

CY1001: Chemistry: Structure, Bonding & Reactivity

PHYSICAL CHEMISTRY PART+

THERMODYNAMICS

- Basics:
- System + Surroundings = Universe
- A thermodynamic system is described in terms of macroscopic variables like (N, V, E) or (N, p, E) or (N, V, T) etc. • These macroscopic variables are called natural variables of a thermodynamic system. The latter is broadly classified as isolated, closed or open.
- The natural variables are independent of each other.
- Isolated System: Energy and Matter can't exchange with surroundings (Variables: $[N, V, E]/[N, P, E]$)
- Closed System: Only Energy exchanges with surroundings $[(N, V, T) \text{ or } (N, P, T)]$
- Open System: Both Energy and Matter can be exchanged with the surroundings. $[(\mu, V, T) (\mu, P, T)]$
- There are two functions in Thermodynamics:
 1. State Function(Path Independent): These functions only depend on Initial and Final conditions, it never depends on the path followed by it.
 2. Path function: It depends on the path followed.

Note : Only Heat and Work are path functions, remaining all are (Enthalpy, Entropy, Internal Energy etc) are State functions.

- **WORK**

- Convention: Work done on the system(Compression) is Positive, Work done by the system(Expansion) is Negative.
- General expression for work: $dw = -(P_{ext})dV$ [P_{ext} is External Pressure; dV is change in volume]
- There are two types of works: 1. Irreversible Work ; 2.Reversible Work
- 1.Irreversible Work: External pressure is applied fast such that $P_{ext} \neq P$; where P_{ext} is the pressure applied, P is pressure of the system.

$$P_{ext} \neq P ; \quad dw = -P_{ext}(dv) ; \quad \omega = -P_{ext}(\Delta v)$$

- 2.Reversible Work: External pressure is applied extremely slowly such that $P_{ext} = P$.

$$dw = -P_{ext}(dv); \quad w = -\int_{V_i}^{V_f} p_{ext}(dV); \quad P_{ext} = P ; \quad \omega = -\int_{V_i}^{V_f} \frac{RT}{V} dV ; \quad \omega_{Re V} = -nRT \ln \left(\frac{V_2}{V_1} \right);$$

(For Isothermal Process at a constant Temp T)

- Note: The magnitude of work of expansion in an irreversible process is less than the reversible one.

- **HEAT** : Convention: If heat enters the system 'q' is positive, if heat leaves the system then q is negative.

- At constant pressure $q = \int_{path} Cp dT$

- At constant Volume $q = \oint C_v dT$

- Note: $\oint dw \neq 0$; $\oint dq \neq 0$ for a cyclic process.

THERMODYNAMICS

- The sum of (infinitesimal change) in heat and work as internal energy change dU (State Function)

- $\oint dU = 0; \quad dU = dq + dw$

- At constant pressure: $dU = C_p dT - P_{ext} dv \quad (1)$

- For fixed number of moles $U(T, V) = \left(\frac{\partial U}{\partial T}\right)_v dT + \left(\frac{\partial U}{\partial v}\right)_T dV \quad (2)$

- From 1 and 2 $\left(\frac{\partial U}{\partial T}\right)_v = C_p = C_v; \quad \left(\frac{\partial U}{\partial v}\right)_T = -P_{ext}$

- By rearranging the equation 1: At constant pressure

- $dH = C_p dT; \quad dH = dU + P dv; \quad H = U + PV;$

- Here new state function defined called Enthalpy (H). $dH = dU + p dv + v dp; \quad dU = q - p dv$

- $dH = q + v dp \quad (3)$

- $H(T, P) \Rightarrow dH = \left(\frac{\partial H}{\partial T}\right)_p dT + \left(\frac{\partial H}{\partial P}\right)_T dP; \quad \left(\frac{\partial H}{\partial T}\right)_p = C_p; \quad \left(\frac{\partial H}{\partial P}\right)_T = v$ (On comparison with 3)

- The change in the enthalpy of a system is equal to the amount of heat exchanged at constant pressure.
- The enthalpy of an ideal gas depends only on temperature $H(T)$ This implies that for an Isothermal process $dH = 0$ for an ideal gas.

THERMODYNAMICS

- **Entropy:**

- $\oint \frac{dq_{rev}}{T} = 0$ (Proved by solving Carnot cycle)

- This defines another state function Entropy(Degree of Randomness)

- $ds = \frac{dq_{rev}}{T} ; \quad \Delta s = \int_1^2 \frac{dq_{rev}}{T} ; \quad = s_2 - s_1$

- Entropy is a state function, but to calculate change in entropy requires a reversible path. Whether it is reversible or irreversible, find a reversible path and calculate Entropy, because entropy is state function.

- For isolated systems:

- $\Delta S_{Total} = \Delta S_{system} + \Delta S_{surroundings}$

- $\Delta S_{Total} > 0$ (*Irreversible*)

- $\Delta S_{Total} = 0$ (*Reversible*)

- $\Delta S_{Total} < 0$ (Impossible, Not spontaneous)

Thermodynamics

- Entropy of Mixing of an Ideal Gas at Constant T

- $$\Delta S_{mi} = -\Delta S_{demix}$$

- Suppose two gases A, B mixed with mole fractions x_A, x_B

- $$\Delta S_{mix} = -nR(x_A \ln(x_A) + x_B \ln(x_B))$$

- Note: Since $x_A, x_B < 1$ $\Delta S_{mix} > 0$; So mixing is spontaneous.

- **Entropy Changes Associated with State Changes**

- **Boiling:** As temperature is constant, $\Delta S = \Delta H_{vap}/T$

- **Melting:** As temperature is constant, $\Delta S = \Delta H_{fus}/T$

- Example: Calculate the entropy during one mole of Ice at -10°C converted to Water at 0°C .

- Solution: $\Delta S_{syst} = (\Delta S_{syste})_{Ice \text{ at } -10^\circ\text{C to } 0^\circ\text{C}} + (\Delta S_{system})_{Ice \text{ at } 0^\circ\text{C to water at } 0^\circ\text{C}}$

- $(\Delta S_{syste})_{Ice \text{ at } -10^\circ\text{C to } 0^\circ\text{C}} = \int_{T_1}^{T_2} \frac{C_P dT}{T} = C_P \ln\left(\frac{T_2}{T_1}\right)$ where $T_2 = 273 \text{ K}$; $T_1 = 263 \text{ K}$

- $(\Delta S_{syst})_{Ice \text{ at } 0^\circ\text{C to water at } 0^\circ\text{C}} = \frac{\Delta_f H}{T}$ where $T = 273 \text{ K}$.

