Chemical kinetics

Chemical kinetics constitutes an important topic in physical chemistry. It concerns itself with measurement of rate of reactions proceeding under given conditions of temperature, pressure and concentrations. The study of this subject has been highly useful in determining the factors which influence rates of reactions as well as in understanding of mechanism of a number of chemical reactions.

Thermodynamic descriptions of chemical reactions involved the Gibbs or Helmholtz energy for a reaction and the corresponding equilibrium constant. These quantities are sufficient to predict the reactant and product concentrations at equilibrium but are of little use in determining the timescale over which the reaction occurs. For example heat of formation of water from gaseous H_2 and O_2 is -285 kJ/mol but the reaction take place very slowly, if at all unless the reaction is initiated by spark. That is, thermodynamics may dictate that a reaction is spontaneous, but it does not dictate the over which the reaction will occur and reach equilibrium. Chemical kinetics provides information on the timescale of chemical reactions.
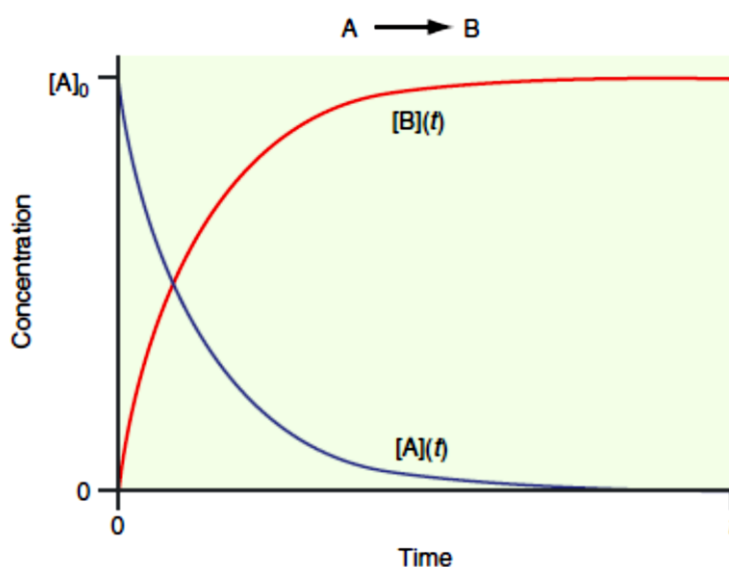

Figure 1: *Concentration as a function of time for the conversion of reactant A into product B. The concentration of A at is $[A]_0$, and the concentration of B is zero. As the reaction proceeds, the loss of A results in the production of B.*

In the course of a chemical reaction, concentrations will change with time as "reactants" become "products." Figure 1 presents possibly the first chemical reaction introduced in introductory chemistry: the conversion of reactant "A" into product "B." The figure illustrates that, as the reaction proceeds, a decrease in reactant concentration and a corresponding increase in product concentration are observed. One way to describe this process is to define the rate of concentration change with time, a quantity that is referred to as the reaction rate. The central idea behind chemical kinetics is that by monitoring the rate at which chemical reactions occur and determining the dependence of

this rate on system parameters such as temperature, concentration, and pressure and catalyst we can gain insight into the mechanism of the reaction.

Rate of reactions

The rate of a chemical reaction is expressed as a change in concentrations of some species with time. Therefore, the dimensions of the rate must be those of concentrations divide by time (mol L^{-1} s^{-1})

Consider a general reaction

$$A + B \rightarrow C$$
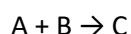
The rate of the above reaction can be expressed either in terms of disappearance of A or B or in terms of appearance of C.

$$\text{The rate of disappearance of A } = -\frac{d[A]}{dt}$$

Concentration of A is decreasing as A is consumed but rates are a positive number.

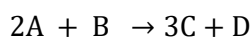$$\text{Rate of disappearance of B} = -\frac{d[B]}{dt}$$

$$\text{The rate of appearance of C } = +\frac{d[C]}{dt}$$

The mathematical equation relating concentrations and time is called rate equation or rate law.

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

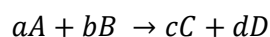Any of those equations can be used to define the rate of the reaction.

Now consider another reaction

$$2A + B \rightarrow 3C + D$$

Appearance of C is three times faster than the disappearance of B.

$$-\frac{1}{2}\frac{d[A]}{dt} = -\frac{d[B]}{dt} = \frac{1}{3}\frac{d[C]}{dt} = \frac{d[D]}{dt}$$

To generalize

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

The rate of reaction

$$-\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = \frac{1}{c}\frac{d[C]}{dt} = \frac{1}{d}\frac{d[D]}{dt}$$

The rate law and rate constants

The rate of the reaction is often found to be proportional to the concentrations of reactants raised to the power. For example, the rate of a reaction may be found to be proportional to the molar concentrations of two reactants A and B, so

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

with each concentration raised to the first power. The coefficient k is called the rate constant for the reaction. The rate constant is independent of the concentrations but depends on the temperature. An experimentally determined equation of this kind is called rate law of the reaction. More formally a rate law is an equation that expresses the rate of reaction as the function of the concentrations for the species present in the overall chemical equation for the reaction of the sometime.

$$Rate = k ([A][B] \dots)$$

The rate law of a reaction is determined experimentally and cannot in general be inferred from the chemical equation for the reaction.

For example

$$CH_3CHO_{(g)} \xrightarrow{hv} CH_{4(g)} + CO_{(g)}$$

$$\frac{d[CH_4]}{dt} = k [CH_3CHO]^{3/2}$$
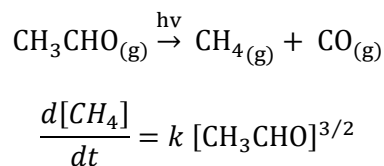
In the above case the rate law does not reflect the stoichiometry of the reaction but reflect a feature of under-laying reaction mechanism.

Reaction order

Experimentally many reaction rates had been made. Many reactions are found to have rate laws of the form

$$Rate = k [A]^{\alpha}[B]^{\beta}$$

α is called order of reaction with respect to   A

β is called order of reaction with respect to   B

$\alpha + \beta$ is called overall order

k is called rate constant

A reaction need not have an integral order as like shown in the dissociation of acetaldehyde with order 3/2. A reaction is said to be of first order if its rate is given by the expression of the type.
$Rate = k_1[A]$; of the second order if the rate is given by the expression of the type $Rate = k_2[A]^2$ or Rate = $k_2[A][B]$; and of third order if reaction rate is given by type $Rate = k_3[A]^3$ or $k_3[A][B][C]$ and so on. For a zero order reaction, the rate equation is written as rate = k_0
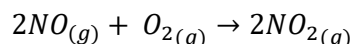
Molecularity of a reaction

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. If only one molecule is involved, the reaction is said to be unimolecular. The example is the dissociation of N_2O_5

$$N_2O_{5\,(g)} \rightarrow N_2O_{4\,(g)} + \frac{1}{2}O_{2\,(g)}$$
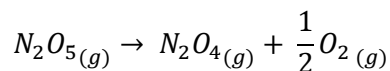
If two molecules are involved, the reaction is said to be bimolecular.

$$2HI_{(g)} \rightarrow H_{2\,(g)} + I_{2\,(g)}$$
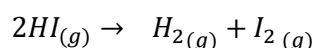
Similarly if three molecules are involved, the reaction is said to be trimolecular. Eg oxidation of nitric oxide

$$2NO_{(g)} + O_{2\,(g)} \rightarrow 2NO_{2\,(g)}$$

Order and molecularity of a simple reactions

From a study of the kinetics of a number of simple reactions, we know that their order is same as molecularity. Thus the order or reaction involving the decomposition of nitrogen pentoxide is 1, that of the reaction involving the dissociation of HI is 2 and that of the reaction involving the 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 reactant is present in large excess. Such reactions are called pseudo order reactions.

Unit of rate constants

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

$$k = \frac{Rate}{[A]^n}$$

$$\text{Unit of k} = \frac{mol\ L^{-1}s^{-1}}{(mol\ L^{-1})^n}$$

(1)   For zero order reactions n = 0

Unit of k = $mol\ L^{-1}s^{-1}$

(2)   For a first order reactions n = 1

Unit of k = s^{-1}

(3)   For a second order reactions n = 2

Unit of k = L $mol^{-1}s^{-1}$

Dependence of rates on concentrations

Rate laws that depend on the concentrations of reactant are in simple ways. Although many complicated cases are well known, there are also a great many reactions for which the dependence on concentration is first order, second order or zero order

Integrated rate laws

Because rate laws are differential equations we must integrate them to find concentrations as a function of time. Even most complex rate laws may be integrated numerically. However in number of simple cases analytical solutions are easily obtained and prove to be useful.

(a) First order reactions

Suppose a reaction can be written as

$$A \rightarrow B$$

and that of rate law of the reaction can be expressed as

$$\text{Rate} = -\frac{d[A]}{dt} = k \, [A]^1$$

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

$$-\int_{[A]_0}^{[A\}} ln[A] = k \int_0^t dt$$

$$-ln\frac{[A\}}{[A]_0} = kt$$

$$ln\frac{[A]_0}{[A]} = kt$$

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

We can also write this equation in another form

$$ln\frac{[A]}{[A]_0} = -kt$$

$$\frac{[A]}{[A]_0} = e^{-kt}$$

$$[A] = [A]_0 e^{-kt}$$

From this equation, it can be seen that the concentration of A decreases with time in an exponential way. Such a relationship is sometimes referred to as an **exponential decay**.

