example the bonds to CH or CD are not broken during the reaction (but there is a change in hybridization at carbon, and thus a change in IR frequency for the CH bonds).

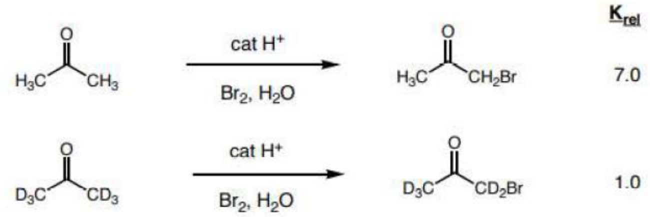
Secondary kinetic isotope effects

A secondary kinetic isotope effect is observed when no bond to the isotopically labelled atom in the reactant is broken or formed. Secondary kinetic isotope effects tend to be much smaller than primary kinetic isotope effects; however, secondary deuterium isotope effects can be as large as 1.4 per deuterium atom, and techniques have been developed to measure heavy-element isotope effects to very high precision, so secondary kinetic isotope effects are still very useful for elucidating reaction mechanisms.

For the aforementioned nucleophilic substitution reactions, secondary hydrogen kinetic isotope effects at the α-carbon provide a direct means to distinguish between S_N1 and S_N2 reactions. It has been found that S_N1 reactions typically lead to large secondary kinetic isotope effects, approaching to their theoretical maximum at about 1.22, while S_N2 reactions typically yield primary kinetic isotope effects that are very close to or less than unity. Kinetic isotope effects that are greater than 1 are referred to as normal kinetic isotope effects, while kinetic isotope effects that are less than one are referred to as inverse kinetic isotope effects. In general, smaller force constants in the transition state are expected to yield a normal kinetic isotope effect, and larger force constants in the transition state are expected to yield an inverse kinetic isotope effect when stretching vibrational contributions dominate the kinetic isotope effect.



A kinetic isotope effect is a mechanistic phenomenon wherein isotopically substituted molecules react at different rates.



Interpretation of the rate differences provides information on the nature of the rate-determining step.

Secondary Kinetic Isotope Effect (Secondary KIE, 2° KIE) Secondary KIE are usually small KIE refer to rate constant ratios, k_H/k_D. There are also equilibrium isotope effects (EIE) which refer to equilibria k_H/k_D, for example,

$$H_2O + D_2O \rightleftharpoons 2HDO \quad K = 3.94$$
$$HT + H_2O \rightleftharpoons H_2 + HTO \quad K = 6.3$$
$$D_2 + 2HCl \rightleftharpoons H_2 + 2DCl \quad K = 1.89$$
$$^{13}CO + {}^{12}CO_2 \rightleftharpoons {}^{12}CO + {}^{13}CO_2 \quad K = 1.09$$

The hydrogen isotopes have special atomic symbols and names

^1H	Protium	H
^2H	Deuterium	D
^3H	Tritium	T

Normal Isotope Effect: Occurs when k_H/k_D is greater than 1.

Inverse Isotope Effect: Occurs when k_H/k_D is less than 1.

Using Primary KIE's to Distinguish Between Reaction Mechanisms

KIE's give useful information about the rate determining step of the reaction mechanism.

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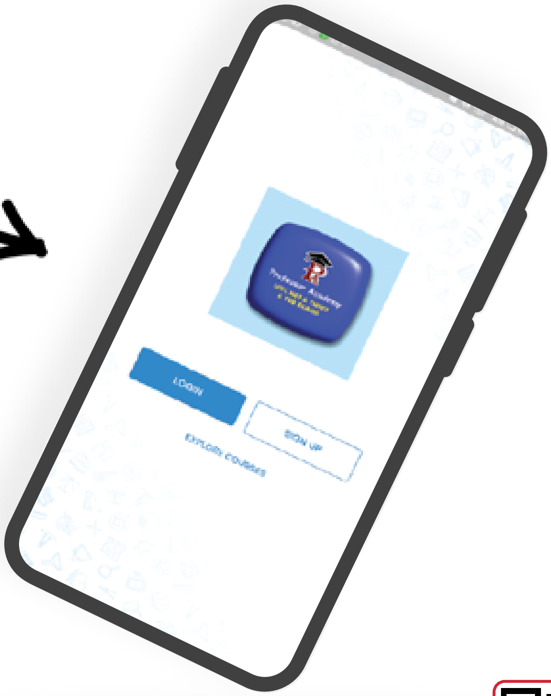

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Principles of Microscopic Reversibility

Principle of microscopic reversibility, principle formulated about 1924 by the American scientist Richard C. Tolman that provides a dynamic description of an equilibrium condition. Equilibrium is a state in which no net change in some given property of a physical system is observable; for example, in a chemical reaction, no change takes place in the concentrations of reactants and products, although the Dutch chemist J.H. van't Hoff had already recognized that this condition results from the equality of the forward and backward rates of a reversible reaction.

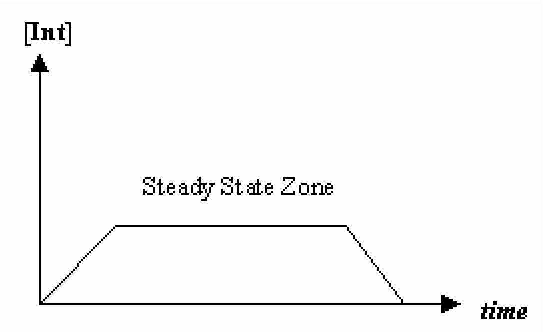
According to the principle of microscopic reversibility, at equilibrium there is continuous activity on a microscopic (i.e., atomic or molecular) level, although on a macroscopic (observable) scale the system may be considered as standing still. There is no net change favouring any one direction, because whatever is being done is being undone at the same rate. Thus, for a chemical reaction at equilibrium, the amount of reactants being converted to products per unit time is exactly matched by the amount being converted to reactants (from products) per unit time. The principle of microscopic reversibility, when applied to a chemical reaction that proceeds in several steps, is known as the principle of detailed balancing. Basically, it states that at equilibrium each individual reaction occurs in such a way that the forward and reverse rates are equal.

The law of microscopic reversibility is a fundamental principle that is extremely useful in both qualitative and quantitative analysis and understanding of rate and equilibrium phenomena. Reference to this principle is made as early as the freshman year, and it and its consequences are frequently cited or invoked in subsequent undergraduate and graduate instruction. In recent years it has seen increasing use as a criterion of validity for approximate theories of rate processes, and as a device by which measurements of rate constants for reactions in one direction may be used to obtain the rate constants for the experimentally inaccessible reverse directions. Despite the importance of the principle of microscopic reversibility, most chemists are rather uncertain about its origin, nature, and limitations. In part, this is because the basis of the principle is usually treated in physics textbooks in terms of rather formal quantum mechanics. In addition, a certain amount of confusion results from the fact that the term 'detailed balance is often encountered in the same context as is microscopic reversibility. According to some authors, microscopic reversibility refers only to mechanical quantities such as transition probabilities, trajectories, and cross sections, whereas detailed balance pertains to statistical mechanical concepts such as rate constants and equilibrium.

Steady State Approximation

When a reaction mechanism has several steps of comparable rates, the rate determining step is often not obvious. However, there is an intermediate in some of the steps. An intermediate is a species that is neither one of the reactants, nor one of the products. The steady-state approximation is a method used to derive a rate law. The method is based on the assumption that one intermediate in the reaction mechanism is consumed as quickly as it is generated. Its concentration remains the same in a duration of the reaction.

When a reaction involves one or more intermediates, the concentration of one of the intermediates remains constant at some stage of the reaction. Thus, the system has reached a steady-state. The concentration of one of the intermediates, [Int], varies with time as shown in Figure . At the start and end of the reaction, [Int] does vary with time $\frac{d[Int]}{dt} = 0$.



When a reaction mechanism has several steps with comparable rates, the rate-determining step is not obvious. However, there is an intermediate in some of the steps. The steady-state approximation implies that you select an intermediate in the reaction mechanism, and calculate its concentration by assuming that it is consumed as quickly as it is generated. In the following, an example is given to show how the steady-state approximation method works.

Example:

Use the steady-state approximation to derive the rate law for this reaction

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

assuming it follows the following three-step mechanism:

$$N_2O_5 \underset{k_b}{\overset{k_f}{\leftrightarrows}} NO_2 + NO_3$$

$$NO_3 + NO_2 \xrightarrow{k_2} NO + NO_2 + O_2$$

$$NO_3 + NO \xrightarrow{k_3} 2NO_2$$

Solution

In these steps, NO and NO_3 are intermediates. You have

$$\text{production rate of NO} = k_2[NO_3][NO_2]$$
$$\text{consumption rate of NO} = k_3[NO_3][NO]$$

A steady-state approach makes use of the assumption that the rate of production of an intermediate is equal to the rate of its consumption. Thus, we have

$$k_2[NO_3][NO_2] = k_3[NO_3][NO]$$

and solving for [NO] gives the result,

$$[NO] = \frac{k_2[NO_3][NO_2]}{k_3[NO_3]}$$

For the other intermediate NO_3,

$$\text{production rate of } NO_3 = k_f[\ N_2O_5]$$
$$\text{consumption rate of } NO_3 = k_2[NO_3][NO_2] + k_3[NO_3][NO] + k_b[NO_3][NO_2]$$

Applying the steady-state assumption gives:

Applying the steady-state assumption gives:

$$k_f[\ N_2O_5] = k_2[NO_3][NO_2] + k_3[NO_3][NO] + k_b[NO_3][NO_2]$$

Thus,

$$[NO_3] = \frac{k_f[\ N_2O_5]}{k_2[NO_2] + k_3[NO] + k_b[NO_2]}$$

Let's review the three equations (steps) in the mechanism:

Step i. is at equilibrium and thus can not give a rate expression.

Step ii. leads to the production of some products, and the active species NO causes further reaction in step iii. This consideration led to a rate expression from step ii. as:

$$\frac{d[O_2]}{dt} = k_2[NO_3][NO_2]$$

Substituting (1) in (2) and then in (3) gives

$$\frac{d[O_2]}{dt} = \frac{k_f k_2[\ N_2O_5]}{k_b + 2k_2} = k[\ N_2O_5]$$

Where $k = \frac{k_f k_2}{k_b + 2k_2}$.

This is the differential rate law, and it agrees with the experimental results. Carry out the above manipulation yourself on a piece of paper. Simply reading the above will not lead to solid learning yet.

