Module III: Kinetics and Catalysis:

Syllabus: Kinetics of Chain, Parallel/Competing/Side, Consecutive reactions; Fast reactions; Outline of Catalysis, Acid-base catalysis, Enzyme catalysis (Michaelis-Menten equation), Important catalysts in industrial processes: Hydrogenation using Wilkinsons catalyst, Phase transfer catalyst.

1. Introduction

- Chemical kinetics deals with the study of rate of chemical reactions. Rate of reaction is defined as change in concentration of reactants or products (or change in physical parameters which depends on the concentration such as conductance, absorbance, current etc.) per unit time.
- Besides information about the speed at which reactions occur, kinetics also sheds light on the reaction mechanism (exactly how the reaction occurs).
- Rate of the reaction is influenced by various factors such as nature of substance, physical state of substance, temperature, concentration (solution), pressure (gaseous reactions), surface area of the reactants, presence of catalyst, intensity of radiation etc.

2. Rate of reactions

$$\text{Rate of reaction} = \frac{\text{Change in the concentration of reactants or (products)}}{Time}$$

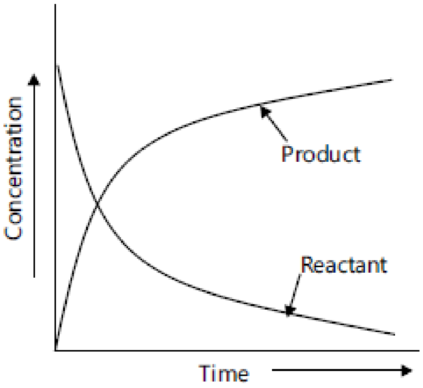
The rate of reaction is expressed in mol L^{-1} s^{-1}.

2.1 Average Rate of Reaction

Average rate of reaction is defined as change in the concentration of reactants (or products) during large interval of time. If ΔC is the change in the concentration of reactants and products in Δt time, then

$$\text{Average rate} = \frac{\text{Change in the concentration of reactants or (products)}}{Time} = \pm\frac{\Delta C}{\Delta t} = \pm\frac{C_2 - C_1}{t_2 - t_1}$$

The graph shows the progress of reaction with respect to time.

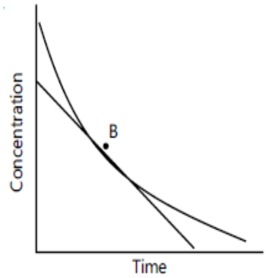


Concentration vs Time plot

2.2 Instantaneous Rate of Reaction

Instantaneous rate of reaction is defined as the reaction rate during a very short interval of time or rate of reaction at a particular time.

$$\text{Instantenious rate} = \pm \lim_{\Delta t \to 0} \frac{\Delta C}{\Delta t} = \frac{dC}{dt} = \text{slope}$$



Instantaneous reaction

For the reaction $n_1A + n_2B \rightarrow m_1C + m_2D$

$$\text{Instantenious rate of reaction} = -\frac{1}{n_1}\frac{d[A]}{dt} - \frac{1}{n_2}\frac{d[B]}{dt} = +\frac{1}{m_1}\frac{d[C]}{dt} = +\frac{1}{m_2}\frac{d[D]}{dt}$$

2.3 Expression of Rate of Reaction

For the following reaction $n_1A + n_2B \rightarrow m_1C + m_2D$

$$\text{Rate of reaction} = -\frac{1}{n_1}\frac{\Delta[A]}{\Delta t} - \frac{1}{n_2}\frac{\Delta[B]}{\Delta t} = +\frac{1}{m_1}\frac{\Delta[C]}{\Delta t} = +\frac{1}{m_2}\frac{\Delta[D]}{\Delta t}$$

For the reaction $2H_2O_2 \rightarrow 2H_2O + O_2$

$$\text{Rate of reaction} = \frac{\Delta[O_2]}{\Delta t} = -\frac{1\Delta}{2}\frac{[H_2O_2]}{\Delta t}$$

3. Rate Law

For the reaction: mA + nB → product, the rate law is

$$Rate \propto [A]^m B^n$$

- It may not depend upon the concentration of each reactant or product of the reaction.
- Rate of chemical reaction is directly proportional to the concentration of reactants.
- The rate law represents the experimentally observed rate of reaction, which depends upon the slowest step of the reaction.
- Rate law cannot be deduced from the equation for a given reaction. It can be found out by experiments only.
- The rate law may not bear a simple relationship for the stoichiometric equation.
- It may not depend upon the concentration of species, which do not appear in the equation for the overall reaction.

4. Rate Constant

Consider a simple reaction A → B

At a particular instant, if C_A is the molar concentration or active mass of A, then

$$\frac{dX}{dt} \propto C_A \text{ or } \frac{dX}{dt} = kC_A$$

where k is a proportionality constant, called velocity constant or rate constant or specific reaction rate.

At a fixed temperature, if $C_A = 1$, then Rate = $\frac{dX}{dt} = k$

Thus, rate constant can be defined as rate of reaction at unit concentration of the reactants.

Units of Rate Constant

For reactions of different order, unit for rate constant is as follows:

$$\text{Unit of rate constant} = [\frac{1}{Unit\ of\ concentration}]^{n-1} \times\ time^{-1}$$

$$= [\frac{1}{mole/litre}]^{n-1} \times\ sec^{-1} = \left\{\left[\frac{litre}{mol}\right]^{n-1} \times\ sec^{-1}\right\}$$

Where n is the order of the reaction.

5. Order of Reaction

The order of any reaction may be defined as the sum of the powers to which the concentration terms are raised in order to determine the rate of reaction.

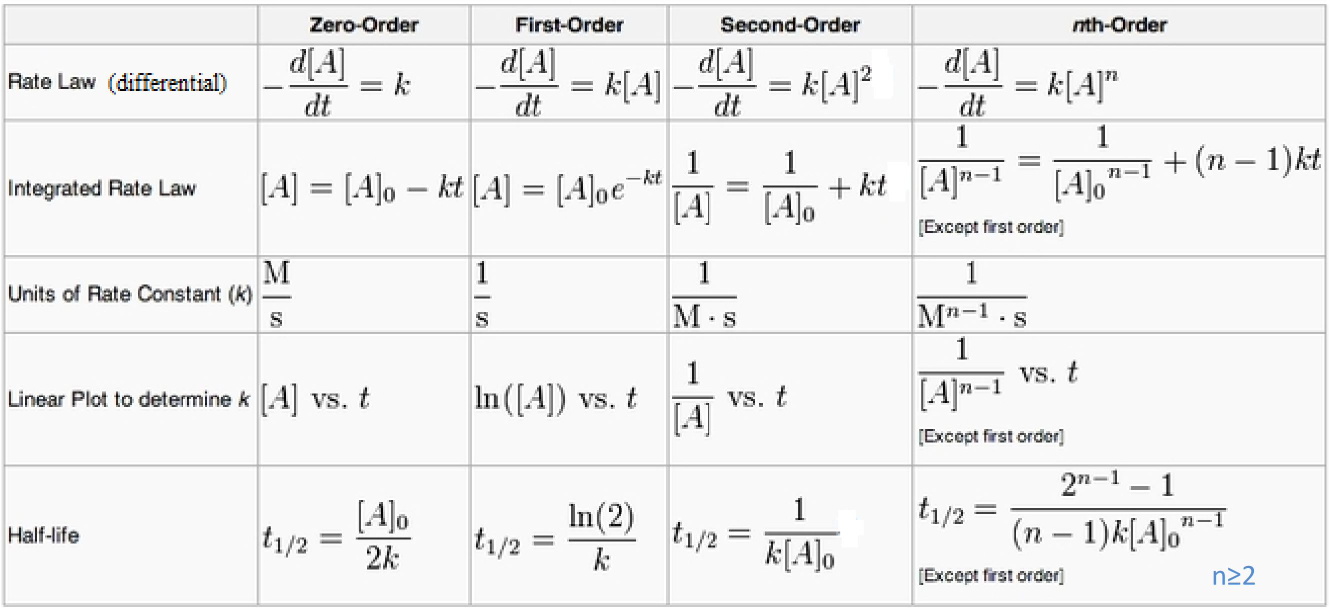
For the reaction: mA+nB → product

The experimental data suggests that

Rate = $k[A]^p[B]^q$; then the order with respect to A = p and the order with respect to B = q and the total order of the reaction n = p + q.

Note: n can be (-) ve, 0, fraction, integers.

A summary of reactions with the differential and integrated equations.



	Zero-Order	First-Order	Second-Order	*n*th-Order
Rate Law (differential)	$-\frac{d[A]}{dt} = k$	$-\frac{d[A]}{dt} = k[A]$	$-\frac{d[A]}{dt} = k[A]^2$	$-\frac{d[A]}{dt} = k[A]^n$
Integrated Rate Law	$[A] = [A]_0 - kt$	$[A] = [A]_0 e^{-kt}$	$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$	$\frac{1}{[A]^{n-1}} = \frac{1}{[A]_0{}^{n-1}} + (n-1)kt$ [Except first order]
Units of Rate Constant (*k*)	$\frac{\mathrm{M}}{\mathrm{s}}$	$\frac{1}{\mathrm{s}}$	$\frac{1}{\mathrm{M}\cdot\mathrm{s}}$	$\frac{1}{\mathrm{M}^{n-1}\cdot\mathrm{s}}$
Linear Plot to determine *k*	$[A]$ vs. t	$\ln([A])$ vs. t	$\frac{1}{[A]}$ vs. t	$\frac{1}{[A]^{n-1}}$ vs. t [Except first order]
Half-life	$t_{1/2} = \frac{[A]_0}{2k}$	$t_{1/2} = \frac{\ln(2)}{k}$	$t_{1/2} = \frac{1}{k[A]_0}$	$t_{1/2} = \frac{2^{n-1}-1}{(n-1)k[A]_0{}^{n-1}}$ [Except first order] n≥2

7. Kinetics of some complex reactions: Chain, Parallel/Competing/Side, Consecutive reactions

7.1. Kinetics of Chain reactions

Chain reactions usually involve free radicals. We will show how to deal with chain reactions by working out several examples. Our first example is the gas phase reaction of hydrogen with bromine to give HBr. (The temperature must be high enough that bromine is a gas and not a liquid.)

$$H_2 + Br_2 \rightarrow 2\,HBr \tag{1}$$

The experimental rate law is obtained by Linde and Bodenstein

$$\frac{d[\mathrm{HBr}]}{dt} = \frac{k'[\mathrm{H_2}][\mathrm{Br_2}]^{1/2}}{1 + k''\frac{[\mathrm{HBr}]}{[\mathrm{Br_2}]}}. \tag{2}$$