Radioactive decay processes follow a first-order rate law. The rate of decay is proportional to the amount of material present, so doubling the amount of radioactive material doubles the measured counting rate of decay products. When the amount of material remaining is one-half of the original amount, the time expired is called the half-life. At time $t_{1/2}$ the concentration of [A] become $\frac{[A]_0}{2}$
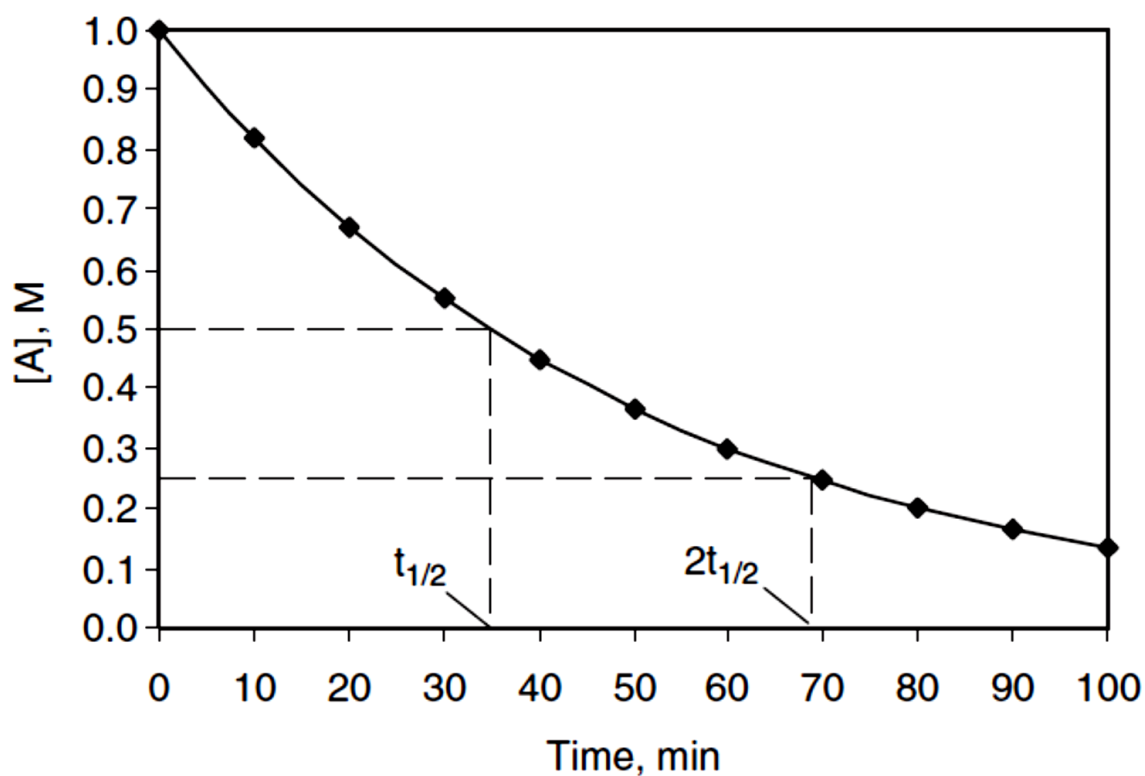
$$k = \frac{2.303}{t} log \frac{[A]_0}{[A]}$$

Become

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

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

Note that for a process that follows a first-order rate law, the half-life is independent of the initial concentration of the reactant. For example, in radioactive decay the half-life is independent of the amount of starting nuclide. It is easy to see that after one half-life the amount of material remaining is one-half of the original; after two half-lives, the amount remaining is one-fourth of the original; after three half-lives, the amount remaining is one-eighth of the original. This is illustrated in below figure

The quantity of reactant left behind after one $t_{1/2} = \frac{[A]_0}{2}$

The quantity of reactant left behind after two $t_{1/2} = \left(\frac{1}{2}\right)^2 [A]_0$

The quantity of reactant left behind after three $t_{1/2} = \left(\frac{1}{2}\right)^3 [A]_0$

The quantity of reactant left behind after n $t_{1/2} = \left(\frac{1}{2}\right)^n [A]_0$

Pseudo order reactions

Under a condition when there exists the presence of a large excess of one or more of the reactant, a reaction may show an order different from its actually expected order. Such a reaction is called pseudo order reaction. Particularly important are the pseudo first order reaction which are not truly first order but under certain condition show an order of 1.

A reaction which is found to follow first order kinetics despite having a molecularity greater than one is called a pseudo first order reactions, here the order of the reaction effectively becomes 1 because reactant other than one are present in large excess.

Consider the hydrolysis of ethyl acetate in dilute aqueous solution (large excess of water) in the presence of a constant concentration of H^+ ions.

$$CH_3COOC_2H_5 \quad + \quad H_2O \quad \xrightarrow{H^+} \quad CH_3COOH \quad + \quad C_2H_5OH$$

Ethyl acetate   Acetic acid   Ethanol

The reaction is bimolecular but it s order is experimentally found to be 1. This is because, as water is present in a large excess, its concentration remains practically constant during the reaction. So, the rate equation

$$\text{Rate} = k^{'} [CH_3COOC_2H_5][H_2O]$$

$$\text{Rate} = k[CH_3COOC_2H_5] \qquad \text{where } k = k^{'}[H_2O]$$

In other words, the rate is effectively determined by the concentration of the ester only. The reaction thus behaves as a first order reaction. It forms an example for a pseudo first order reaction. Another example for a pseudo first order reaction is the hydrolysis of sucrose into glucose and fructose in the presence of a constant of H^+ ions.

$$C_{12}H_{22}O_{11} \quad + H_2O \quad \xrightarrow{H^+} \quad C_6H_{12}O_6 \quad + \quad C_6H_{12}O_6$$

Sucrose   Glucose   Fructose

Here also water is present in large excess, its concentration remains practically constant during the reaction and thus the rate is effectively determined by the concentration of sucrose only.

Hydrolysis of ester in acid medium

$$CH_3COOC_2H_5 \quad + \quad H_2O \quad \xrightarrow{H^+} \quad CH_3COOH \quad + \quad C_2H_5OH$$

Ethyl acetate   Acetic acid   Ethanol

The rate of hydrolysis is usually followed by withdrawing equal volumes (say 2 mL) of reaction mixture at regular intervals and titrating against NaOH solution (added from the burette).The titre value (V_0)

at zero time (t = 0) is directly proportional to the concentration of the acid catalyst (HCl). The titre value at any time (t) is proportional to the concentration of the acetic acid formed plus that of the acid present as catalyst at that instant. The titre value (V_∞) at the completion of the reaction (t= ∞) is proportional to the acetic acid formed from the total hydrolysis plus that of the acid present as catalyst. Then

Total concentration of the ester (a) $\quad\quad\propto\quad\quad V_\infty - V_0$

Concentration of ester hydrolysed (x) at time t $\propto\quad\quad V_t - V_0$

$$\therefore \quad a\text{-}x \quad \propto \quad V_\infty - V_t$$

$$\text{Rate constant, } k \quad = \quad \frac{2.303}{t}\log\left[\frac{a}{a-x}\right]$$

$$= \quad \frac{2.303}{t}\log\left[\frac{V_\infty - V_0}{V_\infty - V_t}\right]$$

Graphical representation

The integrated rate equation for a first order reaction is

$$k \quad = \quad \frac{2.303}{t}\log\left[\frac{A_0}{A}\right]$$

$$\log\left[\frac{A_0}{A}\right] \quad = \quad \frac{kt}{2.303}$$

$$y = mx + 0$$
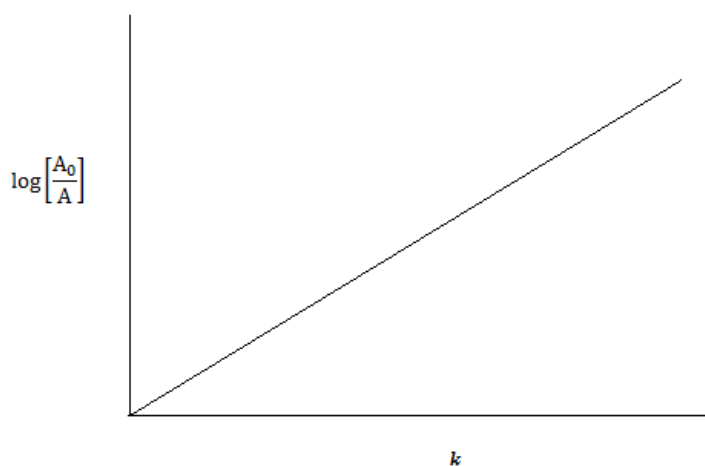
$$k \quad = \quad \frac{2.303}{t}\log\left[\frac{A_0}{A}\right]$$

$$\log[A] = -\frac{kt}{2.303} + \log[A_0]$$

$$\text{Slope} = -\frac{k}{2.303}$$
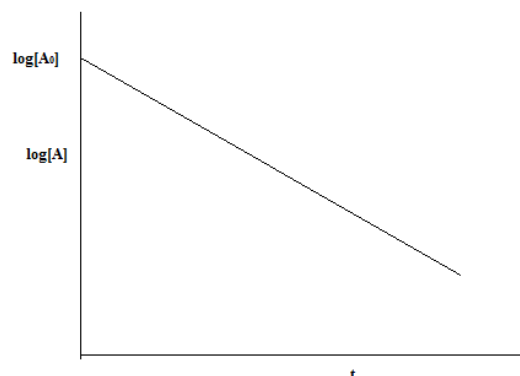
Second order reactions

A reaction that is second-order in one reactant or component obeys the rate law

$$\text{Rate} = k[A]^2 = -\frac{d[A]}{dt} \qquad (1)$$

Such a rate law might result from a reaction that can be written as

$$2A \qquad \rightarrow \qquad products$$
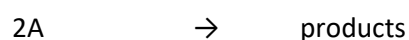
If we rearrange the equation (1) we have

$$-\frac{d[A]}{[A]^2} = kt$$

If the equation is integrated between limit of concentration of $[A_0]$ at t = 0 and [A] at time t. we have

$$\int_{[A_0]}^{[A]} \frac{-d[A]}{[A]^2} = k \int_0^t dt$$

Performing the integration gives the integrated rate law

$$\frac{1}{[A]} - \frac{1}{[A]_0} = kt \qquad (2)$$

Since the initial concentration of A is a constant, the equation can be put in the form of a linear equation

$$\frac{1}{[A]} = kt + \frac{1}{[A]_0} \qquad (3)$$

$$y = mx + c$$

As shown in Figure 1, a plot of 1/[A] versus time should be a straight line with a slope of k and an intercept of 1/[A]o if the reaction follows the second-order rate law. The units on each side of Eq. (3) must be 1/concentration. If concentration is expressed in mole/liter, then 1/concentration will have units of liter/mole. From this we find that the units on k must be liter/mole time (Lmol^{-1}s^{-1}) or M^{-1} time^{-1}.
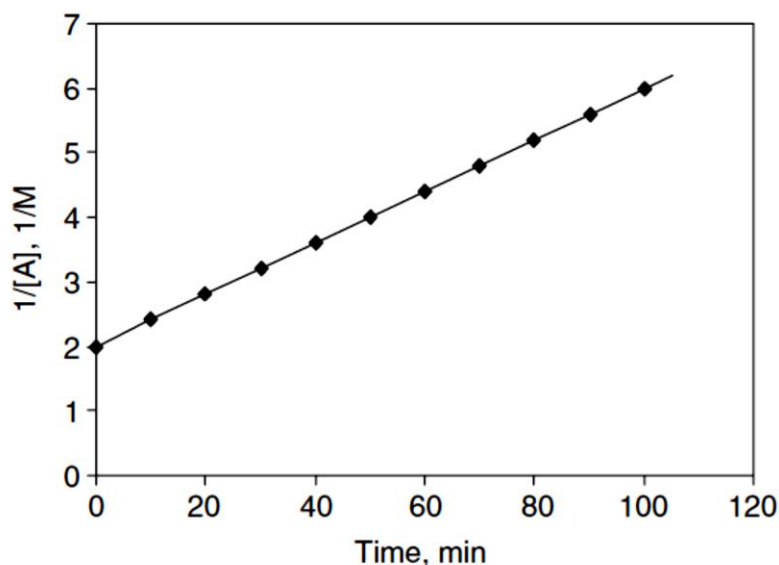
The half-life for a reaction that follows a second-order rate law can be easily calculated. After a reaction time equal to one half-life, the concentration of A will have decreased to one-half its original value. That is, [A] = [A$_0$]/2, so this value can be substituted for [A] in Equation 2 we will get

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

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

$$\frac{1}{k[A]_0} = t_{1/2} \qquad (4)$$

Here we see a major difference between a reaction that follows a second order rate law and one that follows a first-order rate law. For a first-order reaction, the half-life is independent of the initial concentration of the reactant, but in the case of a second-order reaction, the half-life is inversely proportional to the initial concentration of the reactant.

