Colloids and Surface Chemistry

C304 (2 Credits)

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Course contents

- History of Colloids
- Classification of colloids
- Preparation of colloidal sols
- Purification of colloidal sols
- Important properties of colloidal systems
- Emulsions
- Identification of emulsion
- Preparation of emulsions
- Applications of colloids
- Surface Chemistry

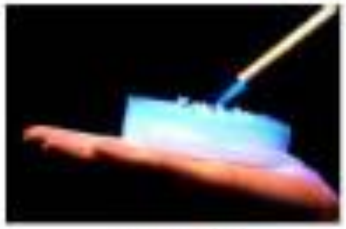
Examples of colloidal systems from daily life


Foams


Milk


Fog, smoke

Detergents


Aerogel


Blood


Paints

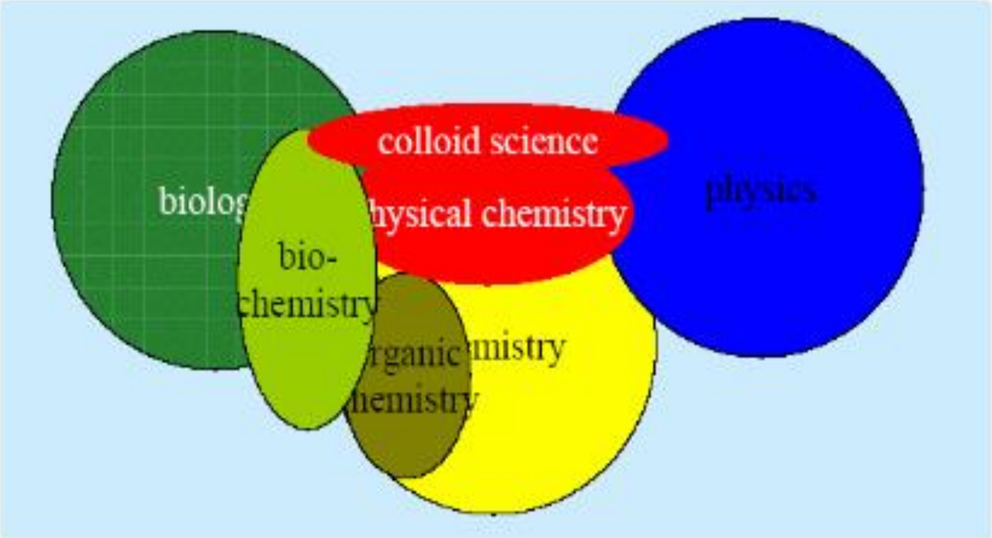
Cosmetics

Colloid science is interdisciplinary

1. partly physical chemistry
   - it is not the chemical composition which is important
   - the state is independent of the composition

2 partly physics
   - the physical properties are of great importance
   - basic law of physics can be applied

3 partly biology
   - biological materials are colloids
   - the mechanisms of living systems are related to colloid- and interfacial chemistry



history of colloids

Thomas Graham
(1805 - 1869)

1827, Robert Brown publishes his famous study on the jittering motion of small clay particles found in pollen grains.

1857, Michael Faraday experiments on colloidal dispersions of gold; salt-induced coagulation of the colloidal particles.

1861, Thomas Graham separates components of a solution using a semi-permeable membrane. He calls the components permeating the membrane *crystalloids*, and the ones that do not permeate the membrane *colloids*, which is derived from the Greek word κωλλα, "glue".

1905, Albert Einstein and William Sutherland formulate the theory of the Brownian **motion.**

1910, Jean-Baptiste Perrin: sedimentation equilibrium and Avogadro's number determined.

1910, Louis Gouy (and David Chapman 1913): theory of surface charge screening.

1937, H.C. Hamaker develops a theory of van der Waals forces between surfaces.

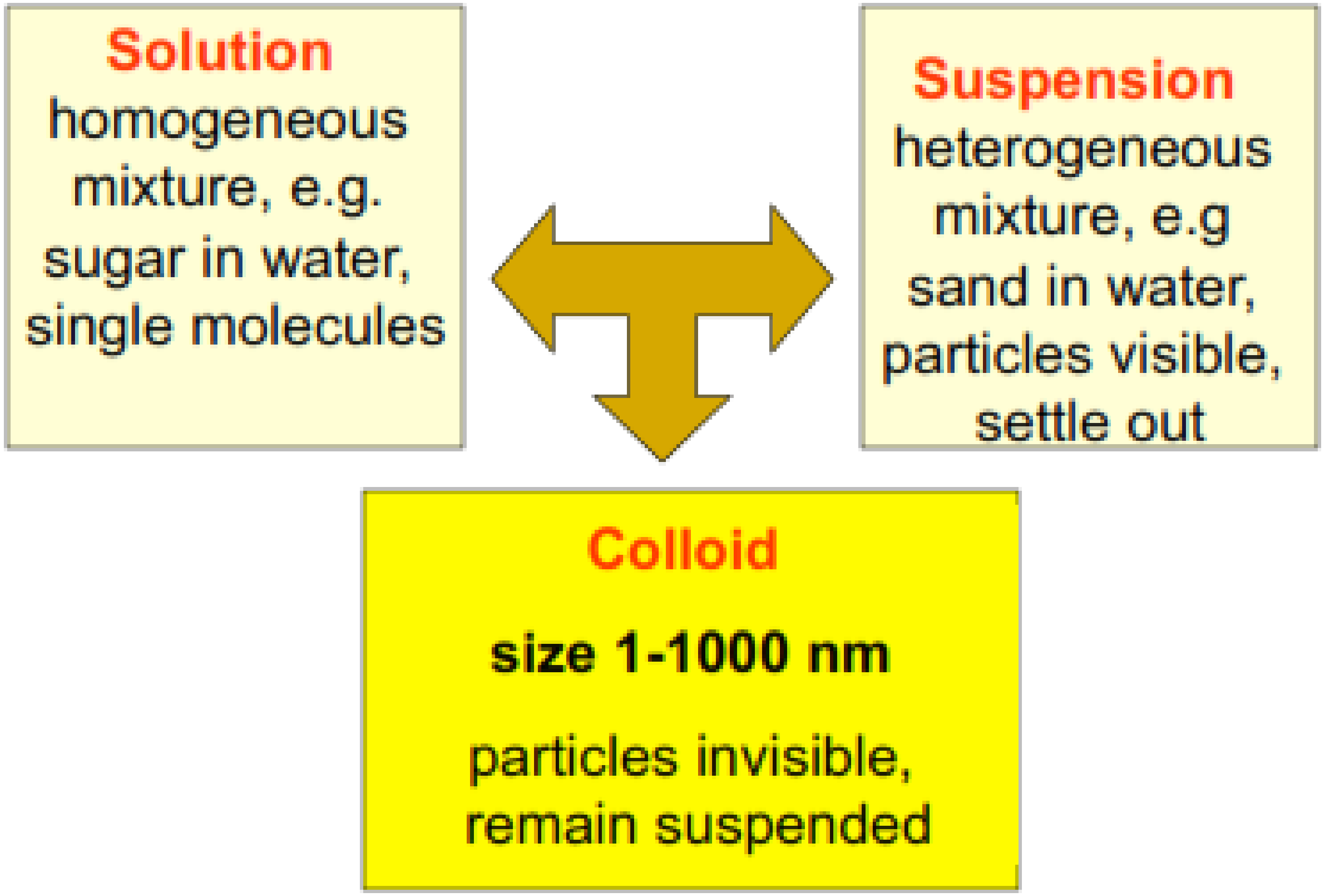
1941, Boris Derjaguin and Lev Landau formulate a theory of colloidal stability.

1948, Evert Verwey and Theo Overbeek improve the forementioned theory; DLVO-theory.

Colloids History

- Thomas Graham (1861) while doing his classical researches on liquid diffusion observed two classes of substances
    - **Crystalloid:** readily pass through animal & vegetable membrances
    - **Colloids**: diffused very slowly & could not pass through membrane
        - Came from the Greek word *kola* which means "glue-like"

What is a Colloid?



Solution
homogeneous mixture, e.g. sugar in water, single molecules

Suspension
heterogeneous mixture, e.g sand in water, particles visible, settle out

Colloid

size 1-1000 nm

particles invisible, remain suspended

Properties of Solutions, Colloids and Suspensions		
Solution	**Colloids**	**Suspensions**
Don't settle	Don't settle	Settles
Doesn't scatter light	Scatters light	Scatters light
Unaffected by membranes	Separated by membrane	Separated by membrane
Pass through filter paper unchanged	Pass through filter paper unchanged	Separated by filter paper

Classification of colloids

Classification is based on following criteria

Physical state of dispersed phase and dispersion medium.

Nature of interaction between dispersed phase and dispersion medium.

Types of particles of the dispersed phase.

Classification based on physical state of dispersed phase and dispersion medium

Eight types of colloidal systems are possible.

Dispersed phase	Dispersion medium	Type of colloid	Example
Solid	Solid	Solid sol	Some coloured glasses, and gem stones
Solid	Liquid	Sol	Paints, glue, ink
Solid	Gas	Aerosol	Smoke, dust
Liquid	Solid	Gel	Cheese butter, jellies
Liquid	Liquid	Emulsion	Milk, cream, crude oil,
Liquid	Gas	Aerosol	Fog, mist, cloud, insecticide sprays
Gas	Solid	Solid foam	Pumice stone, foam rubber
Gas	Liquid	Foam	Froth, whipped cream, soap-lather

Classification of colloidal dispersions in terms of the physical states of the internal and external phases

L/G: fog, mist, spray
(liquid aerosols)

S/G: smoke, loose
soot (powders)
(solid aerosols)

G/L: sparkling water, foam,
whipped cream
(liquid gas dispersions)

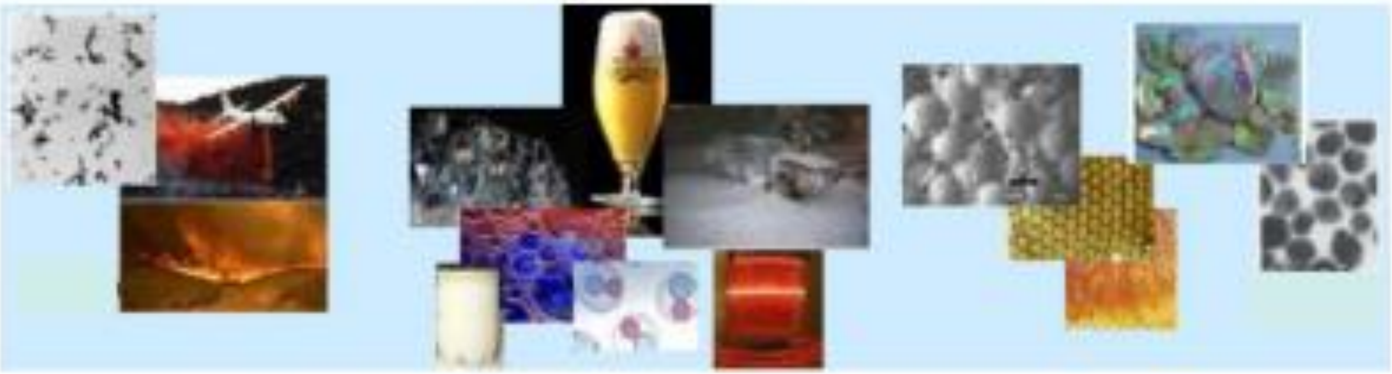
L/L: milk; mayonnaize; crude oil
((micro)emulsions)

S/L: paint, ink, toothpaste
(sols/suspensions)

G/S: polysterene foam,
silica gel
(aerogels, xerogels)

L/S: opal, pearl
(solid emulsions)

S/S: pigmented plastics
(solid suspensions)



Classification based on nature of interaction

Lyophobic colloids (dispersion medium hating colloids)
When metals and their sulphides simply mixed with dispersion medium, they don’t form colloids.

- need stabilizing to preserve them.
- irreversible.
- For example, colloidal solutions of **gold,silver**, $Fe(OH)_3$, As_2S_3, etc.

Lyophilic colloids (dispersion medium loving)
Directly formed by substances like gum, **gelatine** rubber etc. on mixing with a suitable liquid(the dispersion medium).

- self-stabilizing
- reversible sols
- For example, gums, gelatin, starch, albumin in water.

Characteristics of lyophilic & lyophobic

LYOPHILIC	LYOPHOBIC
Stable	Unstable
The particles may or may not migrate in an electrical field	The particles are charged and hence move towards electrode in an electrical field
Viscosity is much higher than that of the medium	Viscosity is same as that of the medium
Reversible	Irreversible
Self-stabilized due to strong attraction between 2 phases	Stabilizer is required
Not easily precipitated by the addition of electrolytes	Coagulated easily by adding electrolytes
Not visible under ultramicroscope	Visible under ultramicroscope
Prepared by directly dissolving	Prepared by indirect method

Specific surface area S_{sp}

the area of the interface per unit volume of the dispersed phase.

D = 1/a , where a = cross section size of particles.

D = degree of dispersion.

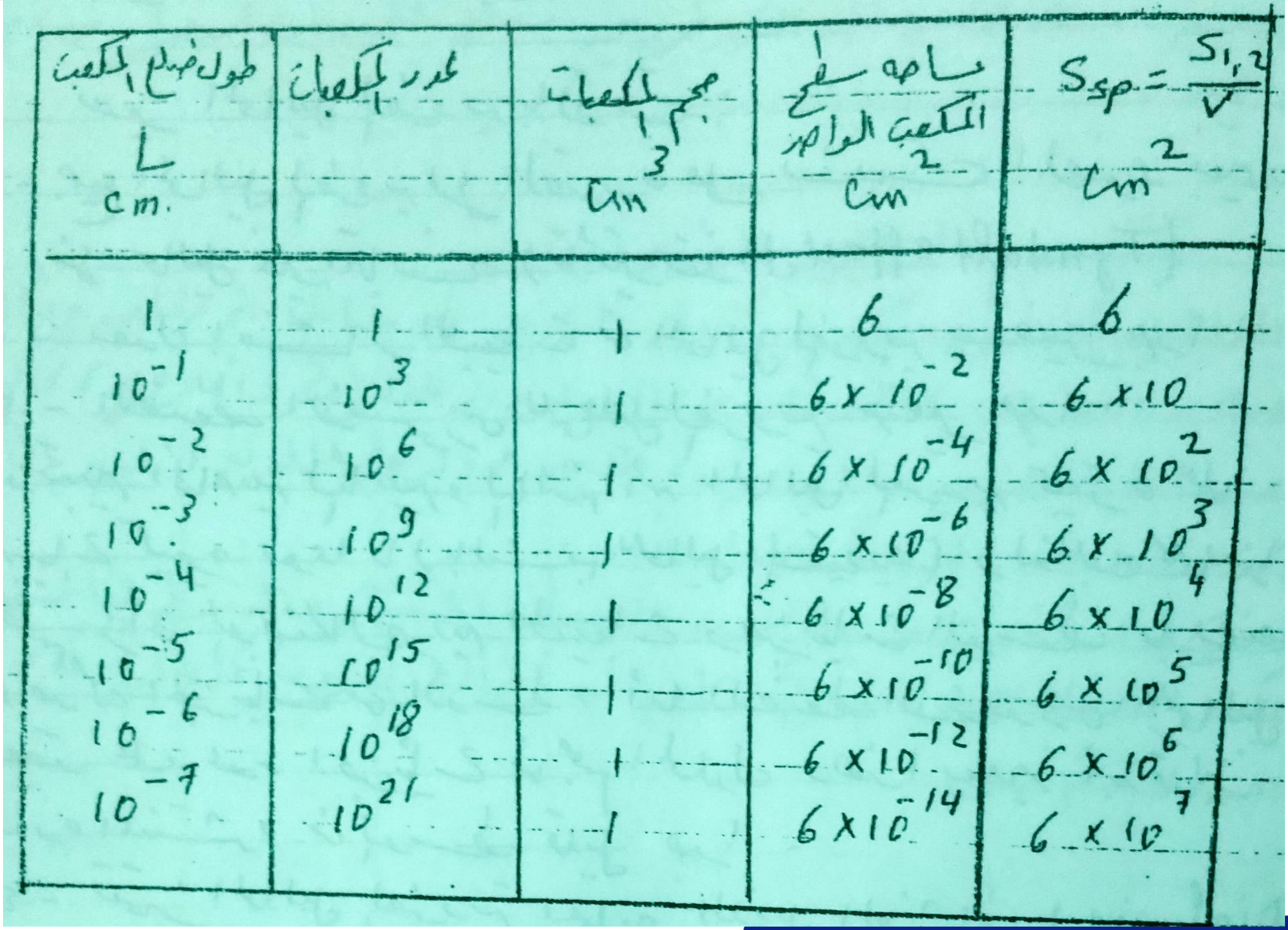
$$S_{sp} = S_{1,2/}V$$

$S_{1,2}$ is the interfacial area between phase 1 and 2. and *V* is the volume of the dispersed phase.