Fundamental equations in thermodynamics

- Helmholtz free Energy: $A = U - TS$
- Gibbs free energy : $G = H - TS$
- Fundamental Equations:
 - $dU(S, V) = T ds - P dv$
 - $dH(S, P) = T dS + v dp$
 - $dA(T, V) = -S dT - p dv$
 - $dG(T, P) = -T ds + v dp$
- Valid for reversible and irreversible processes since they only depends on state variables.
- **Maxwell Relations**
 - Provide relationships between different partial derivatives. Certain thermodynamic quantities, like internal energy, entropy, Helmholtz and Gibbs free energies etc. are hard to measure experimentally.
 - Using Maxwell relations, one can express the above quantities (U, S, A, G...) in terms of experimentally measurable quantities.

Maxwell relations in thermodynamics

Maxwell Relations

$$\begin{aligned} A(T, V) &\Rightarrow dA = \left(\frac{\partial A}{\partial T}\right)_V dT + \left(\frac{\partial A}{\partial V}\right)_T dV \\ G(T, p) &\Rightarrow dG = \left(\frac{\partial G}{\partial T}\right)_p dT + \left(\frac{\partial G}{\partial p}\right)_T dp \end{aligned}$$

A and G are
state functions

$$\begin{aligned} \left(\frac{\partial A}{\partial T}\right)_V &= -S & \left(\frac{\partial A}{\partial V}\right)_T &= -p \\ \left(\frac{\partial G}{\partial T}\right)_p &= -S & \left(\frac{\partial G}{\partial p}\right)_T &= V \end{aligned}$$

$$\begin{aligned} A(T, V) &\Rightarrow dA = -SdT - pdV \\ G(T, p) &\Rightarrow dG = -SdT + Vdp \end{aligned}$$

Fundamental Equations

$$\frac{\partial^2 A}{\partial V \partial T} = \frac{\partial^2 A}{\partial T \partial V} \quad \text{and} \quad \frac{\partial^2 G}{\partial p \partial T} = \frac{\partial^2 G}{\partial T \partial p}$$

Since A, G are exact differentials

Maxwell Relations:

$$\Rightarrow \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V \quad \left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p$$

These can be obtained from equation of state.

Maxwell relations in thermodynamics

Maxwell Relations

$$dU = TdS - pdV \quad \text{Fundamental Equation}$$

$$U(S, V) \Rightarrow dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV \quad \text{U is a state function}$$

$$\left(\frac{\partial U}{\partial S}\right)_V = T \qquad \left(\frac{\partial U}{\partial V}\right)_S = -p$$

$$\frac{\partial^2 U}{\partial V \partial S} = \left(\frac{\partial T}{\partial V}\right)_S$$

$$\frac{\partial^2 U}{\partial S \partial V} = -\left(\frac{\partial p}{\partial S}\right)_V$$

$$\frac{\partial^2 U}{\partial V \partial S} = \frac{\partial^2 U}{\partial S \partial V}$$

U is an exact differential

Maxwell Relations:

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$$

The Four most common Maxwell Relations

$$dU = TdS - pdV$$

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

$$dH = TdS + Vdp$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$

$$dA = -SdT - pdV$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

$$dG = -SdT + Vdp$$

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

Using Maxwell Relations

basic equations	Maxwell relations	working equations
$dU = TdS - PdV$	$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$	$dU = C_V dT + \left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right] dV$
$dH = TdS + VdP$	$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$	$dH = C_P dT - \left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right] dP$
$dA = -PdV - SdT$	$\left(\frac{\partial S}{\partial V}\right)_T = +\left(\frac{\partial P}{\partial T}\right)_V$	$dS = \frac{C_V}{T} dT + \left(\frac{\partial P}{\partial T}\right)_V dV$
$dG = VdP - SdT$	$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$	$dS = \frac{C_P}{T} dT - \left(\frac{\partial V}{\partial T}\right)_P dP$

Gibbs free energy

- $$G(T, P) = H(S, P) - TS \quad \Rightarrow \quad dG = V dp - S dT \quad (1)$$

- $$dG = \left(\frac{\partial G}{\partial T}\right)_P dT + \left(\frac{\partial G}{\partial p}\right)_T dP \quad (\text{On comparison with (1)})$$

- $$\left(\frac{\partial G}{\partial T}\right)_P = -S \quad \Rightarrow \quad G(T, P) = G(T_0, P) - \int_1^2 S dT$$

- $$\left(\frac{\partial G}{\partial p}\right)_T = V \quad \Rightarrow \quad G(T, P) = G(T, P_0) + \int_1^2 v dp$$

- For Ideal gases:
$$G(T, P) = G(T, P_0) + RT \ln \left(\frac{P}{p_0}\right)$$

- Also
$$\left(\frac{\partial G}{\partial T}\right)_P = -S = \frac{G-H}{T} \quad \Rightarrow \quad \frac{\partial \left(\frac{G}{T}\right)}{\partial T} = -\frac{H}{T^2} \quad (\text{or}) \quad \frac{\partial \left(\frac{\Delta_r G}{T}\right)}{\partial T} = -\frac{\Delta_r H}{T^2}$$

Where $\Delta_r G$ is Gibbs energy change of a reaction.

CHEMICAL POTENTIAL

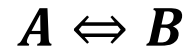
- Consider a system that is allowed to exchange particles. When material equilibrium is reached, the chemical potential of the system and the surroundings is the same.
- Chemical Potential is the intensive variable that is equal in two systems that are in material equilibrium.
- Material equilibrium only possible if matter can be exchanged. Material equilibrium also possible in chemical reactions

$$\mu = \left(\frac{\partial G}{\partial n} \right)_{T,p} \quad \text{kJ/mol OR kcal/mol}$$

- Chemical potential tells about the tendency of the system to give particles
- Lower chemical potential means more stable.
- Chemical potential for a single component homogeneous system is nothing but the molar Gibbs Free Energy.
- For a single component system $dG = v dp - s dT + \mu dn$
- For a multi component system $dG = v dp - s dT + \sum_i \mu_i dn_i$
- Other fundamental equations also changes like: $du = -P dv + T dS + \sum_i \mu_i dn_i$

RELATION BETWEEN EQUILLIBRIUM CONSTANT AND GIBBS FREE ENERGY OF THE REACTION

- Consider the mixture containing two components A and B which react at constant T, p