Another type of second-order reaction is one that is first-order in each of two reactants A and B:

$$A + B \rightarrow P$$
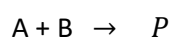
$$-\frac{d[A]}{dt} = k[A][B]$$

$$-\frac{d[A]}{dt} = k([A]_0 - x)([B]_0 - x)$$

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$$\frac{dx}{dt} = k([A]_0 - x)([B]_0 - x)$$

The initial condition is that $x = 0$ when $t = 0$; so the integration required is

$$\int_0^x \frac{1}{([A]_0 - x)([B]_0 - x)} = k\int_0^t dt \qquad (6)$$

The integral on the right is simply kt. The integral on the left is evaluated by using the method of partial fractions in which we write

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

It follows that

$$\int \frac{dx}{(a - x)(b - x)} = \frac{1}{b - a}\left[\int_0^x \frac{1}{a - x} - \int_0^x \frac{1}{b - x}\right]$$

$$= \frac{1}{b-a}\left[\ln\frac{a}{a-x} - \ln\frac{b}{b-x}\right]$$

By putting a = $[A]_0$, b = $[B]_0$, $a\text{-}x$ = $[A]$, $b\text{-}x$ = $[B]$

$$= \frac{1}{[B]_0-[A]_0}\left[\ln\frac{[A]_0}{[A]} - \ln\frac{[B]_0}{[B]}\right]$$

Substituting these values in equation 6.

$$([B]_0 - [A]_0)kt = \ln\left(\frac{[A]_0\,[B]}{[A][B]_0}\right) \qquad (7)$$

This equation is of the form

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

This equation can also be written as

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

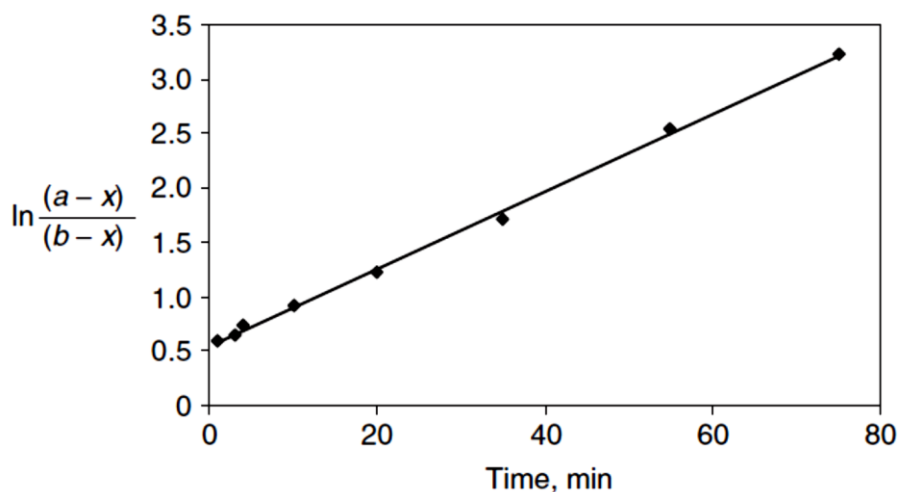$$\ln\frac{(a-x)}{(b-x)} = k(a - b)t + \ln\frac{b}{a}$$

$$y = m\ x + c$$

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Figure : Second order plot for hydrolysis of ethyl acetate in basic solution.

so that a graph of $\ln\frac{(a-x)}{(b-x)}$ versus t should be linear with a slope of k(a −b) and an intercept of $-\ln\frac{b}{a}$.

Zero order reactions

For certain reactions that involve one reactant, the rate is independent of the concentration of the reactant over a wide range of concentrations. For example, the decomposition of hypochlorite on a cobalt oxide catalyst behaves this way. The reaction is

$$2OCl^- \xrightarrow{catalyst} 2\,Cl^- + O_2$$
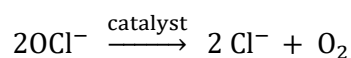
The cobalt oxide catalyst forms when a solution containing Co^{2+} is added to the solution containing OCl^-. It is likely that some of the cobalt is also oxidized to Co^{3+}, so we will write the catalyst as Co_2O_3, even though it is probably a mixture of CoO and Co_2O_3.

The reaction takes place on the active portions of the surface of the solid particles of the catalyst. This happens because OCl^- is adsorbed to the solid, and the surface becomes essentially covered or at least the active sites do. Thus, the total concentration of OCl^- in the solution does not matter as long as there is enough to cover the active sites on the surface of the catalyst. What does matter in this case is the surface area of the catalyst. As a result, the decomposition of OCl^- on a specific, fixed amount of catalyst occurs at a constant rate over a wide range of OCl^- concentrations. This is not true as the reaction approaches completion, and under such conditions the concentration of OCl^- does affect the rate of the reaction because the concentration of OCl^- determines the rate at which the active sites on the solid become occupied.

For a reaction in which a reactant disappears in a zero-order process, we can write

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

Because $[A]^0 = 1$ we can write

$$-d[A] = kt$$

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so that the rate law in integral form becomes

$$\int_{[A_0]}^{[A]} -d[A] = k \int_0^t dt$$

$$[A] = [A]_0 - kt$$

This equation indicates that at any time after the reaction starts, the concentration of A is the initial value minus a constant times t. This equation can be put in the linear form

$$[A] = -kt + [A]_0$$

$$y = mx + c$$

which shows that a plot of [A] versus time should be linear with a slope of -k and an intercept of $[A_0]$. Figure below shows such a graph for a process that follows a zero-order rate law, and the slope of the line is -k, which has the units of M time^{-1}
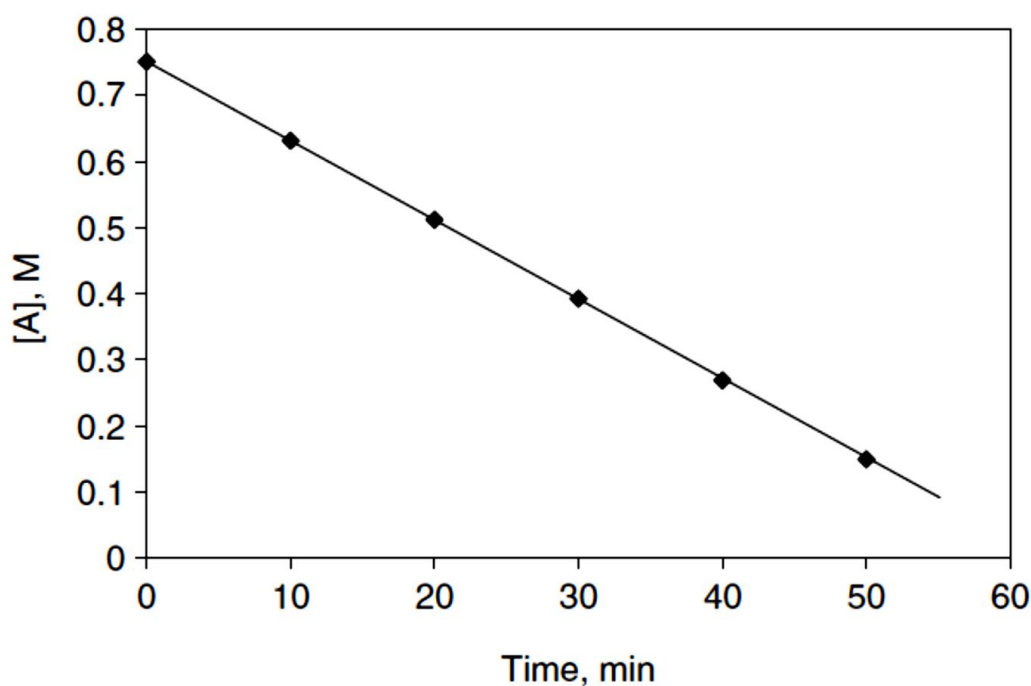
Figure : *A zero order plot where* $[A]_0 = 0.75 M$

As in the previous cases, we can determine the half-life of the reaction because after one half-life, [A] $= \frac{[A_0]}{2}$. Therefore

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

$$t_{1/2} = \frac{[A]_0}{2k} \qquad (8)$$

In this case, we see that the half-life is directly proportional to $[A_0]$, the initial concentration of A.

Although this type of rate law is not especially common, it is followed by some reactions, usually ones in which some other factor governs the rate. This the case for the decomposition of OCl⁻described
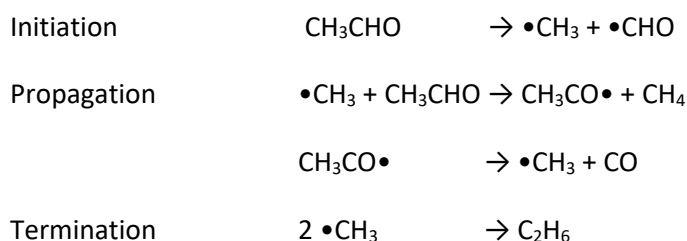
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earlier. An important point to remember for this type of reaction is that eventually the concentration of OCl⁻ becomes low enough that there is not a sufficient amount to replace quickly that which reacts on the surface of the catalyst. Therefore, the concentration of OCl- does limit the rate of reaction in that situation, and the reaction is no longer independent of [OCl⁻]. The rate of reaction is independent of [OCl⁻] over a wide range of concentrations, but it is not totally independent of [OCl⁻]. Therefore, the reaction is not strictly zero-order, but it appears to be so because there is more than enough OCl⁻ in the solution to saturate the active sites. Such a reaction is said to be pseudo zero-order. This situation is similar to reactions in aqueous solutions in which we treat the concentration of water as being a constant even though a negligible amount of it reacts. We can treat the concentration as being constant because the amount reacting compared to the amount present is very small. We will describe other pseudo-order processes in later sections of this book.

