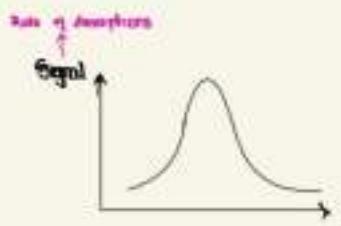


60 min.

$$\frac{d[M-S]}{dT} = -\frac{\tau_0^{-1}}{\alpha} [M-S] e^{-E_a/RT}$$

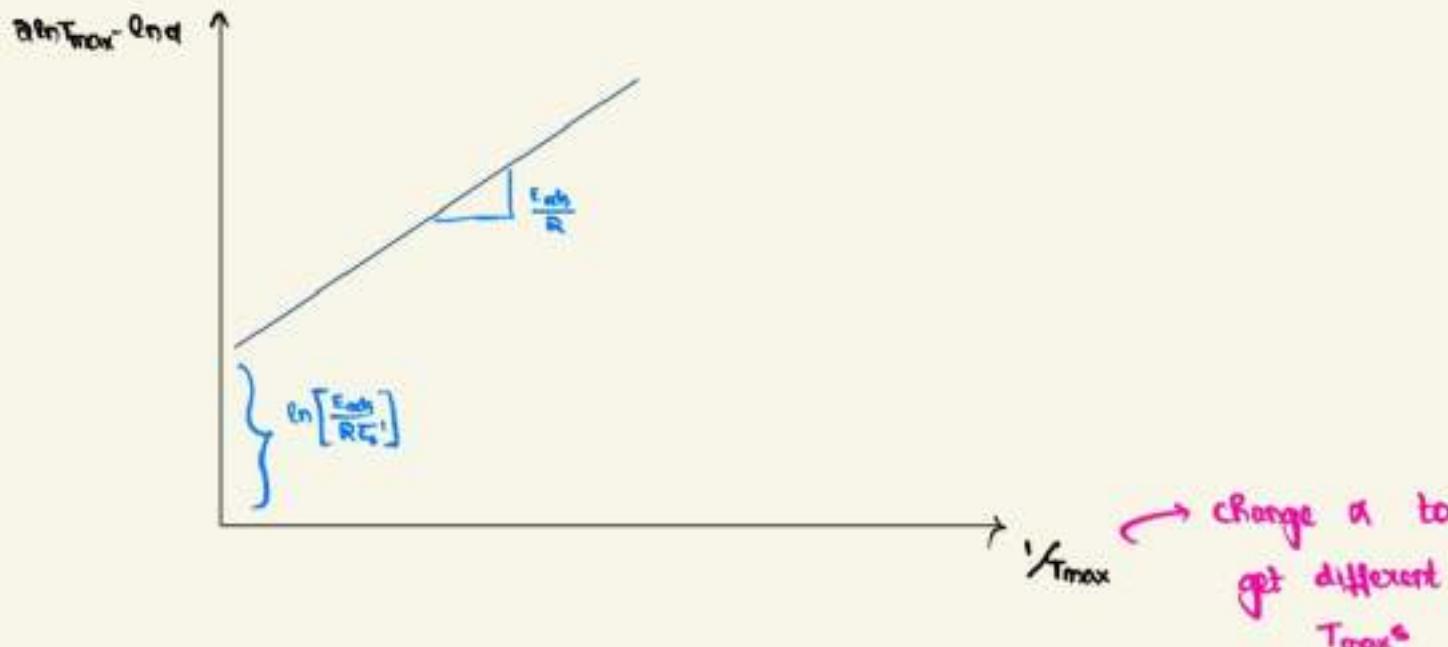


Now, $\frac{d}{dT} \left(\frac{d[M-S]}{dT} \right) = 0 \rightarrow$ for the maxima
 $T = T_{max}$

$$\Rightarrow \frac{E_a}{RT_{max}^2} = -\frac{\tau_0^{-1}}{\alpha} e^{-E_a/RT_{max}}$$

take ln \rightarrow

$$\Rightarrow \ln T_{max} - \ln q = \ln \left[\frac{E_a}{R\tau_0^{-1}} \right] + \frac{E_a}{RT_{max}}$$



We consider \rightarrow
surface homogeneous \rightarrow geometrically
essentially
Adsorption sites \rightarrow equivalent
An really \rightarrow parallel \rightarrow up to date
also essentially different

ENERGY LEVELS FOR THE 4 DIFFERENT TYPES OF MOTION : TRANSLATIONAL , ROTATIONAL, VIBRATIONAL, ELECTRONIC .

I. Translational Motion

Energy Levels

Translational motion is continuous, and molecules can have any kinetic energy:

$$E_{\text{trans}} = \frac{p^2}{2m}$$

where:

- E_{trans} is the translational energy.
- p is the momentum ($p = mv$).
- m is the mass of the molecule.

Quantum Formula

The translational partition function in a box of volume V :

$$Z_{\text{trans}} = \frac{V}{\Lambda^3}$$

where $\Lambda = \frac{\hbar}{\sqrt{2\pi mk_B T}}$ is the thermal de Broglie wavelength, and \hbar is Planck's constant.

2. Vibrational Motion

Energy Levels

For a harmonic oscillator model, the vibrational energy levels are quantized:

$$E_v = \left(v + \frac{1}{2}\right) h\nu$$

where:

- v is the vibrational quantum number ($v = 0, 1, 2, \dots$).
- ν is the vibrational frequency.

Population Distribution

$$\frac{N_v}{N} = \frac{e^{-\frac{E_v}{k_B T}}}{Z_{\text{vib}}}$$

where:

- N_v is the number of molecules in vibrational state v .
- $Z_{\text{vib}} = \sum_v e^{-\frac{E_v}{k_B T}}$ is the vibrational partition function.

Quantum Formula

Approximate vibrational partition function:

$$Z_{\text{vib}} = \frac{1}{1 - e^{-\frac{h\nu}{k_B T}}}$$

3: Electronic Motion

Energy Levels

Electronic energy levels are discrete and depend on the molecule:

$$E_{\text{elec}} = E_0 + \Delta E_i$$

where:

- E_0 is the ground state energy.
- ΔE_i is the energy difference from the ground state to the i -th excited state.

Population Distribution

$$\frac{N_i}{N} = \frac{g_i e^{-\frac{E_i}{k_B T}}}{Z_{\text{elec}}}$$

where:

- g_i is the degeneracy of the i -th state.
- $Z_{\text{elec}} = \sum_i g_i e^{-\frac{E_i}{k_B T}}$ is the electronic partition function.

4. Rotational Motion

Energy Levels

For a rigid rotor (diatomic molecule), the rotational energy levels are quantized:

$$E_J = \frac{J(J+1)h^2}{8\pi^2 I}$$

where:

- J is the rotational quantum number ($J = 0, 1, 2, \dots$).
- I is the moment of inertia of the molecule.
- h is Planck's constant.

Population Distribution

$$\frac{N_J}{N} = \frac{g_J e^{-\frac{E_J}{k_B T}}}{Z_{\text{rot}}}$$

where:

- N_J is the number of molecules in state J .
- $g_J = 2J + 1$ is the degeneracy factor.
- $Z_{\text{rot}} = \sum_J g_J e^{-\frac{E_J}{k_B T}}$ is the rotational partition function.

Quantum Formula

Approximate high-temperature rotational partition function:

$$Z_{\text{rot}} \approx \frac{k_B T}{\sigma \frac{h^2}{8\pi^2 I}}$$

'THE PARTITION FUNCTION'

The partition function Z is a fundamental concept in statistical mechanics. It quantifies the statistical properties of a system in thermodynamic equilibrium and serves as a bridge between microscopic properties (quantum states) and macroscopic observables (thermodynamic quantities like energy and entropy).

$$Z = \sum_i e^{-\beta E_i}$$

$Z \rightarrow$ partition function

$E_i \rightarrow$ energy of i th state

$\beta \rightarrow \frac{1}{k_B T}$ is the inverse temperature

Qualitatively, the partition function indicates how the particles are distributed among the various energy levels.

The following can be obtained from the partition function:

$$\rightarrow \text{Average energy } \langle E \rangle = -\frac{\partial \ln Z}{\partial \beta}$$

$$\rightarrow \text{Entropy } S = k_B (\ln Z + \beta \langle E \rangle)$$

$$\rightarrow \text{Free energy } F = -k_B T \ln Z$$

$$\rightarrow \text{Pressure } P = k_B T \frac{\partial \ln Z}{\partial V}$$

MOLECULAR PARTITION FUNCTIONS FOR GAS :

Molecules are associated with energy of different types (4 types, corresponding to the 4 motions) . All these must be taken into account while mentioning Z .

$$E(\text{total energy}) = E_{\text{rot}} + E_{\text{trans}} + E_{\text{elec}} + E_{\text{vib}}$$

$$\text{Molecular partition function} = \sum_i g_i e^{-\beta E_i}$$

'The total partition function of a gas molecule is the product of translational, rotational, vibrational & electronic contribution'.

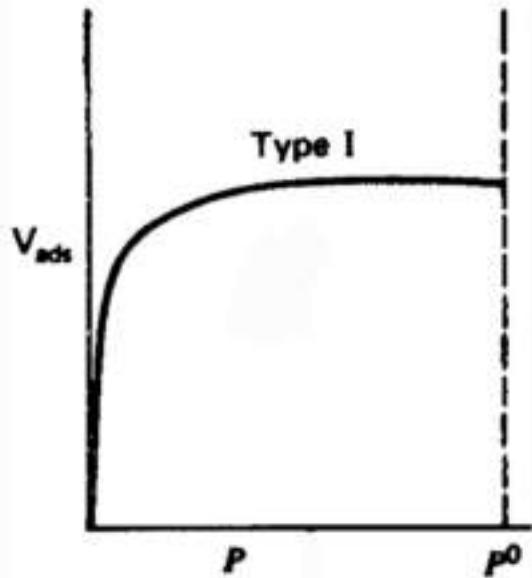
TYPES OF ISOTHERMS

Adsorption isotherms do not all conform to the Langmuir type in terms of shape. Brunauer considered that there are in fact 5 principal forms.

These isotherms describe the relationship between the amount of gas adsorbed V_{ads} and P/P_0 ; where P = pressure of the gas,

P_0 = saturation vapor pressure
of the adsorbate.

or P/P_0 = relative pressure
of the adsorbate gas



TYPE 1 :-

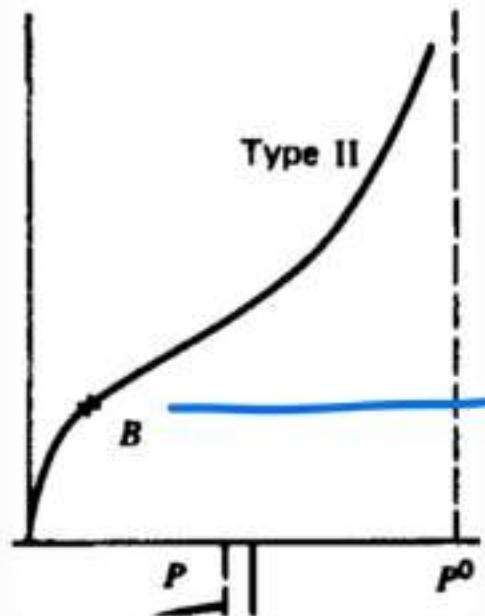
Type 1 is the Langmuir type, roughly characterised by a monotonic approach to a limiting adsorption that corresponds to a complete monolayer.

This is found for porous materials with small pores, where adsorption occurs mainly due to pore filling. (Microporous)

e.g. activated carbons, charcoal (adsorbent)

→ This type is typically observed in chemisorption.

- * The flat region of the type I isotherm has never been observed up to pressures approaching P^0



TYPE 2 : →

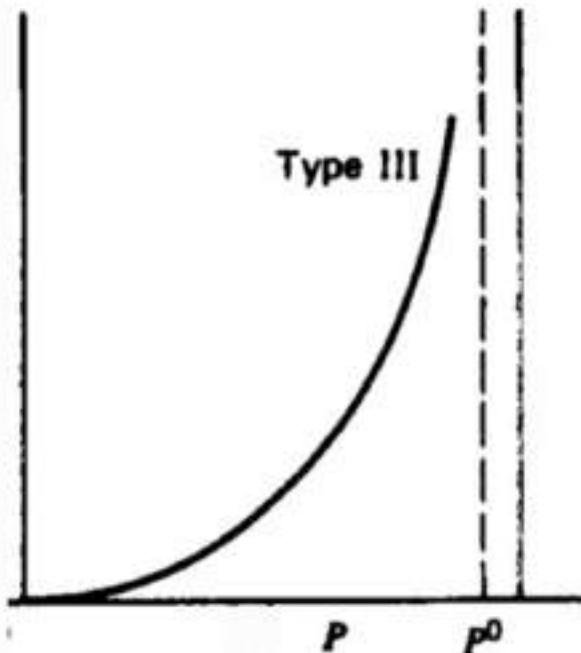
Type II isotherm is common in the case of physical adsorption and corresponds to multilayer formation.

→ Point B, at the knee of the curve corresponds to monolayer adsorption.

After point B, multilayer adsorption occurs as the pressure increases and adsorption continues indefinitely.

→ Experimentally, such behaviour is observed for adsorption on powdered samples and the approach towards infinite film thickness is due to interparticle condensation.*
eg. on non porous materials.

* Interparticle condensation refers to the process where condensation of vapor occurs between particles, typically in the void spaces or gaps that exist in a packed powder or porous material, rather than inside the pores of the individual particles themselves.



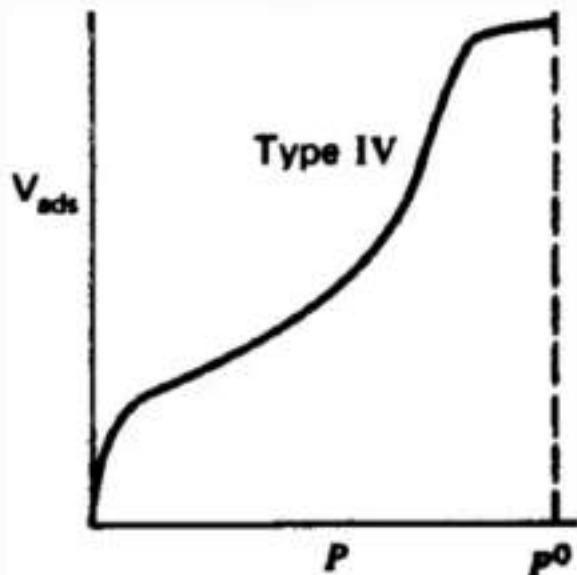
TYPE 3 :→

$$\Delta H \text{ liquefaction} \geq \Delta H \text{ adsorption}$$

of adsorbate

- Graph approaches P^0 asymptotically.
- For materials with cohesive force between adsorbate molecules greater than the adhesive force between adsorbate molecules and adsorbent.

- * e.g. adsorption of nitrogen on ice
(Non porous with weak interaction)



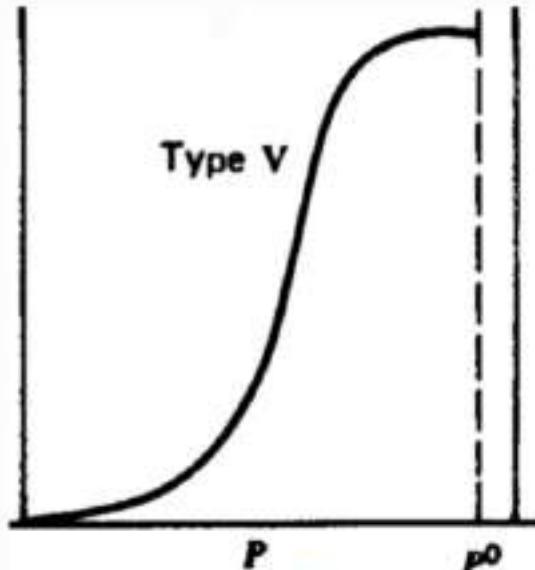
TYPE II :-

→ Type II specifically refers to porous solids. (or mesoporous) This isotherm shows monolayer- multi-layer adsorption followed by capillary condensation*(hysteresis effects).

* Capillary condensation is the phenomenon where vapor condenses into liquid inside the small pores or capillaries of a porous material at a vapor pressure below the saturation pressure (P_0) of the bulk liquid.

→ e.g. Silica gels, MCM-41

MCM-41 a mesoporous silica material exhibits type IV. During adsorption water vapour condenses in its mesopores at high relative pressure. During desorption, the vapour does not evaporate at the same pressure and hence a hysteresis loop forms. → Capillary condensation example.



TYPE 5 →

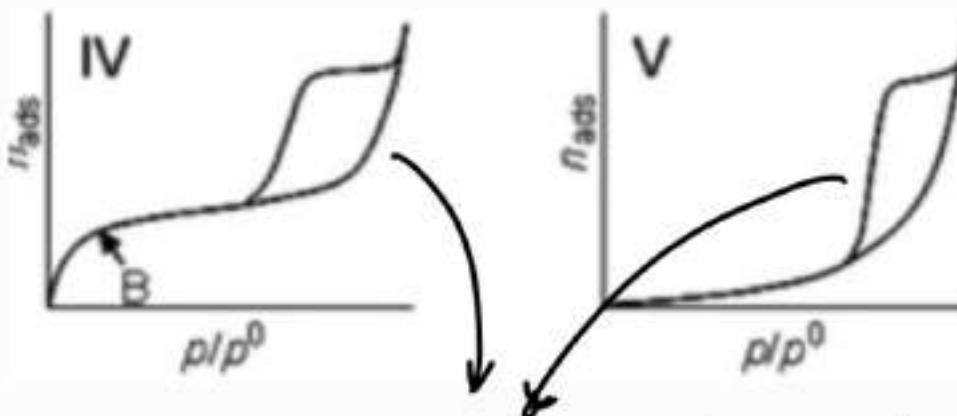
- This isotherm suggests weak adsorbate-adsorbent interactions & capillary condensation within mesopores.
- for mesoporous solids
- it may also exhibit hysteresis loop.

(Type II is for mesoporous solids & weak interactions)

e.g. Adsorption of water on hydrophobic mesoporous materials.

#

For type
4 and 5.



'hysteresis loop'

ADSORPTION - THERMODYNAMICS

The Langmuir adsorption theorem :

1. The adsorption includes a monolayer at the surface.
2. No interaction takes place between the molecules on different sites.
3. Each site can hold only a single adsorbed molecule.
4. The heat of adsorption is not dependent on the number of sites. It is equal for everyone.

$$\theta = \frac{bP}{1+bP} \quad \text{--- ①}$$

where b is the ratio of rate constant of condensation and evaporation. ($b = \frac{k_2}{k_1} \quad (k_1 s_i = k_2 P(s-s_i))$)

where θ is the fraction of the surface of adsorbent covered and can also be written as →

$$\theta = \frac{n}{n_m} \quad \text{--- ②}$$

where n_m : moles / gram adsorbed at the monolayer point and n : moles / gram adsorbed.

Thus, from eq. ① and ②

$$\frac{n}{n_m} = \frac{bP}{1+bP}$$

$$n = \frac{n_m bP}{1+bP} \quad \text{--- } ③$$

At low pressure:

The amount adsorbed becomes directly proportional to the pressure →

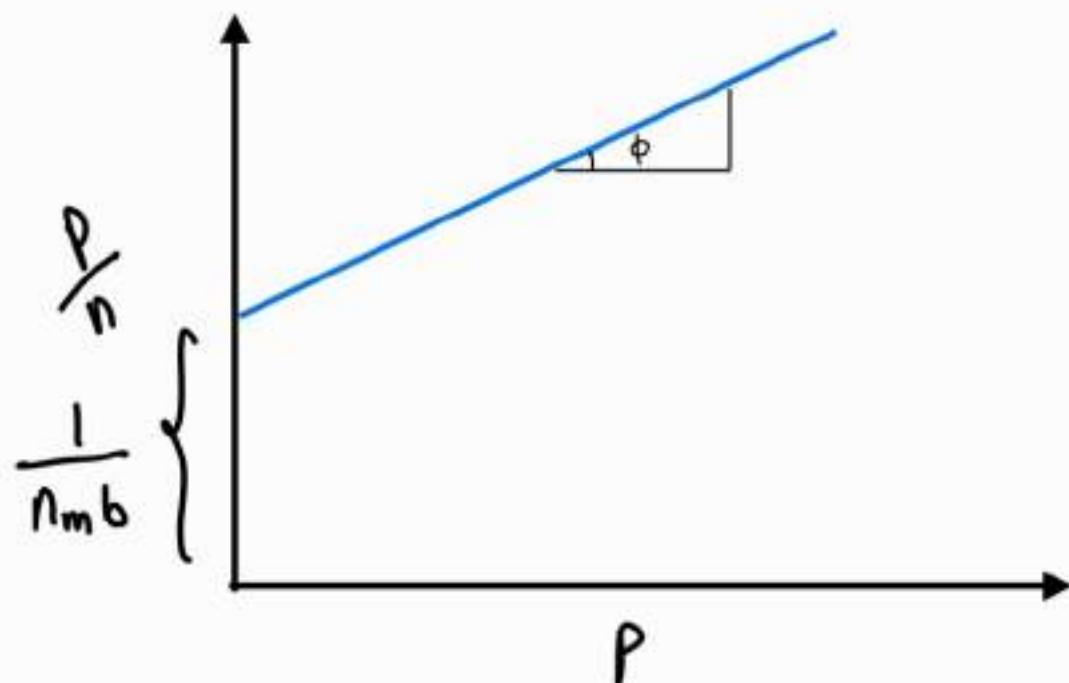
$$n = n_m bP$$

At high pressure: n approaches the limiting value n_m .

equation ③ can be written as :-

$$\frac{P}{n} = \frac{1}{n_m b} + \frac{P}{n_m}$$

A plot of P/n versus P should give a straight line and the 2 constants n_m and b may be evaluated from the slope and the intercept.



$$\tan \phi = \frac{1}{n_m b}$$

$$b = K_d$$

= adsorption equilibrium constant

- * If there are several competing adsorbates, a derivation analogous to the foregoing gives →

$$n_i = \frac{n_{mi} b_i p_i}{1 + \sum_j b_j p_j}$$

where $b = K_d$,

$$\Delta G = -RT \ln K_d \quad \text{--- (4)}$$

$$\Delta G = \Delta H - T \Delta S \quad \text{--- (5)}$$

from (4) and (5)

$$\ln K_d = -\frac{\Delta H}{RT} + \frac{T \Delta S}{RT}$$

$$\left. \frac{\partial (\ln K_d)}{\partial T} \right|_0 = \frac{\Delta H}{RT^2} \rightarrow (\text{Isosteric enthalpy of adsorption})$$

$$\text{Langmuir : } \theta = \frac{KP}{1+KP}$$

↳

$$KP = \frac{\theta}{1-\theta}$$

$$\ln P + \ln K = \ln\left(\frac{\theta}{1-\theta}\right)$$

at fixed θ , $\ln P + \ln K = \text{constant}$

Differentiate \Rightarrow

$$\left(\frac{\partial \ln K}{\partial T} \right)_\theta = - \left(\frac{\partial \ln P}{\partial T} \right)_\theta$$

using vant Hoff equation :

$$\left(\frac{\partial \ln P}{\partial T} \right)_\theta = - \frac{\Delta H^\circ_{AD}}{RT^2}$$

$$\left(\frac{\ln P_1}{P_2} \right)_\theta = \frac{\Delta H^\circ_{AD}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

Note : $\frac{\partial(\frac{1}{T})}{\partial T} = -\frac{1}{T^2}$

$$\left(\frac{\partial(\ln p)}{\partial(\frac{1}{T})} \right)_\theta = \frac{\Delta H_{AD}^\circ}{R}$$

This is a form of the Clausius-Clapeyron Relation

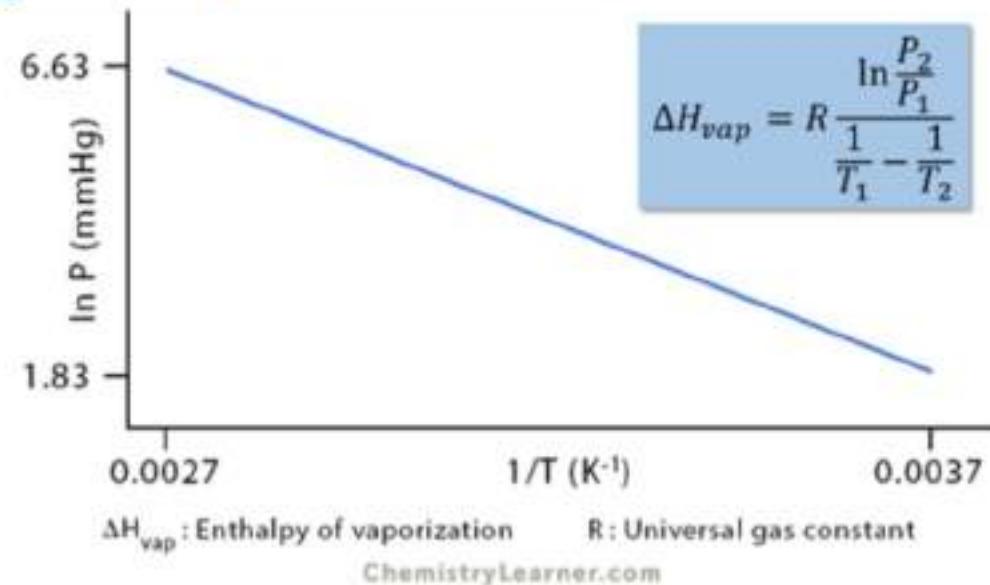
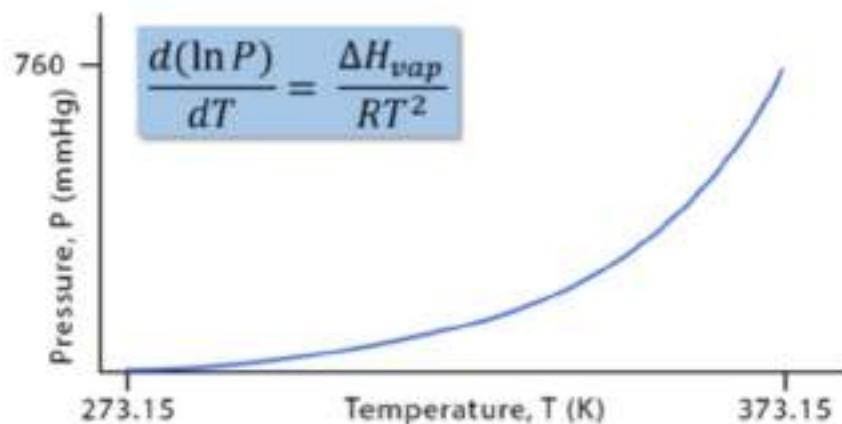
The isosteric heat of adsorption ΔH_{AD}° refers to the heat released or absorbed during the adsorption of a gas onto a solid surface at constant coverage (θ).
 (Isosteric means constant adsorbed amount)

$$\begin{aligned}\text{Isosteric heat of adsorption } Q_{st} &= -\Delta H_{AD}^\circ \\ &= -\left(\frac{\partial(\ln p)}{\partial(\frac{1}{T})} \right)_\theta R\end{aligned}$$

Clausius - Clapeyron Equation

Clausius-Clapeyron Equation

Example: Vapor Pressure of Water



STATISTICAL THERMODYNAMIC DERIVATION OF LANGMUIR ISOTHERM

While kinetic derivations are intuitive, they often make unnecessary assumptions when deriving equilibrium relationships. As an alternative, the equation for Langmuir Isotherm can be derived using statistical thermodynamics by examining the two states involved (adsorbed and gaseous).

From a thermodynamic point of view, the internal energy and entropy of a molecule should be different in the adsorbed state from that in the gaseous state. Hence, in the following derivation we take the following assumptions:

- Adsorbed molecules have different potential energy and partition functions compared to gas molecules
- Instead of moving freely, adsorbed molecules are confined to specific localized sites
- There are no interactions between adjacent adsorbed molecules
- Each adsorption site has an associated energy 'Q'

since translational and internal energy (rotation + vibration) are independent, the partition function for the gas (free) can be written as:

$$\Omega^g = \Omega^g_{\text{trans}} \Omega^g_{\text{int}}$$

And for the adsorbed gas / surface state :

$$Q^s = Q^s_{\text{site}} Q^s_{\text{int}} e^{Q^s_{\text{RT}}}$$

Here, Q^s is a function of temperature only and not of the degree of occupancy of the sites.

The complete partition function is obtained by multiplying Q^s by the number of distinguishable ways of placing 'N' molecules on 'S' sites.

[There are S ways of placing the first molecule, $S-1$ for the second ... and so on]

Hence, for N molecules the number of ways is
 $S(S-1)(S-2) \dots (S-(N-1))$ or $\frac{S!}{(S-N)!}$.

of these, $N!$ are indistinguishable since molecules are not 'labeled' and the complete partition function for N molecules becomes \rightarrow

$$Q_{\text{tot}}^S = (Q^S)^N \binom{S}{N}$$

$S \rightarrow S$ possible sites where gas may adsorb

$N \rightarrow N$ adsorbed gas molecules to the solid

$Q_{\text{tot}}^S \rightarrow$ Partition function for all the adsorbed gas molecules

$Q^S \rightarrow$ Partition function for a single adsorbed gas molecule

Because the gas molecules are indistinguishable from each other, hence $(Q^S)^N \cdot (Q^S \times Q^S \times \dots \times Q^S) \underset{N \text{ times}}{\underline{\times}}$.

The helmholtz free energy of the adsorbed layer is given by \Rightarrow

$$A^S = -kT \ln Q_{st}^S$$

$$A^S = -kT \ln \left(\frac{(\Omega_e)^N S!}{(S-N)! N!} \right)$$

Using Stirling's approximation for factorials $\Rightarrow x! = \left(\frac{x}{e}\right)^x$
we get,

$$A^S = kT \left(-S \ln S + N \ln N + (S-N) \ln (S-N) - N \ln Q^S \right)$$

The chemical potential μ^S is given by $\left(\frac{\partial A^S}{\partial N}\right)_{T,S}$, so that

$$\mu^S = kT \ln \frac{N}{S-N} - kT \ln Q^S$$

And for the gas phase \Rightarrow

$$\mu^g = -kT \ln Q^g$$

At equilibrium $\Rightarrow \mu^S = \mu^g$

$$\cancel{kT \ln \frac{N}{S-N}} - \cancel{kT \ln Q^S} = -kT \ln Q^g$$

$$\ln \frac{N}{S-N} = \ln Q^L - \ln Q^g$$

$$\ln \left(\frac{N}{S-N} \right) = \ln \frac{Q^L}{Q^g}$$

$$\frac{N}{S-N} = \frac{Q^L}{Q^g} \quad (\text{since } \theta = \frac{N}{S})$$

$$\boxed{\frac{\theta}{1-\theta} = \frac{Q^L}{Q^g}} \quad \text{--- equation 1}$$

It is now necessary to examine the partition function in more detail, for which we do the following calculations \Rightarrow

$$P_i = \frac{n_i}{N}$$

where P_i is the probability of occupying the i th energy level in a statistical thermodynamic system.

$$P = \frac{n_i}{N} = \frac{e^{-\epsilon_i/kT}}{\sum_i e^{-\epsilon_i/kT}}$$

↓
Partition function

$n_i \Rightarrow$ no. of particles in i th energy level
 $N \Rightarrow$ total no. of particles
 $k \Rightarrow$ Boltzmann's constant
 $\epsilon_i \Rightarrow$ energy of i th state

This is a form of the Boltzmann distribution, which describes how particles are distributed across different energy levels in a system at thermal equilibrium. The denominator is the partition function, which ensures that all probabilities sum to 1.

Also note that these energy levels are degenerate, meaning multiple quantum states can have the same energy level, with the degeneracy arising from symmetry considerations.

Considering degeneracy (g_i) \rightarrow

$$P_i = \frac{g_i e^{-E_i/kT}}{\sum_i g_i e^{-E_i/kT}}$$

$$\mathcal{G} = \sum_n g_n e^{-\beta E_n} \quad \text{where } \beta = \frac{1}{kT}$$

For translational motion in a 1 d box of length 'a'
we have :-

$$E_n = \frac{n^2 h^2}{8a^2 m}$$

For translation, $g_n = 1$ as motion is continuous
and there is no inherent degeneracy associated with
translational energy levels.

$$Q_{\text{trans}} = \sum_n e^{-En\beta} \simeq \int_0^\infty e^{-\frac{n^2 h^2 \beta}{8a^2 m}} dn \quad \rightarrow \textcircled{*}$$

$$\text{take } \alpha = \frac{\beta h^2}{8a^2 m}$$

The integral is of the type $I = \int_0^\infty e^{-\alpha x^2} dx$

To solve this integral :-

$$I = \int_0^\infty e^{-\alpha x^2} dx$$

$$I = \int_0^\infty e^{-\alpha y^2} dy$$

$$I^2 = I \cdot I = \int_0^\infty \int_0^\infty e^{-\alpha(x^2+y^2)} dx dy$$

Using polar coordinates : $r^2 = x^2 + y^2$
 $dr \cdot r d\theta = dx dy$

$$I^2 = \int_0^{\pi/2} \int_0^\infty e^{-\alpha r^2} r dr d\theta$$

$$\begin{aligned}
 &= \int_0^{\pi/2} d\theta \int_0^{\infty} e^{-\alpha x^2} \mu dr \\
 &= \frac{\pi}{2} \int_0^{\infty} e^{-\alpha t} \frac{dt}{2} = \frac{\pi}{4} \left[\frac{e^{-\alpha t}}{-\alpha} \right]_0^{\infty} \\
 &= \frac{\pi}{4\alpha} (1-0)
 \end{aligned}$$

hence, $I = \sqrt{\frac{\pi}{4\alpha}}$

so $\underset{1\text{dim}}{Q_{\text{trans}}} = \sqrt{\frac{\pi}{4 \cdot \frac{\beta h^2}{8ma^2}}} = a \sqrt{\frac{2m\pi}{\beta h^2}} = \left(\frac{2\pi m k T}{h^2} \right)^{1/2} a$

- * We could convert the summation to the integral as the states are so close together.

For 2 dimensional box,

$$\underset{2\text{dim}}{Q_{\text{trans}}} = \left(\frac{2\pi m k T}{h^2} \right) a^2$$

For 3 dimensional box,

$$Q_{\text{trans}} = \left(\frac{2\pi m kT}{h^2} \right)^{3/2} a^3$$

↑ volume

$$= \left(\frac{2\pi m kT}{h^2} \right)^{3/2} \frac{kT}{P}$$

Now substituting values in equation 1, we get :

$$\frac{\theta}{1-\theta} = \frac{Q^L}{Q^g} = \frac{Q_{\text{int}}^L Q_{\text{int}}^d e^{Q/RT}}{Q_{\text{int}}^g \left(\frac{2\pi m kT}{h^2} \right)^{3/2} kT} \cdot \frac{P}{P}$$

$$\frac{\theta}{1-\theta} = bP$$

$$\theta = bP - bP\theta$$

$$\theta(1+bP) = bP$$

$$\theta = \frac{bP}{1+bP}$$



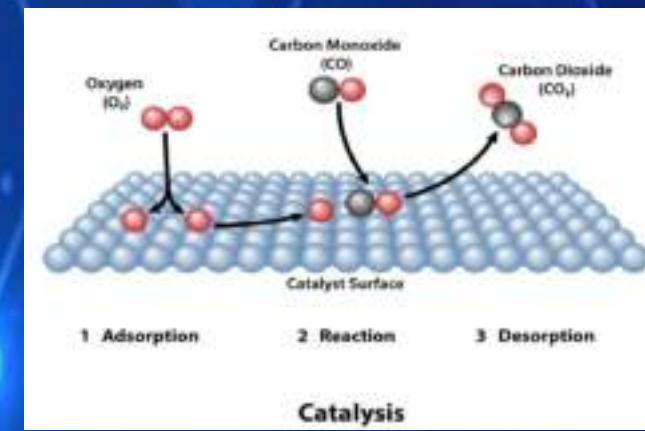
which is the same expression as for the Langmuir isotherm.

THANK YOU!



CML 103

GROUP- 9 (B)



DESORPTION

- A physical process where adsorbed atom are released from surface(reverse of adsorption).
- This occurs when molecule gains enough energy to overcome the activation barrier and binding energy that keep it attached to the surface.
- Desorption is always activated(Energy required to break chemical bonds)
- The average time that a molecule remains adsorbed on the surface is called **Residence time(τ)**.

Let ,

$$\text{Number of sites available} = S$$

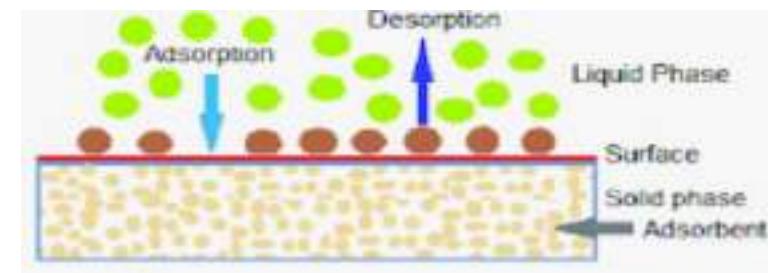
$$\text{Number of sites occupied} = S_0$$

$$\text{Number of sites available} = S - S_0$$

→ Depends on the partial pressure

$$\text{Rate of adsorption} = K_a [S - S_0] P_A$$

$$\text{Rate of desorption} = K_d [S_0]$$



What does K_d physically mean?

Let's dive in ➔

RELATION BETWEEN K_d AND τ

Residence time equation

$$\tau = \tau_0 \cdot e^{\frac{E_{ads}}{RT}}$$

T: residence time

T₀: pre exponential factor(also called vibrational frequency factor)

E_{ads}: The adsorption activation energy.

R: The universal gas constant.

T: Temperature

Arrhenius type equation

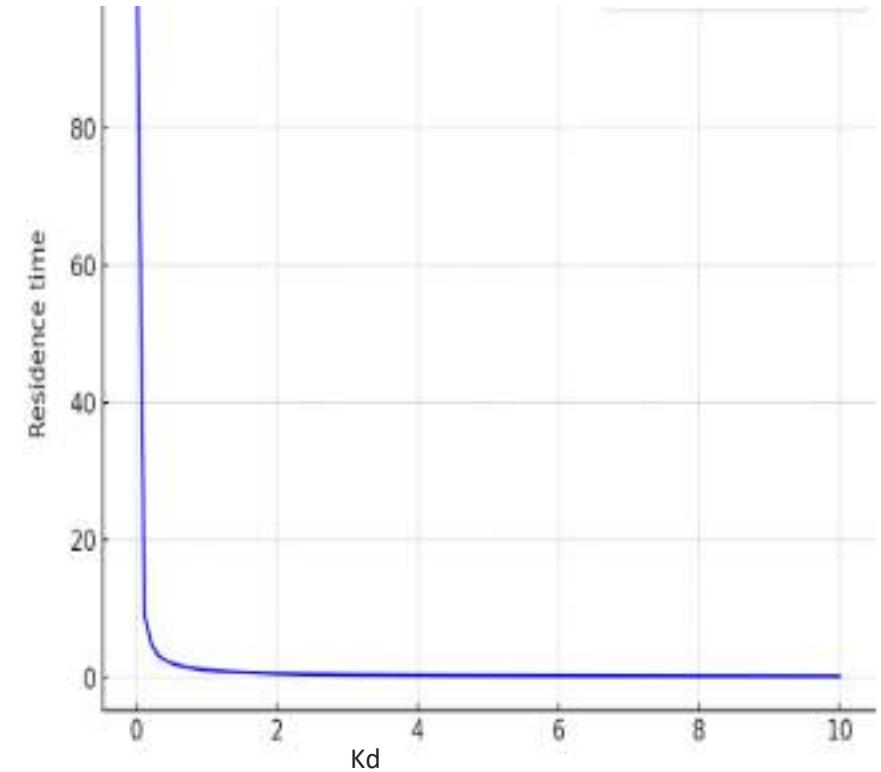
$$K_d = \tau_0^{-1} \cdot e^{-\frac{E_{ads}}{RT}}$$



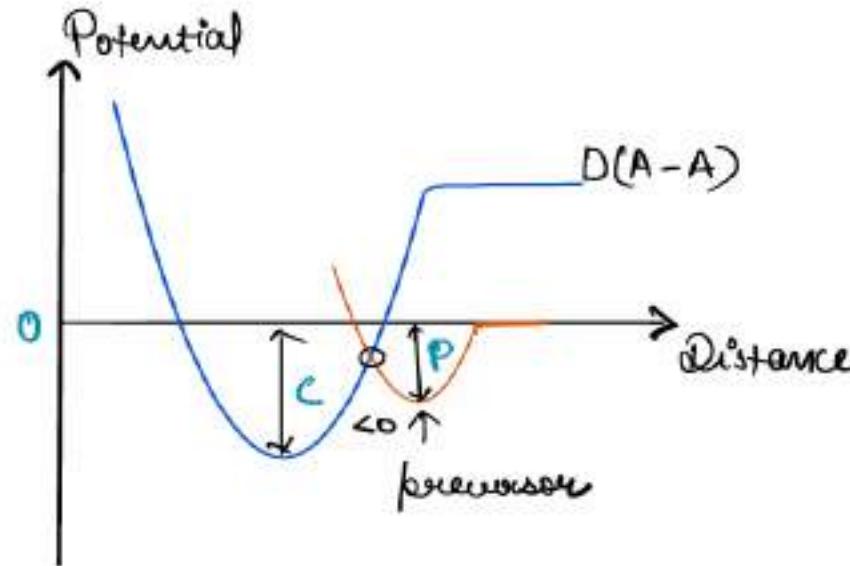
$$\tau \equiv \frac{1}{K_d}$$

PHYSICAL INTERPRETATION OF Kd

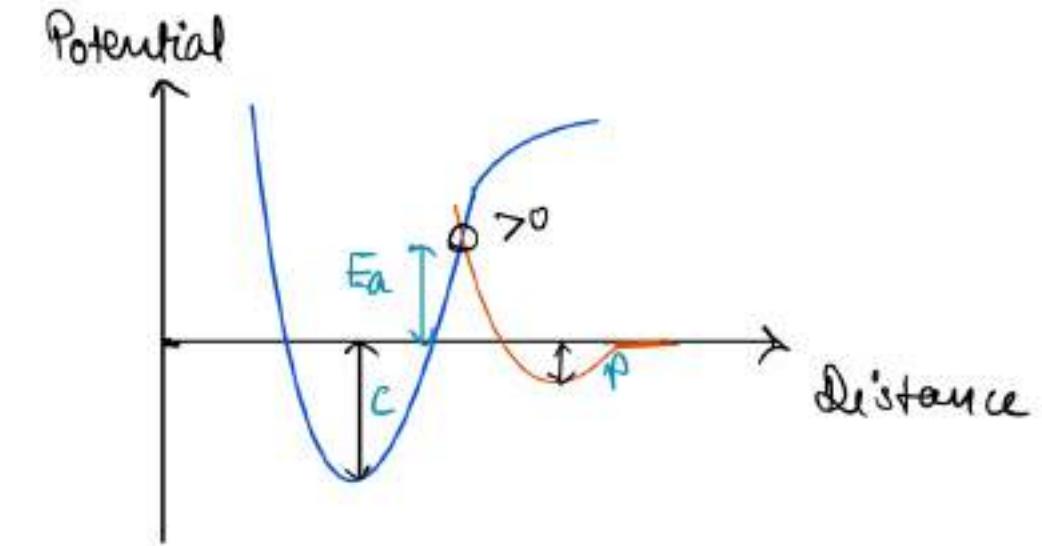
- Kd provides valuable information about the binding affinity between an adsorbate and a surface.
- Kd is inversely proportional to residence time(τ)
- A lower Kd indicates stronger binding and longer residence times.
- This relationship is fundamental in understanding and designing processes involving adsorption and desorption in chemical engineering.



Inverse relationship between residence time and Kd has been shown



Non Activated adsorption



Activated adsorption

c stands for chemisorption
p stands for physisorption

Since the intersection point is -ve , thus no activation energy is required.

The adsorbate needs to overcome a barrier to be adsorbed.
 $E_a > 0$ (as shown in the figure)

TEMPERATURE PROGRAMMED DESORPTION(TPD)

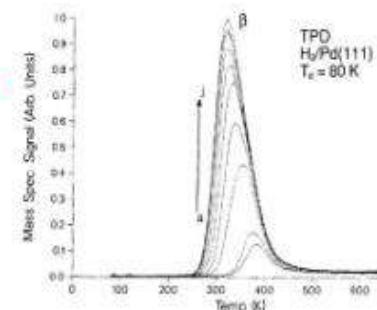
- A surface analysis techniques used to determine desorption rates that were previously adsorbed on a surface .
- We get desorption rates of each product species as a function of Temperature of the surface . This is called TPD spectra.
- As the temperature is known, it is possible to compute the activation energy.

$$T = T_0 + \alpha t$$

What Does TPD do for us?