- $\Delta_r G = G_B - G_A = \mu_B - \mu_A$

- $\Delta_r G > 0$ Backward reaction spontaneous

- $\Delta_r G < 0$ Forward reaction spontaneous

- $\Delta_r G = 0$ Equilibrium

- For Ideal gases $G(T, P) = G(T, P_0) + RT \ln \left(\frac{P}{P_0} \right)$ similarly

$$\mu_A(T, P) = \mu_A(T, P_0) + RT \ln \left(\frac{p_A}{p_0} \right) \quad (1); \quad \mu_B(T, P) = \mu_B(T, P_0) + RT \ln \left(\frac{p_B}{p_0} \right) \quad (2);$$

$$(2)-(1) \quad \Delta_r G = \Delta_r G^0 + RT \ln Q$$

At Equilibrium $\Delta_r G^0 = -RT \ln k_p$ (At Equilibrium $Q = k_p$ (Equilibrium constant))

Phase Diagrams, Coexistence Curves

- **Gibbs Phase Rule**

- Given a mixture consisting of several species in different phases at equilibrium
- P = Total number of phases in the system
- C = total number of components = total number of chemically independent species
- F = variance or degrees of freedom i.e. number of intensive variables that can be changed independently without disturbing the phase equilibrium. According to the Gibbs Phase Rule:

$$F = C - P + 2$$

- **Gas-Liquid and Gas-Solid Coexistence**

- For a given temperature, the gas and liquid coexist only at a certain pressure. This pressure is called vapor pressure and depends on temperature.
- Similarly, solids also have a vapor pressure. The function along the coexistence curve gives how the vapor pressure changes as a function of temperature

Clapeyron Equation and Clausius-Clapeyron Equation

- **Clapeyron Equation:** To find slope of the P-T Curve, for solid –liquid co-existence curve. It also useful to find the vapor pressure of solids at given temperature, by integrating the equation.

$$\frac{dp}{dT} = \frac{\Delta_f H_m}{T \Delta_f v_m} \quad \Delta_f H_m = \text{Molar Enthalpy of Fusion}$$

$$\Delta_f v_m = \text{Change in molar volume} = (v_{\text{liquid}})_m - (v_{\text{solid}})_m$$

- **Clausius-Clapeyron Equation:** It is useful to
- For liquid vapor coexistence, the molar volume of liquid can be taken as much smaller than that of gas. Further the gas can be approximated as an ideal gas.

$$\frac{dP}{dT} = \frac{\Delta_f H_m}{T \Delta_g v} = \frac{P \Delta_f H_m}{RT^2} \quad (\text{or})$$

$$\frac{d \ln P}{dT} = \frac{\Delta_f H_m}{RT^2}$$

Chemical kinetics

• Reaction Mechanisms

1. Opposing Reactions: $A \xrightleftharpoons[k_2]{k_1} B$

Reaction Mechanism: $-\frac{d[A]}{dt} = \frac{d[B]}{dt} = k_1[A] - k_2[B] \quad (1)$

$$\frac{d[B]}{dt} = \frac{dx}{dt} = k_1(A_0 - x) - k_2(B_0 + x) \quad [\text{Where } x \text{ is change in concentration in B or amount of A dissociated}]$$

At Equilibrium $A_e = A_0 - x_e$; $B_e = B_0 + x_e$ substitute in (1)

$$\frac{dx}{dt} = k_1(A_e + x_e - x) - k_2(B_e - x_e + x)$$

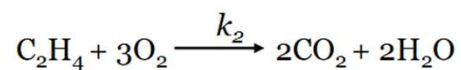
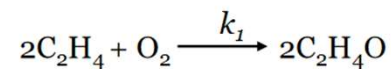
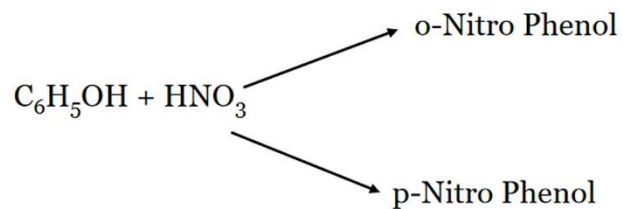
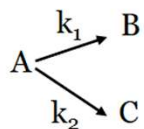
Equilibrium constant $k = \frac{k_1}{k_{-1}} = \frac{[B_e]}{[A_e]}$, by putting all these conditions and integrating from 0 to x we get final solution as

$$x = x_e(1 - \exp(-(k_1 + k_2)t))$$

Now $A(t) = A_e + x_e(\exp(-(k_1 + k_2)t))$ and $B(t) = B_e - x_e(\exp(-(k_1 + k_2)t))$

Parallel reactions

Parallel Reactions



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

$$[A(t)] = [A(o)] \exp\{-(k_1+k_2)t\} ;$$

$$\frac{dB}{dt} = k_1[A]$$

$$\frac{dB}{dt} = k_1[A(o)] \exp\{-(k_1+k_2)t\}$$

$$\int_0^t dB = k_1[A(o)] \int_0^t \exp\{-(k_1+k_2)t\} dt$$

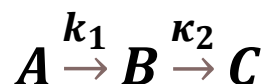
$$[B(t)] = \frac{k_1}{k_1+k_2} [A(o)][1-\exp\{-(k_1+k_2)t\}]$$

$$\frac{dC}{dt} = k_2[A]$$

$$[C(t)] = \frac{k_2}{k_1+k_2} [A(o)][1-\exp\{-(k_1+k_2)t\}]$$

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

Consecutive Reactions



Product of one reaction becomes reactant for the next reaction under same conditions.

$$\frac{d[A]}{dt} = -k_1[A] \quad \text{Integrating, we get} \quad A(t) = A_0 e^{-k_1 t}$$

$$\frac{d[B]}{dt} = k_1[A] - k_2[B] = k_1[A_0]e^{-k_1 t} - k_2[B] ; \quad \text{Integrating we get}$$

$$B(t) = \frac{k_1}{k_2 - k_1} [A_0] (e^{-k_1 t} - e^{-k_2 t})$$

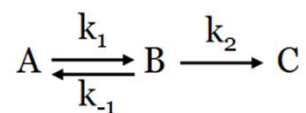
$$\frac{d[C]}{dt} = k_2[B] \quad \text{putting } B(t) \text{ in this equation and integrating, we get}$$

$$[C_t] = [A_0] - ([A_t] + [B_t])$$

$$[C_t] = [A_0] - \left[1 - \frac{k_1}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t}) - e^{-k_1 t} \right]$$

Steady state approximation

- After initial induction period, the change of concentration of any intermediate species is equivalent to zero, provided the concentration of intermediate is always smaller compared to the starting concentrations ($k_2 \gg k_1$).
- This is called steady-state approximation (or quasi-steady state approximation).



