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Chemical Kinetics helps us to understand how chemical reactions occur.

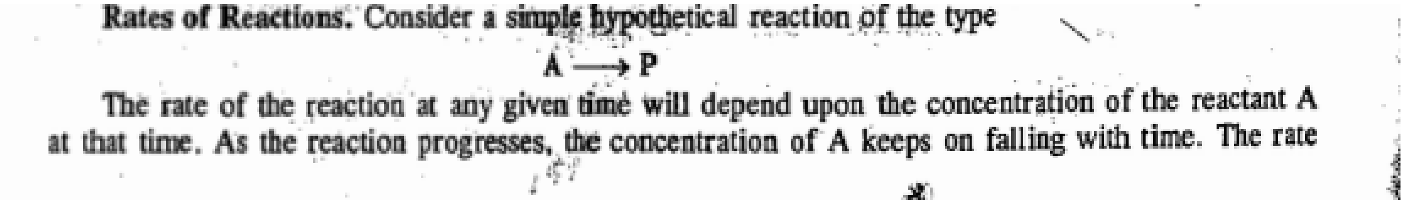
Chemistry, by its very nature, is concerned with change. Substances with well defined properties are converted by chemical reactions into other substances with different properties. For any chemical reaction, chemists try to find out

(a) the feasibility of a chemical reaction which can be predicted by thermodynamics (as you know that a reaction with $\Delta G < 0$, at constant temperature and pressure is feasible);

(b) extent to which a reaction will proceed can be determined from chemical equilibrium;

(c) speed of a reaction i.e. time taken by a reaction to reach equilibrium.

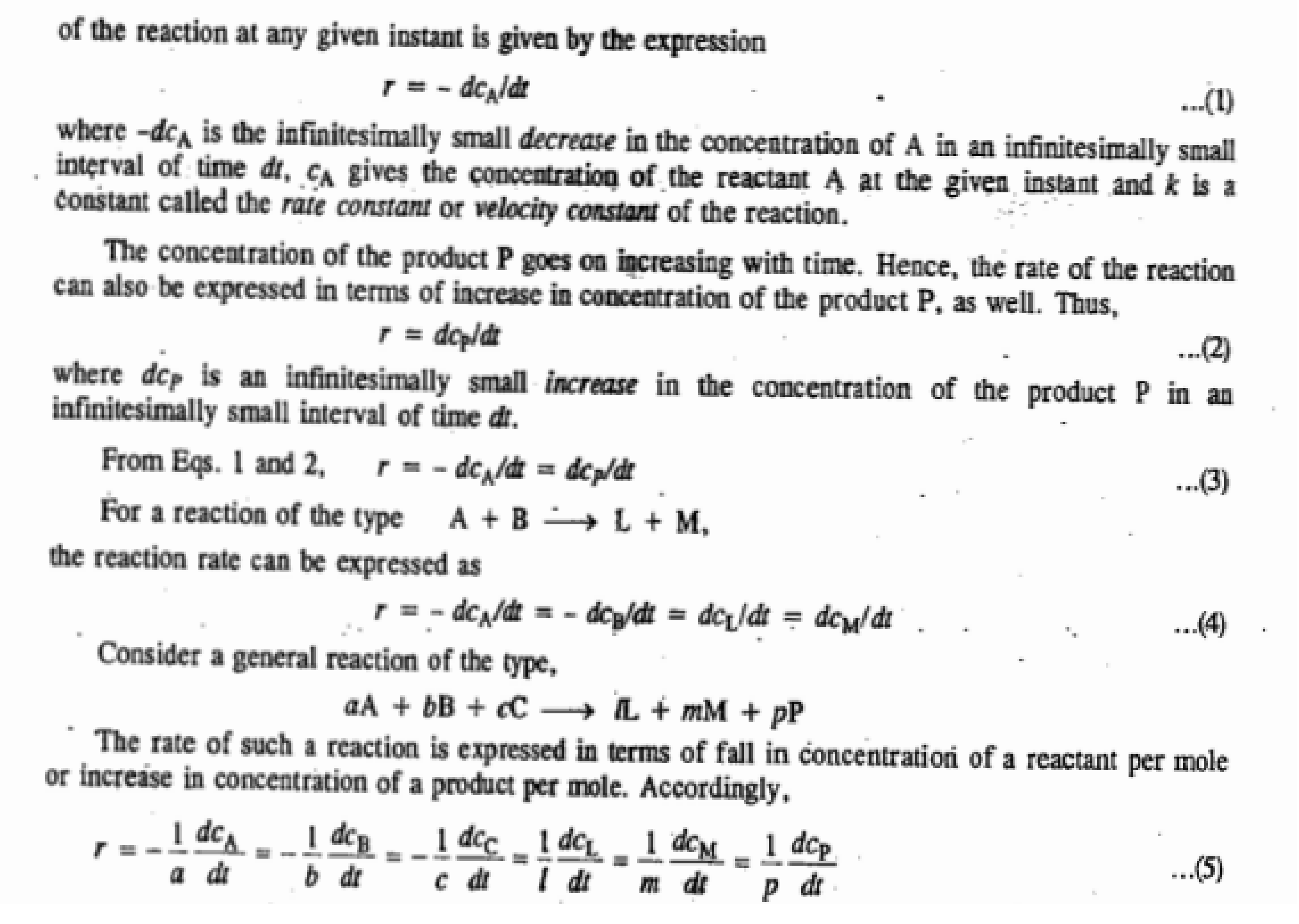
Along with feasibility and extent, it is equally important to know the rate and the factors controlling the rate of a chemical reaction for its complete understanding. For example, which parameters determine as to how rapidly food gets spoiled? How to design a rapidly setting material for dental filling? Or what controls the rate at which fuel burns in an auto engine? All these questions can be answered by the branch of chemistry, which deals with the study of reaction rates and their mechanisms, called **chemical kinetics**. The word kinetics is derived from the Greek word 'kinesis' meaning movement. Thermodynamics tells only about the feasibility of a reaction whereas chemical kinetics tells about the rate of a reaction. For example, thermodynamic data indicate that diamond shall convert to graphite but in reality the conversion rate is so slow that the change is not perceptible at all. Therefore, most people think that diamond is forever. Kinetic studies not only help us to determine the speed or rate of a chemical reaction but also describe the conditions by which the reaction rates can be altered. The factors such as concentration, temperature, pressure and catalyst affect the rate of a reaction. At the macroscopic level, we are interested in amounts reacted or formed and the rates of their consumption or formation. At the molecular level, the reaction mechanisms involving orientation and energy of molecules undergoing collisions, are discussed.



Rates of Reactions. Consider a simple hypothetical reaction of the type

$$A \longrightarrow P$$

The rate of the reaction at any given time will depend upon the concentration of the reactant A at that time. As the reaction progresses, the concentration of A keeps on falling with time. The rate



of the reaction at any given instant is given by the expression

$$r = -dc_A/dt \qquad \text{...(1)}$$

where $-dc_A$ is the infinitesimally small *decrease* in the concentration of A in an infinitesimally small interval of time dt, c_A gives the concentration of the reactant A at the given instant and k is a constant called the *rate constant* or *velocity constant* of the reaction.

The concentration of the product P goes on increasing with time. Hence, the rate of the reaction can also be expressed in terms of increase in concentration of the product P, as well. Thus,

$$r = dc_P/dt \qquad \text{...(2)}$$

where dc_P is an infinitesimally small *increase* in the concentration of the product P in an infinitesimally small interval of time dt.