Gives us information about:

1. Rate of desorption ✓
2. Kinetic order of desorption ✓
3. Number of adsorption sites/packing structures

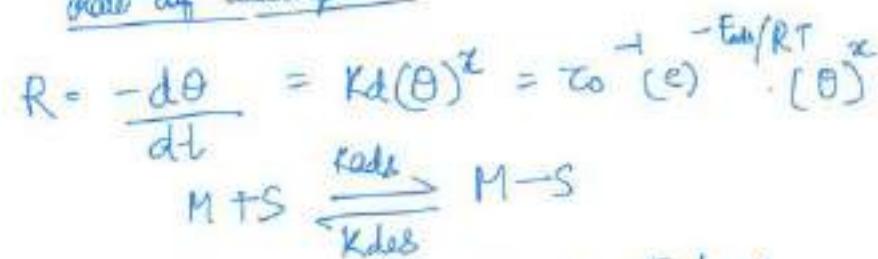


$$T = T_0 + \alpha t$$

α : heating time

t : time

Rate of desorption



$$\frac{d[M-S]}{dT} = -\frac{[M-S]}{\alpha} \left(\tau_0^{-1}(e)^{-E_{ads}/RT} \right)$$

$$\frac{d[M-S]}{dT} = \frac{d[M-S]}{dt} \left(\frac{dt}{dT} \right)$$

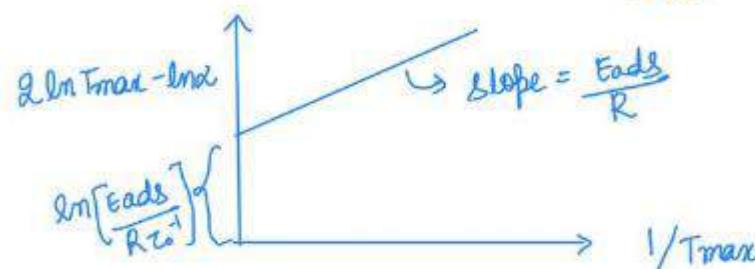
$$\frac{d[M-S]}{dT} = -\frac{\tau_0^{-1}}{\alpha} [M-S](e)^{-E_a/RT}$$

$\left. \begin{array}{l} T = T_0 + \alpha t \\ \frac{dt}{dT} = \alpha \end{array} \right\}$

$$T=T_{max} \quad \frac{d}{dT} \left(\frac{d[M-S]}{dT} \right) = 0$$

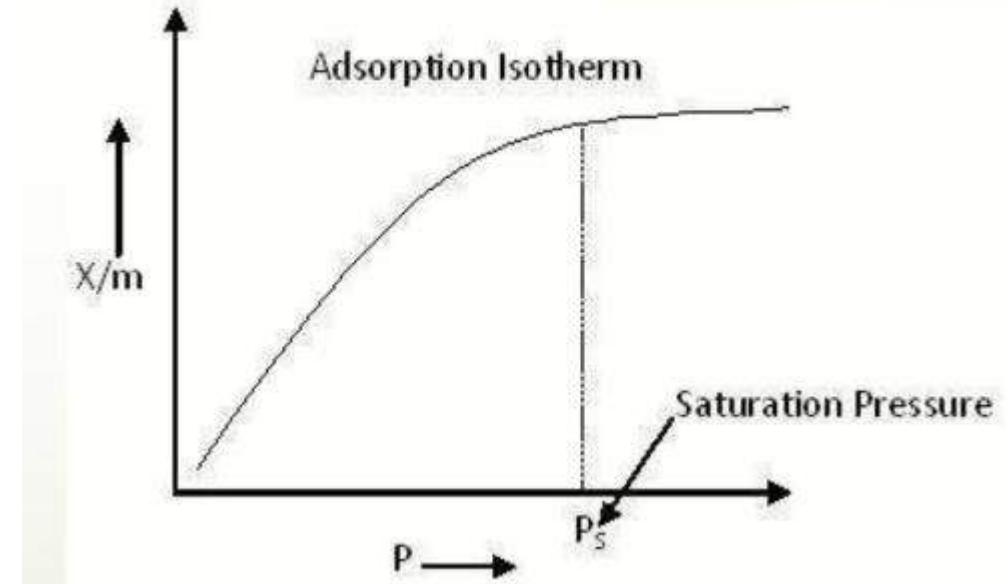
$$\Rightarrow \frac{E_a}{RT_{max}^2} = \frac{\tau_0^{-1}}{\alpha} (e)^{-E_{ads}/RT_{max}}$$

$$2 \ln T_{max} - E_a \alpha = \ln \left[\frac{E_{ads}}{R \tau_0^{-1}} \right] + \frac{E_{ads}}{RT_{max}}$$



ADSORPTION ISOTHERM

- Adsorption Isotherm are usually studied through graph known as **adsorption Isotherm** .
- That is the amount of adsorbate adsorbed on its adsorbent as a function of its pressure at a constant temperature.



Where,

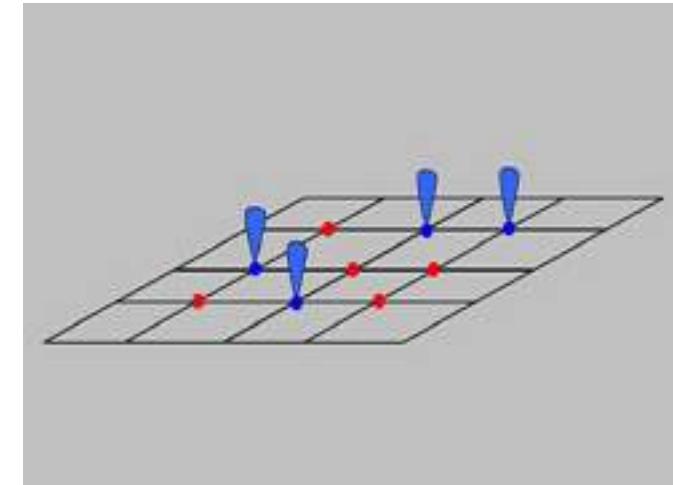
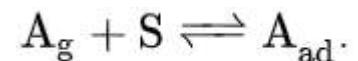
X: Amount of adsorbate

M: weight of adsorbent

P: Pressure

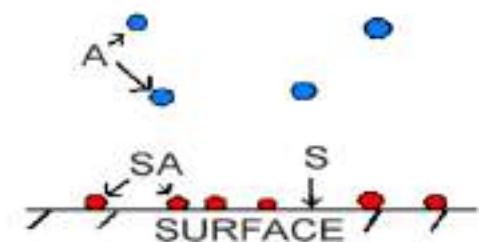
LANGMUIR ADSORPTION ISOTHERM

- Langmuir hypothesised that a given surface has a certain number of equivalent site (*Ref. Fig1*) to which a species can stick either by physisorption or chemisorption.
- A model that explains adsorption of adsorbate as an ideal gas at constant temperature on a solid surface.
- According to this model, desorption and adsorption are reversible process.
- Adsorbate binding is treated as chemical reaction between adsorbate Ag (gas molecule) and empty sorption site S.



equivalent sites on solid surface,
occupied -(blue) unoccupied -(red)

Fig 1



Mathematical form of Langmuir Isotherm

The mathematical form of the Langmuir adsorption isotherm is:

$$\theta = \frac{K \cdot P}{1 + K \cdot P}$$

Where:

- θ is the fraction of the surface covered by the adsorbed species.
- K is the equilibrium constant related to the affinity of the binding sites for the adsorbate.
- P is the pressure of the gas or the concentration of the adsorbate in the liquid phase.

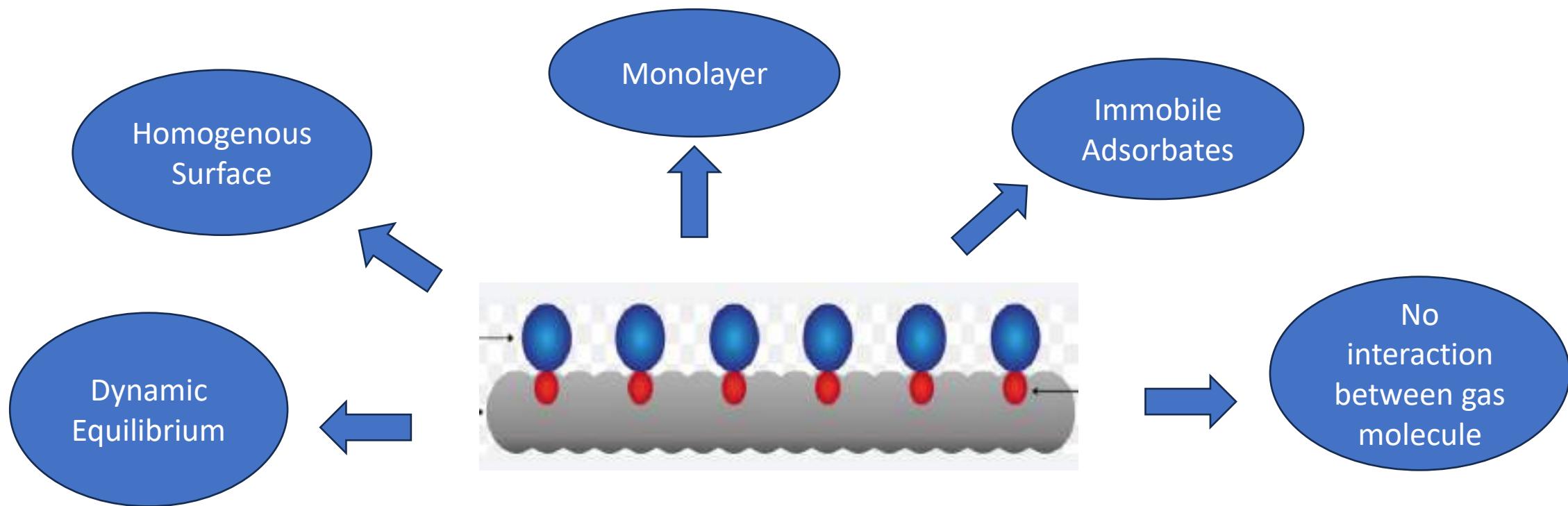
For total adsorption amount q , the equation becomes:

$$q = \frac{q_{\max} \cdot K \cdot P}{1 + K \cdot P}$$

Where q_{\max} is the maximum adsorption capacity (monolayer coverage).

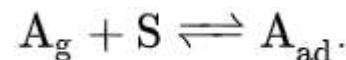
ASSUMPTIONS

- **Monolayer Adsorption**-Adsorption is limited to one layer of molecules, with no further adsorption on top of already adsorbed molecules.
- **Dynamic equilibrium**: A dynamic equilibrium exists between adsorbed and desorbed molecules, meaning adsorption and desorption rates are equal at equilibrium.
- **Homogeneous surface**: All adsorption sites are equivalent.
- **No interaction between adsorbed molecules**: Adsorbed molecules do not interact with each other
- **Immobile adsorbates** - Adsorbates are immobile on the surface of adsorbent.



DERIVATION OF LANGMUIR ADSORPTION ISOTHERM

1) Kinetic Method



$$r_{ad} = k_{ad} p_A [S],$$

$$r_d = k_d [A_{ad}],$$

where p_A is the partial pressure of A over the surface, $[S]$ is the concentration of free sites in number/m², $[A_{ad}]$ is the surface concentration of A in molecules/m² (concentration of occupied sites), and k_{ad} and k_d are constants of forward adsorption reaction and backward desorption reaction in the above reactions.

At equilibrium, the rate of adsorption equals the rate of desorption. Setting $r_{ad} = r_d$ and rearranging, we obtain

$$\frac{[A_{ad}]}{p_A [S]} = \frac{k_{ad}}{k_d} = K_{eq}^A.$$

The concentration of sites is given by dividing the total number of sites (S_0) covering the whole surface by the area of the adsorbent (a):

$$[S_0] = S_0/a.$$

We can then calculate the concentration of all sites by summing the concentration of free sites $[S]$ and occupied sites:

$$[S_0] = [S] + [A_{ad}].$$

Combining this with the equilibrium equation, we get

$$[S_0] = \frac{[A_{ad}]}{K_{eq}^A p_A} + [A_{ad}] = \frac{1 + K_{eq}^A p_A}{K_{eq}^A p_A} [A_{ad}].$$

We define now the fraction of the surface sites covered with A as

$$\theta_A = \frac{[A_{ad}]}{[S_0]}.$$

This, applied to the previous equation that combined site balance and equilibrium, yields the Langmuir adsorption isotherm:

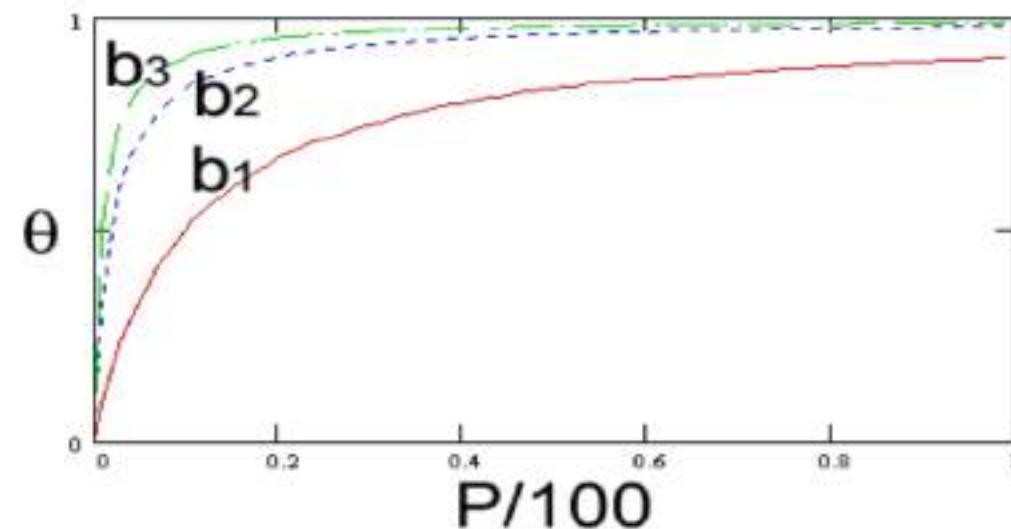
$$\theta_A = \frac{K_{eq}^A p_A}{1 + K_{eq}^A p_A} = \frac{b P_A}{1 + b P_A}$$

where $b = k_a/k_d$.

→ b is only a constant if the enthalpy of adsorption is independent of coverage

As with all chemical equilibria, the position of equilibrium will depend upon a number of factors:

- The relative stabilities of the adsorbed and gas phase species involved.
- The temperature of the system (both the gas and surface, although these are normally the same).
- The pressure of the gas above the surface



where $b_3 > b_2 > b_1$

2) Thermodynamic Method

An equilibrium constant, K, can be written:

$$K = \frac{[SA]}{[S][A]}$$

θ = Fraction of surface sites occupied ($0 < \theta < 1$)

Note that

- **[SA]** is proportional to the surface coverage of adsorbed molecules, or proportional to θ
- **[S]** is proportional to the number of vacant sites, $(1 - \theta)$
- **[A]** is proportional to the pressure of gas, P

Thus it is possible to define the equilibrium constant, b:

$$b = \frac{\theta}{(1-\theta)P}$$

Rearranging gives the expression for surface coverage:

$$\theta = \frac{bP}{1+bP}$$

>> Statistical Thermodynamic
 Derivation of Langmuir Isotherm >>

Since translational and internal energy (Rotational + vibrational) are independent, the partition function for the gas (free) can be written as:

$$\Omega^f = \Omega^f_{\text{trans}} \Omega^f_{\text{internal}}$$

And for adsorbed gas / surface state:-

$$\Omega^s = \Omega^s_{\text{site}} \Omega^s_{\text{int}} e^{Q/RT}$$

Here Ω^s is a function of temperature only and not of the degree of occupancy of the sites.

The complete partition function is obtained by multiplying Ω^s by the number of distinguishable ways of placing 'N' molecules on 's' sites.

[There are S ways of placing the first molecule,
 S-1 for the second ... and so on]

hence for N Molecules the number of ways
 is $S(S-1)(S-2) \dots (S-(N-1))$ or $\frac{S!}{(S-N)!}$

Of these, $N!$ are distinguishable since molecules are not 'labelled' and complete partition

function for N Molecules becomes \Rightarrow

$$Q_{\text{total}}^s = (Q^s)^N \binom{s}{N}$$

- $s \rightarrow s$ Possible sites where gas may adsorbs.
- $N \rightarrow N$ adsorbed gas molecules to the solid.
- $Q_{\text{total}}^s \rightarrow$ Partition function for all the adsorbed gas Molecules.
- $Q^s \rightarrow$ Partition function for a single adsorbed gas Molecules

Because the gas molecules are indistinguishable from each other, hence $(Q^s)^N \cdot (Q \times Q \dots \times Q)$ _{N times}

The helmholtz free energy of the adsorbed layer is given by \rightarrow

$$A^s = -KT \ln Q_{\text{total}}^s$$

$$A^s = -KT \ln \left((Q^s)^N \frac{s!}{(s-N)! N!} \right)$$

using Stirling's approximation for factorials,

$$x! = \left(\frac{x}{e}\right)^x$$

we get,

$$A^s = kT(-S\ln S + N\ln N + (S-N)\ln(S-N) - N\ln Q^s)$$

The chemical Potential μ^s is given by $\left(\frac{\partial A^s}{\partial N}\right)_{T,S}$

so that

$$\mu^s = kT \ln \frac{N}{S-N} - kT \ln Q^s$$

And for the gas phase:-

$$\mu^g = -kT \ln Q^g$$

At equilibrium:-

$$\mu^s = \mu^g$$

$$kT \ln \frac{N}{S-N} - kT \ln Q^s = -kT \ln Q^g$$

$$\ln \frac{N}{S-N} = \ln Q^s - \ln Q^g$$

$$\ln \left(\frac{N}{S-N} \right) = \ln \frac{Q^s}{Q^g}$$

$$\frac{N}{S-N} = \frac{Q^s}{Q^g} \quad (\text{since } Q^s = N)$$

$$\boxed{\frac{\theta}{1-\theta} = \frac{\theta^S}{\Omega^S}} \rightarrow \text{equation 1}$$

It is now necessary to examine the partition function in more detail, for which we do the following calculations :→

$P_i = \frac{n_i}{N}$ where P_i is the probability of occupying the i th energy level in a Statistical thermodynamic System.

$$P = \frac{n_i}{N} = \frac{e^{-E_i/kT}}{\sum_i e^{-E_i/kT}}$$

$n_i \Rightarrow$ no. of particles in i th energy level.
 $N \Rightarrow$ total no. of Particles
 $k \Rightarrow$ Boltzmann's const.

considering degeneracy (g_i) \rightarrow

$$P_i = \frac{g_i e^{-E_i/kT}}{\sum_j g_j e^{-E_j/kT}}$$

$$Q = \sum_n g_n e^{-\beta E_n} \quad \text{where } \beta = \frac{1}{kT}$$

for translational motion in a 1d box of length 'a' we have :-

$$E_n = \frac{n^2 \hbar^2}{8am}$$

\rightarrow for translation, $g_n=1$ as motion is continuous and there is no inherent degeneracy associated with translational energy levels.

$$Q_{\text{trans 1dim}} = \sum_n e^{-E_n \beta} \approx \int_0^\infty e^{-\frac{n^2 \hbar^2 \beta}{8am}} dn \quad \text{--- A}$$

$$\text{take } \alpha = \frac{\beta \hbar^2}{8am}$$

$$\text{Integral is of the type } I = \int_0^\infty e^{-\alpha x^2} dx$$

To solve this integral :-

$$I = \int_0^\infty e^{-\alpha x^2} dx$$

$$I = \int_0^\infty e^{-\alpha y^2} dy$$

$$I^2 = I \cdot I = \int_0^\infty e^{-\alpha(x^2+y^2)} dx dy$$

using polar coordinates : $r^2 = x^2 + y^2$
 $r dr d\theta = dx dy$

$$I^2 = \int_0^{\pi/2} \int_0^\infty e^{-\alpha r^2} r dr d\theta$$

$$= \int_0^{\pi/2} d\theta \int_0^\infty e^{-\alpha r^2} r dr$$

$$r^2 = t + 2\alpha dr = dt$$

$$= \frac{\pi}{2} \int_0^\infty e^{-\alpha t} \frac{dt}{2}$$

$$= \frac{\pi}{4\alpha} (1 - 0)$$

hence , $I = \sqrt{\frac{\pi}{4\alpha}}$

so $Q_{\text{trans}} = \sqrt{\frac{\pi}{4 \cdot B h^2}} = \sqrt{\frac{2m\pi}{Bh^2}} = \left(\frac{2\pi m k T}{h^2}\right)^{1/2} a$

(*) we could convert the summation to the integral as the states are so close together.

for 2 dimensional box,

$$\text{Ostans}_{2\text{dim}} = \left(\frac{2\pi m k T}{h^2} \right) a^2$$

for 3 dimensional box,

$$\begin{aligned}\text{Ostans} &= \left(\frac{2\pi m k T}{h^2} \right)^{3/2} a^3 \\ &= \left(\frac{2\pi m k T}{h^2} \right)^{3/2} \frac{KT}{P} \quad \uparrow\end{aligned}$$

Now Substituting Values in equation 2, we get:-

$$\frac{\theta}{1-\theta} = \frac{Q^s}{Q^d} = \frac{Q^s \int Q^s e^{Q^s/RT}}{Q^d \int \left(\frac{2\pi m k T}{h^2} \right)^{3/2}} \cdot \frac{P}{RT}$$

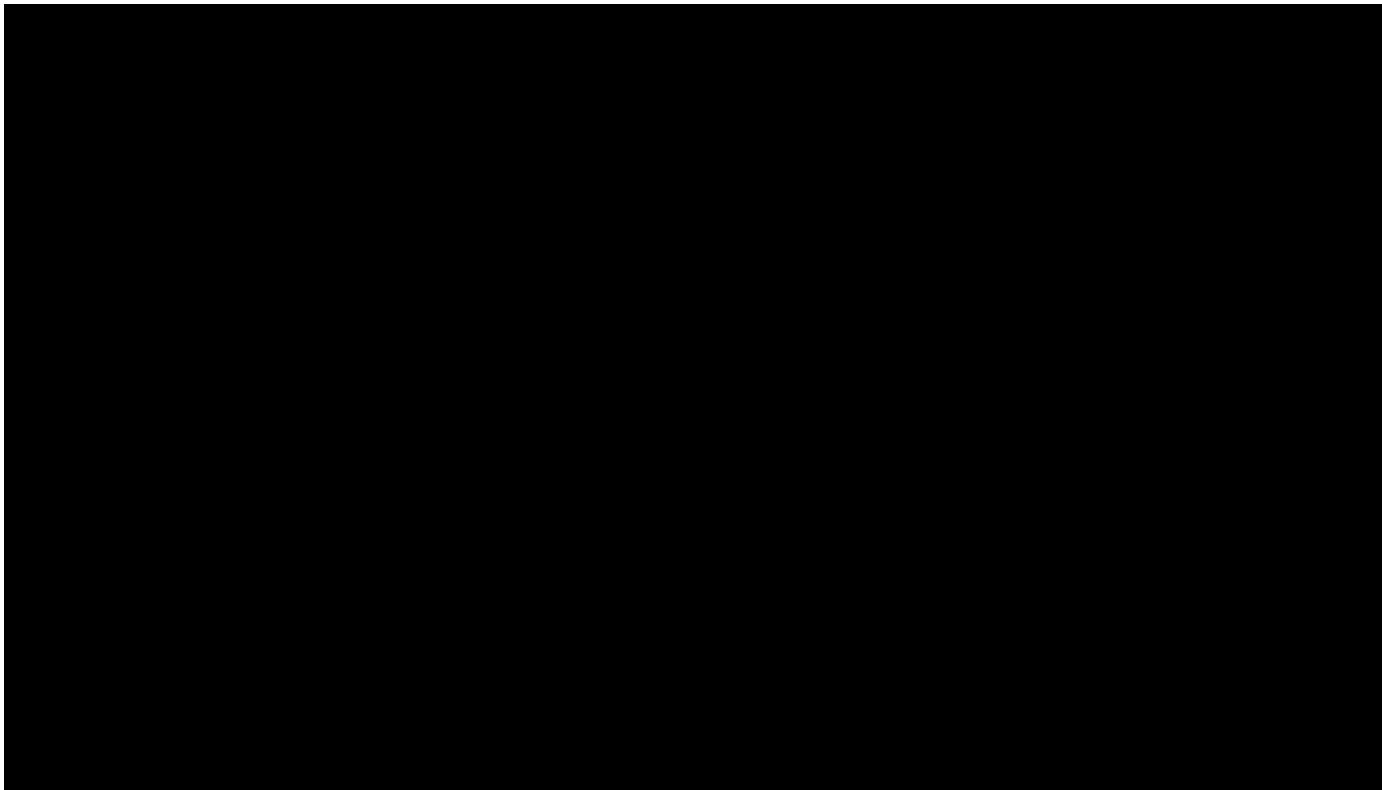
$$\frac{\theta}{1-\theta} = bP$$

$$\theta = bP - bP\theta$$

$$\theta(1+bP) = bP$$

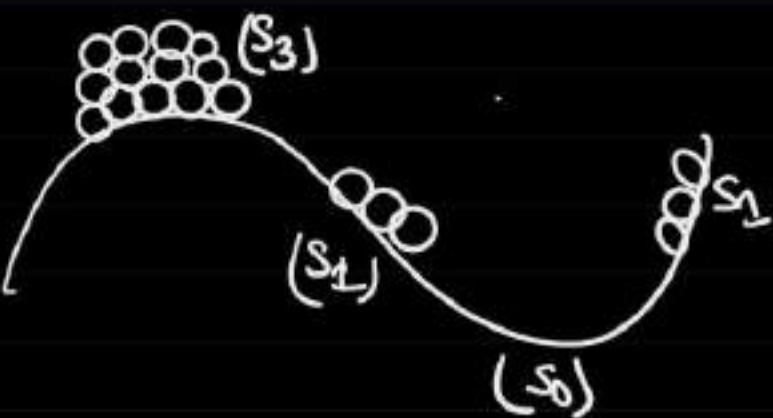
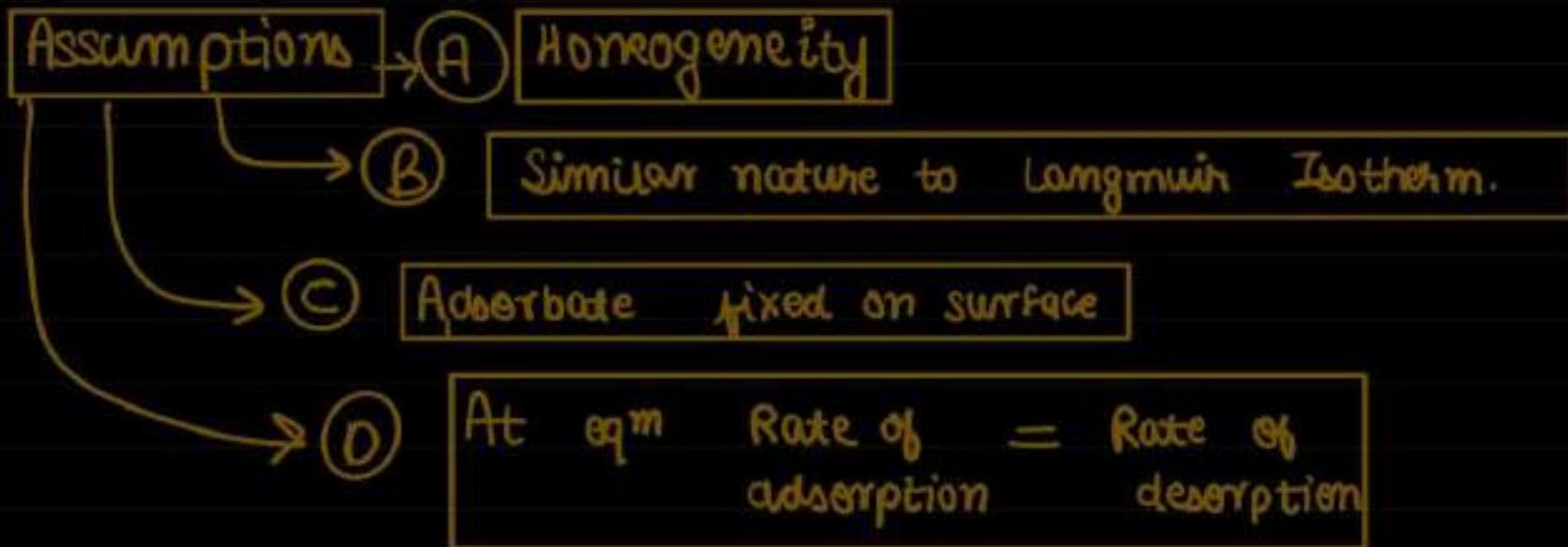
$$\boxed{\theta = \frac{bP}{1+bP}}$$

→ which is the same expression as for Langmuir isotherm.



BET ISOTHERM

This model allows multilayer adsorption



Absorption may or may not be activated
some energy of activation is required for adsorption to take place.

Desorption is always activated energy is required for breaking the molecular adhesion / attraction.

Total number of sites $\Rightarrow S$

$$S = S_0 + S_1 + S_2 + \dots + S_n = \sum_{i=0}^n s_i$$

Equation of dynamic eqm for different layers assuming rate constant for adsorption (k_a) same for all the layers and $k_{d,i}$ being rate constant for desorption for i^{th} layer.

For the first layer interaction is of surface - adsorbate type and for further layers, it is of adsorbate - adsorbate type thus

$$k_{d,1} \neq k_{d,2}$$

$$k_{d,2} = k_{d,3} = k_{d,4} = \dots = k_{d,n}$$

$$\text{First layer} \Rightarrow (K_a)(P)(S_0) = (Kd_1)(S_1)$$

$$S_1 = \left(\frac{K_a}{Kd_1} P \right) S_0$$

$$\text{Second layer} \Rightarrow (K_a)(P)(S_1) = (Kd_2)(S_2)$$

$$S_2 = \left(\frac{K_a P}{Kd_2} \right) S_1 \quad S_2 = \frac{K_a P}{Kd_2} \cdot \frac{K_a P}{Kd_1} S_0 = \frac{(K_a)^2 (P)^2}{(Kd_1)(Kd_2)} S_0$$

$$\text{third layer} \Rightarrow (K_a)(P)(S_2) = (Kd_3)(S_3)$$

$$S_3 = \left(\frac{K_a P}{Kd_3} \right) S_2 \quad S_3 = \frac{K_a P}{Kd_3} \frac{(K_a)^2 (P)^2}{Kd_1 Kd_2} S_0$$

$$S_3 = \frac{(K_a)^3 (P)^3}{Kd_1 Kd_2 Kd_3} S_0$$

we can further say that

$$S_i^* = \frac{(K_a P)^i}{Kd_1 (Kd_i)^i} S_0$$

$$S_i^* = \frac{(K_a)^i (P)^i}{(Kd_1) \underbrace{(Kd_i)}_{i-1} \dots} \quad i \neq 1$$

$$K_d = \nu e^{-E_{\text{ads}}/k_B T} \xrightarrow{\text{Boltzmann's constant } 1.38 \times 10^{-23} \text{ kg m}^2/\text{s}^2\text{K}}$$

frequency factor

$$K_{d1} = \nu e^{-E_{\text{ads}}/k_B T}$$

$$K_{d2} = \nu e^{-E_v/k_B T}$$

vapourization

we may see this adsorption in terms of condensation and evaporation

→ when gas molecules adsorb on the surface they now key condense

$$S_i = \frac{(K_a)^i (P)^i}{(K_{d1}) (K_{d2})^{i-1}} S_0 = \frac{(K_a)^i (P)^i}{(\nu e^{-E_{\text{ads}}/k_B T}) (\nu e^{-E_v/k_B T})^{i-1}} \times \frac{\nu e^{-E_v/k_B T}}{\nu e^{-E_v/k_B T}}$$

$$= \frac{(K_a)^i (P)^i (S_0)}{(\nu e^{-E_v/k_B T})^i} e^{(E_{\text{ads}} - E_v)/k_B T}$$

$$= \left[\frac{(K_a) (P)}{\nu e^{-E_v/k_B T}} \right]^i (S_0) \left(e^{(E_{\text{ads}} - E_v)/k_B T} \right)$$

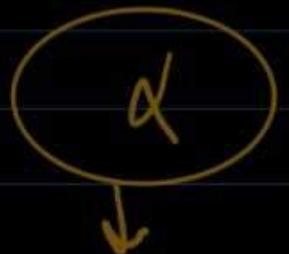
$$S_i = (x)^i (c) (S_0)$$

V = volume of the adsorbate gas on surface

V_m = volume for monolayer formation.

$$V = \sum_{i=1}^n v_i^o \quad (\text{volume of the } i\text{th layer}) \propto \text{no. of molecules in } i\text{th layer}$$

$\sum_{i=1}^n i s_i^o$ (weighted term for number of molecules in diff layers).



Proportionality

$$V \Rightarrow \sum_{i=0}^{\infty} i x^i s_0 = s_0 \sum_{i=0}^{\infty} i x^i = \frac{c s_0 x}{(1-x)^2}$$

$$V_m \propto S = \sum_{i=1}^n s_i^o = s_0 + \sum_{i=1}^n s_i^o = s_0 + \sum_{i=1}^{\infty} x^i c s_0 = \frac{c s_0 (x)}{(1-x)} + s_0$$

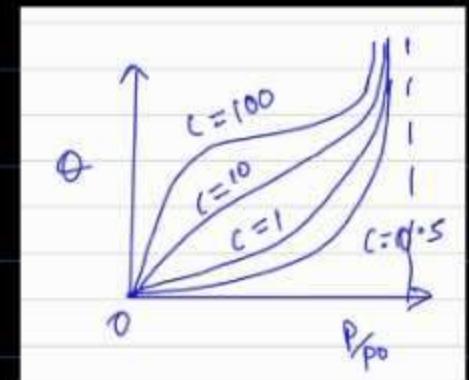
$$Q = \frac{V}{V_m} = \frac{\frac{c s_0 x}{(1-x)^2}}{s_0 + \frac{c s_0 x}{(1-x)}} = \boxed{\frac{c x}{(c x + 1 - x)(1-x)}}$$

$$c = e^{(E_{ads} - \epsilon v)/k_B T}$$

; ;

($v \rightarrow \infty$)

$$\chi = 1 \Rightarrow \chi = \frac{k_a p}{v_e^{-\epsilon v / k_B T}} = \frac{k_a i p}{k_d i \geq 2}$$



$$\text{If } P \rightarrow P_0, \chi = P/P_0$$

(iii) At saturation pressure (P_0)

$$(K_{ai})(P_0)(N) < (K_{di})(N)$$

$$P_0 < \frac{K_{ai}}{K_{di}}$$

<

At saturation

rate of adsorption < Rate of desorption

$$\chi = \frac{K_{ai}}{K_{di}} P < 1$$

$$\chi = \frac{P}{P_0} < 1$$

BET Surface Area

$$\text{specific surface area } A_{sp} = \frac{\text{Total surface area}}{\text{Total mass}}$$

$$\text{for spherical particles} = \frac{n \times 4\pi R_s^2}{n \times \frac{4}{3} \pi R_s^3} = \frac{3}{R_s}$$

$$\text{Also, } Q = \frac{n^s \text{ (mole)} \times N_A \times 6^\circ \text{ (cm}^2\text{)}}{w \text{ (gm)} \times A_{sp} \text{ (gm/cm}^2\text{)}} \quad [\text{at saturation } Q=1]$$

6° = footprint (area of molecule cm^2)

$$A_{sp} = \frac{n^s N_A 6^\circ}{w}$$

Limitations of BET Isotherm model \Rightarrow

only valid when
 $P/P_0 = 0.05 \text{ to } 0.3$

Electrified interfaces

Electrified interfaces occur when there is a potential difference across an interface, such as a metal-solution interface due to the application of an external electric field.

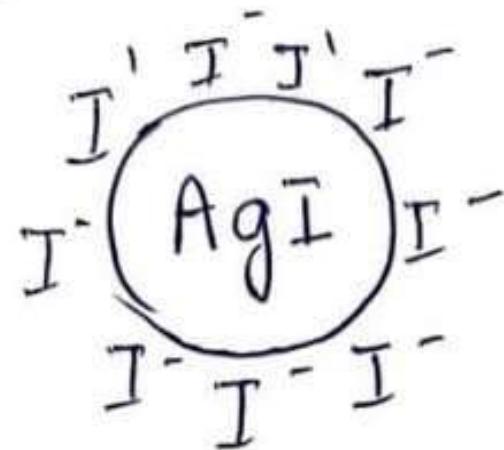
e.g- an electrode-electrolyte

There are Two ways in which electrified interfaces can be formed-

1) Adsorption of Ions:

- When ions from the solution adsorb onto a charged surface, they alter the surface potential. This process is critical in electrochemistry as it impacts reaction rates, potential distribution, and the behaviour of the interface.
- Ion adsorption can either increase or decrease the surface charge density, depending on the type of ions (anions or cations) and the surface's initial charge.

$\text{AgI} \rightarrow \text{I}^-$ ions are adsorbed on the surface of AgI colloidal particles because of which colloidal particles of AgI becomes negatively charged.



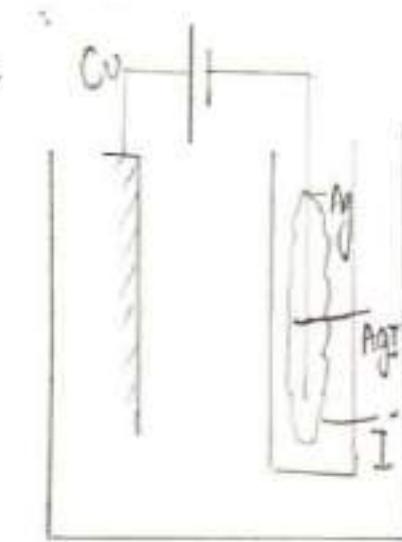
2) Surface Functional Groups and Dissociation:

- Many surfaces have functional groups (e.g., -COOH, -OH) that can dissociate in solution.
- Example: Carboxyl (-COOH) groups on a surface can dissociate to form carboxylate ions (COO^-) and protons (H^+).
- Reaction: $\text{R-COOH} \rightleftharpoons \text{R-COO}^- + \text{H}^+$
- This dissociation affects the surface charge, which in turn influences the electrochemical behaviour of the interface.

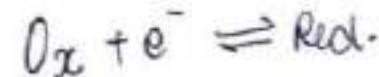
- **Impact on Surface Potential and pH**
- As functional groups dissociate or ions adsorb onto the surface, the pH of the solution near the interface changes, impacting the chemical environment of the interface.
- Changes in surface potential due to ion adsorption and functional group dissociation are essential in applications like corrosion, sensor design, and catalysis.

The electrostatic double layer force at the fluid–fluid and liquid–solid interfaces becomes important when charged molecules are present at the interfaces. The charge may arise by the adsorption of a charged ion (such as an ionic surfactant or a polyelectrolyte) at the interface, or dissociation of an ionisable surface group (e.g. the dissociation of $-COOH$ or $-SiOH$ groups present on the surface of a solid). The dissociated group attached to the surface attracts the counterions by Coulomb force. On the other hand, osmotic pressure forces the counterions away from the surface and from each other. The dispersion of the counterions is thermodynamically favourable because it increases the entropy. A balance between the Coulomb attraction and osmotic repulsion maintains the double layer. Two similarly-charged surfaces encounter osmotic repulsion when they approach each other due to the reduction in entropy. The double layer force is very important in the stabilisation of emulsions, foams, and colloids. The combined effect of van der Waals and double layer forces between two surfaces is described by the Derjaguin–Landau–Verwey–Overbeek (DLVO) theory.

E vs I graph for Ag^{I}



Inversible electrode,
ideally non polarizable
electrode



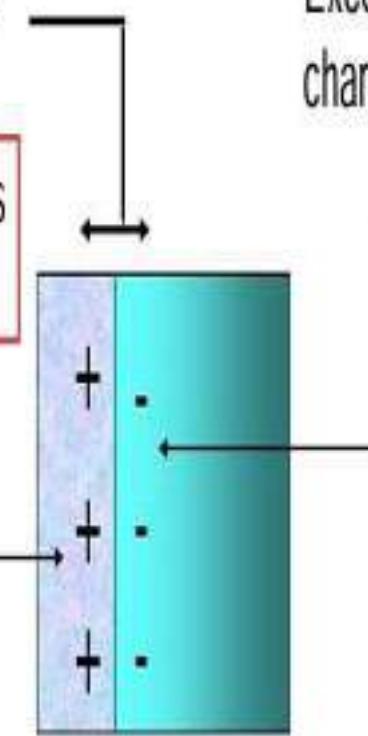
Newt eqn \Rightarrow

$$E = E^\circ + \frac{RT}{nF} \ln \left[\frac{\text{Ox}}{\text{Red.}} \right]$$

E-Field generated

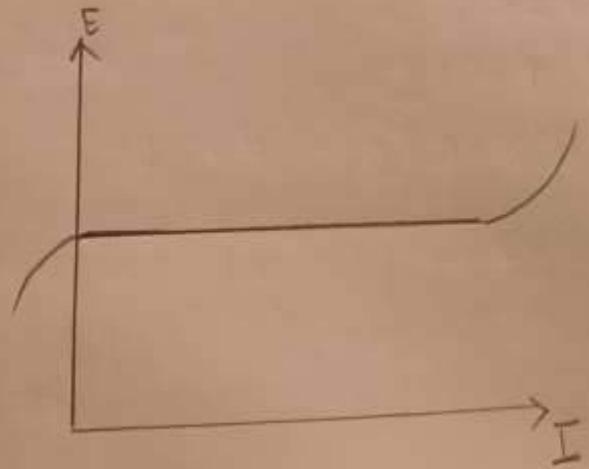
An Electrical Double Layer is set up at M/S interface

Excess positive charge density



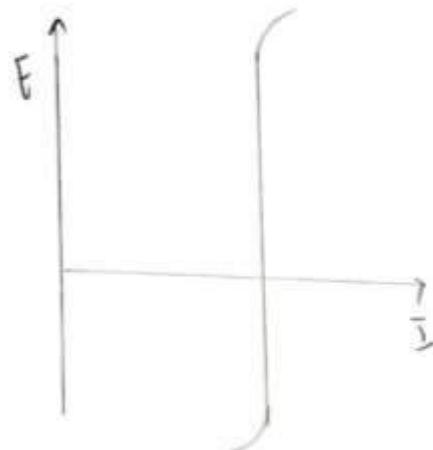
Excess negative charge density

for non polarizable electrode-



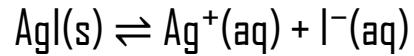
- * since the electrode is non-polarizable, any small change in current result in minimal change in electrode potential.
- * As the current increases significantly, especially in an AgI colloidal solution where ions are involved, the potential may eventually start to shift. However, the reversibility and non-polarizability characteristics mean this shift will still be much less pronounced than for a polarizable electrode. The graph may show a slight upward curve, but much flatter than a typical electrode potential response.

for ideally polarizable electrode



- * The potential increases more significantly with increasing current, especially beyond the low current region.
- * This strong upward trend reflects the polarization effect, where the electrode potential shifts due to increasing current, characteristic of polarizable electrodes.

Finding equilibrium concentration of ions



$$K_{\text{sp}} = [\text{Ag}^+][\text{I}^-] = s^* s = s^2$$

$$s = \sqrt{(7.5 \times 10^{-17})} \approx 8.5 \times 10^{-9} \text{ M}$$

- Nernst equation

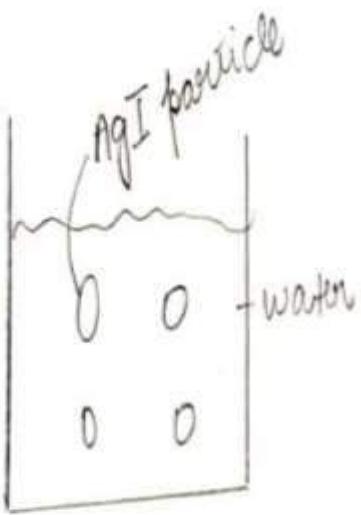
$$E = E^\circ + (RT \ln(\text{Ox} / \text{Red}) / nF)$$

- It is used to calculate the cell potential under non-standard conditions
- The **point of zero charge (PZC)** is the pH value at which the net surface charge of an adsorbent (like a solid surface) is zero.
- Finding potential of zero charge for AgI electrode

$$\Psi_0 = 2.303 (RT \log [C/C_{\text{pzc}}]) / nF$$

At PZC, $E^\circ = 0$, $c = 8.5 \times 10^{-9} \text{ M}$, $C_{\text{pzc}} = 3 \times 10^{-9} \text{ M}$

$$\Psi_0 = -150 \text{ mV}$$



$$K_{sp} = 7.5 \times 10^{-17} \text{ at } 25^\circ\text{C}$$

$$[Ag] = [I] = 8.5 \times 10^{-9}$$

↓

specifically adsorbed
or

preferentially adsorbed

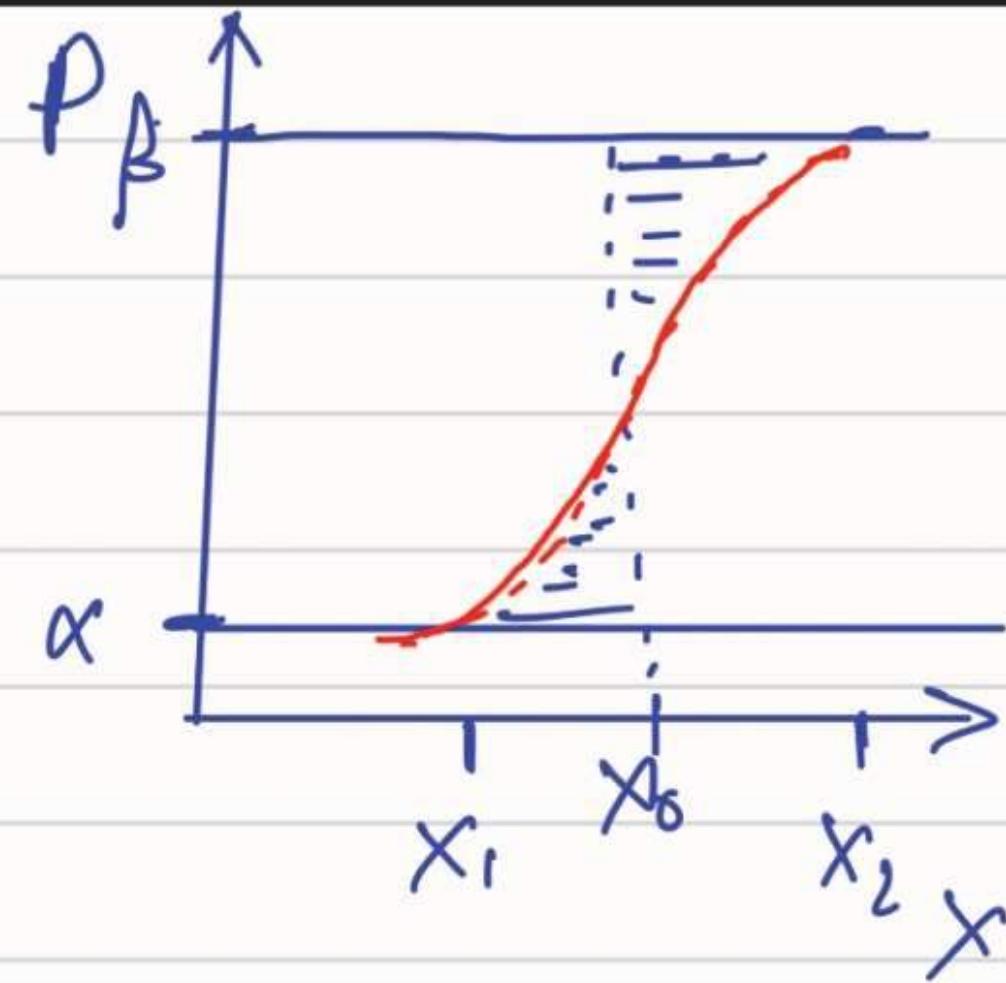
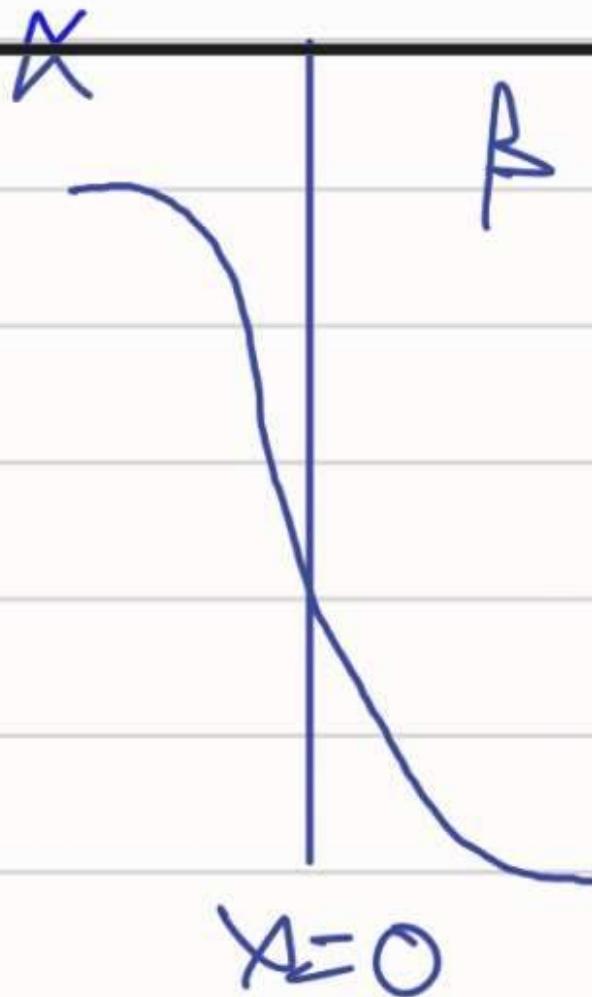
point of zero charge, $C_{pzc, pzc=0V}^{\text{conc}} = 3 \times 10^{-9}$
potential of zero charge ↓

Taking
this
reference

$$\Psi_0 = \frac{2.303}{nF} RT \log \left[\frac{c}{C_{pzc}} \right]$$

if $[Ag^+] = 8.5 \times 10^{-9}$
(surface $\Psi_0 = -150 \text{ mV}$
potential)

Gibbs adsorption isotherm.