A General Reaction to Show the Applicability of the Steady State Approximation

Consider the following reaction $A \rightarrow B$

Let us say that the reaction occurs in two steps

$$A \xrightarrow{k_1} I$$
$$I \xrightarrow{k_2} B$$

The differential rate laws are given by in the Equations respectively:

$$\frac{dc_t(A)}{dt} = -k_1 c_t(A)$$
$$\frac{dc_t(I)}{dt} = k_1 c_t(A) - k_2 c_t(I)$$
$$\frac{dc_t(B)}{dt} = k_2 c_t(I)$$

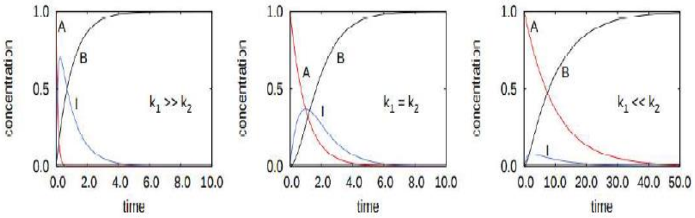
The integrated rate laws which are obtained by solving the coupled differential equations are given by in the Equations given below respectively:

$$c_t(A) - c_0(A)e^{-k_1t}$$

$$c_t(I) = \begin{cases} c_0(A)\dfrac{k_1}{k_1 - k_2}(e^{-k_1t} - e^{-k_2t});\ k_1 \neq k_2 \\ c_0(A)k_1le^{-k_1t};\ k_1 = k_2 \end{cases}$$

$$c_t(B) = c_0(A) - c_t(A) - c_t(I)$$

The concentrations of the reactant, intermediate and the product for the cases i) $k_1 > k_2$ ii) $k_1 = k_2$, and iii) $k_1 < k_2$ are shown below



Clearly the steady state approximation is applicable for the case $k1 < k2$ where the concentration of the intermediate is small and it varies slowly and can be considered to be constant most of the time during the reaction (i.e., to a good approximation, $dct\ (I)/dt = 0$). The situation $k1 < k2$ also means that the intermediate is very reactive and this step is very fast. Also note that the first step is relatively very slow hence the first step determines the rate of the entire reaction. Now let us apply the steady state approximation for this case to derive the rate law. In most of the cases, we look for an expression for ct (I) in terms of the rate constants and the concentration of reactants. Let us apply dct (I)dt $= 0$ which is the steady state approximation to Equation

$$\frac{dc_t(I)}{dt} = 0 \Rightarrow c_t(I) = \frac{k_1}{k_2}c_t(A)$$

Using the above equation we can rewrite the rate laws (differential and integral) as follows

$$\frac{dc_t(A)}{dt} = -k_1c_t(A)$$

$$\frac{dc_t(I)}{dt} = 0$$

$$\frac{dc_t(B)}{dt} = k_1c_t(A)$$

And

$$\begin{aligned} c_t(A) &= c_0(A)e^{-k_1t} \\ c_c(I) &= \text{ constant} \\ c_t(B) &= c_0(A) - c_t(A) - \frac{k_1}{k_2}c_t(A) \\ &= c_0(A)\left\{1 - c_0(A)e^{-k_1t} - \frac{k_1}{k_2}c_0(A)e^{-k_1t}\right\} \\ &= c_0(A)\{1 - c_0(A)e^{-k_1t}\} \end{aligned}$$

In the last equation we have used $k_1k_2 = 0$ because k_2 is large.

Kinetics of Complex Reactions

Introduction

Electrochemical processes considered so far involve simple reactions of a particle with a single electron to produce a reduced ion, or vice versa. Such are the simple ionic redox processes, where the only difference in structure between a reactant and a reaction product may be due to some rearrangement of the neighbouring solvent molecules. When one or more transfers of electrons between the electrode and a species in solution are accompanied by major structural changes, the reaction usually consists of a sequence of events, called elementary acts, or unit steps, constituting the reaction mechanism. Intermediate states between the steps usually involve some unstable intermediate species with higher energy content than those of the reactants or of the reaction products.

Complex reaction mechanisms can consist of a number of electron transfer steps, with some chemical steps preceding or succeeding the electron transfer steps or taking place in between them. Most organic electrochemical reactions are complex, involving large numbers of electrons in the overall reaction. Usually one step in the reaction encounters the largest energy barrier. The rate of occurrence of this step limits the rate of the overall reaction. This step is called the rate determining step and, for most practical purposes, all intermediate steps before and after it can be considered to be in equilibrium.

Parallel, Consecutive And Opposing Or Reversible Reactions

There are many reactions both in nature and in the laboratory which do not take place strictly according to the equation derived. These reactions involve two or more side reactions in addition to the actual reactions and thus, the kinetics of such reactions is complicated. The various complications are due to the following factors:

1. Reversible or Opposing Reactions
2. Consecutive Reactions
3. Side reactions or Parallel Reactions

1. Reversible or Opposing Reactions: So far it has been assumed that a reaction takes place in the forward direction and does not reverse. But, it has been found that majority of the reactions are reversible and forward and the reverse reactions take place simultaneously, for example, oxidation of nitric oxide to nitrogen dioxide, hydrolysis of ethyl acetate in aqueous solutions, etc. These reactions take place as:

$$2\mathrm{NO} + \mathrm{O_2} \underset{k_2}{\overset{k_1}{\leftrightarrows}} 2\mathrm{NO_2}$$

(k_1) is the rate constant for the forward reaction and k_2 is the rate constant for the backward reaction)

$$\mathrm{CH_3COOC_2H_5} + \mathrm{H_2O} \underset{k_2}{\overset{k_1}{\leftrightarrows}} \mathrm{CH_3COOH} + \mathrm{C_2H_5OH}$$

(The symbol $\rightleftharpoons$ indicates that the reaction is reversible.)

Consider a simplest case of this type in which both forward and reverse reactions are of first order:

$$A \underset{k_2}{\overset{k_1}{\leftrightarrows}} B$$

k_1 and k_{-1} are the first order rate constants for the forward and reverse reactions respectively. Initially at $t = 0$. Let ' a ' be the concentration of A and there will be no B. After time t, if x is the amount of A transformed into B, the concentrations of A and B will be $(a - x)$ and x respectively.

Therefore, the rate of the reaction will become

$$\frac{dx}{dt} = k_1(a - x) - k_{-1}x$$

where $k_1(a - x)$ is the actual rate for the forward reaction and $k_{-1}x$ is the rate for the reverse reaction.

At equilibrium, the two rates are equal. If x_e is the amount of the product formed at equilibrium, then

$$k_1(a - x_e) = k_{-1}x_e$$

or

$$k_{-1} = \frac{k_1(a - x_e)}{x_e}$$

Substituting this value of k_{-1} in Equation (2)

$$\frac{dx}{dt} = k_1(a - x) - \frac{k_1x(a - x_e)}{x_e} = \frac{k_1a(x_e - x)}{x_e}$$

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

Separation of variables gives

$$\frac{dx}{x_e - x} = \frac{a}{x_e}k_1dt$$

Rewriting and integrating this equation in the limits that at $t = 0, x = 0$ and at time $t, x = x$, we get

$$\int_0^t k_1dt = \frac{x_e}{a}\int_0^x \frac{dx}{x_e - x}$$

or

$$k_1t = \frac{x_e}{a}|-\ln(x_e - x)|_0^x = \frac{x_e}{a}\ln\frac{x_e}{x_e - x}$$

or

$$k_1\frac{a}{x_e} = \frac{1}{t}\ln\frac{x_e}{x_e - x}$$

Therefore, if x_e is known, the specific rate constant for the forward reaction can be calculated.

Similarly, expressions for second order opposing reactions can also be obtained.

2.Consecutive Reactions. These are those reactions in which the product of one reaction becomes the reactant for the other reaction for example,

$$A \overset{k_1}{\rightarrow} B \overset{k_2}{\rightarrow} C$$

In this reaction, A is the original reactant and gives the product B at the rate constant k_1. This product formed further reacts to give the substance C at some other rate constant k_2. The kinetics of such a reaction is determined by the slowest step. In the above reaction, if first reaction is faster than the second reaction, the kinetics will be determined by the second reaction. In general, it can be stated that if a reaction takes place in series, then the slowest reaction will be the rate-determining reaction.

Let a be the initial concentration of A, x the amount of it decompose after time t and y the amount of C formed at the same time.

Thus, at time t, we have Concentration of A, $C_A = a - x$

Concentration of C, $C_C = y$ and concentration of B, $C_B = x - y$

(because the total amount of B formed is x and y of it decomposes to form C). Therefore, rate of disappearance of A is given by

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

and that of B is given by $\frac{dy}{dt} = k_2(x-y)$ (This is also the rate of formation of C.) To show the variation of concentrations of A, B and C with time, equation (9) is integrated in the limits that $x = a$ when $t = 0$ and $x = x$ at time t. This gives

$$C_A = (a-x) = ae^{-klt}$$

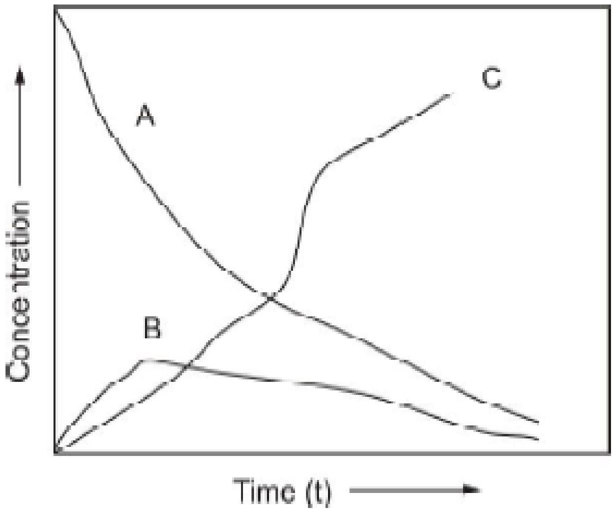
i.e., the concentration of A falls off exponentially. Substituting the value of x from equation (11) into equation (10) and then integrating the latter equation we get,

$$C_B = (x-y) = a\frac{k_2}{k_2-k_1}(e^{-k1t} - e^{k2t})$$

Knowing C_A and C_B at time t, C_C can be found. Its value comes out to be

$$C_C = \frac{a}{k_2-k_1}[(k_2 - k_2 \cdot e^{-k_1 t}) - (k_1 - k_1 e^{-k_2 t})]$$

The general manner in which C_A, C_B and C_C vary with time t is shown by the curves in Figure given below.



(Concentration Versus Time in Consecutive Reactions)

It is clear from the various curves that concentration of A decreases and that of C increases continuously while the concentration of B passes through a maximum and then begins to decrease with time.

Examples:

1. Pyrolysis of Acetone. This takes place in two steps:

(i) $CH_3COCH_3 \rightarrow CH_2{=}CO + CH_4$; and

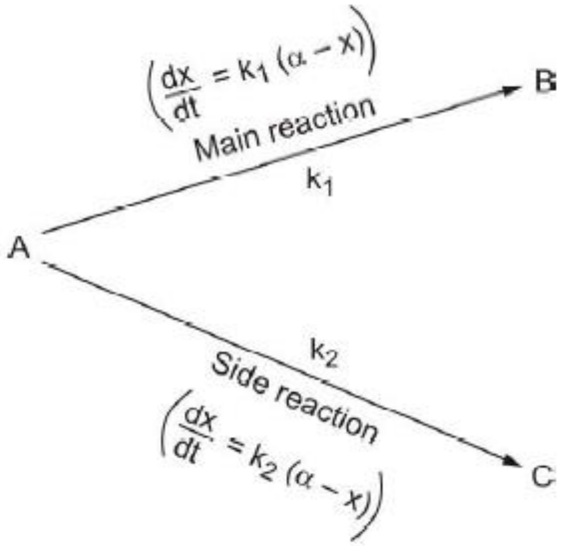
(ii) $CH_2{=}CO \rightarrow 2\ C_2H_4 + CO$

2. Decomposition of Sodium Hypochlorite in Alkaline Solutions:

(i) $2NaClO \rightarrow NaCl + NaClO_2$; and

(ii) $NaClO_2 + NaClO \rightarrow NaCl + NaClO_3$

3. Side Reactions: These are those reactions in which the reactant gives the products in more than one way. The reaction which gives the maximum quantity of the product is called the main reaction and the others yielding poor amount of the products are called the side reactions. Side reactions are quite common in organic chemistry, as shown in figure. k_1 is the rate constant for the main reaction and k_2 the rate constant for the side reaction.



If a is the initial concentration of A and x is the amount of it that decomposes into B and C at time t, the rate of disappearance of A is given by

The overall rate of reactions

$$\frac{dx}{dt} = (k_1 + k_2)(a-x)$$

Integration under the condition that at $t = 0$, $x = 0$ gives

$$k = (k_1 + k_2) = \frac{1}{t}\ln\frac{a}{a-x}$$

This is a typical first order equation. and the rate of formation of B and C is given by

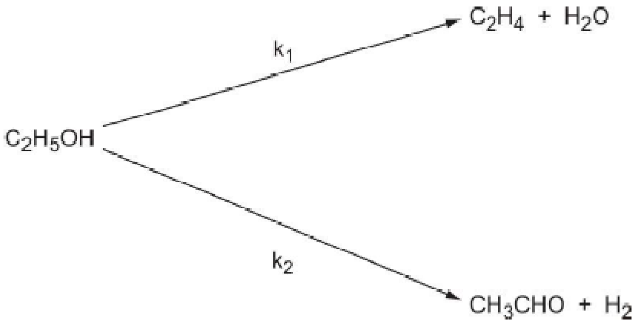
$$\frac{d[B]}{dt} = k_1 x$$

And $\frac{d[C]}{dt} = k_2 x$. Ratio of equations given above gives

$$\frac{d[B]}{d[C]} = \frac{k_1}{k_2}$$

With the help of equations k_1 and k_2 can be calculated.