Our task is to show that the postulated mechanism will give this rate law. (We will not try to invent mechanisms for particular reactions in this course.) The postulated mechanism has five elementary reaction steps:

$$\text{Initiation} \qquad \mathrm{Br_2} \overset{k_a}{\rightarrow} \mathrm{Br}\bullet + \mathrm{Br}\bullet \tag{3}$$

$$\text{Propagation} \qquad \mathrm{Br}\bullet + \mathrm{H_2} \overset{k_b}{\rightarrow} \mathrm{HBr} + \mathrm{H}\bullet \tag{4}$$

$$\text{Propagation} \qquad \mathrm{H}\bullet + \mathrm{Br_2} \overset{k_c}{\rightarrow} \mathrm{HBr} + \mathrm{Br}\bullet \tag{5}$$

Inhibition $\quad H\bullet + HBr \xrightarrow{k_d} H_2 + Br\bullet$ (6)

Termination $\quad Br\bullet + Br\bullet \xrightarrow{k_e} Br_2$ (7)

Our goal is to find the rate law implied by this mechanism and see how it comparaes to the experimental rate law, Equation 2. Our first task will be to define the reaction rate. We will define the reaction rate as rate of production of the product, HBr.

$$\text{Rate} = \frac{d[\text{HBr}]}{dt}. \tag{8}$$

Looking at the mechanism and using only the steps which yield or consume HBr we find that

$$\frac{d[\text{HBr}]}{dt} = k_b[\text{Br}\bullet][\text{H}_2] + k_c[\text{H}\bullet][\text{Br}_2] - k_d[\text{H}\bullet][\text{HBr}]. \tag{9}$$

We see that the rate contains two transient species, Br• and H• , so we set up the equations which show the rate of change of the concentrations of these two species and apply the steady state approximation. The two equations are,

$$\frac{d[\text{H}\bullet]}{dt} = k_b[\text{Br}\bullet][\text{H}_2] - k_c[\text{H}\bullet][\text{Br}_2] - k_d[\text{H}\bullet][\text{HBr}] \approx 0 \tag{10}$$

and

$$\frac{d[\text{Br}\bullet]}{dt} = 2k_a[\text{Br}_2] + \left\{-k_b[\text{Br}\bullet][\text{H}_2] + k_c[\text{H}\bullet][\text{Br}_2] + k_d[\text{H}\bullet][\text{HBr}]\right\} - 2k_e[\text{Br}\bullet]^2 \approx 0. \tag{11}$$

In Equation 11 we have set three of the terms apart by braces { } in order to make it easier to see that the part inside the braces is just the negative of the middle of Equation 10. Since the part inside the braces is zero we conclude that

$$2k_a[\text{Br}_2] - 2k_e[\text{Br}\bullet]^2 = 0, \tag{12}$$

or

$$[\text{Br}\bullet] = \sqrt{\frac{k_a}{k_e}[\text{Br}_2]}. \tag{13}$$

We can solve Equation 10 for [H•] to get

$$[\text{H}\bullet] = \frac{k_b[\text{Br}\bullet][\text{H}_2]}{k_c[\text{Br}_2] + k_d[\text{HBr}]}, \tag{14}$$

which, on substituting the result of Equation13, becomes,

$$[\text{H}\bullet] = \frac{k_b[\text{H}_2]\sqrt{\frac{k_a}{k_e}[\text{Br}_2]}}{k_c[\text{Br}_2] + k_d[\text{HBr}]}. \tag{15}$$

We now go back to the equation for the Rate, Equation 9, and note that the right hand side of Equation 9 is the same as Equation 10 except for the sign of the k_c term. Rewrite Equation 10 as,

$$k_b[\mathrm{Br}\bullet][\mathrm{H}_2] - k_c[\mathrm{H}\bullet][\mathrm{Br}_2] - k_d[\mathrm{H}\bullet][\mathrm{HBr}] = 0, \qquad (10b)$$

or

$$k_b[\mathrm{Br}\bullet][\mathrm{H}_2] - k_d[\mathrm{H}\bullet][\mathrm{HBr}] = k_c[\mathrm{H}\bullet][\mathrm{Br}_2]. \qquad (10c)$$

Combining Equations 9 and 10c we find that,

$$\frac{d[\mathrm{HBr}]}{dt} = 2k_c[\mathrm{H}\bullet][\mathrm{Br}_2]. \qquad (16)$$

Since Equation 15 gives us an expression for [H•] we can combine Equations 15 and 16 to eliminate all the transient concentrations,

$$\frac{d[\mathrm{HBr}]}{dt} = 2k_c \frac{k_b[\mathrm{H}_2]\sqrt{\frac{k_a}{k_e}[\mathrm{Br}_2]}}{k_c[\mathrm{Br}_2] + k_d[\mathrm{HBr}]}[\mathrm{Br}_2], \qquad (17)$$

which rearranges to

$$\frac{d[\mathrm{HBr}]}{dt} = \frac{2k_b\sqrt{\frac{k_a}{k_e}}[\mathrm{H}_2][\mathrm{Br}_2]^{1/2}}{1 + \frac{k_d}{k_c}\frac{[\mathrm{HBr}]}{[\mathrm{Br}_2]}}. \qquad (18)$$

with,

$$k' = 2k_b\sqrt{\frac{k_a}{k_e}} \qquad (19)$$

and

$$k'' = \frac{k_d}{k_c}. \qquad (20)$$

Equation 18 has the same form as Equation 2

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

The two phenomenological rate constants, k' and k'', can be written in terms of the rate constants for the elementary reaction steps in the mechanism.

In the initial stage of the reaction, i.e., t = 0, [HBr] is negligibly small i.e., [HBr] = 0 and hence

$1 + k''$ [HBr]/Br_2] ≈ 1

And the initial rate becomes $\frac{d[HBr]}{dt} = k^{/}[H_2][Br_2]^{1/2}$

That is, in the initial stage, the overall order of the reaction is 1.5 (order 1 w.r.t. H_2 and ½ w.r.t. Br_2).

7.1. Kinetics of consecutive or sequential reactions

In many cases, the product formed in one of the elementary reactions acts as the reactant for some other elementary reaction. One of the examples of consecutive reactions involves the following steps.

$$A \xrightarrow{k_1} B \xrightarrow{k_1'} C$$

Let the initial concentration of A be $[A]_0$ and let after time t, the concentrations of A, B and C

be [A], [B] and [C], respectively. It is obvious that

$$[A]_0 = [A] + [B] + [C] \qquad (1)$$

Differential Rate Law: The differential rate expressions are

$$-\frac{d[A]}{dt} = k_1[A] \qquad \ldots\ldots(2)$$

$$\frac{d[B]}{dt} = k_1[A] - k_1'[B] \qquad \ldots\ldots(3)$$

$$\frac{d[C]}{dt} = k_1'[B] \qquad \ldots\ldots(4)$$

On integrating equation (2), we get

$$[A] = [A]_0 e^{-k_1 t} \qquad \ldots\ldots(5)$$

Substituting [A] from equation (5) into equation (3), we get

$$\frac{d[B]}{dt} = k_1[A]_0 e^{-k_1 t} - k_1'[B]$$

$$\frac{d[B]}{dt} + k_1'[B] = k_1[A]_0 e^{-k_1 t}$$

Integrated Rate Law : Multiplying the above expression throughout by exp (k'_1t), we get

$$\frac{d[B]}{dt} + k_1'[B]e^{k_1't} = k_1[A]_0 e^{-(k_1-k_1')t}$$

The left side of the above expression is equal to $d([B]e^{k_1't})/dt$. Hence, the above expression can written as , $d\{[B]e^{k_1't}\} = k_1[A]_0 e^{-(k_1-k_1')t}dt$

Integrating the above expression with [B] = 0 at t = 0, we get

$$[B]e^{k't} = k_1[A]_0\left[\frac{e^{-(k_1-k_1')t}}{-(k_1-k_1')} + \frac{1}{k_1-k_1'}\right]$$

$$[B] = k_1[A]_0\left[\frac{e^{-k_1t}}{-(k_1'-k_1)} + \frac{e^{-k_1't}}{k_1-k_1'}\right]$$

$$[B] = k_1[A]_0\left(\frac{k_1}{k_1'-k_1}\right)\{e^{-k_1t} - e^{-k_1't}\} \qquad \ldots\ldots(6)$$

Substituting equations (5) and (6) in equation (1), we get

$$[A]_0 = [A]_0e^{-k_1t} + [A]_0\left(\frac{k_1}{k_1'-k_1}\right)(e^{-k_1t} - e^{-k_1't}) + [C]$$

$$[C] = [A]_0\left[1 - \frac{1}{k_1'-k_1}(k_1'e^{-k_1t} - k_1e^{-k_1't})\right] \qquad \ldots\ldots(7)$$

Figure (1) Illustrates the general appearance of the variations of concentrations of A, B and C during the progress of the reaction.

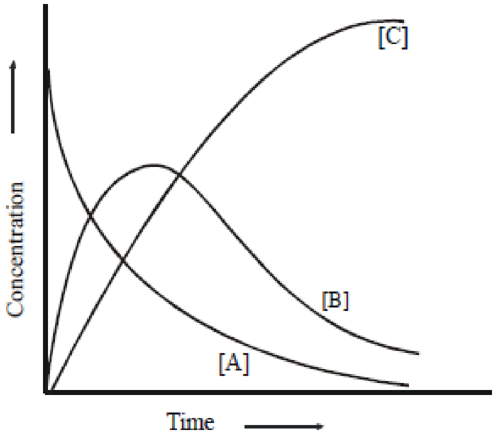


Fig. Typical variations of concentration of A, B and C during the progress of the re action A → B → C. The actual variations on the values of k_1 and k'_1.

In general concentration of A decreases exponentially, the concentration of B initially increases up to a maximum and then decreases thereafter, and the concentration of C increases steadily until it reaches its final value $[A]_0$, when all A has changed into C.

Maximum Concentration of B : Equation (6) is

$$[B] = [A]_0 \left(\frac{k_1}{k_1' - k_1} \right) \{ e^{-k_1 t} - e^{-k_1' t} \} \qquad \ldots\ldots(6)$$

At the maximum concentration of B, we have

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

Hence, differentiating equation (6) with respect to t, we get

$$\frac{d[B]}{dt} = [A]_0 \left(\frac{k_1}{k_1' - k_1} \right) \{ -k_1 e^{-k_1 t} + k_1' e^{-k_1' t} \} \qquad \ldots\ldots(8)$$

Equating equation (8) to zero, we get

$$-k_1 e^{-k_1 t_{max}} + k_1' e^{-k_1' t_{max}} = 0$$

or

$$\frac{k_1}{k_1'} = e^{(k_1 - k_1') t_{max}}$$

or

$$\ln \left(\frac{k_1}{k_1'} \right) = (k_1 - k_1') t_{max}$$

or

$$t_{max} = \frac{1}{k_1 - k_1'} \ln \left(\frac{k_1}{k_1'} \right) \qquad \ldots\ldots(9)$$

substituting equation (9) in equation (6), we get

$$[B]_{max} = [A]_0 \left(\frac{k_1'}{k_1} \right)^{k_1'/(k_1 - k_1')} \qquad \ldots\ldots(10)$$

Examples of 1st order consecutive reactions:

- Radioactive decay
- Decomposition of dimethyl ether in gaseous phase and that of the ethylene oxide. The reactions are

$$CH_3OCH_3 \xrightarrow{k_1} CH_4 + HCHO$$

$$HCHO \xrightarrow{k_2} H_2 + CO$$

and $(CH_2)_2O \xrightarrow{k_1} (CH_3CHO)^* \xrightarrow{k_2} CH_4 + CO$

Important conclusions from equations (5), (6) and (7):

Two important conclusions are (1) the slowest elementary process (i.e. the process having smallest rate constant) is the rate-determining step of the reaction and (2) the steady-state approximation (the reactive intermediate are present in constant concentration) can be assumed to hold good for all reactive intermediates. These conclusions can be derived as follows.