6.3 GIBBS ADSORPTION EQUATION

The exact relationship between adsorption and surface tension was derived by J.W. Gibbs. The Gibbs adsorption equation is one of the most important equations of surface science. It is used to determine the surface activity of a surfactant at air–water or oil–water interface. It is also a basis for deriving the surface equations of state which describe the variation of surface tension with the concentration of surfactant. Many derivations of varying rigidity and complexity are available in the literature. The following derivation is based on the method of Gibbs involving the use of the thermodynamic potential. If γ is the surface energy per unit area and s is the surface area, then the free energy of a two-component system is given by the Gibbs–Duhem equation

$$G = \gamma s + \mu_1 n_1 + \mu_2 n_2 = 0 \quad (6.4)$$

where the μ -terms represent chemical potentials and the n -terms represent the number of moles. The subscript '1' stands for the solvent and the subscript '2' stands for the solute. The term γs represents the surface contribution to the free energy. Upon differentiation, Eq. (6.4) gives,

$$dG = \gamma ds + sd\gamma + \mu_1 dn_1 + n_1 d\mu_1 + \mu_2 dn_2 + n_2 d\mu_2 \quad (6.5)$$

From another Gibbs–Duhem equation at constant temperature and pressure, we have

$$dG = \gamma ds + \mu_1 dn_1 + \mu_2 dn_2 \quad (6.6)$$

where the increase in surface area is ds . Now, from Eqs. (6.5) and (6.6), we get

$$sd\gamma + n_1 d\mu_1 + n_2 d\mu_2 = 0 \quad (6.7)$$

Now, let us imagine to divide the system into two parts: one part consists of the surface region, and the other part consists of the remainder of the solution. The former is called the *surface phase* and the latter is called the *bulk phase*, which is free from the surface effects. If the number of moles of the two components in the bulk phase are denoted by n_1^0 and n_2^0 (corresponding to n_1 and n_2 in the surface phase), the following relationship applies to the bulk phase [whereas Eq. (6.7) holds for the surface phase]:

Now, let us imagine to divide the system into two parts: one part consists of the surface region, and the other part consists of the remainder of the solution. The former is called the *surface phase* and the latter is called the *bulk phase*, which is free from the surface effects. If the number of moles of the two components in the bulk phase are denoted by n_1^0 and n_2^0 (corresponding to n_1 and n_2 in the surface phase), the following relationship applies to the bulk phase [whereas Eq. (6.7) holds for the surface phase]:

$$n_1^0 d\mu_1 + n_2^0 d\mu_2 = 0 \quad (6.8)$$

Let us multiply Eq. (6.8) by n_1 / n_1^0 to obtain

$$n_1 d\mu_1 + n_1 \left(\frac{n_2^0}{n_1^0} \right) d\mu_2 = 0 \quad (6.9)$$

Subtracting Eq. (6.9) from Eq. (6.7), we get

$$sdy + \left(n_2 - \frac{n_1 n_2^0}{n_1^0} \right) d\mu_2 = 0 \quad (6.10)$$

Therefore,

$$-\frac{d\gamma}{d\mu_2} = \frac{n_2 - \frac{n_1 n_2^0}{n_1^0}}{s} \quad (6.11)$$

Now, n_2 moles of the solute are associated with n_1 moles of the solvent in the surface phase, and $n_1 n_2^0 / n_1^0$ moles of the solute are associated with n_1 moles of the solvent in the bulk phase. Therefore, the right side of Eq. (6.11) may be regarded as the excess concentration of solute per unit area of surface. This excess concentration is denoted by Γ_2 . Therefore,

$$\Gamma_2 = -\frac{d\gamma}{d\mu_2} \quad (6.12)$$

Although the arbitrary amount n_1 was used to define Γ_2 , it is independent of this quantity, since the quantity $d\gamma/d\mu_2$ depends on the nature of the surface phase only, not on its amount. The actual amount of the surface phase does not affect the value of Γ_2 as long as the entire part of the system that comes under the influence of the surface is included.

The chemical potential of the solute is related to its activity by the relation

$$\mu_2 = \mu_2^0 + RT \ln a_2 \quad (6.13)$$

At constant temperature, we have

$$d\mu_2 = RT d \ln a_2 \quad (6.14)$$

Therefore, from Eq. (6.12), we get

$$\Gamma_2 = -\frac{1}{RT} \frac{d\gamma}{d \ln a_2} \quad (6.15)$$

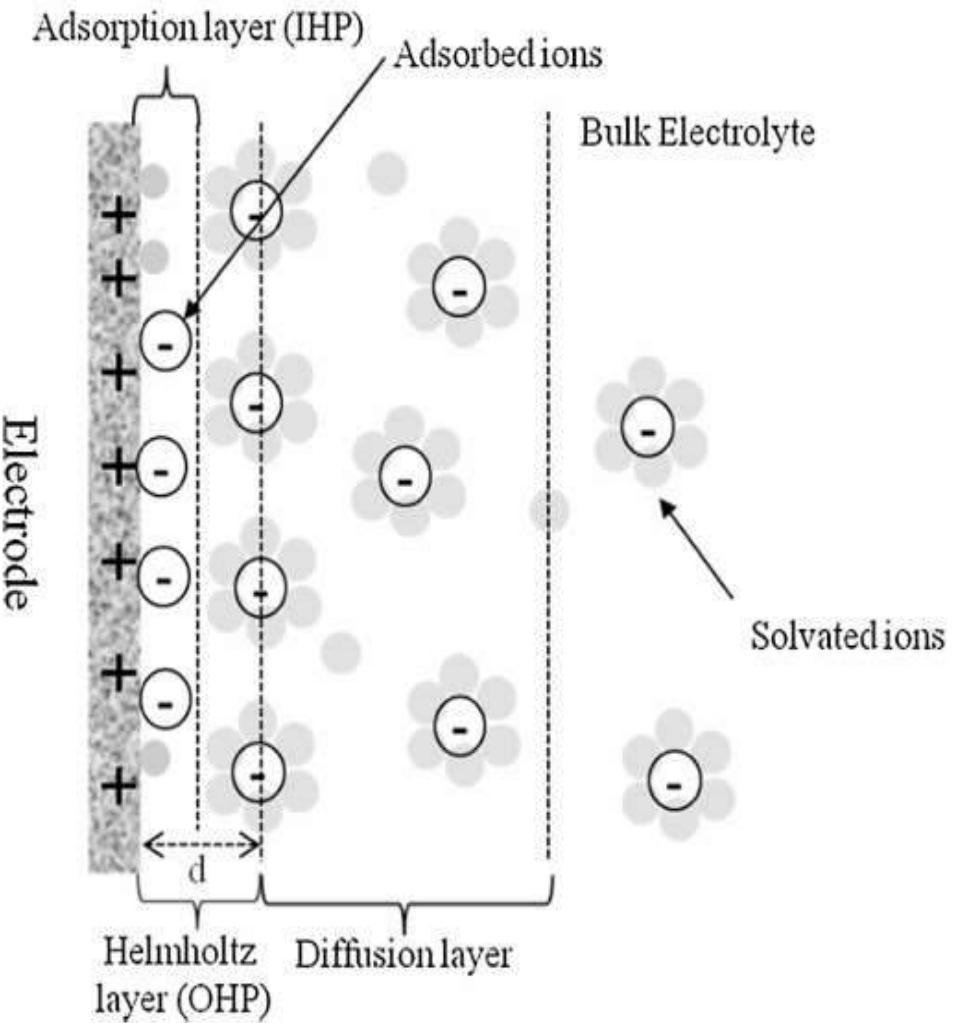
In practice, this equation is usually applied to the solute. However, it should hold for either component of a binary system. The subscript, therefore, can be omitted giving the following equation:

$$\Gamma = -\frac{1}{RT} \frac{d\gamma}{d \ln a} = -\frac{a}{RT} \frac{d\gamma}{da} \quad (6.16)$$

Equation (6.16) is known as the *Gibbs adsorption equation*. In its derivation, we have not made any assumption regarding the system or the surface. Its obvious application is to a gas-liquid or liquid-liquid interface. Therefore, γ represents surface tension in the former case and interfacial tension in the latter. Since Γ is expressed in mol/m², it is not a conventional concentration term. Nonetheless, it is a definite quantity, which can be measured by radiotracer (Tajima, 1970) and neutron reflection (Lu et al., 1993) techniques.

Helmholtz Capacitor

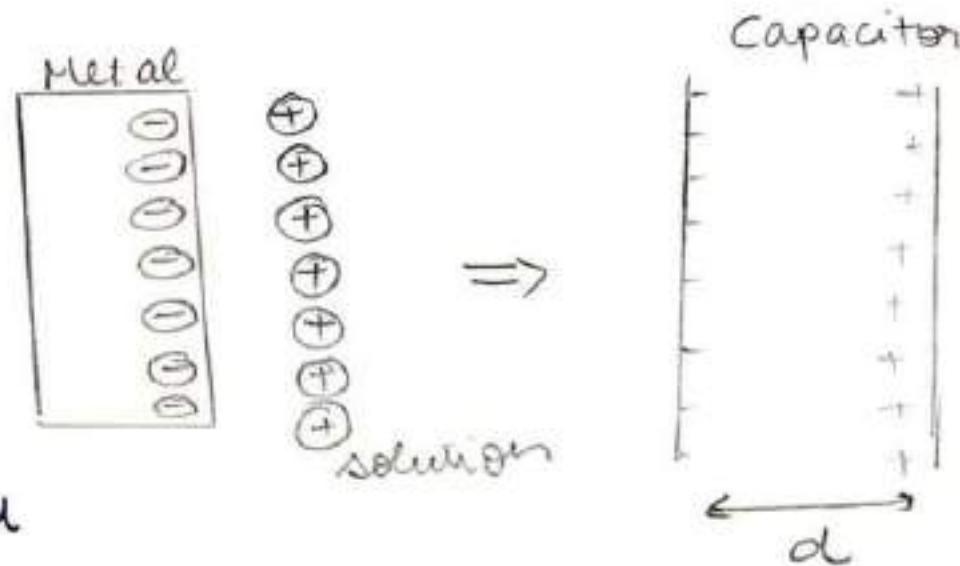
- The Helmholtz Model is a simplified model that describes the structure of the electrical double layer at the interface between a solid electrode and an electrolyte solution.
- In the Helmholtz model, the double layer is simplified as two parallel plates of charge:
- **Inner Helmholtz Plane (IHP):** A layer of ions adsorbed directly onto the electrode surface.
- **Outer Helmholtz Plane (OHP):** A layer of solvated ions that are electrostatically attracted to the electrode but remain separated from the surface by a layer of solvent molecules.



HELMHOLTZ MODEL

Key concepts →

- * In an electrolyte solution near a charged surface, ions of opposite charge are attracted to the surface, forming a compact layer of ions.

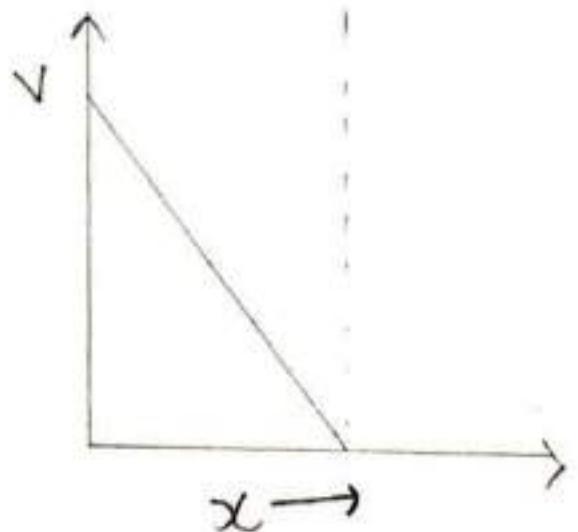
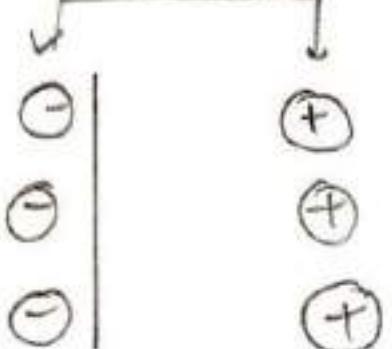


This creates a "double layer" of charge: one layer on the solid surface and an adjacent layer of counter ions in the soln.

* This model treats the double layer as if it were a simple capacitor. The charged surface and the layer of counter-ions are separated by a small distance, d , similar to the plates of a parallel-plate capacitor. This separation creates a potential difference across the double layer.

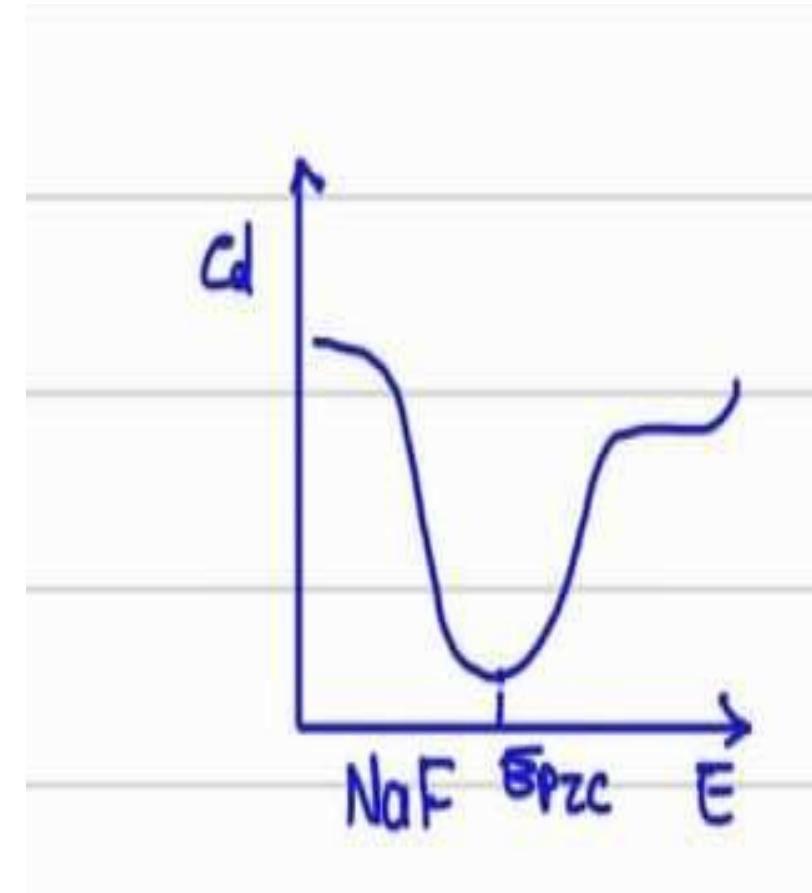
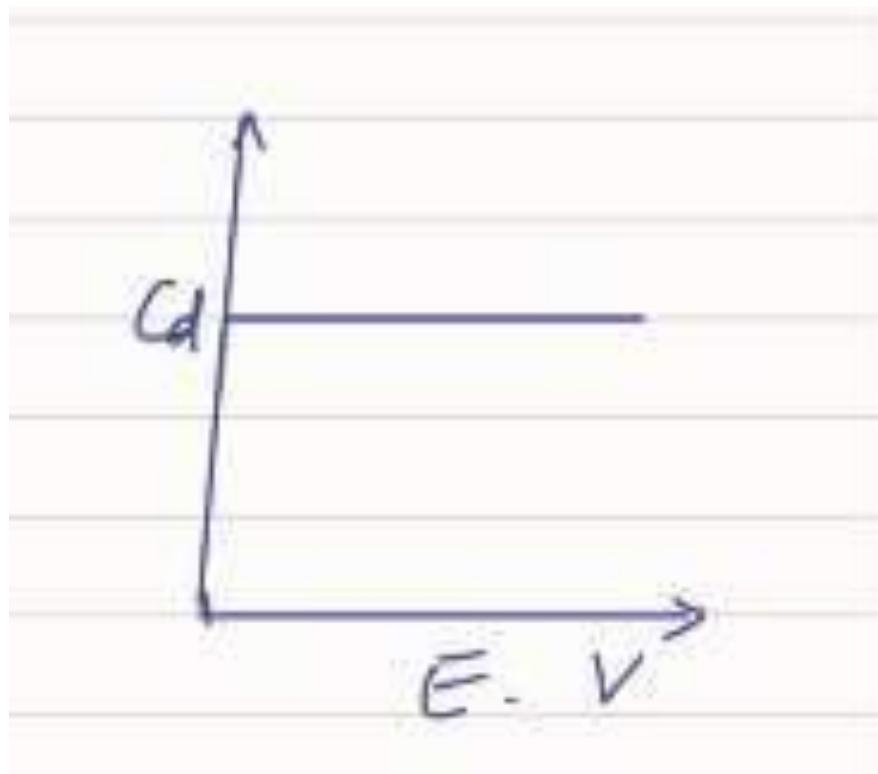
$$\text{Capacitance} = \frac{\epsilon_r \epsilon_0}{d}$$

should be
equal &
opposite



$\tilde{\epsilon}_r \rightarrow$ dielectric const. of medium
 $\epsilon_0 \rightarrow$ permittivity of free
space

Variation of V with distance
(potential decreasing
linearly)



5.3.1 The Models of Electrostatic Double Layer

One of the earliest models of electrostatic double layer was the capacitor model in which the double layer was considered as a parallel-plate condenser in which two parallel plates are separated by a non-conducting medium (i.e. a dielectric) with a potential difference between them (Figure 5.5). The potential drop across two locations separated by a small distance (which is of the order of molecular diameters) is depicted in this figure. Suppose that the surface is positively charged (which is represented by the left plate) and the atmosphere of the negatively charged counterions is represented by the right plate. This visualisation of the ionic atmosphere near a charged surface originated the term *electrostatic double layer*. This is, however, a highly simplified picture of the double layer as evident from the present-day experimental observations and theories. A more realistic description of the double layer involves the diffuse part of the double layer extending into the solution as shown in Figure 5.6.

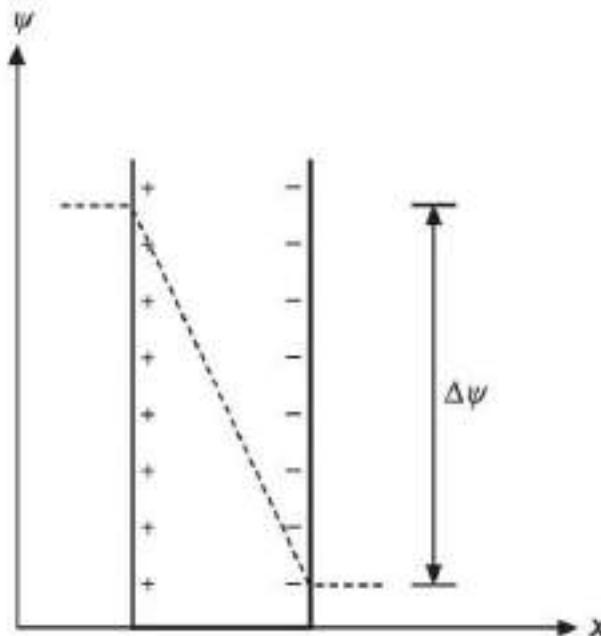
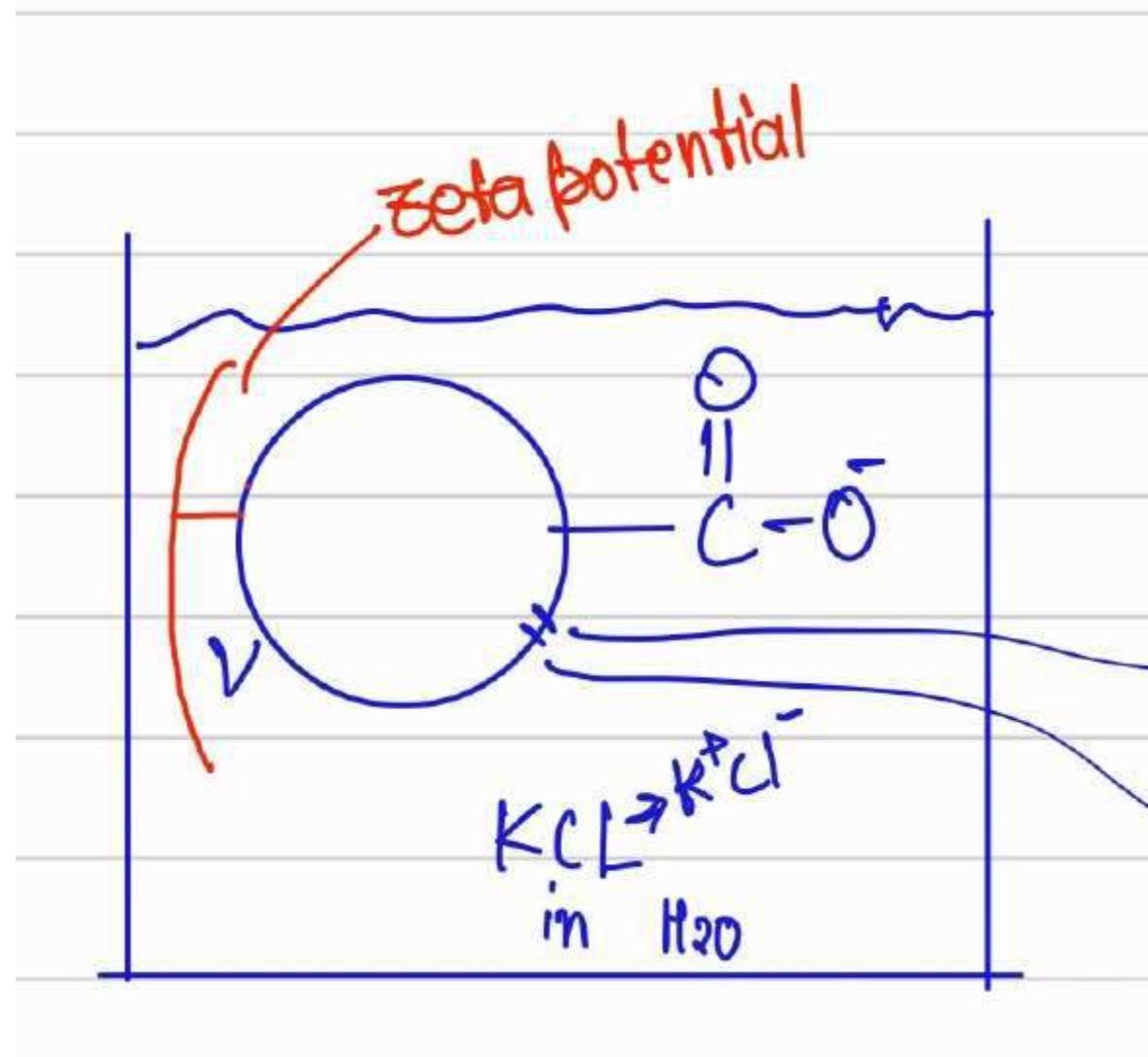


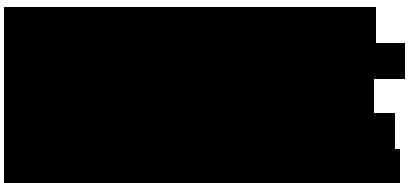
Figure 5.5 The parallel-capacitor model of electrostatic double layer.

The Coulomb attraction by the charged surface groups pulls the counterions back towards the surface, but the osmotic pressure forces the counterions away from the surface. This results in a diffuse double layer. The various parts of the electrostatic double layer have been shown in Figure 5.6. The double layer very near to the surface is divided into two parts: the Stern layer and the Gouy–Chapman diffuse layer. The compact layer of adsorbed ions is known as *Stern layer* in honour of Otto Stern (1924) who proposed the existence of this layer. This layer has a very small thickness (say, 1 nm). The Stern layer has been discussed at various levels of sophistication (Adamson and Gast, 1997; Grahame, 1947; Hiemenz and Rajagopalan, 1997; Hunter, 2005; Lyklema, 1995). The counterions specifically adsorb on the surface in the inner part of the Stern layer, which is known as *inner Helmholtz plane* (IHP). The potential drop in this layer is quite sharp, and it depends on the occupancy of the ions. The *outer Helmholtz plane* (OHP) is located on the plane of the centres of the next layer of non-specifically adsorbed ions. These two parts of the Stern layer are named so because the Helmholtz condenser model was used as a first approximation of the double layer very close to the surface. The diffuse layer begins at the OHP. The potential drop in each of the two layers is assumed to be linear. The dielectric constant of water inside the Stern layer is believed to be much lower (e.g. one-tenth) than its value in the bulk. The value is lowest near the IHP.



When a liquid moves past a solid surface, the relative velocity between the liquid and the surface is zero at the surface. At some distance from the surface, the relative motion sets in between the immobilised layer and the fluid. This boundary is known as the *surface of shear*. The Stern layer is quite immobile. The surface of shear may not coincide with the boundary of the Stern layer, but it may be located somewhat farther. The location of the surface of shear can be estimated from the knowledge about the adsorption from solution and the Stern layer. Therefore, it can be concluded that the surface of shear is located inside the double layer at a distance approximately equal to the thickness of the Stern layer from the surface. The potential at this surface is known as ***zeta potential***.

THANK-YOU

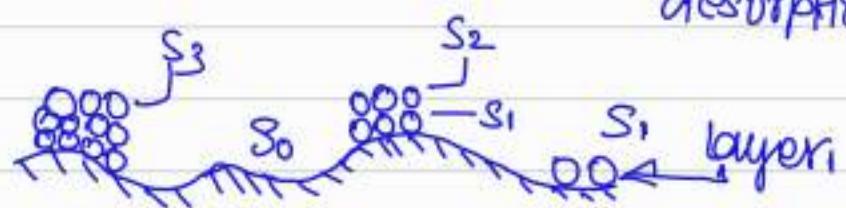


19 Oct

BET isotherm

⇒ Assumptions : Similar to Langmuir

- Homogeneity
- Adsorbate fixed on surface
- At equilibrium ⇒ Rate of adsorption = Rate of desorption.



- Adsorption may or may not be activated
- desorption is always activated.

$$\text{Total site} \Rightarrow S = S_0 + S_1 + S_2 + \dots + S_n = \sum_i S_i$$

$I = 0$

Bare Surface

Rate of qds = Rate of desorption

$$\leftarrow k_a p S_0 = K_d S_1 \Rightarrow S_1 = \left[\frac{k_a}{K_d} p \right] S_0$$

Assuming
rate
constant is
same

$$k_a p S_1 = K_d S_2 \Rightarrow S_2 = \left[\frac{k_a}{K_d} p \right] S_1$$

$$(K_d_2 = K_d_3 \dots)$$

$$S_2 = \left[\frac{\frac{k_a^2}{K_d} p^2}{K_d_1 K_d_2} \right] S_0$$

$$S_3 = \left[\frac{\frac{k_a^2}{K_d} p^2}{K_d_2} \right] S_1$$

$$S_i^\circ = \left[\frac{k_a^{i-1} p^{i-1}}{k_{d_2}^{i-1}} \right] S_1$$

$$S_i^\circ = \left[\frac{k_a^i p^i}{k_{d_2}^{i-1} k_{d_1}} \right] S_0$$

$$k_d = V e^{-E_{ads}/k_B T}$$

$$k_{d_1} = V e^{-E_{ad}/k_B T}, \quad k_{d_2} = V e^{-B_V/k_B T}$$

$$\rightarrow S_i^\circ = \left[\frac{k_a p}{V e^{-E_V/k_B T}} \right] e^{(E_{ad} - B_V)/k_B T} S_0$$



$$S_i^\circ = \chi^i c S_0$$

$$\sum_{i=1}^{\infty} S_i^\circ = CS_0 \sum_{i=1}^{\infty} \chi^i = \frac{CS_0 \chi}{1-\chi}$$

$$S = S_0 + S_1 + S_2 + \dots + S_n$$

$$S = S_0 + \sum_{i=1}^n \chi^i c S_0$$

Let V = Total volume of adsorbed gas on surface.

V_m = Volume for mono layer formation

$$V = \sum_{i=1}^n V_i^\circ \times \sum_{i=1}^n i S_i^\circ = \sum_{n=1}^{\infty} n x^n = \frac{x}{(1-x)^2}$$

$$V_m \propto S \Rightarrow V_m = S_0 + \sum_{i \geq 1} x_i^\circ C S_0$$

$$\frac{V}{V_m} = 0 = \frac{Cx}{(1-x)[1+(C-1)x]}$$

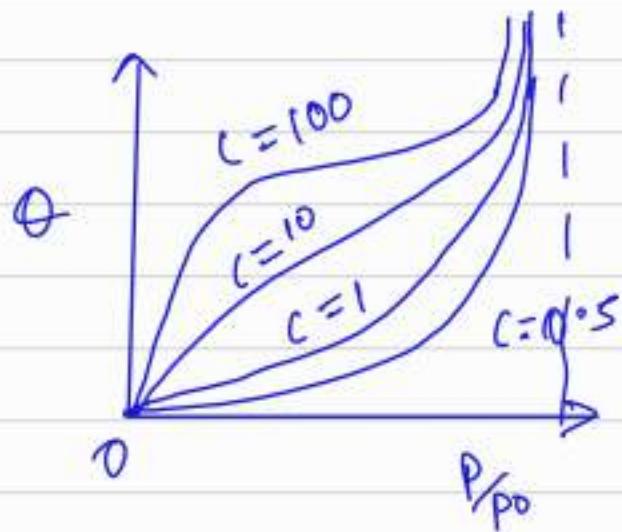
$$C = e^{(E_{\text{ads}} - \bar{B}v)/k_B T};$$

$$V \rightarrow \infty$$

$$1 \Rightarrow x = \frac{k_B P}{\sum_{i=1}^{\infty} i^{-2}} = \frac{k_B P}{\zeta}$$

$$V e^{cv/k_B T} \quad k_{di}, i=2$$

If $p \rightarrow p_0$, $\chi = p/p_0$



BET

$\begin{matrix} 0 & 1 & 1 & 0 & 1 & 0 \\ 1 & 0 & 1 & 0 & 1 & 0 \end{matrix}$

$$\theta_i^0 = \frac{k_{ai}^0}{k_{di}^0} P \theta_{i-1}^0$$

$$\theta_0 = \frac{2}{9}$$

$$\theta_1 = 2/9$$

$$= \frac{k_{d,i-1}^{\circ}}{k_{d,i-1}} P \frac{k_a}{k_d} P \theta_0$$

Similarly $\theta_2 \dots$

$$\chi = P \frac{k_{a,i}^{\circ}}{k_{d,i}^{\circ}} \Rightarrow \chi^i = P \frac{k_{a,i}^{\circ}}{k_{d,i}^{\circ}}$$

$$\theta_i^{\circ} = \chi^i C \theta_0$$

$$\chi = P \frac{k_{a,i}^{\circ}}{k_{d,i}^{\circ}}$$

$$\left(Q = \frac{\text{number of molecules of sites}}{\text{Total number of sites.}} \right)$$

$$Q = \frac{n_a}{n}$$

All equilibrium

at equilibrium,
pressure (P) = P_0

↓
eqm vapour pressure.

$$N_a = \sum_{i=1}^{\infty} i \Theta^i N$$

$$= \sum_{i=1}^{\infty} i \chi^i$$

$$= \frac{2}{(1-\chi)^2}$$

$$K_a^\circ P_0 N = K_d^\circ N$$

$$P_0 = \frac{K_d^\circ}{K_a^\circ}$$

$$\rightarrow \left[\chi = \frac{P}{P_0} < 1 \right]$$

$$C = \frac{P}{\chi} \frac{K_a}{K_d} = \frac{P}{\chi} \frac{e^{-\bar{E}_{ads}/RT}}{e^{-\bar{E}_v/RT}} = e^{(\bar{E}_{ads} - \bar{E}_v)/RT}$$

$$= e^{(\Delta_{\text{ads}}H^\circ - \Delta_{\text{rep}}H^\circ)/RT}$$

Specific Surface Area.

$$\alpha_{\text{sp}} = \frac{\text{Total Area of Sample}}{\text{Total mass.}}$$

$$\Omega = \frac{n^s N_A 6^\circ}{W \cdot \alpha_{\text{sp}}} \Rightarrow \Omega = 1 \text{ at saturation}$$

Foot print = 6° = area of molecule.

$$\alpha_{\text{sp}} = \frac{n^s N_A 6^\circ}{W}$$

w

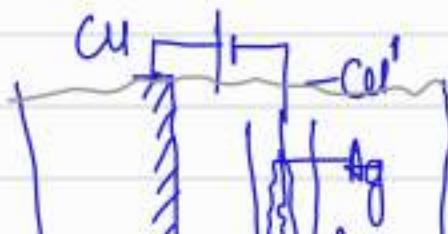
$$\text{Limitation} = \left(\frac{P}{P_0} = 0.05 \text{ to } 0.3 \right)$$

Electrified interfaces

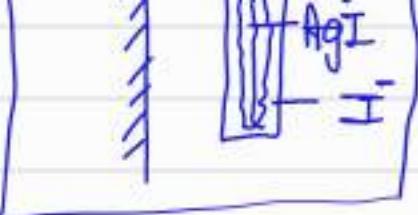
$\text{AgJ} \rightarrow$ negative charge tendency
 $J =$ chemically adsorption.

Book \Rightarrow Pallab Ghosh
colloid and
interfaces

- 1 > Adsorption of ions
- 2 > dissociation of surface functionality.

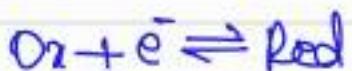


$\text{Ag/AgJ, J}^{(\text{aq})}$

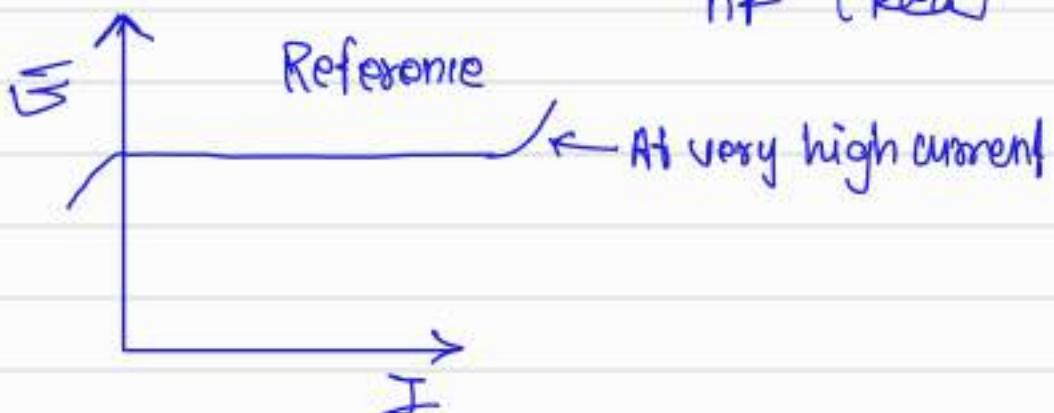


Reversible electrode

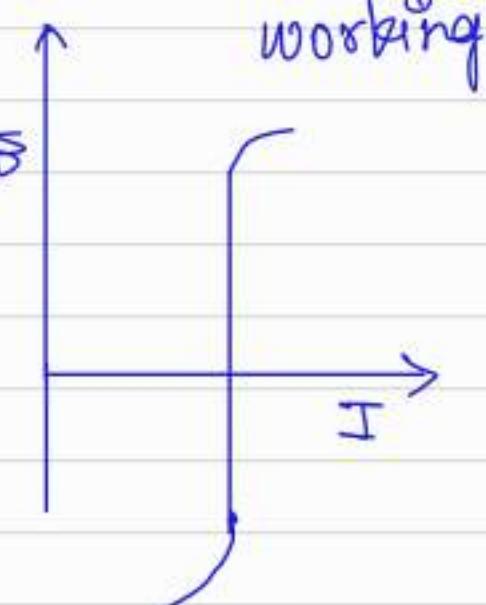
Ideally non-polarizable electrode



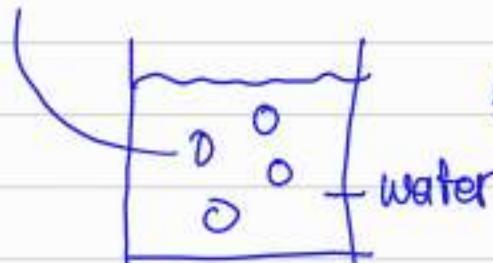
Nernst eqⁿ = $E = E^\circ + \frac{RT}{nF} \ln \left[\frac{O_2}{Red} \right]$



Ideally polarizable electrode



AgI particle



$$K_{sp} = 7.5 \times 10^{-17} \text{ at } 25^\circ\text{C}$$

$$[\text{Ag}] = [\text{I}] = 8.5 \times 10^{-9}$$

→ Specifically adsorbed or preferentially adsorbed

unauthorised.

point of zero charge., $C \xrightarrow{\text{conc.}} C_{PZC}$ \rightarrow PZC = 0V
 potential of zero charge. Taking this reference

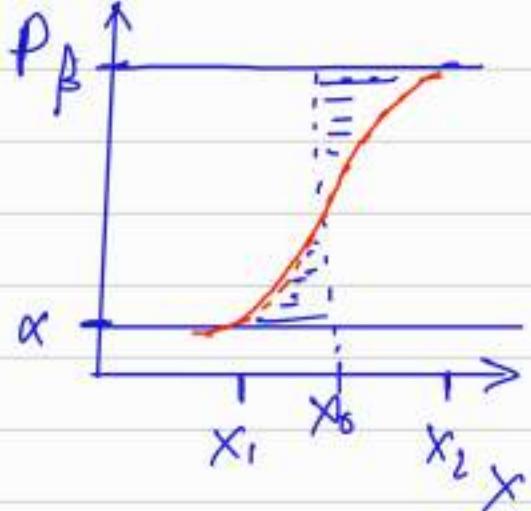
$$\boxed{\psi_0 = 2.303 \frac{RT}{NF} \log \left[\frac{C}{C_{PZC}} \right]}$$

If $[Ag^+] = 8.5 \times 10^{-9}$

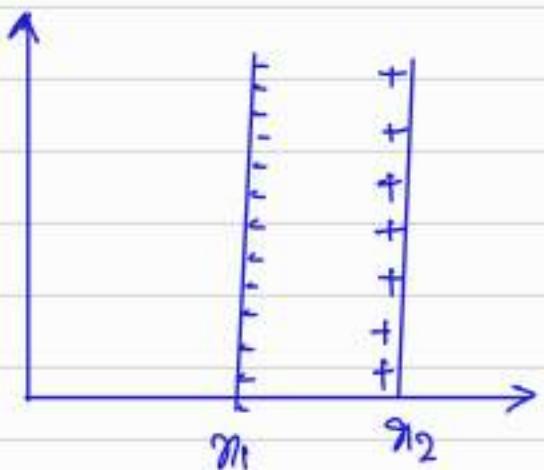
$$\psi_0 = -150 \text{ mV.}$$

C_{PZC} \rightarrow upper behaviour
 \rightarrow nitro benz
 anil.

Gibbs adsorption Isotherm.

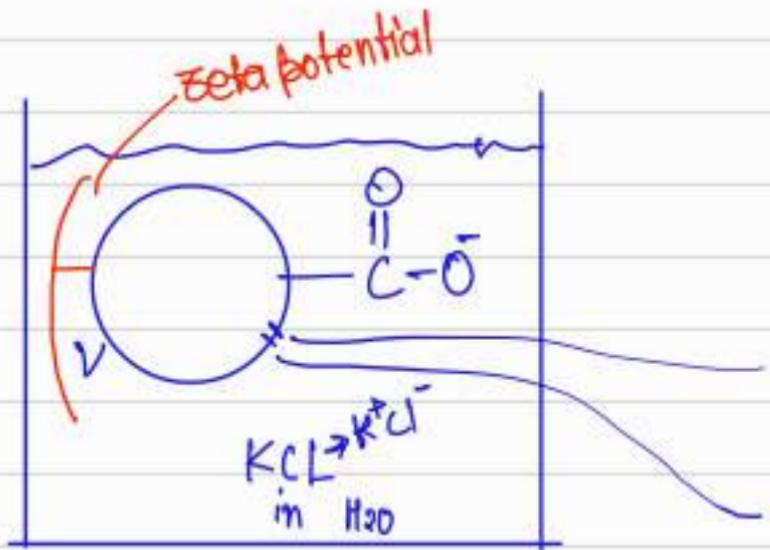


Helmholtz Model



Colloidal
brown
particle

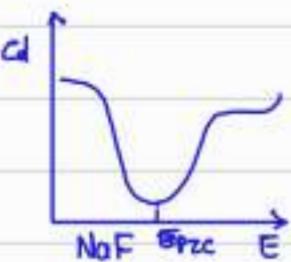
Quantum dot



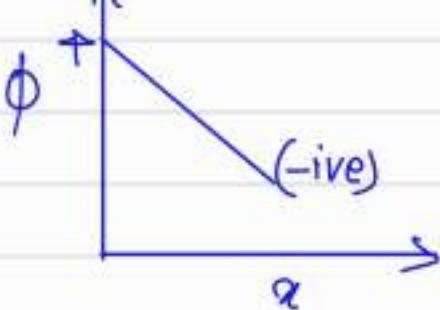
$$\sigma_1^m = -\sigma_2^s$$

should be equal & opp sign

electrical double layer

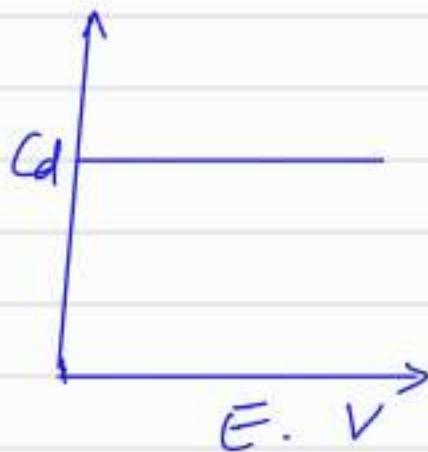


$$\Gamma^m = \frac{q}{A} = \frac{\Sigma \epsilon_0 V}{d}$$

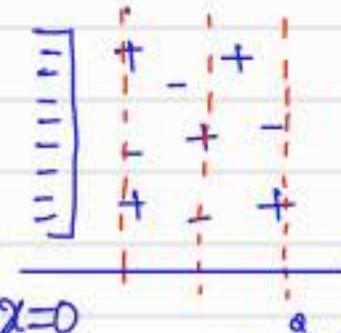
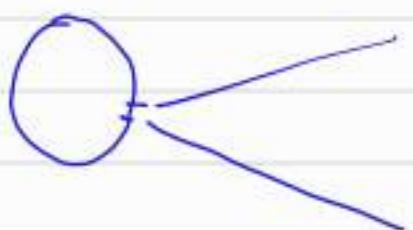


Capacitance = $\frac{\text{Charge}}{\text{Potential}}$

$$C_d = \frac{d\Gamma^m}{dV} = \frac{\Sigma \epsilon_0}{d}$$



Gony - Chapman (Diffuse double layer).