Example: Alcohol can be dehydrated to olefins as well as dehydrogenated to aldehyde:



3 CHAIN REACTIONS

There are some chemical reactions which take place by a series of successive processes involving the formation of free atoms and radicals. The kinetic laws for such reactions are considerably complex. A well known example of these types of reactions is the hydrogen-bromine reaction.

The stoichiometry for this reaction is

$$\text{H}_2 + \text{Br}_2 \rightarrow 2\text{HBr}$$

but it does not follow the simple rate expression

$$\frac{d[\text{HBr}]}{dt} = k[\text{H}_2][\text{Br}_2]$$

analogous to that followed in the hydrogen-iodine reaction but follows the following empirical equation given by Bodenstein and Lind in 1906:

$$\frac{d[\text{HBr}]}{dt} = \frac{k[\text{H}_2][\text{Br}_2]^{\frac{1}{2}}}{1 + k\frac{[\text{HBr}']}{[\text{Br}_2]}}$$

k and k are constants at a given temperature and parentheses indicate the concentration of the species. The appearance of the term [HBr] in the denominator implies that the velocity of the reaction is decreased by the product, HBr and this product acts as an inhibitor of the reaction.

The complexity of equation could not be explained until 1919 when Christiansen. Herzfeld and Polanyi independently and almost simultaneously solved the problem. They proposed a chain of reactions with the following steps:

1 $\text{Br}_2 \overset{k_1}{\rightarrow} 2\text{Br}$ Chain initiation

2 $\text{Br} + \text{H}_2 \overset{k_2}{\rightarrow} \text{HBr} + \text{H}$

3 $\text{H} + \text{Br}_2 \overset{k_3}{\rightarrow} \text{HBr} + \text{Br}$

4 $\text{H} + \text{HBr} \overset{k_4}{\rightarrow} \text{H}_2 + \text{Br}$ Chain inhibition

5 $\text{Br} + \text{Br} \overset{k_5}{\rightarrow} \text{Br}_2$ Chain termination

According to this mechanism, HBr is formed in reactions (2) and (3) and removed in reaction (4). Consequently, the rate of formation of HBr is given by

$$\frac{d[\text{HBr}]}{dt} = \text{k}_2[\text{H}_2][\text{Br}] + k_3[\text{H}][\text{Br}_2] - k_4[\text{H}][\text{HBr}] \ldots$$

This expression involves concentrations of H atoms and Br atoms. Since these atoms are present in very small quantities, their concentrations cannot be directly measured. Thus, equation cannot be solved unless the concentrations of these atoms are expressed in terms of the concentrations of the molecules H_2, Br_2, and HBr. In order to remove this difficulty, it is assumed that the atoms H and Br are short lived intermediates and the steady-state principle can be applied to them. Thus, we get

$$\frac{d[\text{H}]}{dt} = k_2[\text{Br}][\text{H}_2] - k_3[\text{H}][\text{Br}_2] - k_4[\text{H}][\text{HBr}] = 0$$

$$\frac{d[\text{Br}]}{dt} = k_1[\text{Br}_2] + k_3[\text{H}][\text{Br}_2] + k_4[\text{H}][\text{Br}] - k_2[\text{Br}][\text{H}_2] - k_5[\text{Br}]^2 = 0$$

Solving these two equations simultaneously, we get

$$[\text{Br}] = \left(\frac{k_1[Br_2]}{k_5}\right)^{\frac{1}{2}}$$

Substituting these values for [H] and [Br] into equation and rearranging, we get

$$\frac{d[\mathrm{HBr}]}{dt}=\frac{2k_2(k_1/k_6)^{\frac{1}{2}}[\mathrm{H_2}][\mathrm{Br_2}]^{\frac{1}{2}}}{1+(k_4/k_3)\frac{[\mathrm{HBr}]}{[\mathrm{Br_2}]}}$$

This equation is in agreement with equation but now the constants k and k are expressed as composites of constants for step reactions in succession.

A reaction like the above is an example of a chain reaction. Inspection of steps (1) to (5) for the hydrogen-bromine reaction leads to a number of points of interest in the mechanism. The reaction is initiated by thermal dissociation of a bromine molecule into bromine atoms. The introduction of bromine atoms produces a large number of molecules of hydrogen bromide through the sequence of reactions (2) and (3). These two stages repeat themselves until the reactants are used up. These reactions are chain-propagating reactions. Step (4) accounts for the observed inhibition by HBr, since the product HBr is removed by this step, there is a decrease in the rate of formation of HBr . Step (5) results in removal of bromine atoms, and hence in chain termination. In some cases, chain termination may take place by collisions of chain propagators with the walls of the reaction vessel

In some chain reactions, free radicals such as CH_3, C_2H_5, or CH_3CO, act as chain carriers. Consider, for example, the thermal decomposition of acetaldehyde, namely,

$$\mathrm{CH_3CHO \rightarrow CH_4 + CO}$$

The following mechanism has been proposed for this reaction:

1 $CH_3CHO \xrightarrow{k_1} CH_3 + CHO$ Chain initiation

2 $CH_3CHO + CH_3 \xrightarrow{k_2} CH_4 + CH_3CO$
Chain propagation

3 $CH_3CO \xrightarrow{k_3} CH_3 + CO$

4 $CH_3 + CH_3 \xrightarrow{k_4} C_2H_6$

Chain termination

Step (1) initiates the chain, steps (2) and (3) propagate the chain and step (4) terminates the chain. Applying the steady-state principle to the radicals CH_3 and CH_3CO, we get

$$\frac{a[\mathrm{CH_3}]}{dt}=k_1[\mathrm{CH_3CHO}]+k_3[\mathrm{CH_3CO}]-k_2[\mathrm{CH_3CHO}][\mathrm{CH_3}]-k_4[\mathrm{CH_3}]^2=0$$

and $$\frac{d[\mathrm{CH_3CO}]}{dt}=k_2[\mathrm{CH_3CHO}][\mathrm{CH_3}]-k_3[\mathrm{CH_3CO}]=0$$

From these two equations, we get

$k_1[\mathrm{CH_3CHO}]=k_4[\mathrm{CH_3}]^2$

or $[\mathrm{CH_3}]=[k_1/k_4]^{1/2}[\mathrm{CH_3CHO})^{1/2}$.

The overall rate of reaction is determined by the production of CH_4 in step (4). The rate equation is

$$\frac{d[\mathrm{CH_4}]}{dt}=k_2[\mathrm{CH_3CHO}][\mathrm{CH_3}]$$

Substituting the value of $[CH_3]$ into the equation, we get

$$\frac{d[\mathrm{CH_4}]}{dt}=k_2\left(\frac{k_1}{k_4}\right)^{\frac{1}{2}}[\mathrm{CH_3CHO}]^{\frac{3}{2}}$$

The free-radical scheme thus predicts the reaction to be of the $\frac{3}{2}$ order. This is in agreement with the experimental data which shows a first order reaction gradually becoming a second order reaction.

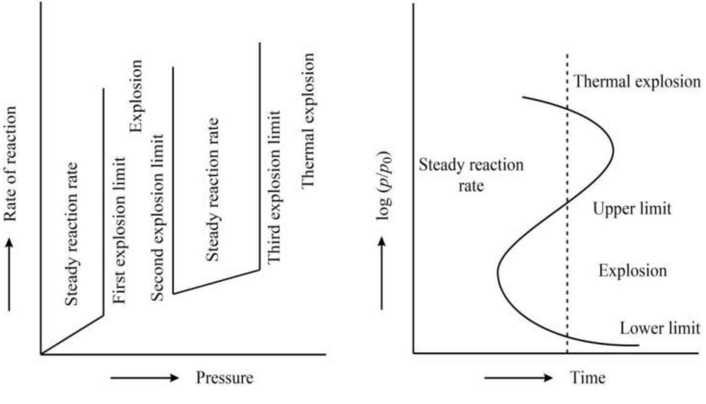
Free radical chains play an important role in the polymerization of many unsaturated compounds, such as ethylene, styrene and vinyl compounds, to produce materials of industrial importance.

4 Branching Chains, Explosive Reactions

In the chain reactions, each propagation phase produces a molecule of product and one chain carrier. This is referred to as a stationary state. In some reactions, it has been frequently observed that more than one chain carrier is produced from the original one in each propagating phase. This results in branching (or nonstationary) chain, in which the number of chain carriers increase rapidly. The reaction then takes place very rapidly and explosion is said to occur. (In fact, explosions do occur if chain carriers are produced more quickly than they can be removed.) A reaction mechanism that involves branching reactions is known as branching chain process.

One of the consequences of the formation of branching chains is the phenomenon of explosion limit discovered by Hinshelwood and his co-workers in 1928. It is exhibited by a number of oxidation reactions, for example, of hydrogen, carbon monoxide, carbon disulphide and phosphine.

Consider the reaction between hydrogen and oxygen. This reaction takes place at a conveniently measurable speed between the temperature range of 450°C and 600°C. Below this range, the rate is very slow, but above this range, the reaction takes place extremely rapidly, i.e., becomes explosive. If the mixture of H_2 and O_2 in the ratio 2:1 is maintained at 550°C and at a pressure of about 2 mm, a steady homogeneous reaction occurs. If the pressure is gradually raised the rate increases. At a certain critical pressure of few millimetres, the reaction suddenly becomes explosive. This is referred to as first (lower) explosion limit. The explosive reaction persists with further increase of pressure but above a pressure of 50 mm at 500°C, there is no longer an explosion and the reaction rate is normal. If the pressure is further increased at about 100 mm, a condition is once again reached at which the reaction is very rapid and explosion reoccurs. This is referred to as second (upper) explosion limit. At about 200 mm pressure, the reaction is again steady. At still higher pressures, a third limit is achieved. This behaviour is displayed in figure given below.



(Explosion limits)

In order to explain the existence of explosion limits, the branching chain mechanism is utilised. At very low pressures, the chain carriers diffuse quickly to the walls of vessel and are destroyed at the surface, thus terminating the chain. The rate of the reaction is, therefore, slow. As the pressure is increased, rate of formation of chain carriers exceed their rate of destruction; the reaction rate then increases enormously and explosion occurs. This represents lower explosion limit which depends on the size and material of the reaction vessel. Further increase of pressure favours destruction of chain carriers by their mutual collisions in the interior of the gas. Eventually, the upper explosion limit is reached when destructive collisions in the gas phase exceed the chain branching. The reaction becomes non-explosive in character and goes smoothly. At still higher pressures, represented by the third explosion limit, the reaction is again so fast that the conditions are no longer isothermal and reaction passes over into a thermal explosion. In a thermal explosion, since the heat liberated is not dissipated, the temperature of the reaction system rises rapidly and the rate of reaction increases practically without bound.

Taking into consideration the views expressed above, the following mechanism is suggested for the hydrogen-oxygen reaction:

1. $H_2 \rightarrow 2H$ Chain initiation
2. $H + O_2 \rightarrow OH + O$ Chain branching
3. $O + H_2 \rightarrow OH + H$
4. $OH + H_2 \rightarrow H_2O + H$ Chain propagation
5. H + wall → Destruction
6. OH + wall → Destruction
7. O + wall → Destruction

Kinetics of Reactions in Solution

The collision theory of bimolecular reactions discussed earlier applies to gas phase reactions. It is not expected to apply to reactions in solution since the solvent would hinder the collisions. And yet, surprisingly, there are certain reactions for which the rate constant and the activation energy are almost the same when the reactions are studied in a solvent as when they are investigated in the gas phase. We conclude, therefore, that the Arrhenius factors for these cases are nearly the same.