Fractional order reactions

In fractional order reactions, the order is a non-integer, which often indicates a chemical chain reaction or other complex reaction mechanism. For example, the pyrolysis of ethanal (CH_3CHO) into methane and carbonmonoxide proceeds with an order of 1.5 with respect to ethanal: rate = $k[CH_3CHO]^{3/2}$. The decomposition of phosgene ($COCl_2$) to carbon monoxide and chlorine has order 1 with respect to phosgene itself and order 0.5 with respect to chlorine:

$$\text{rate} = k[COCl_2]\,[Cl_2]^{1/2}.$$

The order of a chain reaction can be rationalized using the steady state approximation for the concentration of reactive intermediates such as free radicals. For the pyrolysis of ethanal, the Rice-Herzfeld mechanism is

Initiation CH_3CHO → •CH_3 + •CHO

Propagation   •CH_3 + CH_3CHO → CH_3CO• + CH_4

                                CH_3CO•   → •CH_3 + CO

Termination   2 •CH_3 → C_2H_6

To simplify the theory, the reactions of the •CHO to form a second •CH_3 are ignored.

In the steady state, the rates of formation and destruction of methyl radicals are equal, so that

$$\frac{d[\cdot CH_3]}{dt} = k_i[CH_3CHO] - k_t[\cdot CH_3]^2 = 0,$$

so that the concentration of methyl radical satisfies

$$[\cdot CH_3] \quad \propto \quad [CH_3CHO]^{\frac{1}{2}}.$$

The reaction rate equals the rate of the propagation steps which form the main reaction products CH_4 and CO:

$$v = \frac{d[CH_4]}{dt} = k_p[\cdot CH_3][CH_3CHO] \quad \propto \quad [CH_3CHO]^{\frac{3}{2}}$$

in agreement with the experimental order of 3/2.

Nth order reaction

If a reaction takes place for which only one reactant is involved, a general rate law can be written as

$$-\frac{d[A]}{dt} = k[A]^n$$

$$-\frac{d[A]}{[A]^n} = kdt$$

$$\int_{[A_0]}^{[A]} -[A]^{-n} \, d[A] = kt$$

If the reaction is not first-order so that n is not equal to 1, integration of this equation gives

$$\left[-\frac{1}{-n+1} [A]^{-n+1} \right]_{[A]_0}^{[A]} = kt$$

$$\frac{1}{n-1} \left[\frac{1}{[A]^{n-1}} \right]_{[A]_0}^{[A]} = kt$$

$$\frac{1}{n-1} \left[\frac{1}{[A]^{n-1}} - \frac{1}{[A]_0^{n-1}} \right] = kt$$

From this equation, it is easy to show that the half-life can be written as

$$\frac{1}{n-1} \left[\frac{1}{\left[\frac{[A]_0}{2}\right]^{n-1}} - \frac{1}{[A]_0^{n-1}} \right] = kt_{1/2}$$

$$\frac{1}{n-1} \left[\frac{2^{n-1}}{[A]_0^{n-1}} - \frac{1}{[A]_0^{n-1}} \right] = kt_{1/2}$$

$$\frac{1}{n-1} \left[\frac{2^{n-1} - 1}{[A]_0^{n-1}} \right] = kt_{1/2}$$

$$t_{1/2} = \frac{2^{n-1} - 1}{k(n-1)[A]_0^{n-1}} \quad (9)$$

In this case, n may have either a fraction or integer value.

METHODS FOR DETERMINING THE ORDER OF A REACTION

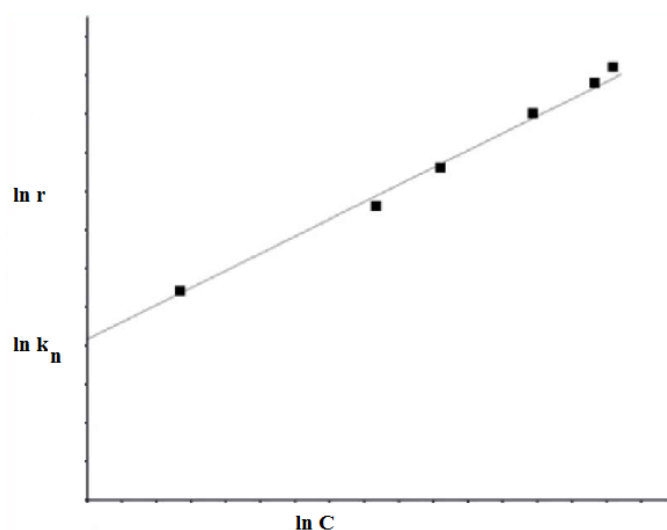(1) **Vant Hoff's method**

Dr. Biju A R

According to this method the rate of an nth order reaction is given by

$$r = k_n C^n$$

Taking logarithms, we have

$$\ln(r) = \ln k_n + n \ln C$$

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 $\ln k_n$.

(2) The use of integral rate expressions.

This method can be used either analytically or graphically. In analytical method we assume a certain order for the reaction and calculate the rate constants from the given data. The consistency 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 [A} versus t is a straight line, the reaction is first order. Similarly the integrated expression for the second order the plot of $\frac{1}{[A]}$ versus time gives a straight line then the reaction is second order and so on.
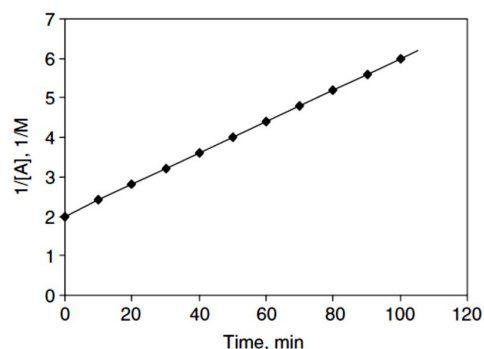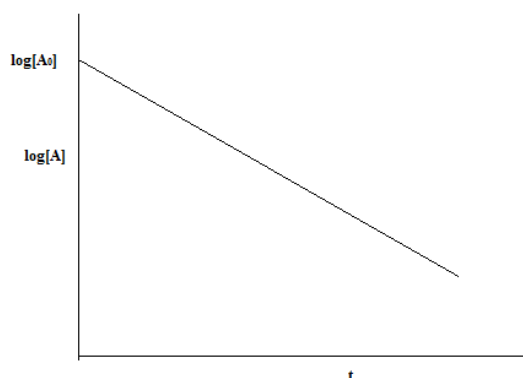
(3) The half-life method

From the equation 9 we have seen that

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

If the two experiments are carried out at different initial concentrations then

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

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

$$n = 1 + \frac{ln\dfrac{\left(t_{1/2}\right)_1}{\left(t_{1/2}\right)_2}}{ln\dfrac{[A]_2}{[A]_1}}$$

This method was suggested by Ostwald. The determination of half-lives of a reaction at two different initial concentration 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 would give 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.

Consecutive reactions

Dr. Biju A R

Simplest consecutive mechanism is

$$A \xrightarrow{1} B \xrightarrow{2} C \quad (10)$$
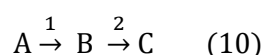
In this case, B is known as an intermediate because it is not the final product. A similar situation is very common in nuclear chemistry where a nuclide decays to a daughter nuclide that is also radioactive and undergoes decay

If the initial concentration of A is [A]o and its concentration at any time t is [A], the rate equation for A is

$$-\frac{d[A]}{dt} = k_1[A]$$

Integration of this equation, subject to the boundary condition that [A] = [A]o when t = 0, gives

$$\ln\frac{[A]}{[A]_0} = -k_1 t$$

$$[A] = [A]_0\, e^{-k_1 t} \quad (11)$$

The net change in the concentration of B is the rate at which it is formed minus the rate at which it reacts. Therefore,

$$\frac{d[B]}{dt} = k_1[A] - k_2[B] \quad (12)$$

where the term k1[A] represents the formation of B from A, and the term -k$_2$[B] represents the reaction of B to form C. The rate of formation of C can be represented as

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

If the stoichiometry as shown in Eq. (10) is followed, it should be apparent that

$$[A] + [B] + [C] = [A]_0$$

Substituting [A] from the equation 11 in the equation 12, we get

$$\frac{d[B]}{dt} = k_1[A]_0\, e^{-k_1 t} - k_2[B] \quad (13)$$

Rearrangement of this equation leads to

$$\frac{d[B]}{dt} + k_2[B] = k_1[A]_0\, e^{-k_1 t}$$

Now we have to integrate this expression to find [B]. Before integration we will modify above equation.

Multiply by $e^{k_2 t}$ on both sides

Dr. Biju A R

$$e^{k_2 t} \left(\frac{d[B]}{dt} + k_2[B] \right) = k_1[A]_0 \, e^{(k_2 - k_1)t}$$

Which can be write in the form

$$\frac{d([B]e^{k_2 t})}{dt} = k_1[A]_0 \, e^{(k_2 - k_1)t}$$

Integrate on both sides

$$\int_0^t \frac{d([B]e^{k_2 t})}{dt} = \int_0^t k_1[A]_0 e^{(k_2 - k_1)t}$$

$$\left([B]e^{k_2 t}\right)_0^t = \frac{k_1[A]_0}{k_2 - k_1} \left[e^{(k_2 - k_1)t} \right]_0^t$$

$$[B]e^{k_2 t} - [B_0]e^0 = \frac{k_1[A]_0}{k_2 - k_1} \left[e^{(k_2 - k_1)t} - 1 \right]$$

$$[B] = \frac{k_1[A]_0}{k_2 - k_1} \left(e^{-k_1 t} - e^{-k_2 t} \right) \quad (14)$$

$[A] + [B] + [C] = [A]_0$

$$[C] = [A]_0 - [B] - [A]$$

$$[C] = [A]_0 - \frac{k_1[A]_0}{k_2 - k_1} \left(e^{-k_1 t} - e^{-k_2 t} \right) - [A]_0 \, e^{-k_1 t}$$

$$= [A]_0 - \frac{k_1[A]_0}{k_2 - k_1} e^{-k_1 t} + \frac{k_1[A]_0}{k_2 - k_1} e^{-k_2 t} - \frac{k_2[A]_0}{k_2 - k_1} e^{-k_1 t} + \frac{k_1[A]_0}{k_2 - k_1} e^{-k_1 t}$$

$$[C] = [A]_0 \left(1 - \frac{1}{k_2 - k_1} [k_2 e^{-k_1 t} - k_1 e^{-k_2 t}] \right) \quad (15)$$

We know that $e^{-k_1 t} = 1 - k_1 t + \frac{(k_1 t)^2}{2!} + \dots$

$$[A] \approx [A]_0 (1 - k_1 t) \quad (16)$$

$$[B] = \frac{k_1[A]_0}{k_2 - k_1} (1 - k_1 t - 1 + k_2 t)$$

$$\cong \frac{k_1[A]_0}{k_2 - k_1} (k_2 - k_1)t$$

$$[B] \cong k_1[A]_0 \, t \quad (17)$$

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

$$d[C] \cong k_1 k_2 [A]_0 \, t \, dt$$

19

On integration we will get

$$[C] \approx \frac{k_1 k_2 [A]_0 t^2}{2} \quad (18)$$
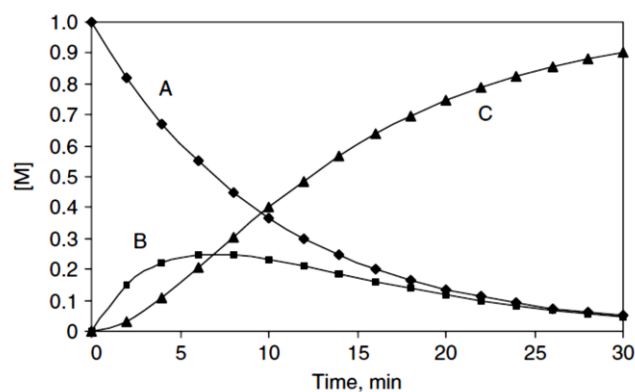
A plot of concentration of [A], [B] and [C] will give

Figure : Series first-order reactions where [A]o = 1.00 M, k_1 = 0.100 min^{-1}, and k_1 = 0.200 min^{-1}.