Total no. of ions = n^o
Ions in layer = n_i

z^o = charge on ion

e = electron charge

ϕ = potential

using Boltzmann distribution,
 $n^o = N^o \exp\left(-\frac{z^o e \phi}{kT}\right)$

Poisson's eqn

$$\rightarrow \frac{d^2\phi}{dx^2} = -\frac{\rho}{\epsilon \epsilon_0}$$

$$\rho = \sum n_i z_i e = \sum n_i z_i e \exp\left(-\frac{z_i e \phi}{kT}\right)$$

charge

density

$$\frac{d^2\phi}{dx^2} = -\frac{e}{\epsilon \epsilon_0} \sum_i n_i z_i \exp\left(-\frac{z_i e \phi}{kT}\right)$$

→ If ϵ : ϵ electrolyte symmetrical.

$$\frac{d^2\phi}{dx^2} = -\frac{e}{\epsilon \epsilon_0} \left[n_i z \exp\left(-\frac{z e \phi}{kT}\right) - n_i z \exp\left(\frac{z e \phi}{kT}\right) \right]$$

$$= -\frac{e n_i z}{\epsilon \epsilon_0} \left[\exp\left(-\frac{z e \phi}{kT}\right) - \exp\left(\frac{z e \phi}{kT}\right) \right]$$

For small ϕ , $\hat{e}^{\pm} = 1 \pm x$

$$= \boxed{\frac{2e^2 n_i z^2 \phi}{\epsilon \epsilon_0 k T}} \quad K^2 = \frac{1}{L^2} = \text{inverse of Debye length}$$

$= K^2 \phi$

↓
जो तक
charge
on influence
रहता है!

$$K^2 = \frac{2e^2 n_i z^2}{\epsilon \epsilon_0 k T}$$

CML103 – Chemistry of Interfaces

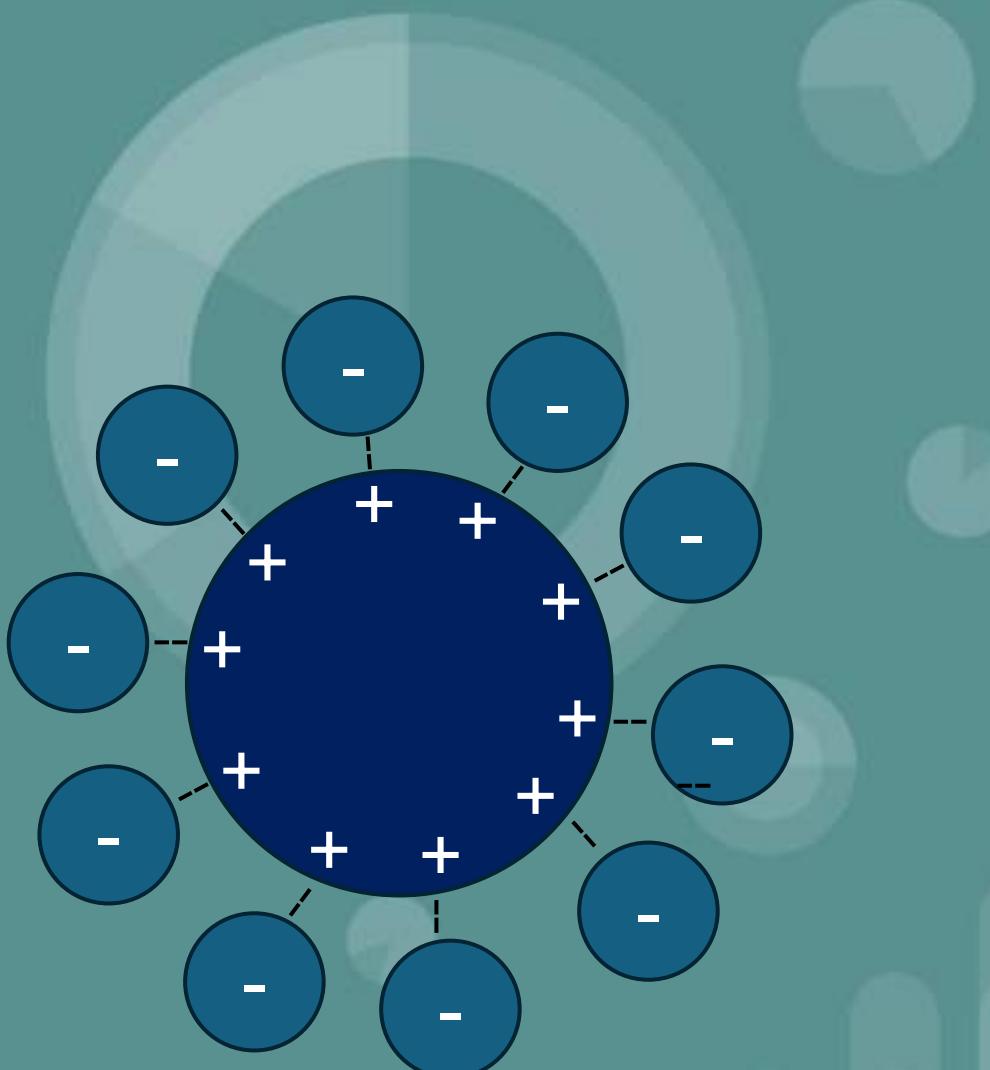
Scribes

Week 11A



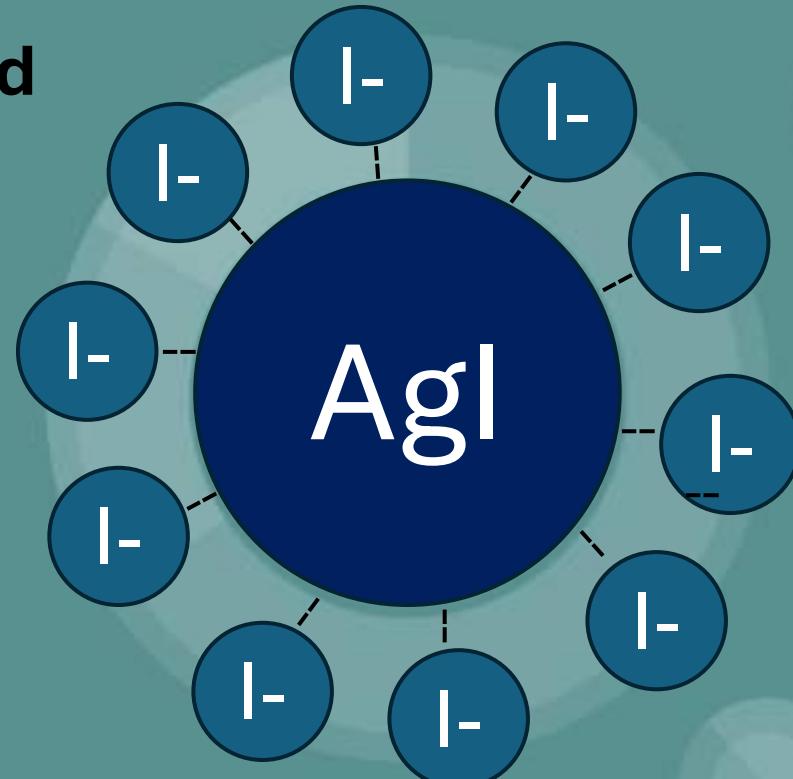
Electrified Surfaces

Electrified interfaces occur when there is a potential difference across an interface or one region where surface can be charged, such as a metal-solution interface due to the application of an external electric field. For example: electrode-electrolyte,



There are two ways of forming electrified interfaces

1. Adsorption of Ions: When ions from the solution adsorb onto a electrified surface, they change the surface potential. This process impacts reaction rates, potential distribution, and the behaviour of the interfaces. For example, AgI behaves as negatively charged particle because of a negatively charged layer of I⁻ being formed on its surface



There are two ways of forming electrified interfaces

2. Dissociation of Surface Functionality: Many surfaces have functional groups that can dissociate in solution.

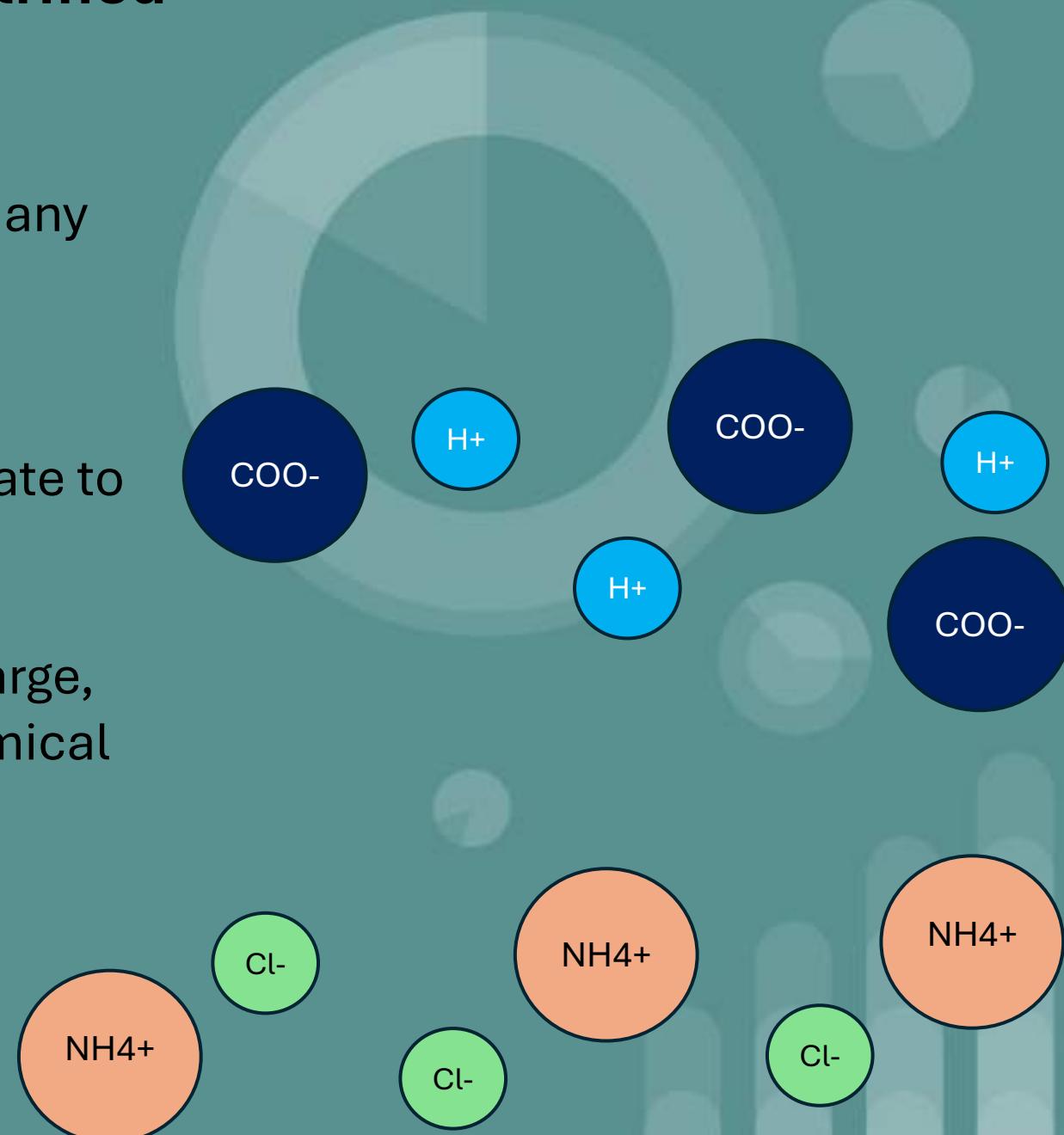
For example:

- i. -COOH groups on a surface can dissociate to form COO⁻ and protons (H⁺). Reaction:



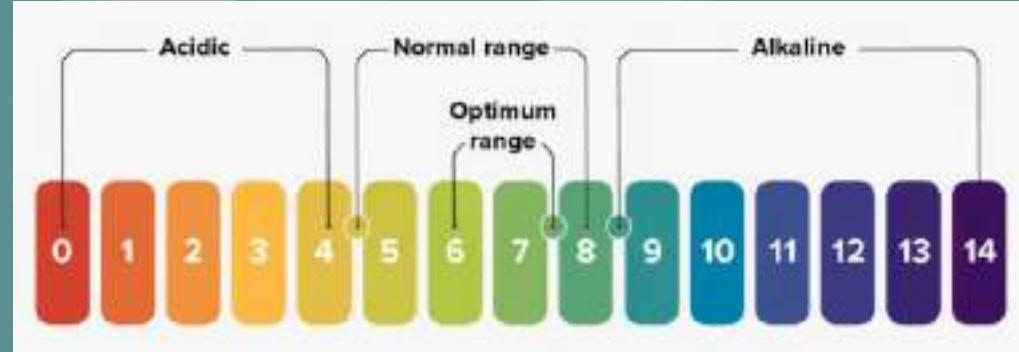
This dissociation affects the surface charge, which in turn influences the electrochemical behaviour of the interface.

- ii. NH₄Cl \rightleftharpoons NH₄⁺ + Cl⁻



Impact on pH and Surface Potential

A. Impact on pH: As functional groups dissociate or ions adsorb onto the surface, the pH of the solution near the interface changes, impacting the chemical environment of the interface.



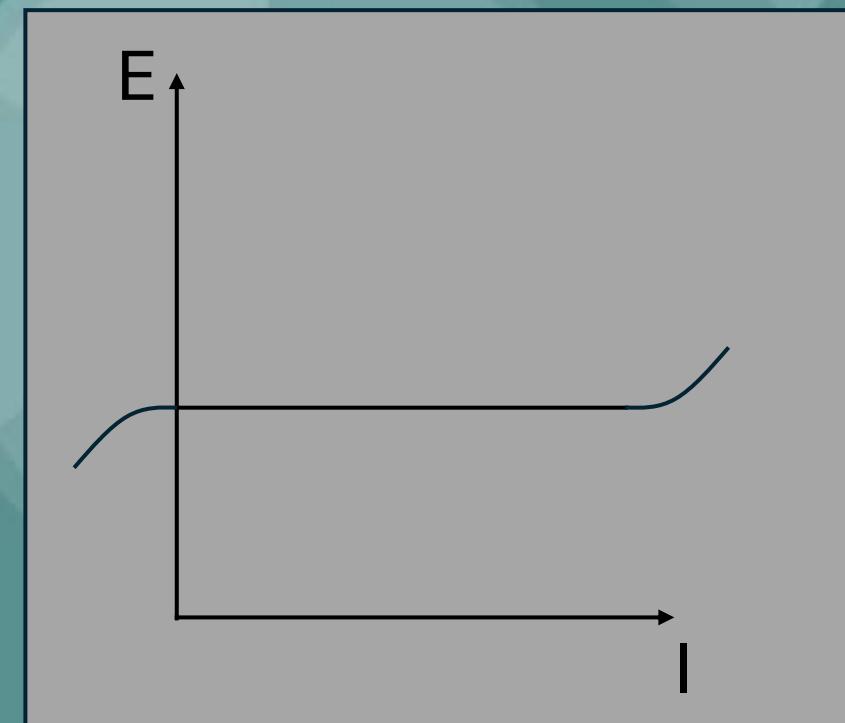
B. Impact on Surface Potential: When ions from the solution adsorb onto an electrified surface, they change the surface potential which is essential in applications like corrosion, sensor design, and catalysis.



The electrostatic double layer force at the fluid-fluid and liquid-solid interfaces becomes important when charged molecules are present at the interfaces. The charge may arise by the adsorption of a charged ion (such as an ionic surfactant or a polyelectrolyte) at the interface, or dissociation of an ionisable surface group (e.g. the dissociation of -COOH or -SiOH groups present on the surface of a solid). The dissociated group attached to the surface attracts the counterions by Coulomb force. On the other hand, osmotic pressure forces the counterions away from the surface and from each other. The dispersion of the counterions is thermodynamically favourable because it increases the entropy. A balance between the Coulomb attraction and osmotic repulsion maintains the double layer. Two similarly-charged surfaces encounter osmotic repulsion when they approach each other due to the reduction in entropy. The double layer force is very important in the stabilisation of emulsions, foams, and colloids. The combined effect of van der Waals and double layer forces between two surfaces is described by the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory.

Reversible Electrode (ideally non-polarizable electrode)

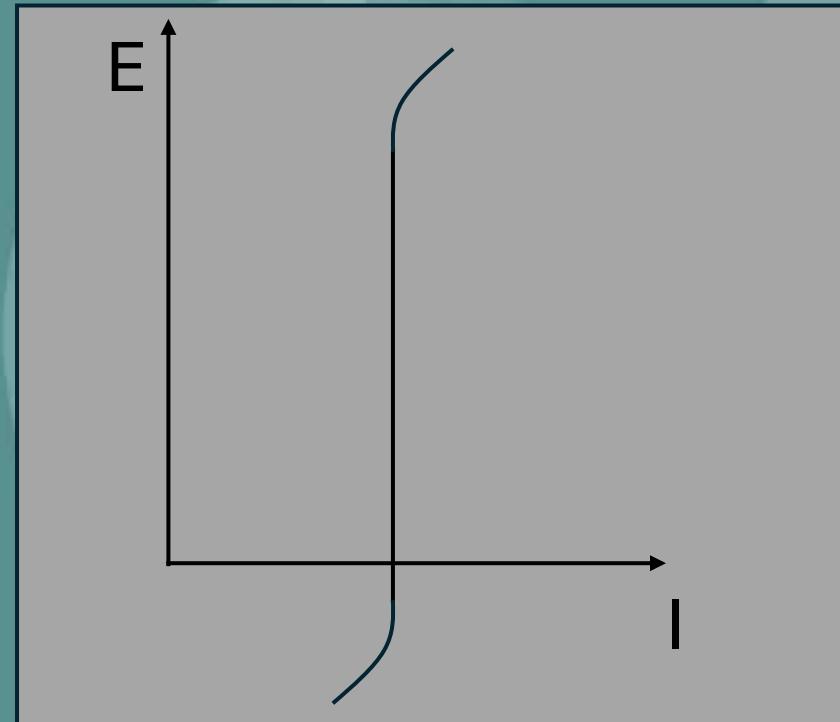
1. Since the electrode is non-polarizable, any small change in current result in minimal change in electrode potential
2. As the current increases significantly, especially in an AgI colloidal solution where ions are involved, the potential may eventually start to shift. However, the reversibility and non-polarizability characteristics mean this shift will still be much less pronounced than a polarizable electrode. The graph may show a slight upward curve, but much flatter than a typical electrode potential response.



Nernst eqⁿ = $E = E^\circ + \frac{RT}{nF} \ln \left[\frac{\text{O}_2}{\text{Red}} \right]$

Ideally Polarizable Electrode

1. The potential increases more significantly with increasing current, especially beyond the low current region.
2. This strong upward trend reflects the polarization effect, under the electrode potential shifts due to increasing current, characteristic of polarizable electrodes.

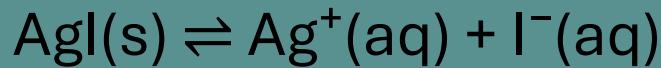


Nernst equation

$$E = E^\circ + (RT \ln(Ox / Red) / nF)$$

1. It is used to calculate the cell potential under non-standard conditions.
2. The **point of zero charge (PZC)** is the pH value at which the net surface charge of an adsorbent (like a solid surface) is zero

Finding equilibrium concentration of ions



$$K_{\text{sp}} = 7.5 \times 10^{-17}$$

$$K_{\text{sp}} = [\text{Ag}^+][\text{I}^-] = s * s = s^2$$

$$s = \sqrt{(7.5 \times 10^{-17})} \approx 8.5 \times 10^{-9} \text{ M}$$

$$[\text{Ag}] = [\text{I}] = 8.5 \times 10^{-9} \text{ M}$$

→ Specifically adsorbed or preferentially adsorbed

Finding potential of zero charge for AgI electrode

$$\Psi_0 = 2.303 (RT \log [C/C_{\text{PZC}}]) / nF$$

$$\text{At Pzc, } E^\circ = 0$$

$$c = 8.5 \times 10^{-9} \text{ M}$$

$$C_{\text{PZC}} = 3 \times 10^{-9} \text{ M (PZC = 0V)}$$

$$\Psi_0 = -150 \text{ mV (surface potential)}$$

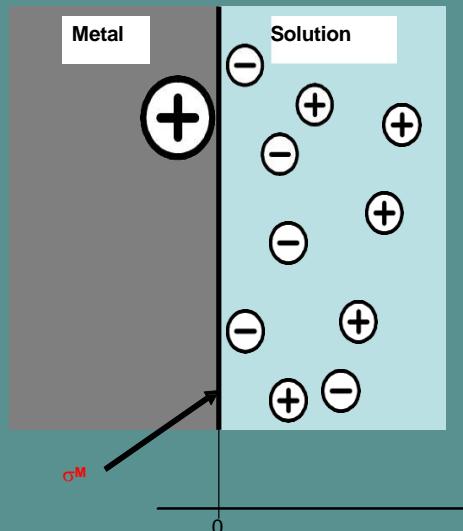
Gouy-Chapman model (1910)

The double layer is not as compact as in Helmholtz rigid layer.

Consider thermal motions of ions:

Tendency to increase the **entropy** and make the layer **diffuse**

(while **electrostatic attraction** tends to keep ions close to interface and make the layer more **rigid**).



Distribution of ions: determined by electrostatics and stat. mechanics

Assumptions:

Ions: point ions, highly mobile

Solvent: dielectric continuum

Metal: perfect conductor

Distribution of ions with distance x from interface: apply Boltzmann statistics

$$n_i = n_i^0 \exp\left(\frac{-z_i F \phi(x) - \phi_s}{RT}\right)$$

n_i : particle density (#particles/cm³)

Regions of large $\phi(x)$: reduced density of positive ions
of enhanced density of anions (compared to bulk).

Gouy - Chapman

$$n_i^* = n_i^0 \exp\left(\frac{-z_i e \phi}{kT}\right) \quad \text{Poisson's equation.}$$

$$\begin{aligned} \frac{d^2\phi}{dx^2} &= -\frac{\epsilon}{\epsilon_0} \sum_i n_i^* z_i \exp\left(\frac{-z_i e \phi}{kT}\right) z_i \\ &= -\frac{\epsilon}{\epsilon_0} \left[n_i^0 z_i \exp\left(\frac{-z_i e \phi}{kT}\right) \right] - n_i^* z_i \exp\left(\frac{-z_i e \phi}{kT}\right) \\ &\quad \curvearrowleft \text{for symmetrical electrolyte.} \end{aligned}$$

Small ϕ

$$\begin{aligned} \frac{d^2\phi}{dx^2} &\approx -\frac{\epsilon n_i^0 z}{\epsilon_0 kT} \left[1 - \frac{z e \phi}{kT} \right] \approx 1 - \frac{z e \phi}{kT} \\ &= \frac{z e n_i^0 z^2 \phi}{\epsilon_0 k T} \end{aligned}$$

if, its asymmetric and ϕ is small,

$$\frac{d^2\phi}{dx^2} = -\frac{\epsilon}{\epsilon_0} \sum_i n_i^* z_i \left(1 - \frac{z_i e \phi}{kT} \right)$$

$$\frac{e^2}{\epsilon_0 k T} \sum_i c_i M_i z_i^2 \phi = \frac{e^2}{\epsilon_0 k T} \sum_i n_i^* z_i^2 \phi$$

$\downarrow K^2$

$$\frac{d^2\phi}{dx^2} = K^2 \phi$$

no. of moles = $\frac{\text{Total no. of ions}}{N_A}$

$$c_i = \frac{n_i^*}{A} \Rightarrow \boxed{c_i N_A = n_i^*}$$

Charge density involving all ionic species:

$$\rho(x) = \sum_i n_i z_i e_0 \quad e_0 = 1.602 \cdot 10^{-19} \text{ C}$$
$$= \sum_i n_i^0 z_i e_0 \exp\left(\frac{-z_i F (\phi(x) - \phi^s)}{RT}\right)$$

Galvani potential in solution obeys Poisson's equation:

$$\frac{d^2\phi(x)}{dx^2} = -\frac{\rho(x)}{\epsilon\epsilon_0}$$

Resulting expression is the Poisson-Boltzmann equation:

$$\frac{d^2\phi_\Delta}{dx^2} = -\frac{1}{\epsilon\epsilon_0} \sum_i n_i^0 z_i q \exp\left(-\frac{z_i F \phi_\Delta(x)}{RT}\right), \text{ where } \phi_\Delta(x) = \phi(x) - \phi^s$$

Note: This equation is precisely equal to the Debye-Hückel theory of ionic interactions in dilute solutions, which determines the charge distribution around a central ion.

Next: Let's consider a z-z-electrolyte

$$\rho(x) = n_0 zq \left[\exp\left(-\frac{z F \phi_\Delta(x)}{RT}\right) - \exp\left(\frac{z F \phi_\Delta(x)}{RT}\right) \right]$$

Debye-Hückel approximation

Let's further assume that the potential variation is small,

$$\frac{zF\phi_A(x)}{RT} \ll 1$$

i.e. potential variations are $\phi_A \ll 25 \text{ mV}$ at room-T. This well-known approximation corresponds to the so-called

Debye-Hückel approximation.

If we use this approximation in the charge distribution (*) of the z-z electrolyte and then insert this charge distribution into the Poisson-Boltzmann equation, then we arrive at the linear Poisson-Boltzmann equation:

$$\frac{d^2\phi_A}{dx^2} = \kappa^2 \phi_A$$

Here, κ is the inverse Debye-length,

$$\kappa = \left(\frac{2(zF)^2 c^0}{\epsilon \epsilon_0 RT} \right)^{1/2} = \frac{1}{L_D}$$

c^0 : bulk electrolyte concentration (far away from interface)

κ : or its inverse are important characteristics of the electrolyte.

Debye-length L_D : quantitative measure of width of space charge region within which $\phi(x)$ decreases from ϕ^M to ϕ^S – tremendous importance in electrochemistry and biology.

at 25°C

Symmetrical

$$K(m^1) = 3.29 \times 10^7 |z_1| e^{-V_2}$$

Asymmetrical

$$2.32 \times 10^7 |z_1| e^{-V_2}$$

$$(m)L_D = \frac{1}{K} \quad 3.04 \times 10^{10} |z_1| e^{-V_2} \quad 4.30 \times 10^{10} \geq |z_1| e^{-V_2}$$

- ④ Let's assume we have 3 sol. ⑤ NaCl, ⑥ CaCl₂,
⑦ AlCl₃ all sol are $[c] = 10 \text{ mol/m}^3$, find L_D ?
Ans ($\text{NaCl} > \text{CaCl}_2 > \text{AlCl}_3$)

$$\frac{d^2\phi}{dx^2} = K^2\phi$$

$$\text{let's, } \phi = Ae^{Kx} + Be^{-Kx}$$

Boundary condt.

$$x=0, \phi = \phi_0 \quad x \rightarrow \infty, \phi = 0$$

$$\phi_0 = A + B$$

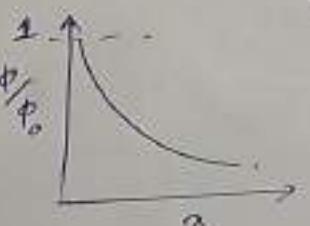
$$B = \phi_0$$

$$\boxed{\phi = \phi_0 e^{-Kx}}$$

$$0 = A(\infty) *$$

$$\underline{A=0}$$

$$\frac{\phi}{\phi_0} = e^{-Kx}$$



$\frac{1}{r^2} \left(\frac{\partial}{\partial r} \left(\gamma \frac{\partial \phi}{\partial R} \right) + \right) = \kappa \phi$

colloidal particle.

$\phi = \frac{c_1}{r} e^{\gamma r} + \frac{c_2}{r} e^{-\gamma r}$

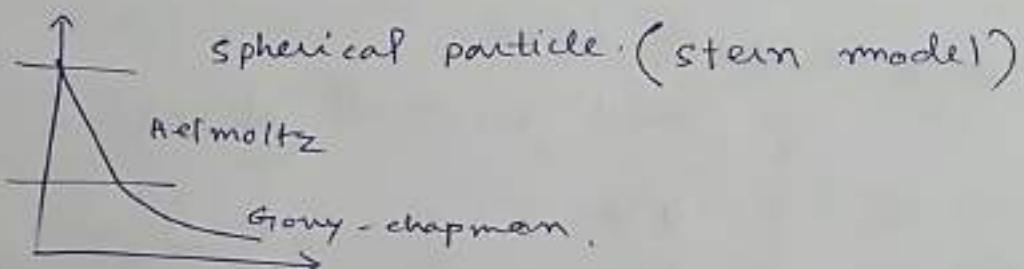
$$\phi = \phi_d \frac{(R_s + d)}{r} e^{\kappa(R_s + d) - \kappa r}$$

$$\begin{cases} r = R_s + d, \phi = \phi_d \\ r = \infty, \phi = 0 \end{cases}$$

$$\phi_d = \frac{c_2}{(R_s + d)} e^{-\kappa(R_s + d)}$$

$$\zeta = (R_s + d) \phi_d e^{\kappa(R_s + d)}$$

$$\phi = \phi_d \frac{(R_s + d)}{r} e^{\kappa(R_s + d - r)}$$



The following effects are important to remember:

Larger electrolyte concentration C^0 smaller L_D

i.a.w: the double layer becomes less diffuse

Higher temperature \rightarrow larger L_D

i.a.w.: the double layer becomes more diffuse

Potential and charge distribution in the electrolyte solution are given

in Debye-Hückel approximation by:

$$\phi_0(x) = \frac{\sigma^M}{\epsilon\epsilon_0 k} \exp(-\kappa x)$$

$$\rho(x) = -\sigma^M k \exp(-\kappa x)$$

interface, i.e. the excess surface charge density σ^M on the metal is balanced by an exponentially decaying space-charge layer in solution.

The double layer capacity in this approximation is given by

$$C_{d,DH} = \epsilon\epsilon_0 k = \frac{\epsilon\epsilon_0}{L_D}$$

i.e. it is given by the plate capacitor formula with the Debye length as the effective plate separation.

**Table: Debye length at various electrolyte concentrations
(1-1 electrolyte)**

$c^0 / \text{mol l}^{-1}$	10^{-4}	10^{-3}	10^{-2}	10^{-1}
$L_D / \text{\AA}$	304	96	30.4	9.6

Higher concentrations:

steeper potential drop in solution

narrower space charge region, smaller L_D

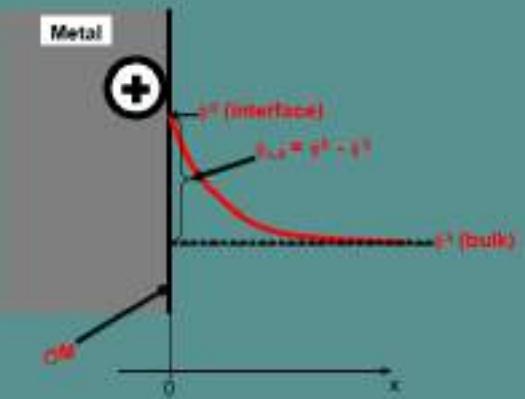
higher double layer capacities, $C_{d,DH}$

In practice: The Debye-Hückel (DH) approximation is not valid at large electrolyte concentration. It works well as long as the potential variation does not exceed $\phi_\Delta \approx 80 \text{ mV}$.

General Case: Nonlinear Poisson-Boltzmann-equation

For a z-z-electrolyte with concentration c^0 the Poisson-Boltzmann equation has an explicit solution. This will be added as an appendix. Here only the main results will be given.

Potential distribution in solution



The relation between potential and charge density of the diffuse layer is given by

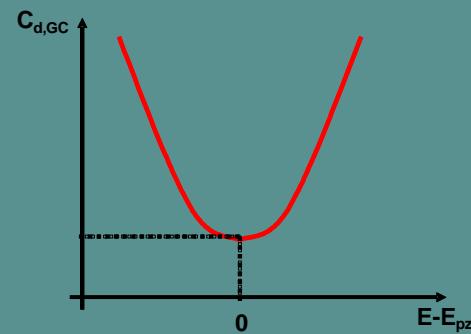
$$\sigma^M = \epsilon \epsilon_0 \left(\frac{dq_A}{dx} \right)_{x^0} = \left(8RT\epsilon \epsilon_0 c^0 \right)^{1/2} \sinh \left(\frac{zF\phi_{A,0}}{2RT} \right)$$

Differentiating this expression gives the differential capacity in the Gouy-Chapman model:

$$C_{A,GC} = \left(\frac{\partial \sigma^M}{\partial \phi_{A,0}} \right) = \frac{\epsilon \epsilon_0}{L_D} \cosh \left(\frac{zF\phi_{A,0}}{2RT} \right) \quad \text{where} \quad \phi_{A,0} = E - \delta p z c$$

The variation of this capacitance with electrode potential

E is thus given by



This model predicts correctly the minimum in capacity at the pzc. For large E , it predicts an unlimited rise of the capacity.



Why would the DL capacity rise unlimitedly in this approach? Which assumption is responsible for this unphysical behaviour?

It is assumed that ions are point charges, which could approach the electrode surface arbitrarily close with increasing E . This leads to a very small charge separation (consider the plate capacitor as an analogue!). **The capacity rises without limit.**

What is the solution out of this “capacity catastrophe”???

Ions have a finite size! Arbitrarily close approach is not possible. Ions are stopped from approaching the electrode at distances that correspond to their radii.

A further refinement of the double layer models takes this effect into account.

The Stern Model (1924)

accounts for finite size of ions
 combines the Helmholtz and Gouy- Chapman models

two parts of double layer:

- (a) compact layer ("rigid layer") of ions at distance of closest approach
- (b) diffuse layer.

The compact layer, $x < x_H$, is charge-free (linear variation of potential)!

Mathematically: two capacitors in series with total capacity

$$\frac{1}{C_D} = \frac{1}{C_{\text{diff},H}} + \frac{1}{C_{\text{diff},GC}} = \frac{\chi_H}{\epsilon \epsilon_0} + \frac{L_D}{\epsilon \epsilon_0 \cos h \left(\frac{zF\phi_{\Delta,0}}{2RT} \right)}$$

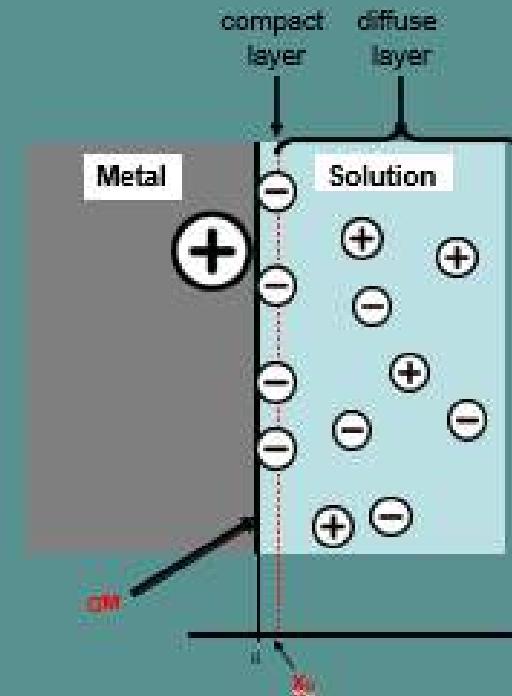
Far from E_{pzc} (large $\phi_{\Delta,0} = E - E_{\text{pzc}}$):

$C_{\text{diff},H} \ll C_{\text{diff},GC} \Rightarrow C_d \approx C_{\text{diff},H}$ Helmholtz, rigid

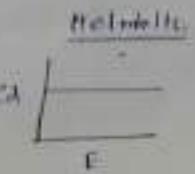
Close to E_{pzc} (small $\phi_{\Delta,0} = E - E_{\text{pzc}}$):

$C_{\text{diff},H} \gg C_{\text{diff},GC} \Rightarrow C_d \approx C_{\text{diff},GC}$ Gouy-Chapman, diffuse

Remember: the smaller guy always wins (well, not always, but here)!



spherical capacitor (Helmholtz model)



$C_H - C_L$

$$C_L \int_{E_b}^{\infty} \frac{d\phi}{\epsilon_r \epsilon_0} = C_H$$

E_b (point of zero charge)

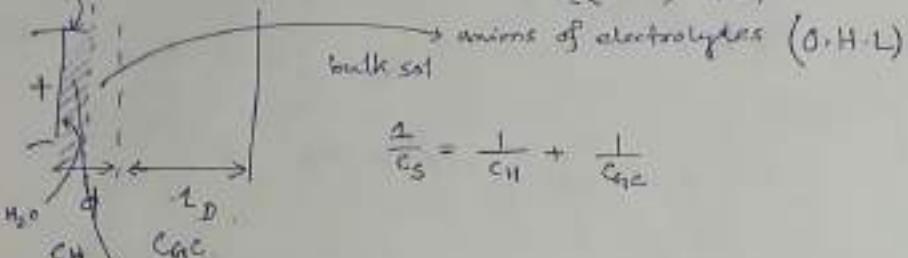
charge density
of metal

$$\frac{d(\sigma_m)}{d\phi} = C_H$$

catastrophy

Stein Model

$\pi_{2,0}$ combines the two models ($H.M.$, $G.C.$)



$$\frac{1}{\epsilon_{ss}} = \frac{1}{\epsilon_{H}} + \frac{1}{\epsilon_{L}}$$

INNER HELMHOLTZ LAYER.

(Valid) (verified) (NOTES) /

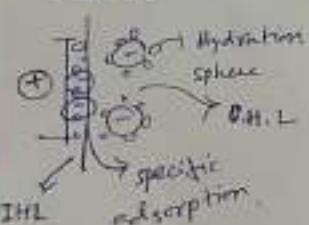
$$\frac{d^2\phi}{dr^2} = -\frac{P}{\epsilon\epsilon_0} = -\frac{e}{\epsilon\epsilon_0} \sum_i m_i^\infty Z_i \exp\left(-\frac{2ie\phi}{k_B T}\right)$$

$$d\left(\frac{d\phi}{dr}\right)^2 = -\frac{2P}{\epsilon\epsilon_0}$$

$$\left(\frac{d\phi}{dr}\right)^2 = \frac{2k_B T}{\epsilon\epsilon_0} \sum_i m_i^\infty \exp\left(-\frac{2ie\phi}{k_B T}\right)$$

final eqn. yours choice.

BDM



$$x \rightarrow \infty, \phi = 0$$

Effect of electrolyte concentration:

smaller electrolyte concentration

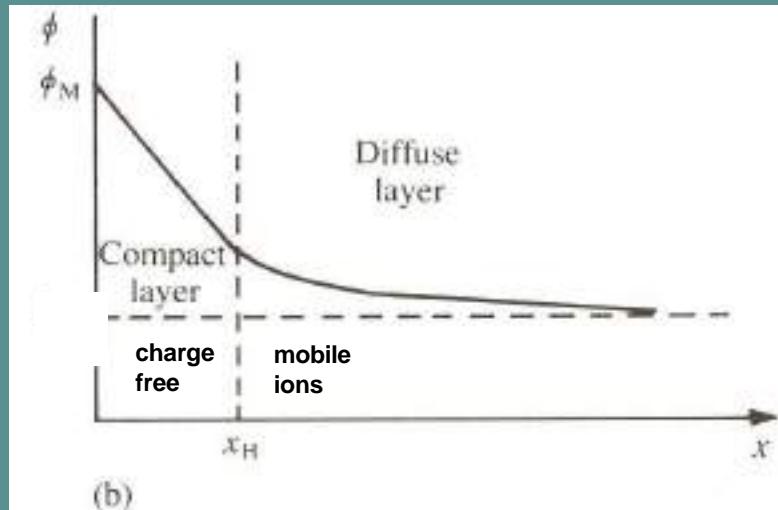
smaller κ (L_D larger), double is more diffuse!

$C_{\text{diff,GC}}$ becomes more important

The **Stern model** reproduces gross features of real systems. Potential distribution in interfacial layer and capacity variation with E are shown in the figures below.

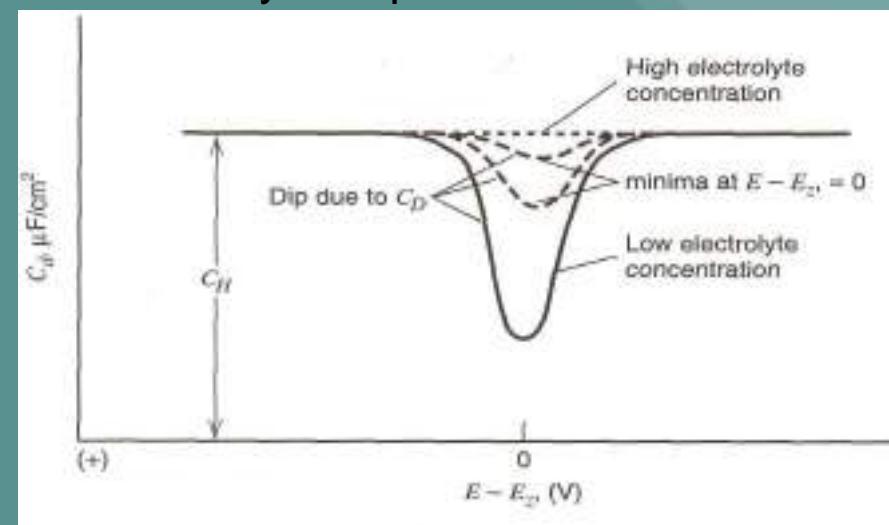
What happens upon increasing the electrolyte concentration?

Potential distribution



(b)

Double layer capacitance



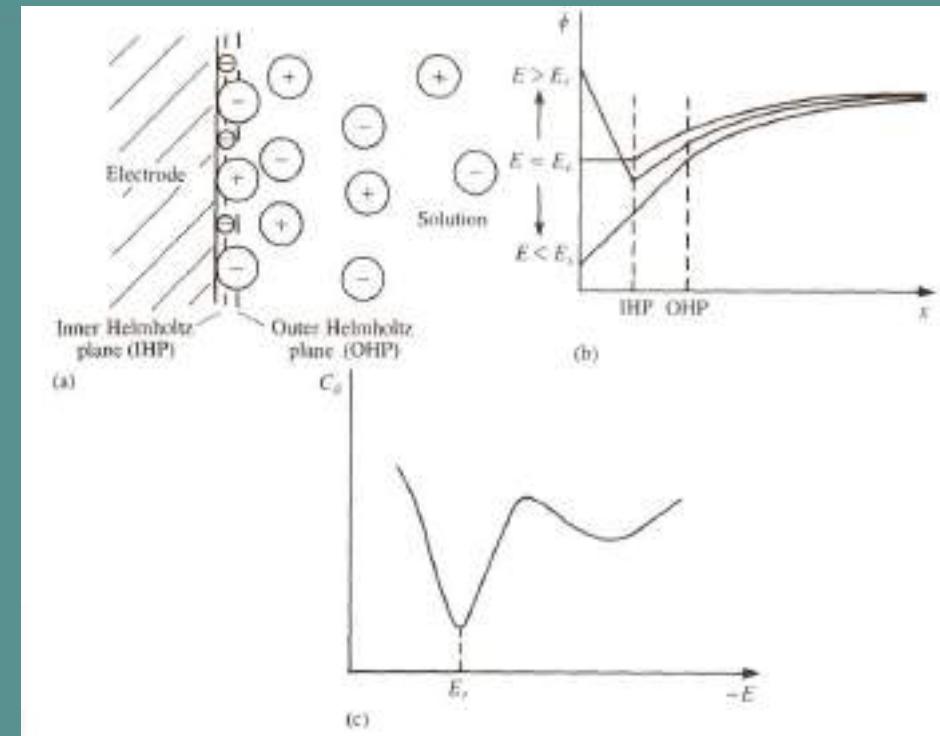
Further refinement: Grahame model (1947)

Some ions (usually anions) loose hydration shell – smaller radii! Ions of smaller radii could approach the electrode closer.
Distinguish **three different regions**!

Inner Helmholtz plane (IHP): through centers of small, partially solvated ions

Outer Helmholtz plane (OHP): through centers of fully solvated ions

Outside OHP: diffuse layer



This is the best model so far. It shows good correspondence to the experimental data.

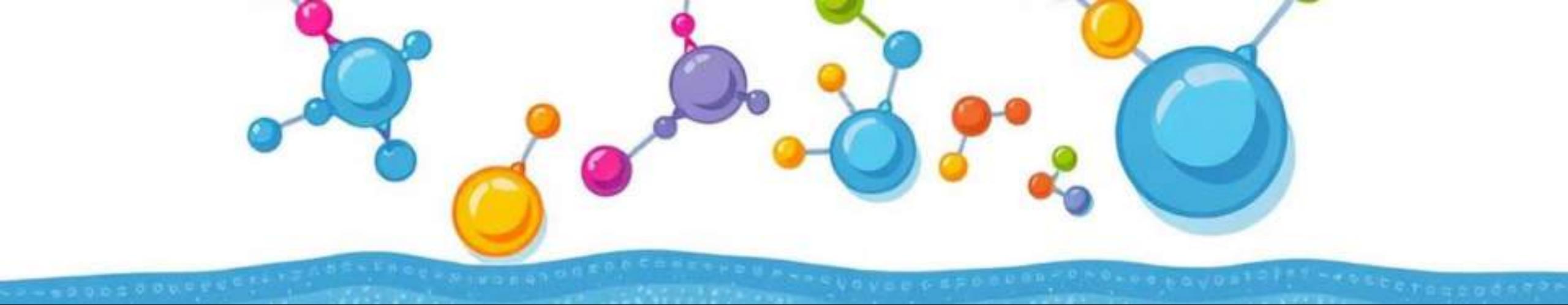
Why are the potential distributions (in (b)) different for positive and negative E ?

This is due to a difference between anions and cations. Anions have a less rigid solvation shell. They become more easily desolvated. Thus, desolvated anions could form the IHP. This happens at positive E . Cations keep their solvation shell. They, thus, cannot approach the electrode closer than to the OHP.



Gibbs Adsorption Isotherm and Thomas-Thomas-Fermi Screening

This presentation will explore the fundamental concepts of the Gibbs Adsorption Isotherm and Thomas-Fermi Screening, two important principles in surface chemistry and materials science.



Introduction to Adsorption

1 Adsorption Basics

Adsorption is the adhesion of atoms, ions, or molecules to a surface, forming a thin film.

2 Importance in Science

Adsorption plays a crucial role in various fields, including catalysis, filtration, and energy storage.

3 Surface Interactions

The strength and nature of surface interactions dictate the adsorption behavior of different substances.

Gibbs Adsorption Isotherm: Derivation and Significance

1

Thermodynamic Basis

The Gibbs Adsorption Isotherm is derived from the principles of thermodynamics, relating surface tension and adsorption.

2

Quantitative Analysis

The isotherm equation provides a way to quantify the amount of adsorption at a given surface pressure.

3

Practical Applications

It is used to characterize adsorption processes and optimize the design of surfaces and interfaces.