From Eqs. 1 and 2, $r = -dc_A/dt = dc_P/dt$ ...(3)

For a reaction of the type $A + B \longrightarrow L + M$,

the reaction rate can be expressed as

$$r = -dc_A/dt = -dc_B/dt = dc_L/dt = dc_M/dt \qquad \text{...(4)}$$

Consider a general reaction of the type,

$$aA + bB + cC \longrightarrow lL + mM + pP$$

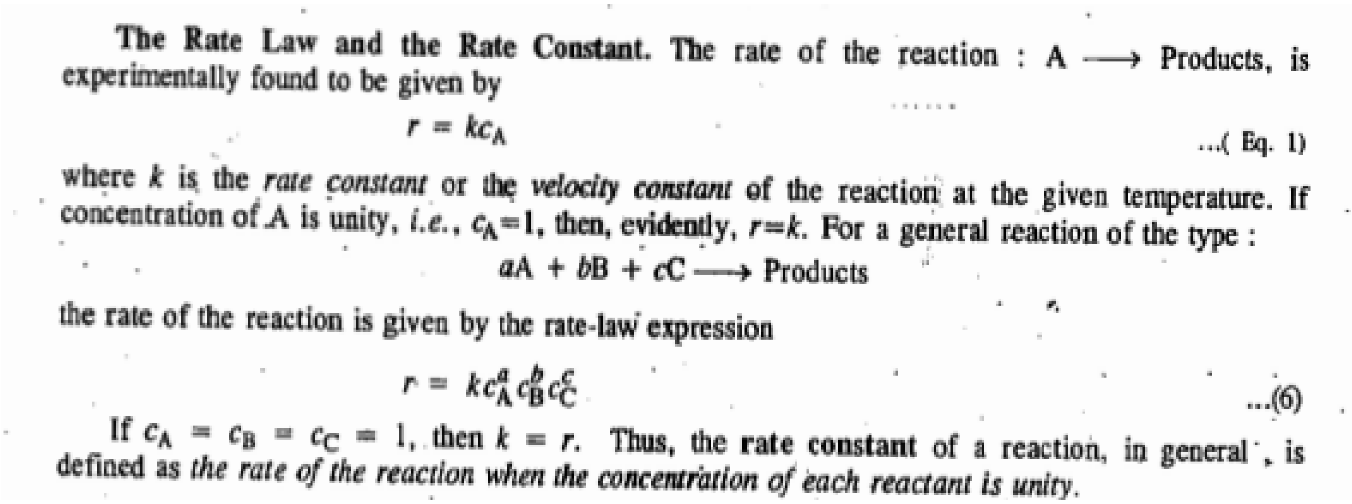
The rate of such a reaction is expressed in terms of fall in concentration of a reactant per mole or increase in concentration of a product per mole. Accordingly,

$$r = -\frac{1}{a}\frac{dc_A}{dt} = -\frac{1}{b}\frac{dc_B}{dt} = -\frac{1}{c}\frac{dc_C}{dt} = \frac{1}{l}\frac{dc_L}{dt} = \frac{1}{m}\frac{dc_M}{dt} = \frac{1}{p}\frac{dc_P}{dt} \qquad \text{...(5)}$$

Units of rate of a reaction

concentration $time^{-1}$.

mol $L^{-1}s^{-1}$.



The Rate Law and the Rate Constant. The rate of the reaction : A $\longrightarrow$ Products, is experimentally found to be given by

$$r = kc_A \qquad ...(\text{Eq. } 1)$$

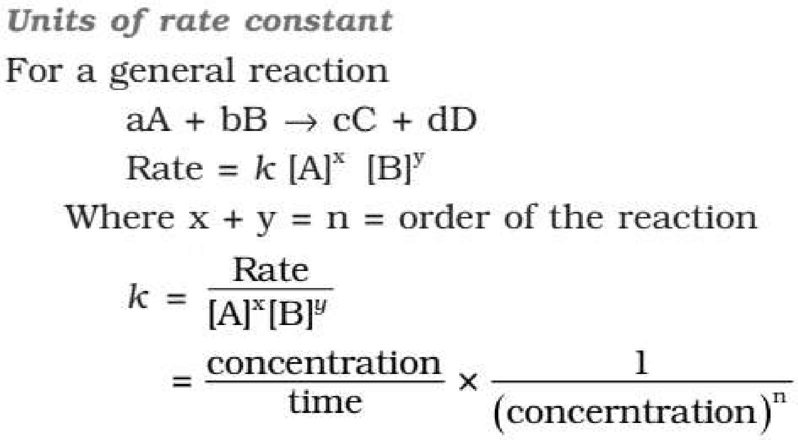
where k is the *rate constant* or the *velocity constant* of the reaction at the given temperature. If concentration of A is unity, *i.e.*, $c_A = 1$, then, evidently, $r = k$. For a general reaction of the type :

$$aA + bB + cC \longrightarrow \text{Products}$$

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

$$r = kc_A^a c_B^b c_C^c \qquad ...(6)$$

If $c_A = c_B = c_C = 1$, then $k = r$. Thus, the **rate constant** of a reaction, in general, is defined as *the rate of the reaction when the concentration of each reactant is unity.*



Units of rate constant

For a general reaction

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

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

Where x + y = n = order of the reaction

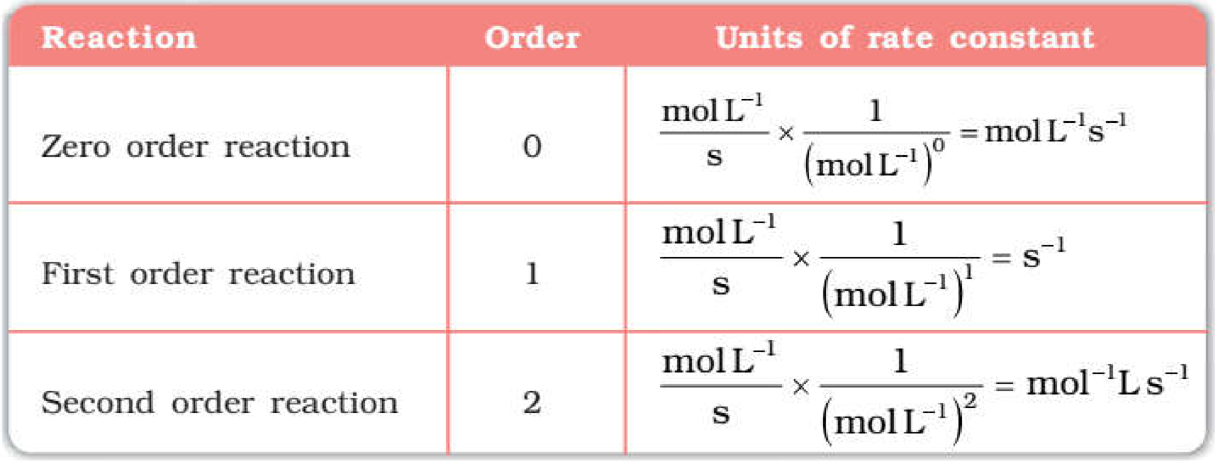
$$k = \frac{\text{Rate}}{[A]^x[B]^y}$$

$$= \frac{\text{concentration}}{\text{time}} \times \frac{1}{(\text{concerntration})^n}$$

$$= \frac{Concentration^{1-n}}{time}$$

SI units of concentration, mol L^{-1} and time.