$$S_{sp} = S_{1,2}/V = 6L^2/L^3 \text{ for cubic particles}$$

$$S_{sp} = 4\Pi r^2/4/3\ \Pi\ r^3 = 3/r = 6/d \text{ for spherical particles.}$$

$$S_{sp} = K/a = KD$$



طول ضلع المكعب L cm.	عدد المكعبات	حجم المكعبات cm^3	مساحه سطح المكعب الواحد cm^2	$S_{sp} = \frac{S_{1,2}}{V}$ cm^2
1	1	1	6	6
10^{-1}	10^{3}	1	6×10^{-2}	6×10
10^{-2}	10^{6}	1	6×10^{-4}	6×10^{2}
10^{-3}	10^{9}	1	6×10^{-6}	6×10^{3}
10^{-4}	10^{12}	1	6×10^{-8}	6×10^{4}
10^{-5}	10^{15}	1	6×10^{-10}	6×10^{5}
10^{-6}	10^{18}	1	6×10^{-12}	6×10^{6}
10^{-7}	10^{21}	1	6×10^{-14}	6×10^{7}

Stability of colloidal systems

- **Thermodynamic stability:**

The aggregative instability of colloidal systems is caused by the positive free surface energy which is concentrated on the interface of a system.

In coagulation, particles adhere and the interface partially disappears thus the Free energy of the system decreases.

- **Kinetic concepts:**

the stability of a colloidal or micro-heterogeneous system is determined by the balance between:

1- Attractive forces (Van der Waals) which ten to bring particles together.

2- Repulsive forces which hinder coagulation. (electrostatic forces).

Preparation of colloidal systems

- Most substances can form colloidal systems
- Starch, gelatin form colloidal systems by simple warming or agitation with water.
- But metals and other inorganic substances can be obtained but with difficulty by using special devices.

- To get a substance in colloidal form, we can either start the material in bulk and break it down into fine particles of colloidal size (This is the Dispersion Method).

- Or, we can bring about a large number of atoms or molecules to from bigger particles of the colloidal size (This is the Condensation method)

1- Dispersion methods

2- Condensation methods

Preparation of Colloids

- Dispersion
  - Large particles are broken down to colloidal dimension & dispersing them to colloidal solution
- Condensation
  - Particles of molecular size are allowed to coalesce or condense to form bigger particles of colloidal size

1- Dispersion methods

Mechanical

Using crusher, mill, mixer

Electro-dispersion

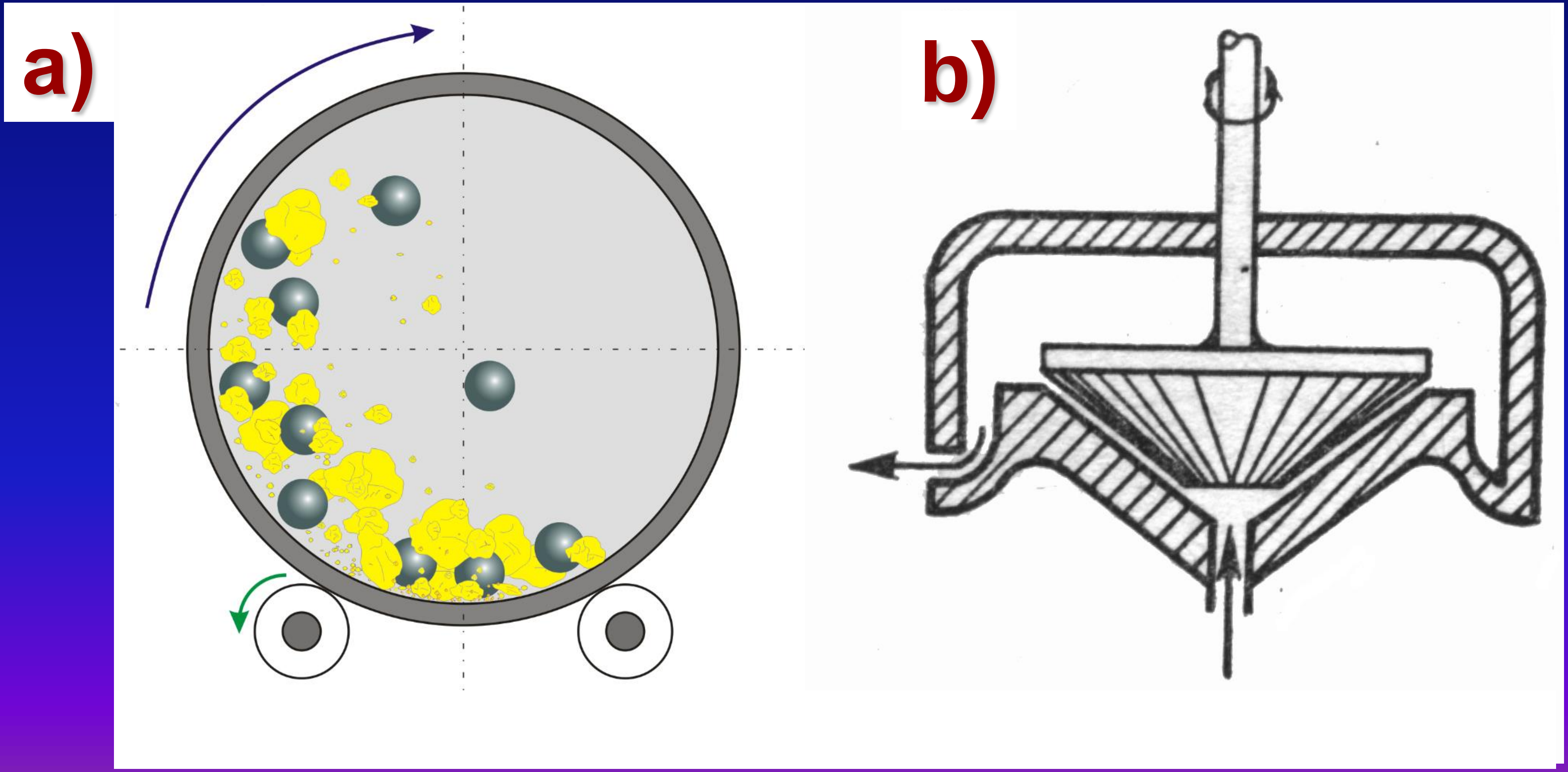
using the instruments for electrolytic spraying

Acoustic

using ultrasound

Peptization

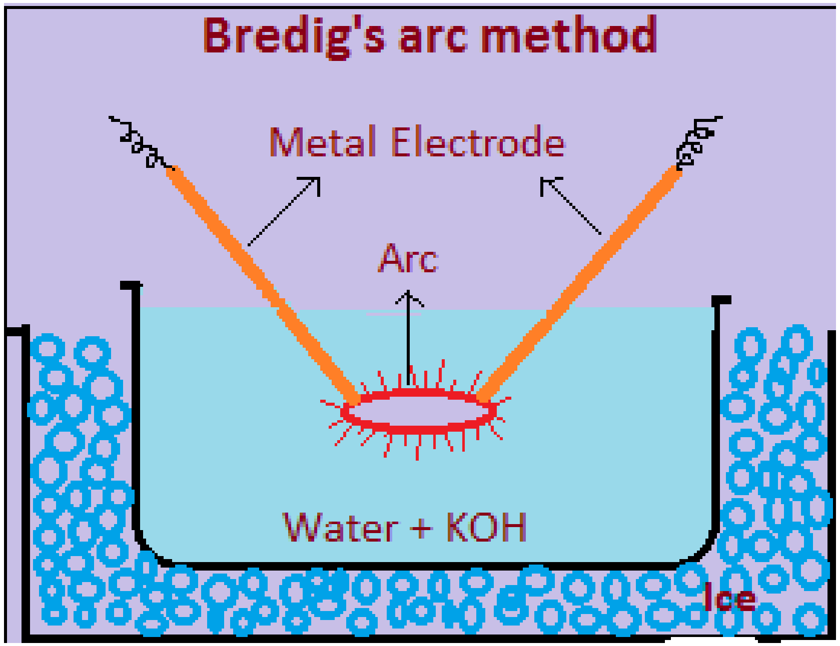
Mechanical methods
(a) Ball and (b) colloid mill



Electro-dispersion

(Bridge's arc method)

- This method is employed for obtaining colloidal solutions of metals e.g. silver, gold, platinum



(Bridge's arc method)

- An electric current is struck between two metallic electrodes placed in a container of water.
- The intense heat of the arc converts the metal into vapours which condensed immediately in the cold water bath.
- This results in the formation of particles of colloidal size.
- Example of particles are Gold, platinum, silver and etc..

Ultrasonic-dispersion

Peptization

- It is a converse of (Coagulation)
- Redispersion of coagulated sol to form stable colloidal particles.
- A reddish brown colored colloidal solution is obtained by adding small quantity of ferric chloride solution to the freshly precipitated ferric hydroxide , $Fe(OH)_3$.
- Ferric chloride is called **peptizing agent**.

Condensation methods

Excessive cooling

Exchange of solvent

Colloidal solution of phosphorus is prepared by addition of alcohol into a solution of phosphorous in excess water.

Passing vapour of an element over a liqiuid

Chemical Action

Double decomposition

Arsenious sulphide colloidal solution is prepared by passing of H_2S gas into a solution of As_2O_3.

Oxidation method

Sulphur colloids are prepared by oxidation of H_2S by O_2.

Reduction

Silver colloids are prepared by passing H_2 through a saturated aqueous solution of silver oxide at 65° C.

Hydrolysis

Dark brown $Fe(OH)_3$ colloidal solution is prepared by adding $FeCl_3$ into boiling water.

i) **Double decomposition:** An Arsenic sulphide sol is prepared by passing a slow stream of hydrogen sulphide gas through a cold solution of arsenious oxide. This is continued till the yellow colour of the sol attains maximum intensity.

$As_2O_3 \quad + \quad 3\,H_2S$ --- --- -- > $As_2S_{3(yellow)} \quad + \; 3\,H_2O$

Excess hydrogen sulphide is removed by passing in a stream of hydrogen.

(ii) **Oxidation** : A colloidal solution of sulphur is obtained by passing H_2S into a solution of sulphur dioxide.

$2H_2S + SO_2$ ---- -- - > $2H_2O + 3\,S$

(iii) **Reduction:** Silver sols and gold sols can be obtained by treating dilute solution of silver nitrate or gold chloride with organic reducing agents like tannic acid or formaldehyde or others.

$AgNO_3$ + tannic acid --- -- > Ag Sol

$2AuCl_3 + 3\,SnCl_2$ -------$2Au + 3SnCl_4$

iv) **Hydrolysis:** Colloidal solutions of the hydroxides of Fe, Cr, Al etc can be prepared by hydrolysis of their salts. A colloidal solution of ferric hydroxide is obtained by boiling a dilute solution of ferric chloride.

$FeCl_3 + 3H_2O$ -- --- - -> $Fe(OH)_{3(red\ sol)} + 3HCl$

Condensation method

Normal crystals are formed in two stages:

1- The Nucleation (formation of crystallization centers) in a supersaturated solution (like in chemical reaction that yields a slightly soluble compound).

2- The growth of nuclei leading to the formation of sufficiently large crystals.

The nucleation rate (U) can be expressed as:

$$U = K\,(C_{sup} - C_s)/C_s$$

Where K is constant
C_{sup} = conc. of supersaturated solution
C_s = conc. of a saturated solution.
$(C_{sup} - C_s)$ is an excess of a substance which is able to form crystals, then can serve as a measure of the rate of liberation from the solution. Cs can serve a measure of resistance to the liberation (interaction between the solute and solvent).
So, the grater the $(C_{sup} - C_s)$ and the smaller Cs, the more rapidly the nuclei formed and the larger is the no. of crystallization centers, hence the smaller are colloidal particles because the liberated substance will be distributed between a large n. of crystallization centers.

Purification of colloids

Dialysis
In this process, the colloidal particles are separated from the impurities (mainly electrolytes) by the diffusion through a porous membrane such as parchment, collodion, etc.

Electrodialysis
This is a special type of dialysis process, which is accelerated by the application of a potential difference across the membrane. So ions migrate faster than the colloids .

Ultrafiltration
In this process the colloidal particles are separated by the process of filtration, through a filter paper, which is impregnated with gelatin or collodion (Nitro celleulose) followed by hardening in formaldehyde.

Purification of colloidal solutions:

- When a colloidal solution is prepared is often contains certain electrolytes which tend to destabilize it. The following methods are used for purification:

1- Dialysis:

- Semipermeable cellophane membrane prevent the passage of colloidal particles, yet allow the passage of small molecules or electrolytes.

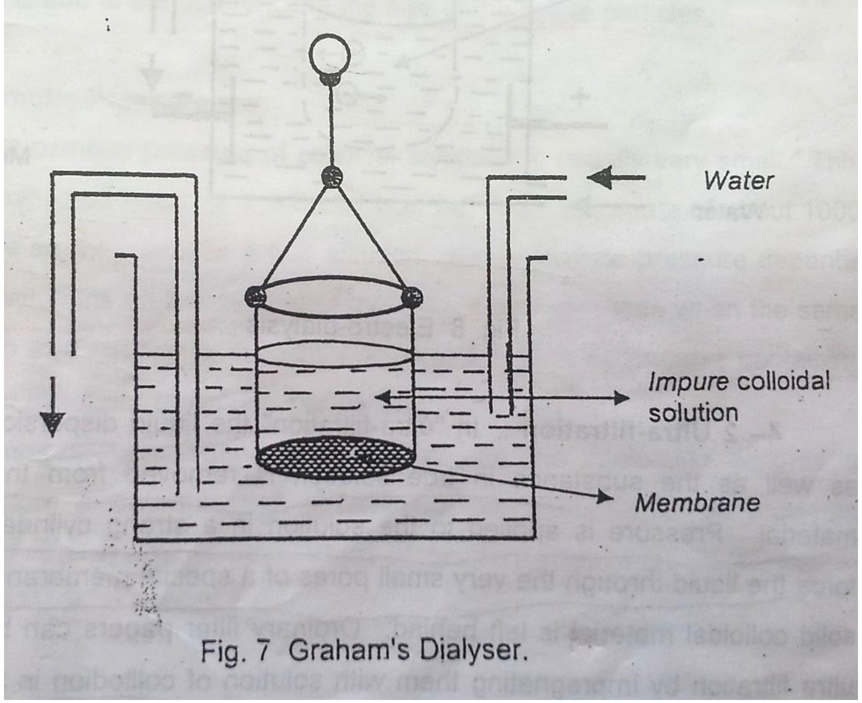


Fig. 7 Graham's Dialyser.