$$\frac{dA}{dt} = -k_1[A] + k_{-1}[B]$$

$$\frac{dB}{dt} = k_1[A] - k_{-1}[B] - k_2[B];$$

$$\frac{dC}{dt} = k_2[B]$$

According to steady-state approximation

$$\frac{dB}{dt} = 0$$

$$k_1[A] - k_{-1}[B] - k_2[B] = 0$$

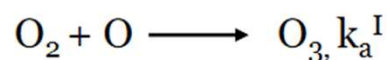
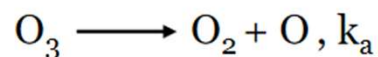
$$k_1[A] = (k_{-1} + k_2)[B]$$

$$\therefore [B] = \frac{k_1[A]}{k_{-1} + k_2}$$

Steady state Approximation

Derive the rate law for the decomposition of Ozone

$2 \text{O}_3 \longrightarrow 3 \text{O}_2$ on the basis of the following mechanism



$$\frac{d[\text{O}_3]}{dt} = -k_a [\text{O}_3] + k_a' [\text{O}_2] [\text{O}] - k_b [\text{O}] [\text{O}_3] \quad \text{--- (1)}$$

$$\frac{d[\text{O}]}{dt} = k_a [\text{O}_3] - k_a' [\text{O}_2] [\text{O}] - k_b [\text{O}] [\text{O}_3] = 0 \quad (\text{S.S approximation})$$

$$\Rightarrow k_a [\text{O}_3] = k_a' [\text{O}_2] [\text{O}] + k_b [\text{O}] [\text{O}_3] \quad \text{--- (2)}$$

Substituting (2) in (1)

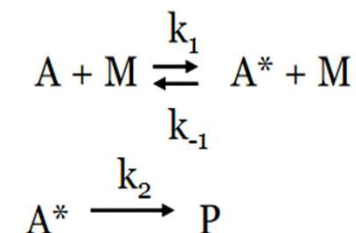
$$\begin{aligned} \frac{d[\text{O}_3]}{dt} &= -\cancel{k_a' [\text{O}_2] [\text{O}]} - k_b [\text{O}] [\text{O}_3] + \cancel{k_a' [\text{O}_2] [\text{O}]} - k_b [\text{O}] [\text{O}_3] \\ &= -2 k_b [\text{O}] [\text{O}_3] \end{aligned}$$

$$\begin{aligned} \text{From (2)} \quad [\text{O}] &= \frac{k_a [\text{O}_3]}{k_a' [\text{O}_2] + k_b [\text{O}_3]} \end{aligned}$$

$$\text{Ans: } \frac{d\text{O}_3}{dt} = -\frac{2k_a k_b [\text{O}_3]^2}{k_a' [\text{O}_2] + k_b [\text{O}_3]}$$

LINDEMANN MECHANISM

$$\frac{d[A^*]}{dt} = k_1[A][M] - k_{-1}[A^*][M] - k_2[A^*]$$



From steady-state approximation, $\frac{d[A^*]}{dt} = 0$, $[A^*] = \frac{k_1[A][M]}{k_2 + k_{-1}[M]}$

$$rate = \frac{d[P]}{dt} = k_2[A^*] = \frac{k_1 k_2 [A][M]}{k_2 + k_{-1}[M]}$$

In the vapour phase,

At high pressures: (Collisions will be higher)

Rate of collisional deactivation \gg Rate of uni-molecular decay

$$k_{-1}[A^*][M] \gg k_2[A^*]$$

$$k_{-1}[M] \gg k_2$$

$$\frac{d[P]}{dt} = \frac{k_1 k_2}{k_{-1}} [A] \text{ - first order reaction}$$

Lindemann Mechanism

At low pressures, (Collisions will be lower)

Rate of collisional deactivation \ll Rate of uni-molecular decay

$$k_{-1}[A^*][M] \ll k_2 [A^*]$$

$$k_{-1} [M] \ll k_2$$

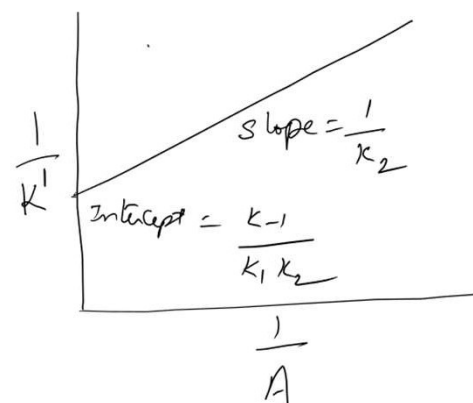
$$\frac{d[P]}{dt} = k_1[A][M] - \text{Second Order reaction}$$

Hence a unimolecular reaction is a first order reaction at high pressures and second order reaction at low pressures.

$$\frac{d[P]}{dt} = \frac{k_1 k_2 [A][M]}{k_2 + k_{-1}[M]} = k' [A], \text{ where } k' = \frac{k_1 k_2 [M]}{k_2 + k_{-1}[M]}$$

$$\frac{1}{k'} = \frac{k_{-1}}{k_1 k_2} + \frac{1}{k_2 [M]}$$

This theory can be proved by plotting the above equation to observe a straight line.



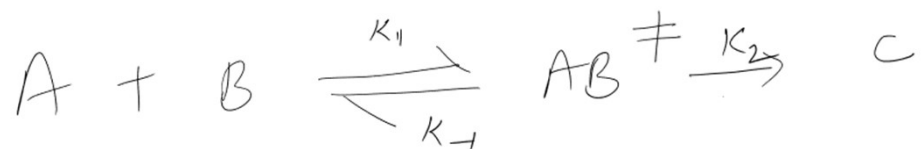
Here A=M

TRANSITION STATE THEORY

- Temperature dependence of reaction rates:
- Rate of a reaction generally increases with increase in temperature.
- Physical observation reveals that the rate of the reaction that occur at room temperature double with a temperature increase of only 10°C.

We know that $K = Ae^{-E_a/RT}$ Where E_a = Activation Energy

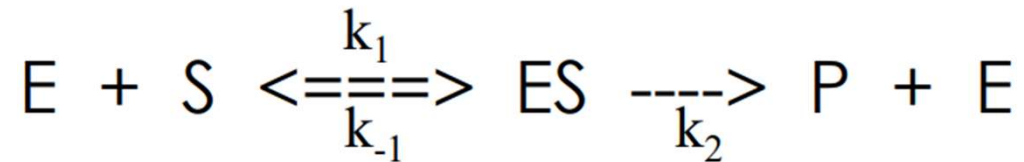
- Now consider the reaction $A + B \rightarrow P$, according to transition state theory, the reaction happens as follows-



Overall reaction rate given by $K = \frac{ek_BT}{h} e^{-\left[\frac{\Delta S}{R} - \frac{E_a}{RT}\right]}$

ENZYME CATALYSIS

- An enzyme-catalyzed reaction of substrate S to product P, is an example of consecutive reaction (with an initial opposing reaction) in biological systems.