Units of Rate constant



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

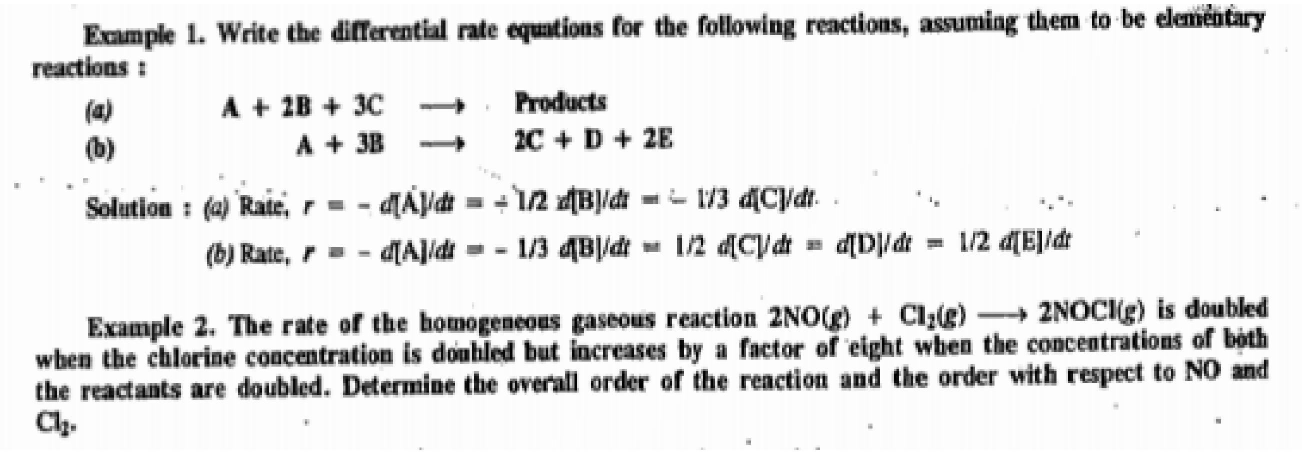
Order of Reaction

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

x and y indicate how sensitive the rate is to the change in concentration of A and B. Sum of these exponents, i.e., x + y in (4.4) gives the overall order of a reaction whereas x and y represent the order with respect to the reactants A and B respectively.

Hence, **the sum of powers of the concentration of the reactants in the rate law expression is called the order of that chemical reaction.**

Order of a reaction can be 0, 1, 2, 3 and even a fraction. A zero order reaction means that the rate of reaction is independent of the concentration of reactants.



Example 1. Write the differential rate equations for the following reactions, assuming them to be elementary reactions :

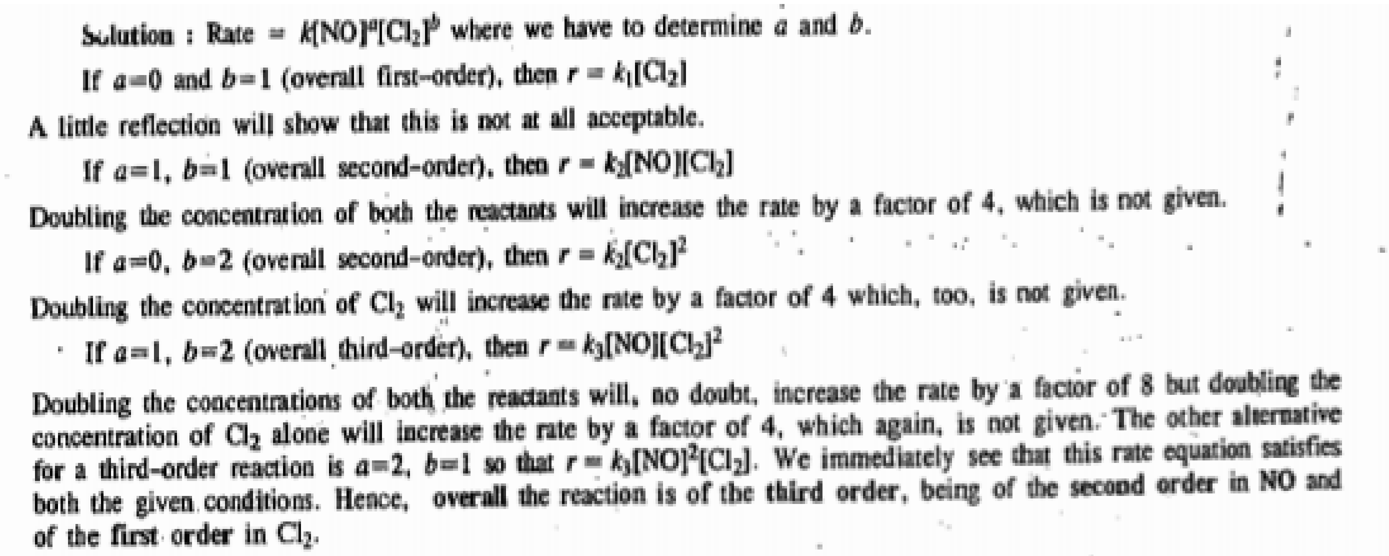
(a) $A + 2B + 3C \longrightarrow$ Products

(b) $A + 3B \longrightarrow 2C + D + 2E$

Solution : *(a)* Rate, $r = -d[A]/dt = -1/2\ d[B]/dt = -1/3\ d[C]/dt$

(b) Rate, $r = -d[A]/dt = -1/3\ d[B]/dt = 1/2\ d[C]/dt = d[D]/dt = 1/2\ d[E]/dt$

Example 2. The rate of the homogeneous gaseous reaction $2NO(g) + Cl_2(g) \longrightarrow 2NOCl(g)$ is doubled when the chlorine concentration is doubled but increases by a factor of eight when the concentrations of both the reactants are doubled. Determine the overall order of the reaction and the order with respect to NO and Cl_2.



Solution : Rate $= k[NO]^a[Cl_2]^b$ where we have to determine a and b.

If $a=0$ and $b=1$ (overall first-order), then $r = k_1[Cl_2]$

A little reflection will show that this is not at all acceptable.

If $a=1$, $b=1$ (overall second-order), then $r = k_2[NO][Cl_2]$

Doubling the concentration of both the reactants will increase the rate by a factor of 4, which is not given.

If $a=0$, $b=2$ (overall second-order), then $r = k_2[Cl_2]^2$

Doubling the concentration of Cl_2 will increase the rate by a factor of 4 which, too, is not given.

If $a=1$, $b=2$ (overall third-order), then $r = k_3[NO][Cl_2]^2$

Doubling the concentrations of both the reactants will, no doubt, increase the rate by a factor of 8 but doubling the concentration of Cl_2 alone will increase the rate by a factor of 4, which again, is not given. The other alternative for a third-order reaction is $a=2$, $b=1$ so that $r = k_3[NO]^2[Cl_2]$. We immediately see that this rate equation satisfies both the given conditions. Hence, **overall the reaction is of the third order, being of the second order in NO and of the first order in Cl_2.**

Integration of Rate Expressions

1. Integration of Rate Expression for First–Order Reactions

The differential rate expression for the first–order reaction, A ⟶ P is given by

$$r = -dc_A/dt = dc_P/dt = kc_A \qquad \text{...(7)}$$

Separating the variables, *i.e.*, bringing concentration terms on one side and the time on the other side, we get

$$-dc_A/c_A = k_1 dt \qquad \text{...(8)}$$

Before performing the actual integration, let us first ascertain the limits of integration. Let the initial concentration at initial time $t=0$ be c_0. Subsequently, at any other time, t, the concentration will be c. On integration, we obtain

$$\int_{c_0}^{c} -dc_A/c_A = k_1 \int_0^t dt \qquad \text{...(9)}$$

$$\therefore \qquad [-\ln c_A]_{c_0}^{c} = k_1 [t]_0^t$$

$$\text{or} \qquad -\ln(c/c_0) = k_1 t \qquad \text{...(10)}$$

$$\text{or} \qquad c = c_0 e^{-k_1 t}$$

From Eq. 10, we can also write

$$k_1 = 1/t \ln c_0/c \qquad \text{...(11)}$$

Eq. 11 gives the expression for the first–order rate constant, k_1.