When the two molecules collide: with each other in solution they are hindered from separating after an unreactive collision (encounter) since they are surrounded by a cage of solvent molecules. Thus, they make many collisions before separating. These collisions (encounters) compensate for the relatively slow diffusion of the reactant molecules towards each other in the liquid phase.

Diffusion-Controlled Reactions in Solution.

Diffusion-controlled reactions in solution are generally very fast, requiring very small, nearly zero, activation energy. Examples of diffusion-controlled reactions are the electron-transfer, the proton-transfer and atom-recombination reactions in organic solvents. For a reaction taking place extremely rapidly in solution, the rate of chemical interaction is often greater than the rate with which the reacting molecules approach each other by diffusing through the liquid. In such a case, the experimentally measured rate is not the rate of interaction between the molecules but is, instead, the rate of diffusion: Such reactions are called diffusion-controlled reactions.

The theory of diffusion-controlled reactions was developed by Peter Debye, ·who made use of the ideas of the Polish physicist, M. Smoluchowsld. In 1917, Smoluchowski had developed a theory of the growth of the colloidal particles and their diffusion towards the surface.

Let us consider two uncharged reactant molecules A and B having radii r_{A} and r_{B} and diffusion coefficients D_{A} and D_{B}, respectively. If n_{A} and n_{B} are the numbers of A and B molecuies per cm^3, then the number of encounters v per cubic centimetre per second between A and B is given by

$$v = 4\pi(D_{\mathrm{A}} + D_{\mathrm{B}})(r_{\mathrm{A}} + r_{\mathrm{B}})n_{\mathrm{A}}n_{\mathrm{B}}\ \mathrm{cm}^{-3}\ \mathrm{s}^{-1}$$

The above also gives the reaction rate in terms of molecules $\mathrm{cm}^{-3}\ \mathrm{s}^{-1}$ if each encounter leads to chemical reaction.

To obtain the rate in mol $\mathrm{cm}^{-3}\ \mathrm{s}^{-1}$ we divide v by N_{A}, the Avogadro's number. Then, evidently,

$$v/N_{\mathrm{A}} = k_D(n_{\mathrm{A}}/N_{\mathrm{A}})(n_{\mathrm{B}}/N_{\mathrm{A}})\mathrm{mol\ cm}^{-3}\ \mathrm{s}^{-1}$$

where k_D. is the diffusion-controlled rate constant (in $\mathrm{cm}^3\ \mathrm{mol}^{-1}\ \mathrm{s}^{-1}$) and $n_{\mathrm{A}}/N_{\mathrm{A}}$ and $n_{\mathrm{B}}/N_{\mathrm{A}}$ are the molar concentrations (molcm^{-3}) of A and B, respeetively.

$$v = k_D n_{\mathrm{A}} n_{\mathrm{B}}/N_{\mathrm{A}}$$

Hence, from equations,

$$k_{\mathrm{D}}^* = 4\pi N_{\mathrm{A}}(D_{\mathrm{A}} + D_{\mathrm{B}})(r_{\mathrm{A}} + r_{\mathrm{B}})\mathrm{cm}^3\ \mathrm{mol}^{-1}\ \mathrm{s}^{-1}$$

The diffusion coefficient of a spherical molecule in a liquid is related to the coefficient of viscosity η of the liquid and the radius r of the molecule by the Stokes equation, viz;

$D = k_B T/6\pi\eta r$. Thus, for the molecules A and B,

$$D_{\mathrm{A}} = k_{\mathrm{B}}T/6\pi inr_{\mathrm{A}};\ D_{\mathrm{B}} = k_{\mathrm{B}}T/6\pi\eta r_{\mathrm{B}}$$

where k_{B} is Boltzmann constant $= R/N_{\mathrm{A}}$.

Then

$$k_D = \frac{2RT}{3\eta} \times \frac{(r_{\mathrm{A}} + r_{\mathrm{B}})^2}{r_{\mathrm{A}}r_{\mathrm{B}}}\ \mathrm{cm}^3\ \mathrm{mol}^{-1}\ \mathrm{s}^{-1}$$

where $R(= N_A k_B)$ is the ideal gas constant. If we assume that $r_A = r_B$, then

$$k_D = (8RT/3\eta)\mathrm{cm}^3\ \mathrm{mol}^{-1}\ \mathrm{s}^{-1}$$

This is the well-known Debye-Smoluchowski equation for the rate constant of a diffusion-controlled reaction. It may be noted that in this equation the radii of the molecules have been cancelled out. Thus, the bimolecular rate constant of a diffusion-controlled reaction is independent of the size of the molecules. Also, we see that *ko* is inversely proportional to the coefficient of viscosity of the solvent.

SALT EFFECTS

It has been observed that the rate of reaction in solution is altered by the presence of inert ionic species in the solution. The effect is observed for most of the reactions. However, it is more significant for reactions between ions. In such cases, the rate of reaction may alter even at low concentration of the salt. Such an effect of ionic species on the rate of reaction is called as **salt effect.** These salt effects are manifested in two different ways and are classified as primary and the secondary salt effects. The primary salt effect is related to the influence of the added electrolyte concentration on the activity coefficient of the reactants and hence on the rate of reaction. On the other hand, the secondary salt effect refers to the change in the concentration of the reacting ions due to the addition of the electrolytes.

1 Primary Salt Effect In case of reactions in solution involving ions, the magnitude of the electrostatic forces between the ions affects the kinetics of the reactions. These forces in turn are affected by the presence of electrolytes whether they are as reactants, products, or an added inert salt. You may note here that an inert salt is the one whose ions do not react either with the reactant (s) or product (s). This effect of inert salts in the reaction rate is called **primary salt effect.** The effect of added inert electrolyte concentration on the rate constants of reactions involving ions in aqueous solutions can be explained in terms of transition state theory and the Debye-Hückel theory.

Let us consider the following reaction between a cation, X having a charge Z_X and an anion, Y having a charge, Z_Y

$$X^{Z_X} + Y^{Z_Y} \rightarrow \text{Products}$$

As above, the reaction scheme can be represented as

$$X^Z X + Y^{Z_Y} \overset{K^{\ddagger}}{\rightleftharpoons} [XY^{\ddagger}]^{(Z_X+Z_Y)} \longrightarrow \text{Product}$$

For such a reaction the activated complex, $[XY^{\ddagger}]^{(Z_x+z_Y)}$ will have a charge equal to $(z_X + z_Y)$. For sake of simplicity the charges on the species are not shown from now on. As explained above, the equilibrium constant for the formation of the transition state can be written in terms of the activities of the species as

$$K_s^{\ddagger} = \frac{\gamma_{\ddagger}[XY^{\ddagger}]}{\gamma_X[X]\gamma_Y[Y]}$$

The rate constant can be expressed as per equation viz.,

$$k_s = \frac{k_B T}{h} K_s^{\ddagger} \frac{\gamma_X \gamma_Y}{\gamma_{\ddagger}}$$

Taking logarithm of equation and expanding the terms we get,

$$\log k_s = \log \frac{k_B T}{h} K_s^{\ddagger} + \log \gamma_X + \log \gamma_Y - \log \gamma_{\pm}$$

The activity coefficients vary with the concentration especially in the presence of added electrolyte. To understand this, Lewis and Randall introduced the quantity called ionic strength. It is a unitless quantity that accounts for the charge and concentration of all ions in a solution and is a measure of the intensity of the electric field due to the ions in a solution.

Mathematically, it is given as

$$I = \frac{1}{2}\sum m_i z_i^2 \text{ or } \frac{1}{2}\sum c_i z_i^2$$

Where, where m_i or C_i is the molar concentration of each individual ion, and Z_i is the charge of each ion. In other words, it is the sum of the terms obtained by multiplying the molarity (concentration) of each ion present in solution by the square of charge on it. Let us take an example to understand the calculation of ionic strength.

If the solution is sufficiently dilute, the dependence of activity coefficient on ionic strength is given by Debye-Huckel limiting law about which you will learn in Unit 13. According to the law,

$$\log \gamma_i = -0.509 Z_i^2 1^{1/2}$$

where Z_i is the charge on the species, and I is the ionic strength of the solution. Substituting in equation we get,

$$\log k_s = \log \frac{kT}{h} K_s^{\ddagger} - 0.509(Z_X^2 + Z_Y^2 - Z_z^2) 1^{1/2}$$

Now, since the charge on the activated complex is $(Z_X + Z_Y)$, we can write

$$Z_{\ddagger}^2 = (Z_x + Z_Y)^2 = Z_X^2 + Z_Y^2 + 2Z_x Z_Y$$

Substituting in the equation, and simplifying we get

$$\log k_s = \log \frac{kT}{h} K_s^{\ddagger} + 1.018 Z_\chi Z_Y I^{1/2}$$

The first term in equation represents $\log k_0$, so we can write

$$\log k_s = \log k_0 + 1.018 Z_X Z_y I^{1/2}$$

In logarithmic form the equation can be written as

$$\log \frac{k_s}{k_o} = 1.018 Z_x Z_Y I^{1/2}$$

The two equations given above are known as the Bronsted-Bjerrum equations and predict that a plot of $\log k$ or $\log \frac{k}{k_o}$ versus the square root of ionic strength, I should be a straight line. For an aqueous solution, the slope is nearly equal to $Z_X Z_Y$, i.e., the product of the ionic charges and the sign of $Z_X Z_Y$ determines the direction of slope as shown in figure given below.

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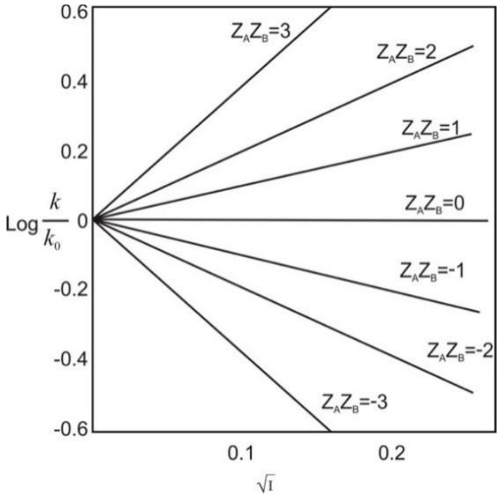


(Schematic Brønsted-Bjerrum plot of log k versus the square root of ionic strength I for different types of ionic reactions in solution)

There are three special cases possible:

I. If Z_X and Z_Y have the same sign (i.e., both the ions are either positive or negative), then Z_XZ_Y is positive and the rate constant increases with ionic strength. This can be rationalised in terms of the fact that when the ionic strength is high, the solvated ions change the dielectric behaviour of the solution in such a way that the ions of like charge do not repel each other significantly. This allows them to approach more closely, whereby increasing the collision frequency and hence an increased reaction rate.

II. If Z_X and Z_Y have different signs, Z_XZ_Y is negative and the rate constant decreases with ionic strength. In this case, an increase in the concentration of ions in the solvent causes a decrease in the attraction between the ions thereby decreasing the number of collisions and thence the decrease in the rate of the reaction between them.

III. If any one of the reactants is uncharged, Z_XZ_Y is zero and the rate constant is independent of the ionic strength.

In order to test these equations we need to make measurements of rate constant of the reaction at different ionic strengths. These are then plotted as a function of square root of the ionic strength. These plots are found to be linear with intercept log k_0. In fact the equation has been verified for a large number of systems and is found to be valid. Some of these reactions are given below.

