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NAAC ACCREDITED ‘A’ GRADE

Topic : Chemical Kinetics
Course Title : Enzymes
Paper : CC4
Unit : II
Semester : 2
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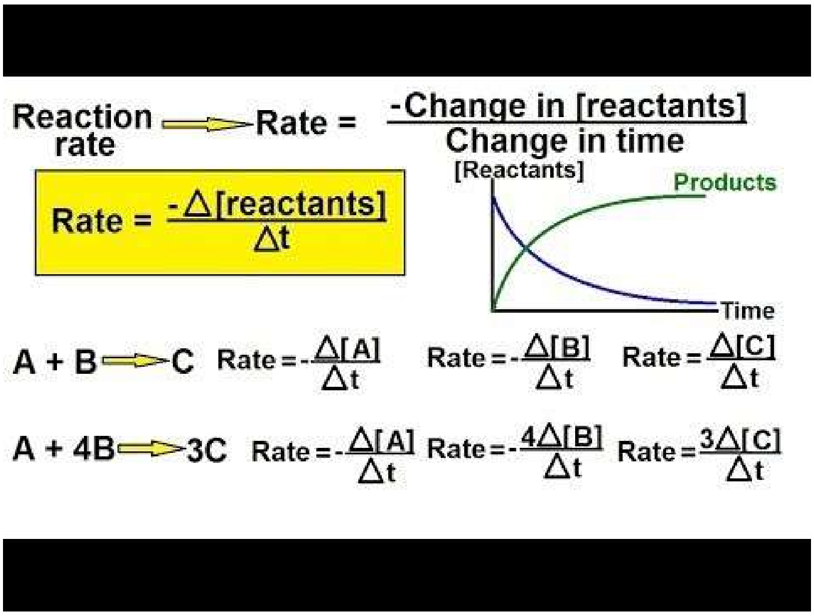
Name of the Department : Biochemistry

Concept of Rate

- The rate of reaction or reaction rate is the speed at which reactants are converted into products.
- In a chemical reaction, products are formed due to the collision between the reactant molecules.

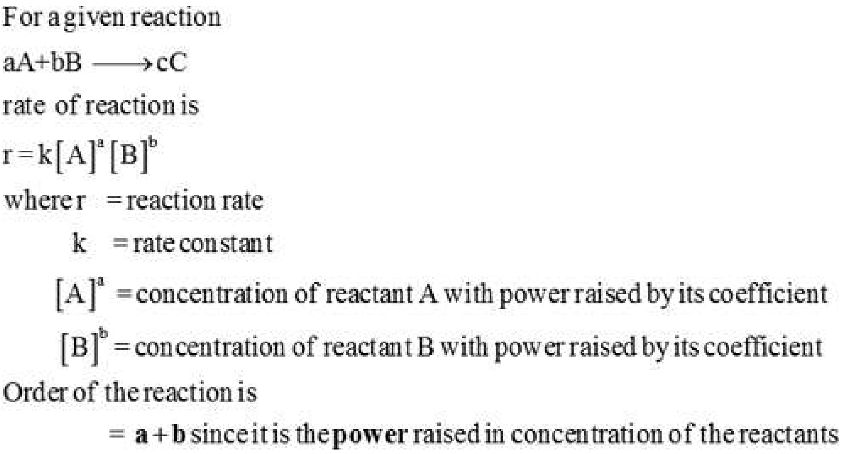


Reaction rate $\Rightarrow$ $\text{Rate} = \frac{-\text{Change in [reactants]}}{\text{Change in time}}$

$$\boxed{\text{Rate} = \frac{-\Delta[\text{reactants}]}{\Delta t}}$$

$A + B \Rightarrow C$ $\quad \text{Rate} = -\frac{\Delta[A]}{\Delta t} \quad \text{Rate} = -\frac{\Delta[B]}{\Delta t} \quad \text{Rate} = \frac{\Delta[C]}{\Delta t}$

$A + 4B \Rightarrow 3C$ $\quad \text{Rate} = -\frac{\Delta[A]}{\Delta t} \quad \text{Rate} = -\frac{4\Delta[B]}{\Delta t} \quad \text{Rate} = \frac{3\Delta[C]}{\Delta t}$