Purification of colloidal systems:

2- Electrodialysis:

- In the dialysis unit, the movement of ions across the membrane can be speeded up by applying an electric current through the electrodes induced in the solution.

- The most important use of dialysis is the purification of blood in artificial kidney machines.

- The dialysis membrane allows small particles (ions) to pass through but the colloidal size particles (haemoglobin) do not pass through the membrane.

Electrodialysis:

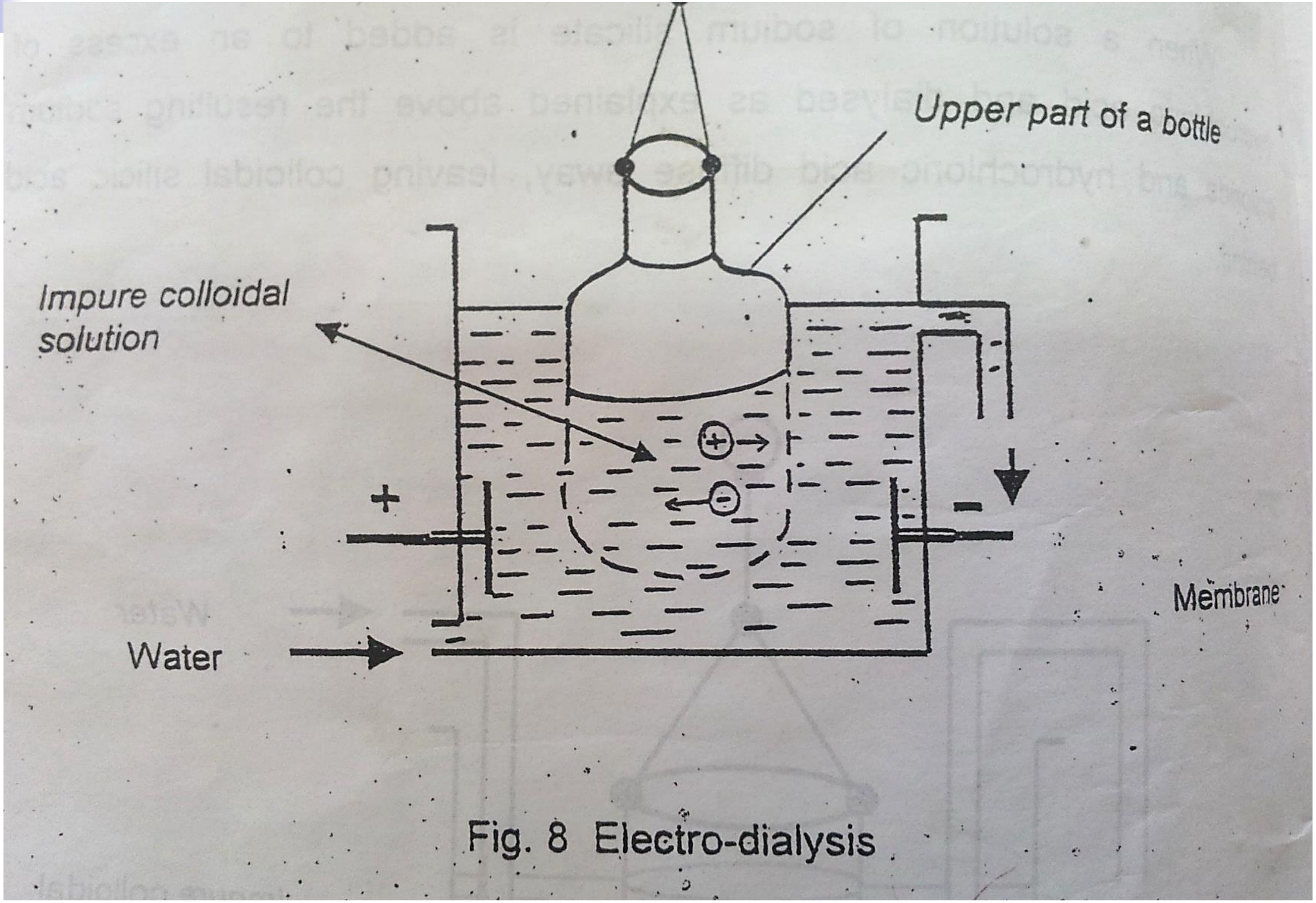


Fig. 8 Electro-dialysis

Purification / Separation of colloids

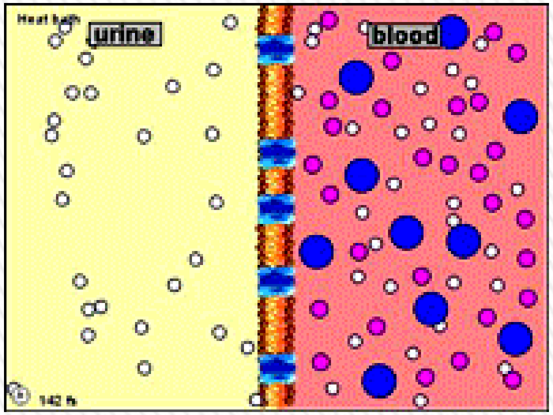
Electro-dialysis

An **electrical potential** may be used to increase the rate of movement of ionic impurities through a dialysis membrane.

Pharmaceutical application of dialysis

Haemodialysis:

Small molecular weight impurities from the body (blood) are removed by passage through a membrane.



Properties of colloidal systems

Optical
Kinetic
Electrical

Properties of Colloids

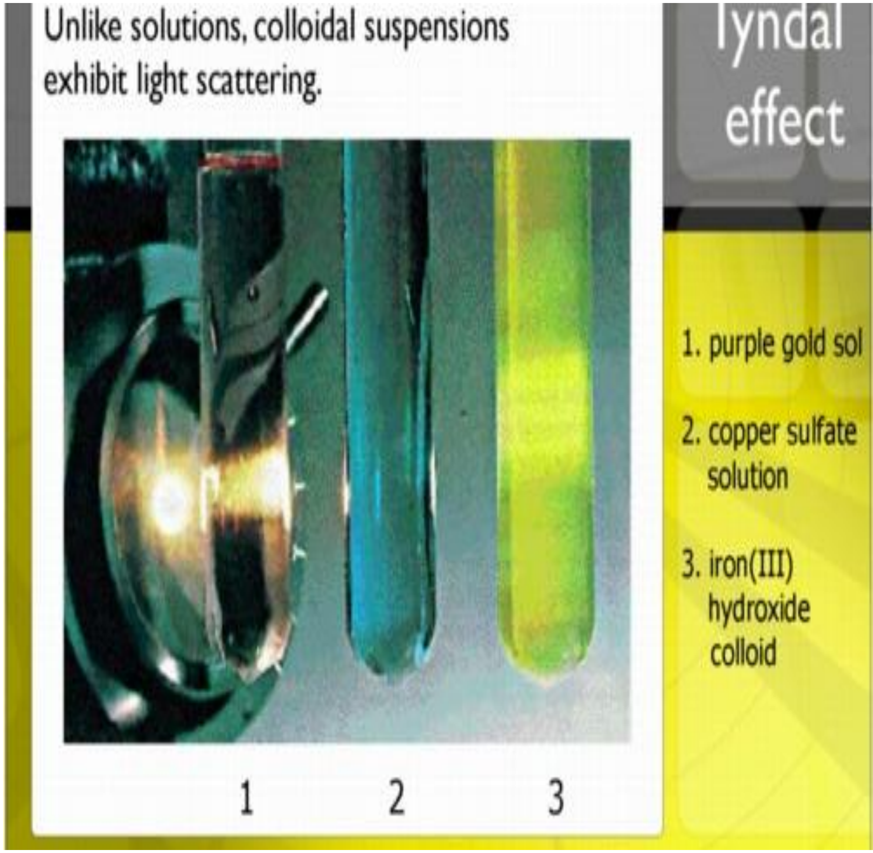
- Due to their small size they do not settle out of solution.
- Particles lying in the colloidal size range possess an **enormous surface area** compared with the surface area of an equal volume of larger particles.
- In order to compare surface area of different systems we use the term **specific surface area** (= surface area per unit weight or volume of material).
- Large specific surface area results in many **unique properties** of colloidal dispersions.
- **Optical properties of colloids. eg. Tyndall (Faraday) Effect**
- **Kinetic properties of colloids eg. Brownian motion, diffusion, osmosis, viscosity etc.**
- **Electrical Properties of Colloids eg. Zeta potential**
- **Electro-kinetic Properties of Colloids eg. Electrophoresis**

Optical Properties of Colloids

1-Faraday-Tyndall effect

– when a strong beam of light is passed through a colloidal sol, the path of light is illuminated (a visible cone formed).

- This phenomenon resulting from the scattering of light by the colloidal particles.



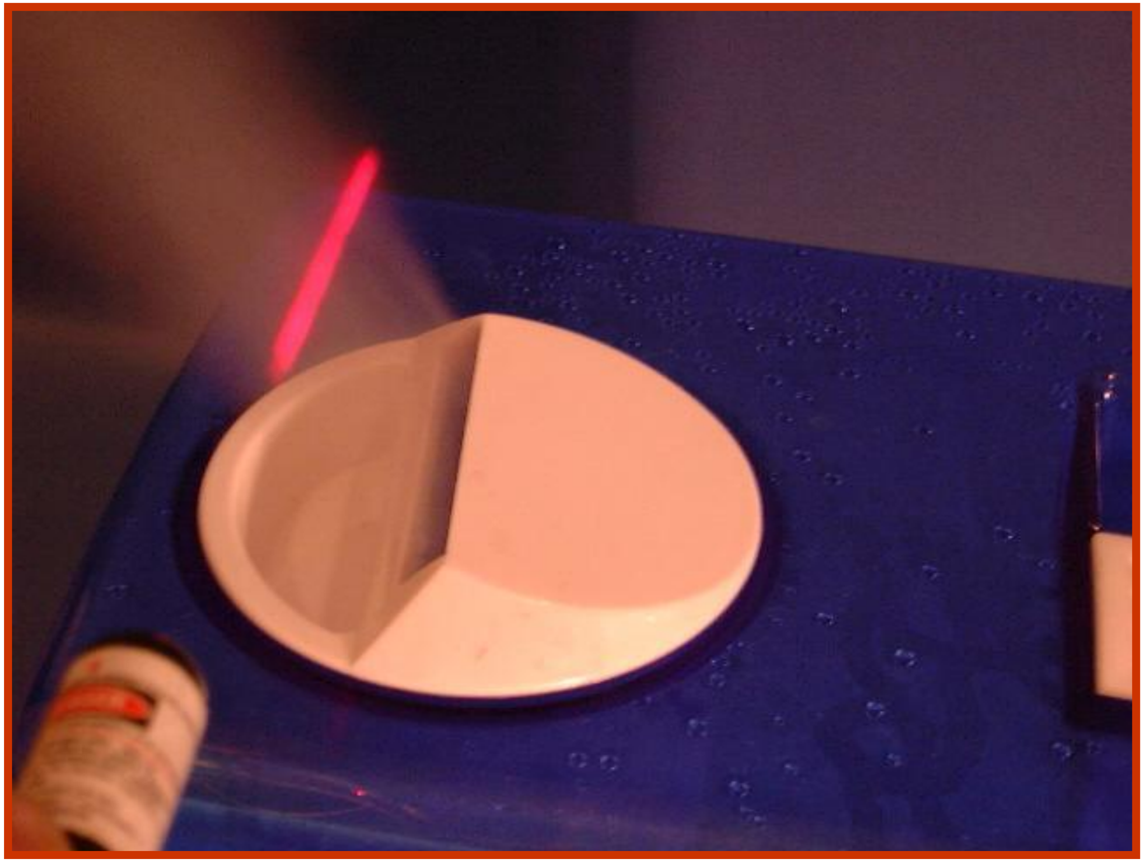
Unlike solutions, colloidal suspensions exhibit light scattering.

Optical Properties of Colloids

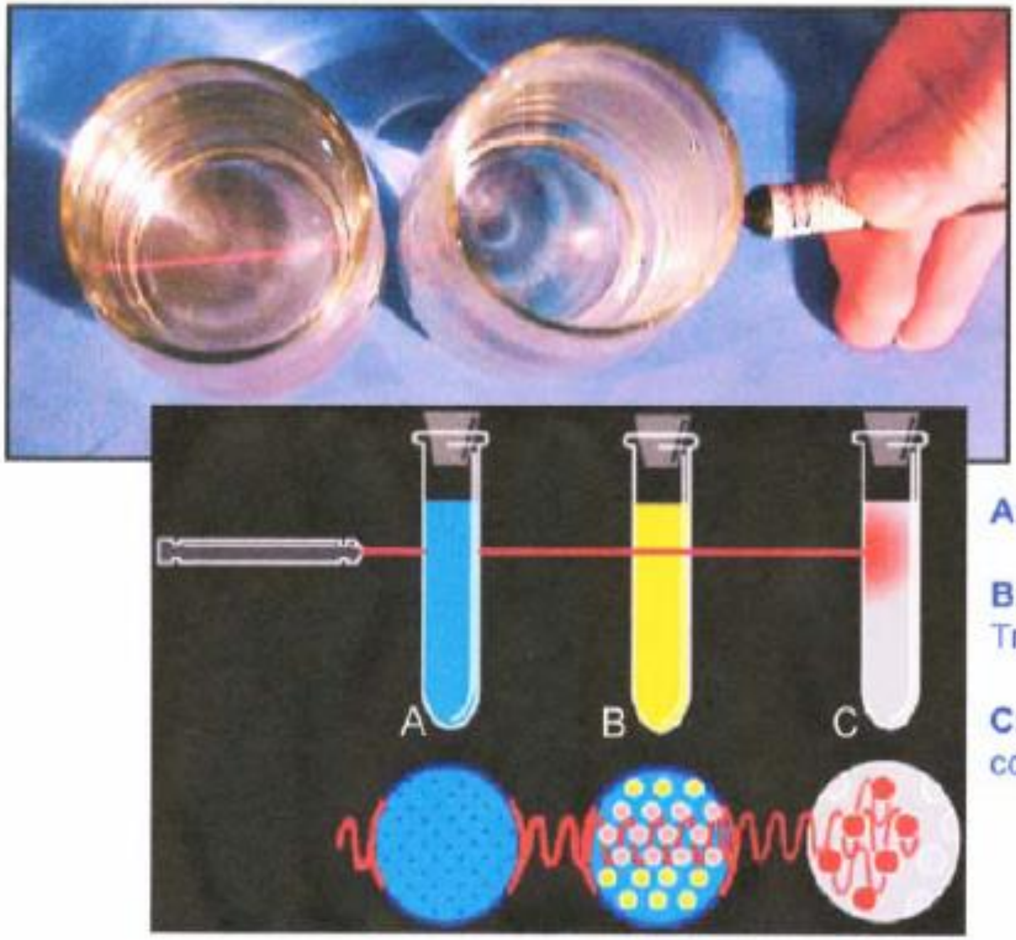
- The same effect is noticed when a beam of sunlight enters a dark room through a slit when the beam of light becomes visible through the room.
- This happens due to the scattering of light by particles of dust in the air.