At t = 0, [B] = 0, but after a very short time, relative to the duration of the reaction, the difference $e^{-k_1 t} - e^{-k_2 t}$ has attained the value of unity and the concentration of B is then $\frac{k_1 [A]_0}{k_2}$ which is much less than $[A]_0$. After this short induction period the concentration of B remains practically constant, so that to a good approximation

$$\frac{d[B]}{dt} = 0$$

This approximation is called steady state approximation.

Steady state approximation

One feature of the calculation so far has probably not gone unnoticed: there is a considerable increase in mathematical complexity as soon as the reaction mechanism has more than a couple of steps. A reaction scheme involving many steps is nearly always unsolvable analytically, and alternative methods of solution are necessary. One approach is to integrate the rate laws numerically. An alternative approach, which continues to be widely used because it leads to convenient expressions and more readily digestible results, is to make an approximation.

The steady-state approximation (which is also widely called the quasi-steady-state approximation, QSSA, to distinguish it from a true steady state) assumes that, after an initial induction period, an interval during which the concentrations of intermediates, B, rise from zero, and during the major part of the reaction, the rates of change of concentrations of all reaction intermediates are negligibly small

$$\frac{d[B]}{dt} \approx 0$$

This approximation greatly simplifies the discussion of reaction schemes. For example, when we apply the approximation to the consecutive first-order mechanism

What has been shown for the very simple scheme of two consecutive first-order reactions is that if the conditions are such that the concentration at the intermediate B is always much smaller than the reactant concentration, the concentration of B rapidly reaches a value that remains practically constant during the course of the reaction.]

From equation 14 we can find $\frac{d[B]}{dt}$

$$\frac{-k_1 k_1 [A]_0}{k_2 - k_1} e^{-k_1 t} + \frac{k_1 k_2 [A]_0}{k_2 - k_1} e^{-k_2 t} = 0$$

$$\frac{k_1 k_2 [A]_0}{k_2 - k_1} e^{-k_2 t} = \frac{k_1 k_1 [A]_0}{k_2 - k_1} e^{-k_1 t}$$

$$k_2 e^{-k_2 t} = k_1 e^{-k_1 t}$$

$$\frac{e^{-k_2 t}}{e^{-k_1 t}} = \frac{k_1}{k_2} \quad , \quad e^{(k_1 - k_2)t} = \frac{k_1}{k_2}$$

$$(k_1 - k_2)t = \ln\frac{k_1}{k_2}$$

which yields the time necessary to reach the maximum in the curve representing [B] as a function of time. Representing that time as t_m and solving for that quantity, we obtain

$$t_m = \frac{\ln\frac{k_1}{k_2}}{k_1 - k_2} \quad (19)$$

Parallel reactions

In many reactions single reactant will be converted to more than one product. There are numerous examples of such reactions in organic chemistry. For example, the reaction of toluene with bromine in the presence of iron at 25 °C produces 65% p-bromotoluene and 35% o-bromotoluene. Similarly, the nitration of toluene under different conditions can lead to different amounts of o-nitrotoluene and p-nitrotoluene, but a mixture of these products is obtained in any event. Tailoring the conditions of a reaction to obtain the most favorable distribution of products is a common practice in synthetic chemistry. We will now illustrate the mathematical analysis of the kinetics of such reactions.

Suppose a compound, A, undergoes reactions to form several products, B and C
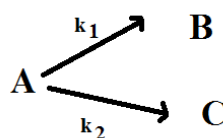
The rate of disappearance of A is the sum of the rates for the

$$-\frac{d[A]}{dt} = k_1[A] + k_2[A]$$

$$= (k_1 + k_2)[A]$$

$$[A] = [A]_0 e^{-(k_1 + k_2)t}$$

Now the rate of the reaction in terms of [B] and [C] can be written as

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

$$\frac{d[C]}{dt} = k_2[A]$$

$$\int_{[B]_0}^{[B]} d[B] = k_1 \int_0^t [A]dt$$

$$[B] - [B]_0 = k_1 \int_0^t [A]_0 e^{-(k_1 + k_2)t} \ dt$$

$$[B] = \frac{k_1[A]_0}{-(k_1 + k_2)} \left[e^{-(k_1 + k_2)t} \right]_0^t$$

$$[B] = \frac{k_1[A]_0}{(k_1 + k_2)} \left[1 - e^{-(k_1 + k_2)t} \right]$$

Similarly

$$[C] = \frac{k_2[A]_0}{(k_1 + k_2)} \left[1 - e^{-(k_1 + k_2)t} \right]$$

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

$\frac{k_1}{k_2}$ is called branching ratio
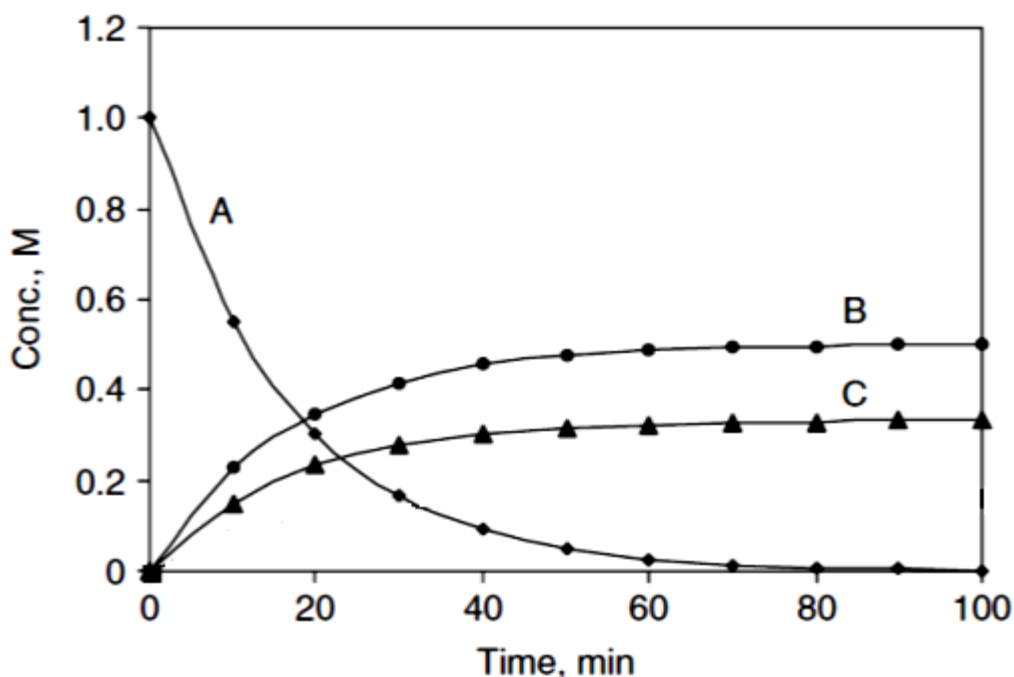
Figure : Concentrations of reactants and products in parallel first order reactions

Reversible reactions

Many reactions do not proceed to completion, and the extent of reversibility must be considered even from the early stages of the reaction. To illustrate the kinetic analysis, a first-order reaction will be considered in which the simplest case is.

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B$$
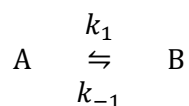
Because A is disappearing in the forward reaction and is produced by the reverse reaction, it should be clear that

$$-\frac{d[A]}{dt} = k_1[A] - k_{-1}[B] \quad (20)$$

Assuming that only A is initially present, the concentration of B is expressed as

$$[B] = [B]_0 + ([A]_0 - [A])$$

Substituting for [B] in equation 20 gives

$$-\frac{d[A]}{dt} = k_1[A] - k_{-1}\big([B]_0 + ([A]_0 - [A])\big)$$

$$-\frac{d[A]}{dt} = (k_1 + k_{-1})[A] - k_{-1}([A]_0 + [B]_0) \quad (21)$$

At equilibrium rate of change of [A] is zero

$$\frac{d[A]}{dt} = 0$$

$$(k_1 + k_{-1})[A]_{eq} = k_{-1}([A]_0 + [B]_0)$$

$$[A]_{eq} = \frac{k_{-1}([A]_0 + [B]_0)}{(k_1 + k_{-1})}$$

$$([A]_0 + [B]_0) = \frac{k_1 + k_{-1}}{k_{-1}}[A]_{eq}$$

Substituting in equation 21

$$-\frac{d[A]}{dt} = (k_1 + k_{-1})[A] - k_{-1}\frac{(k_1 + k_{-1})}{k_{-1}}[A]_{eq}$$

$$-\frac{d[A]}{dt} = (k_1 + k_{-1})\left[[A] - [A]_{eq}\right] \quad (22)$$

$[A] - [A]_{eq}$ is going to change with time and at infinite time $[A] - [A]_{eq} = 0$ since $[A] = [A]_{eq}$

$$-\frac{d[A]}{\left[[A] - [A]_{eq}\right]} = (k_1 + k_{-1})\, dt$$

$$\int_{[A]_0}^{[A]} -\frac{d[A]}{\left[[A] - [A]_{eq}\right]} = (k_1 + k_{-1})\int_0^t dt$$

Therefore

$$-\ln\left[[A] - [A]_0\right]_{[A]_0}^{[A]} = (k_1 + k_{-1})\,[t]_0^t$$

$$\ln\frac{[A] - [A]_{eq}}{[A]_0 - [A]_{eq}} = -(k_1 + k_{-1})\,t \quad (23)$$

$$[A] - [A]_{eq} = [A]_0 - [A]_{eq}\, e^{-(k_1 + k_{-1})\,t}$$

Temperature dependence of reaction rates

The rate constant of most reactions increase as temperature is raised.