For a given reaction

$aA + bB \longrightarrow cC$

rate of reaction is

$r = k[A]^a[B]^b$

where r = reaction rate

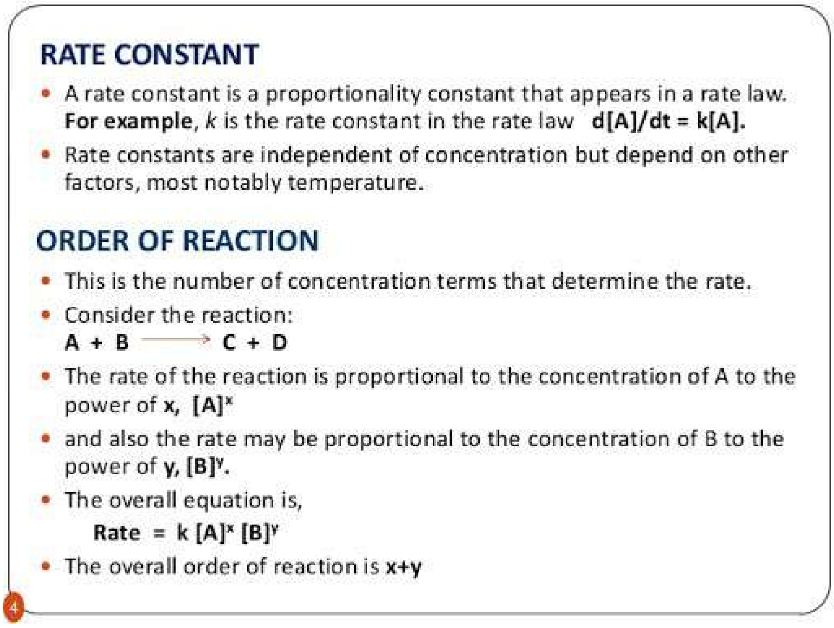
k = rate constant

$[A]^a$ = concentration of reactant A with power raised by its coefficient

$[B]^b$ = concentration of reactant B with power raised by its coefficient

Order of the reaction is

= **a + b** since it is the **power** raised in concentration of the reactants



RATE CONSTANT

- A rate constant is a proportionality constant that appears in a rate law. **For example**, *k* is the rate constant in the rate law **$d[A]/dt = k[A]$.**
- Rate constants are independent of concentration but depend on other factors, most notably temperature.

ORDER OF REACTION

- This is the number of concentration terms that determine the rate.
- Consider the reaction:
  $A + B \longrightarrow C + D$
- The rate of the reaction is proportional to the concentration of A to the power of **x**, **$[A]^x$**
- and also the rate may be proportional to the concentration of B to the power of **y**, **$[B]^y$.**
- The overall equation is,
  $\text{Rate} = k\,[A]^x\,[B]^y$
- The overall order of reaction is **x+y**

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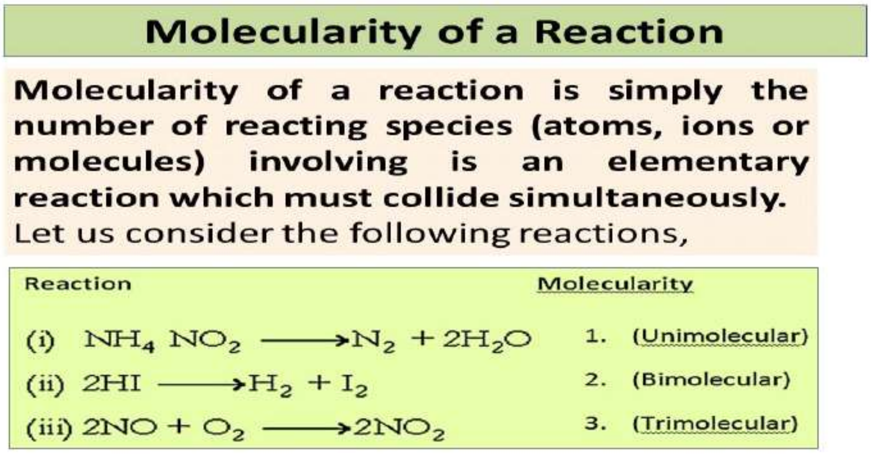
- **The rate constant, k**, is a proportionality constant that indicates the relationship between the molar concentration of reactants and the rate of a chemical reaction.
- The units of the rate constant depend on the order of reaction.
- The rate constant may be found experimentally, using the molar concentrations of the reactants and the order of reaction.
- It isn’t a true constant, since its value depends on temperature and other factors.



Molecularity of a Reaction

Molecularity of a reaction is simply the number of reacting species (atoms, ions or molecules) involving is an elementary reaction which must collide simultaneously.
Let us consider the following reactions,

Reaction	Molecularity
(i) $NH_4NO_2 \longrightarrow N_2 + 2H_2O$	1. (Unimolecular)
(ii) $2HI \longrightarrow H_2 + I_2$	2. (Bimolecular)
(iii) $2NO + O_2 \longrightarrow 2NO_2$	3. (Trimolecular)

The molecularity will be only whole number and never be zero or fraction.