- $-\frac{d[S]}{dt} = k_1[E][S] - k_{-1}[ES]$
- $-\frac{d[E]}{dt} = k_1[E][S] - (k_{-1} + k_2)[ES]$
- $\frac{d[ES]}{dt} = k_1[E][S] - (k_{-1} + k_2)[ES]$
- $\frac{d[P]}{dt} = k_2[ES]$
- We know that $\frac{[E][S]}{[ES]} = \frac{k_1}{k_{-1}}$ and $[E] = [E_0] - [ES]$ substituting and rearranging the terms, we get

Michaelis-Menton KINETICS

- This is was the first Michaelis-Menton equation that related the rate of product formation to the substrate concentration.
- $[S] \ll \frac{k_1}{k_{-1}} \frac{d[p]}{dt} = \frac{k_2 k_{-1}}{k_1} [E_0] [S]$
- $[S] \gg \frac{k_1}{k_{-1}} \frac{d[p]}{dt} = k_2 [E_0]$
- At any chosen instant of an enzyme-catalyzed reaction, the enzyme exists in two forms (the free and the combined). Therefore, the rate of the enzyme-catalyzed reaction will be a maximum when the entire enzyme is present as the ES complex. This should be possible at very high concentration of the substrate.
- In the second reaction of the catalytic cycle, ES breaks down leading to the product and the free enzyme (E). But when [S] is very high, the enzyme will combine instantly with S (limited only by the diffusion of the substrate to the enzyme). Under these conditions, a steady state is reached in which the enzyme is always saturated with its substrate and the reaction rate is maximum.
- Now from steady state approximation $\frac{d[ES]}{dt} = 0$, putting in the above rate equation, we get

$$[ES] = \frac{k_1[E_0][S]}{k_1[S] + k_{-1} + k_2} ; \text{ now } \frac{d[P]}{dt} = \frac{K_2 k_1 [E_0][S]}{k_1[s] + k_{-1} + k_2} = \frac{k_2 [E_0][S]}{K_M + [S]} ; K_M = \frac{k_{-1} + k_2}{k_1}$$

$$\frac{d[p]}{dt} = v = \frac{v_{max}[S]}{K_M + [S]} \quad v_{max} = k_2 [E_0]$$

ENZYME CATALYSIS

- $v_0 = \text{Initial rate}$
- Above Michaelis Menton equation relates substrate concentration and Initial rate.
- **Turnover number (TON):**
 - TON of an enzyme is the number of substrate molecules turned into product by a single enzyme molecule in unit time when the enzyme concentration alone is the rate determining step (high substrate concentration compared to the enzyme).
- **TON = k_2 or k_{cat}**
- Plot of ' v_0 ' (Initial rate) Ver $[S]$ (substrate concentration), $v_0 = v_{max}/2$ when $[S] = K_M$, K_M is Michaelis Menton constant. It is a measure of the enzyme-substrate affinity. The graph will be a rectangular hyperbola.
- As $K_M = \frac{k_{-1} + k_2}{k_1}$ it should be lower, in such a way k_1 is high, and increases the rate of the reaction. Note k_{-1} dissociation rate constants/ k_2 association rate constant. Lower the K_M substrate is bonded in a tight manner.
- A plot of ' v_0 ' (Initial rate) Ver $[E]$ (Enzyme concentration) has a slope equals to k_2 (TON). It will be a straight line.

Chain reactions

- Example 1: $\text{H}_2 + \text{Br}_2 \longrightarrow 2 \text{HBr}$
- Chain initiation, Chain Propagation, Chain termination and Chain Retardation
- $\text{Br}_2 + \text{M} \longrightarrow \text{Br} + \text{Br} + \text{M} \quad (K_i) \text{ [initiation]}; R_i = K_i [\text{Br}_2] [\text{M}]$
- $\text{Br} + \text{H}_2 \longrightarrow \text{HBr} + \text{H} \quad (K_p) \text{ [propagation]}; R_p = K_p [\text{Br}] [\text{H}_2] + K_p' [\text{H}] [\text{Br}_2]$
- $\text{H} + \text{Br}_2 \longrightarrow \text{HBr} + \text{Br} \quad (K_p') \text{ [propagation]}$
- $\text{H} + \text{HBr} \longrightarrow \text{Br} + \text{H}_2 \quad (K_r) \text{ [retardation]}; R_r = K_r [\text{H}] [\text{HBr}]$
- $\text{Br} + \text{Br} + \text{M} \longrightarrow \text{Br}_2 + \text{M}^* \quad (K_t) \text{ [termination]}; R_t = K_t [\text{Br}]^2 [\text{M}]$
- $\frac{d[\text{HBr}]}{dt} = K_p [\text{Br}] [\text{H}_2] + K_p' [\text{H}] [\text{Br}_2] - K_r [\text{H}] [\text{HBr}]$
- $\frac{d[\text{Br}]}{dt} = \frac{d[\text{H}]}{dt} = 0 \text{ (Steady state approximation)}$
- $\frac{d[\text{H}]}{dt} = 0 = K_p [\text{H}_2] [\text{Br}] - K_p' [\text{Br}_2] [\text{H}] - K_r [\text{H}] [\text{HBr}]$
- $\frac{d[\text{Br}]}{dt} = 0 = K_i [\text{Br}_2] [\text{M}] - K_p [\text{H}_2] [\text{Br}] + K_p' [\text{Br}_2] [\text{H}] + K_r [\text{H}] [\text{HBr}] - K_t [\text{Br}]^2 [\text{M}]$
- Rate of product formation
- $\frac{d[\text{HBr}]}{dt} = 2 K_p (K_i / K_t)^{1/2} [\text{Br}_2]^{3/2} [\text{H}_2] / \{ [\text{Br}_2] + (K_r / K_p') [\text{HBr}] \}$

Chain reactions

- Let us consider the thermal polymerization of the monomer vinyl chloride (M = monomer) initiated by benzoyl peroxide (I = initiator).
- $$\text{C}_6\text{H}_5\text{-CO-O-O-OC-C}_6\text{H}_5 + n \text{CH}_2=\text{CH}(\text{Cl}) \longrightarrow \text{--[CH}_2\text{-CH}(\text{Cl})\text{--]}_n\text{--I}$$