Tyndall Effect

- ❑Tyndall effect: ability of a Colloid to scatter light.
- ❑The beam of light can be seen through the colloid.



The Faraday-Tyndall effect



Tyndall Effect: Laser Pointer traveling through a solution (right) and through a colloidal suspension (left).

A: Solution

B: Colloidal Suspension Transparent

C: Colloidal Suspension completely absorbing light

Optical Properties of Colloids

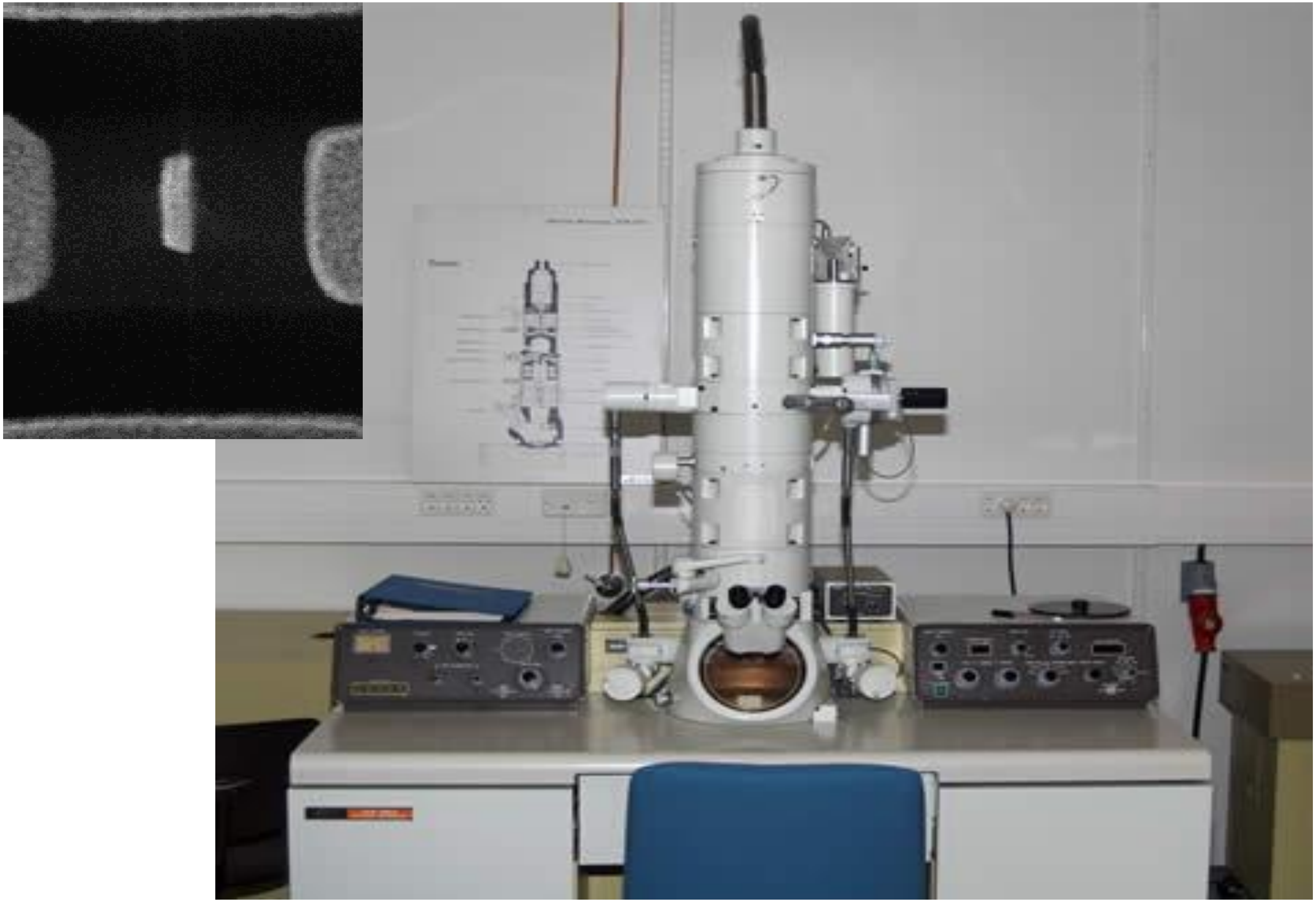
2- Electron microscope

- Ultra-microscope has declined in recent years as it does not able to resolve lyophilic colloids.

- so electron microscope is capable of yielding pictures of actual particles size, shape and structure of colloidal particles.

- Electron microscope has high resolving power, as its radiation source is a beam of high energy electrons, while that of optical microscope is visible light.

Electron Microscope



Optical Properties of Colloids

3- Light Scattering

- depend on tyndall effect.
- used to give information about particle size and shape and for determination of molecular weight of colloids.
- Used to study proteins, association colloids and lyophobic sols.
- Scattering described in terms of turbidity, T

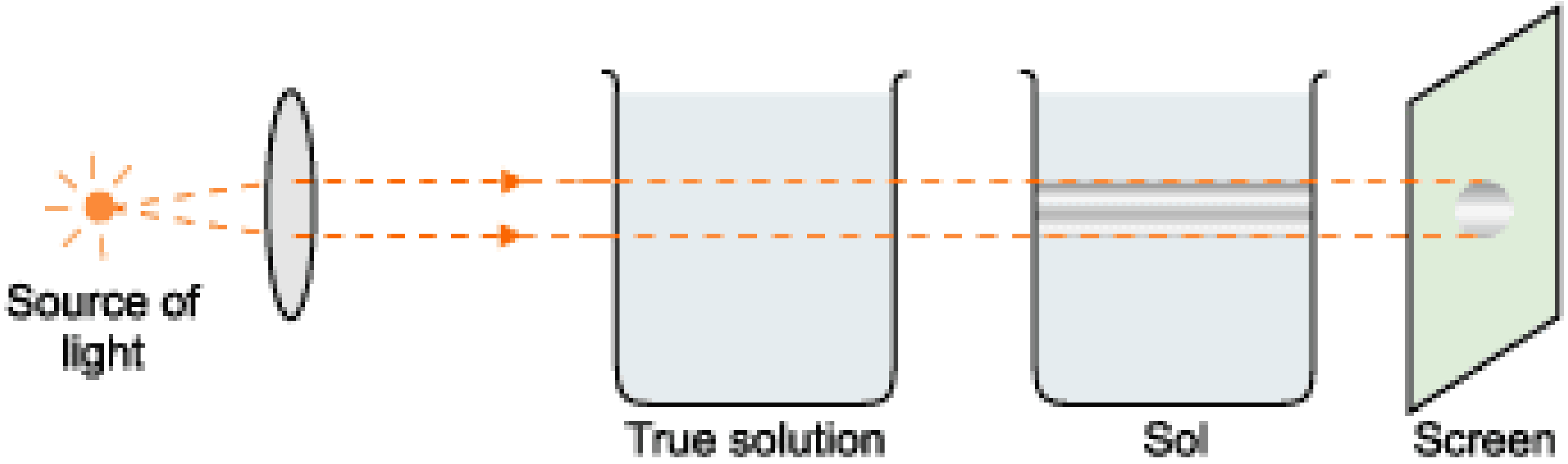
- *Turbidity:* the fractional decrease in intensity due to scattering as the incident light passes through 1 cm of solution.

- Turbidity is proportional to the molecular weight of lyophilic colloid

Properties of Colloids

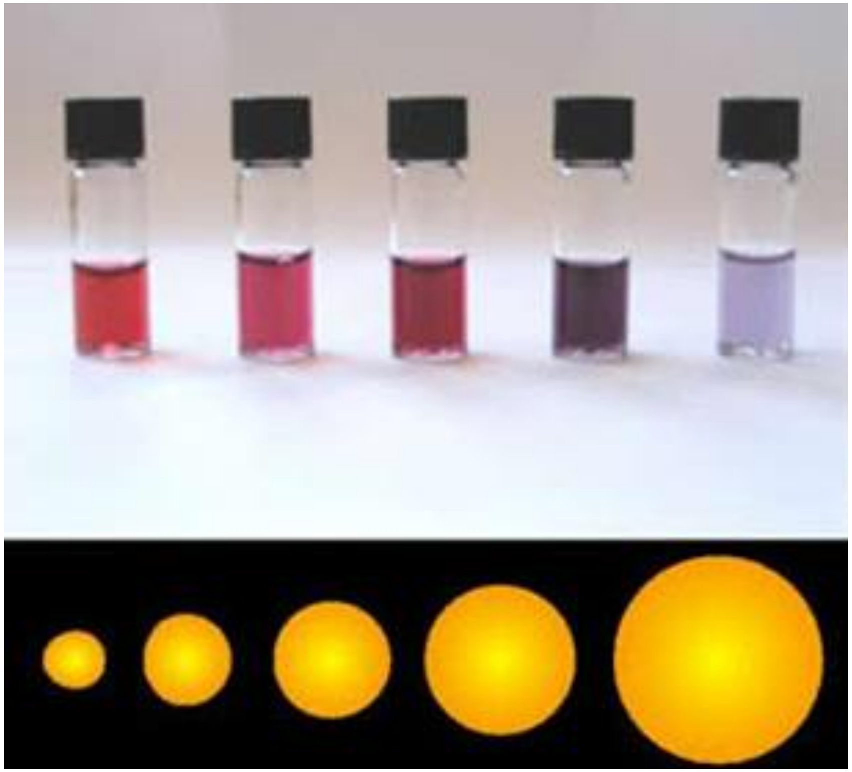
Optical properties: Tyndall effect

When a beam of light falls at right angles to the line of view through a solution, the solution appears to be luminescent and due to scattering of light the path becomes visible.



Quite strong in lyophobic colloids while in lyophilic colloids it is quite weak.

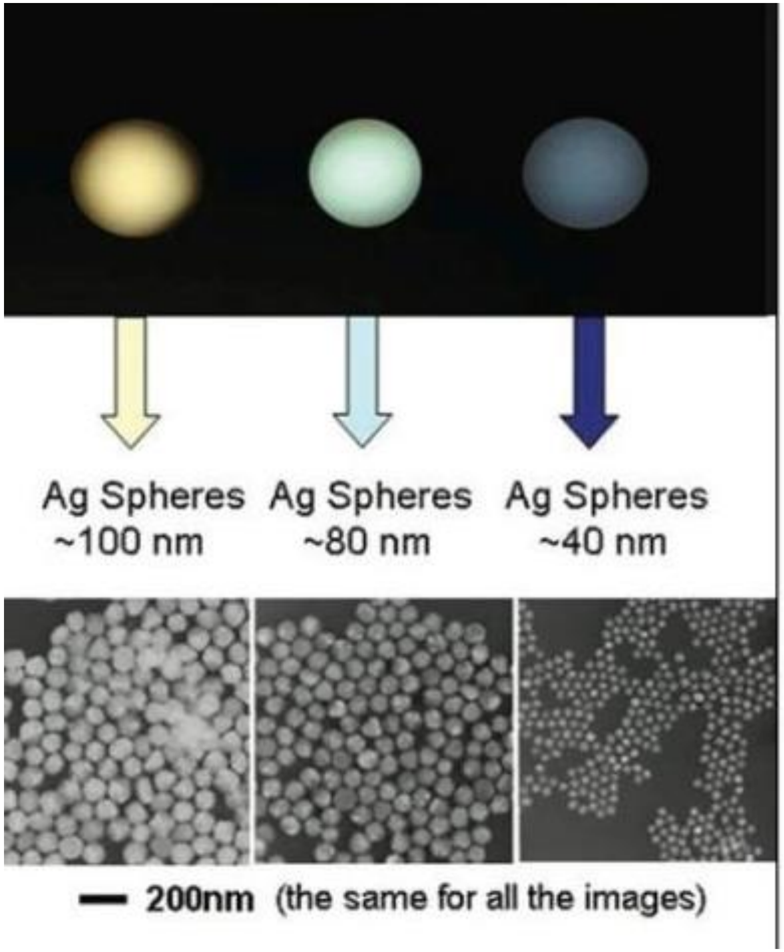
Stained Glass: Size Matters



Gold particles

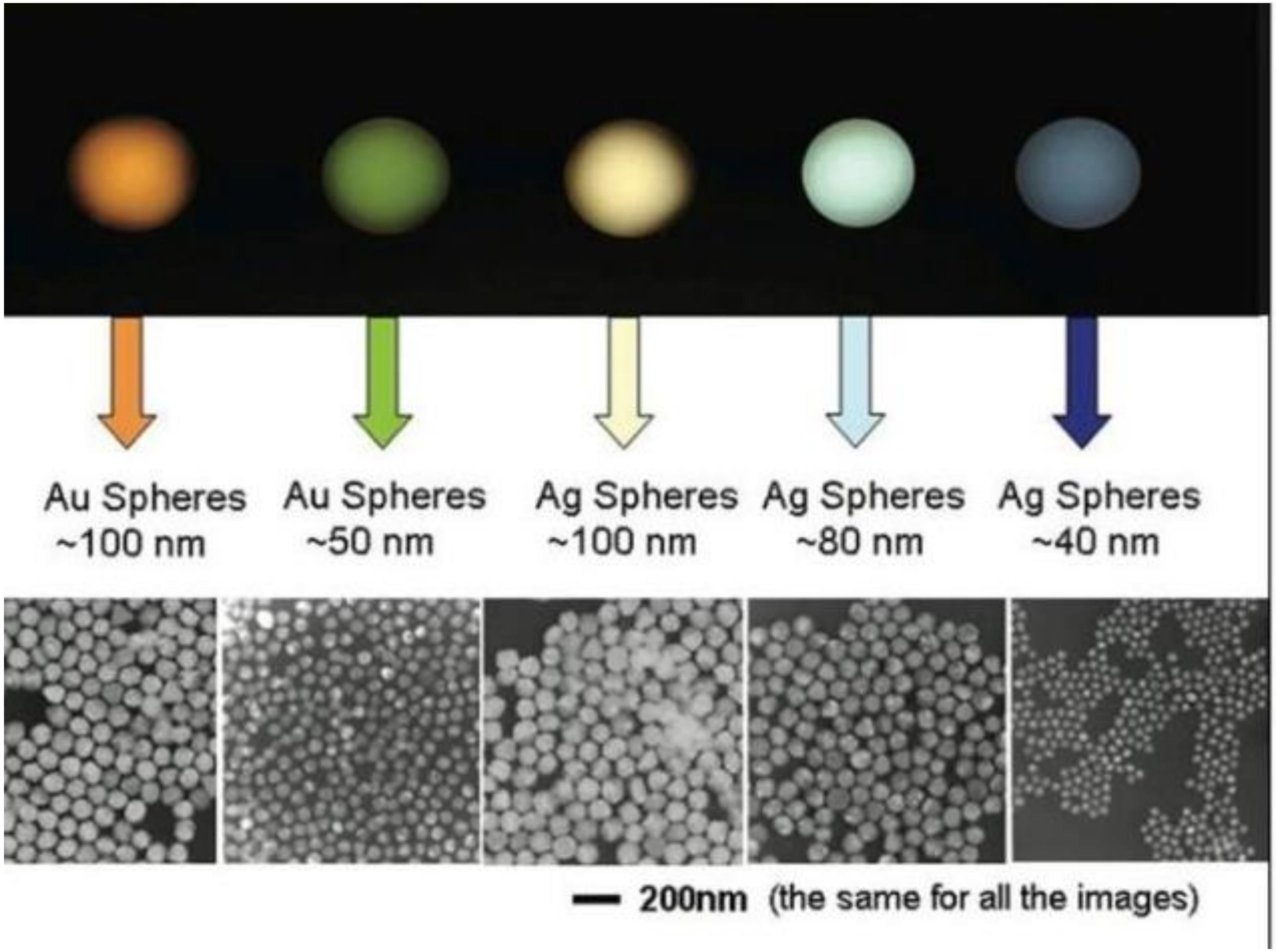
http://www.cas.muohio.edu/nanotech/education/k_12.html http://www.horiba.com/scientific/