Order of a Reaction

- The Order of Reaction refers to the power dependence of the rate on the concentration of each reactant.
- Thus, for a first-order reaction, the rate is dependent on the concentration of a single species.
- A second-order reaction refers to one whose rate is dependent on the square of the concentration of a single reactant (e.g., in a homo-dimerization reaction, $A + A \rightarrow A_2$) or the combined first-order dependence on the concentrations of two different reactants ($A + B \rightarrow C$).
- The order of reaction is an experimentally determined parameter and can take on a fractional value. This is distinct from the *molecularity* (or stoichiometry) of the reaction which is the theoretical integer value of the number of molecules involved in the reaction. For simple one-step reactions, the *order* and *molecularity* should have the same value.
- For example, **the rate of a first-order reaction is dependent solely on the concentration of one species in the reaction.**

Integrated form of rate expressions of first order reaction

Rate constant of a first order reaction:

- The rate of any reaction is determined by concentration of the reactant or substrate and by a rate constant, k. In the first order reaction, unit of k is time^{-1} or sec^{-1}.

For a unimolecular reaction i.e. for first order reaction, $A \rightarrow P$, the rate of a reaction i.e. the amount of substrate reacts per unit time and is expressed by a rate equation:

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

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

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

Integrating it, when t = 0, [A] = [A_0] (initial concentration) and when t = t, [A] = [A_t]

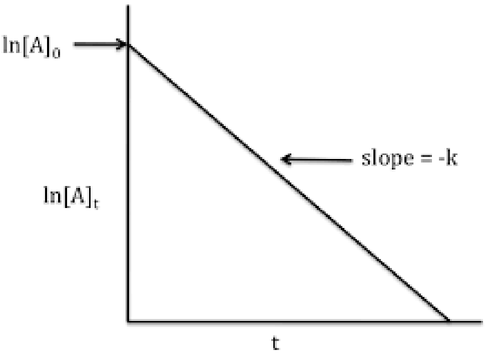
$$\int_{A_0}^{A_t} \frac{-d[A]}{[A]} = \int_0^t kdt$$

$$\int_{A_0}^{A_t} -d\ln[A] = kt$$

$$\ln[A_0] - \ln[A_t] = kt$$

$$\ln[A_t] = -kt + \ln[A_0]$$

This is a linear equation in terms of the variable ln [A_t] and *t*.



Plot of ln $[A]_t$ vs t gives a straight line whose slope is - k and intercept on the ln $[A]_t$ axis is ln $[A]_0$.

Half-life period and its significance

- Half-life (symbol $t_{1/2}$) is the time required for a quantity to reduce to half its initial value.
- The term is commonly used in nuclear physics to describe how quickly unstable atoms undergo, or how long stable atoms survive, radioactive decay.
- In a chemical reaction, the **half-life** of a species is **the time it takes for the concentration of that substance to fall to half of its initial value**.
- In a first-order reaction the half-life of the reactant is ln (2)/λ, where λ is the reaction rate constant.

In general, using the integrated form of the first order rate law we find that:

$A \rightarrow B$

$ln\,[A] = -kt + ln\,[A]_0$

From the definition of half-life of a reaction, at $t = t_{\frac{1}{2}}$; $[A] = \frac{[A]_0}{2}$