(1) The Arrhenius parameters

The Arrhenius equation is given below

$$k = Ae^{-E_a/RT} \quad (25)$$

Where A is called frequency parameter and E_a is called activation energy of the reaction. It is found experimentally for many reactions that a plot of lnk against 1/T gives a straight line. This behaviour is

normally expressed mathematically by introducing two parameters, one representing the intercept and the other the slope of the straight line, and writing the Arrhenius equation.

$$\ln k = \ln A - \frac{E_a}{RT} \qquad (26)$$

The parameter A, which corresponds to the intercept of the line at 1/T = 0 (at infinite temperature, Fig.), is called the pre-exponential factor or the 'frequency factor'. The parameter Ea, which is obtained from the slope of the line (−Ea/R), is called the activation energy. Collectively the two quantities are called the Arrhenius parameters.
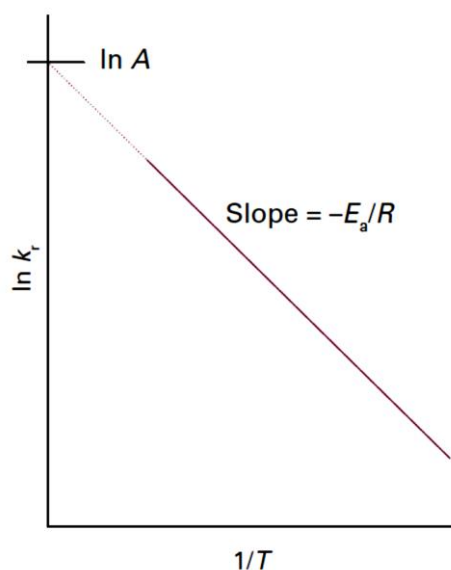
Figure : *A plot of ln kr against 1/T is a straight line when the reaction follows the behaviour described by the Arrhenius equation (eqn 26). The slope gives −Ea/R and the intercept at 1/T = 0 gives ln A.*

The fact that Ea is given by the slope of the plot of $\ln k_r$ against 1/T means that, the higher the activation energy, the stronger the temperature dependence of the rate constant (that is, the steeper the slope). A high activation energy signifies that the rate constant depends strongly on temperature. If a reaction has zero activation energy, its rate is independent of temperature. In some cases the activation energy is negative, which indicates that the rate decreases as the temperature is raised. We shall see that such behaviour is a signal that the reaction has a complex mechanism.

The temperature dependence of some reactions is non-Arrhenius, in the sense that a straight line is not obtained when ln k is plotted against 1/T. However, it is still possible to define an activation energy at any temperature as

$$E_a = RT^2 \left[\frac{d \ln k}{dT} \right] \qquad (27)$$

This definition reduces to the earlier one (as the slope of a straight line) for temperature independent activation energy. However, the definition in eqn 27 is more general than eqn 26, because it allows E_a

to be obtained from the slope (at the temperature of interest) of a plot of ln k against 1/T even if the Arrhenius plot is not a straight line.

(2) The interpretation of parameters

As of now we shall regard the Arrhenius parameters as purely empirical quantities that enable us to discuss the variation of rate constants with temperature; however, it is useful to have an interpretation in mind.

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

Next, to interpret Ea we consider how the molecular potential energy changes in the course of a chemical reaction that begins with a collision between molecules of A and molecules of B
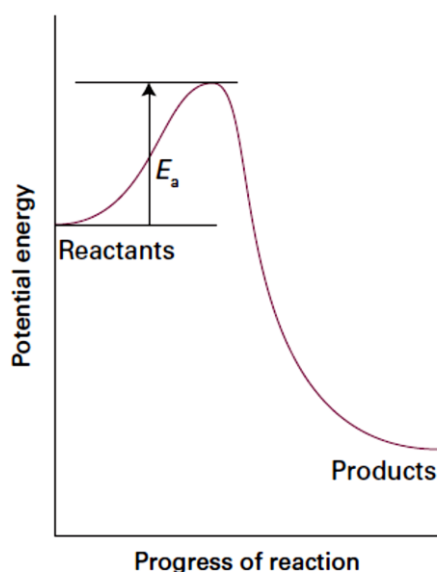

Fig. *A potential energy profile for an exothermic reaction. The height of the barrier between the reactants and products is the activation energy of the reaction.*

As the reaction event proceeds, A and B come into contact, distort, and begin to exchange or discard atoms. The reaction coordinate is the collection of motions, such as changes in interatomic distances and bond angles, that are directly involved in the formation of products from reactants. (The reaction coordinate is essentially a geometrical concept and quite distinct from the extent of reaction.) The potential energy rises to a maximum and the cluster of atoms that corresponds to the region close to the maximum is called the activated complex. After the maximum, the potential energy falls as the atoms rearrange in the cluster and reaches a value characteristic of the products. The climax of the reaction is at the peak of the potential energy, which corresponds to the activation energy E_a. Here two reactant molecules have come to such a degree of closeness and distortion that a small further distortion will send them in the direction of products. This crucial configuration is called the transition state of the reaction. Although some molecules entering the transition state might revert to reactants, if they pass through this configuration then it is inevitable that products will emerge from the encounter.

We also conclude from the preceding discussion that, for a reaction involving the collision of two molecules, the activation energy is the minimum kinetic energy that reactants must have in order to form products. For example, in a gas-phase reaction there are numerous collisions each second, but only a tiny proportion are sufficiently energetic to lead to reaction. The fraction of collisions with a kinetic energy in excess of an energy E_a is given by the Boltzmann distribution as $e^{-E_a/RT}$. The pre-exponential factor is a measure of the rate at which collisions occur irrespective of their energy. Hence, the product of A and the exponential factor, $e^{-E_a/RT}$, gives the rate of successful collisions.

Unimolecular mechanisms

A number of gas-phase reactions follow first-order kinetics, as in the isomerization of cyclopropane

  Rate = k[cyclo-C$_3$H$_6$]
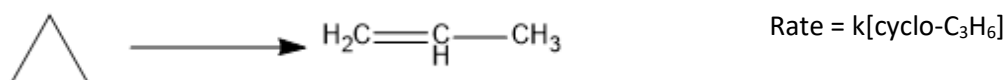
First-order gas-phase reactions are widely called 'unimolecular reactions' because they also involve an elementary unimolecular step in which the reactant molecule changes into the product. This term must be used with caution, though, because the overall mechanism has bimolecular as well as unimolecular steps

The Lindemann-Hinshelwood Mechanism

The first successful explanation of unimolecular reactions was provided by Frederick Lindemann in 1921 and then elaborated by Cyril Hinshelwood. In the Lindemann– Hinshelwood mechanism it is supposed that a reactant molecule A becomes energetically excited by collision with another A molecule in a bimolecular step.

$$A + A \; \rightarrow \; A^* + \; A \qquad \frac{d[A^*]}{dt} = k_a[A]^2$$
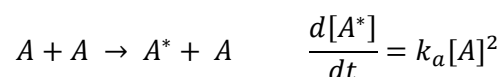
The energized molecule (A*) might lose its excess energy by collision with another molecule:

$$A + A^* \rightarrow A + A \quad \frac{d[A^*]}{dt} = -k_a' \, [A] \, [A^*]$$
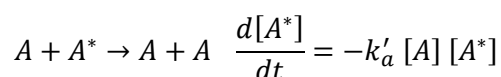
Alternatively, the excited molecule might shake itself apart and form products P. That is, it might undergo the unimolecular decay

$$A^* \; \rightarrow P \qquad \frac{d[A^*]}{dt} = \; -k_b \, [A^*]$$
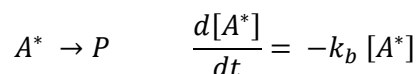
If the unimolecular step is slow enough to be the rate-determining step, the overall reaction will have first-order kinetics, as observed. This conclusion can be demonstrated explicitly by applying the steady-state approximation to the net rate of formation of A*

$$\frac{d[A^*]}{dt} = \; k_a[A]^2 - k_a' \, [A] \, [A^*] - k_b \, [A^*] \; \approx 0$$

This equation solves to

$$[A^*] = \frac{k_a[A]^2}{k_a'[A] + k_b}$$

$$\frac{d[P]}{dt} = k_b[A^*] = \frac{k_b k_a[A]^2}{k_a'[A] + k_b} \qquad (28)$$

At this stage the rate law is not first-order. However, if the rate of deactivation by (A*, A) collisions is much greater than the rate of unimolecular decay, in the sense that

$$k_a'[A][A^*] \gg k_b[A^*] \quad or \quad k_a'[A] \gg k_b$$

Then we can neglect K$_b$ in the denominator and obtain

$$\frac{d[P]}{dt} = k[A] \quad where \quad k = \frac{k_a k_b}{k_a'} \qquad (29)$$

The equation 29 is a first order rate law.

The Lindemann–Hinshelwood mechanism can be tested because it predicts that, as the concentration (and therefore the partial pressure) of A is reduced, the reaction should switch to overall second-order kinetics. Thus, when k_a'[A] << k_b, the rate law in eqn 28 is

$$\frac{d[P]}{dt} \approx k_a[A]^2$$

The physical reason for the change of order is that at low pressures the rate determining step is the bimolecular formation of A*. If we write the full rate law in eqn 28 as

$$\frac{d[P]}{dt} = k'[A] \quad where \ k' = \frac{k_a k_b[A]}{k_a'[A] + k_b}$$

Then the expression for the effective rate constant k' can be rearranged to

$$\frac{1}{k'} = \frac{k_a'}{k_a k_b} + \frac{1}{k_a[A]}$$

Hence, a test of the theory is to plot 1/kr against 1/[A], and to expect a straight line. This behaviour is observed often at low concentrations but deviations are common at high concentrations.

The transition state theory

This is the activated-complex theory (also known as the transition-state theory or absolute-reaction-rate theory) developed mainly by **Henry Eyring** and his co-workers, which since the 1930s has been one of the main approaches used in theoretical discussion of chemical kinetics. Most often it serves to provide a conceptual framework for discussion, but it is also very widely used for full rate calculations. To describe the theory in a convenient but somewhat simplified way, it reduces the dynamics of a reactive collision to equilibrium between the reactants and an intermediate state called the activated complex, conceived as a well-defined species; this equilibrium is then treated by the familiar methods of statistical mechanics. The activated complex has a short lifetime and dissociates either into products or back to reactants. The terms "activated complex" and "transition state" have the same meaning.