Eq. 11 is usually written in another form. If initial concentration of the reactant is a and x moles of it react in time t; then the concentration of the reactant left behind at time t will be a–x. In such a case, $c_0 \propto a$ and $c \propto (a-x)$. Hence, Eq. 11 takes the form

$$k_1 = \frac{1}{t} \ln \frac{a}{a-x} \qquad \text{...(12)}$$

Eq. 12 shows that the concentration of reactant in a first–order reaction decreases exponentially with time : this is shown graphically in Fig. 1. The plot of ln c versus t is shown in Fig. 2.

For a first-order reaction, the concentration of the reactant decreases and that of the product increases exponentially with time, as illustrated in Fig. 3.

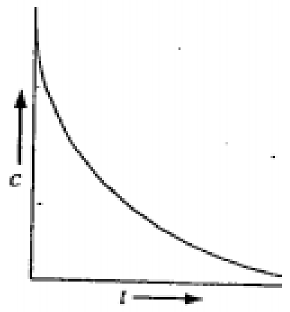


Fig. 1. The plot of concentration versus time for a first-order reaction.

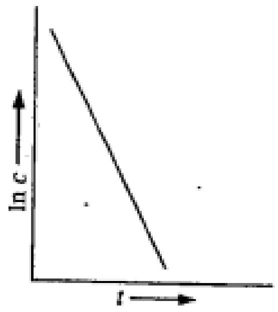


Fig. 2. The plot of ln c versus time t for a first-order reaction.

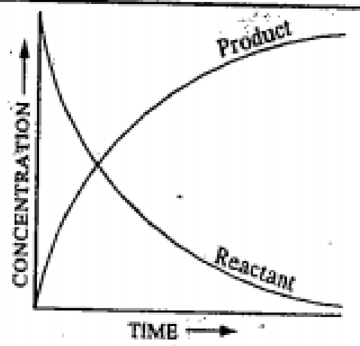


Fig. 3. Concentration versus time plot for the reactant and the product of a first-order reaction.

2. Integration of Rate Expressions for Second-Order Reactions.

The differential rate expressions for the second-order reactions are as follows :

Case I. When the Reactants are Different. Consider a second-order reaction

$$A + B \longrightarrow P$$

where the initial concentration of A is a mol dm^{-3} and that of B is b mol dm^{-3}. After time t, x mol dm^{-3} of A and x mol dm^{-3} of B react to form x mol dm^{-3} of the product. Thus, the reactant concentrations at time t are $(a - x)$ and $(b - x)$, respectively. The differential rate expression for the second-order reaction is, evidently,

$$r = -d[A]/dt = -d[B]/dt = d[P]/dt = k_2[A][B]$$

This can be written as $r = dx/dt = k_2(a-x)(b-x)$ ...(13)

where k_2 is the second-order rate constant. Separating the variables, we have

$$dx/(a-x)(b-x) = k_2dt \qquad \text{...(14)}$$

Resolving into partial fractions (assuming that $a > b$), we have

$$\frac{1}{(a-x)(b-x)} = \frac{1}{a-b}\left[\frac{1}{b-x} - \frac{1}{a-x}\right] \qquad \text{...(15)}$$

Using this result, we can integrate Eq. 14 as follows :

$$\int\frac{dx}{(a-x)(b-x)} = \frac{1}{a-b}\left[\int\frac{dx}{b-x} - \int\frac{dx}{a-x}\right] = k_2\int dt \qquad \text{...(16)}$$

We have taken the factor $1/(a-b)$ outside the integral sign because this quantity is a constant. Carrying out the integration, we have

$$\frac{1}{a-b}\left[-\ln(b-x) - \{-\ln(a-x)\}\right] = k_2t + C$$

or

$$\frac{1}{a-b}\ln\left[\frac{a-x}{b-x}\right] = k_2t + C \qquad \text{...(17)}$$

where C is the constant of integration. To determine C, we recall that at $t=0$, $x=0$. Hence, from Eq. 17,

$$C = \frac{1}{a-b}\ln\left(\frac{a}{b}\right) \qquad \text{...(18)}$$

Substituting this value of C in Eq. 17, we have

$$\frac{1}{a-b}\ln\left(\frac{a-x}{b-x}\right) = k_2t + \frac{1}{a-b}\ln\left(\frac{a}{b}\right)$$

Rearranging and solving for k_2, we get

$$k_2 = \frac{1}{(a-b)t}\left[\ln\left(\frac{a-x}{b-x}\right) - \ln\left(\frac{a}{b}\right)\right] = \frac{1}{(a-b)t}\ln\frac{b(a-x)}{a(b-x)} \qquad \text{...(19)}$$

Eq. 19 is the required integrated expression for the rate constant of a second-order reaction. Here we have assumed that $a > b$. If we had assumed that $b > a$, then the reader can easily verify that

$$k_2 = \frac{1}{(b-a)t}\ln\frac{a(b-x)}{b(a-x)} \qquad \text{...(20)}$$

It can be easily seen that neither Eq. 19 nor Eq. 20 is applicable when the concentrations of both the reactants are the same, *i.e.*, when $a=b$.

If we write Eq. 19 in the form

$$\frac{1}{a-b}\ln\frac{b(a-x)}{a(b-x)} = k_2t \qquad \text{...(21)}$$

we see that it is the equation of a straight line passing through the origin (*viz.*, $y=mx$), where

$$y \equiv \frac{1}{a-b}\ln\frac{b(a-x)}{a(b-x)}\ ;\ m \equiv k_2\ ;\ x \equiv t$$

The plot of the left-hand side of Eq. 21 versus t gives a straight line (Fig. 5) whose slope is equal to the rate constant, k_2.

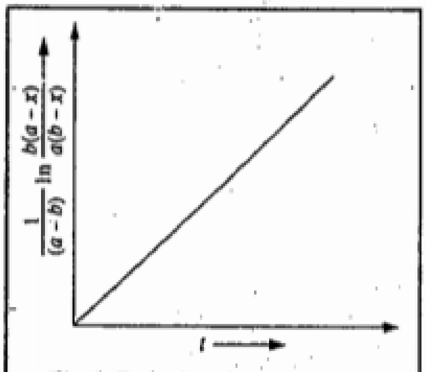


Fig. 5. Evaluation of rate constant for a second-order reaction.

Case II. When Both the Reactants are the Same. This, in effect, means that two molecules of the same reactant are involved in the chemical reaction. The second-order reaction in this case would be represented as

$$2A \longrightarrow P$$

and the rate of the reaction would be expressed as

$$r = dx/dt = k_2(a - x)^2 \qquad \text{...(22)}$$

where, as before, a is the initial concentration of A, x is the concentration of the product formed after time t and $(a - x)$ is the concentration of A remaining at time t.

Separating the variables and integrating, we have

$$\int \frac{dx}{(a-x)^2} = k_2 dt \qquad \text{...(23)}$$

$$\left[-\frac{1}{a-x}\right](-1) = k_2 t + C \quad \text{or} \quad \frac{1}{a-x} = k_2 t + C \qquad \text{...(24)}$$

We know that at t=0, x=0 so that C=1/a. Hence,

$$\frac{1}{a-x} = k_2 t + \frac{1}{a}$$

Transposing and solving for k_2, we get

$$k_2 = \frac{1}{t}\left[\frac{1}{a-x} - \frac{1}{a}\right] = \frac{1}{t}\left[\frac{x}{a(a-x)}\right] \qquad \text{...(25)}$$

which is the required integrated expression for the rate constant of a second-order reaction in which two molecules of the same reactant are involved in the reaction.

The classic example of the above type of the second-order reaction is the gaseous decomposition of hydrogen iodide.

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

The rate expression for this reaction is

$$r = -d[HI]/dt = k_2[HI]^2$$

The plot of r versus reactant concentration is shown in Fig. 6.

The rate constants of second-order reactions in which the two reactants, although different, have the same initial concentration, are also determined with the help of Eq. 25.