$$\Rightarrow ln\frac{[A]_0}{2} - ln\,[A]_0 = -\,kt_{\frac{1}{2}}$$

$$\Rightarrow ln\,\frac{\frac{[A]_0}{2}}{[A]_0} = -kt_{\frac{1}{2}}$$

$$\Rightarrow ln\,\frac{1}{2} = -kt_{\frac{1}{2}}$$

$$\Rightarrow t_{\frac{1}{2}} = \frac{ln\,2}{k}$$

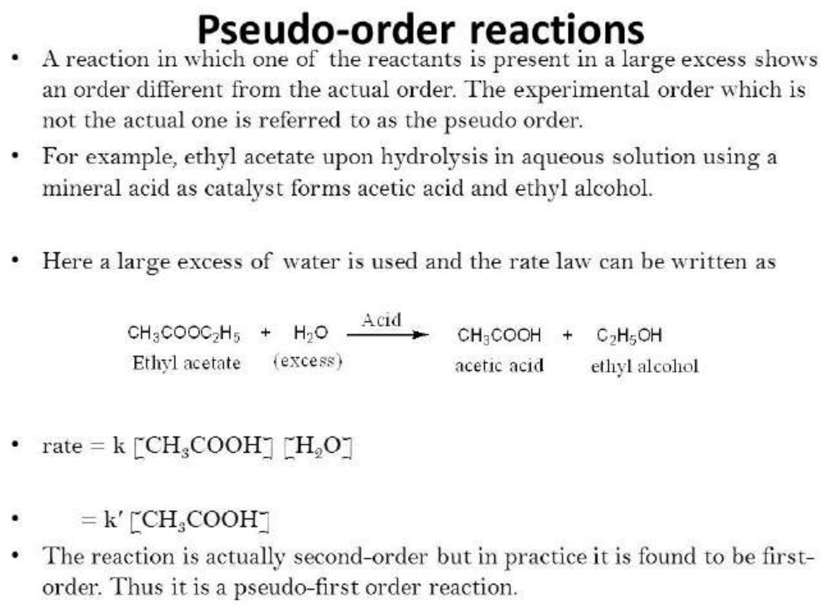
$$\Rightarrow t_{\frac{1}{2}} = 2.303\frac{log_{10}2}{k}$$

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

- **First order reaction**: For a first order reaction the half-life depends only on the rate constant:
  $$t_{1/2} = \frac{\ln 2}{k}$$
- **Second order reaction**: For a second order reaction (of the form: rate=k $[A]^2$) the half-life depends on the inverse of the initial concentration of reactant A:
  $$t_{1/2} = \frac{1}{k[A]_0}$$

Pseudo-unimolecular reaction

In a chemical reaction if two or more reactants are involved but the rate of reaction depends only upon the concentration of any one of the reactant and independent of other reactants then it is said to be pseudo unimolecular reaction.



Pseudo-order reactions

- A reaction in which one of the reactants is present in a large excess shows an order different from the actual order. The experimental order which is not the actual one is referred to as the pseudo order.
- For example, ethyl acetate upon hydrolysis in aqueous solution using a mineral acid as catalyst forms acetic acid and ethyl alcohol.
- Here a large excess of water is used and the rate law can be written as

$$\underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + \underset{\text{(excess)}}{H_2O} \xrightarrow{\text{Acid}} \underset{\text{acetic acid}}{CH_3COOH} + \underset{\text{ethyl alcohol}}{C_2H_5OH}$$

- rate = k $[CH_3COOH]$ $[H_2O]$
- = k′ $[CH_3COOH]$
- The reaction is actually second-order but in practice it is found to be first-order. Thus it is a pseudo-first order reaction.

- Thus order of reaction is one but molecularity of the reaction is two.

- **Acid Catalysed hydrolysis of sucrose**

  $C_{12}H_{22}O_{11} + H_2O + H^+$ ——————> $C_6H_{12}O_6 + C_6H_{12}O_6$

- The above reaction is bimolecular but is found to be of first order, as experimentally it is observed that the **rate of reaction α $[C_{12}H_{22}O_{11}]$ only**.
- The reason for such a behaviour is obvious from the fact that water is present in such a large excess that its concentration remains almost constant during the reaction.
- Such reactions which are not truly of the first order but under certain conditions become reactions of the first order are known as pseudo unimolecular reactions.

Multi step reactions

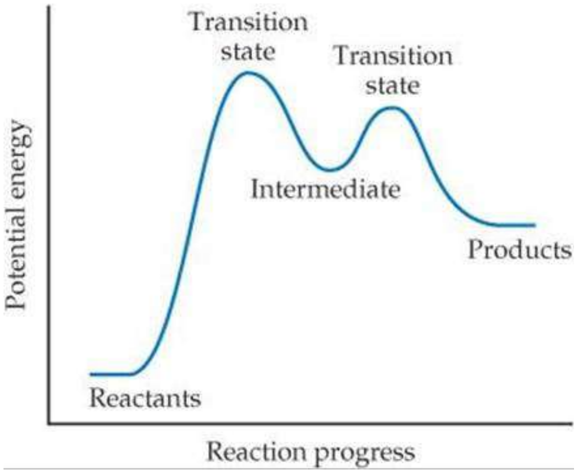
- A multi-step reaction is a combination of two or more elementary steps.
- An elementary step is a single, simple step involving one or two particles.
- The rate-determining step is the slowest step in a multi-step reaction, and the overall reaction rate will be exactly the same as the rate of the slowest step.