Stained Glass: Size and Shape Matter



Controlling the Quantum World: The Science of Atoms, Molecules, and Photons, 2007

Stained Glass: Size and Shape Matter



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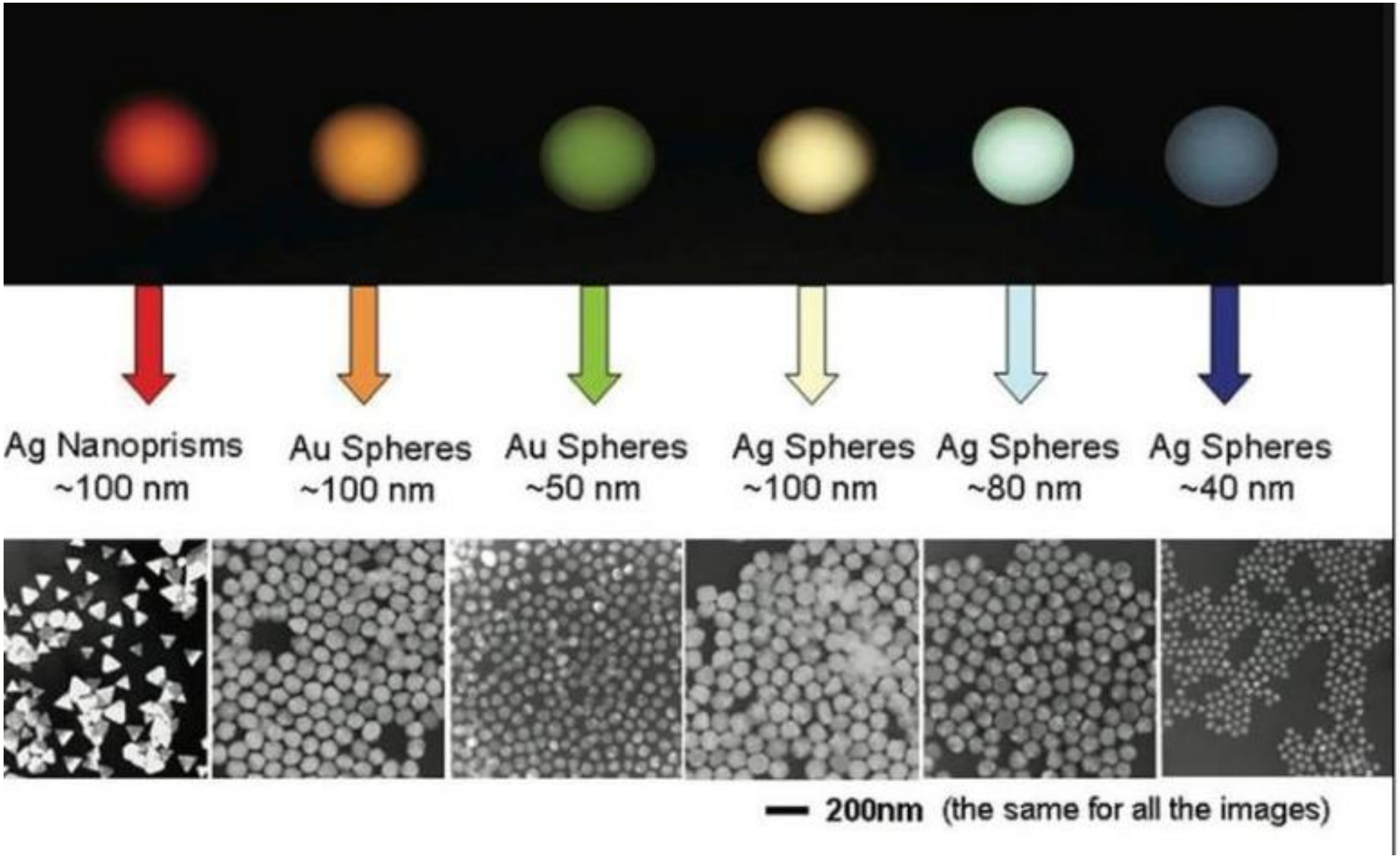
Stained Glass: Size and Shape Matter



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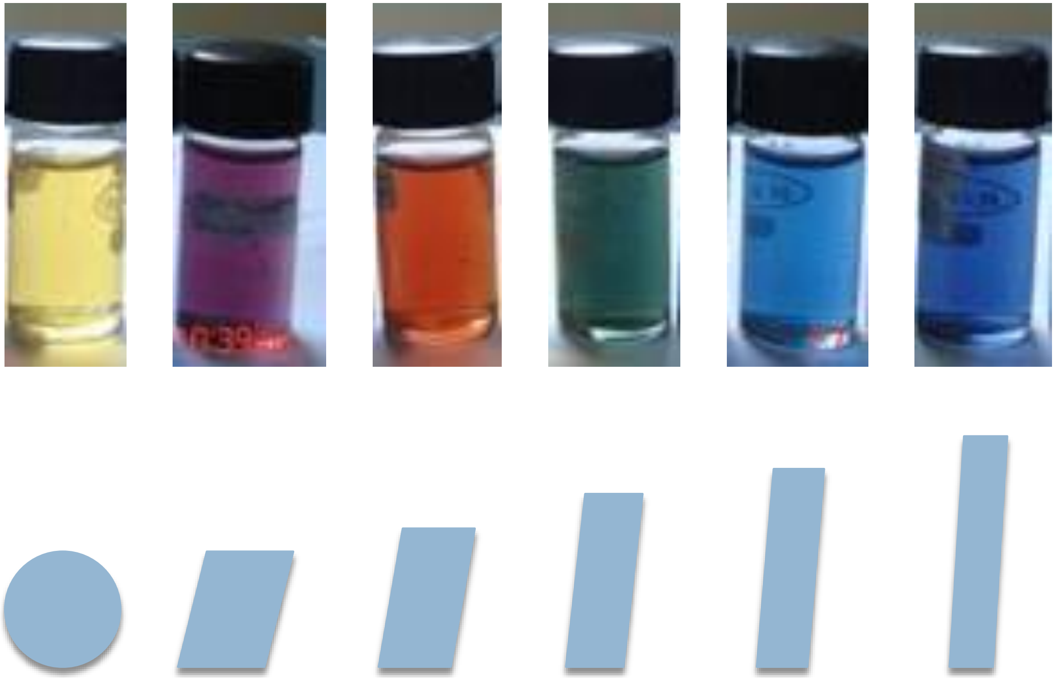
Stained Glass: Size and Shape Matter

Particle shape also affects the color!



http://commons.wikimedia.org/wiki/File:Native_gold_nuggets.jpg
http://www.cat.gov.in/technology/laser/lpas/pps.html

History of Nanotechnology - Colloids

Nanoparticles “stay in solution”, leading to one of the most enduring images of nanotechnology:

The rainbow array of solutions made by the suspension of a variety of sizes of nanoparticles.

This was discovered by Michael Faraday in 1857.

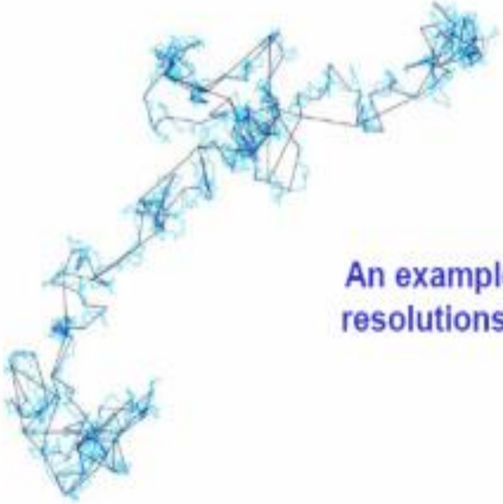
Brownian motion

Robert Brown (1773-1858)

In 1827, the botanist Robert Brown published a study *"A brief account of microscopical observations on the particles contained in the pollen of plants...",* where we reported his observations of irregular, jittery motion of small (clay) particles in pollen grains.

He repeated the same experiment with particles of dust, showing that the motion could not be due to the pollen particles being alive.

Although several people worked on this phenomenon over the years, a proper physical explanation of it had to wait for almost 80 years.

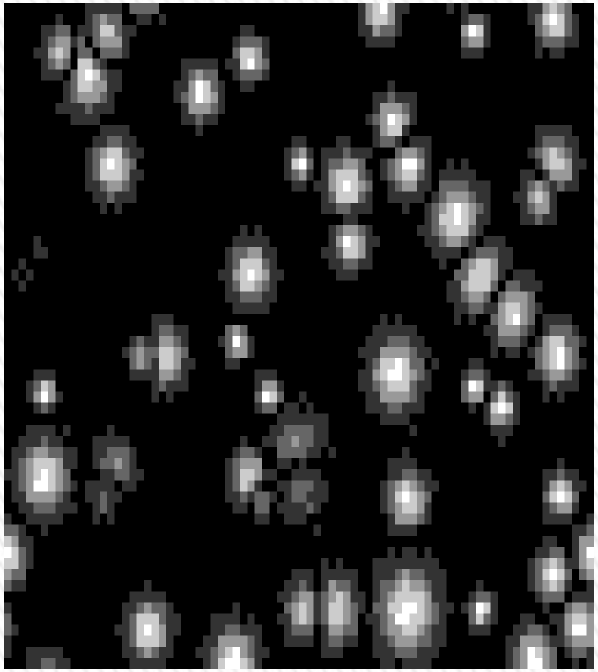


An example of Brownian motion of a particle, recorded for three different resolutions in time (time steps).

Kinetic properties of colloids

Properties which are related to the motion of particles with respect to the dispersion medium

1. Brownian motion



Random movement of the colloidal particles.
The erratic motion is due to the random collision (accident) of the colloidal particles with the molecules of the dispersion medium.
The velocity of the particles increase with decreasing particle size.

2. Diffusion

Particles spontaneously diffuse from a region of higher concentration to a region of lower concentration until the concentration of the system is uniform throughout.
Diffusion is a direct result of Brownian movement.

Kinetic Properties of Colloids

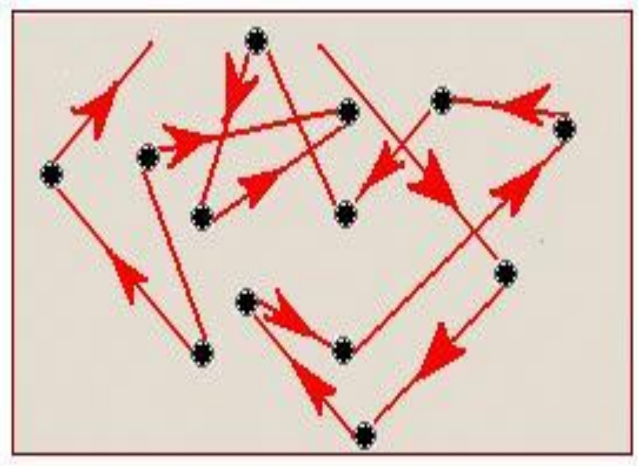
1-Brownian motion

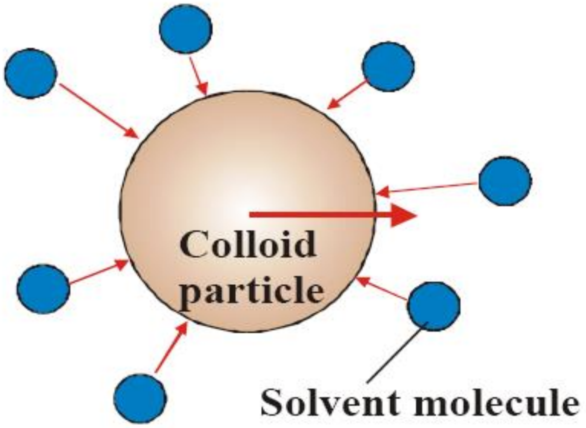
- The zig-zag movement of colloidal particles continuously and randomly.

- This brownian motion arises due to the uneven distribution of the collisions between colloid particle and the solvent molecules.

- Brownian movement was more rapid for smaller particles.

- It decrease with increase the viscosity of the medium.





Brownian motion

- Colloidal particles are kept dispersed throughout the dispersing medium by random collisions with other molecules or atoms.

- A colloidal particle moves through a solvent in a jittery motion along a random path caused by collisions with molecules in the liquid, called *Brownian motion* (first described by botanist Robert Brown in 1827). [Einstein's analysis of Brownian motion in 1905 provided one of the final confirmations of the atomic nature of matter.)

LOADING...

