



Chemical Kinetics

Lecture - 1

Rate of the reaction:

Reaction rate: $A \rightarrow B$

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

Unit of Rate: mole/litre.sec

Rate law:

Rate is directly proportional to $[A]^n$

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

where, proportionality constant 'k' is called the rate constant

Case I: For a Simple reaction

Case II: For a Complex reaction

Order of a reaction:

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

$$\text{Order} = m + n$$

Multistep reactions (Steady State Approximation)

When a reaction mechanism has several steps of comparable rates, the rate-determining step is often not obvious. However, there is an intermediate in some of the steps.

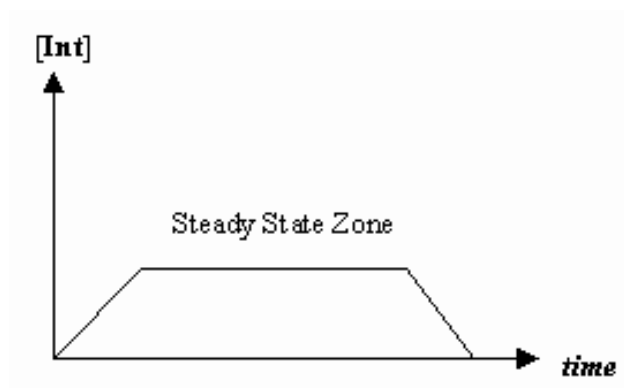
An intermediate is a species that is neither one of the reactants, nor one of the products.

The steady-state approximation is a method used to derive a rate law. The method is based on the assumption that one intermediate in the reaction mechanism is consumed as quickly as it is generated. Its concentration remains the same in duration of the reaction.



When a reaction involves one or more intermediates, the concentration of one of the intermediates remains constant at some stage of the reaction. Thus, the system has reached a **steady-state**.

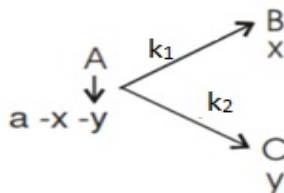
- The concentration of one of the intermediates, $[Int]$ varies with *time* as shown in the following figure.
- The steady-state approximation implies that you select an intermediate in the reaction mechanism, and calculate its concentration by assuming that it is consumed as quickly as it is generated as in Equation-1



$$d[Int]/dt=0 \text{-----(1)}$$

Lecture - 2

Parallel 1st order reaction



$$t=0 \quad [A]=a \quad [B]=[C]=0$$

Calculate effective $t_{\frac{1}{2}}$ for $[A]$ & $[B]$, $[C]$ & $[B] / [C]$



Solution:

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

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

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

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

$$\frac{\ln 2}{T_{eff}} = \frac{\ln 2}{T_1} + \frac{\ln 2}{T_2} \quad (\text{Where } T \text{ presents half-life})$$

$$\boxed{\frac{1}{T_{eff}} = \frac{1}{T_1} + \frac{1}{T_2}} \quad (\text{Remember})$$

$$\text{Now, } [A]_1 = a e^{-k_{eff}t} = a e^{-(k_1+k_2)t}$$

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

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

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

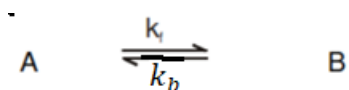
Similarly

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

$$\boxed{\frac{[B]}{[C]} = \frac{k_1}{k_2}} \quad k_{eff} = k_1 + k_2$$

Lecture - 3

Reversible 1st order reaction (Both forward and backward)



$$t = 0 \quad \quad \quad a \quad \quad \quad 0$$

$$t = t \quad \quad \quad a - x \quad \quad \quad x$$

$$t = t_{eq} \quad \quad \quad a - x_{eq} \quad \quad \quad x_{eq}$$



x_{eq} = eq conc. Of product

$$\frac{d[A]}{dt} - \frac{d[B]}{dt} = 0 \text{ At eq. } (\because \text{At equilibrium conc. is not changed})$$

$$\frac{d[A]}{dt} = -k_f[A] + k_b[B]$$

$$\frac{d[B]}{dt} = -k_b[B] + k_f[A]$$

$$\frac{d(a-x)}{dt} = -k_f(a-x) + k_b x$$

$$-\frac{dx}{dt} - k_f a + (k_f + k_b)x$$

$$\int_0^x \frac{dx}{k_f a - (k_f + k_b)x} = \int_0^t dt$$

$$\frac{\ln[k_f a - (k_f + k_b)x]_0^x}{k_f + k_b} = t$$

$$\Rightarrow \frac{1}{k_f + k_b} \left(-\ln \left(\frac{k_f a - (k_f + k_b)x}{k_f a} \right) \right) = t$$

$$\Rightarrow \frac{1}{k_f + k_b} \ln \left(\frac{k_f a}{k_f a - (k_f + k_b)x} \right) = t$$