For Example:

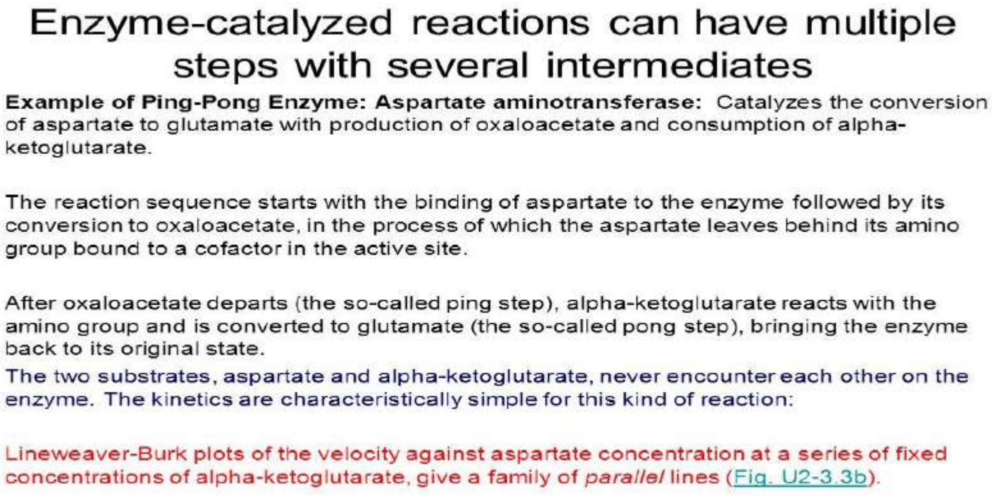
- Nitrogen dioxide and carbon monoxide react in a two-step process to form nitrogen monoxide and carbon dioxide.

- The two steps making up the **reaction mechanism**, which describes what occurs for each stage in the reaction, is shown below.

$$\begin{array}{lllll} \text{Step 1:} & NO_2(g) + NO_2(g) & \xrightarrow{k_1} & NO_3(g) + NO(g) & \text{(slow)} \\ \text{Step 2:} & NO_3(g) + CO(g) & \xrightarrow{k_2} & NO_2(g) + CO_2(g) & \text{(fast)} \\ \hline \text{Overall:} & NO_2(g) + CO(g) & \longrightarrow & NO(g) + CO_2(g) & \end{array}$$



For two step overall reaction, Reactants → Intermediate → Products, as the 1^{st} step is slower than the 2^{nd} step, then the reaction barrier of the 1^{st} step must be higher than that of the 2^{nd} step which is called rate determining step (RDS).



Enzyme-catalyzed reactions can have multiple steps with several intermediates

Example of Ping-Pong Enzyme: Aspartate aminotransferase: Catalyzes the conversion of aspartate to glutamate with production of oxaloacetate and consumption of alpha-ketoglutarate.

The reaction sequence starts with the binding of aspartate to the enzyme followed by its conversion to oxaloacetate, in the process of which the aspartate leaves behind its amino group bound to a cofactor in the active site.

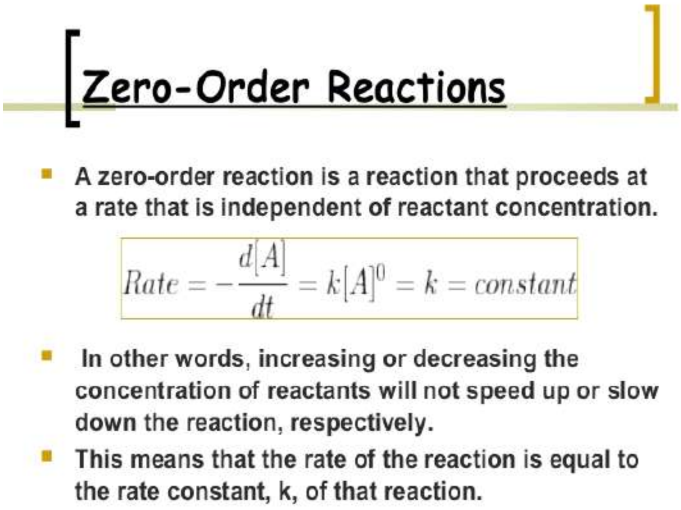
After oxaloacetate departs (the so-called ping step), alpha-ketoglutarate reacts with the amino group and is converted to glutamate (the so-called pong step), bringing the enzyme back to its original state.

The two substrates, aspartate and alpha-ketoglutarate, never encounter each other on the enzyme. The kinetics are characteristically simple for this kind of reaction:

Lineweaver-Burk plots of the velocity against aspartate concentration at a series of fixed concentrations of alpha-ketoglutarate, give a family of *parallel* lines (Fig. U2-3.3b).