The reactions represented in the figure are:

1. $[\mathrm{Co(NH_3)_sBr}]^{2+} + \mathrm{Hg}^{2+}$, $(z_A\mathrm{Z_B} = 4)$
2. $\mathrm{S_2O_3}^{2-} + \mathrm{I}^-$, $(z_Az_B = 2)$
3. $[\mathrm{Co(OC_2H_5)N{:}NO_2}]^- + \mathrm{OH}^-$ $(z_Az_B = 1)$
4. $\mathrm{CH_3COOC_2H_5} + \mathrm{OH}^-$ $(z_Az_B = 0)$
5. $\mathrm{H}^+ + \mathrm{Br}^- + \mathrm{H_2O_2}$. $(z_Az_B = -1)$
6. $\left[\mathrm{CO(NH_3))_5Br}\right]^{2+} + \mathrm{OH}^-$ $(z_Az_B = -2)$
7. $\mathrm{Fe}^{2+} + [\mathrm{Co(C_2O_4)_3}]^{3-}$ $(z_Az_B = -6)$

Now, for reactions involving uncharged reactants, the ionic strength of the solution is expected to have little or no effect on the reaction rate. In cases where the ions are consumed or generated, the overall ionic strength of the medium will change with the progress of the reaction. This may alter the kinetics of the reaction. Therefore, we need to factor in the change in ionic strength with the progress of reaction. In one of the ways to do so is to determine the change in ionic strength during the reaction and adjust results to compensate for the change. Alternatively, the reaction is carried out at a relatively high ionic strength by using a medium containing a large concentration of an inert electrolyte. Minor changes in the concentrations of the ions of reactants and or products do not change the ionic strength of the mediumWe see that if one of the reactants is a neutral molecule, the product $z_Az_B = 0$ and the rate constant will be independent of the ionic strengthighis is true for the base-catalyzed hydrolysis of ethyl acetate.

2 Secondary Salt Effects

In case of the reactions in which one of the species is neutral ($z = 0$), ionic strength should not have any effect as shown above by the Bjerrum equation. However, in practice, for catalytic reactions, especially the ones catalysed by acids or bases there are small effects of changing ionic strength. These effects are not manifested in terms of the change in activity coefficient, instead these are a consequence of the change in the effective concentration of the catalysing species due to the addition of the electrolytes. This phenomenon is independent of primary salt effect and is known as the secondary salt effect. In the reactions catalysed by acids or bases, the addition of inert electrolyte affects the concentration of H^+or OH^-ions. This in turn, alters the rate of the reaction. Let us consider a reaction which is catalysed by H^+ions produced by a weak acid HA. The ionisation equilibrium of the weak acid is given as

$$\mathrm{HA} \rightleftharpoons \mathrm{H^+} + \mathrm{A^-}$$

The corresponding thermodynamic ionization constant is given by the following expression

$$K = \frac{a_{\mathrm{H^+}} \times a_{A^-}}{a_{HA}}$$

You know that the activity of a species equals the product of activity coefficient and the concentration. Substituting in the above

$$K = \frac{\gamma_{\mathrm{H^+}}[\mathrm{H^+}] \times \gamma_{\mathrm{A^-}}[\mathrm{A^-}]}{\gamma_{\mathrm{HA}}[\mathrm{HA}]} \text{ or,}$$

$$K = \frac{\gamma_{\mathrm{H^+}}[\mathrm{H^+}] \times}{[\mathrm{HA}]}\frac{\gamma_{\mathrm{A^-}}[\mathrm{A^-}]}{\gamma_{\mathrm{HA}}}$$

Rearranging, we get

$$[\mathrm{H^+}] = K\frac{[\mathrm{HA}]}{[\mathrm{A^-}]}\frac{\gamma_{HA}}{\gamma_{\mathrm{H^+}}\gamma_{A^-}}$$

Since, for a given acid salt mixture the ratio $\frac{[HA]}{[\mathrm{A^-}]}$ is a constant, we can write

$$[\mathrm{H^+}] = K'\frac{\gamma_{HA}}{\gamma_{\mathrm{H^+}}\gamma_{A^-}}$$

Where K' is a constant. Now since the rate of the reaction depends on the concentration of hydrogen ions besides other species, we can write rate constant expression as

$$k = k_0\frac{\gamma_{HA}}{\gamma_{\mathrm{H^+}}\gamma_{A^-}}$$

Where, k_0 is the rate constant in the absence of secondary salt effect. It includes the primary salt effect. Taking logarithms, we get

$$\log\, k = \log\, k_0 + \log\, \frac{\gamma_{HA}}{\gamma_{\mathrm{H^+}}\gamma_{A^-}}$$

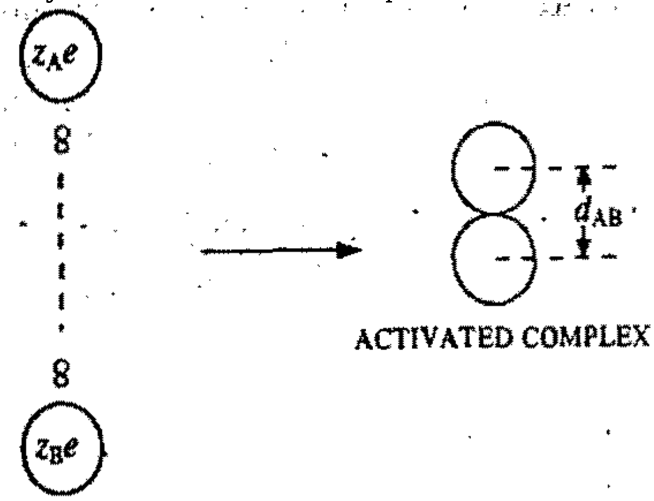
The second term on the right-side equals $1.018\sqrt{1}$, so we get

$$\log\, k = \log\, k_0 + 1.018\sqrt{1}$$

Thus, an increase in the ionic strength increases the rate constant and hence the rate. The Equation suggests that while studying acid / base catalysed reactions we must keep the ionic strength constant. Else the rate will keep varying.

Influence of Solvent on the Rates of Ionic Reactions

Ionic reactions in solution are affected by electrostatic interactions. Let us consider an ionic reaction involving two ions A and B of radius r_{A} and r_{B} and charge $z_{\mathrm{A}}e$ and $z_{\mathrm{B}}e$ in solution. Suppose that the two ions are initially at infinite distance apart but they touch each other when they form the activated complex.



(Double-sphere model for a simple ionic reaction)

The work done in bringing the two ions together from infinity to a distance d_{AB} is given by

$$w = z_{\mathrm{A}}z_{\mathrm{B}}e^2/(\varepsilon_r d_{\mathrm{AB}})$$

where ε_r is the dielectric constant of the solvent. This work is equal to the electrostatic contribution to the Gibbs free energy increase in going from the initial to the transition state. If the signs of charges on the ions are the same, this work is positive; if they are different, it is negative. There is also a molar non-electrostatic term, $\Delta G^{\#}$ n.e.s. The free energy of activation per molecule may thus be written as

$$\frac{\Delta G^{\#}}{N_{\mathrm{A}}} = \frac{\Delta G^{\#}_{\mathrm{n.e.s.}}}{N_{\mathrm{A}}} + \frac{z_{\mathrm{A}}z_{\mathrm{B}}e^2}{\varepsilon_r d_{\mathrm{AB}}}$$

From the activated complex theory, the rate constant is given by

$$k = (k_{\mathrm{B}}T/h)\exp\,(-\Delta G^{\#}/RT)$$

Substitution of equation gives

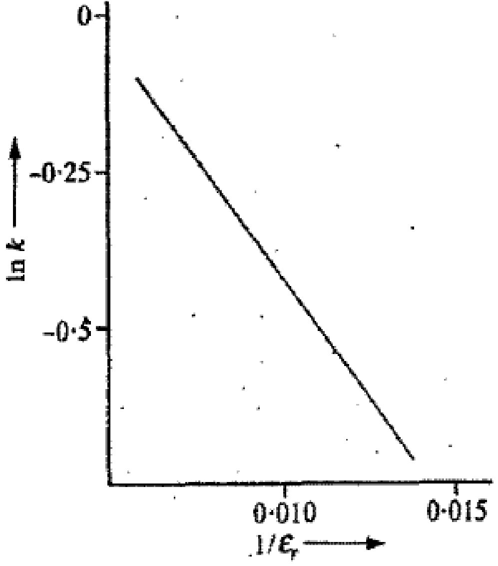
$$k = \left(\frac{k_{\mathrm{B}}T}{h}\right)\exp\,\left(\frac{-\Delta G^{\#}_{\mathrm{n.e.s.}}}{RT}\right)\exp\,\left(-\frac{z_{\mathrm{A}}z_{\mathrm{B}}N_{\mathrm{A}}e^2}{\varepsilon_r RT d_{\mathrm{AB}}}\right)$$

Taking logs,

$$\ln k = \ln (k_{\mathrm{B}}T/h)\left(\frac{-\Delta \mathrm{G}^{\#}{}_{\mathrm{B,e,\,S}}}{RT}\right) - \frac{z_{\mathrm{A}}z_{\mathrm{B}}N_{\mathrm{A}}e^2}{\varepsilon_r RTd_{\mathrm{AB}}}$$

$$= \ln k_0 - \frac{z_{\mathrm{A}}z_{\mathrm{B}}N_{\mathrm{A}}e^2}{\varepsilon_r RTd_{\mathrm{AB}}}$$

The above equation is the equation of a straight line. It shows that the logarithm of the rate constant of an ionic reaction varies inversely with the dielectric constant of the solvent at a given temperature. Several ionic reactions obey this plot over a limited range. The measurement of the slope, which equals $N_{\mathrm{A}^{z}\mathrm{A}^{z}B}\mathrm{e}^2/RTd_{\mathrm{AB}}$ can lead to the estimation of d_{AB}.



(A plot of log k *versus* the reciprocal of the dielectric constant for a typical ionic reaction)

The Hammett Equation and Linear Free Energy Relationship

Hammett Equation

Consider an organic reaction is carried out on a substrate which can be denoted as XRY, X a variable substituent and Y is the reaction spot, and R represents the basic substrate structure. In this type of case, replacing X = H with X = CH_3 results in an increment in the rate of reaction up ten times. However, it is still a mystery what part of the rate enhancement comes from resonance effect, field-effect, or steric effect. To do so, it is reasonable to use compounds where one or two effects are so small that they simply can be neglected. Although it is the oversimplification of the problem, quantitative results can still be obtained. The Hammett equation is the first attempt to give numerical values for the quantitative treatment of structure on reactivity. Hammett proposed the equation for the cases of *m*- and *p*-XC_6H_4Y as given below.

$$\log \frac{k}{k_0} = \sigma\rho$$

where k and k_0 are the constant for the group X ≠ H and X = H; ρ and σ are the constants for reaction conditions and substituent X , respectively.

Derivation of Hammett Equation

To derive the Hammett equation, we need to recall the quantitative relationship between the structure and reactivity first. To do so, we need to find some mathematical parameter that can be used to represent the combined magnitude of inductive and resonance effects of different substituents. This can be achieved by considering the hydrolysis of a series of different benzoic acids as given below.

$$\mathrm{XC_6H_4COOH + H_2O \overset{K_a}{\rightleftharpoons} XC_6H_4COO^- + H_3O^+}$$

Where X is a substituent at the m - or p-position and K_a is the dissociation constant. As expected, the dissociation constant was found to be different for differently substituted substrates.

Since an electron-withdrawing group will better stabilize the conjugate base (i.e., $\mathrm{XC_6H_4COO^-}$), resulting in a larger magnitude of K_a (lower p K_a). On the other hand, an electron-donating group will destabilize the conjugate base (i.e., $\mathrm{XC_6H_4COO^-}$), resulting in a smaller magnitude of K_a (higher p K_a). Therefore, we can say that the electronic effect (inductive plus mesomeric effect) of a substituent can be represented as the difference between the p K_a value of its benzoic acid derivative and the p K_a value of benzoic acid itself, mathematically, we can say

$$\sigma_X = \log(K_a) - \log(K_a)_0 = -p(K_a) + p(K_a)_0$$

Where the parameter σ_{x} (or simply σ) is called as substituent constant, and was found for several different groups just subtracting its benzoic acid derivative's p K_a value from p K_a value of benzoic acid.