(1 weight % of VC or M)
VC or M (liquid)
PVC (solid)
- $R_i = r_i = \frac{d[M\cdot]}{dt} = 2f k_d [I]$ (Rate of Initiation)-- “f” is a fraction; it represents fraction of benzoyl peroxide radical available for addition with monomer. k_d is rate constant of thermal decomposition.
- $R_p = r_p = -\frac{d[M\cdot]}{dt} = \frac{d[p]}{dt} = k_p [M] [M\cdot]$ (Rate of product formation)
- $R_t = r_t = -\frac{d[M\cdot]}{dt} = 2 k_t [M\cdot]^2$ (Rate of Termination)
- By using Steady state approximation, $-\frac{d[M\cdot]}{dt} = 0$
- Rate of polymerization = $R_p = -\frac{d[M\cdot]}{dt} = f k_p \left(\frac{k_d}{k_t}\right)^{\frac{1}{2}} [M] [I]^{\frac{1}{2}}$
- Composite rate constant = $k_p \left(\frac{k_d}{k_t}\right)^{\frac{1}{2}}$

Quantum Chemistry _ PART-1_Basic Concepts of Quantum Chemistry

- The dynamics of microscopic systems:
- Quantum mechanics acknowledges the wave–particle duality of matter and the existence of quantization by supposing that, rather than travelling along a definite path, a particle is distributed through space like a wave.

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + V(x)\psi = E\psi \quad , \text{where } \psi \text{ is the wave function of the particle.}$$

The same equation can be written as $\frac{\partial^2 \psi}{\partial x^2} = -\frac{2m}{\hbar^2} (E - V)\psi$, has possible solutions

$$\psi = \cos kx \quad \text{where } k = \left(\frac{2m(E-V)}{\hbar^2} \right)^{\frac{1}{2}}$$

- Amplitude square of a wave = intensity = probability of finding more photons/particles $\Rightarrow |\psi|^2$ should give us the probability of finding particle/matter.
- $|\psi|^2$ is the probability density, and $|\psi|^2 = (\psi^*)\psi$. $|\psi|^2$ has the units of inverse length (volume) in 1D (3D).
- Note that, ψ can be negative or complex, but not $|\psi|^2$.

Quantum Chemistry

- Normalization of wave function. If ψ is a solution of TISE, then so is $N\psi$, where N is any constant. \Rightarrow we can find a normalization constant, N , such that the proportionality of the Born interpretation becomes an equality.

- $$\int_{-\infty}^{\infty} N\psi (N\psi)^* d\tau = 1 \quad \text{Where } N \text{ is a Constant} \quad N = \frac{1}{\left(\int_{-\infty}^{\infty} \psi\psi^* d\tau\right)^{\frac{1}{2}}}$$

Probability= 1

- Wavefunctions for which the above integral exists (being finite) are called square integrable.
- ψ must be:
 - continuous (because SH is a 2nd order differential equation)
- Have a continuous slope (because SH is 2nd order)
- Be single-valued (otherwise, two probabilities at the same x)
- Be square-integrable (normalization is not possible)).

Note: For a free particle, $V=0$. So, the TISE can be written as:

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} = E\psi$$

Principles of Quantum Mechanics

❖ Position and momentum of a free particle:

- The locations where the probability density is zero correspond to nodes in the wavefunction. Specifically, a node is a point where a wavefunction passes through zero.

❖ Operators, eigenvalues, eigenvectors:

- $\hat{H}\Psi = E\Psi$ Operator form of the SH eqn. Also, known as the eigenvalue equation.
- Hamiltonian operator in 1D
- Eigenvalue equation is: (Operator)(function) = (constant factor)*(same function) General eigenvalue equation, with omega as the eigenvalue and psi as the eigenfunction of the operator.
- **(Operator)(eigenfunction) = (eigenvalue)*(eigenfunction)**
- Example: Hamiltonian Operator: $\hat{H} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x)$ and its eigen value is Energy.
- Position and Momentum operators: $\hat{x} = x$; $\hat{P} = -i\hbar \frac{\partial}{\partial x}$ in 1D. In 3D -- $-i\hbar \left(\frac{\partial}{\partial x} + \frac{\partial}{\partial y} + \frac{\partial}{\partial z} \right)$
- We can construct other operators like
$$E = \frac{p_x^2}{2m} = \left(i\hbar \frac{\partial}{\partial x} \right) \left(i\hbar \frac{\partial}{\partial x} \right) = -\hbar^2 \frac{\partial^2}{\partial x^2}$$
- Note: Condition for two wave functions Ψ_1, Ψ_2 are Orthogonal is
$$\int_{-\infty}^{\infty} \Psi_1 \Psi_2^* d\tau = 0$$

Quantum Mechanics Postulates

❖ Hermiticity, real eigenvalues, orthogonal eigenfunctions:

- We know that, Eigen values of a Hermitian matrix ($A=A^*$) are real, in quantum mechanics, the eigen values for different operators are real (energy, momentum), so the operator must be Hermitian.
- Eigen functions for same operator of an wave function, all are orthogonal.
- Any wave function can be expressed as linear combination of eigen functions of an operator. (let us assume that it is ψ)
- Linear combination of basis functions: $\psi = C_1\Psi_1 + C_2\Psi_2 + \dots + \Psi_n = \sum_{i=1}^n C_i\Psi_i$

where the c_k are numerical (possibly complex) coefficients and the Ψ_i correspond to different momentum states.

- The probability of measuring a particular eigenvalue in a series of observations is proportional to the square modulus $|c_n|^2$.
- The average value of a large number of observations is given by the **Expectation value**, $\langle \Omega \rangle$, of the operator.
- $\langle \Omega \rangle = \int \Psi^* \hat{\Omega} \Psi d\tau$ Expectation values Definition of expectation (average) value If ψ is an eigenfunction of with eigenvalue ω , then the expectation value is (assuming ψ is a normalized function)

$$\int \Psi^* \hat{\Omega} \Psi d\tau = \int \Psi^* \omega \Psi d\tau \text{ because } (\hat{H}\Psi = \omega\Psi) = \omega \int \Psi^* \Psi d\tau = \omega$$