Zero order

- The reaction rate is independent of the concentration of a reactant, so that changing its concentration has no effect on the speed of the reaction.
- Many enzyme-catalysed reactions are zero order, provided that the reactant concentration is much greater than the enzyme concentration which controls the rate, so that the enzyme is saturated.
- For example, the biological oxidation of ethanol to acetaldehyde by the enzyme liver alcohol dehydrogenase (LADH) is zero order in ethanol.
- Reactions with heterogeneous catalysis can be zero order if the catalytic surface is saturated. For example, the decomposition of phosphine (PH_3) on a hot tungsten surface at high pressure is zero order in phosphine which decomposes at a constant rate.

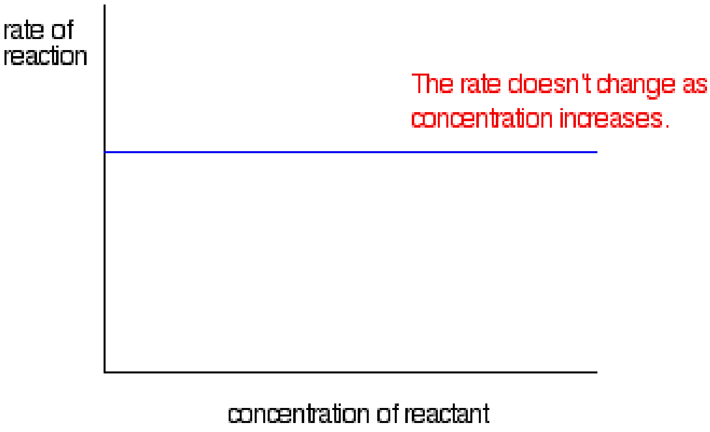


Zero-Order Reactions

- A zero-order reaction is a reaction that proceeds at a rate that is independent of reactant concentration.

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

- In other words, increasing or decreasing the concentration of reactants will not speed up or slow down the reaction, respectively.
- This means that the rate of the reaction is equal to the rate constant, k, of that reaction.



Reaction of fractional order

- The order is a non-integer, which often indicates a chemical chain reaction or other complex reaction mechanism.
- For example, the pyrolysis of acetaldehyde (CH_3CHO) into methane and carbon monoxide proceeds with an order of 1.5 with respect to acetaldehyde:

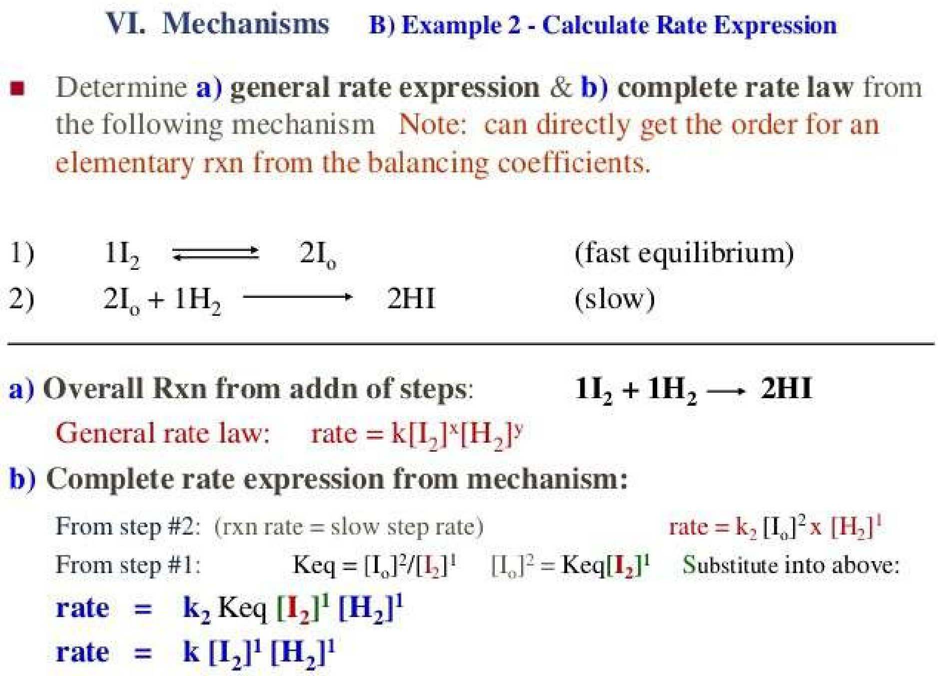
  $r = k[CH_3CHO]^{3/2}$
- $H_2 + Br_2 \rightarrow 2HBr$

  $Rate = k[H_2]\,[Br_2]^{1/2}$

  Order = 1+1/2 = 3/2

Complex reaction and rate expression

In kinetics, the term '**complex reaction**' simply refers to a **reaction** whose mechanism comprises more than one elementary step.