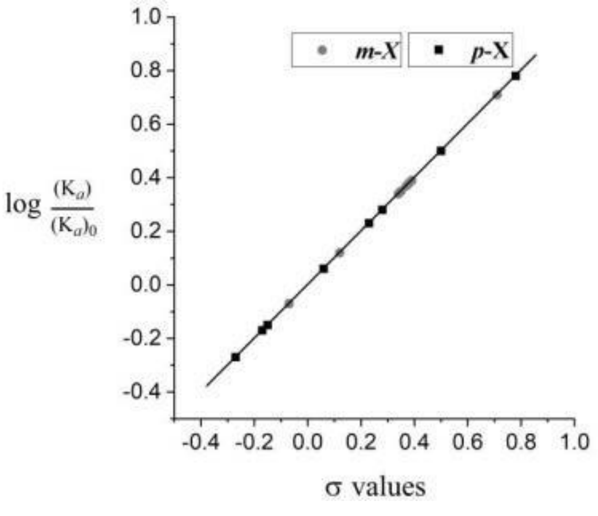
pK_a values and substituent constants for XC_6H_6COOH using benzoic acids $p(K_a)_0 = 4.21$.

Substituent	$p_m(K_a)$	$p_p(K_a)$	$\sigma_m = p(K_a)_0 - p_m(K_a)$	$\sigma_p = p(K_a)_0 - p_p(K_a)$
NO_2	3.50	3.43	0.71	0.78
CH_3	4.28	4.38	−0.07	−0.17
OCH_3	4.09	4.48	0.12	−0.27
$CH(CH_3)_2$	4.28	4.36	−0.07	−0.15
F	3.87	4.15	0.34	0.06
Br	3.82	3.98	0.39	0.23
Cl	3.84	3.98	0.37	0.23
I	3.86	3.93	0.35	0.28
$COCH_3$	3.83	3.71	0.38	0.50

Using $\log m - \log n = \log m/n$, the above equation can also be written as

$$log\frac{(K_a)}{(K_a)_0} = \sigma$$

Now if we plot a curve between $\log(K_a)/(K_a)_0$ vs σ, we will definitely get a straight line with a slope = 1.



(Variation of $\log(K_a)/(K_a)_0$ vs σ for substituted benzoic acids.)

Now we need to check if these σ values (i.e., of substituted benzoic acids) can also be used for other meta- or para-substituted benzene derivatives. To do so, consider two series of reactions; the first one is the acid dissociation of phenyl phosphonic acid, and the second one is the base hydrolysis of substituted ethyl benzoate. Here we will find if different substituents affect their dissociation constants or rates in the same manner as affected in the case of substituted benzoic acid. Also, we did not use ortho-substituents or substituents in the aliphatic system because they also contain steric factors and don't not linear variation.

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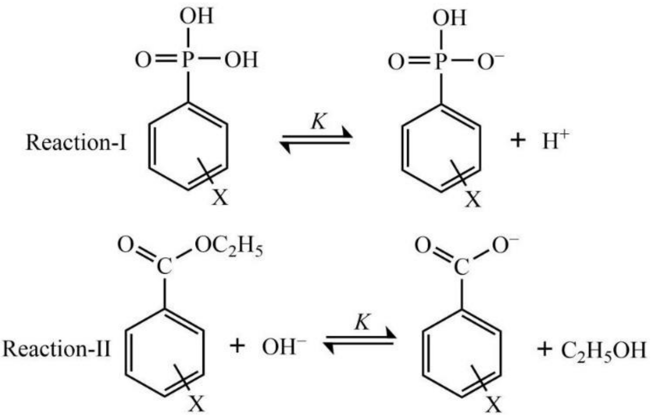
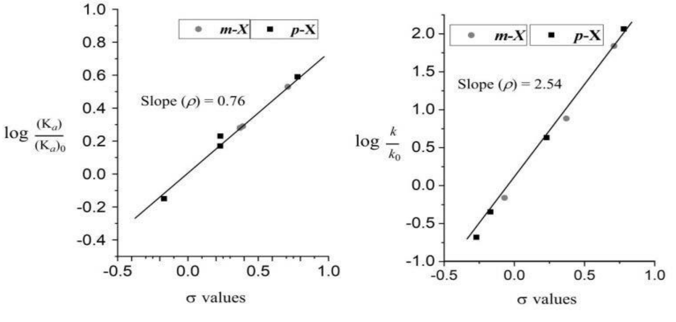
Table : Experimental values of $\log(K_a)/(K_a)_0$ and $\log k/k_0$ for the acid dissociation of phenyl phosphonic acid and base hydrolysis of substituted ethyl benzoates, respectively.

Substituent	*meta*-$\log(K_a)/(K_a)_0$	*para*-$\log(K_a)/(K_a)_0$	*meta*-$\log k/k_0$	*para*-$\log k/k_0$
NO_2	0.53	0.59	1.83935	2.06423
Br	0.29	0.23	–	–
Cl	0.28	0.17	0.88536	0.63347
CH_3	–	−0.15	−0.16115	−0.34679
OCH_3	–	–	–	−0.67923

The experimental $\log(K_a)/(K_a)_0$ for the reaction-I and experimental $\log k/k_0$ for reaction-II are given above.



When plotted the experimental $\log(K_a)/(K_a)_0$ for the reaction-I and experimental $\log k/k_0$ for reaction-II vs the substituent constants obtained for the substituted benzoic acids, we get the following curves.



($\log(K_a)/(K_a)_0$ and $\log k/k_0$ vs σ for reaction-I and reaction-II)

It is obvious that the plots are still linear like in figure but the slope has changed. This implies that the order and relative effects for different substituents on both reactions remain the same though the magnitude has been changed which can be attributed to the different nature reaction considers from 'base reaction'.

Therefore, our aim, in this case, should be the determination of the slope (let us say ρ). Since on the vertical side we have '$[\log(K_a)/(K_a)_0]_{sppa}$' for reaction-I (acid dissociation of phenyl phosphonic acid) and on the horizontal side we have 'σ *or* $[\log(K_a)/(K_a)_0]_{sba}$' for base reaction (hydrolysis of substituted benzoic acid), the slope should be

$$\rho = \frac{[\log\,(K_a)/(K_a)_0]_{seb}}{[\log\,(K_a)/(K_a)_0]_{sba}}$$

or

$$\rho[\log\,(K_a)/(K_a)_0]_{sba} = [\log\,(K_a)/(K_a)_0]_{seb}$$

But from equation, we know that $[\log\,(K_a)/\log\,(K_a)_0]_{sba} = \sigma$; and therefore, equation takes the form

$$\left[\log\frac{(K_a)}{(K_a)_0}\right]_{seb} = \rho\sigma$$

For any reactions,

$$\log\,K_a = \rho\sigma - \log\,(K_a)_0$$

Similarly, on the vertical side we have '$\log\,k/k_0$' for reaction-II (base hydrolysis of substituted ethyl benzoate) and on the horizontal side we have 'σ or $[\log\,(K_a)/(K_a)_0]_{sba}$' for base reaction (hydrolysis of substituted benzoic acid), the slope should be

$$\rho = \frac{[\log\,k/k_0]_{\text{seb}}}{[\log\,(K_a)/(K_a)_0]_{sba}}$$

or

$$\rho[\log\,(K_a)/(K_a)_0]_{sba} = [\log\,k/k_0]_{seb}$$

But we know that $[\log\,(K_a)/\log\,(K_a)_0]_{sba} = \sigma$; and therefore, equation takes the form

$$\left[\log\frac{k}{k_0}\right]_{sppa} = \rho\sigma$$

For any reactions,

$$\log k = \rho\sigma - \log k_0$$

The results given by equations given above are called as Hammett's equations', which shows that the rates of ortho and para-substituted benzene derivatives can be obtained offthe substituent contents for substituted benzoic acid are known. Now we will discuss the substituent and reaction constants in more detail.

Linear Free Energy Relationship (LFER)

The Hammett equation is a linear free energy relationship that can be proved for any group X by recalling the kinetics of organic reactions is ith the framework of "Activated complex Theory", which states that the rate constant (k) for a typical reaction is

$$-NETR+\frac{RT}{Nh}e^{-\frac{\Delta G^*}{RT}}$$

$$k=\frac{1}{2}$$

Where ΔG^* is the free energy change of the activation step at temperature T. The symbols R, N, and h are the gas constant, Avogadro number, and Planck's constant, respectively. Similarly, for k_0 we have

$$k_0=\frac{RT}{Nh}e^{\frac{\Delta G_0^*}{RT}}$$

After putting the value of above two equations in Hammett equation, we get

$$\log\frac{\frac{RT}{Nh}e^{-\frac{\Delta G^*}{RT}}}{\frac{RT}{Nh}e^{-\frac{\Delta G_0^*}{RT}}}=\sigma\rho$$

$$\log\frac{e^{\frac{\Delta G^*}{RT}}}{e^{\frac{\Delta G_0^*}{RT}}}=\sigma\rho$$

Multiplying both sides by 2.303, we have

$$2.303\ \log\frac{e^{\frac{\Delta G^*}{RT}}}{e^{\frac{\Delta G_0^*}{RT}}}=2.303\sigma\rho$$

Or

$$\ln\frac{e^{\frac{\Delta G^*}{RT}}}{e^{\frac{\Delta G_0^*}{RT}}}=2.303\sigma\rho$$

Or

$$\ln e^{\frac{\Delta G^*}{RT}}-\ln e^{\frac{\Delta G_0^*}{RT}}=2.303\sigma\rho$$

Or

$$\left(\frac{\Delta G^*}{RT}\ln e\right)-\left(\frac{\Delta G_0^*}{RT}\ln e\right)=2.303\sigma\rho$$

Or

$$\left(-\frac{\Delta G^*}{RT}\right)+\left(\frac{\Delta G_0^*}{RT}\right)=2.303\sigma\rho$$

Which implies

$$\frac{\Delta G_0^*}{RT}-\frac{\Delta G^*}{RT}=2.303\sigma\rho$$

Or

$$\frac{\Delta G_0^*-\Delta G^*}{RT}=2.303\sigma\rho$$

Or

$$\Delta G_0^*-\Delta G^*=2.303RT\sigma\rho$$

Or

$$-\Delta G^*=2.303RT\sigma\rho-\ \Delta G_0^*$$

Hence, the variation of negative of the free energy of activation varies linearly with slope $2.303RT\rho$ and $-\Delta G_0^*$ as intercept.

Reactions in Flow Systems

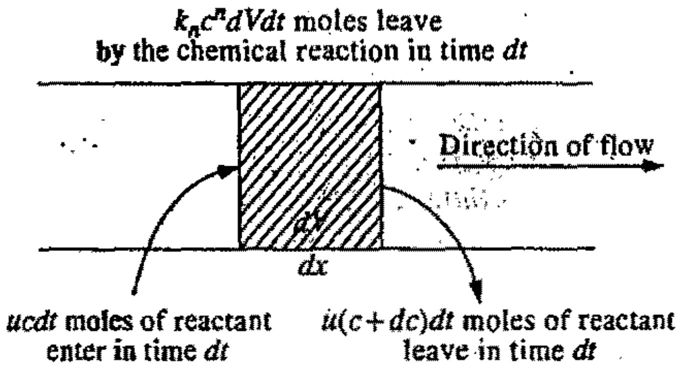
The rate equations for reactions of various orders developed so far apply to static systems, i.e., systems in which reactants are introduced in a reaction vessel and their concentration changes are followed as the reaction proceeds. In some cases, however, it is desirable to study the kinetics of reactions in flow systems in which the reaction mixture is flowing through a reaction vessel known as a reactor. Kinetic measurements in flow systems are generally useful when the reactants are at extremely low pressures or concentrations. Flow systems are also used for studying kinetics of fast reactions.

Types of Flow Systems

Flow systems are of two types. In the first type, there is no stirring in the reactor and the flow through it is often called the plug flow. In the second type, there is stirring which is vigorous enough to cause complete mixing in the reactor. This is called stirred flow. Intermediate situations, though possible, are difficult to analyze.

Plug Flow

The following figure shows the schematic representation of the plug flow.



The reaction mixture is passed through the reactor at a volumetric flow rate (units: $m^3\ s^{-1}$) equal to u.

Let us consider an element of volume dV in the reactor. Assume that the reaction rate depends upon the concentration c of a single reactant. We know that for an n th-order reaction, the rate of consumption of the reactant is given by $r = k_n c^n$. Hence, the rate of consumption of the reactant in volume $dV = k_n c^n dV$.