$$x = \frac{k_f a}{k_f + k_b} (1 - e^{-(k_f + k_b)t}) \quad (\text{remember})$$

$$k_{eq.} = \frac{k_f}{k_b} = \frac{[B]_{eq.}}{[A]_{eq.}} = \frac{X_{eq.}}{(a - X_{eq.})}$$

$$\frac{k_f + k_b}{k_f} = \frac{a}{X_{eq.}}$$

$$X = X_{eq.}(1 - e^{-(K_f + K_b)t}) \quad t \rightarrow \infty, X \rightarrow X_{eq.}$$

$$k_f + k_b = \frac{1}{t} \ln \left(\frac{X_{eq.}}{X_{eq.} - X} \right) \quad (\text{remember})$$

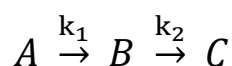
Where $X_{eq} = a \times \left[\frac{k_f}{k_f + k_b} \right]$

$$X_{eq} = \frac{k_f \times a}{k_f + k_b}$$



Consecutive or Sequential Reactions

This reaction is defined as that reaction which proceeds from reactants to final products through one or more intermediate stages. The overall reaction is a result of several successive or consecutive steps.



Example of Sequential Reactions:

(a) Decomposition of ethylene oxide.

(b) The pyrolysis of acetone

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

Lecture - 4

Collision Theory: model that emphasizes the energy and orientation of molecular collisions to explain and predict reaction kinetics

Collision theory is based on the following postulates:

1. The rate of a reaction is proportional to the rate of reactant collisions:
 2. The reacting species must collide in an orientation that allows contact between the atoms that will become bonded together in the product.
 3. The collision must occur with adequate energy to form new bonds (and new chemical species).
- Every reaction requires a certain amount of activation energy for it to proceed in the forward direction, yielding an appropriate activated complex along the way.
 - In the study of reaction mechanisms, each of these three arrangements of atoms is called a proposed **activated complex** or **transition state**.



Arrhenius equation

The Arrhenius equation is $k = Ae^{(-E_a/RT)}$, where A is the frequency or pre-exponential factor and $e^{(-E_a/RT)}$ is the fraction of collisions that have enough energy to react (i.e., have energy greater than or equal to the activation energy E_a) at temperature T. This equation can be used to understand how the rate of a reaction depends on temperature.

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

Forms of the Arrhenius equation

How to write different forms of the Arrhenius equation.

Using the Arrhenius equation to look at how changing temperature and activation energy affects collisions.

Using the Arrhenius equation

How to use the Arrhenius equation to calculate the activation energy.

Evaluation of Activation energy:

(i) Graphical Method: $E_a = \text{slope} \times 2.303 R$

(ii) Analytical Method:

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left[\frac{T_2 - T_1}{T_2 T_1} \right]$$

Lecture - 5

Activation Energy

Activation energy is the energy that must be overcome in order for a reaction to occur. It is the minimum energy that is required to start a chemical reaction

- **Arrhenius equation** to relate the activation energy and the rate constant, k , of a given reaction:

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

$$\frac{\ln k_1}{\ln k_2} = \frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

Theory of unimolecular reactions (Lindemann's time lag theory)

Mathematical treatment

$$\text{Rate} = k_1[A]^2 / k_2[A] + k_3$$

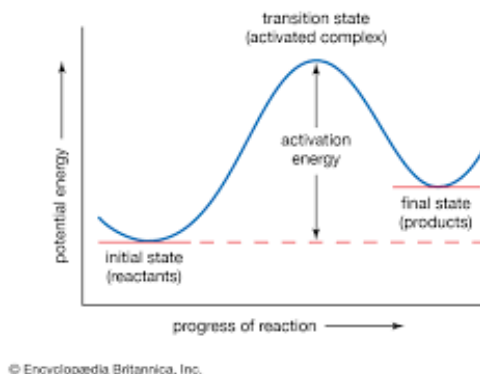
Case I: $k_2[A] \gg k_3$

Case II: $k_3 \gg k_2[A]$

Lecture - 6

Absolute reaction rate theory (ART)

- Transition state theory (TST), which is also known as theory of absolute reaction rates (ART) and the theory of activated state (complex), is essentially a refined version of crude collision theory, which explains the rate of chemical reaction assuming a special type of chemical equilibrium (quasi-equilibrium) between the reactants and activated state (transition state complex).



- This special molecule decomposes to form the products of reaction.
- The rate of this reaction is then equal to the rate of decomposition of activated complex.

$$v = k_B T / h$$

k_B is the Boltzmann's constant (1.381×10^{-23} J/K),

- T is the absolute temperature in Kelvin (K) and
- h is Planck's constant (6.626×10^{-34} Js).
- v is the frequency of vibration

$$k = k_B T / h K^\ddagger$$

- k is the rate constant and
- K^\ddagger is the thermodynamic equilibrium constant.