VI. Mechanisms **B) Example 2 - Calculate Rate Expression**

- Determine **a) general rate expression** & **b) complete rate law** from the following mechanism Note: can directly get the order for an elementary rxn from the balancing coefficients.

1) $1I_2 \rightleftharpoons 2I_o$ (fast equilibrium)

2) $2I_o + 1H_2 \longrightarrow 2HI$ (slow)

a) Overall Rxn from addn of steps: $\mathbf{1I_2 + 1H_2 \longrightarrow 2HI}$

General rate law: $rate = k[I_2]^x[H_2]^y$

b) Complete rate expression from mechanism:

From step #2: (rxn rate = slow step rate) $rate = k_2\,[I_o]^2 \times [H_2]^1$

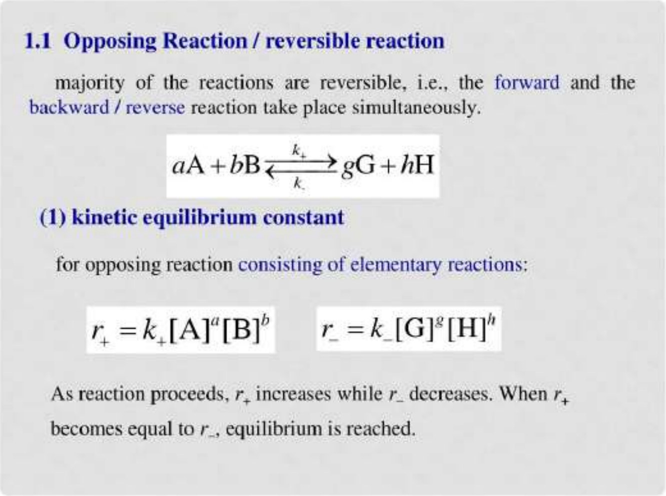
From step #1: $Keq = [I_o]^2/[I_2]^1$ $[I_o]^2 = Keq[I_2]^1$ Substitute into above:

$$\mathbf{rate} = k_2\,Keq\,[I_2]^1\,[H_2]^1$$

$$\mathbf{rate} = k\,[I_2]^1\,[H_2]^1$$

Opposing reaction

- The products formed react back simultaneously to form the reactants. These reactions are also called as reversible reactions.



1.1 Opposing Reaction / reversible reaction

majority of the reactions are reversible, i.e., the forward and the backward / reverse reaction take place simultaneously.

$$aA + bB \underset{k_-}{\overset{k_+}{\rightleftharpoons}} gG + hH$$

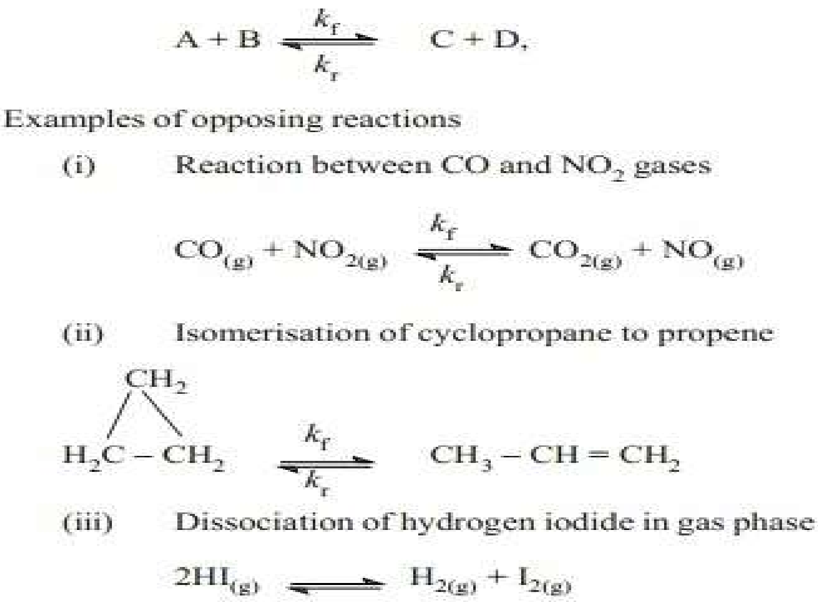
(1) kinetic equilibrium constant

for opposing reaction consisting of elementary reactions:

$$r_+ = k_+[A]^a[B]^b \qquad r_- = k_-[G]^g[H]^h$$

As reaction proceeds, r_+ increases while r_- decreases. When r_+ becomes equal to r_-, equilibrium is reached.