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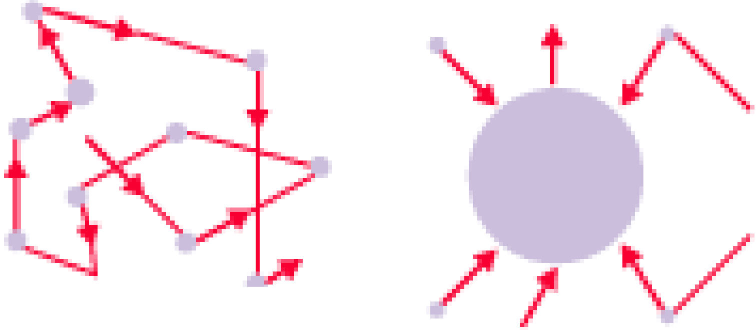
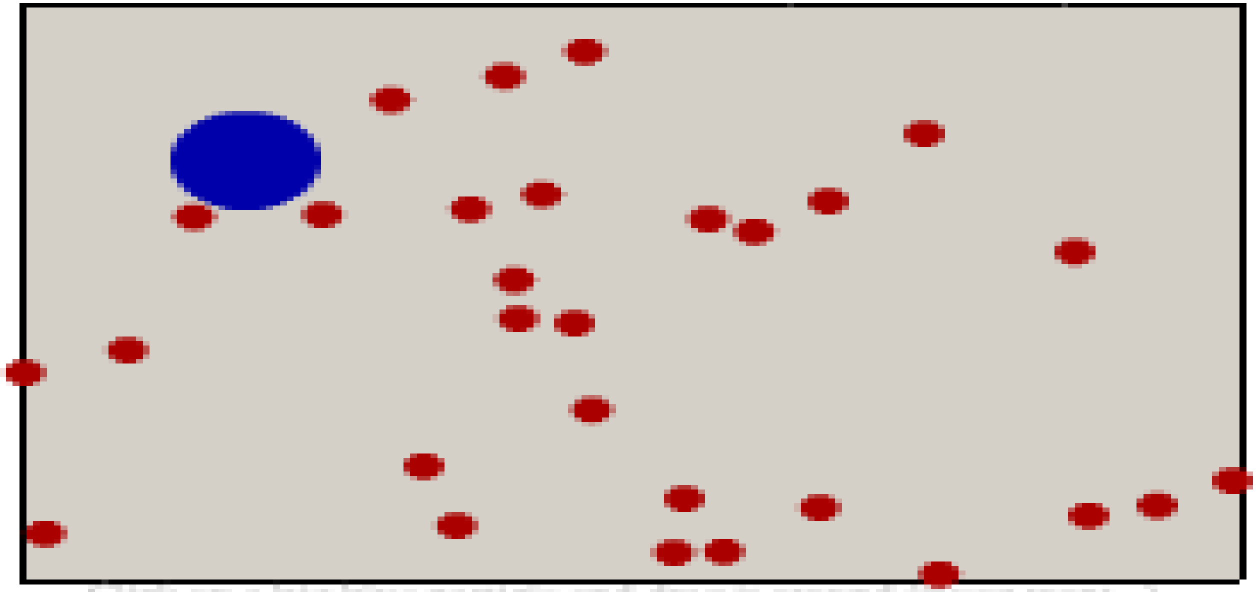
Properties of colloids

Brownian movement: Zig- zag movement of colloidal particles in a colloidal sol





Click on a big blue particle and drag it around (if you want...)

Coagulation

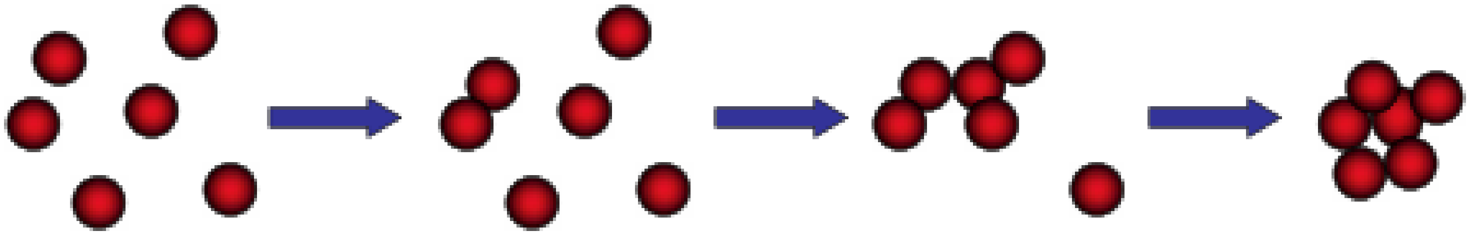
Coagulation is the process of formation of aggregates of colloidal particles, which stick together under the action of forces of molecular attraction, in the course of Brownian motion. Coagulation can be either rapid or slow. Rapid coagulation occurs when all the particles in Brownian motion stick together as they approach each other. In slow coagulation, only some particles stick together upon approach because the electric double layer partially remains on the surface of colloidal particles. The reversal of coagulation or flocculation is the dispersion of aggregates to form a colloidally stable suspension or emulsion is called deflocculation or peptization. The rate of aggregation is determined by the frequency of collisions and the probability of cohesion during collision. If the collisions are caused by Brownian motion, the process is called perikinetic aggregation, if by hydrodynamic motion (i.e. convection or sedimentation), the process is called orthokinetic aggregation.

stable $Fe(OH)_3$ sol

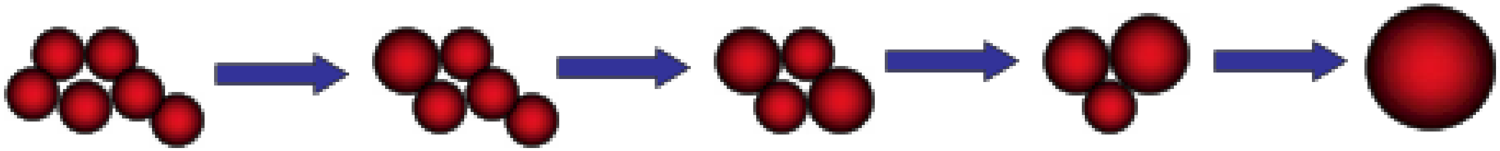
The sol undergoes coagulation upon the addition of $Al_2(SO_4)_3$ solution

Instability of liophobic colloids

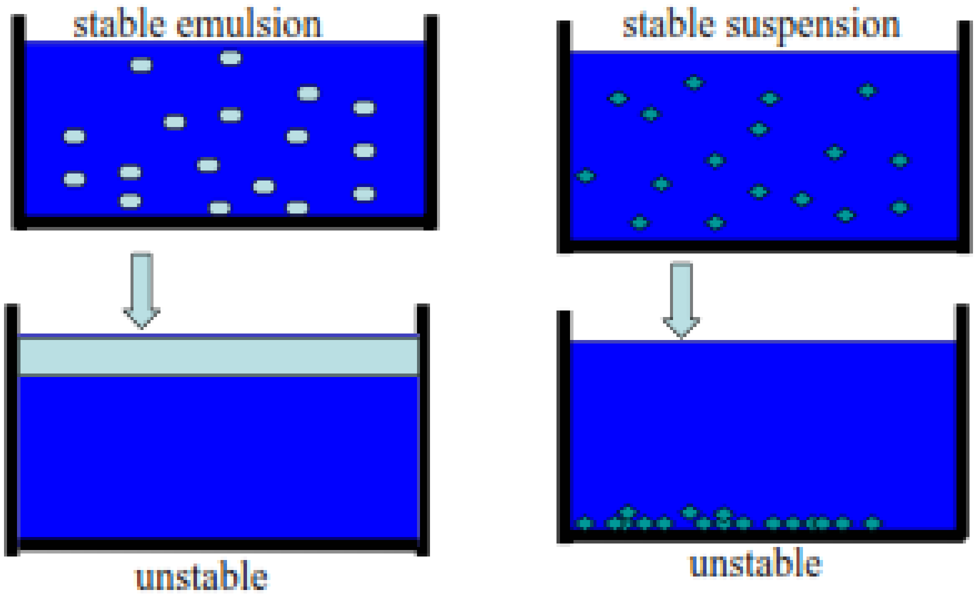
aggregation:



coalescence:



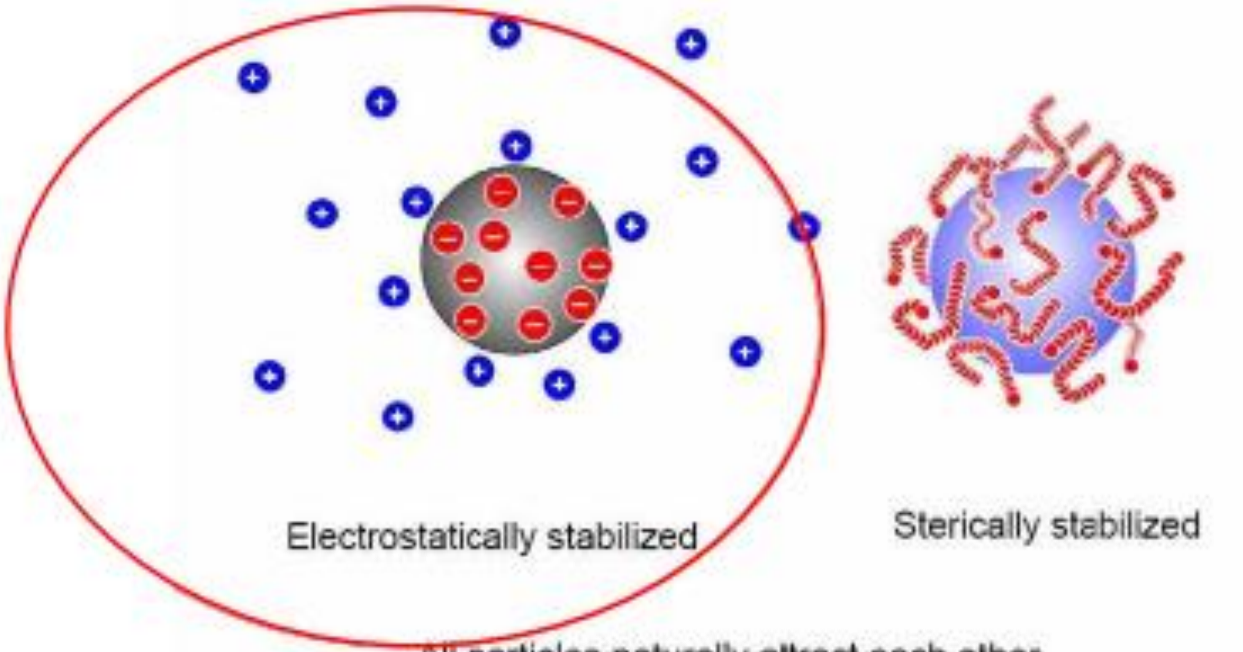
Colloid stability/flocculation/coagulation/ are controlled by the relative magnitudes of the van der Waals and the Coulombic forces



(coagulation; creaming and coalescence)

(coagulation / flocculation; sedimentation)

Colloid stability requires repulsive forces between colliding particles

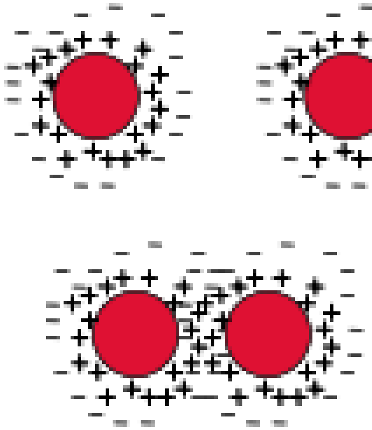


All particles naturally attract each other.

Electrical charges or attached polymer layers screen the attraction.

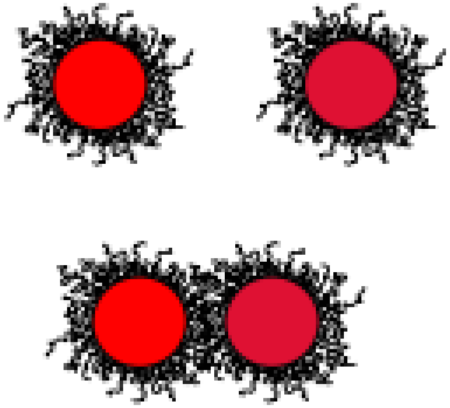
Main types of (de)stabilization of colloidal dispersions

electrostatic potential



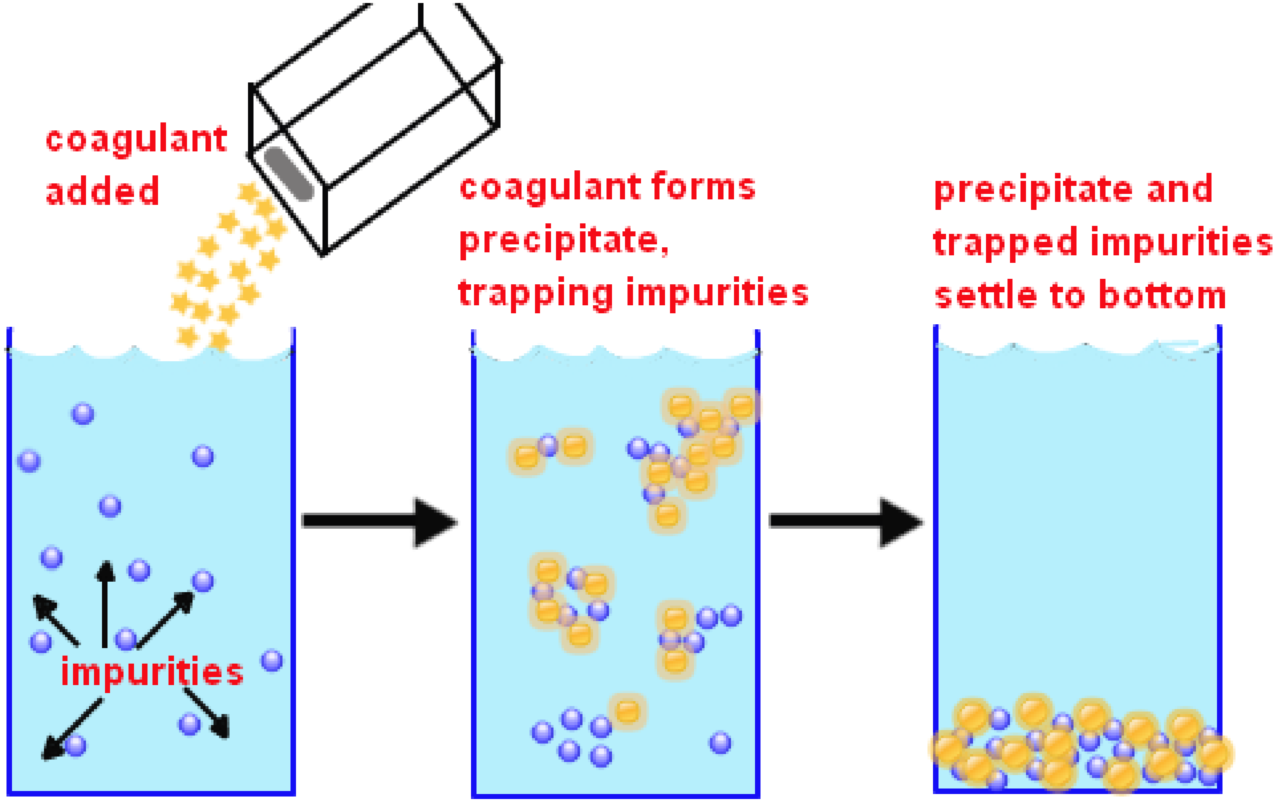
Coulombic repulsion →
→ electrostatic stabilization