(i) Rate-determining step: In the consecutive reactions

$$\mathrm{A} \xrightarrow{k_1} \mathrm{B} \xrightarrow{k_1'} \mathrm{C}$$

the reaction rate constant $k'_1 >> k_1$ i.e. reaction A→B is much slower than the reaction B→C. Thus the rate of formation of the product C depends wholly on the rate at which the intermediate B is formed from A. The same conclusion can be derived from the equation (7). We have

$$[\mathrm{C}] = [\mathrm{A}]_0 \left\{1 - \frac{1}{k_1' - k_1}\left(k_1' \mathrm{e}^{-k_1 t} - k_1 \mathrm{e}^{-k_1' t}\right)\right\}$$

Since $k'_1 >> k_1$, the $\mathrm{e}^{-k_1' t}$ will be much smaller than $\mathrm{e}^{-k_1 t}$ and hence $k_1 \mathrm{e}^{-k_1' t}$ may be ignored in comparison to $k_1' \mathrm{e}^{-k_1 t}$.

Hence, the above equation simplifies to

$$[\mathrm{C}] \simeq [\mathrm{A}]_0 \left\{1 - \frac{k_1'}{k_1' - k_1} \mathrm{e}^{-k_1 t}\right\}$$

Since k_1 is much smaller than k'_1, we may ignore $k_1$in comparison to k'_1. Thus, the above equation becomes

$$[\mathrm{C}] \simeq [\mathrm{A}]_0 \left(1 - \mathrm{e}^{-k_1 t}\right) \qquad (11)$$

Equation (11) can be obtained directly if we consider alone the reaction
A→C

Now $$\frac{\mathrm{d}[\mathrm{C}]}{\mathrm{d}t} = k_1[\mathrm{A}] = k_1([\mathrm{A}]_0 - [\mathrm{C}])$$

or $$\frac{\mathrm{d}[\mathrm{C}]}{[\mathrm{A}]_0 - [\mathrm{C}]} = k_1 \mathrm{d}t$$

or $$\int_0^{[\mathrm{C}]} \frac{\mathrm{d}[\mathrm{C}]}{[\mathrm{A}]_0 - [\mathrm{C}]} = k_1 \int_0^t \mathrm{d}t$$

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

or $$\frac{[\mathrm{A}]_0 - [\mathrm{C}]}{[\mathrm{A}]_0} = \mathrm{e}^{-k_1 t}$$

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

This is identical to equation (11). Thus we may conclude that the reaction with the smaller rate constant is the rate-determining step.

The same conclusion would be obtained if we consider the 1st step is much faster than 2nd step, i.e.

$k_1 >> k'_1$. In this case we will ignore k'_1 in comparison to k_1 and $k'_1 e^{-k_1 t}$ in comparison to $k_1 e^{-k'_1 t}$

Hence, equation (7) in the present case will simplify to

$$[C] = [A]_0 (1 - e^{-k'_1 t})$$

The above equation can be obtained directly if we consider alone the reaction

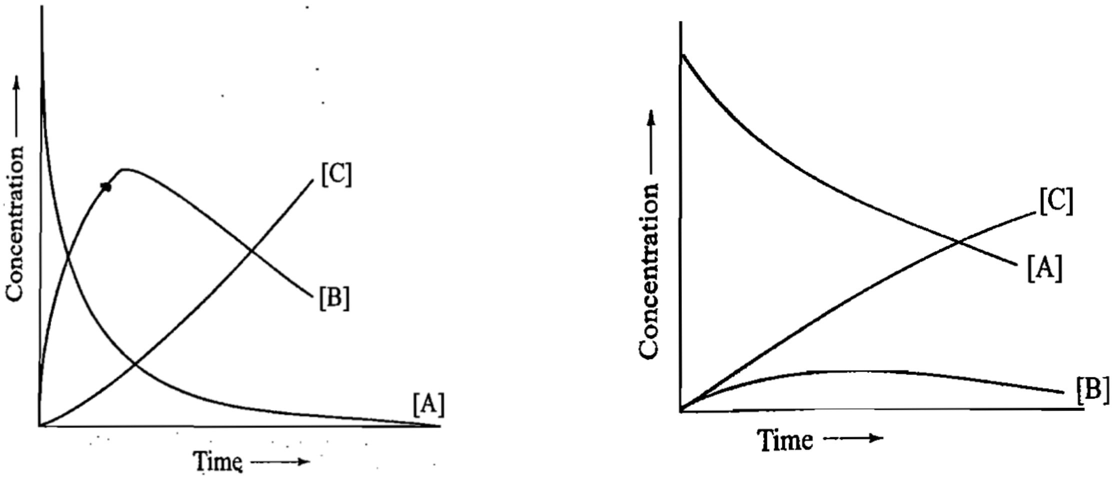
B→C

With $[B]_0 = [A]_0$ as the transformation of A to B is very fast.

(ii) Steady-state approximation: The typical variation of concentration of A, B and C for the two consecutive 1st order reactions

$$A \xrightarrow{k_1} B \xrightarrow{k'_1} C$$

with (a) $k_1 >> k'_1$ and (b) $k_1 << k'_1$, respectively



(a) $k_1 >> k'_1$

(b) $k_1 << k'_1$

Fig. Variation of concentration of A, B and C for the two consecutive 1st order reactions with (a) $k_1 >> k'_1$ and (b) $k_1 << k'_1$.

In Fig. 2(a), the concentration of A disappears very rapidly as $k_1 >> k'_1$ and since the rate at which B disappears is relatively slow, the concentration of B increases rapidly and after attaining the maximum in a small time interval, starts decreasing.

In Fig. 2(b), the concentration of A decreases slowly as the reaction rate constant k_1 has a small value. The concentration of B practically remains constant for reasonable time, except at very beginning and at the end. This constancy results from the fact that the intermediate B is very reactive as its transformation to C occurs at very fast rate. In fact, the concentration of B at any instant will be much smaller than that of A.

From equation (6)

$$[B] = [A]_0 \left(\frac{k_1}{k_1' - k_1} \right) \{ e^{-k_1 t} - e^{-k_1' t} \}$$

on ignoring k_1 in comparison to k'_1 and $e^{-k'_1 t}$ comparison to $e^{-k_1 t}$, we get

$$[B] \simeq [A]_0 \frac{k_1}{k_1'} e^{-k_1 t} \tag{12}$$

Since at any instant the concentration of A is given by equation (5), we get

$$[B] \simeq \frac{k_1}{k_1'} [A] \tag{13}$$

That is, the concentration of B is smaller than the concentration of A by a factor of about (k_1/ k'_1). The concentration of the reactive intermediate B has a small value and that it practically remains constant throughout the reaction is known as the *steady-state approximation*.
Mathematically, it can be written as

$$\frac{d[B]}{dt} = 0 \tag{14}$$

The use of this equation very much simplifies the kinetics of the reaction.
For example, in a consecutive 1st order reaction with $k'_1 >> k_1$, equation (3) gives

$$\frac{d[B]}{dt} = k_1[A] - k_1'[B] = 0$$

$$\text{or} \quad [B] = \frac{k_1}{k_1'} [A] \tag{15}$$

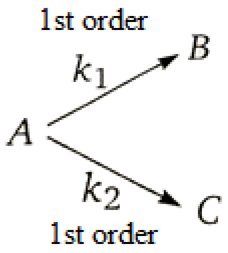
Substituting the above equation in equation (4), we get

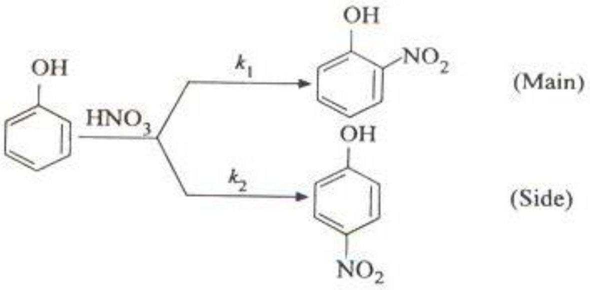
$$\frac{d[C]}{dt} = k_1'[B] = k_1' \frac{k_1}{k_1'} [A] = k_1[A] \tag{16}$$

Note the identity of equations (13 & 15) and equations (10 & 16).

7.2. Kinetics of Parallel / Side/ Competing Reactions:

Consider the reaction





The differential rate expressions are

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

$$\frac{d[C]}{dt} = +k_2[A] \quad (2)$$

The overall reaction rate for the consumption of A can be written as:

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

Or

$$\frac{d[A]}{dt} = -(k_1 + k_2)[A] \quad (3)$$

We can solve for the concentrations of A, B and C at any time ‘t’. To solve for [B] or [C], we must know [A].

Integrating $[A]$ with respect to t, we obtain the following equation:

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

Plugging this expression into the equation for $\frac{d[B]}{dt}$, we obtain:

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

Integrating $[B]$ with respect to t, we obtain:

$$[B] = -\frac{k_1[A]_0}{k_1+k_2}\left(e^{-(k_1+k_2)t}\right) + c_1$$

At t = 0, $[B] = 0$. Therefore,

$$c_1 = \frac{k_1[A]_0}{k_1+k_2}$$

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

Likewise,

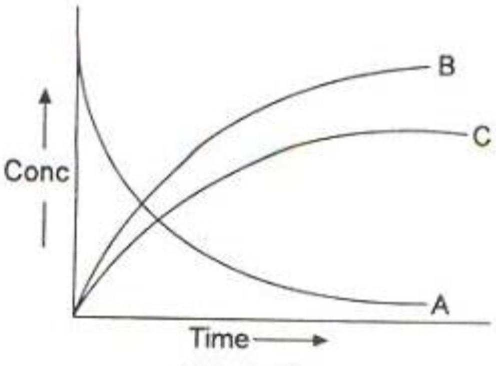
$$[C] = \frac{k_2[A]_0}{k_1+k_2}\left(1 - e^{-(k_1+k_2)t}\right)$$

The ratio of $[B]$ to $[C]$ is simply:

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

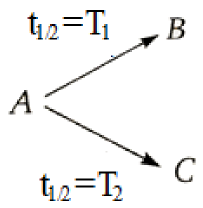
The ratio of concentrations of B and C at any time is constant.