After the system has been operating for a sufficient time, a steady state is reached, i.e., there occurs no further change in the concentration of the reactant with time in the volume element dV. Three processes contribute to the steady state. These are:

1 The reactant molecules enter the slab (shown by slanting lines) through the left face, the amount entering in time dt being $ucdt$.

2 The molecules leave the slab by the right face, the amount leaving in time dt being $u(c+dc)dt$.

3 Molecules disappear by chemical reaction. For an nth-order reaction, the amount consumed in time dt is $k_n c^n dVdt$.

We can obtain the steady-state equation by equating the rate of entry of reactant into the slab (by process 1) to the sum of the rates of its removal (by processes 2 and 3):

$$ucdt \doteq u(c+dc)dt + k_n c^n dVdt \text{ or } -dc/c^n = dVk_n/u$$

The above equation needs to be integrated over the volume V_0 of the reactor. At the entrance to the reactor $V = 0$ and $c = c_i$ (the initial concentration) while at the exit $V = V_0$. and $c = c_f$ (the final concentration of the reactant). Hence,

$$-\int_{c_i}^{c_f} \frac{dc}{c^n} = \frac{k^n}{u}\int_0^{v_0} dV$$

For a first-order reaction ($n = \text{i}$), integration of Eq, 168 yields

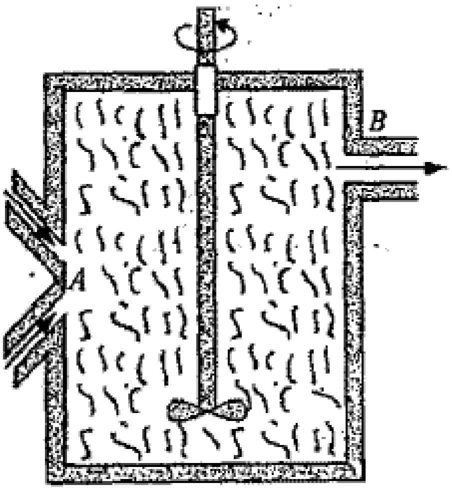
$$-\ln\left(c_f/c_i\right) = k_1 V_0/u \text{ or } c_f = c_i \exp\left(-k_1 V_0/u\right)$$

Comparing this equation with that for a static first-order reaction, wiz., $c_f = c_i \exp\left(-k_1 t\right)$, we see that the two are equivalent if V_0/u is replaced by t. The quantity V_0/u is called the contact time for the reaction. The contact time is the average time that a molecule takes to pass through the reactor. The above equation may be tested by varying V_0/u (by changing either the volume of the reactor or the flow rate), just as time is varied in a static system. Reactions that are too rapid for convenient iivestigation in a static system may be studied in a flow system, the contact time being reduced by dsing a high flow rate and a small volume.

For an n th-order reaction ($n > 1$), integration of equation yields

$$\frac{n}{n-1}\left[\frac{1}{c_f^{n-1}}\right] = \frac{k_n v_0}{u}$$

This equation can be compared with the equation for the rate constant of a static n th-order reaction with $V_0/u = 1$. We have assumed above that there is no volume change during the course of the reaction ; any such change will cause the volumetric flow rate to vary. The consideration of volume change, however, complicates the integration of the rate equation.



(A Stirred flow reactor)

In a stirred-flow reactor, the reactants enter the vessel at A. The concentrations are maimained constant within the reactor by stirring at a high speed (about 3000 rpm). The mixing occurs within a second or so. In this case it is not necessary to consider a thin slab; instead, we consider the reactor as a whole. After a steady state is reached, the product mixture is withdrawn at B. The rate of flow of reactants into the reactor is uc_i and the rate of flow out is uc_f. The difference between these gives the rate of reaction in the reactor which is rV where r is the rate per unit volume. Thus,

$$uc_i - uc_f = rV \quad \text{or} \quad r = u(c_i - c_f)V$$

By measuring c_i and c_f at a given flow rate, the reaction rate can be calculated. The order of the reaction and the rate constant can then be determined by working at different initial concentrations and flow rates.

The stirred-flow reactor finds application in the study of transient reaction intermediates, the concentrations of which in a static system might quickly reach a maximum and then fall to zero. It is interesting to note that there is an analogy between a living cell and a continuous stirred-flow reactor. The theoretical principles of kinetics are the same in each case. Though there is no obvious 'internal stirrer' in the case of a cell, the process of diffusion of molecules across the cell can maintain the 'well-stirred' conditions. Again, though there are no inlets and outlets in a cell as are in the case of a reactor, the entire cell wall adequately serves these functions.

Kinetics of Complex Reactions–Fast Reaction, Flow And Relaxation Methods

There are chemical reactions which take place at a very fast rate, i.e., these reactions can take place in seconds or in minutes. In general the reactions between ionic compounds are fast. For example, combustion of LPG gas in kitchen takes place in a few seconds, i.e., it takes place at a very fast rate in 10-15 seconds so it is a fast reaction.

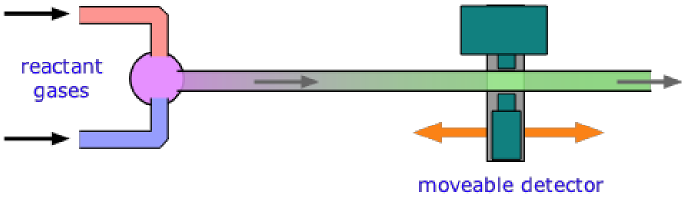
The most frequently flow methods used for the study of fast reactions is the stopped-flow method. Due to the short analysis time and feasibility, flow based systems have become one of the most powerful analytical tools used for studying fast reactions. Flow methods use flow instruments which are a rapid mixing devices for studying the chemical kinetics of fast reactions in solution.

Flow Methods

Flow method was the first technique invented to study fast-reaction and is an important method used till today. The method was introduced by Hartridge and Roughton in 1923 in their study of the reaction between haemoglobin and oxygen and makes use of a continuous-flow system. Since then, a number of variants of flow methods have been employed to study the fast reactions. These have been used to study the kinetics of reactions in liquid and gas phases and are applicable for the reactions both with small or large equilibrium constants.

Continuous Flow Approach

For reactions that take place in milliseconds, the continuous flow technique is used, for example to study fast gas-phase reactions in which one of the reactants is a free radical, such as OH that can be produced by an intense microwave discharge acting on a suitable source gas mixture. This gas, along with the other reactant being investigated, is made to flow through a narrow tube at a known velocity.



(A Continuous Flow Fast Kinetic System)

If the distance between the point at which the reaction is initiated and the product detector is known, then the time interval can be found from the flow rate. By varying this distance, the time required to obtain the maximum yield can then be determined.

In a typical measurement using continuous flow method, the reactants are injected continuously into the mixing chamber. As a consequence, the profile of concentration of reactants and products along the detection tube, does not change with time. In other words, the composition of the reaction mixture varies as a function of the distance from the mixing chamber and not the time of measurement.

If we know the rate of flow and the diameter of the tube leading from the mixing chamber, we can relate the reaction time to the distance between the mixing chamber and the place where the reactants (or products) are measured I detected along the tube. In a way, in the flow techniques, the clock as a timer in conventional methods is replaced by distance along the detection tube. The rate of change of concentration of a reactant (say A) with time can be obtained by dividing the rate of change in its concentration with distance by the flow rate i.e.,

$$-\frac{dA}{dt} = \frac{-\frac{dA}{dx}}{\frac{dx}{dt}} = \frac{-\frac{dA}{dx}}{\text{Flowrate}}$$

The measurement at a distance of 10 cm from the mixing chamber in a system having a flow rate of 10 $\mathrm{m\ s^{-1}}$ corresponds to a reaction time of 0.01 second. Similarly, the measurements at a distance of 20 cm, 50 cm and 1 m along the detection tube will correspond to a time of 0.02,0.05 and 0.1 s respectively. The reaction mixture is analysed at different points along the observation tube and is a measure of the progress of the reaction at different times. Using the measurements made at different distances (representing different times) we can prepare a concentration versus time plot, which in turn, can provide the rate constant for the reaction being studied.

Limitations of continuous flow method

Though the continuous flow method is quite simple and provides good results it has a few limitations such as

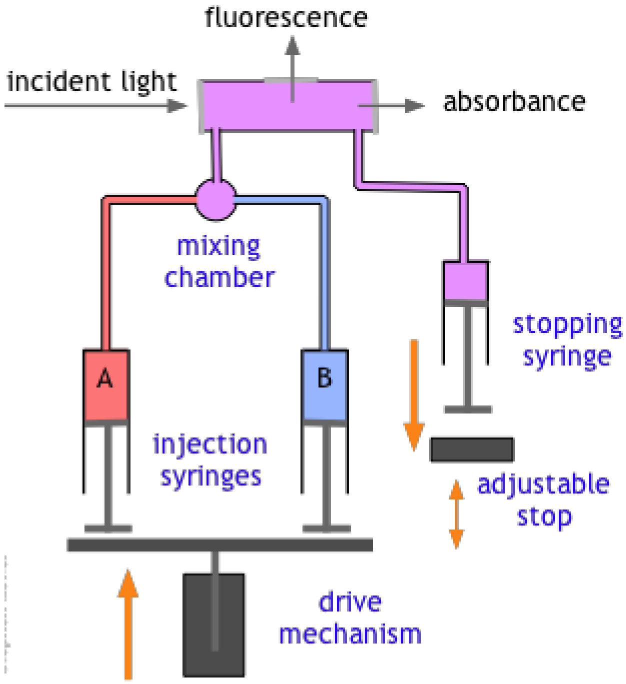
- We can study reactions having a half-life of $\geq 10^{-3}$ s only. Increasing the flow rate may permit the measurement at a still lesser time, however, then the flow will no more be lamellar and the results will not be reliable.
- We need to use high pressures to study gaseous reactions by continuous flow method. It is so because we need to measure the concentration changes due to reaction only. In case of low pressures the reaction mixture moves slowly along the detection tube. This may also allow the diffusion of the reactants and products thereby affecting their concentrations leading to an error in the determination of the kinetic parameters.
- We need a large volume of the reactant. The earlier experiments, required $3-4\mathrm{dm}^3$ of reactants per run. This becomes an issue when the reactants are somewhat expensive. However, with the use of narrow-bore tubing and mechanically-operated hypodermic syringes, the requirements of the reactant volumes have been considerably reduced.

In a variant of the continuous flow method, the rate of flow is continuously varied and the analysis is made at a fixed point along the observation tube. The method is called accelerated flow method. In such a case, as the rate of flow changes with time, the reactants reach at the fixed observation point at different times. The measured value of the concentration at different times helps generate a time-concentration plot which can then be used for the rate study. The advantage of this method is that it requires very small quantities of the reactant and is useful for studying enzyme reactions.

Stopped Flow Approach

Owing to the rather large volumes required, continuous flow method is more practical for the study of gas-phase reactions than for solutions, for which the stopped-flow method described below is generally preferred. These are by far the most common means of studying fast solution-phase reactions over time intervals of down to a fraction of a millisecond. The use of reasonably simple devices is now practical even in student laboratory experiments. These techniques make it possible to follow not only changes in the concentrations of reactants and products, but also the buildup and decay of reaction intermediates.

The stoppered flow technique, developed for solutions, is an improvement over the continuous flow method and addresses the issue of the requirement of large volume of the reactants. In this method, the solutions containing the reactants are taken in separate syringes and their pistons are pushed rapidly by a mechanical system to inject the reactants simultaneously into the mixing chamber, where the reaction starts. This acts as an efficient and rapid mixing device. The reaction mixture then exits into a tube and the flow of the reaction mixture is suddenly (in about 10^{-3} s) stopped. This is achieved by interrupting the flow by a stop syringe, which also controls the volume of the reaction mixture studied. A schematic diagram of the stoppered flow apparatus is given in figure. The smaller the distance from the mixing chamber at which the flow is stopped, the shorter is the time from the start of the reaction at the time of mixing. The reaction between the reactants continues here and the changes in the concentrations of reactants (or products) are followed in real time.