steric potential

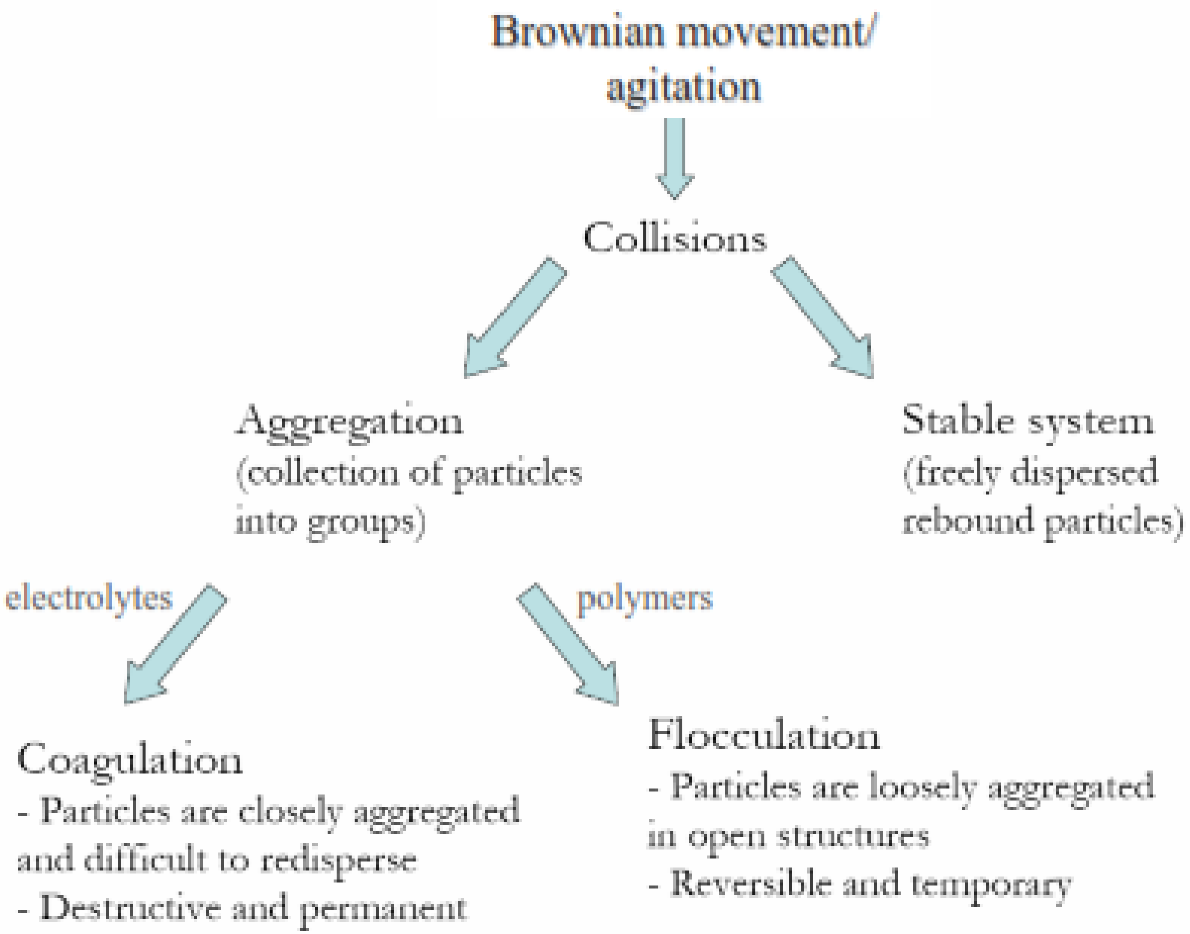


entropy hindrance →
→ steric stabilization

The coagulant chemical is added. It helps in neutralization of the particles in the water. So the particles come closer and make large clumps.



Physical stability of colloidal system



Brownian movement/
agitation

Collisions

Aggregation
(collection of particles
into groups)

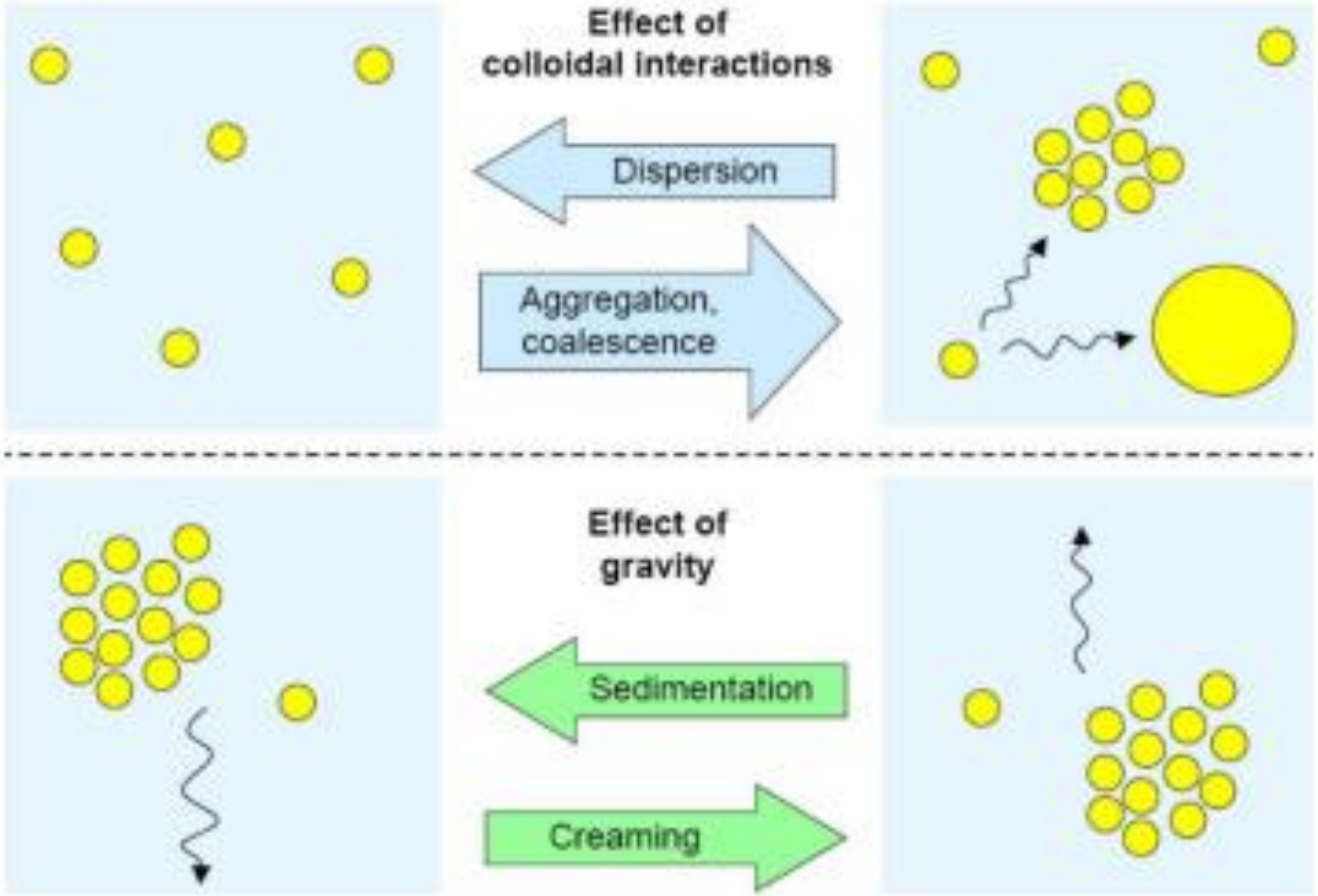
Stable system
(freely dispersed
rebound particles)

electrolytes

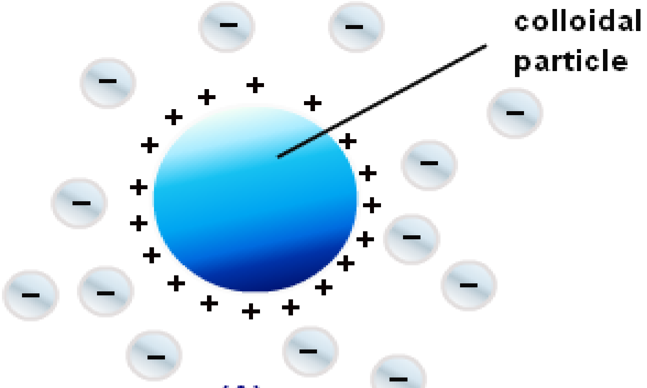
polymers

Coagulation
- Particles are closely aggregated and difficult to redisperse
- Destructive and permanent

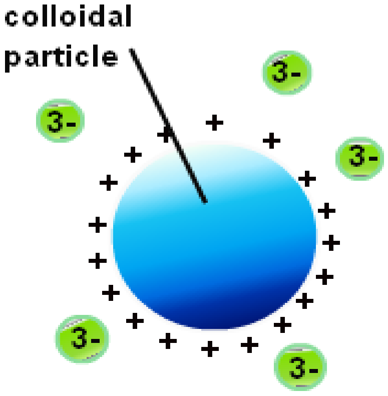
Flocculation
- Particles are loosely aggregated in open structures
- Reversible and temporary


Effect of colloidal interactions
Dispersion
Aggregation, coalescence
Effect of gravity
Sedimentation
Creaming

An iron (III) hydroxide sol can be made to aggregate by addition of an ionic solution. A positively charged particle of iron (III) hydroxide gathers a layer of anions around it. The thickness of this layer is determined by the charge on the anions. The greater the magnitude of the negative charge, the more compact the layer of charge. For e.g., phosphate ions gather more closely to the positively charged iron (III) particle than chloride ions.



(A)



(B)

Layers of ions surrounding a charged particle of iron (III) hydroxide.

- A: $Fe(OH)_3$ surrounded by Cl^- ions
- B: $Fe(OH)_3$ surrounded by PO_4^{3-} ions

If the ion layer is gathered close to the colloidal particles, the overall charge is effectively neutralized and two colloidal particles can approach close enough to aggregate and precipitate out.
The coagulation of colloids by an electrolyte takes place only when the electrolyte has a certain minimum concentration. The minimum concentration of electrolyte in milli moles that is added to one liter of the colloidal sol to bring about complete coagulation is called the critical coagulation concentration (CCC).

Properties of colloids

Hardy Schulze law : Coagulating power of an electrolyte increases rapidly with the increase in the valency of cation or anion.

For negatively charged sol, the coagulating power of electrolytes are

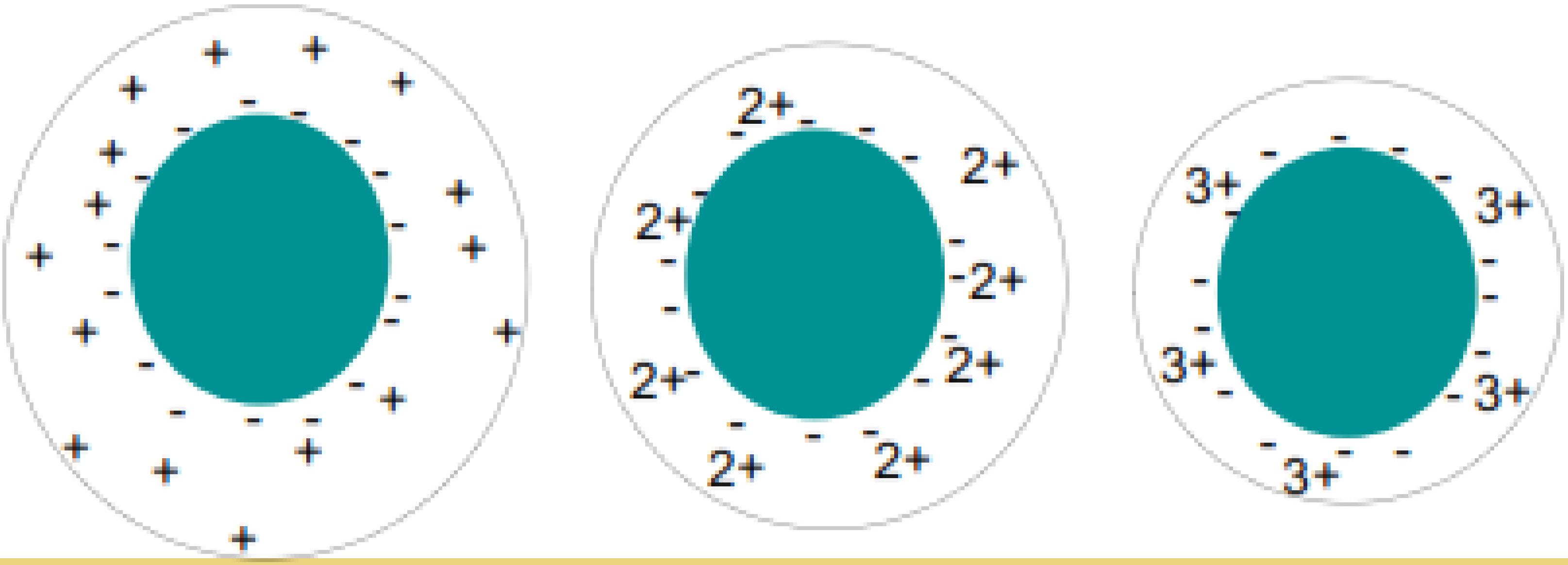
$AlCl_3 > BaCl_2 > NaCl$ or $Al^{3+} > Ba^{2+} > Na^+$

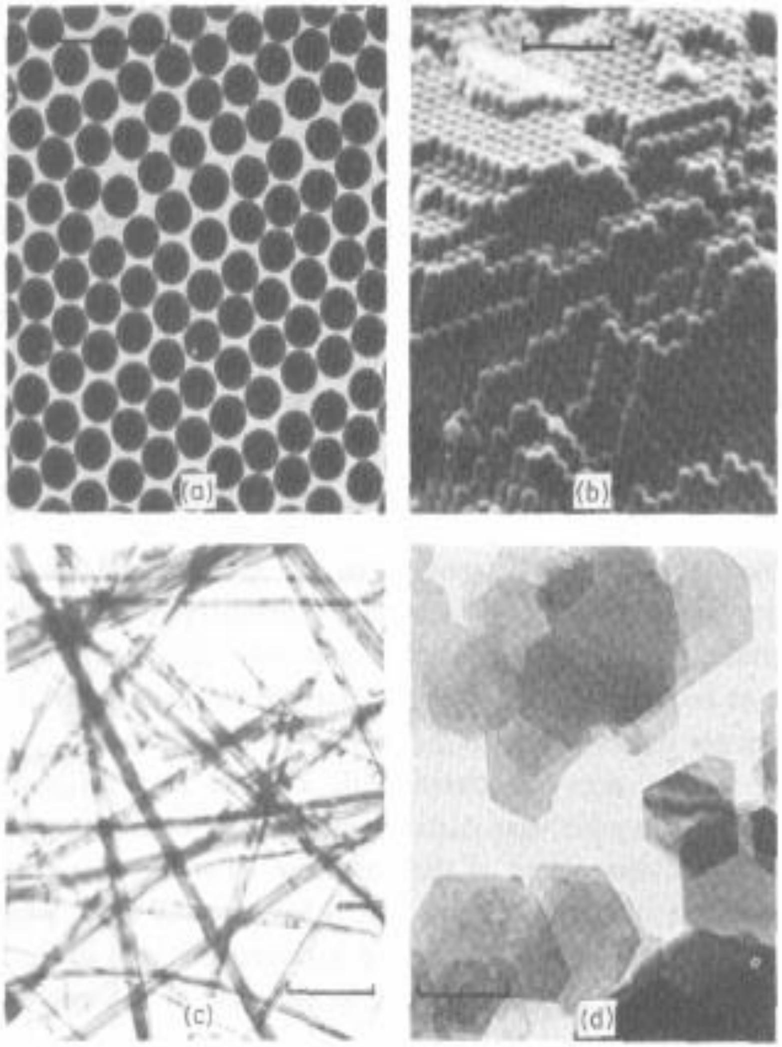
For positively charged, then the coagulating power of electrolytes follow the following order:

$PO_4^{3-} > SO_4^{2-} > Cl^-$

Hardy-Schulze Rule

- Flocculation is controlled by the valency of the counter-ion (added electrolyte with charge opposite that of the particle surface)
- Fewer 3+ ions than 2+ than 1+ ions are needed to cancel out colloid charge on negatively charged colloid → *more compact* counter-ion cloud (the critical coagulation concentration is lower for 3+ than 2+)