Concentration vs Time Plot:



$K_1 > k_2$

The Effective Half-life:



For 1st order reaction, $t_{1/2} = \frac{ln2}{k}$

Hence, $T_1 = \frac{ln2}{k}_{1}$

$$T_2 = \frac{ln2}{k}_{2}$$

Therefore, effective half-life

$$T_2 = \frac{ln2}{k}_{eff}$$

$$k_{eff} = \frac{ln2}{T}_{eff}$$

Since, $k_{eff} = k_1 + k_2$

$$\frac{ln2}{T_{eff}} = \frac{ln2}{T_1} + \frac{ln2}{T_2}$$

$$\boxed{\frac{1}{T_{eff}} = \frac{1}{T_1} + \frac{1}{T_2}}$$

Thermodynamic vs Kinetic control product:

$$A \xrightarrow{k_1} B \qquad A \xrightarrow{k_2} C$$

Consider the reverse reactions

$$B \xrightarrow{k_{-1}} A \qquad C \xrightarrow{k_{-2}} A$$

Moreover $B \leftrightarrow C$

At equilibrium

$$\frac{K_1}{K_2}=\left\{\frac{[B]/[A]}{[C]/[A]}\right\}=\frac{[B]}{[C]}$$

Thermodynamic control

K=Eqbm. Const.

When any reverse reactions or interconversion of B and C can be neglected

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

Kinetic control

k=Rate Const.

8. Methods to Study Kinetics of Fast Reactions:

The chemical reaction which completes in less than 1 ps (one pieco second) (10-12 s) time, is known as the fast reactions. It is practically impossible to measure the speed of such reactions. The reason for a very fast rate of such reaction is that no chemical bonds are to be broken among the reactants.

Examples: ionic reactions, organic substitution reactions, neutralization reactions

Characteristics of Fast Reactions

- The chemical reactions in which the rate constant lies between $10^{1} – 10^{11}$ s^{-1} are called fast reactions. They have very short half-life of $10^{-1} – 10^{-15}$ s.
- They are so fast that they occur as soon as the reactants are brought together.
- The special experimental techniques used for measuring the rate constant of fast reactions include: Relaxation methods, Flow methods, Ultrasonic and Resonance techniques etc.

Relaxation Methods:

Relaxation methods are classified into three groups based on the extent of perturbation to attain a new equilibrium. They include:

- Small perturbation method
  Examples: Temperature jump method and Pressure jump method
- Large perturbation method
  Examples: Shock tube method and Flash photolysis
- Periodic perturbation method
  Example: Ultrasonic method

- In relaxation techniques, a chemical equilibrium is disturbed (perturbed) by a rapid change in one of the possible parameters like temperature or pressure or electric field intensity.
- The relaxation is followed by using spectrometer or conductivity meter techniques.
- The time during which the reaction gets relaxed from the equilibrium is called relaxation time.
- The relaxation time can be determined by T-jump method or by P-jump method.

Relaxation by Temperature Jump Method (T-Jump Method):

- In T-jump method, a high voltage power supply charges the capacitor (C).
- When a certain voltage is reached, the spark gap (G) breaks down and thereby discharging the capacitor and sending a strong current through the cell containing reactive system at equilibrium (Fig. 3).
- As the current passes, the temperature of the reactive system rises by about 10°C in few microseconds. This temperature rise perturbs the system in such a way that the concentration of reactive species adjusts to a new equilibrium value.
- The speed with which the system approaches new equilibrium is monitored through spectrometer in which the intensity of light leaving the cell is measured by using a suitable photodetector (Photo multiplier tube-PMT).
- The output of PMT is displayed as the variation of concentration versus time on the oscilloscope screen.

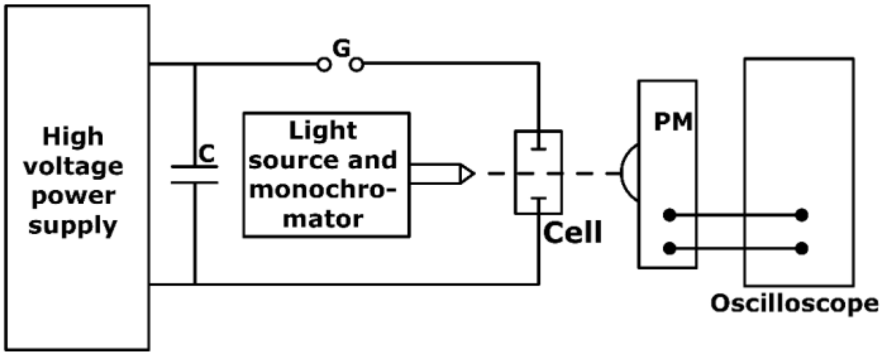


Fig. Apparatus for the temperature jump method

Rate Constant Expression for Fast Reactions by T-Jump Method:

If the displacement from equilibrium is very small, the rate of relaxation (restoration of equilibrium) always follows the first order kinetics.

Consider a reversible first- order reaction:

$$\mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{B}$$

Let '*a*' be the total concentration of A, and '*x*' be the concentration of B at any interval of time '*t*'.

Therefore, the rate of reaction is given by:

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

At equilibrium $dx/dt = 0$ and $x = x_e$, and from the equation (1) we have:

$$0 = k_1(a - x_e) - k_{-1}x_e \quad \ldots(2)$$

(or)

$$k_1(a - x_e) = k_{-1}x_e \quad \ldots(3)$$

The deviation from equilibrium (Δx) may be defined as:

$$\Delta x = x - x_e$$

Where x_e is equilibrium concentration.

(or)

$$x = \Delta x + x_e \quad \ldots(4)$$

The deviation of Δx with time is given by:

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

But $x = \Delta x + x_e$ and hence, we have:

$$\frac{d(\Delta x)}{dt} = k_1[a - \Delta x - x_e] - k_{-1}[\Delta x + x_e] \quad \ldots(5)$$

$$\frac{d(\Delta x)}{dt} = k_1 a - k_1\Delta x - k_1 x_e - k_{-1}\Delta x - k_{-1}x_e$$

$$\frac{d(\Delta x)}{dt} = k_1(a - x_e) - k_1\Delta x - k_{-1}\Delta x - k_{-1}x_e$$

$$\frac{d(\Delta x)}{dt} = k_1(a - x_e) - k_1\Delta x - k_{-1}\Delta x - k_{-1}x_e \quad \ldots(6)$$

From equation (3), we have:

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

Therefore, the equation (6) is written as:

$$\frac{d(\Delta x)}{dt} = k_{-1}x_e - k_1\Delta x - k_{-1}\Delta x - k_{-1}x_e$$

(or)

$$\frac{d(\Delta x)}{dt} = -\Delta x[k_1 + k_{-1}]$$

$$\frac{d(\Delta x)}{dt} = -\Delta x . k_r \quad \ldots(7)$$

Where $k_r = [k_1 + k_{-1}]$ is known as relaxation constant.

The reciprocal of relaxation constant is known as relaxation time (τ*).

$$\tau^* = \frac{1}{k_r} = \frac{1}{[k_1 + k_{-1}]}$$

Rearranging equation (7), we have:

$$\frac{d(\Delta x)}{\Delta x} = -\, k_r dt \quad \ldots(8)$$

Since the quantity Δx varies with time, integrating the equation (8) subjected to the boundary conditions $\Delta x = \Delta x_o \rightarrow \Delta x$ when $t = 0 \rightarrow t$, we have:

$$\int_{\Delta x=\Delta x_o}^{\Delta x=\Delta x} \frac{d(\Delta x)}{\Delta x} = -\, k_r \int_{t=0}^{t=t} dt$$

$$ln\frac{\Delta x}{\Delta x_o} = -\, k_r t$$

$$\frac{\Delta x}{\Delta x_o} = e^{-\,k_r t}$$

$$\Delta x = \Delta x_o e^{-\,k_r t}$$

Where $k_r = k_1 + k_{-1}$.

Exercise: 1

The relaxation time for fast reaction $A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B$ is 10 μs and the equilibrium constant is $1x10^{-3}$. Calculate the rate constant for forward and reversible reaction.

The relaxation time for the given fast reaction is given as:

$$\tau^* = \frac{1}{[k_1 + k_{-1}]} = 10\ \mu s = 10 \times 10^{-6} s = 10^{-5} s$$

Since the k1 is far greater than k-1 (k1 <<<k-1),

$$\tau^* = \frac{1}{k_1}$$

(or)

$$10^{-5} s = \frac{1}{k_1}$$

$$k_1 = 10^5 s^{-1}$$

We know that the equilibrium constant (*K*) for the given reversible reaction is:

$$K = \frac{k_1}{k_{-1}}$$

Given that the equilibrium constant for the given fast reaction is 1×10^{-3}. Therefore, the rate constant for reversible reaction is:

$$k_{-1} = \frac{k_1}{K}$$

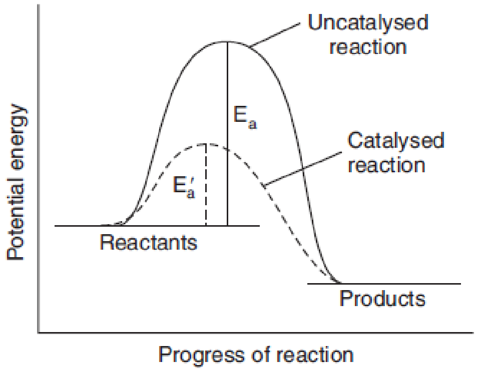
$$k_{-1} = \frac{10^5}{1 \times 10^{-3}} s^{-1}$$

$$k_{-1} = 10^8 s^{-1}$$

9. Catalysis:

9.1. Role of a catalyst:

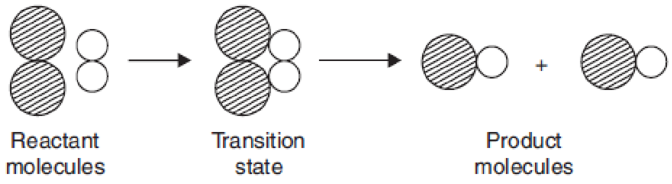
We can employ catalyst for increase the rate of a reaction because catalyst can provide an alternative pathway with low activation energy, so more reactant molecules can cross the activation energy barrier at given concentration and temperature.

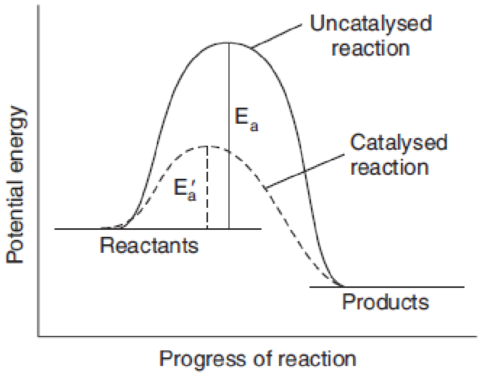


E_T = threshold energy of the uncatalysed reaction
$E^{/}_T$ = threshold energy of the catalyzed reaction
E_R = Energy of the reactant
E_p = Energy of the product

Advantages of using catalyst instead of using high temperature to promote a chemical reaction
(a) Better to control of the reaction
(b) Low energy cost due to lower temperature (more economical)
(c) Fewer side reactions thereby providing higher yield of the desired products.