Gibbs Adsorption Isotherm

Deriver of the Gibbsisoterm ith the quanls and the larhis edpostior and variables. soing hove the say blut.

$$A, \quad Y_{\pi} = -6(A_i = 1 + 0)$$

$$Y_{\pi} = -\frac{V}{2} \left(+ \right) \frac{-4,331,5}{5+2}$$

$$B, \quad Y_{\pi} = -Y_{\pi} = - + 36 \left(\right) = a,$$

$$Y_{\pi} = 2_{\pi} = 2_y = + 24 \left(\right)$$

$$Y_{\pi} = 2_{\pi} = S(x_i = + 21) \left(= 4,2_i - 4,1_i \right) + = -5(,41)$$

$$B, \quad Y_{\pi} = 19_j = + 4,5)$$

$$2_{\pi} = F_{\pi} = \left(= Y_{\pi} \right) = + Y_y \left(, \right) ez_a + 3 = ^2:2 + + 18)$$

Factors Affecting Adsorption: Temperature, Pressure, and Surface Characteristics

Temperature

Increased temperature generally decreases the amount of adsorption due to increased thermal energy.

Pressure

Higher pressure leads to greater adsorption, as more adsorbate molecules are available for surface interactions.

Surface Characteristics

Surface area, porosity, and chemical composition all influence the adsorption capacity and kinetics.

Graphical Representation of Gibbs Adsorption Isotherm Isotherm

Curve Shapes

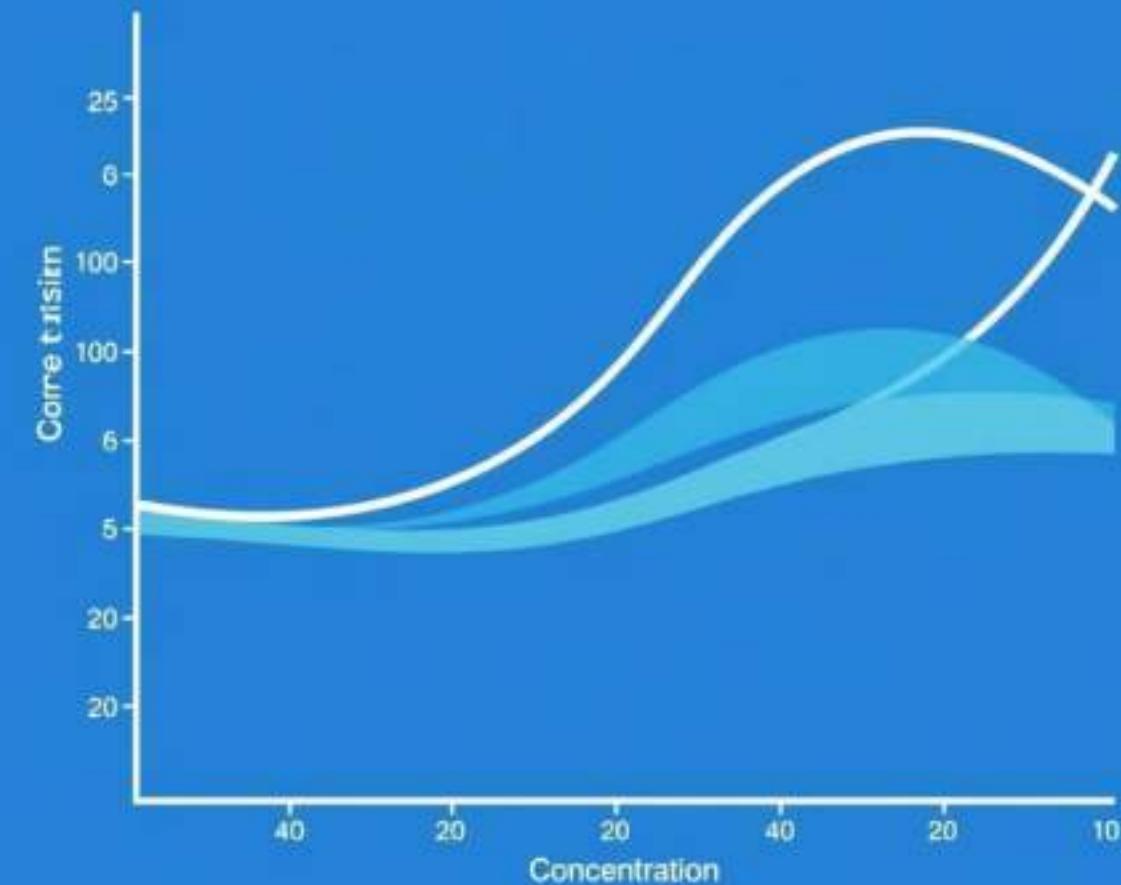
The isotherm can exhibit different curve shapes, depending on the adsorption mechanism and system properties.

Interpreting the Graph

The slope of the curve provides information about the adsorption behavior and surface excess.

Practical Applications

The isotherm graph is used to determine the optimal conditions for adsorption-based processes.



Thomas-Fermi Screening: Concept and Theoretical Background

Electrostatic Screening

Thomas-Fermi screening describes how charged particles in a material can shield each other's electric fields.

Practical Implications

It is used to understand the behavior of materials, interfaces, and nanostructures at the atomic scale.



Quantum Mechanics

The model combines classical electrostatics with quantum mechanical principles of electron density distributions.

Graphical Representation of Thomas-Fermi Screening



Atomic Scale

The screening potential decays exponentially with distance from the charged particle.



Electron Density

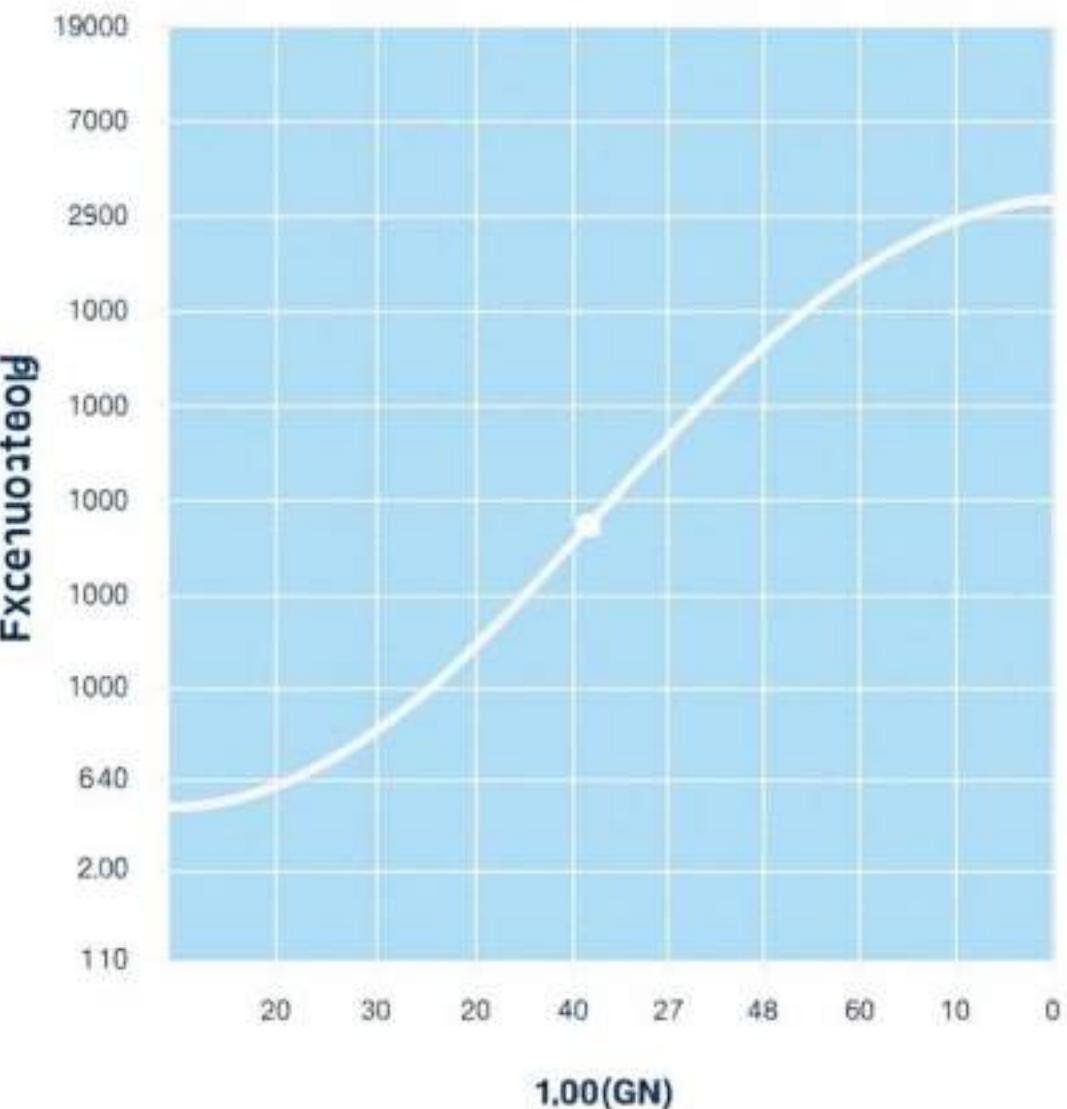
The screening effect is determined by the distribution of electron density in the material.



Energy Considerations

The screening phenomenon is a result of the system minimizing its total electrostatic energy.

Thomas-Fermi potential screening potential



Practical Applications and Implications

1

Catalysis

Adsorption plays a crucial role in the design of efficient catalytic systems.

2

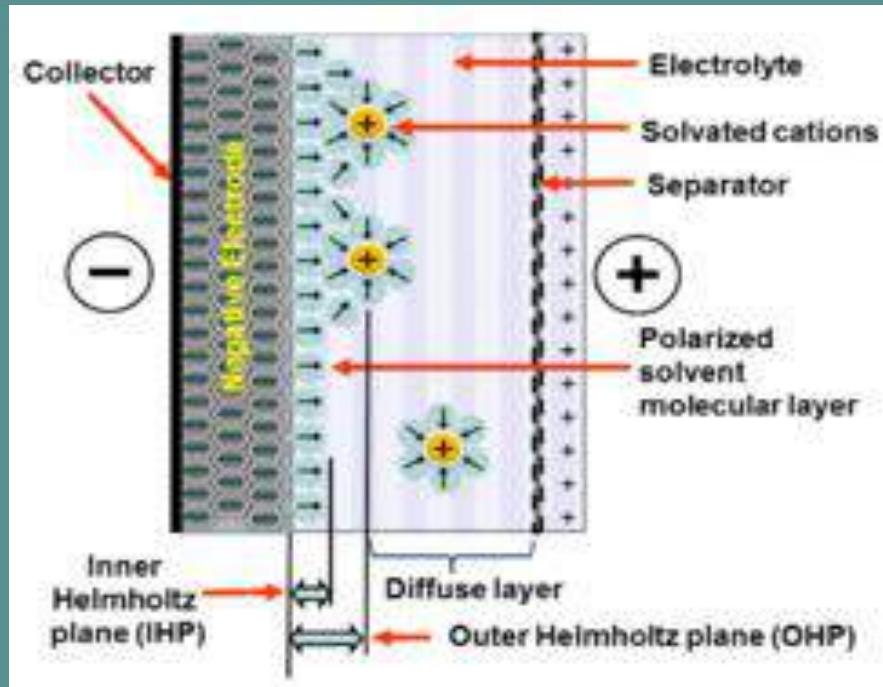
Energy Storage

Understanding adsorption and screening is key for developing advanced energy storage materials.

3

Material Engineering

Controlling adsorption and screening can enable the fabrication of novel functional materials.



Helmholtz Capacitor

Every capacitor has two electrodes, mechanically separated by a separator. These are electrically connected via the electrolyte, a mixture of positive and negative ions dissolved in a solvent such as water.

Capacitance

Capacitance is the capacity of a material object or device to store electric charge. It is measured by the charge in response to a difference in electric potential expressed as the ratio of those quantities.

Spherical Capacitor

They consist of an inner conducting sphere and an outer conducting shell, with a gap between them. The inner sphere carries a positive charge, while the outer shell is negatively charged, creating an electric field between them.

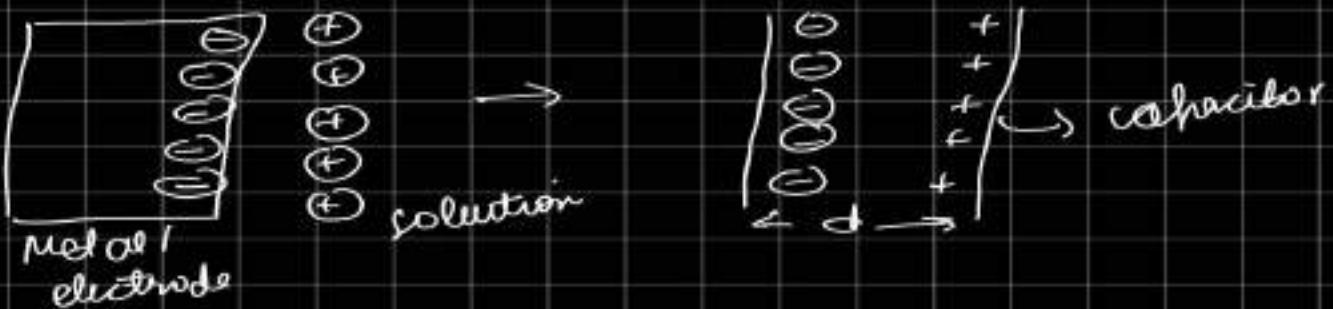
Helmholtz capacitor

The Helmholtz Model is a simplified model that describes the structures of the electrical double layer at the interface between a solid electrode and an electrolyte solution.

In the Helmholtz model, the double layer is simplified as two parallel plates of charge.

Inner Helmholtz plane (IHP): A layer of ions adsorbed directly onto the electrode surface.

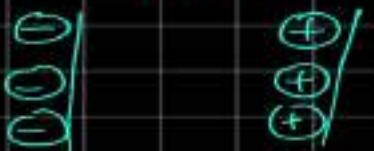
Outer Helmholtz plane (OHP): A layer of solvated ions that are electrostatically attracted to the electrode but remain separated from the surface by a layer of solvent molecules.



The separation creates a potential difference across the double layer.

$$\text{Capacitance} = \frac{\epsilon_0 \epsilon_r}{d}$$

∴ should be equal & opposite

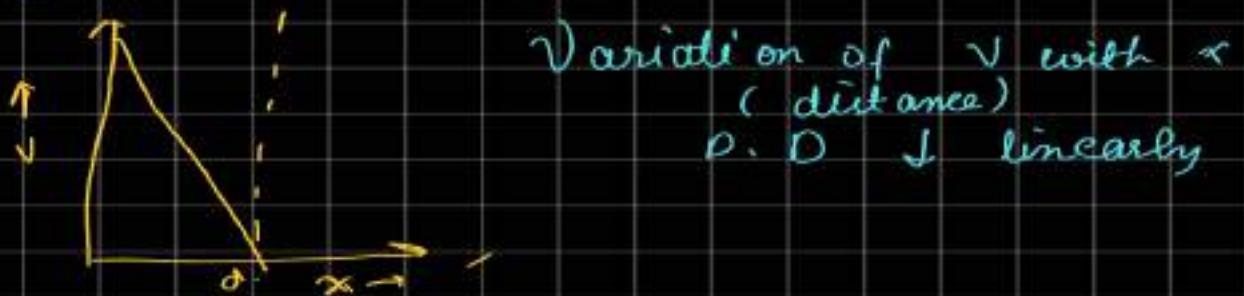


Here,

$\epsilon_r \rightarrow$ dielectric const.
of medium

$\epsilon_0 \rightarrow$ permittivity of
free space

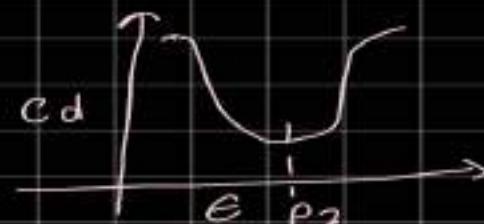
Graph of P.d vs $x \rightarrow$



Helmholtz Σ



$C_1 - C$



Sterm model and BDM model

Scaffolded Theory-Experiment-Modeling and Bond-Dependent Model

How they work?

Theory of Stern Model

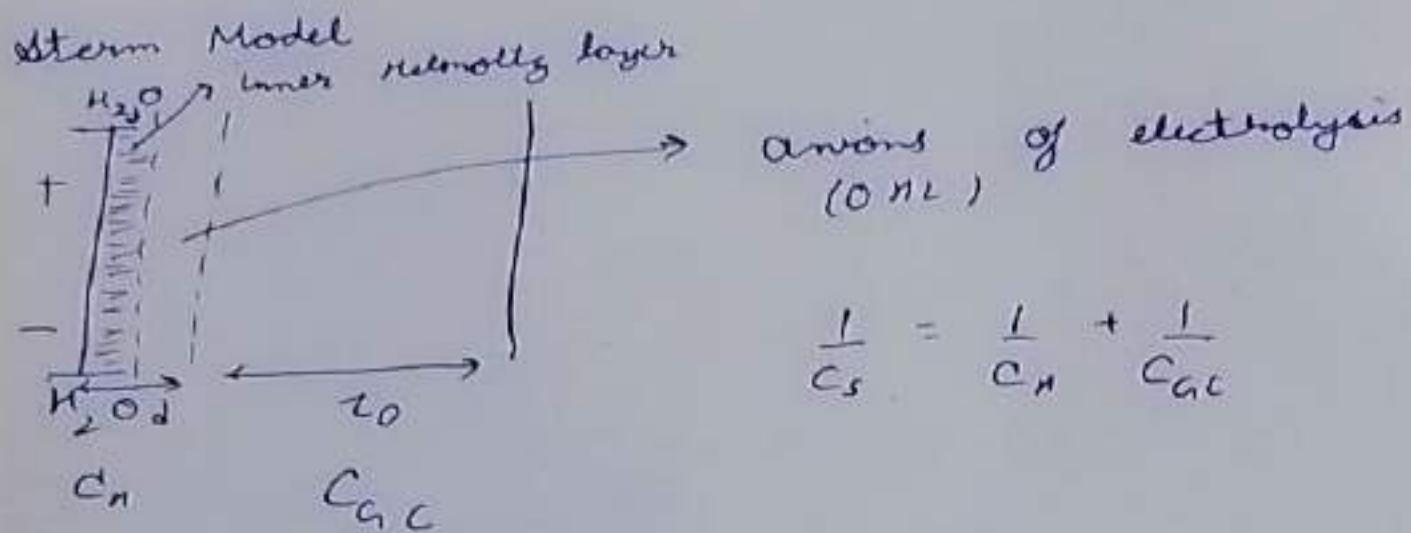
- Quantum chemistry and molecular orbital theory help describe electronic interactions at surfaces, providing insights into bonding, charge transfer, and surface reactivity.
- Surface reactions can be studied under controlled conditions (e.g., ultra-high vacuum) to understand molecular behavior without interference from environmental factors.
- Computational modeling allows researchers to simulate molecular interactions on surfaces, often at the atomic level.

- Density Functional Theory (DFT) is widely used to predict adsorption sites, binding energies, and reaction pathways on surfaces.
- Modeling enables visualization of molecule-surface interactions and predicts outcomes of surface reactions, helping optimize surface properties for applications like catalysis, sensor design, and material development.
- From this theory we understand that it enhance catalyst surface structure, optimize active sites.

Theory of BDM

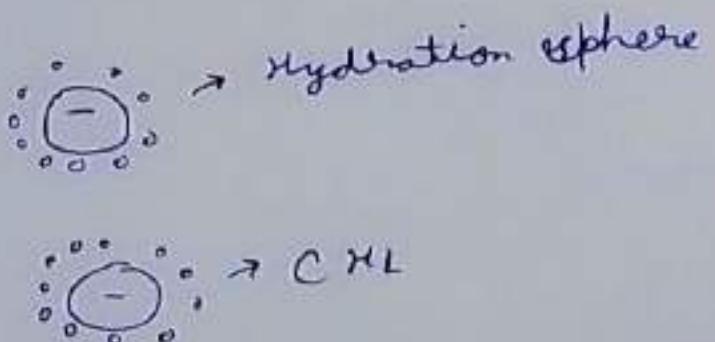
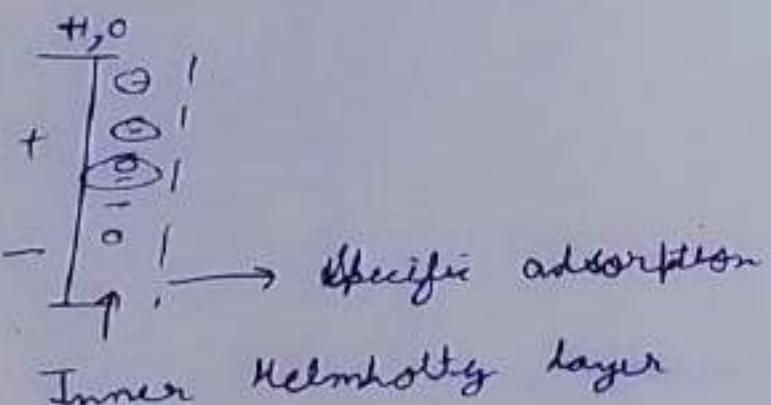
- The BDM model emphasizes that the strength of the bond between an adsorbate and the surface significantly impacts how the molecule behaves on the surface. Stronger bonds may lead to more stable adsorption but can inhibit further reactions.
- The model considers the unique characteristics of different surfaces, such as the types of atoms, surface geometry, and electronic structure, all of which influence bond formation.

- In the BDM model, adsorption sites on a surface can vary significantly in reactivity. For instance, edges, kinks, or defect sites may provide unique bonding environments, altering the chemical behavior of adsorbed molecules.
- The BDM model aids in understanding the transition states of reactions on surfaces. The model helps describe how the bond-dependent properties of a surface influence the activation energy of reactions.
- The BDM model is widely applied in catalysis research, where optimizing the surface bonds can maximize catalytic efficiency and selectivity.



H_2O combine the two model (NM, AC)

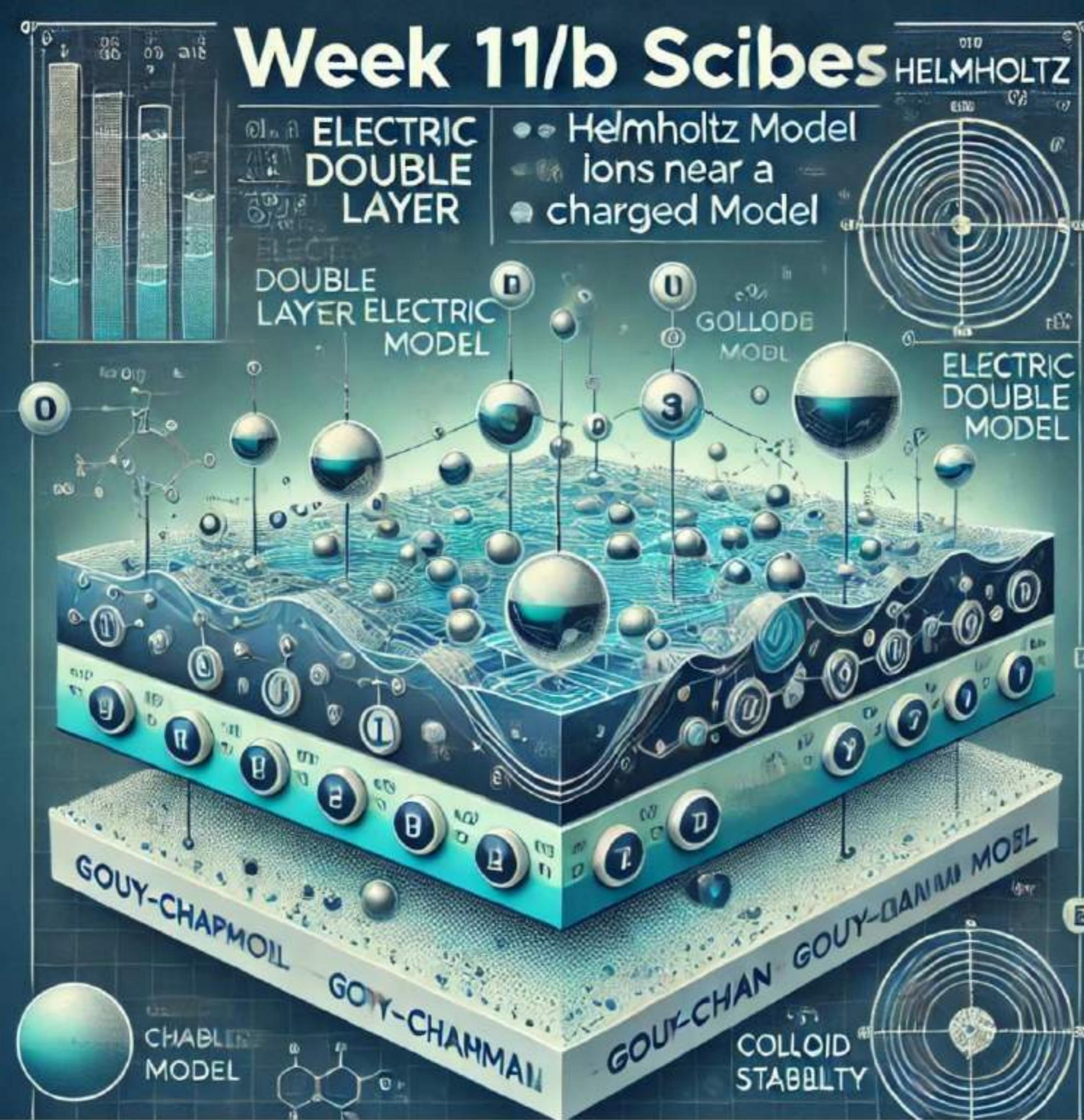
BMM model



Thank you!



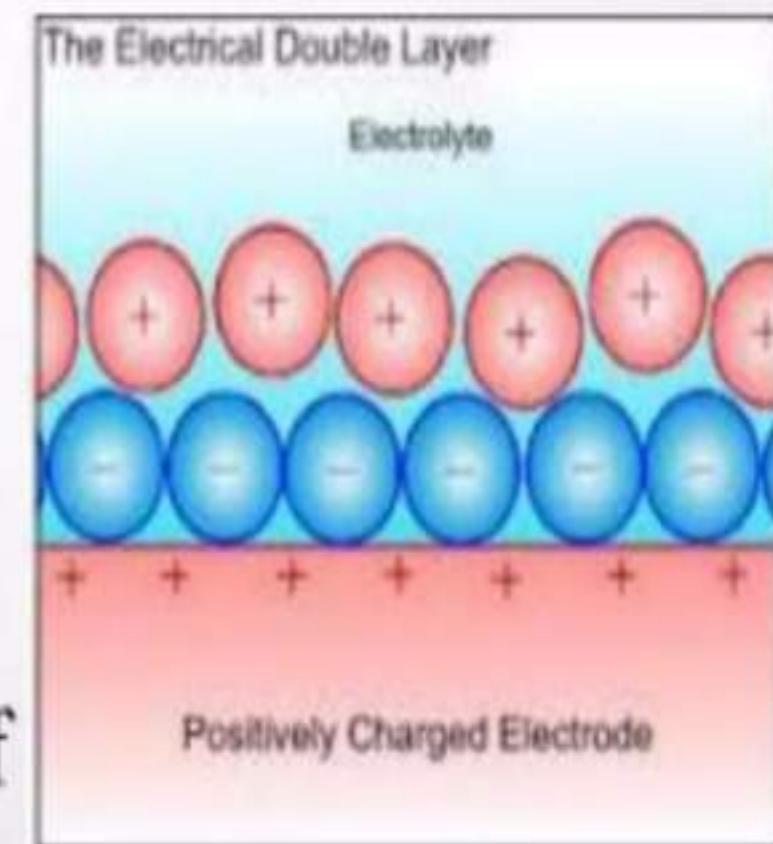
Week 11/b Scribes



Scribes
Week 11(B)

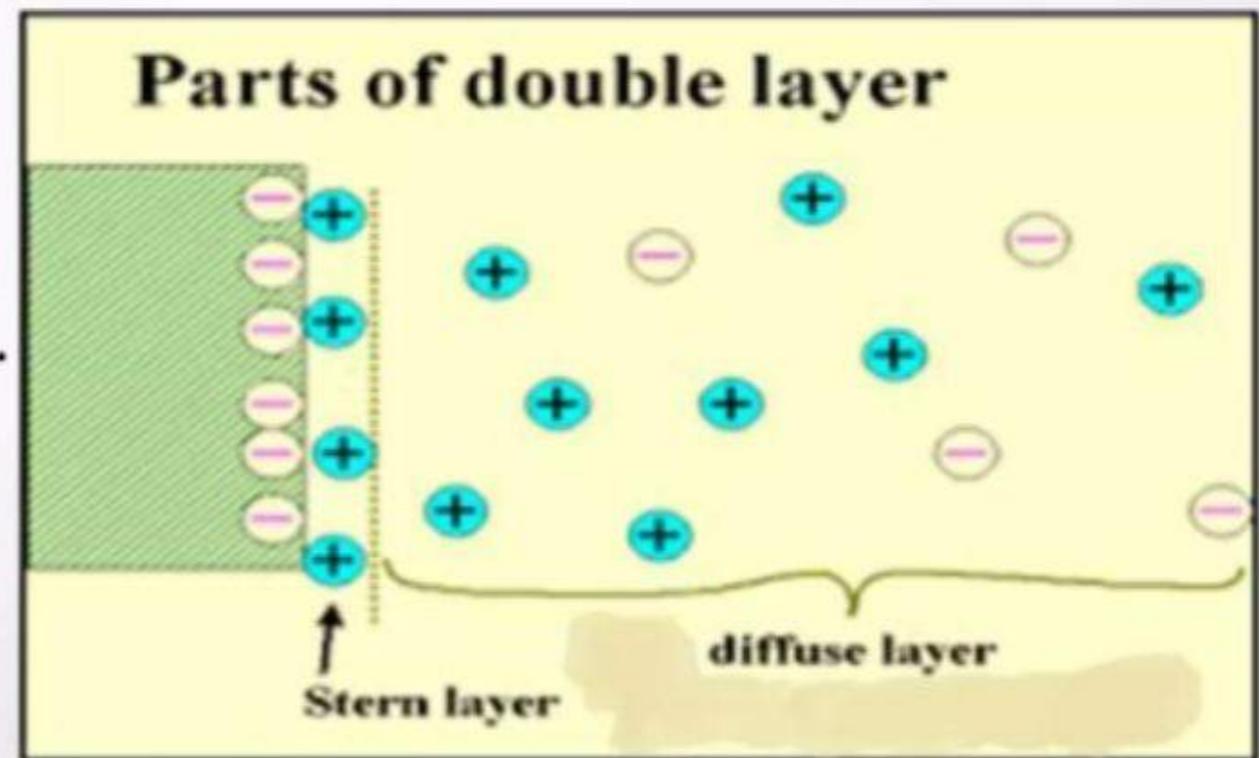
Electrical double layer

- Occurs between ions/molecules in solution and electrode surface.
- There is strong attraction between both.
- It uses to visualize the ionic environment in charged surface.
- Here ion distribute surrounding the charged surface. Therefore increases concentration of counter ions.
- Liquid droplet, solid particles, gas bubble use as object.



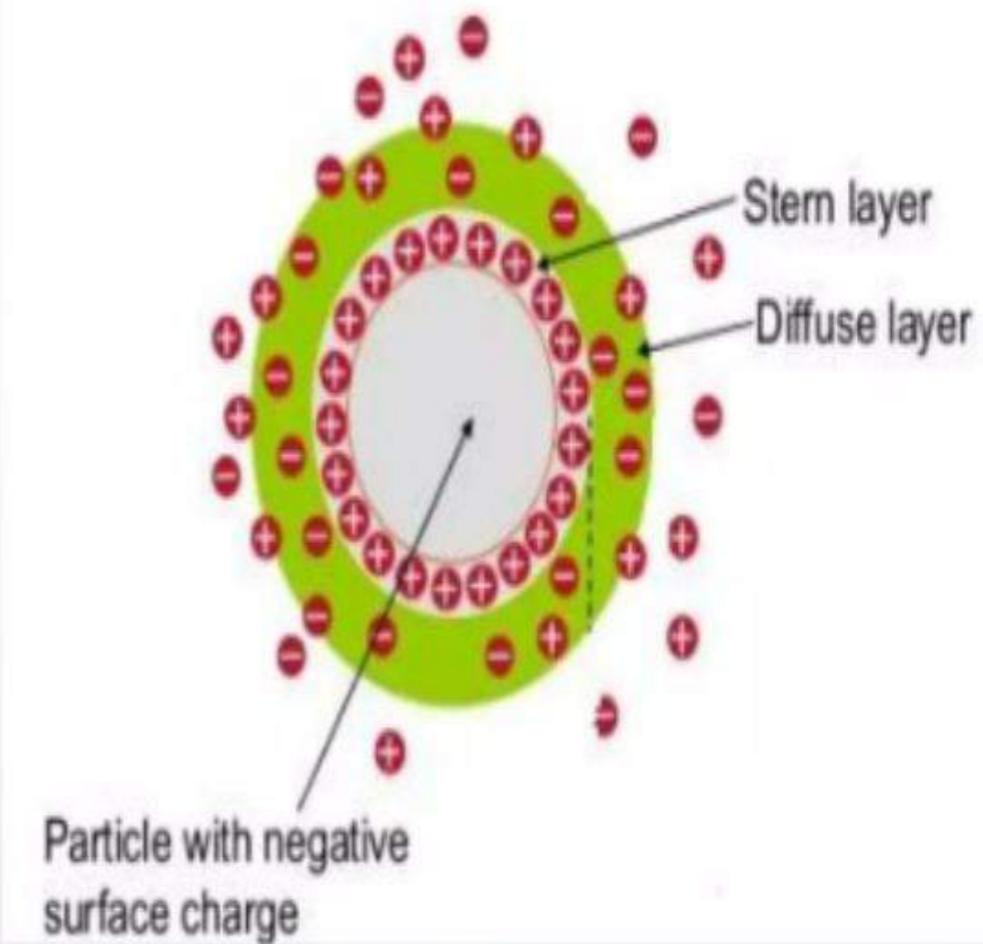
Electrical double layer consist of follows

- Diffuse double layer.
- Stern layer (tightly bound layer).



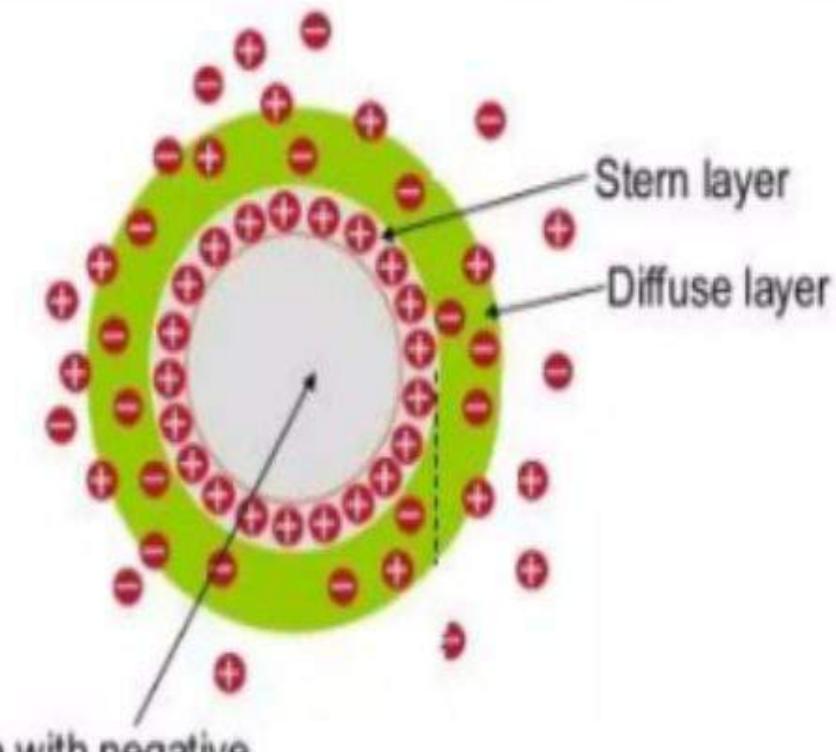
Diffuse double layer

- This layer is loosely associated with the layer.
- This layer called as bulk liquid layer.
- There are excess of negative ion after uniform distribution.



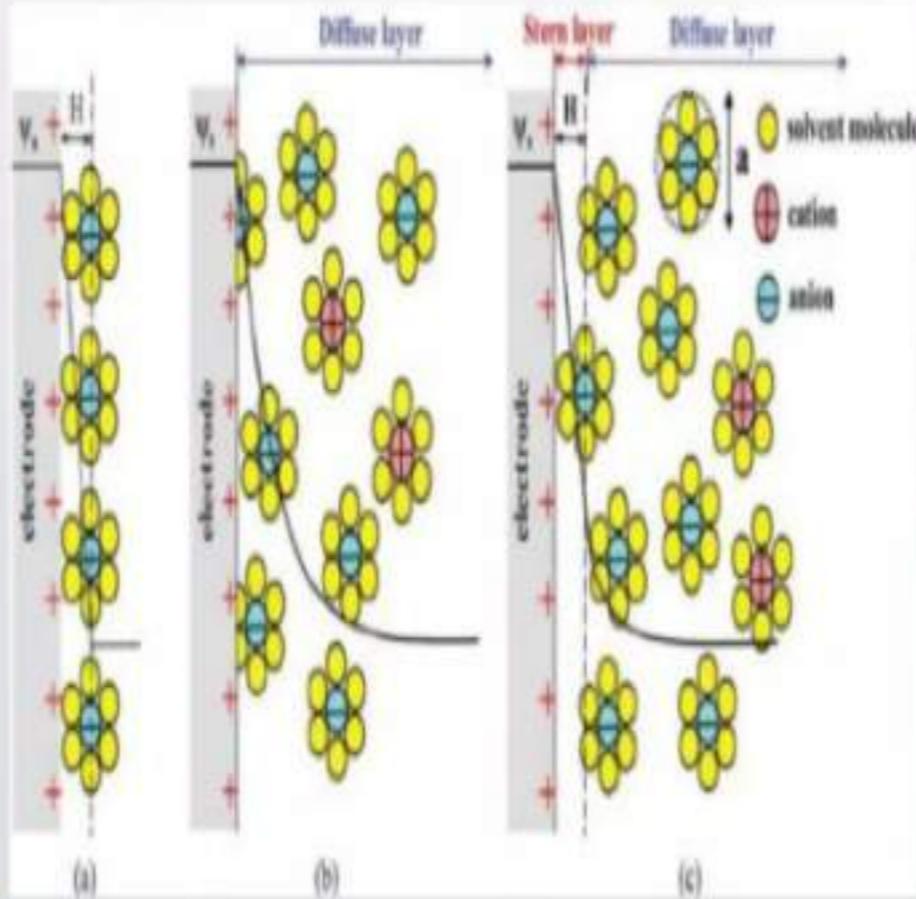
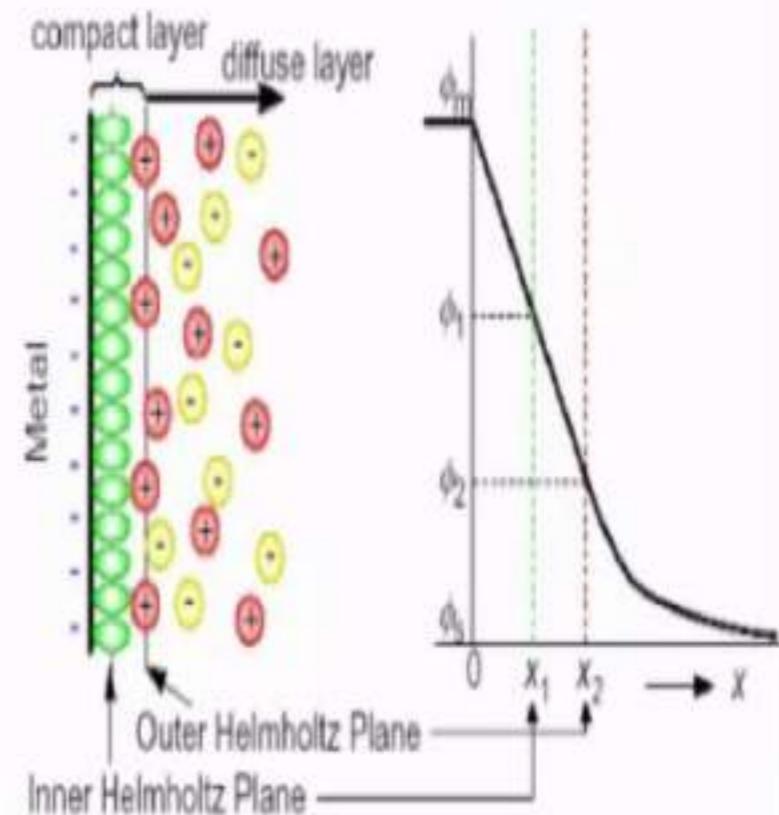
Stern layer

- This is the inner region.
- Here adsorbed ion due to chemical interaction.
- Cations are adsorbed by the negative surface.
- Counter ions is positive charged cations.



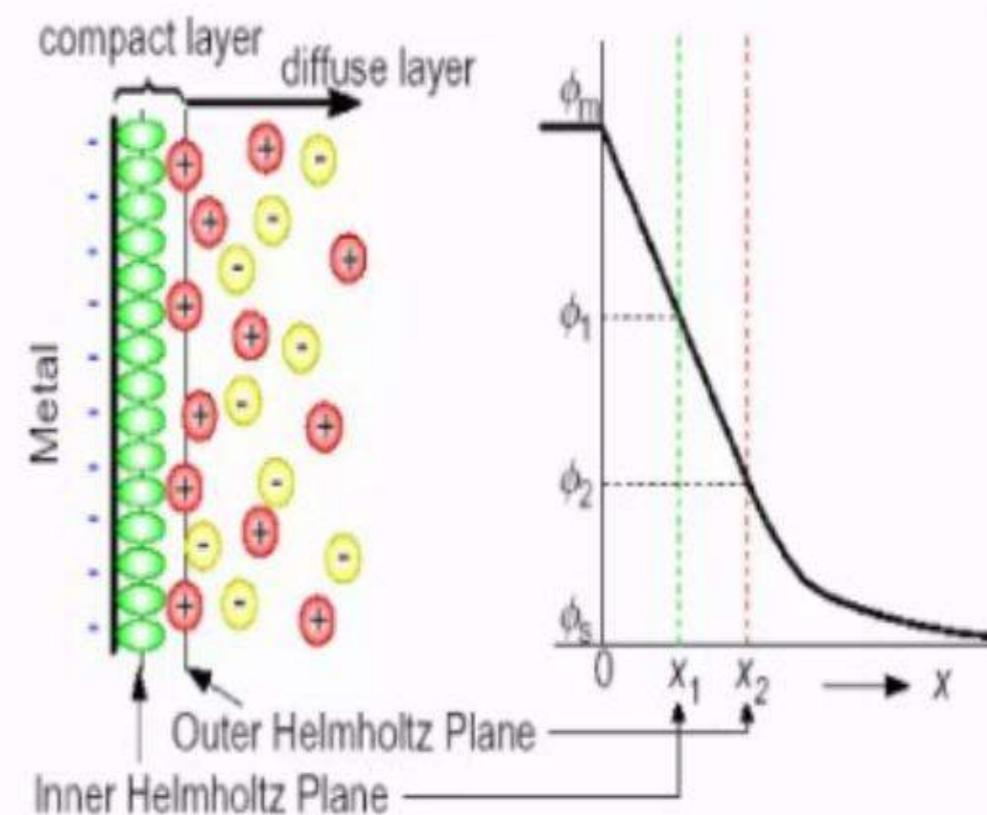
Model of electrical double layer

1. Helmholtz model
2. Gouy-Chapman model
3. Gouy-Chapman stern model



Helmholtz model

- Introduced by the Helmholtz in 1879.
- Describe about charge separation between solid surface and electrolyte solution.
- He proposed that surface charge is balanced by a layer of oppositely charged ions.
- Counter ions are cations.