Quantum Chemistry

- If Ψ is not a eigen function of operator $\hat{\Omega}$, it can be written as linear combination of eigen functions of the operator, then expectation value can be written as

$$\langle \Omega \rangle = \int \Psi^* \hat{\Omega} \Psi d\tau = \int (C_1 \Psi_1 + C_2 \Psi_2)^* \hat{\Omega} (C_1 \Psi_1 + C_2 \Psi_2) d\tau = \int (C_1 \psi_1^* + C_2 \psi_2^*) (C_1 \hat{\Omega} \Psi_1 + C_2 \hat{\Omega} \Psi_2) =$$

$$\int (C_1 \Psi_1^* + C_2 \Psi_2^*) (C_1 \omega_1 \Psi_1 + C_2 \omega_2 \Psi_2) d\tau = |C_1|^2 \omega_1 \int \Psi_1 \Psi_1^* d\tau + |C_2|^2 \omega_2 \int \Psi_2 \Psi_2^* d\tau = |C_1|^2 \omega_1 + |C_2|^2 \omega_2$$

- **Heisenberg's Uncertainty Principle:**

- It is impossible to specify simultaneously, with arbitrary precision, both the momentum and the position of a particle.

$$\Delta p \Delta q \geq \frac{\hbar}{2} \quad \text{where } \Delta P = \{\langle p^2 \rangle - \langle P \rangle^2\}^{\frac{1}{2}} \quad \Delta q = \{\langle q^2 \rangle - \langle q \rangle^2\}^{\frac{1}{2}}$$

- $\hat{\Omega}_2(\hat{\Omega}_1 \Psi) \neq \hat{\Omega}_1(\hat{\Omega}_2 \Psi)$ Complementary variables definition

- $[\hat{\Omega}_1, \hat{\Omega}_2] = \hat{\Omega}_1 \hat{\Omega}_2 - \hat{\Omega}_2 \hat{\Omega}_1$ Definition of commutator (and useful for identifying complementary variables)

- Example: $[\hat{x}, \hat{p}] = i\hbar$

- $\Delta \Omega_1 \Delta \Omega_2 \geq \frac{1}{2} |\langle [\Omega_1, \Omega_2] \rangle|$ HUP for any two complementary variables

- If commutator is zero, then the Wave function is an eigenfunction of both those operators.

Quantum Chemistry: Applications of Quantum Theory: Translation Motion

❖ Translational energy of a free particle is not quantized. Because

- $\hat{H}\Psi = E\Psi$ if $\Psi = Ae^{ikx} + Be^{-ikx}$ then solving we get $E_k = \frac{k^2\hbar^2}{2m}$

- Notice that 'k' can take any value. So, E_k is not quantized (it can have any value).

❖ **Particle in a box:**

- Problem definition: Let us consider a particle in a box, in which a particle of mass m is confined between two walls at $x = 0$ and $x = L$. The potential energy is zero inside the box (i.e., $V=0$ for $0 \leq x \leq L$) but rises abruptly to infinity at the walls ($V = \infty$, otherwise).

- $\hat{H}\Psi = E\Psi$ $\hat{H} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2}$; Solving we get possible solutions for wave function and E as

- $\Psi = C \sin kx + D \cos kx$ $E = \frac{k^2\hbar^2}{2m}$ to find the constants, we have to apply the boundary conditions

- (a) the wavefunction must be zero where V is infinite, at $x < 0$ and $x > L$.

- Reason: If ψ is finite at $x < 0$ and $x > L \Rightarrow$ there is a probability to find the particle in that region \Rightarrow particle must possess infinite potential energy \Rightarrow which is physically impossible. So, ψ should be zero.

- (b) The continuity of the wavefunction then requires it to vanish just inside the well at $x = 0$, $x = L$.

- Putting these conditions, for $x=0$ $\Psi(0)=0$; $D = 0$; for $x = L$; $C \sin kL = 0$; If $C = 0$; Wave function becomes zero, so not possible. $\sin kL = 0$; $k = n\pi/L$.

- C can be determined by $\int_{-\infty}^{\infty} \Psi(\Psi)^* d\tau = 1$ where $\Psi = C \sin n(\pi/L)x$

Quantum Chemistry _ PART-2 _ The Quantum Hydrogen Atom

- Let us consider a nucleus of charge $+Ze$ at the origin and a single electron at a distance r away from it. And coordinates of nucleus are (x_2, y_2, z_2) and (x_1, y_1, z_1) .

- Then the Time Independent Equation for the Hydrogen atom:

$$\left[-\frac{\hbar^2}{2m_1} \left(\frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial y_1^2} + \frac{\partial^2}{\partial z_1^2} \right) - \frac{\hbar^2}{2m_2} \left(\frac{\partial^2}{\partial x_2^2} + \frac{\partial^2}{\partial y_2^2} + \frac{\partial^2}{\partial z_2^2} \right) \right] \Psi(x_1, y_1, z_1, x_2, y_2, z_2) + V(x_1, y_1, z_1, x_2, y_2, z_2) \Psi(x_1, y_1, z_1, x_2, y_2, z_2) = E \Psi(x_1, y_1, z_1, x_2, y_2, z_2) \quad (1)$$

- Here V is the potential depends only on ' r ', distance between the nucleus and electron. So it is better to shift cartesian coordinate system to spherical polar coordinate system, then the potential only depends on ' r ' only. Keeping nucleus at origin.

- For that $x = r \sin \theta \cos \phi$; $y = r \sin \theta \sin \phi$; $z = r \cos \theta$; $r = \sqrt{x^2 + y^2 + z^2}$

- $\phi = \tan^{-1} \left(\frac{y}{x} \right)$; $\theta = \tan^{-1} \left(\frac{\sqrt{x^2 + y^2}}{z} \right)$

- In polar coordinates (1) can be written as

$$\left(\frac{-\hbar^2}{2\mu} \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] + V(r, \theta, \phi) \right) \Psi(r, \theta, \phi) = E \Psi(r, \theta, \phi)$$

$$-\hbar^2 \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + 2\mu r^2 \left(E + \frac{e^2}{4\pi\epsilon_0} \right) \right] \Psi(r, \theta, \phi) + \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] \Psi(r, \theta, \phi) = 0$$

- ' r ' dependent

' θ ' dependent

- From variable separable method we can write $\Psi(r, \theta, \phi) = R(r)\Psi(\theta, \phi)$