What is catalyst
Catalyst is defined as a substance, a small quantity of which alter (increase or decrease) the velocity of a chemical reaction by its mere presence, without itself undergoing any change in mass and composition at the end of the reaction.
The phenomenon of altering the velocity of a chemical reaction by the presence of a catalyst is called catalysis.





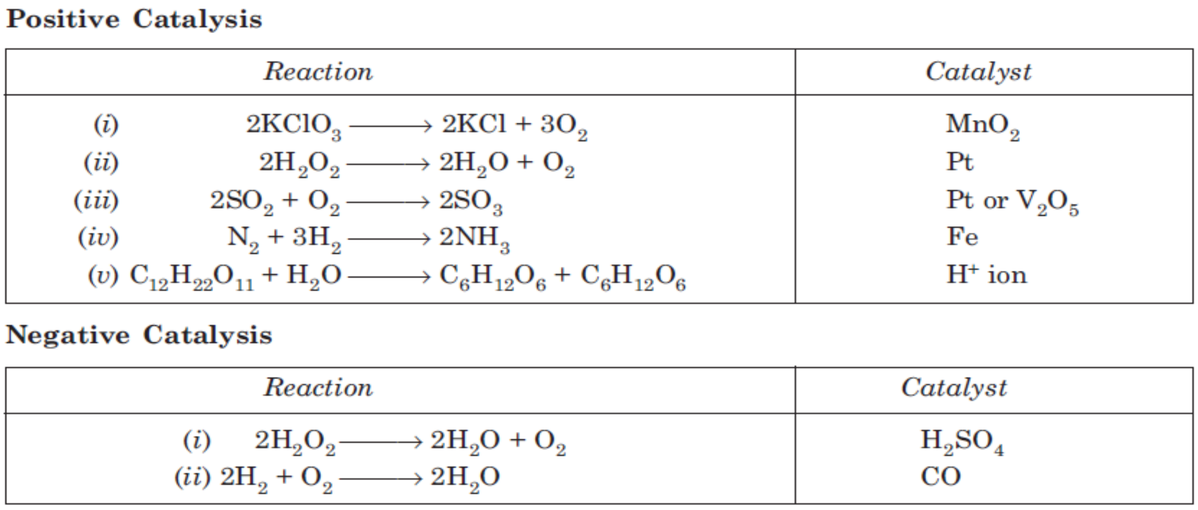
9.2. Types of catalyst:

(a) Positive catalyst: A positive catalyst is a catalyst which accelerates the speed of the reaction (also known as accelerator)

Examples: (i) In hydrogenation reaction of oil during the manufacture of vegetable ghee by Nickel (150-300^{0}C)
(ii) MnO_2 in the decomposition of $KClO_3$ into KCl and O_2
(iii) Platinum black or V_2O_5 in the oxidation of SO_2 by atmospheric oxygen to SO_3 (contact process)

(b) Negative catalyst: If the catalytic substances retard the chemical reaction, it is called negative catalyst (also known as inhibitor)

Examples: (i) Alcohol retard the oxidation of chloroform to poisonous phosgene
(ii) Tetraethyl lead acts as anti-knock material in internal combustion engine.



Positive Catalysis

Reaction	*Catalyst*
(*i*) $2KClO_3 \longrightarrow 2KCl + 3O_2$	MnO_2
(*ii*) $2H_2O_2 \longrightarrow 2H_2O + O_2$	Pt
(*iii*) $2SO_2 + O_2 \longrightarrow 2SO_3$	Pt or V_2O_5
(*iv*) $N_2 + 3H_2 \longrightarrow 2NH_3$	Fe
(*v*) $C_{12}H_{22}O_{11} + H_2O \longrightarrow C_6H_{12}O_6 + C_6H_{12}O_6$	H^+ ion

Negative Catalysis

Reaction	*Catalyst*
(*i*) $2H_2O_2 \longrightarrow 2H_2O + O_2$	H_2SO_4
(*ii*) $2H_2 + O_2 \longrightarrow 2H_2O$	CO

9.3. Characteristics of catalysts:

1. A catalyst remains unchanged in mass and composition at the end of the reaction though a change in physical state, color etc. may occur.

As for example, granular MnO_2 (manganese dioxide) used as a catalyst during the decomposition of Potassium Chlorate ($KClO_3$), is recovered as fine powder after the reaction.

It is believed that MnO_2 catalyzed reaction for the preparation of oxygen takes place as follows-

$$2KClO_3 + 2MnO_2 \rightarrow 2KMnO_4 + Cl_2 + O_2$$

$$2KMnO_4 \rightarrow K_2MnO_4 + MnO_2 + O_2$$

$K_2MnO_4 + Cl_2 \rightarrow 2KCl + MnO_2 + O_2$

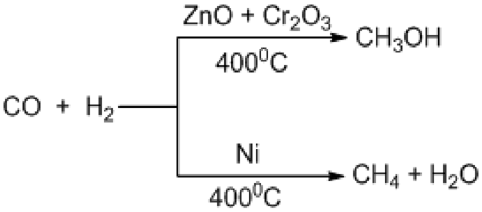
2. A small amount of catalyst is sufficient to bring an appreciable change in the velocity of the reaction. Example: The presence of even 1 mg of fine pt powder is enough to catalyze the combination of 2.5 liters mixtures of H_2 and O_2 to form water. Rate also increases in the increase in the surface area of the catalyst.

3. A catalyst can exert a selective action like a key can open a particular lock. Some catalysts are very specific in respect of reaction and change of a catalyst may divert the path of the same reaction to different products.

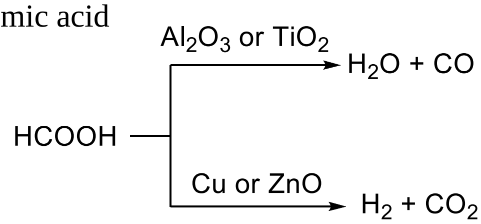
Examples: (i) water gas (a mixture of CO and H_2) is converted to –

(a) Methanol when passed over ZnO and Cr_2O_3 at 400^0C

(b) Methane when passed over a Nickel catalyst at 400^0C



(c) Decomposition of formic acid



Enzymes also have specific catalytic activity.

4. A catalyst can only alter the speed of the reaction but does not affect the final state of equilibrium since it alters the rate of the forward as well as backward reaction to the same extent, thereby the composition of the equilibrium remains the same.

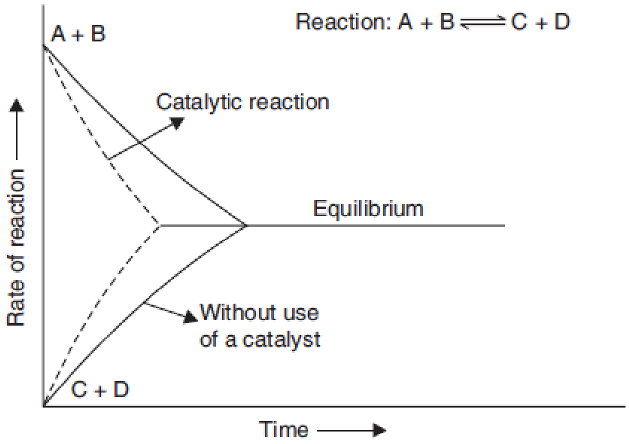


Fig. Effect of catalyst on time to attain equilibrium

5. According to Ostowald, a catalyst cannot initiate the reaction but can only decrease or increase its rate. Initiations of reactions by catalyst are rather rare but not unknown. Example- Perfectly dry H_2 and O_2 does not combine to form water even if they are left in contact for years, but in presence of little water (catalyst), the reaction proceeds quite rapidly.

6. A catalyst is most active at a particular temperature, called the optimum temperature.

7. The addition of a small amount of foreign substances, which are not themselves catalytically active, sometimes increase the catalytic activity of the catalyst. Such substances which catalyze the catalyst are called promoters.

Examples: In the manufacture of ammonia by Habers Process, finely divided Fe acts as a catalyst while Molybdenum (or a mixture of alumina, Al_2O3 and K_2O) acts as a promoter.

Similarly, in the manufacture of methanol from CO and H_2, the activity of the catalyst ZnO is greatly enhanced by the presence of Chromium sesquioxide, the promoter.

The properties of promoters are- (i) Selectively enhancement of the reactions; (ii) Increase catalyst lifetime.

8. The activity of a catalyst is inhibited or completely destroyed by the presence of even minute traces of certain substances, called catalystic posion or anti-catalyst.

Example: In the manufacture of H_2SO_4 by contact process, a trace of As_2O_3 destroys the catalytic activity and efficiency of spongy Platinum.

9.4. Types of catalysis (homogenous, heterogeneous and auto catalysis with example)

Generally there are two types of catalysis-

(i) Homogenous and (ii) Heterogeneous catalysis

(A) Homogenous catalysis: In this catalysis, the catalyst is present in the same phase as the reacting substances (either in gas phase or liquid phase). Examples are given below-

(a) In gas phase:

(i) In the lead chamber process, for the manufacture of H_2SO_4, nitric oxide (NO) catalyses the oxidation of the SO_2

$$2SO_2(g) + O_2\,(g) \xrightarrow{NO(g)} 2SO_3(g)$$

(ii) Decomposition of acetaldehyde is catalysed by Iodine vapour

$$CH_3CHO\ (g) \xrightarrow{I_2\ Vapor} CH_4(g) + CO(g)$$

(iii) Nitric oxide acts as a catalyst in the combination of CO and O_2

$$2CO\ (g) + O_2(g) \xrightarrow{NO(g)} 2CO_2$$

(iv) Formation of HCl from H_2 and Cl_2 using N_2O as catalyst.

$$H_2(g) + Cl_2(g) \xrightarrow{N_2O(g)} 2HCl(g)$$

(b) In Liquid phase: In acid-base catalysis- inversion of cane sugar and hydrolysis of esters.

Acid catalysis:

$$\underset{\text{Cane Sugar}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H_3O^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

$$RCOOR' + H_2O \xrightarrow{H^+} RCOOH + R'OH$$

Base catalysis:

$$RCOOR' + H_2O \xrightarrow{OH^-} \underset{\text{Carboxylate ion}}{RCOO^-} + R'OH$$

(B) Heterogeneous catalysis:

In such reactions, the catalyst is present in different phase from the reacting substances and the reaction proceeds at an interface between the two discrete phases. Catalysts are usually solid and the reactants are in different phase (either liquid or gaseous).