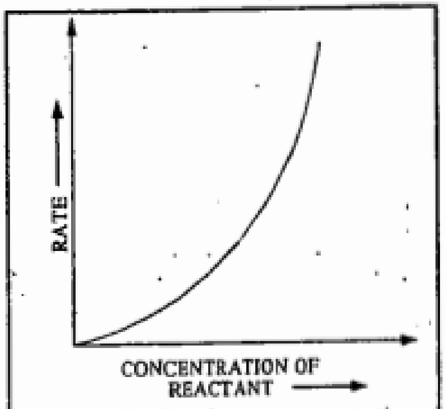
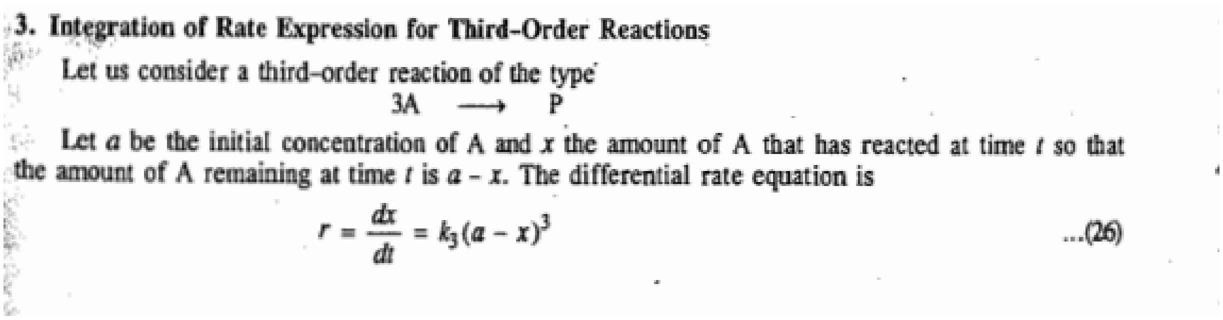


Fig. 6. The plot of r *versus* concentration for a second-order reaction.



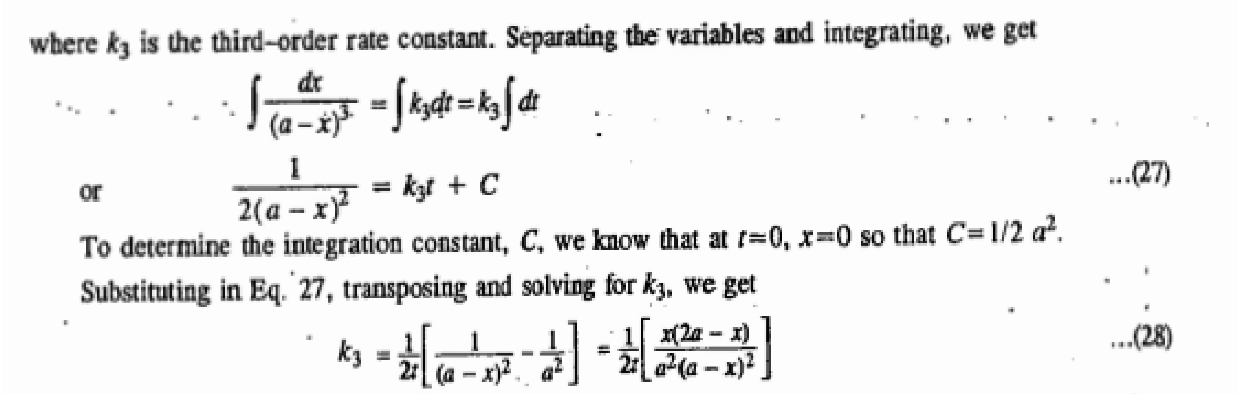
3. Integration of Rate Expression for Third-Order Reactions

Let us consider a third-order reaction of the type

$$3A \longrightarrow P$$

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

$$r = \frac{dx}{dt} = k_3(a-x)^3 \qquad \text{...(26)}$$



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

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

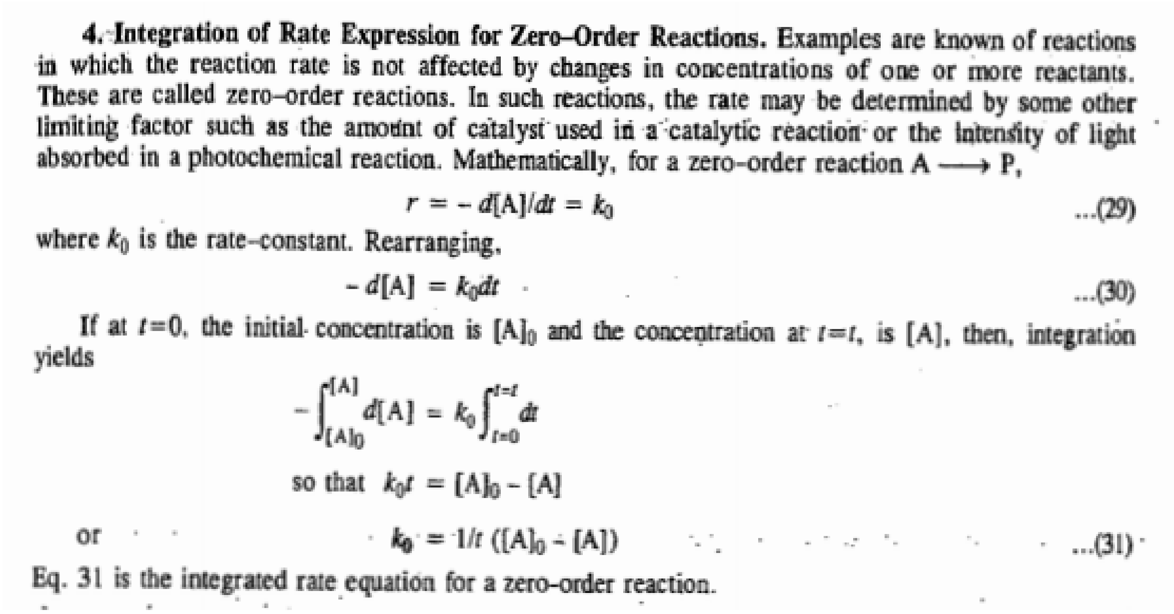
or

$$\frac{1}{2(a-x)^2} = k_3 t + C \qquad \text{...(27)}$$

To determine the integration constant, C, we know that at $t=0$, $x=0$ so that $C = 1/2\ a^2$.

Substituting in Eq. 27, transposing and solving for k_3, we get

$$k_3 = \frac{1}{2t}\left[\frac{1}{(a-x)^2} - \frac{1}{a^2}\right] = \frac{1}{2t}\left[\frac{x(2a-x)}{a^2(a-x)^2}\right] \qquad \text{...(28)}$$



4. Integration of Rate Expression for Zero-Order Reactions. Examples are known of reactions in which the reaction rate is not affected by changes in concentrations of one or more reactants. These are called zero-order reactions. In such reactions, the rate may be determined by some other limiting factor such as the amount of catalyst used in a catalytic reaction or the intensity of light absorbed in a photochemical reaction. Mathematically, for a zero-order reaction A ⟶ P,

$$r = -d[A]/dt = k_0 \qquad \text{...(29)}$$

where k_0 is the rate-constant. Rearranging,

$$-d[A] = k_0 dt \qquad \text{...(30)}$$

If at $t=0$, the initial concentration is $[A]_0$ and the concentration at $t=t$, is $[A]$, then, integration yields

$$-\int_{[A]_0}^{[A]} d[A] = k_0 \int_{t=0}^{t=t} dt$$

$$\text{so that } k_0 t = [A]_0 - [A]$$

or

$$k_0 = 1/t\ ([A]_0 - [A]) \qquad \text{...(31)}$$

Eq. 31 is the integrated rate equation for a zero-order 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 from Eq. 12 that at $x=a/2$, $t=t_{1/2}$. Hence,

$$k_1 = \frac{1}{t_{1/2}} \ln \frac{a}{a-(a/2)} = \frac{1}{t_{1/2}} \ln 2 = \frac{0{\cdot}693}{t_{1/2}}$$

Thus, $$t_{1/2} = 0{\cdot}693/k_1 \qquad \text{...(32)}$$

Example 20. The rate constant for a first-order reaction is $1{\cdot}54\times10^{-3}\ s^{-1}$. Calculate its half-life time.