- Potential of Helmholtz layer is described by the Poisson's equation.

$$\frac{\partial^2 \varphi}{\partial x^2} = -\frac{\rho(x)}{\epsilon_r \epsilon_0}$$

- When consider point charge equation can rewrite as:

$$\frac{\partial^2 \varphi}{\partial x^2} = 0$$

- Potential of capacitors:

$$C_H = \frac{\epsilon_0 \epsilon_r}{l}$$

l-thickness of double layer

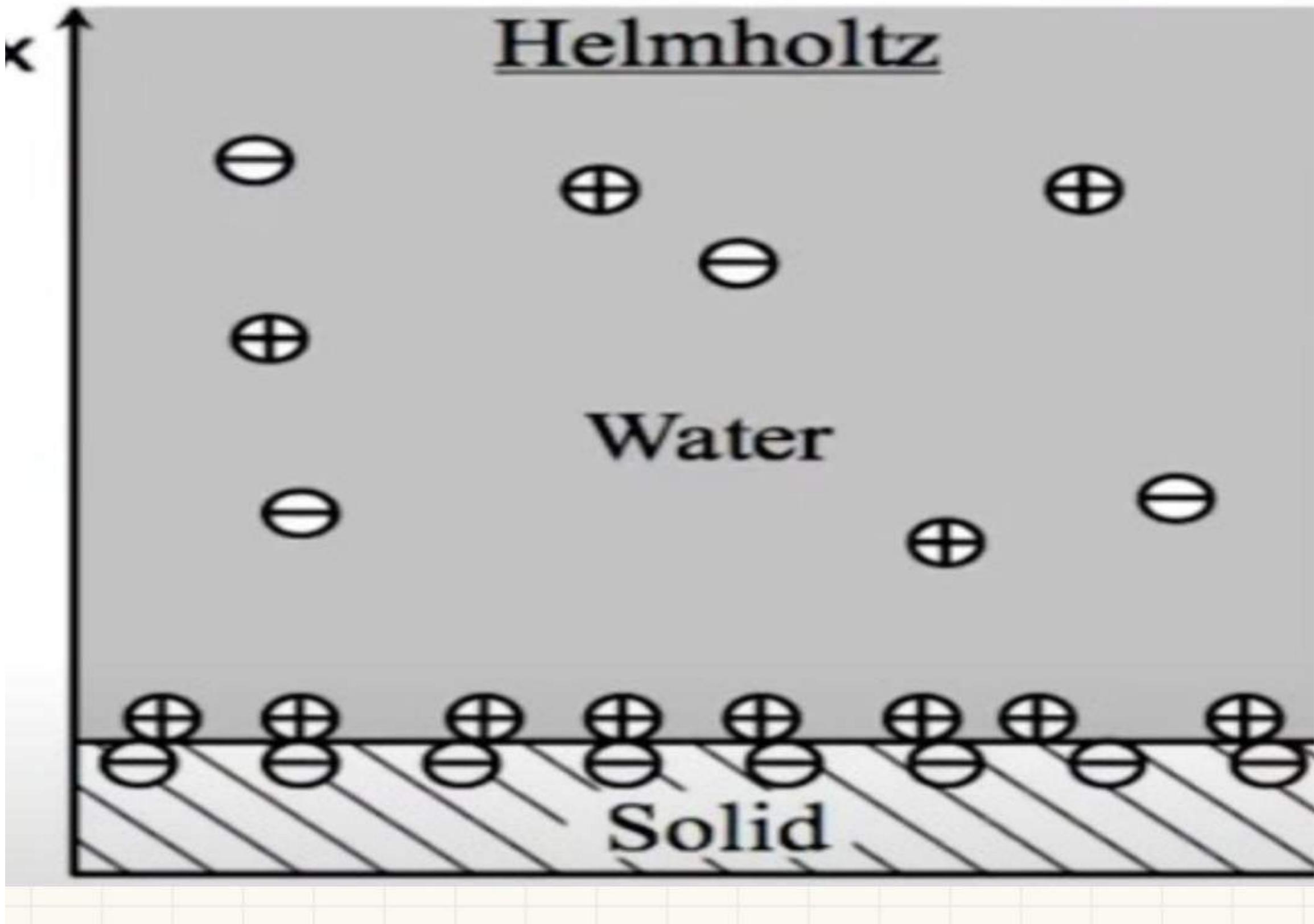
φ - Electric potential

ρ - Charge density

x - Distance from the electrode

ϵ_r - Permittivity of vacuum

ϵ_0 - Relative permittivity of the medium



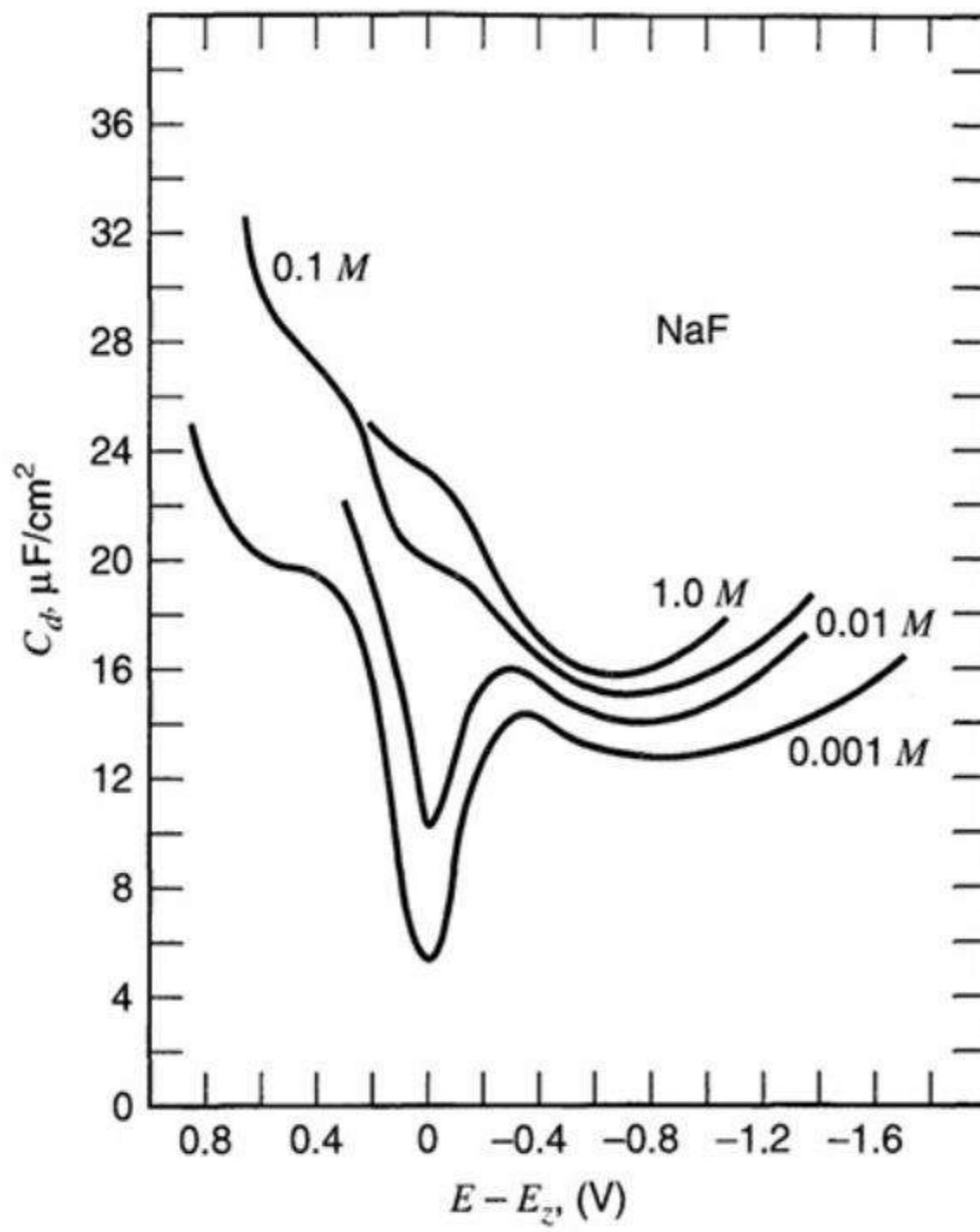


Figure 13.3.1 Differential capacitance *vs.* potential for NaF solutions in contact with mercury at 25°C. [Reprinted with permission from D. C. Grahame, *Chem. Rev.*, **41**, 441 (1947). Copyright 1947, American Chemical Society.]

Since the metallic electrode is a good conductor, it supports no electric fields within itself at equilibrium. In Chapter 2, we saw that this fact implies that any excess charge on a metallic phase resides strictly at the surface. Helmholtz, who was the first to think consequentially about charge separation at interfaces, proposed that the counter-charge in solution also resides at the surface. Thus there would be two sheets of charge, having opposite polarity, separated by a distance of molecular order. In fact, the name *double layer* arises from Helmholtz's early writings in this area (20–22).

Such a structure is equivalent to a parallel-plate capacitor, which has the following relation between the stored charge density, σ , and the voltage drop, V , between the plates (23):

$$\sigma = \frac{\epsilon\epsilon_0}{d}V \quad (13.3.1)$$

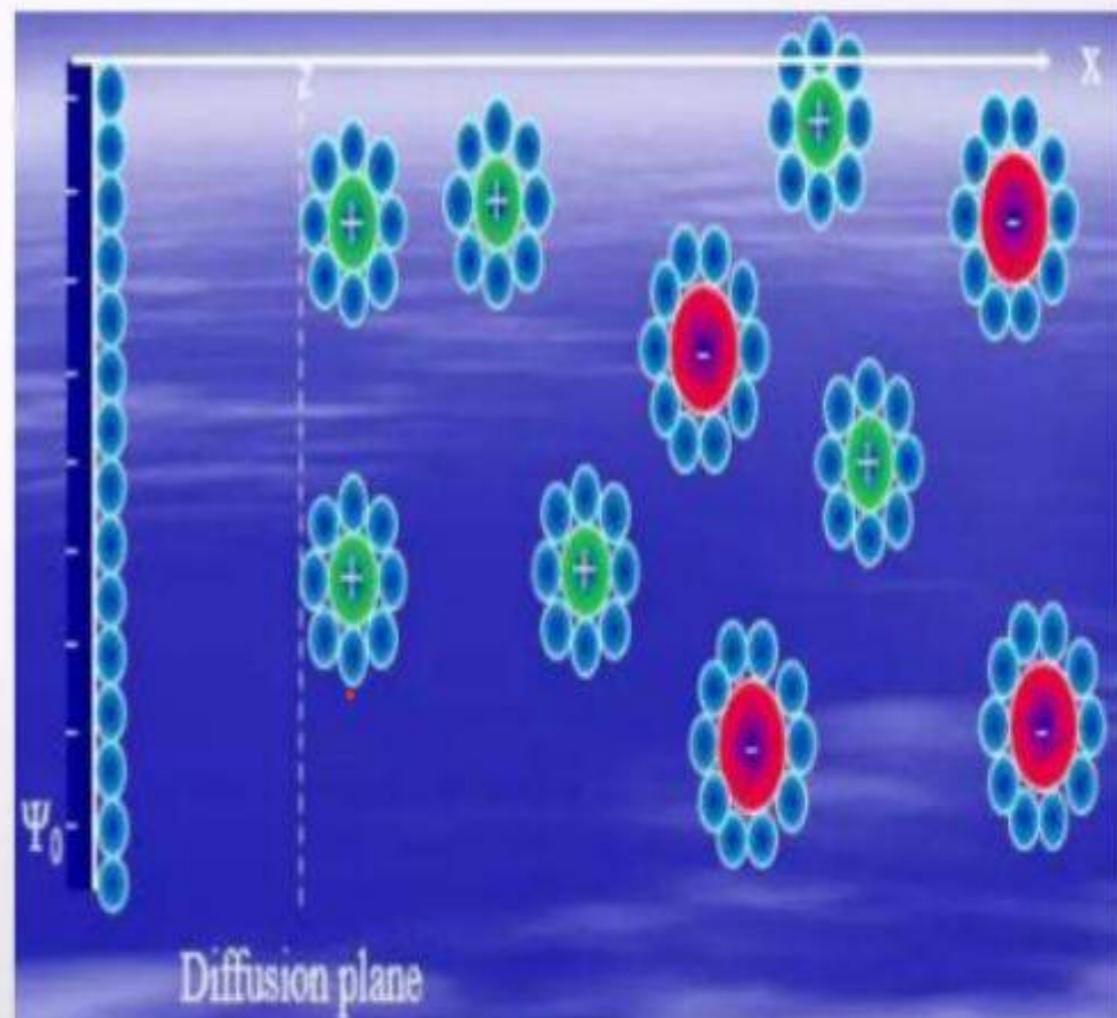
where ϵ is the dielectric constant of the medium, ϵ_0 is the permittivity of free space, and d is the interplate spacing.² The differential capacitance is therefore

$$\frac{\partial \sigma}{\partial V} = C_d = \frac{\epsilon \epsilon_0}{d} \quad (13.3.2)$$

The weakness of this model is immediately apparent in (13.3.2), which predicts that C_d is a constant. We know from our earlier discussion that it is not a constant in real systems. Figure 13.3.1 is a dramatic illustration for interfaces between mercury and sodium fluoride solutions of various concentrations. Variations in C_d with potential and concentration suggest that either ϵ or d depends on these variables; hence a more sophisticated model is clearly in order.

Gouy-Chapman model

- Here assumes ions are point charges.
- Ions don't interact with each other.
- Assume diffuse layer starts at some distance from the surface.
- Counter ions are cations.
- Those are affect for thickness of double layer.



- Concentration of counter ion follow the Boltzmann distribution.

$$n_i = n_i^0 \exp\left(\frac{-z_i e \varphi}{kT}\right)$$

- Counter ion concentration decrease.
- Bulk solution ion concentration increases.
- Exponential potential decrease.

Where,

n_0 - bulk concentration

z - Charge on the ion

e - Charge on a proton

k - Boltzmann constant

Stern's Modification to the Gouy-Chapman Model

Limitations of the Gouy-Chapman Model:

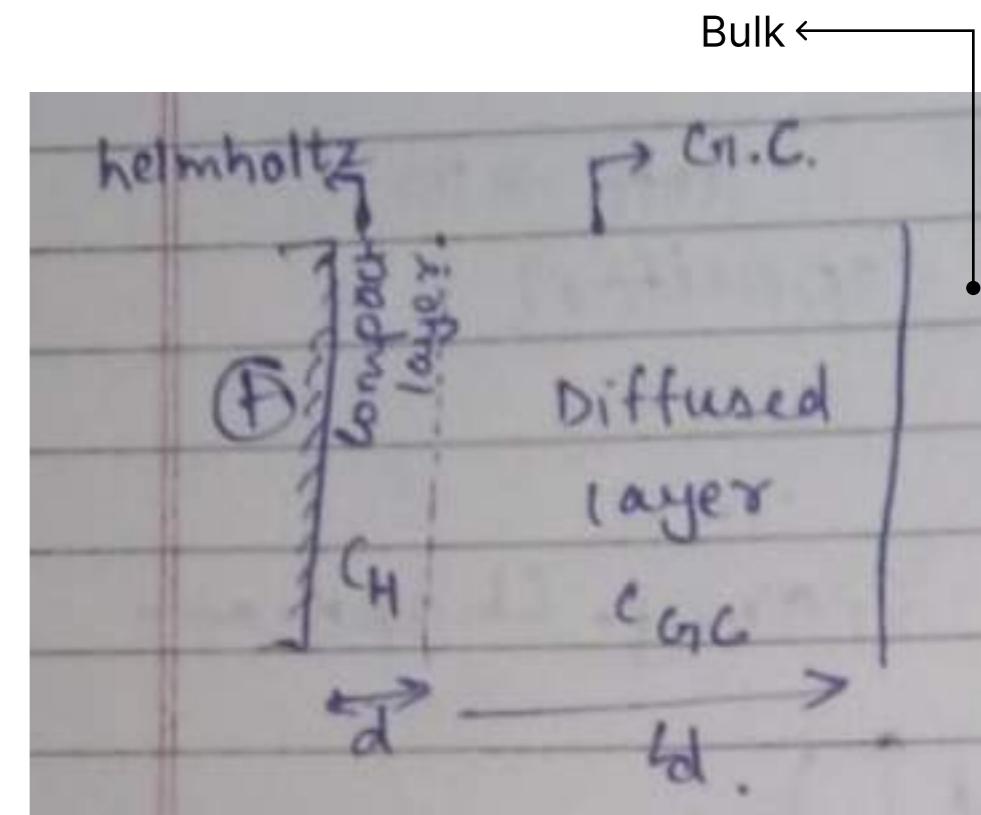
- In the Gouy-Chapman model, ions in solution are treated as point charges that can approach the electrode surface arbitrarily closely, leading to an unlimited increase in differential capacitance at high polarization.
- This model **ignores the finite size of ions** and assumes they are free to move all the way to the electrode surface.

Stern's Solution:

- To address these limitations, Stern introduced the concept of a **plane of closest approach** for ions, accounting for their finite size and solvation layers.
- This leads to **the Outer Helmholtz Plane** (OHP), a fixed distance from the electrode where solvated ions can **approach but not penetrate**.

Layer Structure

- **Compact Layer (Helmholtz Layer)**: Contains ions that are adsorbed or closely associated with the electrode surface up to the OHP.
- **Diffuse Layer**: Extends beyond the OHP, where ions are distributed based on their thermal motion and obey the Poisson-Boltzmann distribution.



Capacitance in the GCS Model

Capacitive Components:

- **Helmholtz Capacitance (C_H):** Represents the capacitance of the compact layer. It is largely independent of potential and depends on the dielectric constant and thickness of the compact layer.
- **Diffuse Capacitance (C_D):** Associated with the diffuse layer where ions are distributed according to the electrostatic potential. It varies with potential, showing a V-shaped dependence near the Potential of Zero Charge (PZC).

Behaviour of C_{GC}

- **Near PZC:** The diffuse capacitance C_D dominates, causing a significant dip in C_D .
- **At Higher Polarizations:** In systems with high electrolyte concentrations or at large polarizations, C_D becomes very large and no longer contributes significantly, so C_D approaches C_H

$$\frac{1}{C_d} = \frac{1}{C_H} + \frac{1}{C_D}$$

↓ ↓ ↓

Stern Model Capacitance Helmholtz Capacitance Diffuse Capacitance

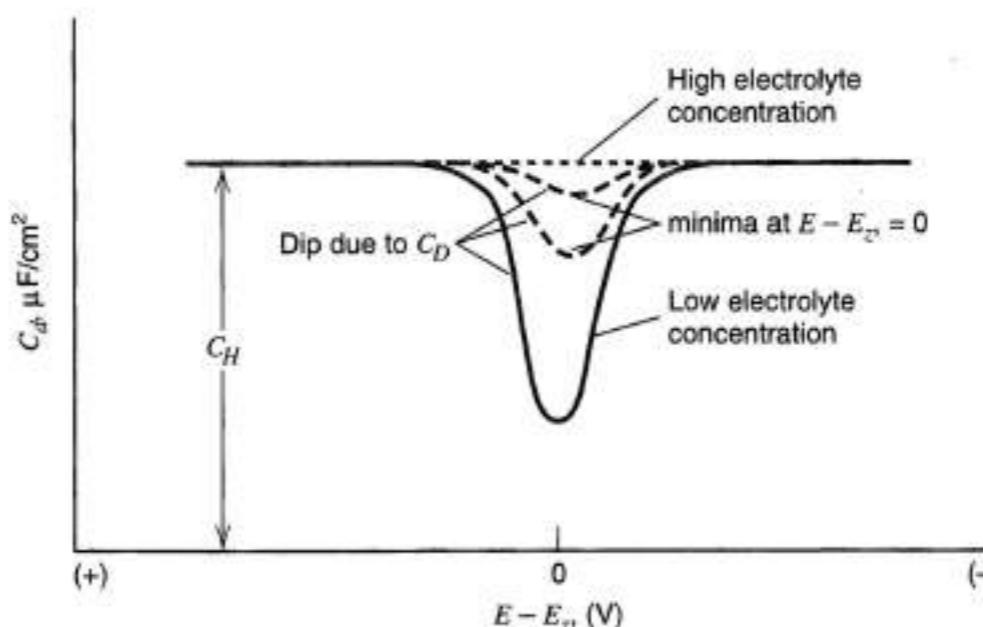
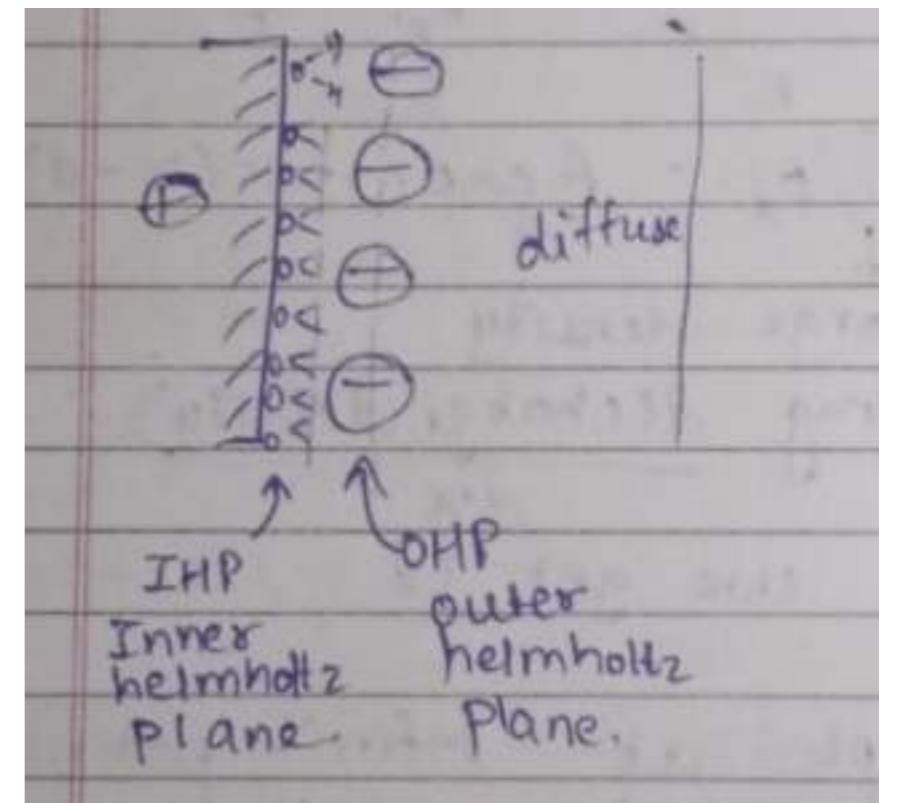


Figure 13.3.7 Expected behavior of C_d according to GCS theory as the electrolyte concentration changes.

Other Models

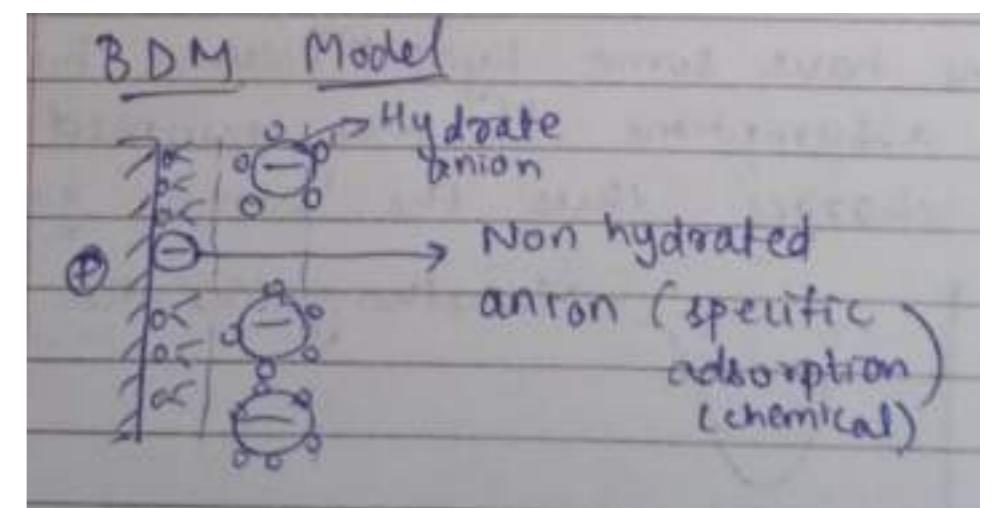
Grahame's Model

- Grahame's model of the electrical double layer builds on the GCS model, further dividing the double layer into three regions:
 - a. **Inner Helmholtz Plane (IHP)**: Closest to the electrode, with specifically adsorbed ions directly interacting with the surface.
 - b. **Outer Helmholtz Plane (OHP)**: Contains solvated ions that are attracted electrostatically but are not directly adsorbed.
 - c. **Diffuse Layer**: Extends beyond the OHP, with ions loosely spread out, gradually neutralizing the surface charge



BDM Model

- The BDM Model of the electrical double layer considers the presence of hydrated and non-hydrated anions near the electrode:
 - a. **Hydrated vs. Non-Hydrated Anions**: Hydrated anions, surrounded by water molecules, stay further from the electrode, while non-hydrated anions can come closer.
 - b. **Double Layer Structure**: Non-hydrated anions form the Inner Helmholtz Plane (IHP), while hydrated anions stay in the Outer Helmholtz Plane (OHP).
 - c. **Effect on Capacitance**: This arrangement impacts the double layer's capacitance and the reaction rates at the electrode, especially in systems where specific adsorption is significant.



The Relation Between σ^M and ϕ_0

$$q = \epsilon\epsilon_0 \oint_{\text{surface}} \mathcal{E} \cdot d\mathbf{S} \quad (13.3.17)$$

Since the field strength, \mathcal{E} , is zero at all points on the surface except the end at the interface [where the magnitude of the field strength is $(d\phi/dx)_{x=0}$ at every point], we have

$$q = \epsilon\epsilon_0 \left(\frac{d\phi}{dx} \right)_{x=0} \int_{\substack{\text{end} \\ \text{surface}}} dS \quad (13.3.18)$$

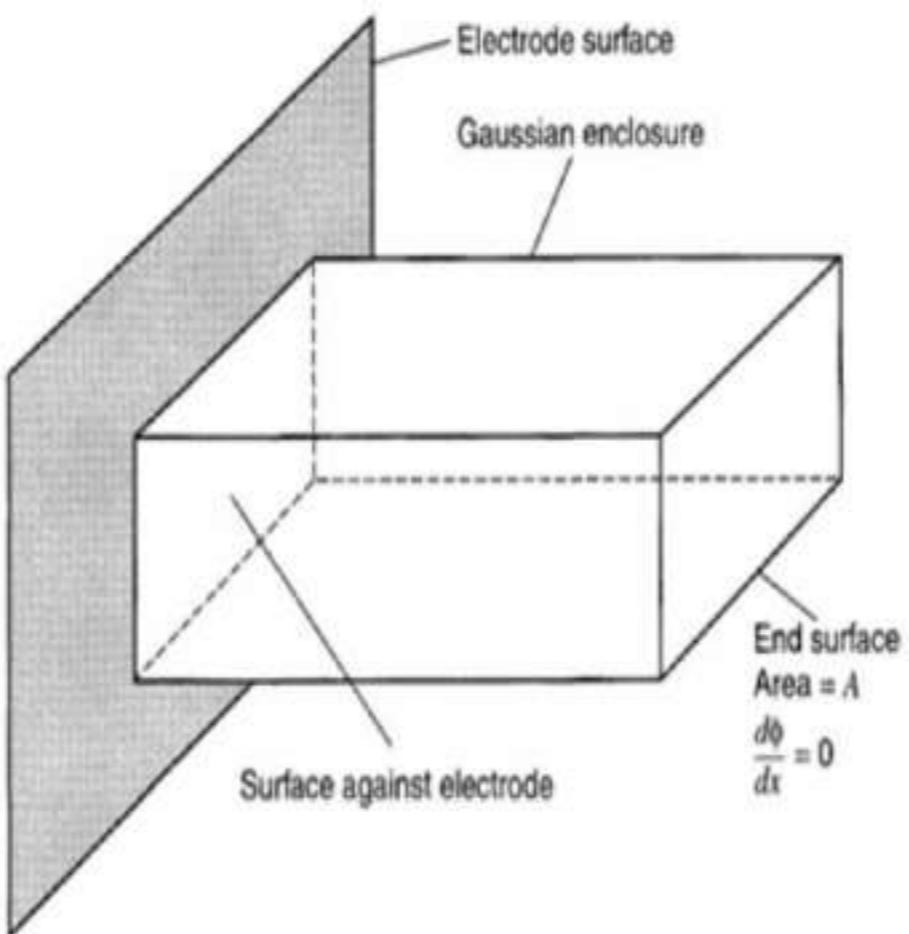


Figure 13.3.4 A Gaussian box enclosing the charge in the diffuse layer opposite an area, A , of the electrode surface.

$$q = \epsilon \epsilon_0 A \left(\frac{d\phi}{dx} \right)_{x=0} \quad (13.3.19)$$

Substituting from (13.3.11) and recognizing that q/A is the solution phase charge density σ^S , we obtain

$$\sigma^M = -\sigma^S = (8\kappa T \epsilon \epsilon_0 n^0)^{1/2} \sinh\left(\frac{ze\phi_0}{2\kappa T}\right) \quad (13.3.20a)$$

For dilute aqueous solutions at 25°C, the constants can be evaluated to give

$$\sigma^M = 11.7 C^*^{1/2} \sinh(19.5 z \phi_0) \quad (13.3.20b)$$

where C^* is in mol/L for σ^M in $\mu C/cm^2$. Note that ϕ_0 is related monotonically to the state of charge on the electrode.

(c) Differential Capacitance

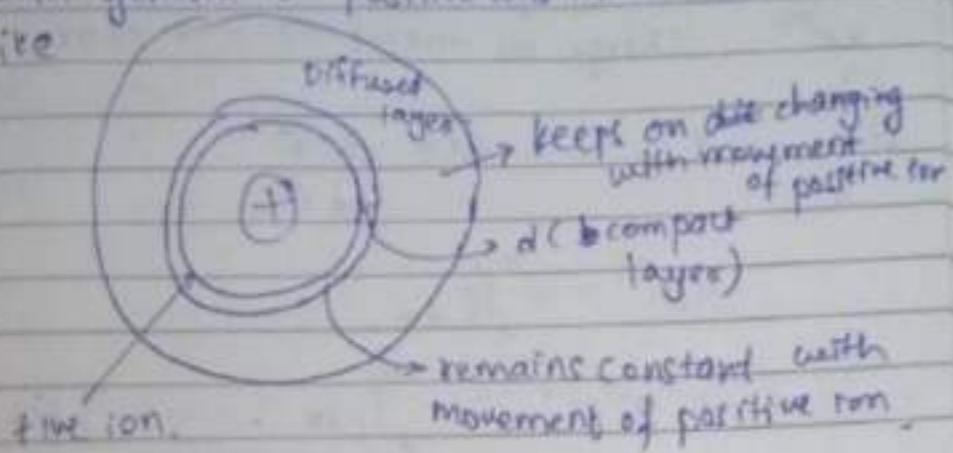
Now we are in a position to predict the differential capacitance by differentiating (13.3.20):

$$C_d = \frac{d\sigma^M}{d\phi_0} = \left(\frac{2z^2 e^2 \epsilon \epsilon_0 n^0}{\kappa T} \right)^{1/2} \cosh\left(\frac{ze\phi_0}{2\kappa T}\right) \quad (13.3.21a)$$

For dilute aqueous solutions at 25°C, this equation can be written,

$$C_d = 228 z C^*^{1/2} \cosh(19.5 z \phi_0) \quad (13.3.21b)$$

\Rightarrow In general a positive ion move in solvent like



$$\frac{d^2\phi}{dx^2} = -\frac{\rho}{\epsilon \epsilon_0} = -\epsilon \sum_i n_i z_i \exp(-z_i e \phi) / kT$$

$$\frac{d^2\phi}{dx^2} = \frac{1}{2} \frac{d}{dx} \left(\frac{d\phi}{dx} \right)^2$$

$$\Rightarrow \frac{d}{dx} \left(\frac{d\phi}{dx} \right)^2 = -\frac{2\epsilon}{\epsilon \epsilon_0} \sum_i n_i z_i \exp(-z_i e \phi) / kT.$$

on integrating.

$$\left(\frac{d\phi}{dx} \right)^2 = +\frac{2\epsilon}{\epsilon \epsilon_0} \sum_i n_i z_i \left(\frac{kT}{e} \right) \exp(-z_i e \phi) / kT + C.$$

on solving using Boundary conditions,

$$IMR: \frac{d\phi}{dx} = \left[\frac{2kT n^*}{\epsilon \epsilon_0} \right]^{1/2} \left[\exp\left(-\frac{ze\phi}{2kT}\right) - \exp\left(\frac{ze\phi}{2kT}\right) \right]$$

NOW $\sigma_m = -\sigma^d$
charge on metal \rightarrow -ve charge in soln.

$$\sigma^d \sim ? \quad Cd = d \frac{\sigma^d}{d\phi}$$

$$\sigma^d = -\frac{\epsilon \epsilon_0}{\epsilon \epsilon_0} \int_0^\infty dx.$$

$$\Rightarrow \sigma^d = - \int_0^\infty \frac{d\phi}{dx} dx = \epsilon \epsilon_0 \frac{d^2\phi}{dx^2} dx \\ = \epsilon \epsilon_0 \left[\frac{d\phi}{dx} \Big|_0 - \frac{d\phi}{dx} \Big|_\infty \right]$$

$$\Rightarrow \sigma^d = -\epsilon \epsilon_0 \frac{d\phi}{dx} \Big|_{x=d}$$

$$= -\epsilon \epsilon_0 \left[\frac{2kT n^*}{\epsilon \epsilon_0} \right]^{1/2} \left[\exp\left(-\frac{ze\phi_d}{2kT}\right) - \exp\left(\frac{ze\phi_d}{2kT}\right) \right]$$

$$= \left[\frac{2kT n^*}{\epsilon \epsilon_0} \right]^{1/2} \left[\exp\left(\frac{ze\phi_d}{2kT}\right) - \exp\left(-\frac{ze\phi_d}{2kT}\right) \right] \\ e^x - e^{-x} = \sinh x$$

$$\Rightarrow \sigma^d = \left[\frac{2kT n^*}{\epsilon \epsilon_0} \right]^{1/2} \left[\sinh\left(\frac{ze\phi_d}{2kT}\right) \right]$$

$$\Rightarrow \frac{d\sigma^d}{d\phi} = \text{constant} \cosh\left(\frac{ze\phi_d}{2kT}\right)$$

COLLOIDAL STABILITY

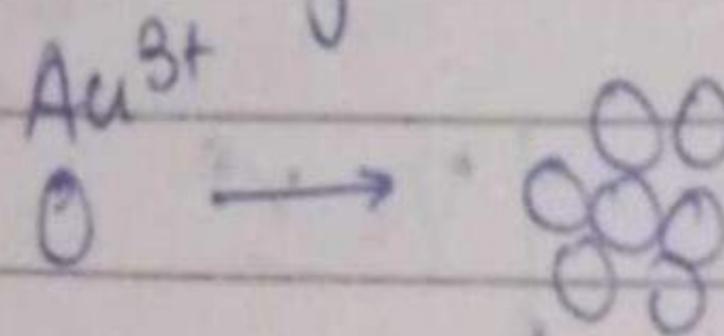
It is the ability of particles in a colloid to remain evenly spread out without clumping together or settling over time. Stable colloids keep their particles suspended, maintaining a consistent appearance and performance.

Why Colloidal stability matter

In a stable colloid, particles don't clump together or settle at the bottom, so the mixture stays uniform. This stability is essential in various products like pain, food medicines and cosmetics, where clumping or settling would make them ineffective or unpleasant to use;

➤ Faraday's gold colloid very stable

Nucleation and growth, [Problem]



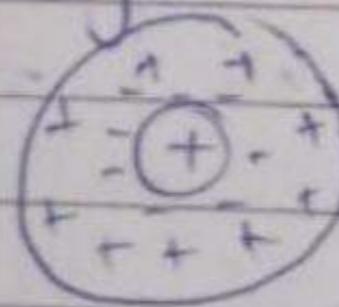
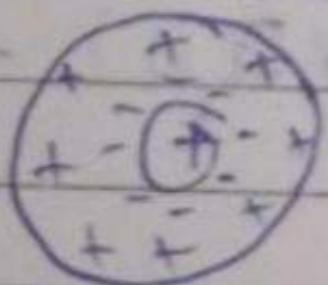
come together &
thus precipitate
(agglomerate)

➤ WAYS TO STABILISE COLLOIDS

1. ELECTRIC DOUBLE LAYER

An electric double layer is a phenomenon that plays a fundamental role in the mechanism of the electrostatic stabilization of colloids. Colloidal particles gain negative electric charge when negatively charged ions of the dispersion medium are adsorbed on the particle surface. A negatively charged particle attracts the positive counterions surrounding the particle. An electric double layer is the layer surrounding a particle of dispersed phase, including the ions adsorbed on the particle surface and a film of the counter charged dispersion medium. The electric double layer is electrically neutral.

i) Electrical double layer:

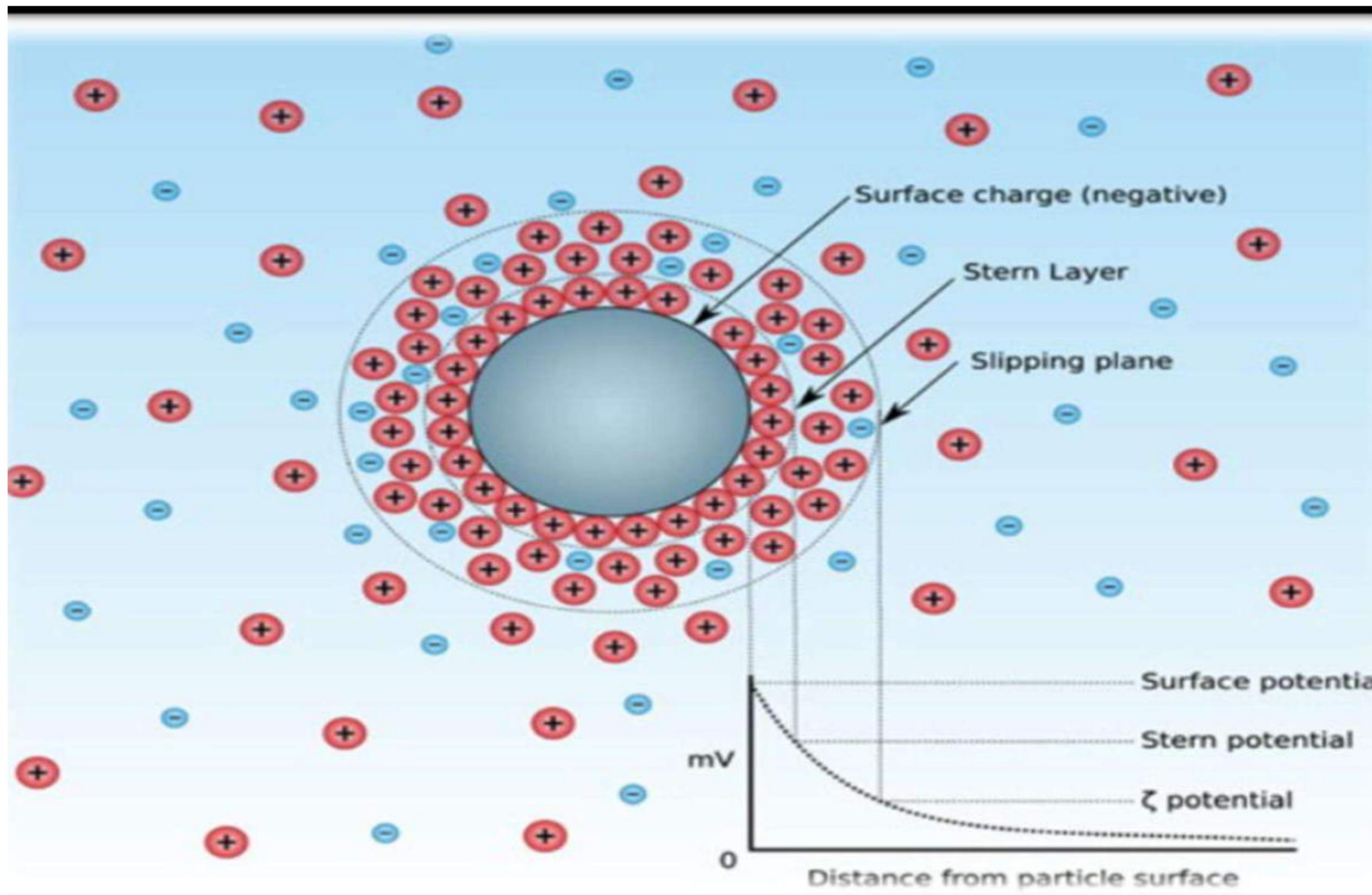


The layer makes the coming closer difficult

- The value of zeta potential (ζ) tells us about stability of colloidal particles

ZETA POTENTIAL

Zeta potential is a parameter that measures the electrochemical equilibrium at the particle-liquid interface. It measures the magnitude of electrostatic repulsion/attraction between particles and thus, it has become one of the fundamental parameters known to affect stability of colloidal particles. It should be noted that that term stability, when applied to colloidal dispersions, generally means the resistance to change of the dispersion with time. Figure below illustrates the basic concept of zeta potential.



<i>Zeta Potential (mV)</i>	<i>Stability behaviour of the particles</i>
<i>0 to ±5</i>	Rapid Coagulation or Flocculation
<i>±10 to ±30</i>	Incipient Instability
<i>±30 to ±40</i>	Moderate Stability
<i>±40 to ±60</i>	Good Stability
<i>More than ±61</i>	Excellent Stability

Principle of Zeta Potential Analysis

Electrokinetic Phenomena

Because an electric double-layer (EDL) exists between a surface and solution, then any relative motion between the rigid and mobile parts of the EDL will result in the generation of an electrokinetic potential. As described above, zeta potential is essentially a electrokinetic potential which rises from electrokinetic phenomena. So it is important to understand different situations where electrokinetic potential can be produced. There are generally four fundamental ways which zeta potential can be produced, via electrophoresis, electroosmosis, streaming potential, and sedimentation potential as shown in the Figure .

DP = Disperse Phase

LP = Liquid Phase

Electrophoresis

DP – in Movement
LP – Stationary

Electro-Osmosis

DP – Stationary
LP – in Movement

Applied
electrical field
causes movement

Zeta Potential

Mechanical force
results in electric
potential

Streaming Potential

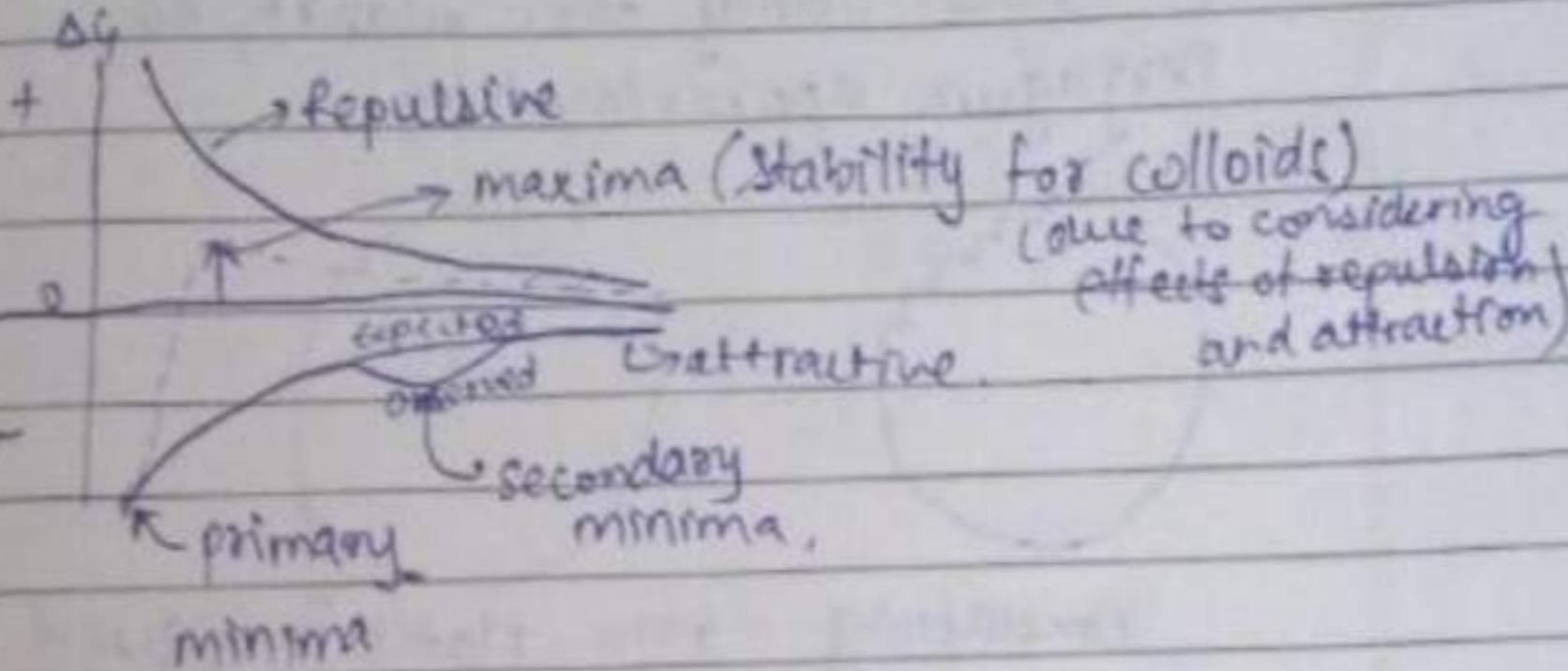
DP – Stationary
LP – in Movement

Sedimentation Potential

DP – in Movement
LP – Stationary

Zeta potential is measured at the shear plane which is just outside of the outer Helmholtz plane

⇒ Higher ζ , better stability of colloids.
if $\zeta \geq \pm 25 \text{ mV}$ → stable colloids.



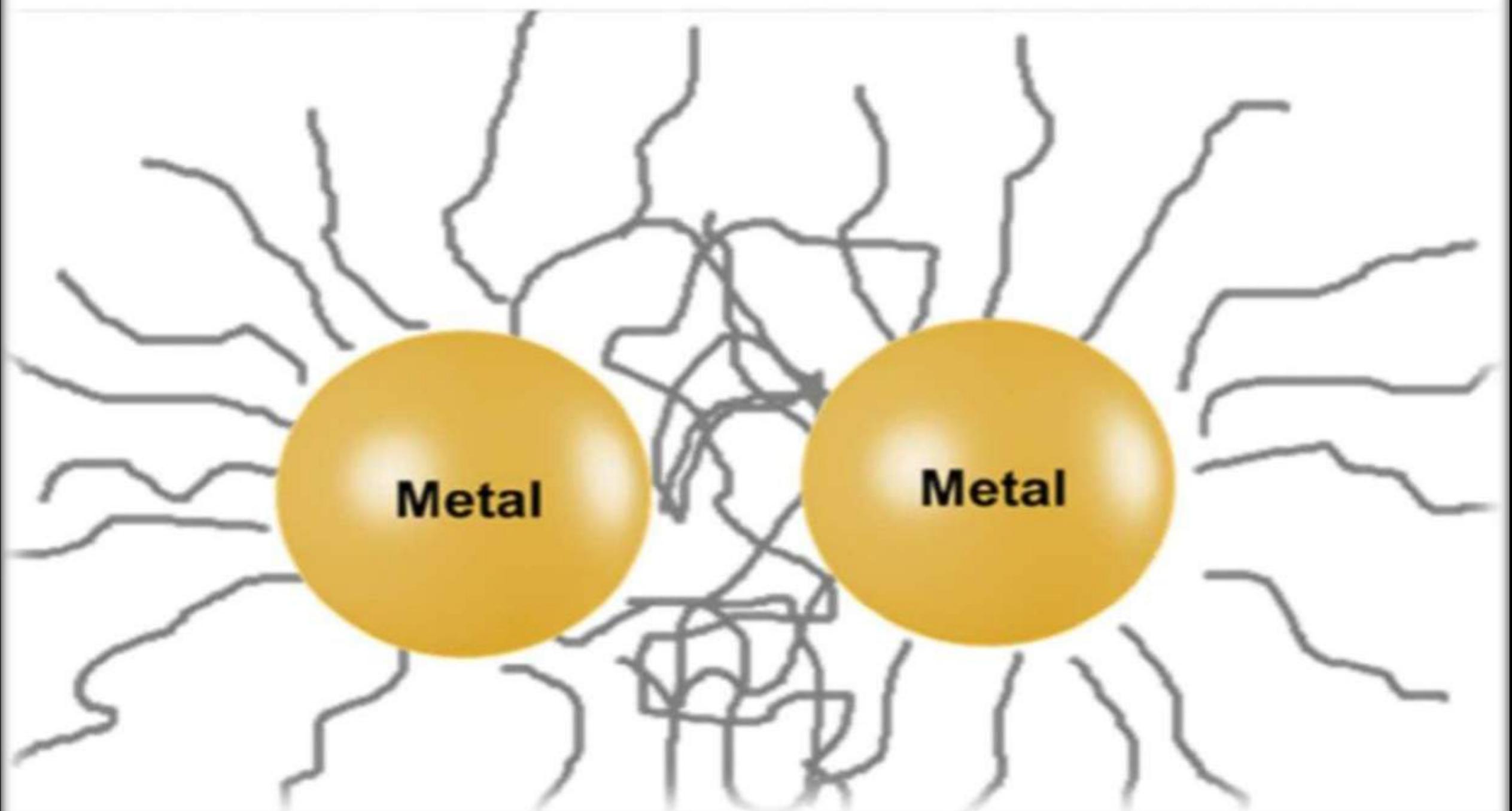
Primary Minima → Agglomeration (From where separation becomes difficult & precipitation occurs)

Secondary Minima → Flocculation (From where separation again in molecules is possible)

2. STERIC STABILISATION

Steric stabilization is way to keep tiny particles in liquid from clumping together. This is done by attaching long molecules to the surfaces of each particle. These molecules form a cushion around the particles, which keeps them from getting too close to each other. This technique is useful in things like paint's medicines, and cosmetics, where it's important for particles to stay evenly mixed without clumping.