(a) In contact Process for the manufacture of H_2SO_4, sulfur dioxide is directly oxidized to sulfur trioxide by atmospheric oxygen in the presence of Pt or vanadium pentoxide V_2O_5 as catalyst.

$$2SO_2\ (g) + O_2(g) \xrightarrow[V_2O_5\,(s)]{Pt\ (s)\ or} 2SO_3$$

(b) In Haber's process, for the manufacture of NH_3, nitrogen and hydrogen gases in the volume ratio 1:3 are passed over heated iron catalyst which contains a promoter, molybdenum.

$$N_2\,(g) + 3H_2(g) \xrightarrow[\text{Mo}]{Fe_2O_3\,(s)} 2NH_3$$

(c) Oxidation of ammonia to nitric oxide in presence of Pt-gause as catalyst

$$NH_3\,(g) + 5O_2(g) \xrightarrow{\text{Pt (s)}} 4NO(g) + 6H_2O(l)$$

(d) Hydrogenation of unsaturated hydrogen in presence of nickel as a catalyst.

$$R{-}HC{=}CH{-}R^{/} \; + \; H_2 \xrightarrow{\text{Ni}} R{-}H_2C{-}CH_2{\cdot}R^{/}$$

Auto-catalysis:

When a product formed in the course of the reaction enhances the velocity of the reaction (or acts as a catalyst), the phenomenon is called autocatalysis. In other words, if one of the product of a reaction is capable of catalyzing the same reaction in which it is produced this is called autocatalysis.

Examples: when an oxalate reacts with acidified $KMnO_4$ solution, the Mn(II) ions (resulting from the reduction of permanganate) catalyze the reaction. When oxalic acid is added to an acidified solution of Potassium permanganate, no appreciable de-colorization occurs for a comparatively long period of time but once the de-colorization occurs, it proceeds rapidly.

$$\begin{array}{l}
C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^- \;\;] \times 5 \\
MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O \;] \times 2 \\
\hline
5C_2O_4^{2-} + 2\,MnO_4^- + 16H^+ \longrightarrow 10CO_2 + 2Mn^{2+} + 8H_2O
\end{array}$$

Many hydrolysis reactions are catalysed by acids. When esters are hydrolysed since one of the products is an acid, the reaction is autocatalytic.

$$RCOOR^{/} + H_2O \xrightarrow{H^+} RCOOH + R^{/}OH$$

Mn(II) ions are not present before the reaction starts and so it starts off extremely slowly at room temperature. However, once the Mn(II) is produced, the reaction proceeds rapidly.

9.5 Acid-base catalysis:

Acid-base catalysis is an example of homogenous catalysis which is catalyzed by Bronsted acid or base or both.

(i) Specific proton catalyzed reaction (H^+ ion catalysis): A reaction which is catalyzed by H^+ or H_3O^+ ions but not by other proton donors (Bronsted Acids) e.g. solvolysis of esters, inversion of cane sugar, keto-enol tautomerism.

The term specific acid catalysis is used when the reaction rate is dependent on the equilibrium for protonation of the reactant and is governed by concentration of H^+ ion, not other Bronsted acids.

(ii) General acid Catalysis: These are the reactions which are not only catalyzed by H^+ ions but also acids including water. E.g. iodination of acetone

(iii) Specific OH^- ion catalysis: A reaction which is catalyzed by OH^- ion only. E.g. conversion of acetone to diacetone alcohol which is catalyzed by OH^- ion.

(iv) Generalized base catalysis: These are the reactions which are not only catalyzed by OH^- ions but also by other bases eg. OAc^-

(v) Reaction catalyzed by both H^+ and OH^- ions: Hydrolysis of ester is an example where both H^+ ion and OH^- ion can catalyze the hydrolysis process.

Kinetics of acid catalyzed reaction:

Mechanism 1:

We assume that a proton is transferred from an acid AH^+ to the substrate S. The acid form the substrate SH^+ then reacts with water molecule to form the product P.

$$S + AH^+ \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} SH^+ + A$$

$$SH^+ + H_2O \xrightarrow{K_2} P + H_3O^+$$

Applying steady state approximation for SH^+, we have,

Rate of formation of SH^+ = rate of consumption of SH^+

$$K_1[S][AH^+] = K_{-1}[A]\,[SH^+] + K_2[SH^+][H_2O]$$

For very dilute solution, concentration of $[H_2O]$ almost remain constant, so

$$K_1[SH][AH^+] = K_{-1}[A][SH^+] + K_2[SH^+]$$

Solving for $[SH^+]$. We have

$$[SH^+]\,(K_{-1}[A] + K_2) = K_1[S]\,[AH^+]$$

$$K_2[SH^+] = \frac{K_1K_2[S]\,[AH^+]}{K_{-1}[A] + K_2}$$

The rate of formation of product is given by,

$$d[P]/dt = K_2[SH^+] = \frac{K_1K_2[S]\,[AH^+]}{K_{-1}[A] + K_2}$$

Let us discuss two limiting cases,

Case I: If $K_2 >> K_{-1}[A]$, so there is always only a small $[SH^+]$.

$$d[P]/dt = K_1[S][AH^+]$$

As the rate depends on $[AH^+]$, hence the reaction is **generalized acid catalysis**.

Case II: If $K_2 << K_{-1}[A]$, SH^+ may be considered to be in equilibrium with reactant.

$$d[P]/dt = \frac{K_1K_2[S]\,[AH^+]}{K_{-1}[A]} \times \frac{[H^+]}{[H^+]} = \frac{K_1K_2[S]\,[H^+]}{K_{-1}K}$$

Where K is the ionization constant of $[AH^+]$

$$AH^+ \rightleftharpoons A + H^+ \qquad K = \frac{[A]\,[H^+]}{[AH^+]}$$

From the equation the rate is proportional to the $[H^+]$, it is an example of **specifically acid catalyzed reaction**.

Mechanism 2:

$$S + AH^+ \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} SH^+ + A$$

$$SH^+ + A \xrightarrow{K_2} P + SH^+$$

We assume that in the second step, the acid form of the substrate reacts with a base instead of water molecule.

Applying steady state approximation, $K_1[S][AH^+] = K_{-1}[A]\,[SH^+] + K_2[SH^+][A]$

$$[SH^+]\,(K_{-1}[A] + K_2[A]) = K_1[S]\,[AH^+]$$

$$[SH^+] = \frac{K_1[S]\,[AH^+]}{K_{-1}[A] + K_2[A]}$$

The rate of the reaction is

$$d[P]/dt = K_2[SH^+][A]$$

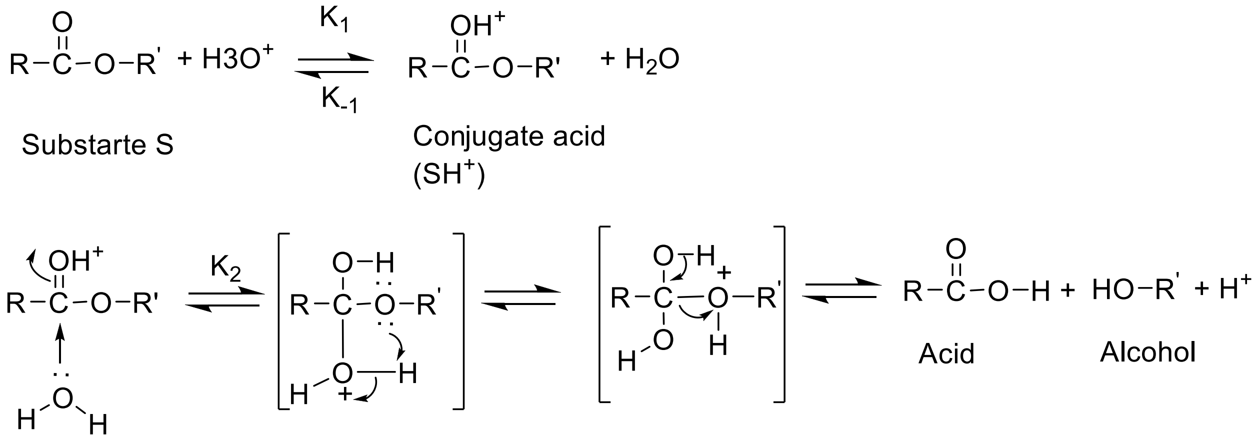
$$= \frac{K_1K_2[A][S]\,[AH^+]}{(K_{-1} + K_2)[A]}$$

$$= \frac{K_1K_2[S]\,[AH^+]}{K_{-1} + K_2}$$

From the above equation, it is obvious that the rate of the reaction is proportional to $[AH^+]$, it is an example of **general acid catalysis**.

Examples:

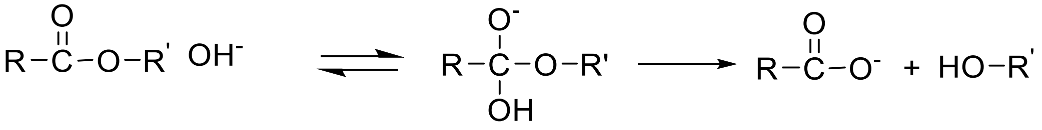
(i) Hydrolysis of esters: This is a specific acid catalyzed reaction when the reaction rate is dependent on the equilibrium for the protonation of reaction.



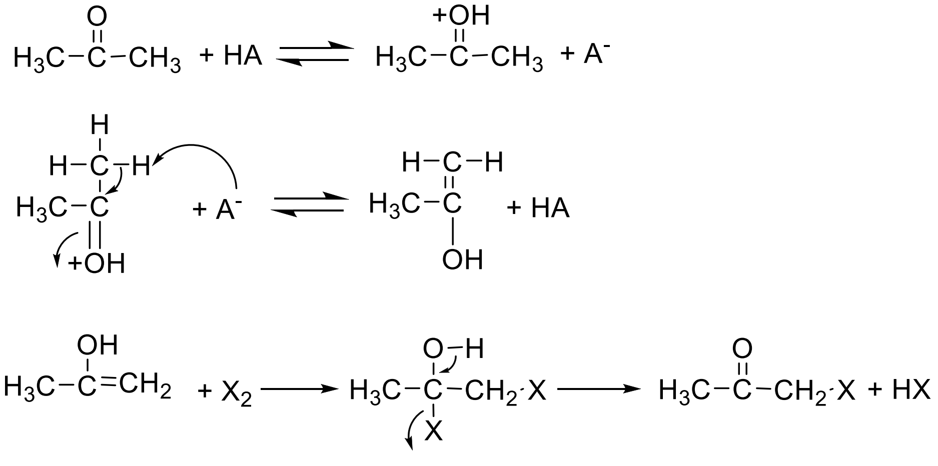
$$\text{Rate} = K_2[SH^+]$$

$$[SH^+] = \frac{K_1K_2[RCOOR]\,[H^+]}{K_{-1} + K_2}$$

Base catalyzed hydrolysis of esters.