- **Examples**:



$$A + B \underset{k_r}{\overset{k_f}{\rightleftharpoons}} C + D,$$

Examples of opposing reactions

(i) Reaction between CO and NO_2 gases

$$CO_{(g)} + NO_{2(g)} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} CO_{2(g)} + NO_{(g)}$$

(ii) Isomerisation of cyclopropane to propene

$$\overset{CH_2}{H_2C - CH_2} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} CH_3 - CH = CH_2$$

(iii) Dissociation of hydrogen iodide in gas phase

$$2HI_{(g)} \rightleftharpoons H_{2(g)} + I_{2(g)}$$

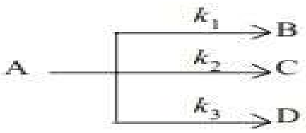
- Most of the enzymatic reactions in Metabolic system: for e.g. In glycolysis conversion of Glucose -6-phosphate to Fructose -6-phosphate by phosphoglucose isomerase.

Parallel reaction

- One or more reactants react simultaneously in two or more pathways to give two or more products. The parallel reactions are also called as side reactions.

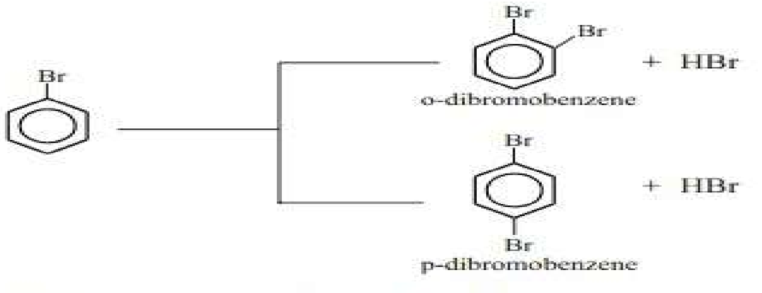
- The reactant A reacts to give products B,C,D separately by following three different reaction pathways involving different k_1, k_2, k_3 rate constants respectively.

- Among the many side reactions, the reaction in which maximum yield of the product obtained is called as the main or major reaction while the other reactions are called as side or parallel reaction.

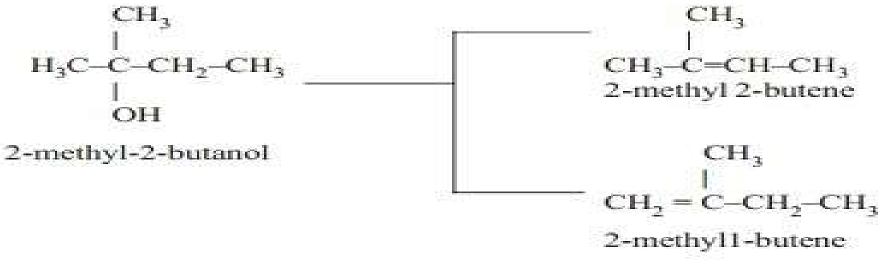


Examples of parallel reaction :

(i) Bromination of bromobenzene :



(ii) Dehydration of 2-methyl-2-butanol



$H_3C-C(CH_3)(OH)-CH_2-CH_3$ → $CH_3-C(CH_3)=CH-CH_3$; $CH_2=C(CH_3)-CH_2-CH_3$

- Some of the enzymatic reactions in metabolic system : for e.g. In pentose phosphate pathway, Ribulose -5-phosphate is converted to Ribose -5-phosphate by ribulose-5-phosphate isomerase or Xylulose-5-phosphate by ribulose-5-phosphate epimerase.

Consecutive reaction

- The reactions in which the reactant forms an intermediate and the intermediate forms the product in one or many subsequent reactions are called as **consecutive** or sequential reactions.
- In such reactions the product is not formed directly from the reactant.
- Various steps in the consecutive reaction are shown as below :

A --- --- > B --- --- > C

A = reactant ; B = intermediate ; C = product.

- Initially only the reactant A will be present. As the reaction starts, A produces an intermediate B through k_1 rate constant.
- When B is formed, it produces the product C through k_2 rate constant.
- After the completion of reaction only 'C' is present and concentrations of A and B will be zero.

- **Example**:

Saponification of a di-ester in presence of an alkali :

R'OOC- $(CH_2)_n$-COOR --- --- > R'OOC-$(CH_2)_n$-COOH -- -- --- > HOOC - $(CH_2)_n$ – COOH

Examples of First Order Consecutive Reactions

(*a*) Decomposition of dimethyl ether is gaseous phase

$$CH_3COCH_3 \xrightarrow{k_1} CH_4 + HCHO \xrightarrow{k_2} H_2 + CO$$

(*b*) Decomposition of Ethylene oxide

- Enzymatic reactions in many Metabolic pathways : such as Lipid metabolism (beta oxidation).

Reference :

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