Transition state theory pictures a reaction between A and B as proceeding through the formation of an activated complex, (AB)‡ by a bimolecular reaction.
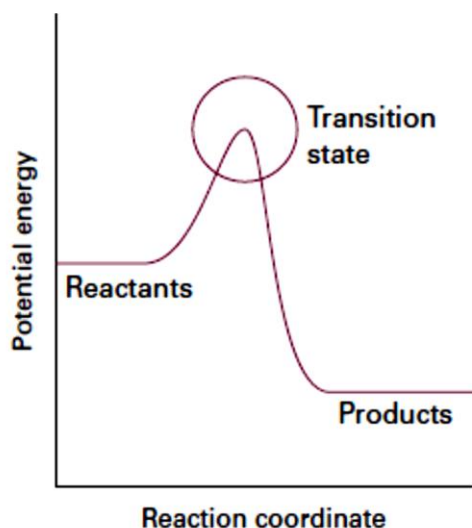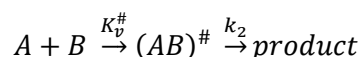

Figure*: A reaction profile (for an exothermic reaction). The horizontal axis is the reaction coordinate, and the vertical axis is potential energy. The activated complex is the region near the potential maximum, and the transition state corresponds to the maximum itself.*

$$A + B \xrightarrow{K_v^\#} (AB)^\# \xrightarrow{k_2} product$$

Where (AB)# is the activated complex; although theory can be formulated more generally, we shall consider only bimolecular case. The equilibrium constant in terms of concentrations defined as

$$K_v^\# = \frac{[(AB)^\#]}{[A][B]} \qquad (30)$$

Since activated complex is not an ordinary stable species, equation 30, should more properly labelled as quasiequilibrium constant. From the equation 30 the concentration of activated complex is

$$[(AB)^\#] = K_v^\#[A][B]$$

All of the activated complexes which reach on the top the barrier will not move forward but some of them will go back to form the reactants. We therefore introduce a transmission coefficient κ, formally defined as the fraction of those systems forming an activated complex that pass directly through it to form products. The value of κ depends on the shape of the potential energy surface; the maximum value possible for a reaction is 1. Assuming for a moment κ =1, the actual mechanism of breaking up of the activated complex depends up on the vibrational excited state at the dissociation limit. This gives a breakup rate is approximately equal to $v\,[(AB)^\#]$, where v is the frequency of vibration at the question.

$$-\frac{d[A]}{dt} = v\,[(AB)^\#] = \frac{k_B T}{h} K_v^\#[A][B] = k\,[A][B]$$

$$k = \frac{k_B T}{h} K_v^\# \qquad (31)$$

The equilibrium constant $K_v^{\#}$ can be expressed in terms of the standard free energy change for the activation process, $(\Delta G^0)^{\#}$, called standard Gibbs free energy of activation and $(\Delta H^0)^{\#}$, is the standard enthalpy activation. Since for activated complex, we can write

$$(\Delta G^0)^{\#} = -RT \ln K_v^{\#} \quad \text{and} \quad (\Delta G^0)^{\#} = (\Delta H^0)^{\#} - T(\Delta S^0)^{\#}$$

$$\ln K_v^{\#} = -\frac{(\Delta G^0)^{\#}}{RT}$$

$$K_v^{\#} = e^{-\frac{(\Delta G^0)^{\#}}{RT}} = e^{\frac{(\Delta S^0)^{\#}}{R}} e^{-\frac{(\Delta H^0)^{\#}}{RT}}$$

Substituting in equation 31, we get

$$k = \frac{k_B T}{h} e^{\frac{(\Delta S^0)^{\#}}{R}} e^{-\frac{(\Delta H^0)^{\#}}{RT}} \qquad (32)$$

The equation 32 is the well known **Eyring equation** for the rate constant of a simple bimolecular gaseous reaction. Here $(\Delta S^0)^{\#}$ is the standard entropy of activation and $(\Delta H^0)^{\#}$ is the standard enthalpy of activation.

Collision theory of reaction rates

The simplest collision theory is applicable only to bimolecular elementary reactions. All of the collisions are perfectly elastic and molecules are considered as hard and spherical. The distance $d_{AB} = r_A + r_B$.
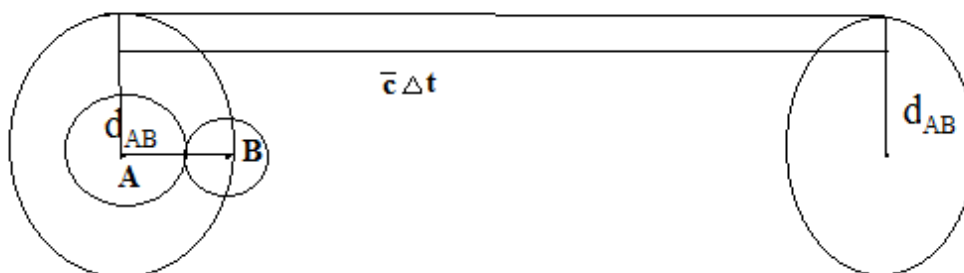
If the molecule A and B at the distance d_{AB}, we can say that collision has occurred. If a molecule A is moving with speed of $\tilde{c}$ and after a time Δt, the volume covered by the A molecule is $\pi d_{AB}^2 \tilde{c} \Delta t$. If the centre of the molecule B is inside this volume, we can say that collision will occur. If the number density (the number of molecules of A in cubic meter) of the molecule A is C_A

$$\frac{-dC_A}{dt} = Z_{AB} e^{-E_c/RT} \qquad (33)$$

$e^{-E_c/RT}$ is the fraction of the total molecule that have energy equal and above than the threshold energy. Z_{AB} is collision rate.

Collision rate of single A with B can be given as

$$Z_{A \to B} = \pi (r_A + r_B)^2 \bar{v}_{AB} C_B$$

Where $\bar{v}_{AB}$ is average velocity of A and B

If the number density of the molecule A is C_A, the total collision rate per unit volume can be given as

$$Z_{AB} = \pi (r_A + r_B)^2 \bar{v}_{AB} C_A C_B \quad (34)$$

The expression for average velocity of A and B, $\bar{v}_{AB}$ has given from Maxwells relation

$$\bar{v}_{AB} = \left(\frac{8k_B T}{\pi \mu}\right)^{1/2} where \ \mu = \frac{m_A m_B}{m_A + m_B}$$

Substituting in equation 34, we get

$$Z_{AB} = \pi (r_A + r_B)^2 \left(\frac{8k_B T}{\pi \mu}\right)^{1/2} C_A C_B \quad (35)$$

On substituting the value of Z_{AB} in the equation 33, we get

$$\frac{-dC_A}{dt} = \pi (r_A + r_B)^2 \left(\frac{8k_B T}{\pi \mu}\right)^{1/2} C_A C_B e^{-E_c/RT}$$

If the number of molecules per cubic meter (per liter) has to be expressed as in concentration terms

$$\frac{C_A L^{-1}}{N_A mol^{-1}} = c_A \ mol L^{-1} \ , C_A = N_A c_A$$

$$N_A \frac{-dc_A}{dt} = (N_A)^2 \ \pi \ (r_A + r_B)^2 \left(\frac{8k_B T}{\pi \mu}\right)^{1/2} c_A c_B e^{-E_c/RT}$$

$$\frac{-dc_A}{dt} = N_A \pi \ (r_A + r_B)^2 \left(\frac{8k_B T}{\pi \mu}\right)^{1/2} e^{-E_c/RT} c_A c_B$$

$$\frac{-dc_A}{dt} = k c_A c_B$$

$$k = N_A \pi \ (r_A + r_B)^2 \left(\frac{8k_B T}{\pi \mu}\right)^{1/2} e^{-E_c/RT} \quad (36)$$

The Arrhenius equation has the same form as equation 36

$$k = A e^{-E_a/RT} \quad (37)$$

By comparing equations 36 and 37,

$$A = N_A \pi \ (r_A + r_B)^2 \left(\frac{8k_B T}{\pi \mu}\right)^{1/2} \quad (38)$$

Strictly speaking A should be independent of temperature. The collision theory predicts the value of the rate constant satisfactorily for reactions that involve relatively simple molecules if the activation

energy is known. Difficulties are encountered with reactions between complicated molecules. The rates tend to be smaller than the collision theory predicts, in many cases by a factor of 10^5 or more. To account for this, an additional factor P, called the probability factor or the steric factor, is inserted in the expression for k:

$$k = P\, A\, e^{-E_a/RT}$$

The steric factor is supposed to be equal to the fraction of molecular collisions in which molecules A and B posses the relative orientations necessary for the reaction. However the steric factor cannot be reliably calculated.

Enzyme catalysis

Enzymes are homogeneous biological catalysts. These ubiquitous compounds are special proteins or nucleic acids that contain an active site, which is responsible for binding the substrates, the reactants, and processing them into products. As is true of any catalyst, the active site returns to its original state after the products are released. Many enzymes consist primarily of proteins, some featuring organic or inorganic co-factors in their active sites. However, certain RNA molecules can also be biological catalysts, forming ribozymes. A very important example of a ribozyme is the ribosome, a large assembly of proteins and catalytically active RNA molecules responsible for the synthesis of proteins in the cell. The structure of the active site is specific to the reaction that it catalyses, with groups in the substrate interacting with groups in the active site by intermolecular interactions, such as hydrogen bonding, electrostatic, or van der Waals interactions. Figure shows two models that explain the binding of a substrate to the active site of an enzyme. In the lock-and-key model, the active site and substrate have complementary three-dimensional structures and dock perfectly without the need for major atomic rearrangements. Experimental evidence favours the induced fit model, in which binding of the substrate induces a conformational change in the active site. Only after the change does the substrate fit snugly in the active site.
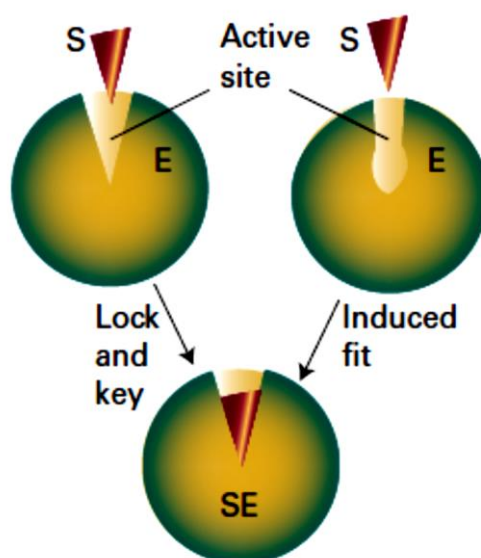

Figure : *Two models that explain the binding of a substrate to the active site of an enzyme. In the lock-and-key model, the active site and substrate have complementary three-dimensional structures and dock perfectly without the need for major atomic rearrangements. In the induced fit model, binding of*

the substrate induces a conformational change in the active site. The substrate fits well in the active site after the conformational change has taken place.