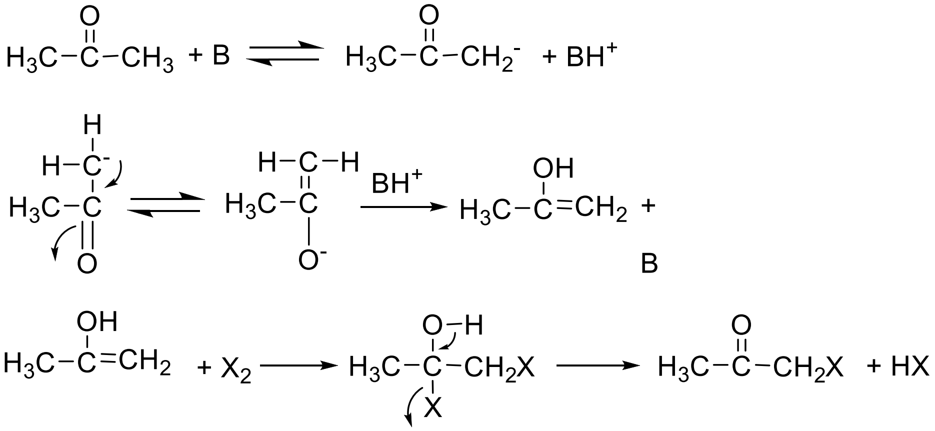


(ii) Halogention of acetone:



Rate determining step is the enolisation of acetone followed by a rapid addition of halogen to the enol. The enolisation of acetone is catalyzed by acids or bases.

Base catalyzed enolisation of acetone and halogenation:



9.6. Enzymes or biological catalyst:

Enzymes are highly complex, non-living nitrogenous organic substances produced by living animals and plants. They possess the incredible capacity in bringing about many complex chemical reactions like hydrolysis, oxidation, reduction etc. They are highly specific and each enzymes can catalyze a specific reaction. It also lowers the activation energy for a particular reaction. Examples:

(i) Starch is catalyzed by diastage to form maltose in turn by maltase into glucose.

$$\underset{\text{Starch}}{2(C_6H_{10}O_5)_n} + nH_2O \xrightarrow{\text{Diastage}} \underset{\text{Maltose}}{n(C_{12}H_{22}O_{11})}$$

$$\underset{\text{Maltose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\text{Maltage}} \underset{\text{Glucose}}{2\ C_6H_{12}O_6}$$

(ii) Invertage converts cane sugar into a mixture of glucose and fructose while zyamase converts glucose and fructose into alcohol.

$$\underset{\text{Cane sugar}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\text{Invertage}} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

$$C_6H_{12}O_6 \xrightarrow{\text{Zyamage}} 2C_2H_5OH + 2CO_2$$

(iii) The enzymes urease (present in Soyabeans) converts urea quantitatively into ammonia and CO_2 or $(NH_4)_2CO_3$.

$$NH_2CONH_2 + 2H_2O \xrightarrow{\text{Urease}} 2NH_3 + CO_2$$

The enzymes ptyalin present in human mouth (saliva) converts starch into glucose.

$$\underset{\text{Starch}}{(C_6H_{10}O_5)_n} + nH_2O \xrightarrow{\text{Ptyalin}} \underset{\text{Glucose}}{n(C_6H_{12}O_6)}$$

9.6.1. Characteristics of Enzymes:

(i) Enzymes are protein that can acts as enormously effective catalyst and can speed up the reaction by high factors of upto 10^{12}.

(ii) They are highly specific and each enzymes catalyze a particular reaction. (Key and Lock).

(iii) All enzyme reaction exhibits maximum efficiency at optimum temperature. Above this temperature the enzymes gets denatured, thereby losing its activity.

For most enzymes, the reaction rates increases upto 450C and above 450C, thermal denaturation take place. Above 550C, rapid thermal denaturation destroys completely the catalytic activity of the enzyme protein. Enzyme decreases the activation energy of a reaction at a given temperature.

(iv) Enzyme catalyzed reactions are much more sensitive to catalytic poison such as HCN, CS2, H2S etc. the inhibitors (or poisons) interact with the functional groups present on the enzyme surface and often reduce or completely destroy the catalytic activity of the enzyme.

(v) Activity of certain enzymes depends upon certain non-protien substances called co-enzymes. For each enzyme, there is only one co-enzymes.

(vi) Enzymes loose their activity when exposed to UV radiation or in presence of electrolyte.

(vii) The effect of PH on the rate of enzyme catalysed reaction is of complex nature. Usually the rate possess through a maximum as the PH increased. (PH 5-7)

(viii) Even a small amount of an enzyme can be highly efficient in bringing about a particular biological reaction.

(ix) Enzyme does not disturb the final state of equilibrium.

9.6.2. Mechanism and kinetic of enzyme catalysed reaction:

L. Michaelis and Mary Menten proposed a mechanism for the kinetics of enzyme catalysed reactions which involves the following steps-

Step 1: Formation of enzyme-substrate complex

$$\underset{\text{Enzyme}}{E} + \underset{\text{Substrate}}{S} \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} \underset{\text{Enzyme-substrate complex}}{ES} \text{ (Fast)}$$

Step 2: Decomposition of the enzyme-substrate complex to give the products.

$$ES \overset{K_2}{\rightleftharpoons} P + E \text{ (Slow)}$$

Overall reaction,

$$ES \xrightarrow{E} P$$

Now the enzyme is consumed in step 1 and but regenerated in backward step. Since step 2 is slow (rate determining) so the rate of the reaction is given by,

$$\text{Rate} = \frac{-d[S]}{dt} = +\frac{d[P]}{dt} = K_2[ES]$$

Using the steady state approximation with respect to ES,

Rate of formation of ES = Rate of consumption of ES

$$K_1[E]\,[S] = K_{-1}[ES] + K_2[ES]$$

$$\frac{d[ES]}{dt} = K_1[E]\,[S] - K_{-1}[ES] - K_2[ES] = 0$$

The equilibrium between the free and bound enzyme E and ES is given by the equation,

$$[E]_o = [E] + [ES]$$

$$[E] = [E]_o - [ES]$$

Where, $[E]_o$ = total enzyme concentration which can be measured

$[E]$ = free enzyme concentration which cannot be measured

$[ES]$ = Reacted or bound enzyme concentration

$$\frac{d[ES]}{dt} = K_1[E]\,[S] - K_{-1}[ES] - K_2[ES] = 0$$

$$= K_1\{[E]_o - [ES]\}\,[S] - K_{-1}[ES] - K_2[ES] = 0$$

$$= K_1[E]o[S] - K_1[ES]\,[S] - (K_{-1} + K_2)[ES] = 0$$

$$[ES] = \frac{K_1[E]o\,[S]}{K_1[S] + K_{-1} + K_2}$$

Dividing by K_1, we get, $$\text{Rate (r)} = \frac{K_2[E]o\,[S]}{\dfrac{(K_{-1} + K_2)}{K_1} + [S]} = \frac{K_2[E]_o\,[S]}{K_m + [S]}$$

$$\text{where,} \quad K_m = \frac{K_{-1} + K_2}{K_1}$$

This equation is known as Michaelis-Menten equation and K_m is known as Michaelis constant.
When all the enzymes has reacted with the substrate at high concentration, the rate of the reaction will be maximum. Under this condition, no free enzyme will be remain and hence,

$$[E]_o = [ES]$$

Maximum rate = $V_{max} = K_2[ES] = K_2[E]_o$

Where K_2 is called turn over number of the enzyme. The number of molecules converted in unit time by one molecule of enzyme is called turn over number and its value ranges from 100-1000s^{-1} but can be 10^5-10^6 s^{-1}.

Now the rate is given by,

$$\text{Rate (r)} = \frac{V_{max}\,[S]}{K_m + [S]}$$

Case I: If, $K_m >> [S]$, then we get, neglecting S in the denominator,

Thus, the enzyme catalyzed reaction is of first order, when the substrate concentration is low.

$$\text{Rate (r)} = \frac{V_{max}\,[S]}{K_m} = K'\,[S]$$

Case II: If Km << [S], so that we can neglect K_m, then,

$$\text{Rate (r)} = \frac{V_{max}\,[S]}{K_m} = V_{max} = \text{constant}$$

Enzyme catalyzed reaction is zero order when substrate concentration is high.

Case III: If, $K_m = [S]$, then,

$$\text{Rate (r)} = \frac{V_{max}\,[S]}{[S] + [S]} = \frac{1}{2}V_{max}$$

i.e. Michaelis constant is that concentration of the substrate at which rate of formation of products is equal to half the maximum rate of formation of products at high concentration of the substrate.

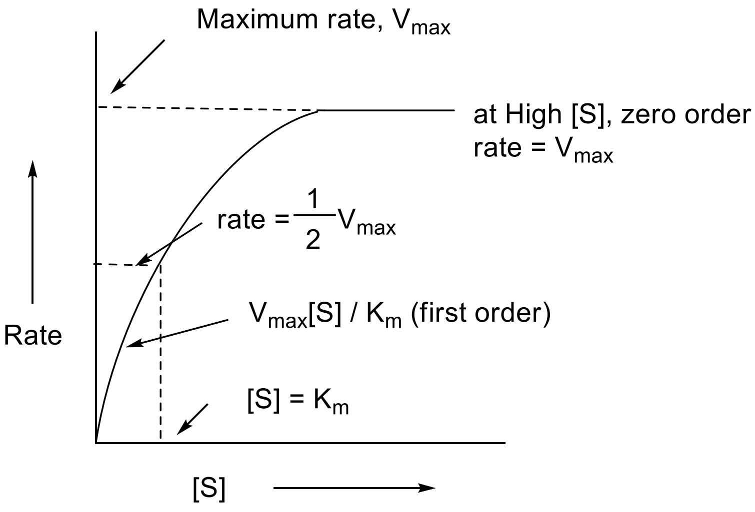


Fig. A plot of Michaelis-Menten equation

N.B.: Why the reaction rate of an enzyme-catalyzed reaction changes from 1st order to zero order as the substrate concentration is increased?

Ans: Each enzyme molecule has one or more 'active' sites at which the substrate must be bound in order that the catalytic action may occur. At low substrate concentration, most of these active sites unoccupied at any time. As the substrate concentration is increased, the number of active sites which are occupied increases and hence the reaction rate also increases. However, at very high substrate concentration, virtually all the active sites are occupied at any time so that further increase in substrate concentration can not further increase the formation of enzyme-substrate complex.

The Lineweaver-Burk method: It is rather difficult to determine V_{max} (and hence K_m) directly from the plot of rate vs [S]. It is possible by rearranging Michaelis-Menten equation

$$\frac{1}{\text{Rate (r)}} = \frac{K_m + [S]}{V_m\,[S]} = \frac{K_m}{V_{max}\,[S]} + \frac{1}{V_{max}}$$

A plot of 1/r against 1/[S] gives a straight line whose intercept on the x-axis and y-axis are $(-1/K_m)$ and $1/V_{max}$, respectively and slope is (K_m/V_{max}), as shown in the Fig. below.