Quantum Chemistry

- Putting in the equation, divided by $R(r)\Psi(\theta, \phi)$ and separate we get
- $$-\frac{1}{R(r)}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R(r)}{\partial r}\right)+2\mu r^2\left(E+\frac{e^2}{4\pi\epsilon_0}\right)R(r)\right]-\hbar^2\left[\frac{1}{\Psi(\theta,\phi)\sin\theta}\frac{\partial\Psi(\theta,\phi)}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2\Psi(\theta,\phi)}{\partial\phi^2}\right]=0$$
- Let 'r' dependent $-\frac{1}{R(r)}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R(r)}{\partial r}\right)+2\mu r^2\left(E+\frac{e^2}{4\pi\epsilon_0}\right)R(r)\right] = -\beta$ and
- $$(\theta, \phi) \text{ dependent } -\hbar^2\left[\frac{1}{\Psi(\theta,\phi)\sin\theta}\frac{\partial(\sin\theta\frac{\partial\Psi(\theta,\phi)}{\partial\theta})}{\partial\theta}+\frac{1}{\sin^2\theta}\frac{\partial^2\Psi(\theta,\phi)}{\partial\phi^2}\right] = \beta$$
, by separating this equation into θ and ϕ parts same as above we get (Note: $\Psi(\theta, \phi) = \Psi(\theta)\Psi(\phi)$; Variable separable method)
- θ dependent will be $\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Psi(\theta)}{\partial\theta}\right)+\beta\sin^2\theta\Psi(\theta, \phi) = m^2$ and
- ϕ dependent part will be $\frac{1}{\psi(\theta,\phi)}\frac{\partial^2\Psi(\phi)}{\partial\phi^2} = -m^2$, by solving this equation by assuming $\Psi(\phi) = A_m e^{im\phi}$ or $Ae^{-im\phi}$ by using $\int_{-\infty}^{\infty} \Psi(\Psi)^* d\tau = 1$, we get $|A_m| = \frac{1}{\sqrt{2\pi}}$;
- $\Psi(\theta) = C P_l^m(\cos\theta)$ where $P_l^m(\cos\theta)$ is the legendary polynomial.
- Note: Here 'm' is principle quantum number whose values are: $\pm 1, \pm 2, \pm 3 \dots \dots \dots$
- and $\beta = l(l+1)$ where 'l' is angular momentum quantum number whose values are 0, 1, 2...

Quantum Chemistry

- Now let's solve 'r' part of the equation

- “ $-\frac{1}{R(r)} \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial R(r)}{\partial r} \right) + 2\mu r^2 \left(E + \frac{e^2}{4\pi\epsilon_0} \right) R(r) \right] = -\beta$ ”

- Let us quickly define ' a_0 ' for H like atom with in terms other fundamental constants.

$$\frac{Ze^2}{4\pi\epsilon_0} = \frac{\mu v^2}{r}, \text{ we know that } \mu v r = n\hbar \text{ for } n = 1, v = \frac{\hbar}{\mu r}, \text{ substituting, we get}$$

$$r = \frac{4\pi\epsilon_0 \hbar^2}{\mu Z} = a_0 \text{ with } n=1. \text{ For first Bohr orbit.}$$

- Solving radial part of the equation we get

- $R(r) = \left\{ \frac{(n-l-1)!}{2n\{(n+l)!\}^3} \right\}^{\frac{1}{2}} \left(\frac{2}{na_0} \right)^{\frac{3}{2}+l} r^l e^{-\frac{r}{na_0}} \left[L_{n+l}^{2l+1} \left(\frac{2r}{na_0} \right) \right]; \left[L_{n+l}^{2l+1} \left(\frac{2r}{na_0} \right) \right]$ is Lagrange Polynomial.

- $\Psi(r, \theta, \phi) = R(r) \Psi(\theta) \Psi(\phi) = N R_{n,l}(r) P_l^m(\cos \theta) e^{im}$; where N is obtained by normalization and includes the coefficients of each partial solution.

- Probability = $P = \int_0^\infty r^2 dr \int_0^\pi \sin \theta d\theta \int_0^{2\pi} \Psi_{nlm} (\Psi_{nlm})^* d\phi = 1$ (in spherical polar coordinates)

Quantum Chemistry

Definition of Angular Momentum

$$\vec{L} = \vec{r} \times \vec{p} = \begin{vmatrix} \vec{i} & \vec{j} & \vec{k} \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix}$$

$$\vec{r} = x\vec{i} + y\vec{j} + z\vec{k}$$

$$\vec{p} = p_x\vec{i} + p_y\vec{j} + p_z\vec{k}$$

$$= (y p_z - z p_y) \vec{i} + (z p_x - x p_z) \vec{j} + (x p_y - y p_x) \vec{k}$$

$$\quad \quad \quad \parallel \quad \quad \quad \parallel \quad \quad \quad \parallel$$

$$\quad \quad \quad L_x \quad \quad \quad L_y \quad \quad \quad L_z$$

$$\left. \begin{aligned} L_x &= y p_z - z p_y \\ \hat{L}_x &= \hat{y} \hat{p}_z - \hat{z} \hat{p}_y \\ &= y \left(-i\hbar \frac{\partial}{\partial z} \right) - z \left(-i\hbar \frac{\partial}{\partial y} \right) \\ \hat{L}_x &= -i\hbar \left[y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right] \end{aligned} \right\} \begin{aligned} L_y &= z p_x - x p_z \\ \hat{L}_y &= \hat{z} \hat{p}_x - \hat{x} \hat{p}_z \\ &= z \left(-i\hbar \frac{\partial}{\partial x} \right) - x \left(-i\hbar \frac{\partial}{\partial z} \right) \\ \hat{L}_y &= -i\hbar \left[z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right] \end{aligned} \left\{ \begin{aligned} L_z &= x p_y - y p_x \\ \hat{L}_z &= \hat{x} \hat{p}_y - \hat{y} \hat{p}_x \\ &= x \left(-i\hbar \frac{\partial}{\partial y} \right) - y \left(-i\hbar \frac{\partial}{\partial x} \right) \\ \hat{L}_z &= -i\hbar \left[x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right] \end{aligned} \right.$$

$$L^2 = L_x^2 + L_y^2 + L_z^2$$

$$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$$

$$[\hat{L}^2, \hat{L}_x] = 0 \quad [\hat{L}_x, \hat{L}_y] = i\hbar \hat{L}_z$$

$$[\hat{L}^2, \hat{L}_y] = 0 \quad [\hat{L}_y, \hat{L}_z] = i\hbar \hat{L}_x$$

$$[\hat{L}^2, \hat{L}_z] = 0 \quad [\hat{L}_z, \hat{L}_x] = i\hbar \hat{L}_y$$

one of its components!

L is the angular momentum operator and L_x, L_y, L_z are its projections in x, y, z directions.

Acknowledgements & References

- **References:**

- For Complete derivation of Schrodinger Equation for H atom , you can refer to following G-Drive folder :
- <https://drive.google.com/drive/folders/1T1-ftTlpC2raiU8B4deuPadsXThQ6wZB?usp=sharing>

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