Solution : Substituting the data directly in Eq. 32, we have

$$t_{1/2} = \frac{0{\cdot}693}{k_1} = \frac{0{\cdot}693}{1{\cdot}54\times10^{-3}\,s^{-1}} = 450\ s$$

Example 21. The half-life of the homogeneous gaseous reaction $SO_2Cl_2 \longrightarrow SO_2 + Cl_2$, which obeys first-order kinetics, is 8·0 minutes. How long will it take for the concentration of SO_2Cl_2 to be reduced to 1% of the initial value ?

Solution : From Eq. 32, by rearranging, we get

$$k_1 = \frac{0{\cdot}693}{t_{1/2}} = \frac{0{\cdot}693}{8{\cdot}0\ \text{min}} = 0{\cdot}087\ \text{min}^{-1}$$

For a first-order reaction, $k_1 = \frac{1}{t} \ln \frac{a}{a-x}$

or $$t = \frac{1}{k_1} \ln \frac{a}{a-x} = \frac{1}{0{\cdot}087\ \text{min}^{-1}} \ln\left(\frac{100}{1}\right) = 52{\cdot}93\ \text{min}$$

Example 22. In an enzyme solution, sucrose undergoes fermentation. If 0·10 M solution of sucrose is reduced to 0·05 M in 10 hours and to 0·025 M in 20 hours, what is the order of the reaction and what is the rate constant?

Solution : Since on doubling the time from 10 hours to 20 hours, fractional reduction of sucrose concentration is also doubled, the reaction must be of the first order.

Since for a first-order reaction, $t_{1/2}=0{\cdot}693/k_1$, hence

$$k_1 = \frac{0{\cdot}693}{t_{1/2}} = \frac{0{\cdot}693}{10\times60\times60 s} = 1{\cdot}9\times10^{-5}\ s^{-1}$$

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

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

Thus, $$t_{1/2} = 1/(k_2 a) \qquad \text{...(33)}$$

From Eq. 33, we find that $t_{1/2}$ of a second-order reaction is inversely proportional to the initial concentration of the reactant and, thus, it does not remain constant as the reaction proceeds.

Example 25. The rate constant for a second-order reaction is $3{\cdot}33 \times 10^{-2}$ dm^3 mol^{-1} s^{-1}. If the initial concentration of the reactant is 0·05 mol dm^{-3}, calculate its half-life.

Solution : Substituting in Eq. 33, we have

$$t_{1/2} = \frac{1}{(3{.}33 \times 10^{-2}\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1})(5 \times 10^{-2}\ \text{mol dm}^{-3})} = 600\ \text{s} = 10\ \text{min}$$

3. $t_{1/2}$ for an nth-Order Reaction. In general, for an nth-order reaction, $n\text{A} \longrightarrow$ Products,

$$r = d[\text{A}]/dt = k_n[\text{A}]^n.$$

It has been shown in Example 26, that

$$t_{1/2} = \frac{2^{n-1} - 1}{k_n(n-1)a_0^{n-1}} \qquad \text{...(34)}$$

where a_0 is the initial concentration of A and k_n is the nth-order rate constant. From Eq. 34 we see that

$$t_{1/2} \propto 1/a_0^{n-1} \qquad \text{...(35)}$$

It is easy to see from Eq. 35 that 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.

Example 26. Derive an expression for the half-life of an *n*th-order reaction where $n \geq 2$.

Solution : An *n*th-order reaction may be represented as

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

The differential rate equation is

$$-d[\mathrm{A}]/dt = k_n[\mathrm{A}]^n \qquad \ldots(i)$$

where k_n is the *n*th-order rate constant.

Separating the variables and integrating, we obtain

$$\int -\frac{d[\mathrm{A}]}{[\mathrm{A}]^n} = k_n \int dt \qquad \ldots(ii)$$

or

$$t = \frac{1}{k_n(n-1)[\mathrm{A}]^{n-1}} + C \qquad \ldots(iii)$$

where C is the constant of integration which we have to determine.

Let $[\mathrm{A}] = a$ and $[\mathrm{A}]_0 = a_0$, the initial concentration. Then, Eq. *(iii)* can be written as

$$t = \frac{1}{k_n(n-1)a^{n-1}} + C \qquad \ldots(iv)$$

At $t=0$, $a=a_0$, so that $C = \dfrac{1}{k_n(n-1)a_0^{n-1}}$ ...(v)

Substituting for C in Eq. *(iv)*, we get

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

When $t=t_{1/2}$, $a=a_0/2$ so that from Eq. *(vi)*,

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

or

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

which is the desired expression. This expression shows that for an nth-order reaction, $t_{1/2} \propto (1/a_0)^{n-1}$ where $n \geq 2$.

METHODS FOR DETERMINING THE ORDER OF A REACTION

The order of a reaction is never known before hand, though majority of reactions are of the first or of the second order. The following methods are commonly used for determining the order of a reaction.

1. The Use of Differential Rate Expressions. According to this method, which was devised by van't Hoff, the rate of an *n*th–order reaction is given by

$$r = k_n c^n \qquad \text{...(36)}$$

Taking logs, we have

$$\ln r = \ln k_n + n \ln c\,. \qquad \text{...(37)}$$

Thus, if the double–logarithmic plot of rate versus concentration gives a straight line, then the slope gives the value of n and the intercept gives $\ln k_n$ (Fig. 7).

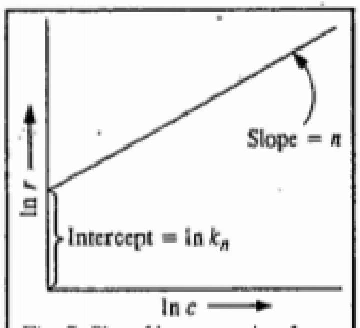


Fig. 7. Plot of $\ln r$ versus $\ln c$ for an nth-order reaction.

Also, if r_1 and r_2 are the rates at two different reactant concentrations c_1 and c_2, then

$$\frac{r_1}{r_2} = \frac{-dc_1/dt}{-dc_2/dt} = \frac{k_n c_1^n}{k_n c_2^n} = \left(\frac{c_1}{c_2}\right)^n$$

Taking logs,
$$\ln\frac{r_1}{r_2} = n \ln\frac{c_1}{c_2} \quad \text{whence } n = \frac{\ln(r_1/r_2)}{\ln(c_1/c_2)} \qquad \text{...(38)}$$

2. The Use of Integral Rate Expressions. We have already demonstrated this method in solving problems for reactions of various orders. This method can be used either analytically or graphically. In the analytical method, we assume a certain order for the reaction and calculate the rate constants from the given data. The constancy of the k–values obtained suggests that the assumed order is correct. If the k-values obtained are not constant, we assume a different order for the reaction and again calculate the k–values using the new rate expression and see if k is constant.

In the graphical method, if the plot of $\ln c$ versus t is a straight line, the reaction is of the first order. Similarly, the integrated expression for the second–order reaction can be utilized graphically to ascertain if the reaction is of the second order, and so on.