Thermodynamics of Transition state theory

$$\ln k/T = -\Delta H^\ddagger/R \cdot 1/T + \ln k_B/h + \Delta S^\ddagger/R$$

$$E_a = \Delta H^\ddagger + RT$$

Lecture - 7

Catalyst

- **Catalyst** is a substance which can change (enhance) the speed of a chemical reaction without itself undergoing any change in its mass and chemical composition. And the phenomena is called **Catalysis**
- **Positive Catalysts:** Catalysts which increase the rate of a chemical reaction are positive catalysts. It increases the rate of reaction by lowering the activation energy barriers such that a large number of reaction molecules are converted into products, thereby the percentage of yield of products increases.

Example: In the preparation of NH_3 by **Haber's process** Iron oxide acts as a positive catalyst and increases the yield of ammonia in spite of less reaction of Nitrogen.

- **Negative Catalysts:** Catalysts which decrease the rate of reaction and negative catalyst. It decreases the rate of reaction by increasing the activation energy barrier which decreases the number of reactant molecules to transform into products and hence the rate of reaction decreases.

Example: Decomposition of Hydrogen peroxide into water and oxygen is retarded by using Acetanilide, this acts as a negative catalyst to decrease the rate of decomposition of hydrogen peroxide.

- **Promoter or Accelerators:** A substance which increases the catalyst activity are known as Promoters or accelerators.

Example: In Haber's process molybdenum or a mixture of potassium and Aluminium oxides act as Promoters.

- **Catalyst Poisons or Inhibitors:** Substances which decrease the catalyst activity are known as catalyst poisons or inhibitors.

Example: In the hydrogenation of alkyne to an alkene, catalyst palladium is poisoned with barium sulphate in quinoline solution and the reaction is stopped at alkene level. The catalyst is known as Lindler's catalyst.

What are the Types of Catalysis?

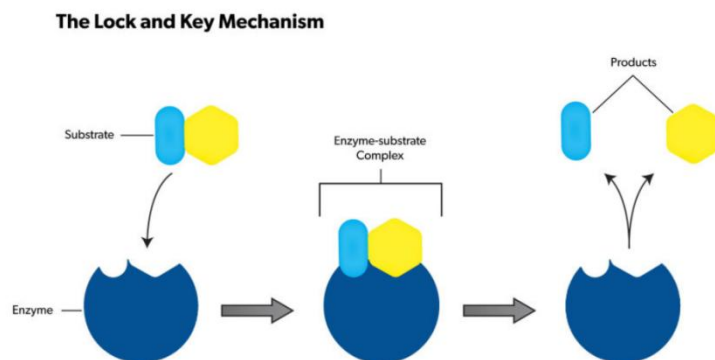
On the basis of nature and the physical state of substance employed in the chemical reaction, catalysis is of three types;

- Homogeneous catalysis
- Heterogeneous catalysis
- Autocatalysis

Lecture - 8

Kinetics of enzyme catalysis: Michaeli's Menten mechanism

Enzyme Catalysis



Enzymes are highly complex protein molecules produced by living organisms or, cells which catalyzes physiological reactions.

Examples of common Enzymes:

Amylase: degrades starches and sugars present in potatoes, fruits, vegetables.

Lactase: degrades lactose present in milk.

Protease: cleaves proteins to peptides.

Lipase: degrades fats in diary products, nuts, oils and meat.

Kinetics of enzyme action (Michaelis and Menten mechanism)

$$r = k_2[ES] \text{-----(1)}$$

$$[ES] = \frac{[E][S]}{k_M} \text{-----(2)}$$

$$r = \frac{k_2[E][S]}{k_M} \text{-----(3)}$$

$$[E] = [E_0] - [ES] \text{-----(4)}$$

$$r = \frac{k_2[E_0][S]}{k_M + [S]} \text{-----(5)}$$

Evaluation of Michaelis constant

$$k_M = \text{Slope/Intercept}$$

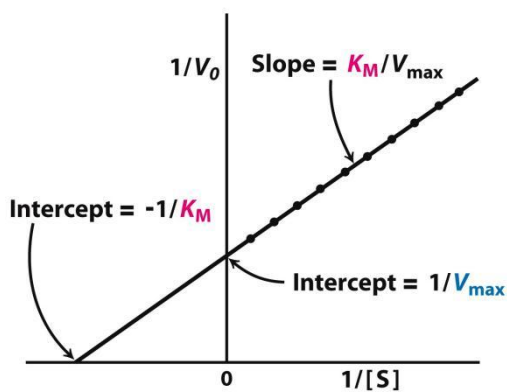


Figure 8.12
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