In may cases, enzymes require the presence of another species before they are able to act as catalysts. Such additional species are called cofactors, and there are several types of cofactors known. The enzyme along with its cofactor is called the holoenzyme, while the protein portion alone is known as the apoenzyme. Of the types of cofactors known, the most common are coenzymes, prosthetic groups, and metal ions. A coenzyme is some other organic material that is loosely attached to the protein enzyme (apoenzyme). If the organic compound is strongly attached to the apoenzyme, it called a prosthetic group. Metal ions (e.g., Fe^{2+}, Ca^{2+}, Mg^{2+}, K^+, Cu^{2+}, etc.) may enhance enzyme activity by binding to the enzyme (forming a complex). On the other hand, some materials known as inhibitors reduce the activity of enzymes. Such cases may result from competitive inhibition in which some material can bind to the enzyme preventing its attachment to the substrate. In another mode of enzyme inhibition, known as noncompetitive inhibition, some material is present that binds to the enzyme, changing its configuration so that it can no longer bind to the substrate effectively.

Experimental studies of enzyme kinetics are typically conducted by monitoring the initial rate of product formation in a solution in which the enzyme is present at very low concentration. Indeed, enzymes are such efficient catalysts that significant accelerations may be observed even when their concentration is more than three orders of magnitude smaller than that of the substrate. The principal features of many enzyme-catalysed reactions are as follows:

> ➢ For a given initial concentration of substrate, $[S]_0$, the initial rate of product formation is proportional to the total concentration of enzyme, $[E]_0$.
> ➢ For a given $[E]_0$ and low values of $[S]_0$, the rate of product formation is proportional to $[S]_0$.
> ➢ For a given $[E]_0$ and high values of $[S]_0$, the rate of product formation becomes independent of $[S]_0$, reaching a maximum value known as the maximum velocity, v_{max}.

The Michaelis–Menten mechanism accounts for these features. According to this mechanism, an enzyme–substrate complex is formed in the first step and either the substrate is released unchanged or after modification to form products:

$$E + S \overset{k_1}{\leftrightarrow} ES \overset{k_2}{\rightarrow} E + P$$

Here E and S are enzyme and substrate, P is the product and ES is an addition complex. The steady state treatment was first applied to this mechanism by Briggs and Haldane. The steady state equation is

$$k_1[E][S] - k_{-1}[ES] - k_2[ES] = 0 \quad (39)$$

In studies of enzyme reaction the molar concentration of the substrate is very much greater than that of the enzyme, only small portion of the substrate is therefore is bound to the enzyme. The total concentration enzyme, $[E]_0$ is equal to the concentration of the free enzyme $[E]$ plus concentration of the complex $[ES]$.

$$[E]_0 = [E] + [ES]$$

$$[E] = [E]_0 - [ES]$$

Substituting this value in 39

$$k_1([E]_0 - [ES])[S] - k_{-1}[ES] - k_2[ES] = 0$$

$$k_1[E]_0[S] = k_{-1}[ES] + k_2[ES] + k_1 [S][ES]$$

$$[ES] = \frac{k_1[E]_0[S]}{k_{-1} + k_2 + k_1 [S]}$$

The rate of the reaction is

$$Rate = v = k_2[ES]$$

$$v = \frac{k_2 k_1[E]_0[S]}{k_{-1} + k_2 + k_1 [S]}$$

$$= \frac{k_2[E]_0[S]}{(k_{-1} + k_2)/k_1 + [S]}$$

$$v = \frac{k_2[E]_0[S]}{K_m + [S]} \quad (40)$$

In this equation K_m equal to $(k_{-1} + k_2)/k_1$ is known as Michaelis constant and equation of the form 40 is known as Michaelis-Menten equation.

When substrate concentration [S] is very small, it may be neglected in the denominator in comparison with K_m

$$v = \frac{k_2}{K_m} [E]_0[S]$$

So the kinetics are first order with respect to substrate concentration. When on other hand [S] >>> K_m

$$v_{max} = k_2 [E]_0$$

and the kinetics are zero order, the enzyme is then saturated with substrate and further increase in S has no effect on rate. The equation 40 can be rewritten as

$$v = \frac{V [S]}{K_m + [S]} \quad (41)$$

Where V is equal to $k_2 [E]_0$ is the limiting rate at high substrate concentration. It is often known as maximal velocity v_{max}. When [S] is equal to K_m equation 41 becomes

$$v = \frac{V [S]}{[S] + [S]} = \frac{V}{2}$$

This relationship is illustrated in Fig. The Michaelis constant K_m can be determined from the plot of v versus [S], by finding the concentration of the substrate that gives one half of the limiting rate. In practice however this procedure does not provide very reliable value.

Substrate concentration [S]
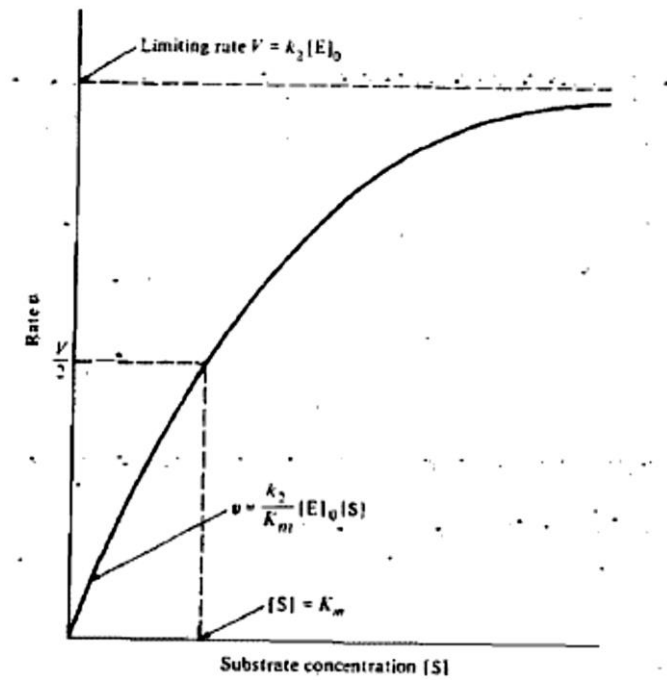
To see whether experimental data are consistent with the equation 41, the equation can recast into a form which gives a linear plot. If reciprocals are taken the result is

$$\frac{1}{v} = \frac{K_m}{V\,[S]} + \frac{1}{V} \quad (42)$$

Therefore the plot of $\frac{1}{v}$ versus 1/[S] gives a straight line. This type of plot is suggested by Lineweaver and Burk is shown below which gives the intercept and slope.
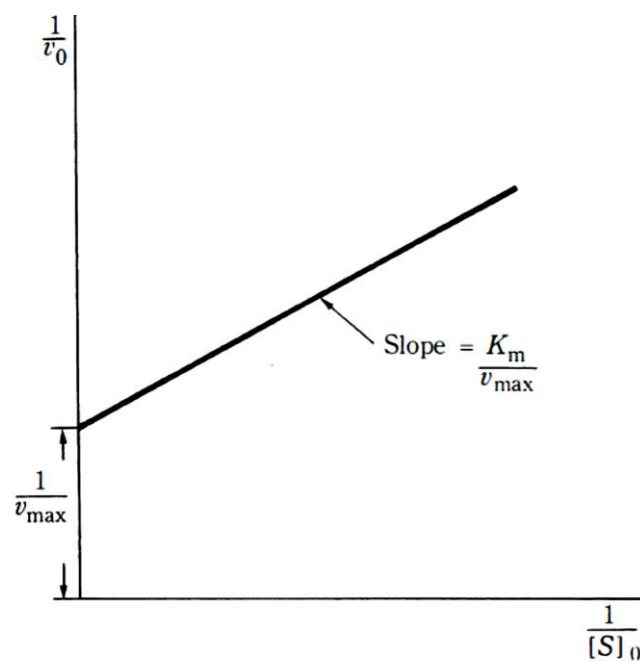
Lineweaver burk plot.

35

The parameters V and K_m can be derived from such a plot. If the enzyme concentration $[E]_0$ is known k_2 can be calculated, since according to the simple mechanism $V = k_2[E]_0$.

ADSORPTION

The most important result that has emerged from investigations of surfaces catalysts is that there must be specific adsorption of reactant molecules. This was first suggested by Faraday, who carried out studies of the adsorption of gases at surfaces and of some surface catalyzed reactions. However this cannot be generally true, since in some cases different surface causes a substance to react in different ways for example, on alumina catalyst ethanol decomposes mainly into ethylene and water, while on copper it decomposes mainly into acetaldehyde and hydrogen. These and many other results indicate that specific forces are involved at surfaces.

Two main types of adsorption may be distinguished. In the first type the forces are of a physical in nature and adsorption is relatively weak. The forces in this type of adsorption are called van der waals forces. This type of adsorption is called van der waals adsorption or physical adsorption or physisorption. The heat evolved in van der waals adsorption is usually small, less than 20 kJmol^{-1}. The second type of adsorption is called chemisorption which was given by Langmuir in 1916. In chemisorptions the adsorbed molecules are held to the surface by covalent forces. The heat evolved for this type is usually comparable to that evolved in chemical bonding 300-500 kJmol^{-1}. An important consequence of chemisorption is that the surface has become covered with a single layer of adsorbed molecules. If it is saturated by a single layer additional adsorption can occur only on the layer already present and this is generally physisorption.

Adsorption isotherm

The work on chemisorption has been concerned with equilibria and with rates. The amount of gases adsorbed after equilibrium is established depends on various factors including nature of the surface and substance adsorbed the temperature, and the pressure. The studies of the amount of adsorption as a function of pressure by keeping temperature constant are called adsorption isotherms. The simplest isotherm is Langmuir isotherm which is ideal adsorption just like ideal gas equation pV = nRT.

Simple Langmuir Isotherm

The simplest situation is when the gas atoms or molecules occupy single sites on the surface and are not dissociated. The process can be represented as

$$A + -S- \leftrightharpoons -S-A$$
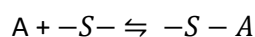
Let θ be the fraction of surface that is covered $1 - \theta$ is the bare fraction. The rate of adsorption is then $k_a[A](1 - \theta)$ where [A] is the gas concentration and k_a is a constant. The rate of desorption is $k_{-a}\theta$. At equilibrium rates are equal to

$$k_a[A](1 - \theta) = k_{-a}\theta$$

$$\frac{\theta}{1 - \theta} = \frac{k_a}{k_{-a}}[A]$$

$$= K[A]$$

Where K is equal to $\frac{k_a}{k_{-a}}$ is an equilibrium constant for the adsorption process. This equation can be written as

$$\theta = K[A] - K[A]\,\theta$$

$$\theta + K[A]\theta = K[A]$$

$$\theta = \frac{K[A]}{1 + K[A]}$$

The bare fraction can be written as

$$1 - \theta = 1 - \frac{K[A]}{1 + K[A]}$$

$$1 - \theta = \frac{1}{1 + K[A]}$$

The variation of θ with [A] is shown in figure. At sufficiently low concentration K[A] is small compared to unity and then θ is proportional to [A]. At sufficiently high concentrations a bare fraction is given by $K[A] \gg 1$ so

$$1 - \theta = \frac{1}{K[A]}$$