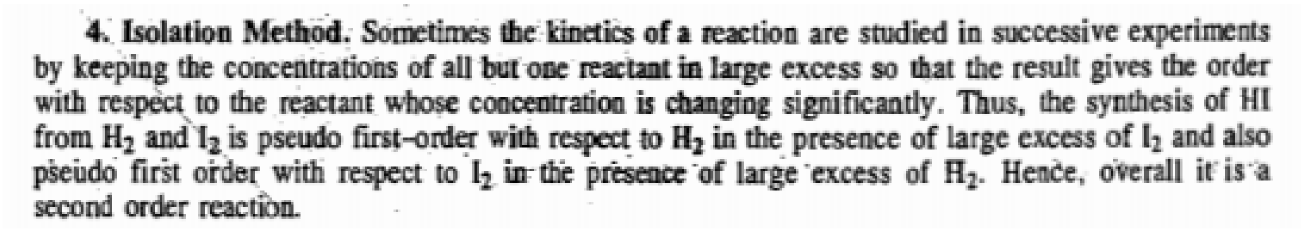
3. The Half–life Method. We have shown above that, provided all reactants are present in the same molar concentrations, the half–life, $t_{1/2}$, of an nth–order reaction is given by Eq. 35.

If two experiments are carried out at different initial molar concentrations, then

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

or
$$n = 1 + \frac{\ln(t_{1/2})_1/\ln(t_{1/2})_2}{\ln(a_2/a_1)} \qquad \text{...(39)}$$

This method was suggested by Ostwald. The determination of half–lives of a reaction at two different initial concentrations leads to the determination of n.



4. Isolation Method. Sometimes the kinetics of a reaction are studied in successive experiments by keeping the concentrations of all but one reactant in large excess so that the result gives the order with respect to the reactant whose concentration is changing significantly. Thus, the synthesis of HI from H_2 and I_2 is pseudo first-order with respect to H_2 in the presence of large excess of I_2 and also pseudo first order with respect to I_2 in the presence of large excess of H_2. Hence, overall it is a second order reaction.

Molecularity of Reaction

Another property of a reaction called molecularity helps in understanding its mechanism. **The number of reacting species (atoms, ions or molecules) taking part in an elementary reaction, which must collide simultaneously in order to bring about a chemical reaction is called molecularity of a reaction**. The reaction can be unimolecular when one reacting species is involved, for example, decomposition of ammonium nitrite.

$$NH_4NO_2 \rightarrow N_2 + 2H_2O$$

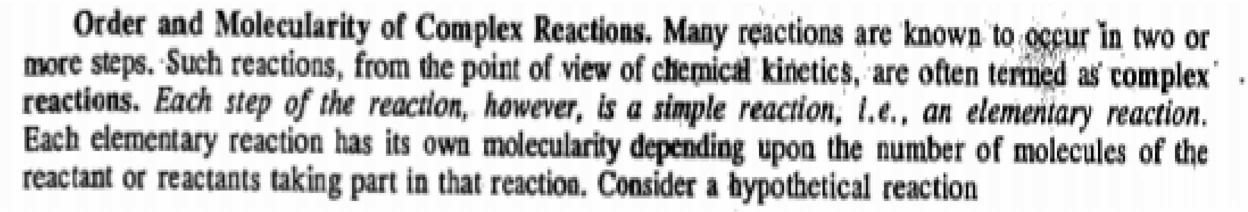
Bimolecular reactions involve simultaneous collision between two species, for example, dissociation of hydrogen iodide.

$$2HI \rightarrow H_2 + I_2$$

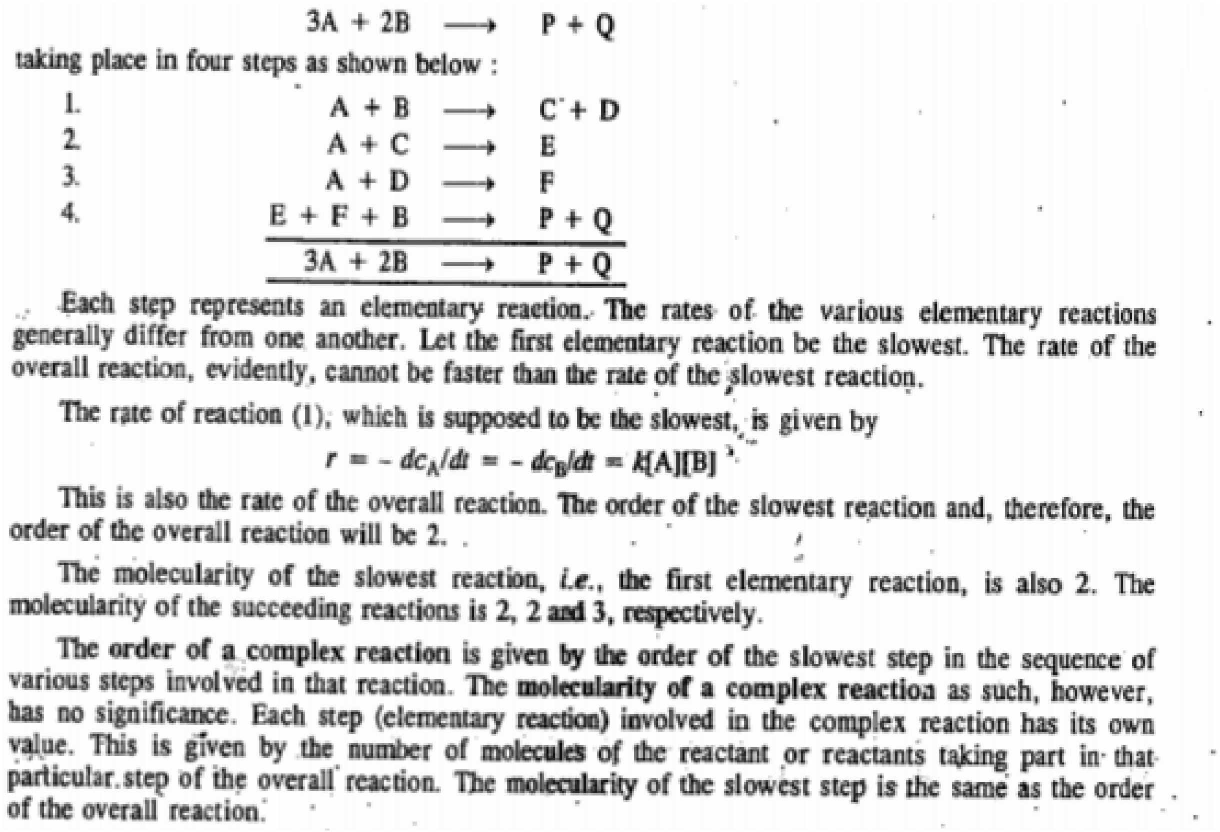
Trimolecular or termolecular reactions involve simultaneous collision between three reacting species, for example,

$$2NO + O_2 \rightarrow 2NO_2$$

The probability that more than three molecules can collide and react simultaneously is very small. Hence, the molecularity greater than three is not observed.



Order and Molecularity of Complex Reactions. Many reactions are known to occur in two or more steps. Such reactions, from the point of view of chemical kinetics, are often termed as **complex reactions**. *Each step of the reaction, however, is a simple reaction, i.e., an elementary reaction.* Each elementary reaction has its own molecularity depending upon the number of molecules of the reactant or reactants taking part in that reaction. Consider a hypothetical reaction



$$3A + 2B \longrightarrow P + Q$$

taking place in four steps as shown below :

$$
\begin{array}{lrcl}
1. & A + B & \longrightarrow & C + D \\
2. & A + C & \longrightarrow & E \\
3. & A + D & \longrightarrow & F \\
4. & E + F + B & \longrightarrow & P + Q \\
\hline
 & 3A + 2B & \longrightarrow & P + Q
\end{array}
$$

Each step represents an elementary reaction. The rates of the various elementary reactions generally differ from one another. Let the first elementary reaction be the slowest. The rate of the overall reaction, evidently, cannot be faster than the rate of the slowest reaction.