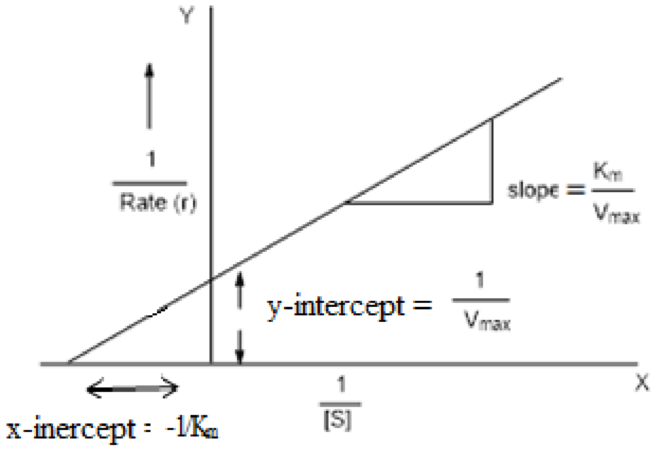


Fig. A plot of 1/r vs 1/[S] i.e. Lineweaver-Burk plot

Important catalysts in industrial processes, Hydrogenation using Wilkinsons catalyst, Hydroformylation by using Cobalt-catalyst

Applications of Catalysts for industrially important Processes:

Sl No	Process	Catalyst	Temp	Reaction	Remarks
1	Haber's Process	Fe	450^0C	$N_2 + 3H_2 \rightarrow 2NH_3$	It is used for the manufacture of ammonia; Al_2O_3 + K_2O or Mo is also used as Promoters

2	Contact Process	V_2O_5 or Platinised asbestos	450^0C	$2SO_2 + O_2 \rightarrow 2SO_3$	It is used for the manufacture of sulfuric acid
3	Chamber Process	NO		$2SO_2 + O_2 \rightarrow 2SO_3$	It is used for the manufacture of sulfuric acid
4	Bosch's Process	Fe_2O_3	$400\text{-}450^0C$	$(CO + H_2) + H_2O \rightarrow CO_2 + 2H_2$	It is used for the manufacture of H_2. Cr_2O_3 is used as promoter.
5	Ostwald Process	Platinised Asbestos	300^0C	$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$; $2NO + O_2 \rightarrow 2NO_2$ $4NO_2 + 2H_2O + O_2 \rightarrow 4HNO_3$	Excess of air (as promoter) is also required.
6	Bergius Process	Tin or Nickel oleate	450^0C	Coal → Gasoline	Heavy oil is also required for making paste of coal with catalyst.
7	Hardening of oil	Nickel	$150\text{-}300^0C$	Oils → Fats $H_2C{=}CH_2 + H_2 \xrightarrow{Cat} CH_3CH_3$	It is used for the manufacture of vegetable ghee from vegetable oil.

Hydrogeneation reaction by Wilkinson's Catalyst: $(PPh_3P)_3RhCl$

Tris-triphenyl phosphine Rhodium Chloride,**$(PPh_3P)_3RhCl$** which is generally known as Wilkinson's Catalyst acts as a homogenous catalyst for the hydrogenation of alkenes and alkynes. The catalyst is not able to reduce other functional groups although it is very reactive compound. The mechanism of the reaction is given below:

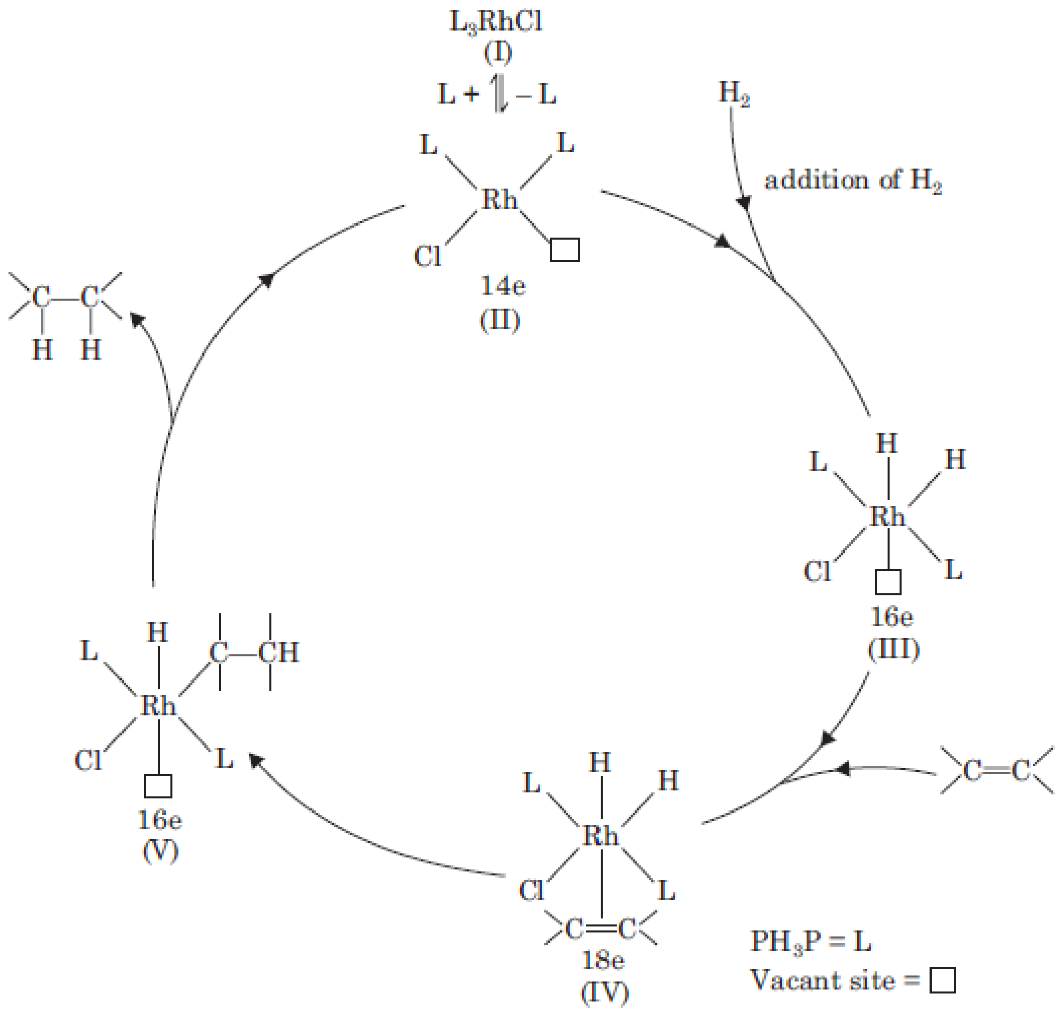


Figure: Mechanism of hydrogenation reaction using Wilkinson's Catalyst

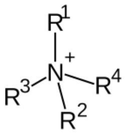
Phase Transfer Catalyst:

In chemistry, a phase-transfer catalyst (PTC) is a catalyst that facilitates the migration of a reactant from one phase into another phase where reaction occurs. Phase-transfer catalysis is a special form of heterogeneous catalysis. Ionic reactants are often soluble in an aqueous phase but insoluble in an organic phase in the absence of the phase-transfer catalyst. The catalyst functions like a detergent for solubilizing the salts into the organic phase. Phase-transfer catalysis refers to the acceleration of the reaction upon the addition of the phase-transfer catalyst.

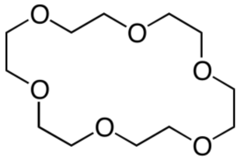
By using a PTC process, one can achieve faster reactions, obtain higher conversions or yields, make fewer byproducts, eliminate the need for expensive or dangerous organic solvents that will dissolve all the reactants in one phase, eliminate the need for expensive raw materials and/or minimize waste problems.

Phase-transfer catalysts are especially useful in **green chemistry**—by allowing the use of water, the need for organic solvents is reduced.

Examples of Phase-transfer catalysts:



X^- and



Quaternary ammonium salts (Q^+X^-) Crown ether

NB: Because of the presence of non-polar hydrocarbon chain polar N^+ ion quaternary ammonium salts are soluble in organic as well as aqueous medium.

Mechanism of Phase-transfer Catalysis:

The mechanism of phase transfer catalysis involves two fundamental processes (i) transfer of one reagent from its normal phase to the phase of other reagent and (ii) reaction of the transferred reagent or ion-pair with the non-transferred reagent within the organic layer.

Phase transfer catalysis can be easily explained using the following common nucleophilic displacement reaction using Q^+X^- as PTC,

$$\mathrm{RCl} \quad + \quad \mathrm{NaCN} \xrightarrow{Q^+X^-} \mathrm{RCN} + \mathrm{NaCl}$$

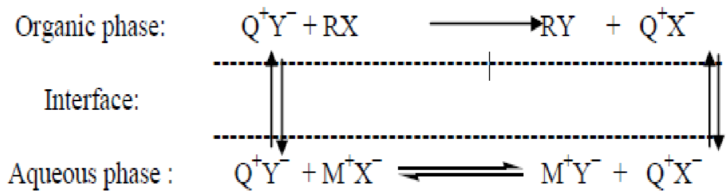
In general,

$$\mathrm{RX} \quad + \quad M^+Y^- \xrightarrow{Q^+X^-} \mathrm{RY} + \mathrm{MX}$$

(Alkyl halide soluble in organic solvent but insoluble in water)	(Inorganic salt soluble in water but insoluble in organic solvent)

The reaction cannot be carried out only in organic solvent or in aqueous medium.

This problem can be solved on addition of Q^+X^- as catalyst, the nucleophile Y^- available in the aqueous solution reacts with alkyl halide RX which is present in organic phase.



An overview of PTC reactions is given in the scheme above:

The ion pair (Q^+Y^-) is generated in aqueous phase by reaction between salt of alkali metal M^+Y^- and catalyst (Q^+X^-). Owing to the oleophilic character of Q^+, the anion Y^- is extracted into the organic phase across the interface. Here the necessary contact with alkyl halide is established and displacement reaction takes place. The displaced anion X^- is transferred back into aqueous phase in the form of an ion pair Q^+X^- and the cycle is completed.

Applications of phase-transfer catalyst:

PTC are not only used in organic chemistry but also a broadly useful tool in several other areas of chemistry viz., inorganic chemistry, electrochemistry, photochemistry, heterocyclic chemistry, industrial chemistry, medicinal chemistry and especially in polymer chemistry. The field of PTC has grown-up spectacularly over the past few decades, paving many new applications in the chemical, fine chemical and pharmaceutical industries. Primary applications are in nucleophilic substitution reactions and in reactions in the presence of bases involving the deprotonation of moderately and weakly acidic organic compounds. Typical reactions where PTCs employs as catalysts include, alkylation, displacements reactions, oxidation, transition metal co-catalyzed reactions (carbonylation, reduction and hydrogenation), condensations, carbene reactions, additions, polymerization, dehydrohalogenation, and so on, which are often part of a multi-step synthetic process for the manufacture of fine chemicals.