Steric stabilization





A stylized illustration of a beach scene. The background features large, expressive waves in shades of orange, white, and teal. In the foreground, there's a white beach chair with a striped cushion, a small white umbrella, and a brown beach bag with white stripes. The overall style is graphic and modern.

THANK YOU

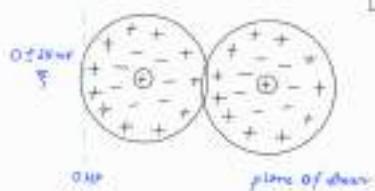
4, 5, 7, 14 Now defined

Colloidal stability

Factors: ΔG , ζ , d

Ways to disrupt :-

① Electrical double layer



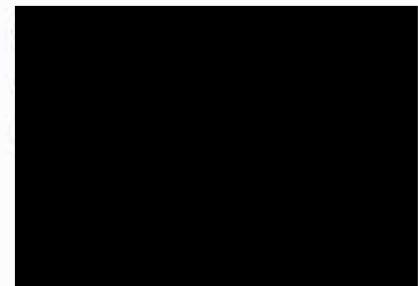
IHP (Inner Helmholtz Plane) layer of ions next to the surface

Composed of water and of electrodes.
Ions adsorbed.

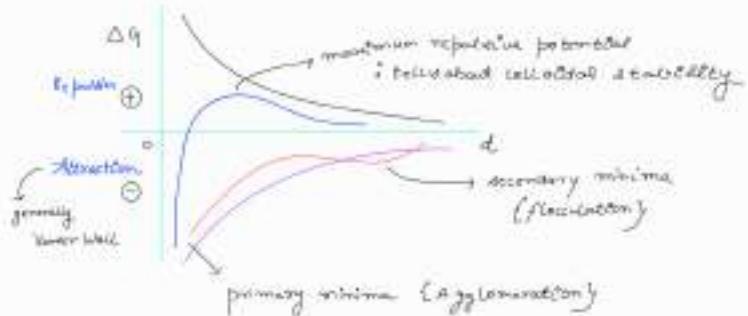
OHP (outer Helmholtz Plane)

Composed of hydrated ions
in a ratio to a certain
distance

The layer beyond OHP, called
the Gouy-Chapman Layer, it where
excess ions are present



ΔG w.r.t. to charged :

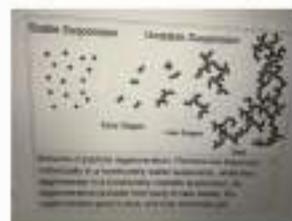


Due to decrease of distance of particles, after a certain threshold, their orbits will overlap and form an interactive bond (sign of instability for colloid)

Flocculation : The process where colloidal particles clump together to form a larger particle (flocs)
→ This occurs on addition of flocculant.



Agglomeration : The process when colloidal particles come together to form clusters



② Steric stabilization: Prevention of colloid from aggregating by adding non-ionic macromolecules to their surface.

steric hindrance

DLVO (Derjaguin - Landau - Verway - Oortbeck)

Derjaguin Approximation

$$\frac{d\phi}{dr} = 0$$

$P_m = \text{max pressure}$

Here we approximate the union surface as a flat surface for ease of calculation.

Two forces

For symmetrical charges

$$f = \pi r^2 Z \left[\exp\left(\frac{-Zc\phi}{kT}\right) - \exp\left(\frac{Zc\phi}{kT}\right) \right]$$

$$f = -2\pi r^2 Z \sinh\left(\frac{Zc\phi}{kT}\right)$$

$\int \frac{dp}{P_s} = 2\pi c Z \int_0^{R/2} \tanh\left(\frac{Zc\phi}{kT}\right) d\phi$

$\Phi = \frac{4\pi r}{Zc} \tanh\left(\frac{Zc\phi}{kT}\right) \exp\left(-\frac{Zc\phi}{kT}\right)$

$F_e = \frac{d\Phi}{dr}$

$$F_{elec} = -\int \frac{d\Phi}{dr} = -\int \pi r^2 Z \exp\left(\frac{-Zc\phi}{kT}\right) d\phi$$

$$\left(\int \sum_i \pi r^2 Z_i \exp\left(\frac{-Z_i c \phi}{kT}\right) d\phi \right)$$

$$= -2\pi r^2 Z \exp\left(\frac{-Zc\phi}{kT}\right)$$

$d\Phi = -f d\phi$

$$P_{h/2} - P_s = 2kTn^2 \left[\tanh\left(\frac{Zc\phi_{h/2}}{kT}\right) - 1 \right]$$

Apply Taylor series and take 2 terms for small $\phi_{h/2}$ potential

$$\Pi_{EDL} = kTn^2 \left(\frac{Zc\phi_{h/2}}{kT} \right)^2 \text{ for small } \phi_{h/2}$$

$$\Pi_{EDL} = 64kTn^2 \tanh^2\left(\frac{Zc\phi_{h/2}}{4kT}\right) \exp(-R\lambda) \text{ for } \lambda = h/2$$

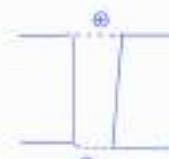
$6N_A \frac{d\Phi}{dr} = F_{edr} \Rightarrow \text{integrate this after putting } F_e = \Pi$

$\bar{\Phi}_{Electrostatic PE} = 64kTn^2 \tanh\left(\frac{Zc\phi_0}{4kT}\right) \exp(-\lambda) \lambda^{-2}$

Electrophoresis

Electrical force QE

Visual force = $F_v = 6\pi\eta_r Rv$



At steady state: $QE = 6\pi\eta_r Rv$, $\frac{dv}{E} = \frac{Q}{6\pi\eta_r R}$ Electrophoresis mobility

Potential Distribution around spherical surface Dudy Hückel Approximation

$$\frac{1}{r} \cdot \frac{\partial}{\partial r} \left(\frac{r^2 \partial V}{\partial r} \right) = \frac{\rho^2}{k_BT} [2\pi r Zc^+] V$$

$$r \frac{\partial^2 V}{\partial r^2} = \tau K^2 \alpha \quad (\text{where } \alpha = r^2)$$

Generalized solution: $\frac{C_1}{r} \exp(-kr) + \frac{C_2}{r} \exp(kr)$

By Gauss law $\Phi = \frac{Q}{4\pi\epsilon_0 r}$

$$\begin{cases} \Phi = \frac{C_1}{r} \exp(-kr) \\ C_1 = \Phi r \end{cases} \rightarrow \text{at } r \text{ very large}$$

$$\oint d\phi = 4\pi k \epsilon_0 \rho r \rightarrow \frac{\nu}{E} = \frac{4\pi k \epsilon_0 \rho r}{4\pi n_2 R} = \frac{1}{3} \frac{8\pi \phi}{n}$$

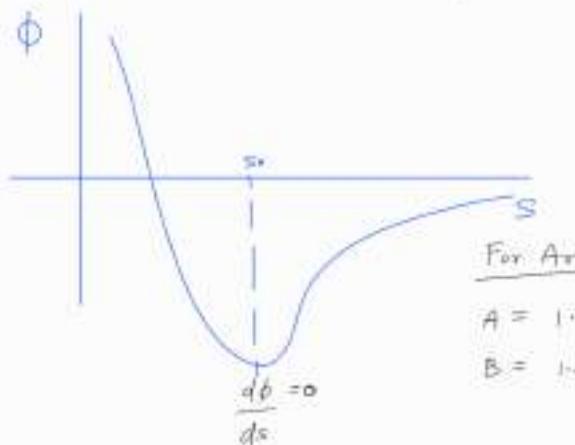
$$\phi = \frac{\pi}{2} \text{ zero potential} \rightarrow \frac{\nu}{E} = \frac{1}{3} \frac{8\pi \phi}{n}$$

ideal gas $PV = nRT$
 Real gas $\left(\rho + \frac{a n^2}{V^2}\right)(V - nb) = nRT$

$$M_i \in \phi = -\frac{A}{S^2} + \frac{B}{S^4}$$

$$\text{London} \rightarrow \phi = -\frac{A}{S^2} + \frac{B}{S^4}$$

Lennard-Jones potential
 LJ pot. or 6-12 pot



$$CA_{S_0}^{-6} - 12BS_0^{-12} = 0 \Rightarrow \frac{6A}{12B} = S_0^{-6} \Rightarrow S_0 \left(\frac{2B}{A} \right)^{1/2}$$

$$S_0 = 1.65 \times 10^{-10} \text{ m}$$

$$\phi_{VDW} = -\frac{A_{vdw}}{S^6} = -\left(\frac{A_L + A_r + A_d}{S^6} \right)$$

A_H = Hamaker const

$$\Phi_{net} = \Phi_{RDC} + \Phi_{VDW} = \left(64 \pi F n^2 R^{-1} \right) \tanh^2 \left(\frac{Ze\phi_0}{4kT} \right) \times \exp(-kT) = A_H \frac{1}{12\pi h^2}$$

$$A_H = \pi^4 n_1 n_2 A_L$$

for 2 diff. types
 of molecules

$$A_L = \frac{9ab}{4\pi^2 h^3 c^3} \text{ Van der Waals}$$

Parameterized

On real gas eqn

$$\text{For CH}_4: a = 0.248 \text{ m}^6 \text{ mol}^{-2}$$

$$b = 4.3 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$$

$$A_L = 1.02 \times 10^{-72} \text{ J m}^6$$

$$3A_L = 1 \text{ J m}^6$$

$$A_L = \frac{3\pi_1 \pi_2 h v_1 v_2}{2(v_1 + v_2)} \left(\frac{1}{4\pi \epsilon_0} \right)^2$$

$\alpha \rightarrow$ polarizability

If $\alpha_1 = \alpha_2$: same molecular interaction

$$A_L = \frac{3\alpha^2 h v}{4} \left(\frac{1}{4\pi \epsilon_0} \right)^2$$

Eg. Neon Gas, $h\nu = 3.46 \times 10^{-8} \text{ J}$

$$\frac{a}{4\pi \epsilon_0} = 3.9 \times 10^{-8} \text{ m}^6$$

$$A_L = 3.35 \times 10^{-72} \text{ J m}^6$$

$$A_H = n^2 n_r n_a A_0^{1/2} +$$

(1) in vacuum

$$A_H^{1/2} = A_0^{1/2} + A_H^{S^2} - A_H^{V^2} - A_H^{W^2}$$

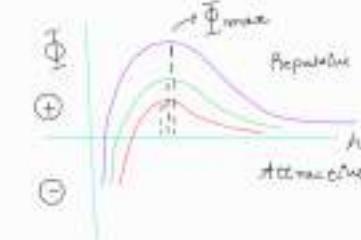


$$\Phi_{net} = \Phi_{vac} + \Phi_{ext}$$

$$= \left(64\pi F \hbar k T \right) \tanh^2 \left(\frac{2e\phi_0}{4kT} \right) \exp(-ex)$$

$\frac{A_H}{12\pi h^2}$ Attract force

Effect of K^{+} concentration

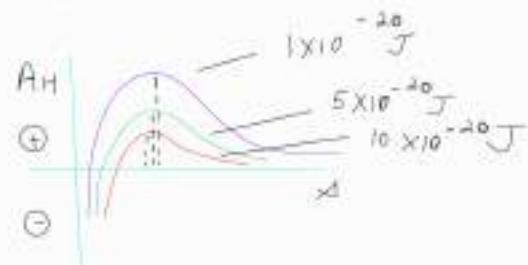
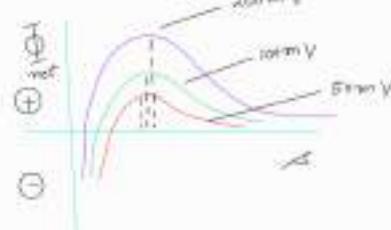


$$K^+ (10^{-5} \text{ cm}) = 0.1 \leftarrow 1$$

$$1.0 \leftarrow 2$$

$$3.3 \leftarrow 3$$

$$10 \leftarrow 4$$



14 Nov (I part)



obtain the $\text{O}_2, \text{SO}_2 \Rightarrow$ L-H Pathway }
 E-R Pathway } Rate laws
 Qualitative plots

Q Adsorption of $\text{N}_2(g)$ on Au(s) follows Langmuir adsorption Isotherm.

$$V_{ad}(\text{Ne}) = 527 \times 10^{-4} \text{ m}^2 \text{ at 26 bar}$$

and $328 \times 10^{-4} \text{ m}^2 \text{ at 3 bar}$

determine b & V_m

A few question → All in the blanks
 ex: Haber process happens at ___ T & ___ P.

(II Part)

Q - Calculate Debye length using different type of electrolyte
 $\text{NaCl}, \text{CaCl}_2, \text{AlCl}_3$
 or Surface potential (Φ_s) can be asked

(II Part)

Q - Calculate Debye length using different type of electrolyte.

NaCl, CaCl₂, AlCl₃.
or Surface potential (Φ_s) can be asked.
↳ need to memorize.

Q - Draw qualitatively curves for ϕ vs z or ϕ vs concentration

Q - Hamaker constant

Calculation of interaction energy using London dispersion force

Q - DLVO approach, Total Interaction Energy

Q - Collative graph (behaviour) of some parameter

Q - Few descriptive question like Define term

Gosh book
NPTEL (est)
Electrolyte
double layer
force point
II or III

WEEK 12B SCRIBES

4,6,7 & 14 NOVEMBER

~You don't have to be great to start, but you have to start to be great.

Colloidal stability refers to the ability of a colloidal system (a mixture where one substance is finely dispersed within another, like milk or paint) to remain uniformly dispersed over time without the particles clumping, aggregating, or settling out. In a stable colloidal system, the dispersed particles remain evenly distributed and do not separate from the continuous phase.

Key Factors Influencing Colloidal Stability

1. Electrostatic (Charge) Repulsion:

- Many colloidal particles carry a surface charge, either positive or negative.
- When particles have like charges, they repel each other, preventing aggregation.
- Electrostatic repulsion is often achieved by adjusting the pH of the solution to charge the particles or by adding electrolytes.
- The **zeta potential** (a measure of the particle's surface charge) is crucial in predicting colloidal stability; higher zeta potentials (either positive or negative) generally indicate more stability.

2. Steric Stabilization:

- This occurs when polymers or other stabilizing agents are adsorbed onto the surface of colloidal particles, creating a "protective" layer around each particle.
- This layer physically prevents particles from coming close enough to aggregate, as it creates a barrier.
- Steric stabilization is particularly important in non-aqueous colloidal systems where charge repulsion might be minimal.

3. Van der Waals Attraction:

- These are weak attractive forces between particles that can lead to aggregation if not countered by other forces like electrostatic repulsion or steric hindrance.
- Van der Waals forces act at short distances and can overcome repulsion if particles get close enough, leading to coagulation or flocculation (formation of clusters)

4. Brownian Motion:

- This is the random motion of particles due to thermal energy, which keeps colloidal particles suspended and dispersed in the medium.
- Brownian motion helps counteract sedimentation (settling of particles due to gravity), especially for very small particles.

5. Hydration and Solvent Effects:

- Water and other solvents can create a hydration layer around particles, stabilizing them by forming a shield that resists aggregation.

Hydration effects are particularly significant for colloids in aqueous solutions, where water molecules can form structured layers around the particles

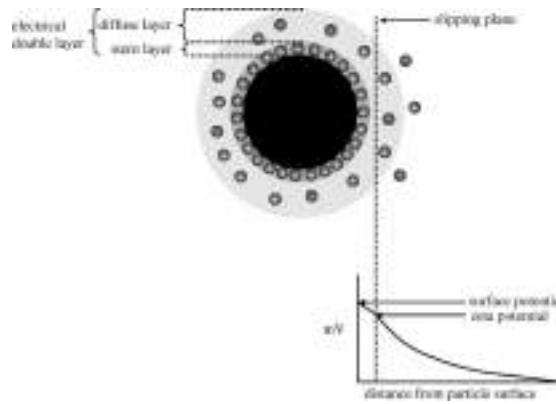
Types of Colloidal Instability

- **Aggregation:** Particles clump together to form larger aggregates due to attractive forces overcoming repulsive forces.
- **Coagulation:** This is an irreversible process where particles come together to form a more solid-like structure, often due to added electrolytes reducing the zeta potential.
- **Flocculation:** Particles form loose clusters or flocs that can be separated more easily, as the process is usually reversible.
- **Sedimentation:** Larger particles may settle at the bottom due to gravitational forces if Brownian motion is insufficient to keep them suspended.

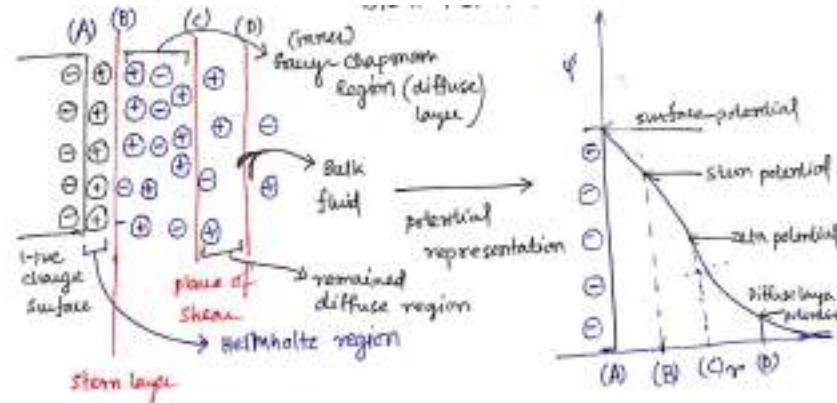
First stable colloidal suspension by Faraday :- Gold colloidal suspension

Colloidal stability:

Zeta Potential and Plane of Shear: The concept of Zeta Potential and Plane of Shear is related to the theory of electrical double layer, more specifically Stern Model of electro Surface Chemistry. Let's have a look



Charged spherical particle



Charged plate

Plane of Shear: It's not a distinct line or a planer separation, it lies somewhere in Diffuse Electrical Double layer region. It's more likely a plane that separates the bound charges(to the charged surface) from unbounds. You can see from the pictorial representation. More close the ions more strong the force of attraction that's why some portion of the Gouy-Chapman layer also falls under the bound region. Rest of the diffuse layer and Bulk fluid falls under unbound region.

Zeta Potential: Potential at any point on the Plane of shear is called zeta potential.

DLVO Theory

DLVO Theory : This theory describes colloidal stability or the stability of charge stabilized colloidal dispersion. It was proposed by **Derjaguin, Landau, Verwey, Overbeek.**

In charge stabilized colloidal dispersion charged ions face two kinds of interaction :

Attractive Interactions: Van der waal (A)

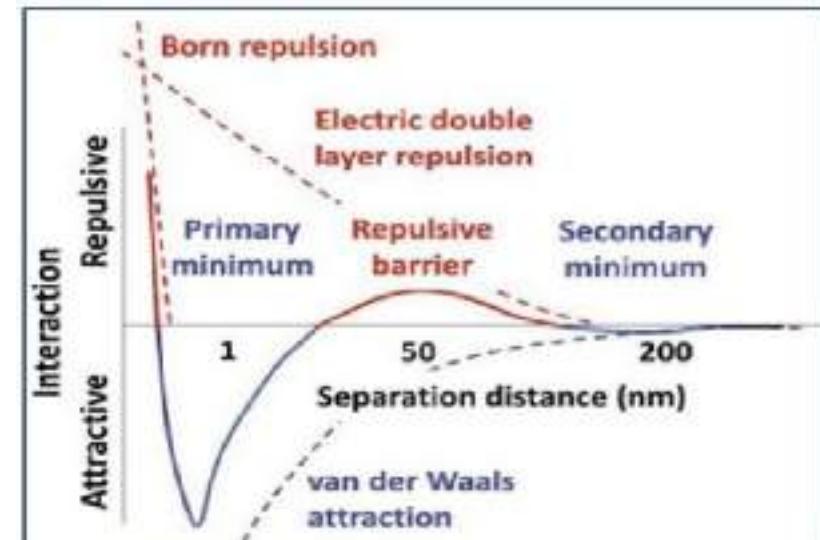
Repulsive Interactions: Overlap of electrical double layer (R)

Net interaction of this two , is represented in terms of potential.

$$V(\text{DLVO}) = V(A) + V(R) ;$$

Difference btw secondary minimum and repulsive barrier is energy barrier of coagulation

SECONDARY MINIMA: FLOCCULATION
PRIMARY MINIMA: AGGLOMERATION



Overlapping Double Layers and Interparticle Repulsion :

Consider two similar charged plates are at a distance h from each other, dipped inside electrolyte. From the knowledge of electrical double layer we can imagine that there will be a overlap between these two double layers from different plates.

It causes a different potential curve btw the intermediate region. Potential in outer region is unaffected.

Due to this special arrangement charge plates face two kind of forces:

Osmotic Pressure Force(due to concentration diff of electrolyte btw inner and outer region)

Electrostatic Forces(due to co-ions and counter-ions)

Derivation:

Consider a volume element and one dimensional parameter x .

X component of pressure force per unit volume ; $F_p = -(dp/dx)$

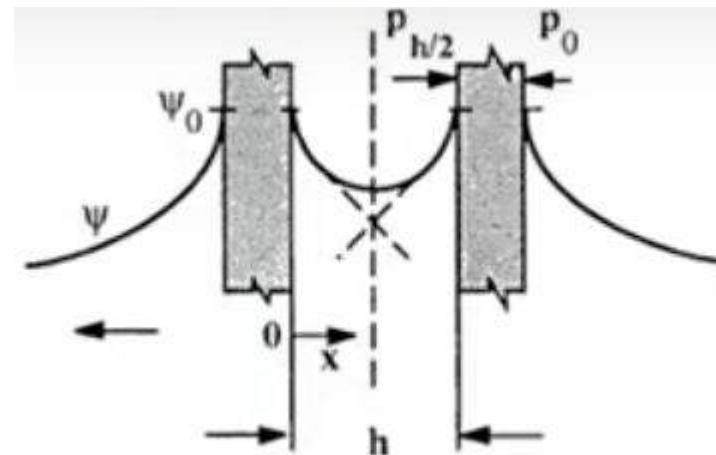
Electrostatic force per unit volume ;

$$Fe = -p^*(dV/dx)$$

(p^* is the charge density)

At equilibrium $F_p + Fe = 0$;

$$(dp/dx) + p^*(dV/dx) = 0$$



Charge density can be expressed in terms of boltzmann factor

$$P^* = \sum_i z_i e n_i$$

$$= \sum z_i e n_i \exp\left(-\frac{z_i e \psi}{k_B T}\right)$$

for symmetrical electrolyte

$$= -2e n^o \exp\left(\frac{ze\psi}{k_B T}\right) + 2e n^o \exp\left(-\frac{ze\psi}{k_B T}\right)$$

$$= 2e n^o \left(\exp\left(-\frac{ze\psi}{k_B T}\right) - \exp\left(\frac{ze\psi}{k_B T}\right) \right)$$

$$= -2ze n^o \sinh\left(\frac{ze\psi}{k_B T}\right)$$

(1)

$$\therefore \frac{dp}{dx} = -P^* \frac{d\psi}{dx}$$

$$\therefore \int dp = - \int P^* d\psi$$

$$\int_{P_{H_2}}^{P_o} dp = \int_{\psi_{H_2}}^{\psi_o} 2ze n^o \sinh\left(\frac{ze\psi}{k_B T}\right) d\psi$$

$$\Rightarrow P_o - P_{H_2} = \frac{2ze n^o}{ze} \left(\cosh\left(\frac{ze\psi_o}{k_B T}\right) - \cosh\left(\frac{ze\psi_{H_2}}{k_B T}\right) \right)^o$$

$$\Rightarrow P_o - P_{H_2} = 2k_B T n^o \left(1 - \cosh\left(\frac{ze\psi_{H_2}}{k_B T}\right) \right)$$

$$\Rightarrow P_{H_2} = P_o + 2k_B T n^o \left(\cosh\left(\frac{ze\psi_{H_2}}{k_B T}\right) - 1 \right)$$

← Representing excess pressure →

Excess pressure or Pressure force per unit Area ; $F(R)$ this is the force responsible for repulsive interactions,

There in the above equation $P(0)$ is the pressure of the bulk fluid,
There potential would be zero, for same reason
(potential at infinity)

And $P(h/2)$ is the pressure exerted by intermediate fluid so there diff would be the force due to excessive repulsive interactions.

$$F_R = 2K_B T n^o \left(\cosh \frac{ze \Psi_{h_2}}{K_B T} - 1 \right)$$

Apply, $\cosh x = \left(1 + \frac{x^2}{2!} \right) + \frac{x^4}{4!} + \dots$
only

$$F_R = K_B T n^o \left(\frac{ze \Psi_{h_2}}{K_B T} \right)^2 = K_B T n^o \left(\frac{ze}{K_B T} \right)^2 (\Psi_{h_2})^2$$

special case, when, h_2 is long enough, least overlap
btw double layers,

its found that, $\Psi_{h_2}^{(\text{Gr-C Potential})} = \Psi_1 + \Psi_2 = 2\Psi$
 $= 2 \left(\frac{4K_B T}{\pi e} \gamma_o \exp(-\kappa h_2) \right)$

When we move far away from a (single) metal plate potential exponentially decays and comes to zero, but that's at infinity, here it's not infinity but large (r) .

It's only a mathematical expression to relate the distance and potential.

$$F_R = k_B T m^{\circ} \left(\frac{ze}{k_B T} \right)^2 64 \left(\frac{k_B T}{ze} \right)^2 \gamma_0^2 \exp(-\kappa r)$$

$$= 64 k_B T m^{\circ} \gamma_0^2 \exp(-\kappa r)$$

Here $\Phi(R)$ and $\Phi(EDL)$ both are same you know it.

$$\gamma_0 \text{ is constant} = \tanh \left(\frac{ze\Phi_0}{4kT} \right)$$

$$\text{Potential energy } \int_0^R \Phi_R = - \int_{\infty}^R F_R dr$$

$$= 64 k_B T m^{\circ} \kappa^2 \gamma_0^2 \exp(-\kappa/\kappa^{-1})$$

This potential energy is due to double layer.

$$\Phi_{net} = \Phi_{vdw} + \Phi_{EDL}$$

In this whole case only potential of diffuse layer is being considered, actually stern layer or helmholtz layer is very thin wrt G.C. layer so that will not affect considerably.

Electrostatic Potential in Electrolyte Solutions

In an electrolyte solution, electrostatic potential varies between charged surfaces due to the distribution of ions. The potential distribution is influenced by the electrolyte's properties and the separation distance between the charged plates.

The diagram below illustrates the potential profile between two parallel charged plates, with key points labeled, including the surface potential (Φ_0) and the midpoint potential (Φ_M).

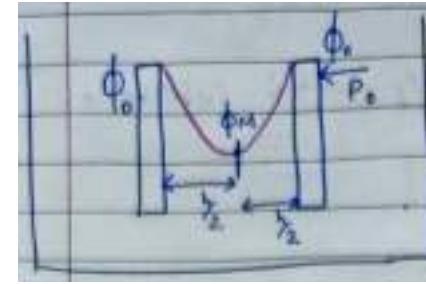
The electrostatic potential (Φ) at a distance 'x' from a reference point is given by:

$$\Phi = \frac{4kT}{ze} \tanh\left(\frac{ze\Phi_0}{4kT}\right) \exp(-k(x-d))$$

where:

- k: Boltzmann constant
- T: Temperature
- z: Valency of ions
- e: Elementary charge
- Φ_0 : Surface potential
- x: Distance from the surface
- d: Separation distance
- κ : Debye screening parameter, describing the decay of potential with distance

This formula describes how the potential decays with distance from the charged surface, governed by the Boltzmann distribution of ions. The parameter 'd' represents the distance between the plates.



Electrostatic Potential Profile
Between Two Charged Plates

Derivation

→ Using Poisson-Boltzmann Eq² for electrostatic potential.

$$\frac{d^2\phi}{dx^2} = -\rho(x)/\epsilon$$

$$\text{since, } \rho(x) = -ze n_0 \left(e^{-\frac{ze\phi(x)}{kT}} - e^{\frac{ze\phi(x)}{kT}} \right)$$

$$\rho(x) = -ze n_0 \sinh \left(\frac{ze\phi(x)}{kT} \right)$$

$$\frac{d^2\phi}{dx^2} = \frac{2ze n_0}{\epsilon} \sinh \left(\frac{ze\phi}{kT} \right)$$

for small $\phi(x) \ll kT/ze$

$$\frac{d^2\phi}{dx^2} \approx \frac{2ze^2 n_0 \phi(x)}{kT}$$

$$\text{Debye length } \kappa T = \sqrt{\frac{kT}{2z^2 e^2 n_0}}$$

$$\therefore \frac{d^2\phi}{dx^2} = \kappa^2 \phi$$

$$\rightarrow \phi(x) = Ae^{-\kappa x} + Be^{\kappa x}$$

Boundary condition: $x=d$ $\phi(d) = \phi_0$

$$\phi(d) = Ae^{-\kappa d} + Be^{\kappa d} = \phi_0$$

assuming $B=0$ (surface symmetry)

$$\phi(x) = \phi_0 e^{-\kappa(x-d)}$$

including non-linear effects for larger potential, using tanh

$$\phi(x) = \frac{4kT}{ze} \tanh \left(\frac{ze\phi_0}{4kT} \right) e^{-\kappa(x-d)}$$

For asymmetric electrolytes, additional factors influence the potential profile. The midpoint potential (Φ_{\square}) is calculated as the average potential between the surfaces, assuming symmetry around this midpoint.

The electric double layer (EDL) potential (Φ_{EDL}) also affects the stability of charged particles within the electrolyte. A derived formula for the mean potential energy across this layer is:

where:

$$\bar{\Phi}_{\text{EDL}} = 64kTn_0 \tanh^2 \left(\frac{ze\Phi_0}{4kT} \right) \exp(-\kappa h)$$

- n_o : Number density of ions
- h : Distance between two points where the potential is measured
- κ : Inverse Debye length, related to ionic concentration

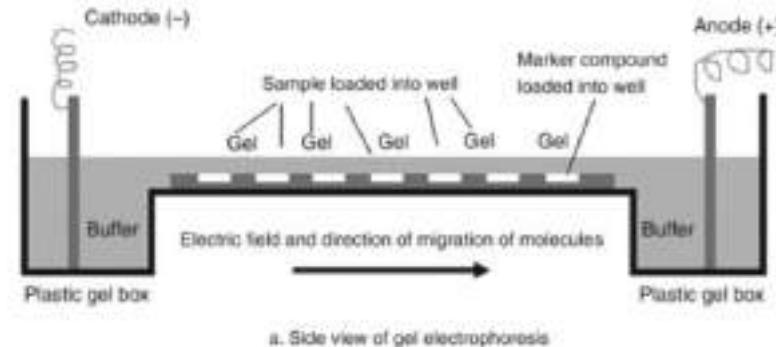
Electrophoresis

Electrophoresis is a technique used to **separate charged particles**, like ions or colloidal particles, by applying an electric field that causes them to move through a medium, typically a gel or liquid. This method is particularly useful in separating molecules such as proteins and nucleic acids based on their charge and size.

Principle of Electrophoresis

In an electric field, charged particles experience an electrostatic force that drives them toward the electrode with the opposite charge. The rate at which they move depends on several factors:

- **Charge** of the particle: Higher charge results in greater force and faster movement.
- **Size and Shape** of the particle: Smaller and more streamlined particles generally move faster.
- **Viscosity** of the medium: Movement is slower in more viscous mediums.
- **Electric Field Strength**: Higher field strength increases particle velocity.



Derivation of Electrophoretic Mobility

To derive electrophoretic mobility, we start by analyzing the forces acting on the particle under the influence of an electric field.

Electrostatic Force: The force acting on a particle with charge q in an electric field E is: $F_{\text{elec}} = qE$

Drag Force: As the particle moves through the medium, it experiences a viscous drag force opposing its motion. For small spherical particles in a viscous medium (following Stokes' Law),

where:

$$F_{\text{drag}} = 6\pi\eta rv$$

- η = dynamic viscosity of the medium
- R = radius of the particle
- v = particle velocity

Equilibrium Condition: When the particle reaches a steady velocity, the electrostatic force and the drag force balance each other:

$$qE = 6\pi\eta rv$$

$$\frac{v}{E} = \frac{q}{6\pi\eta r}$$

$$ue(\frac{v}{E}) = \frac{q}{6\pi\eta r}$$

Electrophoretic Mobility:

Higher charge and smaller particle size increase mobility, while higher viscosity decreases it.

Potential Distribution Around a Spherical Particle

Using the Poisson equation, the fundamental relationship for the electrostatic potential as a function of charge density can be established. In cases of low potential, the **Debye-Hückel approximation** simplifies the analysis by expressing charge density in terms of potential.

The equation:

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d\psi}{dr} \right) = \frac{e^2}{\epsilon k_B T} \left(\sum_i z_i^2 n_i \right) \psi = \kappa^2 \psi$$

relates the potential, ψ , to the distance r from a charged particle, where κ is the Debye-Hückel parameter. This parameter, often simplified by the ionic strength of the solution, **depends on constants like permittivity and temperature**.

By introducing a substitution $x=r\Phi$, this differential equation can be transformed and solved for Φ , leading to a general solution of the form:

$$\Phi = \frac{C_1}{r} \exp(-kr) + \frac{C_2}{r} \exp(kr)$$

C_1, C_2 are constants.

Further solving it by using Boundary condition ($r \rightarrow \infty$, $\Phi = 0$), we get:

$$\Phi = \frac{C_1}{r} \exp(-kr)$$

For large values of k , Φ decreases rapidly.

$$\text{at } h=0, \quad \phi = q/r \Rightarrow q = \phi r$$

$$\text{As per gauss law } \phi = Q/4\pi\epsilon_0 r^2$$

substituting into the electrophoretic mobility expression,

$$\frac{u}{E} = \frac{4\pi\epsilon_0 k \phi}{6\pi\eta r} = \frac{2\epsilon_0 \phi}{3\eta}$$

$$= \frac{2\epsilon_0 \phi}{3\eta} \leftarrow \text{zeta potential}$$



Zeta potential decreases as pH approaches the isoelectric point (where the net charge is zero), making particles more prone to aggregation. Higher electrolyte concentration compresses the electric double layer, reducing zeta potential and often destabilizing colloids.

This equation is known as Hückel equation, which is valid in dilute solutions (k is small). In non-aqueous solutions, the ionic concentration is low and the Hückel equation is applicable.

If the value of k is large (i.e. small k^{-1} , thin double layer), the zeta-potential can be calculated from Smoluchowski equation

$$\frac{u}{E} = \frac{\epsilon \epsilon_0 \zeta}{\xi}$$

- ★ **Zeta potential is a measure of the charge-induced repulsion or attraction among particles in suspension, impacting the stability of colloidal systems.**

Vanderwaal Forces

As, Real gases do not obey the ideal gas law, $PV = mRT$. Two correction terms should be included to improve the accuracy of the ideal gas law.

In ideal gas law, intermolecular attraction and the space occupied by the gas molecules were ignored. According to van der Waals, there should be correction terms for

PRESSURE (due to the attraction between the molecules, which is valid for polar as well as nonpolar molecules),

VOLUME (due to the finite size of the molecules, which act as hard spheres during collision).

$$\left(P + \frac{m^2 a}{V^2} \right) (V - mb) = mRT$$

The van der Waals constants a and b are different for different gases.

Two types of forces were proposed by van der Waals: the **short-range repulsive forces** which give rise to the excluded volume constant b , and **long-range attractive forces** which lead to the constant a .

The constant a varies with temperature. The attractive force decreases with the rise of temperature. The effect of temperature on b is comparatively small (b decreases slightly with rise in temperature for some gases).

These two correction terms are related to the interaction energy between the gas molecules

Semi-empirical correlations were proposed for the interaction energy.

Mie gave the following correlation: $\phi = -\frac{A}{s^p} + \frac{B}{s^q}$

The first term represents attraction and the second term represents repulsion between two molecules separated by a distance s.

The force is given by $F = -\frac{d\phi}{ds}$

Another correlation was proposed by Lennard-Jones, which can be considered as a **special case of the correlation proposed by Mie**.

$$\phi = -\frac{A}{s^6} + \frac{B}{s^{12}}$$

ϕ given by this equation is also known as L-J potential or 6-12 potential.

These equations were developed based on the hypothesis that the pair of molecules is subject to two distinct forces in the limits of large and small separations: an attractive force at the long ranges and a repulsive force at short ranges.

The attraction is due to the **dispersion interactions**.

The short-range repulsion term is due to the **overlap of the molecular orbitals (known as Pauli repulsion or Born repulsion)**.

Q. Given, Lennard-Jones parameters for Ar,
 $A = 1.022 \times 10^{-21} \text{ J m}^6$, $B = 1.579 \times 10^{-14} \text{ J m}^{12}$

To draw a Energy profile and calculate the distance at which the energy will be minimum.

Soln: from the correlation proposed by Lennard-Jones,

$$\phi = -\frac{A}{\delta^6} + \frac{B}{\delta^{12}}$$

Putting the values of A and B,

$$\phi = -\frac{1.022 \times 10^{-21}}{\delta^6} + \frac{1.579 \times 10^{-14}}{\delta^{12}}$$

for the energy will be minimum when

$$\frac{d\phi}{d\delta} = 0$$

and let this occurs at $\delta = \delta_c$

Then,

$$\frac{6A}{\delta_c^7} = \frac{12B}{\delta_c^{13}}$$

$$\Rightarrow \delta_c = \left(\frac{2B}{A} \right)^{1/6}$$

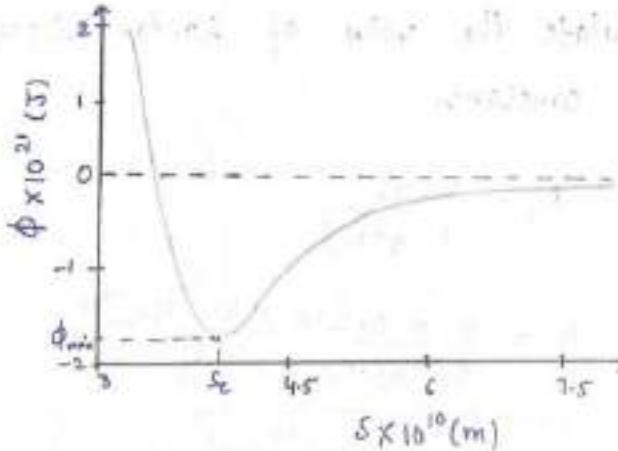
On solving,

$$\delta_c = 3.816 \times 10^{-10} \text{ m}$$

The minimum energy, is,

$$\begin{aligned}\phi_{\min} &= \phi|_{\delta_c} = -\frac{A^2}{2B} + \frac{A^2}{4B} \\ &= -\frac{A^2}{4B}\end{aligned}$$

$$\therefore \boxed{\phi_{\min} = -1.651 \times 10^{-21} \text{ J}}$$



The total van der Waals interaction between molecules has three components:

- (i) interaction between two induced dipoles, which is known as **London dispersion force A_L** ,
- (ii) interaction between two permanent dipoles, which is known as **Keesom orientation force A_K** , and
- (iii) interaction between one permanent dipole and one induced dipole, which is known as **Debye induction force A_D** .

Each of these contributions towards the total interaction energy varies with s^{-6} .

$$\phi_{vdW} = -\frac{A_{vdW}}{s^6} = -\frac{A_L + A_K + A_D}{s^6}$$

These forces exist between all atoms and molecules, even the non-polar molecules. At any given instant, a non-polar molecule will have a dipole moment because of the fluctuations in the distribution of the electrons in the molecule. This dipole creates an electric field that polarises another molecule located nearby, and an induced dipole results.

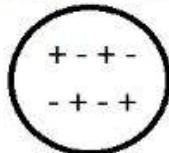
The molecules of hydrocarbons and liquefied gases are held together mainly by these forces.

The interaction between these dipoles leads to the **attractive energy**. The time-averaged dipole moment of each molecule is zero but the time-averaged interaction energy is finite due to these temporarily interacting dipoles.

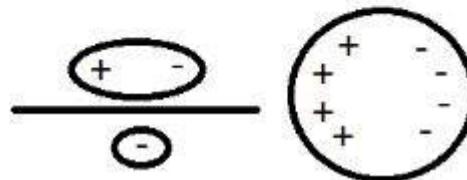
The dispersions forces are probably the most important of the three forces which constitute the total van der Waals force. They are always present, but the presence of the other two types depends upon the properties of the molecules (need at-least 1 polar molecule)

The dispersion forces play very important roles in adhesion, adsorption, wetting, physical properties of gases and liquids, thin films, coagulation, coalescence and many other phenomena. They are often called **long-range forces** because they can **operate up to ~10 nanometres**. The dispersion interaction between two bodies is influenced by the other bodies present nearby. Two molecules interact directly as well as indirectly through the reflection from other molecules since they are also polarised by the electric field. Therefore, if we sum up all pair potentials of a molecule to obtain its net interaction energy with the other molecules, the result will be approximate.

Neutral Molecule



upon introducing
an ion or a dipole:



$$\phi_{\text{vdW}} = - \left[\frac{1}{(4\pi\epsilon_0)^2 s^6} \left[\left\{ \frac{3\alpha_1\alpha_2 h\nu_1\nu_2}{2(\nu_1 + \nu_2)} \right\} + \left(\frac{\mu_1^2 \mu_2^2}{3kT} \right) + (\mu_1^2 \alpha_2 + \mu_2^2 \alpha_1) \right] \right]$$

where u is the dipole moment, α is the polarisability, h is Planck's constant, ν is the orbiting frequency of electron, k is Boltzmann's constant and ϵ_0 is the permittivity of the free space

$$\phi_{\text{vdW}} = - \frac{A_{\text{vdW}}}{s^6} = - \frac{A_L + A_K + A_D}{s^6}$$

By comparing above two formulae.

$$A_L = \left(\frac{1}{4\pi\epsilon_0} \right)^2 \left(\frac{3\alpha_1\alpha_2 h\nu_1\nu_2}{2(\nu_1 + \nu_2)} \right)$$

$$A_K = \left(\frac{1}{4\pi\epsilon_0} \right)^2 \left(\frac{\mu_1^2 \mu_2^2}{3kT} \right)$$

$$A_D = \left(\frac{1}{4\pi\epsilon_0} \right)^2 (\mu_1^2 \alpha_2 + \mu_2^2 \alpha_1)$$

$$\text{Where, } A_L = \frac{3\alpha_1\alpha_2 h\nu_1\nu_2}{2(\nu_1 + \nu_2)} \left[\frac{1}{4\pi\epsilon_0} \right]^2$$

subscripts 1, 2 refers to the 2 molecules
when interaction is b/w single type
of molecules

$$A_L = \left[\frac{3\alpha^2 h\nu}{4} \right] \left[\frac{1}{4\pi\epsilon_0} \right]^2$$

Q: Calculate the London dispersion force constant (A_L) for neon.

$$\text{Given, } h\nu = 3.45 \times 10^{-18} \text{ J}, \frac{c}{4\pi\epsilon_0} = 3.9 \times 10^{-31} \text{ m}^3$$

$$\text{Soln: } A_L = \frac{3}{4} \left(\frac{c}{4\pi\epsilon_0} \right)^2 h\nu$$

$$A_L = \frac{3}{4} \times (3.9 \times 10^{-31})^2 \times 3.45 \times 10^{-18}$$

$$A_L = 3.95 \times 10^{-73} \text{ Jm}^6$$

Q: Given, For CH₄,

$$a = 0.228 \text{ m}^6 \text{ Pa mol}^{-2}$$

$$b = 4.3 \times 10^{-5} \text{ m}^3/\text{mol}$$

To calculate the value of London dispersion force constant.

$$\text{Soln: } A_L = \frac{9}{4} \frac{ab}{\pi^2 N_A^3}$$

$$A_L = \frac{9 \times 0.228 \times 4.3 \times 10^{-5}}{4\pi^2 (6.023 \times 10^{23})^3}$$

$$A_L = 1.62 \times 10^{-71} \text{ Jm}^6$$

When two molecules are far apart, the electric field from one may take longer to reach the other than the time it takes for the dipole to fluctuate. This delay causes the second molecule to re-emit a field that, upon reaching the first molecule, may no longer align with its dipole orientation, weakening the attraction. This decay of dispersion energy at distances beyond s^{-6} is known as the **retardation effect**, which typically becomes significant at about 5 nm in free space and at shorter distances in media with a slower speed of light. **Only dispersion forces experience this effect; orientation and induction forces are unaffected.**

The London dispersion constant relates to the van der Waals parameters a and b .

$$A_L = \frac{9}{4} \frac{ab}{\pi^2 N_A^3}$$

Hamaker constant (A_H)

Hamaker constant quantifies the van der Waals interaction strength and is key to understanding particle interactions across different media.