The rate of reaction (1), which is supposed to be the slowest, is given by

$$r = -dc_A/dt = -dc_B/dt = k[A][B]$$

This is also the rate of the overall reaction. The order of the slowest reaction and, therefore, the order of the overall reaction will be 2.

The molecularity of the slowest reaction, *i.e.*, the first elementary reaction, is also 2. The molecularity of the succeeding reactions is 2, 2 **and** 3, **respectively**.

The **order of a complex reaction** is given **by the** order of the slowest step in the sequence of various steps involved in that reaction. The **molecularity of a complex reaction** as such, however, has no significance. Each step (elementary reaction) involved in the complex reaction has its own value. This is given by the number of **molecules** of the reactant or reactants taking part in that particular step of the overall reaction. The **molecularity** of the slowest step is the same as the order of the overall reaction.

Thus, from the discussion, till now, we conclude the following:

(i) Order of a reaction is an experimental quantity. It can be zero and even a fraction but molecularity cannot be zero or a non integer.

(ii) Order is applicable to elementary as well as complex reactions whereas molecularity is applicable only for elementary reactions. For complex reaction molecularity has no meaning.

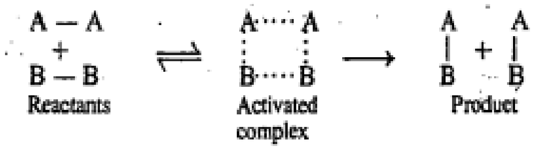
(iii) For complex reaction, order is given by the slowest step and generally, molecularity of the slowest step is same as the order of the overall reaction.

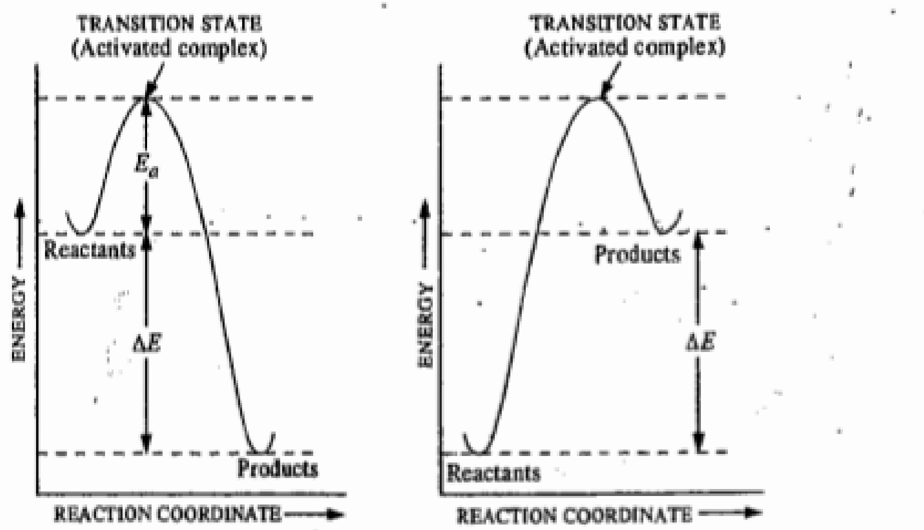
Activated Complex Theory (ACT) of Bimolecular Reactions

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 :

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

or





(a) Exothermic reaction (b) Endothermic reaction

Fig. 12. The profile of energy versus reaction coordinate in ACT in the case of an exothermic and an endothermic reaction.

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

$$A + B \overset{K^{\neq}}{\rightleftharpoons} (AB)^{\neq} \xrightarrow{k_2} \text{Products} \quad ...(58)$$

where $(AB)^{\neq}$ is the activated complex and $K^{\neq}$ is the equilibrium constant between the reactants and activated complex. As said above, in $(AB)^{\neq}$ 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_BT where k_B is the Boltzmann constant) whereas from quantum mechanics, it is given by $h\nu$ so that $h\nu = RT/N_A$ or $\nu = RT/N_Ah = k_BT/h$. 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

$$-d[A]/dt = \kappa k_2[(AB)^{\neq}] = \kappa(k_BT/h)[(AB)^{\neq}] \quad ...(59)$$

where the factor κ, 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 thus omitted from the rate expression. The concentration of the activated complex, $[(AB)^{\neq}]$, can be obtained by writing the equilibrium expression

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

whence $$[(AB)^{\neq}] = K^{\neq}[A][B] \quad ...(60)$$

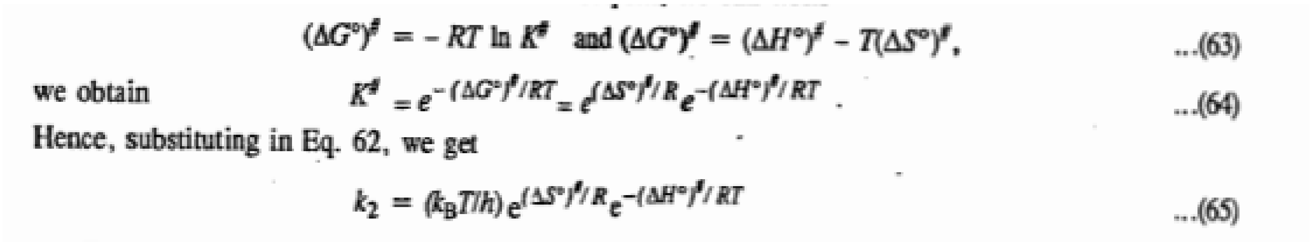
Substituting in Eq. 59, we obtain

$$-d[A]/dt = (k_BT/h)\, K^{\neq}[A][B] \quad ...(61)$$

Thus, the rate constant k_2 may be expressed as

$$k_2 = (k_BT/h)\, K^{\neq} \quad ...(62)$$

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



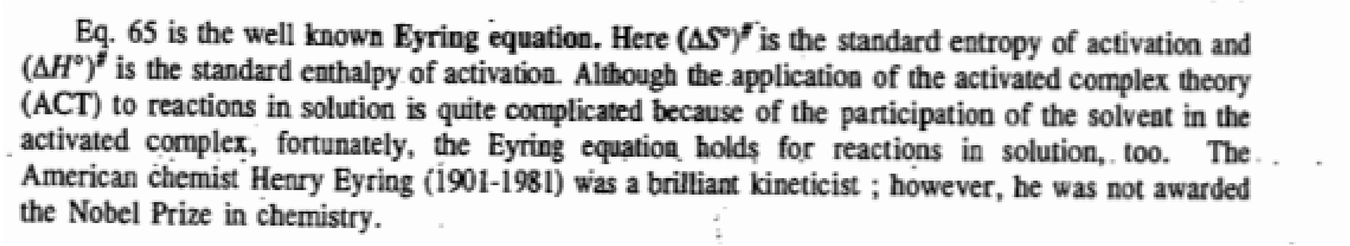
$$(\Delta G^\circ)^\neq = -RT \ln K^\neq \quad \text{and} \quad (\Delta G^\circ)^\neq = (\Delta H^\circ)^\neq - T(\Delta S^\circ)^\neq, \qquad ...(63)$$

we obtain

$$K^\neq = e^{-(\Delta G^\circ)^\neq/RT} = e^{(\Delta S^\circ)^\neq/R}\, e^{-(\Delta H^\circ)^\neq/RT} \qquad ...(64)$$

Hence, substituting in Eq. 62, we get

$$k_2 = (k_B T/h)\, e^{(\Delta S^\circ)^\neq/R}\, e^{-(\Delta H^\circ)^\neq/RT} \qquad ...(65)$$



Eq. 65 is the well known **Eyring equation.** Here $(\Delta S^\circ)^\neq$ is the standard entropy of activation and $(\Delta H^\circ)^\neq$ 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.