(A Stop Flow Fast Kinetic System)

It is important that the time of analysis must be very rapid and an inbuilt timing device is required. That is the detector response time must be much shorter than the reaction half-life. The time intervals at which concentration measurements are made is determined by the speed at which successive analyses are allowed by the detection method. The technique permits to follow changes in optical (or other) properties of solutions with a time resolution in the range of milliseconds to seconds. The concentration of the sample is normally measured by using spectroscopic methods; the detector is placed at the position of halting.

The basic stopped-flow apparatus consists of two or more coupled syringes that rapidly inject the reactants into a small mixing chamber and then through an observation cell that can be coupled to instruments that measure absorption, fluorescence, light scattering, or other optical or electrical properties of the solution.

As the solution flows through the cell, it empties into a stopping syringe that, when filled, strikes a backstop that abruptly stops the flow. The volume that the stopping syringe can accept is adjusted so that the mixture in the cell has just become uniform and has reached a steady state; at this point, recording of the cell measurement begins and its change is followed.

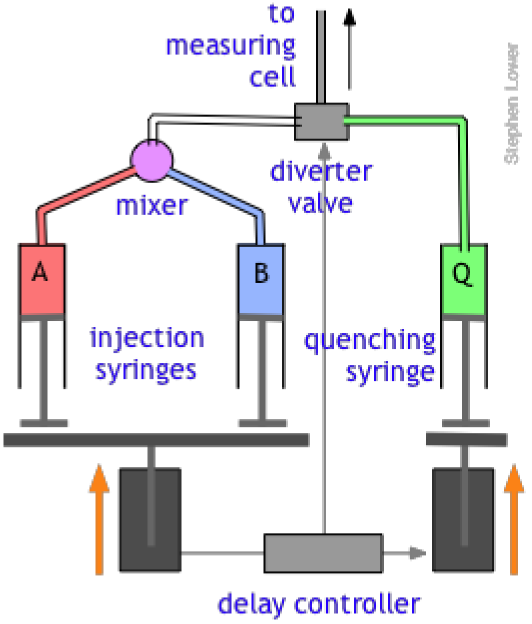
The advantages of the stopped flow method over continuous flow method are as under:

- small volumes of solutions are required, If the mixing is proper, the rate and character of flow does not affect the study Concentration-time plot is obtained that gives a complete record of the progress of reaction The rate equations for modelling the reactions are equivalent to those used in conventional methods.

The flow methods are good but have limitations of their applicability to study reactions having reaction times of the order of 1 ms . For faster reactions we need to use relaxation methods. Let us learn about them. However, before that answer the following simple questions to assess your understanding of flow methods.

Quenched Flow Approach

In a quenched flow instrument, the reaction is stopped after a certain amount of time has passed after mixing. The stopping of the reaction is called quenching and it can be achieved by various means, for example by mixing with another solution, which stops the reaction (chemical quenching), quickly lowering the temperature (freeze quenching) or even by exposing the sample to light of a certain wavelength (optical quenching).



(A quench flow fast kinetic system)

There are many reactions that cannot be followed by changes in light absorption or other physical properties that are conveniently monitored. In such cases, it is often practical to quench (stop) the reaction after a desired interval by adding an appropriate quenching agent. For example, an enzyme-catalyzed reaction can be stopped by adding an acid, base, or salt solution that denatures (destroys the activity of) the protein enzyme. Once the reaction has been stopped, the mixture is withdrawn and analyzed in an appropriate manner.

The quenched-flow technique works something like the stopped-flow method described above, with a slightly altered plumbing arrangement. The reactants A and B are mixed and fed directly through the diverter valve to the measuring cell, which is not shown in this diagram. After a set interval that can vary from a few milliseconds to 200 sec or more, the controller activates the quenching syringe and diverter valve, flooding the cell with the quenching solution.

PRACTICE QUESTIONS

1)The rate equation for a zero-order reaction is:

a) $r=k[A]^0$ b) $r=k[A]^1$

c) $r=k[A]^2$ d) $r=k[A]^3$

2)The unit of the rate constant for a first-order reaction is:

a) mol $L^{-1}s^{-1}$ b) s^{-1}

c) $mol^{-1}L\ s^{-1}$ d) $mol^{-2}L^2s^{-1}$

3)For a second-order reaction, which of the following is correct?

a) The rate is independent of reactant concentration

b) The rate constant has units of L $mol^{-1}s^{-1}$

c) The reaction follows an exponential decay curve

d) The half-life is independent of concentration

4)Which of the following reactions follows a third-order rate law?

a) $2A \rightarrow B$ with rate $r=k[A]^2$

b) $A+2B \rightarrow CA + 2B$ with rate $r=k[A][B]^2$

c) $A \rightarrow BA$ with rate $r=k[A]$

d) $A+B \rightarrow CA + B$ with rate $r=k[A][B]$

5)The half-life ($t_{1/2}$) of a zero-order reaction is proportional to:

a) Initial concentration ($[A]_0$)

b) Square root of concentration

c) Inverse of concentration

d) Independent of concentration

6)The molecularity of a reaction refers to:

a) The sum of the reaction orders

b) The number of molecules involved in an elementary step

c) The overall reaction order

d) The rate at which the reaction occurs

7)A bimolecular reaction involves:

a) One reactant molecule

b) Two reactant molecules

c) Three reactant molecules

d) A catalyst

8)The half-life of a first-order reaction:

a) Depends on the initial concentration

b) Is constant

c) Increases with decreasing concentration

d) Decreases with increasing concentration

9)If the rate equation of a reaction is given by r=k[A][B], the order of reaction is:

a) Zero b) One

c) Two d) Three

10)Which reaction order exhibits a straight-line graph when plotting concentration vs. time?

a) Zero order b) First order

c) Second order d) Third order

11) According to collision theory, the rate of a reaction depends on:

a) The energy of reactant molecules

b) The orientation of colliding molecules

c) The frequency of collisions

d) All of the above

12) The activation energy of a reaction:

a) Is always positive

b) Is the minimum energy required for a reaction to occur

c) Can be negative in exothermic reactions

d) Is dependent on catalyst presence

13) A major failure of collision theory is that:

a) It assumes all collisions lead to reactions

b) It does not consider molecular orientation

c) It cannot explain catalysis

d) It assumes energy is always sufficient for reaction

14) The Arrhenius equation describes:

a) The effect of temperature on reaction rate

b) The probability of molecular collisions

c) The equilibrium constant

d) The molecularity of a reaction

15) In the Lindemann mechanism for unimolecular reactions, the rate-determining step is:

a) The initial collision

b) The formation of an activated intermediate

c) The breakdown of the activated complex

d) The adsorption of molecules

16) Transition State Theory assumes that:

a) A high-energy transition state is formed

b) Molecules must collide with proper orientation

c) The reaction occurs without an intermediate

d) The reactants directly convert to products

17) The activated complex in Transition State Theory is:

a) More stable than reactants

b) A short-lived intermediate at the highest energy point

c) A reaction by-product

d) A stable molecule

18) The rate constant according to Transition State Theory is proportional to:

a) Temperature

b) Activation energy

c) The Gibbs free energy of activation

d) The collision frequency

19) The potential energy surface of a reaction represents:

a) The energy changes along the reaction coordinate

b) The probability of molecular collisions

c) The rate at which the reaction occurs

d) The equilibrium concentration of products

20) A saddle point on a potential energy surface corresponds to:

a) Reactants b) Products

c) The transition state d) The intermediate

21) Which factor affects the rate of a reaction?

a) Temperature b) Concentration

c) Catalyst d) All of the above

22) The order of a reaction can be determined from:
a) The balanced chemical equation
b) The experimental rate law
c) The stoichiometric coefficients
d) The equilibrium constant

23) A catalyst increases the reaction rate by:
a) Increasing reactant concentration
b) Decreasing the activation energy
c) Increasing the temperature
d) Changing the reaction order

24) If a reaction follows first-order kinetics, the plot of ln [A] vs. time will be:
a) A straight line with positive slope
b) A straight line with negative slope
c) A parabolic curve
d) Exponential growth

25) Hinshelwood theory is mainly applied to:
a) Homogeneous catalysis
b) Heterogeneous catalysis
c) Gas-phase unimolecular reactions
d) Radical chain reactions

ANSWERS									
1. a	**2. b**	**3. b**	**4. b**	**5. a**	**6. b**	**7. b**	**8. b**	**9. c**	**10.**
11. d	**12. b**	**13. a**	**14. a**	**15. c**	**16. a**	**17. b**	**18. c**	**19. a**	**20. c**
21. d	**22. b**	**23. b**	**24. b**	**25. c**					

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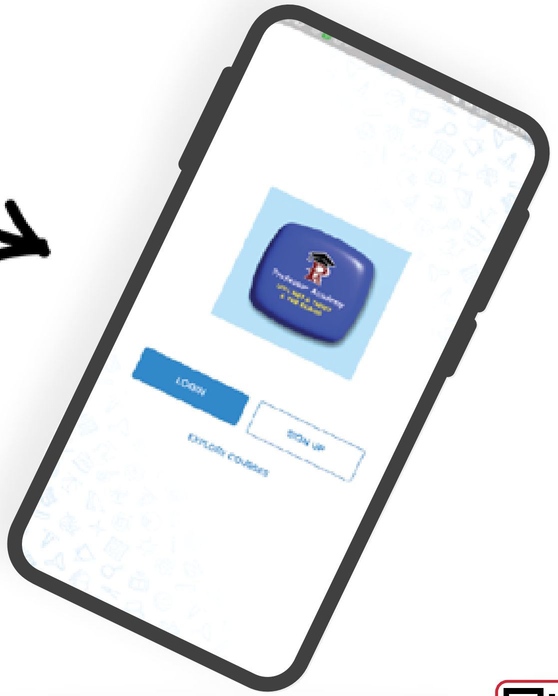

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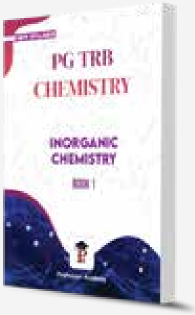

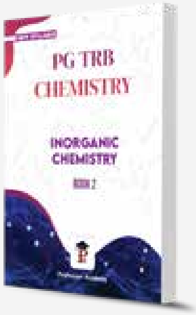

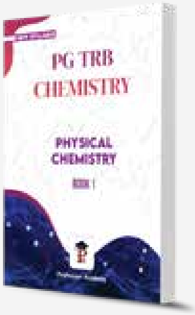

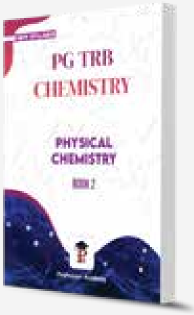

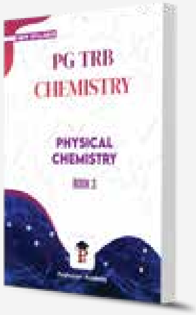

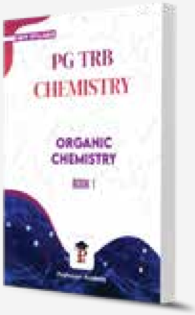

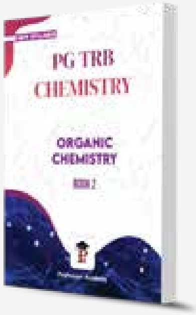

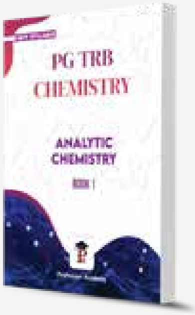

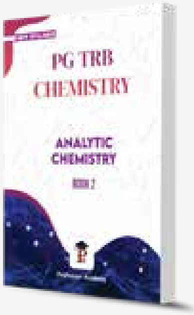

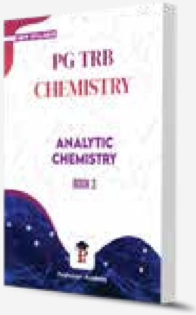

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