The quantity $\Pi^2 n_1 n_2 A_L^{1,2}$ is known as Hamaker constant (A_H). If the interaction between the molecules of type 1 and type 2 is being considered, then

$$A_H = \pi^2 n_1 n_2 A_L^{1,2}$$

where $A_L^{1,2}$ is the London constant for molecules of types 1 and 2, and n_1 and n_2 are the number of molecules per unit volumes of the two types of material respectively.

When two interacting bodies (represented by the superscripts 1 and 2) are separated by a third medium (represented by the superscript 3), the Hamaker constant can be calculated by the following equation:

$$A_H^{1,3,2} = A_H^{1,2} + A_H^{3,3} - A_H^{1,3} - A_H^{3,2}$$

A_{23} and A_{13} are excluded because they don't contribute to the mediated interaction between materials 1 and 2 through medium 3. Only the cross-interactions involving the third medium and self interaction is effective in contributing hamaker constant. There's a negative sign as some of the interaction energy ($A_{1,3}$ & $A_{3,2}$) is consumed in reacting with medium 3 and they're not available now.

$A_H^{i,j}$ represents the Hamaker constant for the interacting materials i and j in vacuo. The presence of a third medium does not change the distance-dependence of the van der Waals force, but its magnitude is affected by the modified value of the Hamaker constant ($A_H^{1,3,2}$).

Using the equation,

$$[A_H^{1,3,2} = A_H^{1,2} + A_H^{3,3} - A_H^{1,3} - A_H^{3,2}]$$

it is apparent that, $A_H^{1,3,2} < A_H^{1,2}$, if $A_H^{3,3} < A_H^{1,3} + A_H^{3,2}$

This condition holds quite often, which indicates that the Hamaker constant is likely to be reduced in presence of the third medium.

Several combining relations are available which can be used to calculate the approximate value of the Hamaker constant in terms of the known values.

$$\text{for Ex: } A_H^{i,j} = \sqrt{A_H^{i,i} A_H^{j,j}}, i \neq j$$

Thus, we can conclude,

$$A_H^{1,3,2} = \left(\sqrt{A_H^{1,1}} - \sqrt{A_H^{3,3}} \right) \left(\sqrt{A_H^{1,2}} - \sqrt{A_H^{3,2}} \right)$$

Note: Hamaker constant for air is $\frac{7.6 \times 10^{-20}}{\text{J}}$.

Q. Calculate the Hamaker constants ($A_H^{1,3,2}$) for Fused quartz (1) - Air (2) - Tetradecane (3)

$$\text{Sol: } A_H^{1,1} = 6.5 \times 10^{-20} \text{ J}, A_H^{3,3} = 0 \text{ J}$$

$$A_H^{1,2} = 5.1 \times 10^{-20} \text{ J}$$

$$A_H^{1,3,2} = \left(\sqrt{A_H^{1,1}} - \sqrt{A_H^{3,3}} \right) \left(\sqrt{A_H^{1,2}} - \sqrt{A_H^{3,2}} \right)$$

$$= \left(\sqrt{6.5} - \sqrt{5.1} \right) (0 - \sqrt{5.1}) \times 10^{-20}$$

$$= -0.66 \times 10^{-20} \text{ J}$$

THE DLVO (Derjaguin–Landau–Verwey–Overbeek) THEORY

The net interaction between two surfaces involves both the electrostatic double layer force and the van der Waals force. The van der Waals force dominates when the separation between the surfaces is small. It is also rather insensitive on the concentration of the electrolytes.

On the other hand, the electrostatic double layer repulsion is strong at larger separations, and it is quite sensitive on the concentration of electrolytes. This theory has proved to be quintessential for explaining the stability of a variety of colloidal materials.

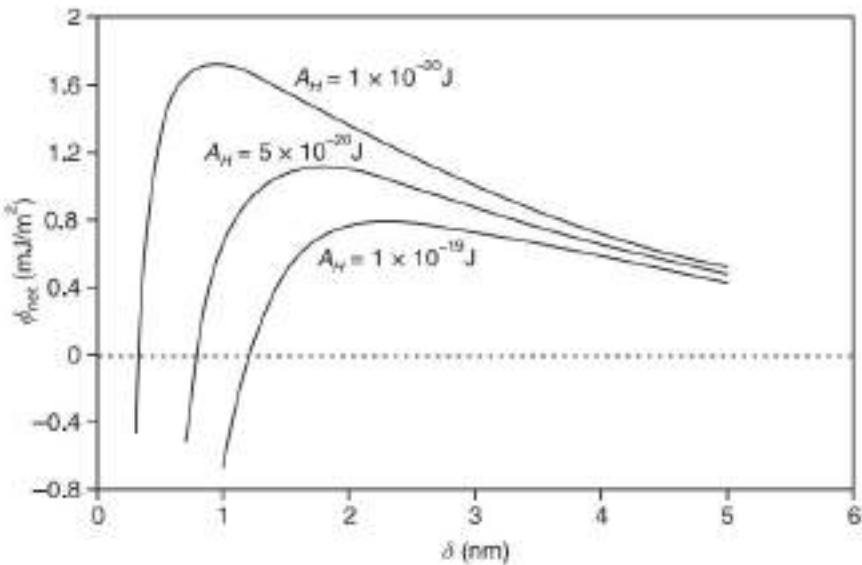
It proposed that an energy barrier resulting from the repulsive force prevents two particles approaching one another and adhering together. If the particles collide with sufficient energy to overcome the barrier, the van der Waals attractive force will attract them strongly and cause them adhere together irreversibly.

If the particles repel each other strongly, the dispersion will resist coagulation and the colloidal system will be stable. If the repulsion is not sufficient then coagulation will take place.

For planar surfaces:-

$$\phi_{\text{net}} = \phi_{\text{EDL}} + \phi_{\text{vdW}} = (64kTn^{\infty}\kappa^{-1}) \tanh^2\left(\frac{ze\psi_0}{4kT}\right) \exp(-\kappa\delta) - \frac{A_H}{12\pi\delta^2}$$

The effect of variation of Hamaker constant on the energy profiles.



The effect of variation of Hamaker constant on the net interaction energy profiles
 $c^* = 10 \text{ mol/m}^3$, $\kappa^{-1} = 3 \text{ nm}$, $\psi_0 = 0.1 \text{ V}$.

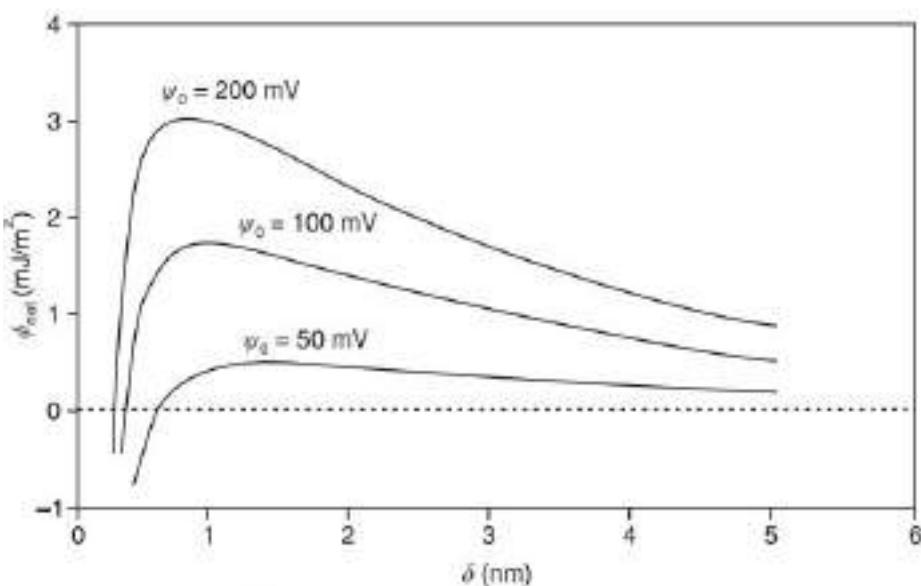
The profiles in Figure were drawn for Hamaker constants of 1×10^{-20} J, 5×10^{-20} J and 1×10^{-19} J for surfaces placed in a 10 mol/m^3 aqueous solution of a 1:1 electrolyte (at 298 K).

The energy barrier (i.e. the peak of the curves) decreased with the increase in the value of Hamaker constant making it easier for them to interact.

The energy barrier shifted to larger separations with the increase in Hamaker constant indicating that attractive forces act over a longer range.

An increased Hamaker constant strengthens van der Waals attraction, reducing the energy barrier and shifting it to larger separations. This facilitates particle coagulation, as particles can more easily overcome the barrier and aggregate at greater distances.

The effect of variation of Surface Potential on the energy profiles.



The effect of variation of surface potential on the net interaction energy profiles.
 $c^* = 10 \text{ mol/m}^3$, $\pi^{-1} = 3 \text{ nm}$, $A_H = 1 \times 10^{-20} \text{ J}$.

It can be observed from this figure that the energy barrier increased as the potential is increased

$$\text{The term } \tanh^2\left(\frac{ze\psi_0}{4kT}\right)$$

approaches unity at the high values of ψ_0 .

Therefore, the effect of surface potential begins to reduce at the higher values. Slow coagulation of the colloid particles occurs when the energy barrier is low. At very low values of ψ_0 , the energy barrier drops below $\phi_{\text{net}} = 0$ (shown by the dotted line in the figure) and coagulation occurs rapidly.

The effect of concentration of electrolyte on the energy profiles.

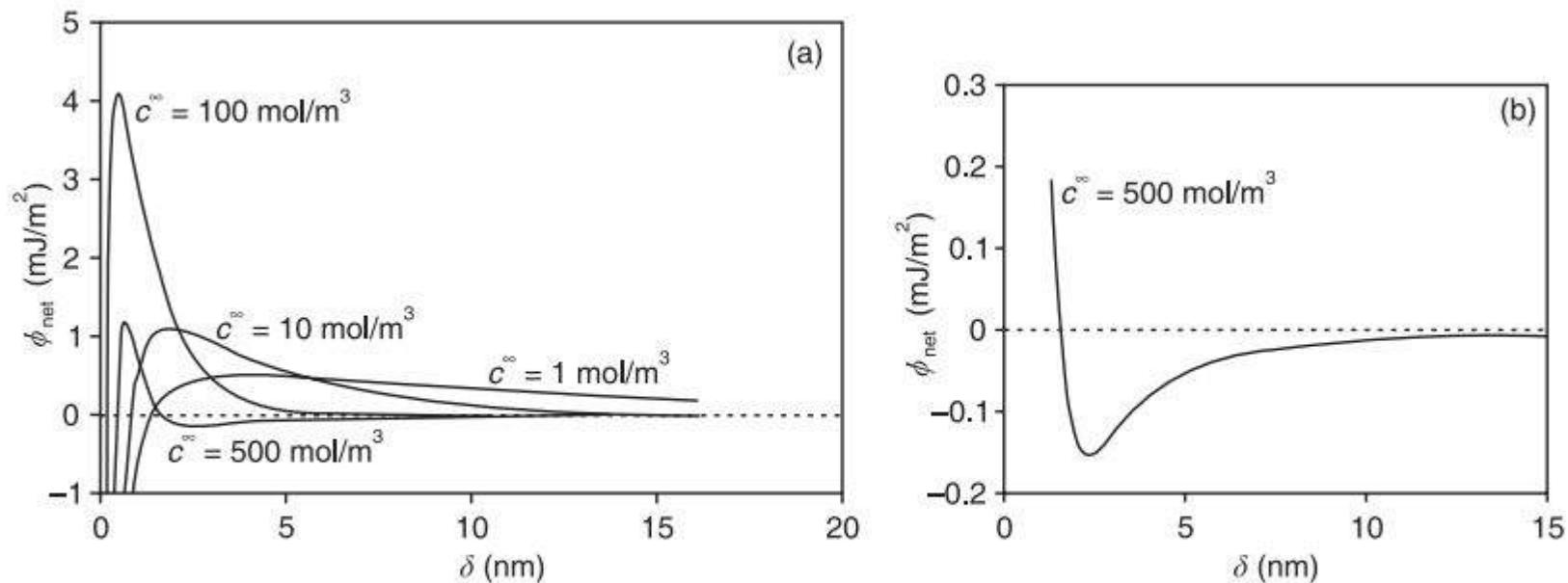


Figure 5.16 (a) The effect of variation of electrolyte concentration on the net interaction energy profiles. $A_H = 5 \times 10^{-20} \text{ J}$, $\psi_0 = 100 \text{ mV}$. Figure (b) shows the secondary minimum in detail.

The effect of concentration of electrolyte on net interaction energy is depicted in Figure 5.16(a).

As the concentration of the electrolyte is increased, n^{\square} increases but ζ^{-1} decreases. The resulting effect is the shift in the energy barrier to a lower separation and the emergence of a secondary minimum [shown in Figure 5.16(b)].

The energy is minimum at contact, which is known as the primary minimum. For a colloidal system, the thermodynamic equilibrium state may be reached when the particles are in deep primary minimum.

However, the energy barrier may be too high so that it is difficult to overcome. In such a situation, the colloid particles may sit in the **secondary minimum, which is weaker than the primary minimum.** The adhesion at secondary minimum can be reversible. The secondary minimum usually appears beyond $\delta = 2 \text{ nm}$ depending on the value of the Hamaker constant.

Energy Barrier and Electrolyte Concentration:

- At lower electrolyte concentrations ($1\text{--}100 \text{ mol/m}^3$), the energy barrier height increases with concentration due to the expansion of the diffuse double layer.
- At higher concentrations (500 mol/m^3), the energy barrier decreases.
- At very high concentrations ($>1000 \text{ mol/m}^3$), attraction dominates, and particles aggregate at all separations.

- **Verwey and Overbeek (1948):**
 - Energy barrier decreases with increasing electrolyte concentration for spherical particles due to the divergence of force lines.
- **Surface Potential:**
 - In many cases, surface potential decreases with electrolyte concentration(e.g. due to the binding of counterions), aiding coagulation at lower electrolyte levels.
- **Critical Coagulation Concentration:**
 - The concentration where the energy barrier drops below the net = 0 line, causing coagulation, is known as the **critical coagulation concentration**.

LET'S SOLVE SOME QUESTIONS ...

REFER THESE AS SUGGESTED BY PROF. FOR BETTER UNDERSTANDING 😊

- COLLOID AND INTERFACE SCIENCE BY PALLAB GHOSH
- [COURSE FROM NPTEL](#)

$$\kappa^{-1} = \left[5.404 \times 10^{15} \sum_i z_i^2 c_i^\infty \right]^{-1/2} \quad (5.41)$$

EXAMPLE 5.11 Calculate the Debye lengths in 10 mol/m³ aqueous solutions of NaCl, CaCl₂ and AlCl₃ at 298 K.

Solution Let us calculate the Debye lengths using Eq. (5.41).

For NaCl: $\sum_i z_i^2 c_i^\infty = (1)^2 \times 10 + (1)^2 \times 10 = 20 \text{ mol/m}^3$

$$\kappa^{-1} = [5.404 \times 10^{15} \times 20]^{-1/2} = 3.04 \times 10^{-9} \text{ m}$$

For CaCl₂: $\sum_i z_i^2 c_i^\infty = (2)^2 \times 10 + (1)^2 \times 2 \times 10 = 60 \text{ mol/m}^3$

$$\kappa^{-1} = [5.404 \times 10^{15} \times 60]^{-1/2} = 1.76 \times 10^{-9} \text{ m}$$

For AlCl₃: $\sum_i z_i^2 c_i^\infty = (3)^2 \times 10 + (1)^2 \times 3 \times 10 = 120 \text{ mol/m}^3$

$$\kappa^{-1} = [5.404 \times 10^{15} \times 120]^{-1/2} = 1.24 \times 10^{-9} \text{ m}$$

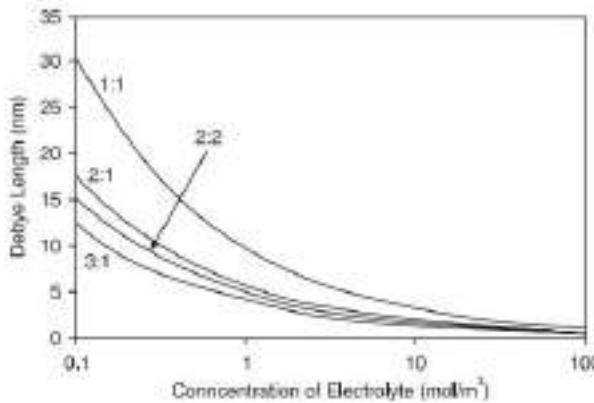


Figure 5.7 Variation of Debye length with electrolyte concentration.

The variation of Debye length for various types of electrolytes (such as NaCl, CaCl₂, MgSO₄ and AlCl₃) with the electrolyte concentration is shown in Figure 5.7. As the concentration of electrolyte is increased, the Debye length decreases by a large extent. For a 1:1 electrolyte like NaCl, the Debye length is 30.4 nm at 0.1 mol/m³ concentration, which reduces to ~1 nm when the concentration is 100 mol/m³. For 2:1 electrolytes, the Debye length is smaller. The effect of electrolytes in reducing the Debye length varies in the order: 1:1 < 1:2 < 2:2 < 3:1, as predicted by Eq. (5.41). The effect of valence decreases progressively as the concentration of the electrolyte increases. Note that the effects of 1:2 and 2:1 electrolytes are same.

Q) Given, $V_{ads}(N_2) = 5.27 \times 10^{-2} m^3$ at 26 bar
 $= 3.28 \times 10^{-2} m^3$ at 3 bar

determine the values of constant b & V_m for adsorption process

\Rightarrow We have Langmuir adsorption isotherm

$$\theta = \frac{V}{V_m} = \frac{bP}{1+bP}$$

V = vol. of adsorbed gas, P = pressure

V_m = vol. of gas req. to form a monolayer

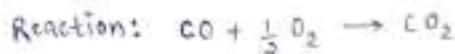
1) $P = 26$ bar $\Rightarrow 5.27 \times 10^{-2} = V_m \cdot \frac{b \cdot 26}{1 + b \cdot 26}$

2) $P = 3$ bar $\Rightarrow 3.28 \times 10^{-2} = V_m \cdot \frac{b \cdot 3}{1 + b \cdot 3}$

Solve these for V_m & b .

- $b \approx 0.448 m^3 bar^{-1}$
- $V_m \approx 0.0572 m^3$

Q. Rate of reaction between carbon monoxide and oxygen on platinum is found under certain circumstances to be directly proportional to the oxygen pressure and inversely proportional to the carbon monoxide pressure. Suggest a suitable mechanism consistent with the observation.



Given Rate Dependency:

- * The reaction rate is directly proportional to P_{O_2} .
- * The reaction rate is inversely proportional to P_{CO} .

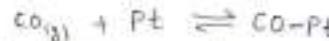
This suggests that:

1) Oxygen adsorption is essential for the reaction, with higher oxygen pressures accelerating the reaction rate.

2) Higher CO pressures inhibit the reaction by occupying surface sites, which reduces the availability of oxygen on the surface.

Proposed Mechanism:

1) Adsorption of CO on the Pt surface,



where, CO-Pt represents carbon monoxide adsorbed on the platinum surface.

2) Adsorption of O_2 on the Pt surface, with O_2 dissociating upon adsorption:



3) Surface Reaction b/w adsorbed CO and adsorbed O₂ form CO_2 (RDS)



4) Desorption of CO_2 : CO_2 (gas) leaves the surface.

Rate Law Derivation: Assume that the surface rxn b/w CO-Pt and O-Pt is RDS.

Using Langmuir adsorption isotherm:

$$\theta_{\text{CO}} = \frac{k_{\text{CO}} P_{\text{CO}}}{1 + k_{\text{CO}} P_{\text{CO}} + k_{\text{O}_2} P_{\text{O}_2}}, \quad \theta_{\text{O}} = \frac{k_{\text{O}_2} P_{\text{O}_2}}{1 + k_{\text{CO}} P_{\text{CO}} + k_{\text{O}_2} P_{\text{O}_2}}$$

where,

* θ_{CO} & θ_{O} are the fractional coverages of CO and O on Pt.

* k_{CO} and k_{O_2} are the adsorption equilibrium constants.

$$\rightarrow \text{Rate} = k \cdot \theta_{\text{CO}} \cdot \theta_{\text{O}}$$

Substitute the expression for θ_{CO} and θ_{O}

$$\text{Rate} = k \cdot \frac{k_{\text{CO}} P_{\text{CO}}}{1 + k_{\text{CO}} P_{\text{CO}} + k_{\text{O}_2} P_{\text{O}_2}} \cdot \frac{k_{\text{O}_2} P_{\text{O}_2}}{1 + k_{\text{CO}} P_{\text{CO}} + k_{\text{O}_2} P_{\text{O}_2}}$$

Assume that $k_{\text{CO}} P_{\text{CO}} \gg 1$ (high CO concn)

$$\text{Rate} \approx k \frac{k_{\text{O}_2} P_{\text{O}_2}}{k_{\text{CO}} P_{\text{CO}}} \propto \frac{P_{\text{O}_2}}{P_{\text{CO}}}$$

Hence, the rate expression matches the experimental observations.

THANK YOU

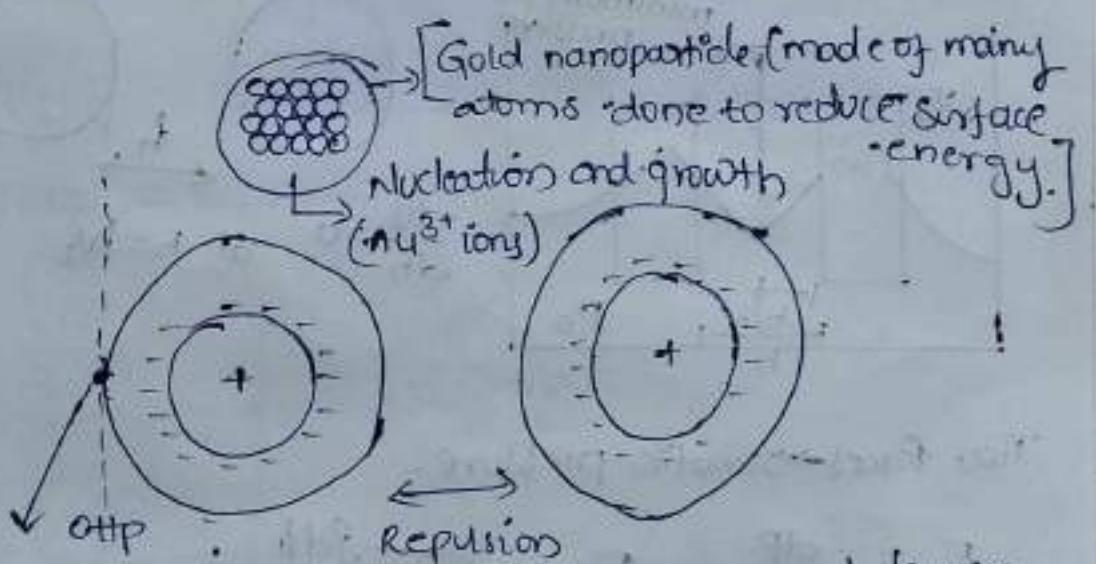


-; COLLOIDAL STABILITY :-

- colloidal stability :- The ability of colloidal particles to remain dispersed without settling or aggregating over time.

Factors influencing colloidal stability :-

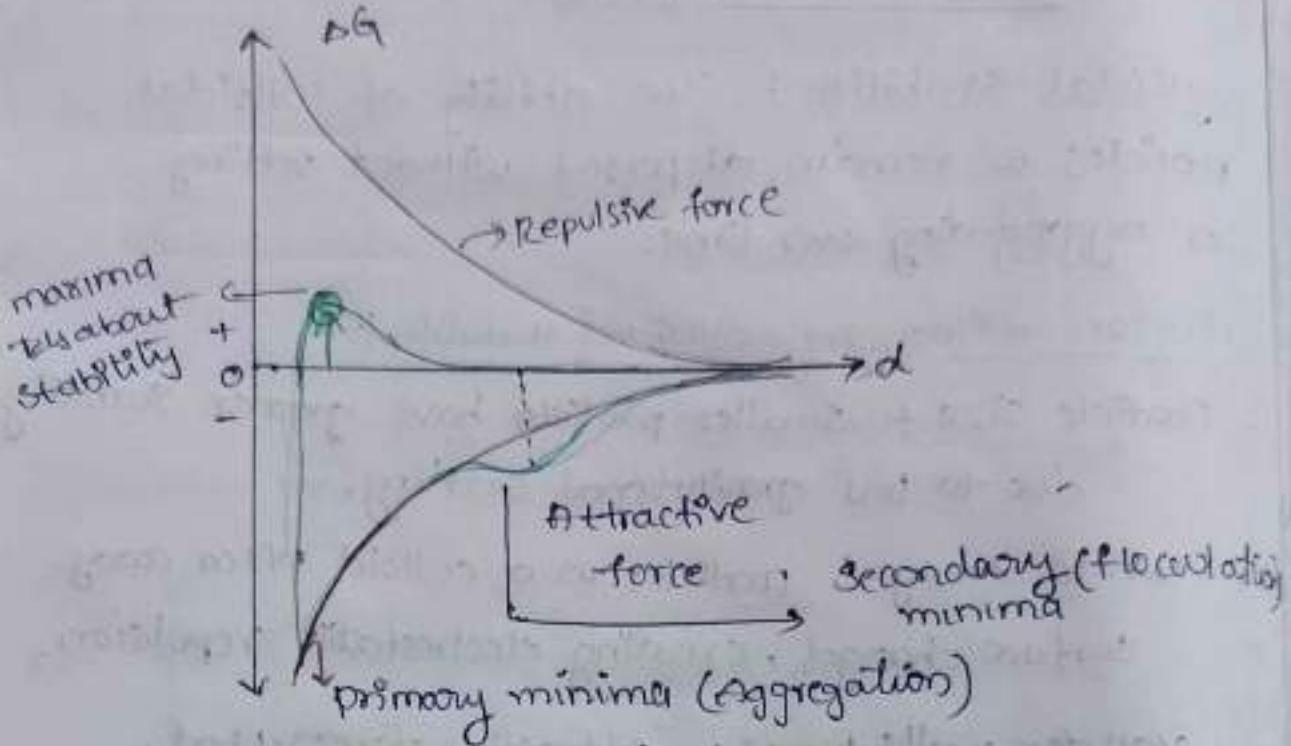
- Particle Size :- Smaller particles have greater stability due to less gravitational settling.
- Surface charge :- particles in a colloid often carry surface charges, creating electrostatic repulsion.
- van der waals forces :- Attractive forces that, when stronger than repulsive force can cause aggregation.
- DLVO Theory [Oerjagrin - Landau - verwey - overbeek] explains stability through the balance of electrostatic repulsion and van der waals attraction.



Potential at this point
is zeta potential (ζ)
 $\approx \pm 25 \text{ mV}$

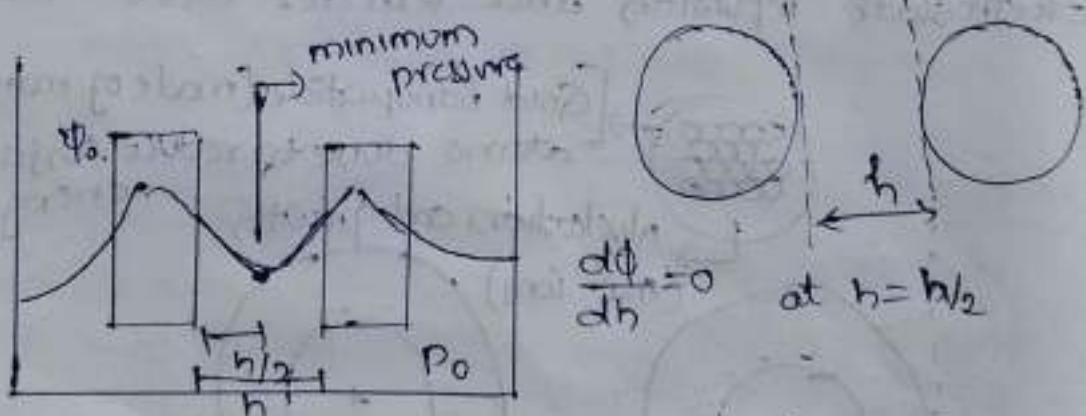
Then colloid is stable.

The compact layer moves with the particle the outer layers keep on changing with new ions as the particle moves.



DLVO (Derjaguin - Landau - Verwey - Overbeek)

explains the stability of colloidal dispersions by examining the interplay between attractive and repulsive forces acting on colloidal particles.



Two forces \rightarrow osmotic pressure.

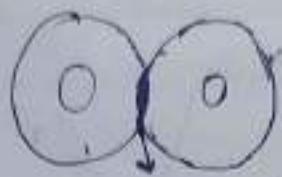
$$F_2 = -\frac{dP}{dz}$$

\downarrow
osmotic

$$F_{electrostat} = -\frac{g d\phi}{dz}$$

$$g = \sum_{i=1}^n n_i z_i c$$

$$= \sum_{i=1}^n n_i z_i e^{-\frac{z_i c \phi}{kT}}$$



overlap of compact layer

fluid entering to prevent overlap

$$F_{ele} = - \sum_{i=1}^n n_i e z_i e \exp\left(-\frac{ze\phi}{kT}\right) \frac{d\phi}{dx}$$

At equilibrium $-fd\phi = dp$

For symmetrical electrolyte

$$n e z \left[\exp\left(-\frac{ze\phi}{kT}\right) - \exp\left(\frac{ze\phi}{kT}\right) \right] d\phi = dp$$

$$\int_{P_0}^{P_{h/2}} dp = \int_0^{\phi_{h/2}} n e z \sinh\left(\frac{ze\phi}{kT}\right) d\phi \quad \therefore \sinh = \frac{e^x - e^{-x}}{2}$$

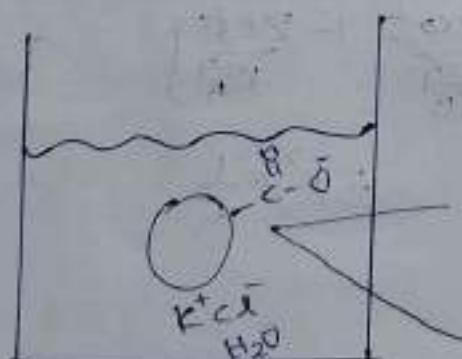
$$2 \sinh = e^x - e^{-x}$$

$$P_{h/2} - P_0 = 2 k T n^o \left[\cosh\left(\frac{ze\phi_{h/2}}{kT}\right) - 1 \right]$$

$\downarrow \pi_{EDL}$ \rightarrow osmotic pressure at electrical double layer, assuming small $\phi_{h/2}$ and expansion of cosh being.

$$\pi_{EDL} = k_B T n^o \left(\frac{ze\phi_{h/2}}{kT} \right)^2 \text{ for small } \phi$$

$$\pi_{EDL} = 64 k T n^o \tan h^2 \left(\frac{ze\phi_0}{4 kT} \right) e^{(-\phi_0)}$$



electrical double layer

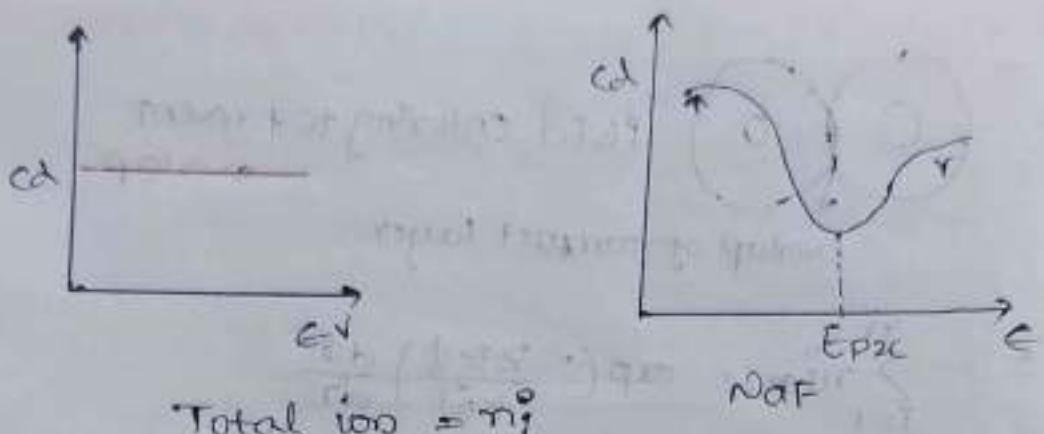
quantum dot

C_m C_s Helmholtz

$$C_s^2 \frac{q}{m} = \frac{\epsilon \epsilon_0}{d} V$$

capacitance = $\frac{\text{charge}}{\text{potential}}$.

$$Cd = \frac{dC_m}{dV}$$



$$\text{Total ions} = n^o$$

$$\text{ions in layer} = n^o_i$$

$$n^o_i = n^o e^{-\frac{zicd}{k_B T}}$$

Poisson's equation

$$\frac{d^2\phi}{dx^2} = \frac{-f}{\epsilon \epsilon_0}$$

$$f = \sum_i n_i z_i e = \sum_i n^o_i z^2 e \exp\left(-\frac{zic\phi}{k_B T}\right)$$

$$\frac{d^2\phi}{dx^2} = \frac{-e}{\epsilon \epsilon_0} \sum_i n_i z_i e \left(\frac{-zic\phi}{k_B T}\right)$$

If z & electrolyte symmetrical

$$\begin{aligned} \frac{d^2\phi}{dx^2} &= -\frac{e}{\epsilon \epsilon_0} \left[n^o z \exp\left(-\frac{zc\phi}{k_B T}\right) - n^o z \exp\left(\frac{zc\phi}{k_B T}\right) \right] \\ &\approx -\frac{en^o z}{\epsilon \epsilon_0} \left[\exp\left(-\frac{zc\phi}{k_B T}\right) - \exp\left(\frac{zc\phi}{k_B T}\right) \right] \end{aligned}$$

$$\phi = \frac{d^2\phi}{dx^2} = \frac{en^o z}{\epsilon \epsilon_0} \left[1 - \frac{2c\phi}{k_B T} - \frac{2c\phi}{k_B T} \right]$$

$$= \frac{2e^2 n^o z^2 \phi}{\epsilon \epsilon_0 k_B T}$$

$$\therefore K^2 = \frac{1}{L}$$

$$K^2 = \frac{2e^2 n^o z^2}{\epsilon \epsilon_0 k_B T}$$

$$\phi_{\text{net}} = \phi_{\text{vans}} + \phi_{\text{EOF}}$$

L van der
waal

electrical
double layer.

$$\phi_m = \phi_{h=0} = \phi_v + \phi_i = 2\phi$$

$$\text{Asymmetrical electrolyte} \rightarrow \phi = \frac{4kT}{zc} \tanh \left(\frac{zc\phi}{4kT} \right) \exp(-k(x-a))$$

$$\phi_{\text{potential}} = -F_e dx \quad \text{then integrate}$$

energy

$$U_{\text{EOF}} = 64k_B T \tanh \left(\frac{zc\phi}{4kT} \right) \exp(-kh)$$

constant

$$\phi_{\text{pe}} = 64k_B T \tanh \left(\frac{zc\phi_0}{4kT} \right) \exp(-kh) E'$$

Electrophoresis?

Electrophoresis is a laboratory technique used to separate charged particles, such as molecules, in a gel or fluid medium under the influence of an electric field.

Viscous force \rightarrow Stoke eqn $\rightarrow F_v = 6\pi\eta r v$

Electric force $= qE_{\text{fluid}}$

At steady state $qE = 6\pi\eta r v$

$$\frac{V}{r} = \frac{qE}{6\pi\eta r} \rightarrow \text{Electrophoretic mobility}$$

Jelly like fluid
in which DNA
proteins are suspended

$$\phi = \frac{C_1}{r} \exp(kr) + \frac{C_2}{r} \exp(kr)$$

At $r \rightarrow \infty, \phi \rightarrow 0 \Rightarrow C_2 = 0$

$$\phi = \frac{C_1}{r} \exp(kr)$$

Also at very large r i.e. very small k

$$C_1 = \phi r$$

$$\text{using } \phi = \frac{Q}{4\pi\epsilon_0 R}$$

$$Q = 4\pi\epsilon_0\phi R$$

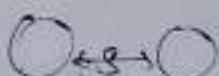
$$\cdot \frac{V}{\epsilon} = \frac{4\pi\epsilon_0\phi R}{8\pi n R} = \frac{2}{3} \frac{\epsilon_0 \phi}{n}$$

$$\boxed{\frac{V}{\epsilon} = \frac{2}{3} \frac{\epsilon \epsilon_0}{n} \phi} \rightarrow \text{Zeta potential.}$$

$$Pv = nRT$$

$$\text{Real gas} \rightarrow \left(P + \frac{am^2}{v^2} \right) (v - nb) = nRT$$

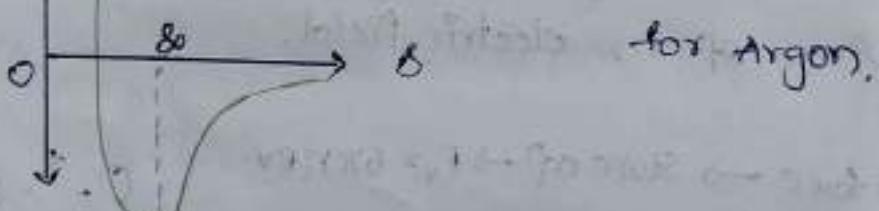
London $\rightarrow \frac{-A}{r^6} + \frac{B}{r^{12}}$ Also called Lennard-Jones potential (L-J potential or 6-12 potential)



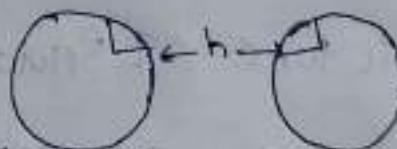
$A, B \rightarrow$ characteristic of gas

$$e \uparrow \rightarrow A = 1.02 \times 10^{-7} \text{ J nm}^6$$

$$B = 1.57 \times 10^{-134} \text{ J m}^2$$



for Argon.



$$\Phi_{\text{vow}} = -\frac{AV_{\text{vow}}}{r^6} = -\left(\frac{A_L + A_K + A_D}{r^6} \right) \rightarrow \text{Hamaker constant}$$

\hookrightarrow composed of 3 & b forces.

But London dispersion are dominant.

$$\Phi_{\text{net}} = \Phi_{\text{ext}} + \Phi_{\text{vow}} = (64k_B n^2)^2 \tanh\left(\frac{2e\phi_0}{4k_B T}\right)$$

$$V_{\text{vow}} = \frac{A_L + A_K + A_D}{r^6}$$

A_K = Debye const. (for 2 permanent dipole)

A_L = London const. (for dipole induced dipole moment)

A_D = Debye constant

(Permanent dipole + induced dipole)

$$A_H = \pi^2 n_1 n_2 A_L$$

for same molecules, $A_H = \pi^2 n^2 A_L$

$$A_L = \frac{q}{4} \frac{ab}{\pi^2 N_A^3}$$

$$A_L = \frac{3\alpha_1 \alpha_2 \hbar v_1 v_2}{2(v_1 + v_2)} \left(\frac{1}{v_1 v_2 \epsilon_0} \right)^2$$

$v \rightarrow$ frequency of orbiting e^- in atom

Note : ①

in vacuum

$$A_H = \pi^2 n_1 n_2 A_L^{1/2}$$

① | ② | ③

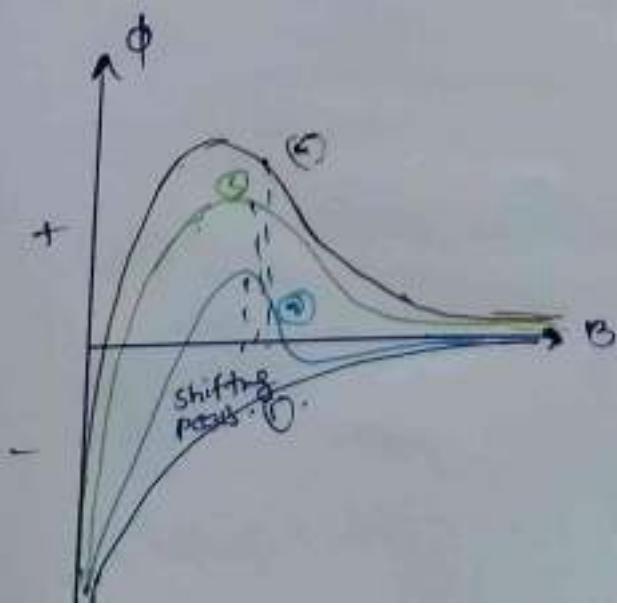
• 2 separate by medium ③.

$$A_H^{1/2} = A_H^{1/2} + A_H^{3/2} - (A_H^{1/2} + A_H^{3/2})$$

$$A_H^{1/2} = \sqrt{A_H^{1/2} A_H^{3/2}}$$

$$\phi_{\text{inct}} = (64 \pi \epsilon_0 k T) \tanh \left(\frac{2e\phi_0}{4kT} \right) \exp(-\phi) - \frac{A_H}{12 \pi h^2}$$

Effect of ϵ' / concentration



$$\epsilon' (10^6 \text{ cm})$$

$$0 \rightarrow 1$$

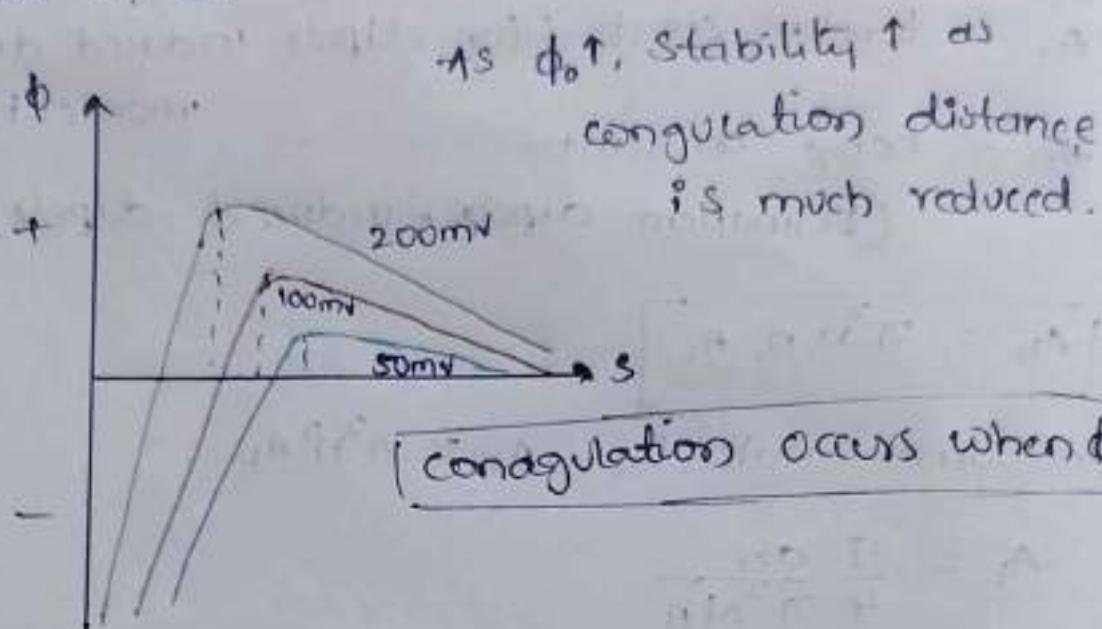
$$1 \rightarrow 2$$

$$3 \rightarrow 3$$

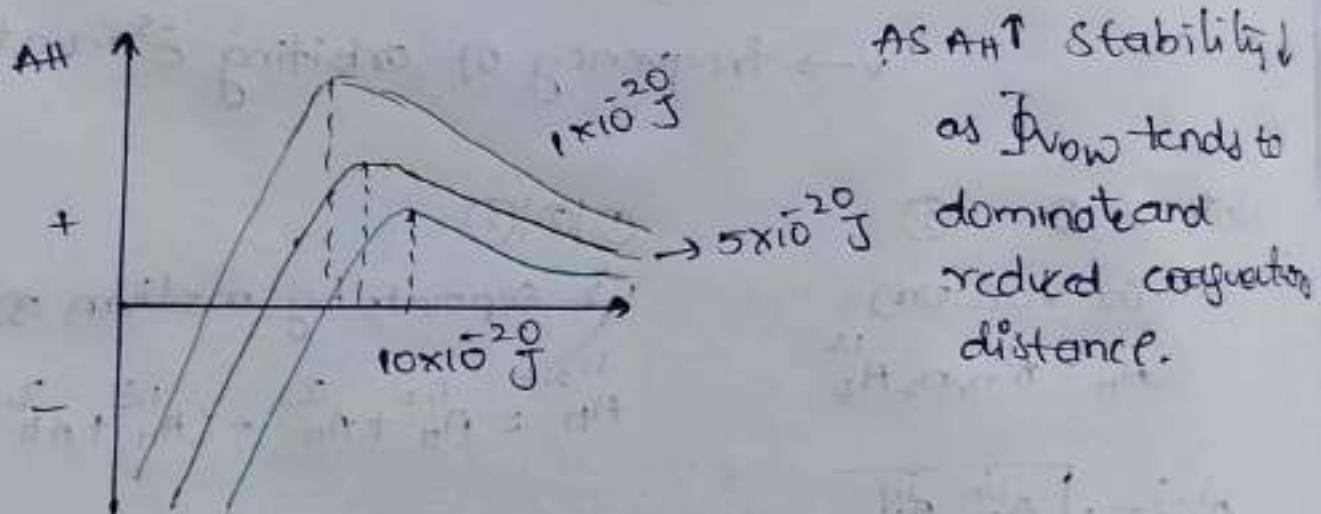
$$10 \rightarrow 4$$

as $\epsilon' \uparrow$, stability \uparrow

Effect of ϕ_0



Effect of A_H



Bigger particles co-agulate faster than smaller particles.