Colloid systems may have a large variety of shapes and structures:

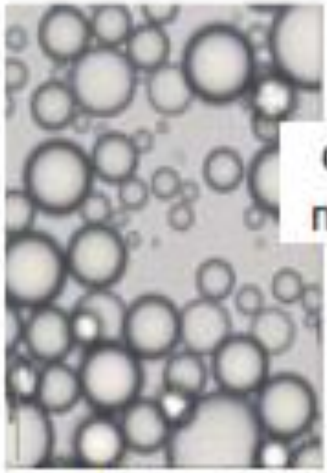
a) spherical particles of monodisperse polystyrene latex;

b) 3D colloidal crystal of monodisperse latex particles

c) asbestos fibres

d) thin plates of kaolinite

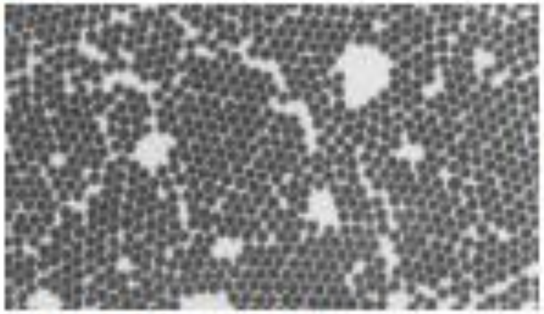
(colloidal) dispersions


opt micr

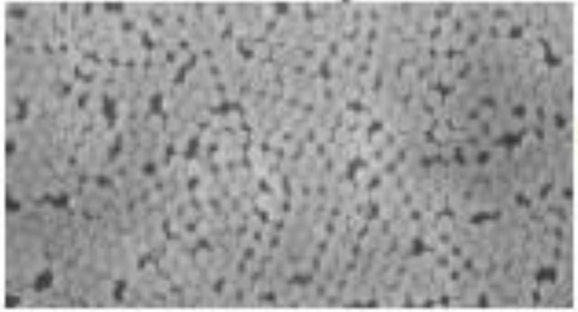
3.2 ± 41% μm O / W emulsion particles


cryo TEM

22 ± 20% nm O / W microemulsion particles

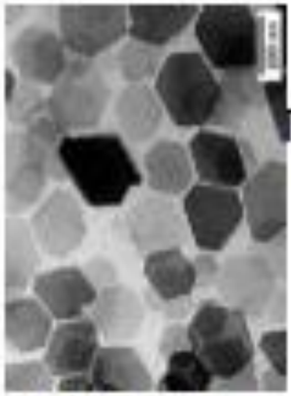

TEM

198 ± 17% nm SiO_2 particles

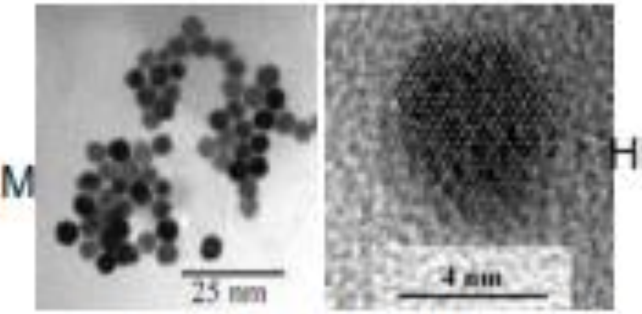

SEM


TEM

4 ± 31% nm Pd particles


TEM

224 ± 21% nm LDH particles



TEM

HRTEM

4 ± 25 % nm cubooctahedral Pd particles

Applications of colloidal solutions:

1- Therapy--- Colloidal system are used as therapeutic agents in different areas.

e.g- Silver colloid-germicidal
Copper colloid-anticancer
Mercury colloid-Antisyphilis

2- Stability---e.g. lyophobic colloids prevent flocculation in suspensions.

e.g- Colloidal dispersion of gelatin is used in coating over tablets and granules which upon drying leaves a uniform dry film over them and protect them from adverse conditions of the atmosphere.

Applications of colloidal solutions:

4- Absorption--- As colloidal dimensions are small enough, they have a huge surface area. Hence, the drug constituted colloidal form is released in large amount.

e.g- sulphur colloid gives a large quantity of sulphur and this often leads to sulphur toxicity.

5-Targeted Drug Delivery--- Liposomes are of colloidal dimensions and are preferentially taken up by the liver and spleen.

Applications of colloidal solutions:

6- Photography:

A colloidal solution of silver bromide in gelatine is applied on glass plates or celluloid films to form sensitive plates in photography.

7- Clotting of blood:

- Blood is a colloidal system and is negatively charged.
- On applying a solution of $FeCl_3$ bleeding stops and blood **clotting occurs as Fe^{+3} ions neutralize** the ion charges on the colloidal particles.

Chapter 2

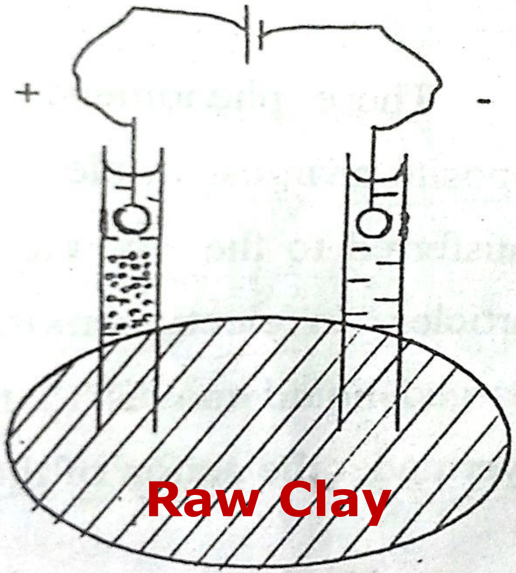
Electrical properties of colloidal systems

- Electrokinetic phenomena.
- Structure of the Electric Double Layer (EDL).
- Factors affecting the Electrokinetic potential.

The fact that the particles of colloidal dispersed phases carry an electric charge dated back to 1808 by F. Reuss in Moscow university.

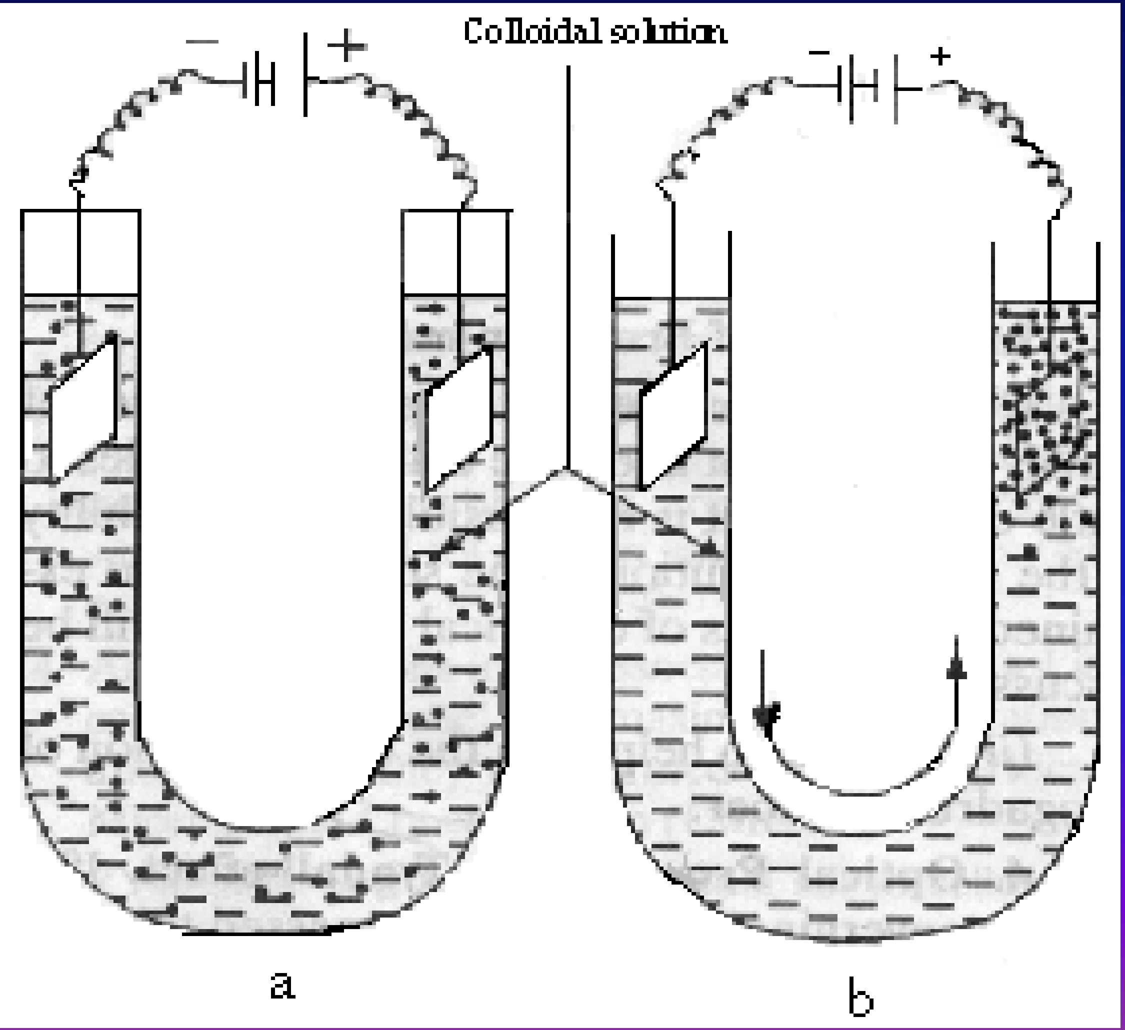
He applied electric potential gradient to electrodes immersed in glass tubes filled with water and stuck into a piece of raw clay. The liquid in the tube with +ve electrode turned cloudy while the –ve side was clear. This indicates that the clay particles transferred to the + ve electrode under the action of the applied electric filed.

- It was discovered later that the particles move at constant rate which depends on the the potential gradient and the dielectric constant of the dispersion medium.



The movement of colloidal particles under the influence of an electric field is called

electrophoresis or **cataphoresis**.



a) Before electrophoresis

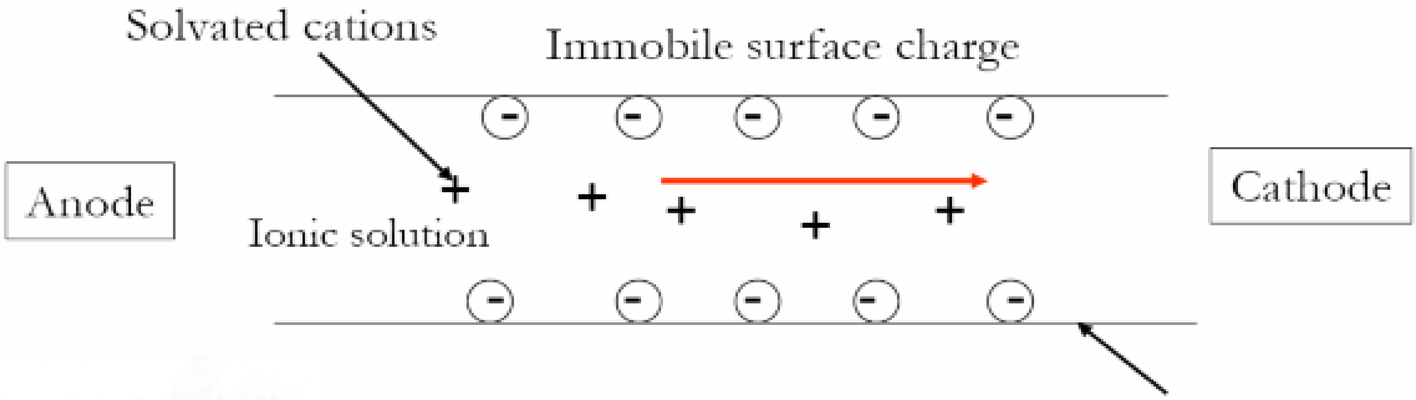
(b) After electrophoresis

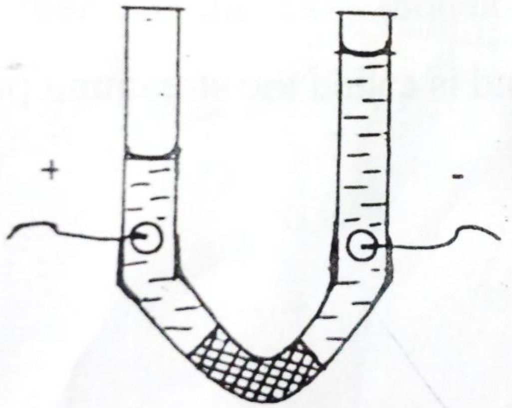
Electro-osmosis (electroendosmosis)

- It is the opposite in principal to that of electrophoresis.
- When electrodes are placed across a clay (or fine quartz sand) mass in a U tube forming porous diaphragm and a direct current is applied, water in the clay or sand pore space is transported to the cathodically –ve charged electrode by electro-osmosis.
- Electro-osmotic occurs at constant rate which is directly proportional to the potential gradient (or current density) and dielectric constant and inversely proportional to the viscosity of the medium. The amount of passing liquid is independent on the cross section area of the diaphragm.

Electroosmosis

The movement of a liquid relative to an immobile charged surface of a capillary tube under the influence of an electric field





These phenomena show that the liquid and solid phases carry <u>opposite charges.</u>

Sedimentation Potential (*Dorn Effect, 1878*)

- **It is the potential induced by the fall of a charged particle under an external force field.**

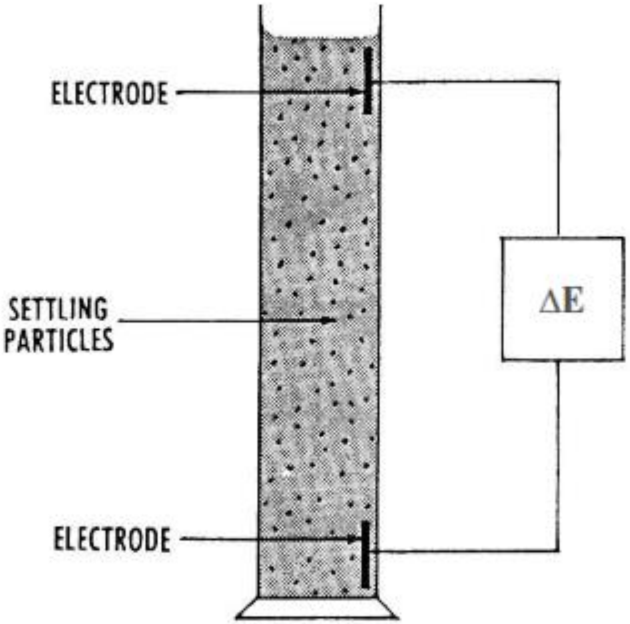
- **It is analogous to electrophoresis in the sense that a local electric field (electromotive forces) is induced as a result of its motion.**

- **if a colloidal suspension has a gradient of concentration (such as is produced in sedimentation or centrifugation), then an electric field is generated by the charge imbalance appearing at the top and bottom of the sample column.**

Sedimentation Potential

Sedimentation potential ("Dorn-effect)

creation of an electric field when a charged particle moves relative to stationary fluid



ΔE = sedimentation potential

Streaming Potential

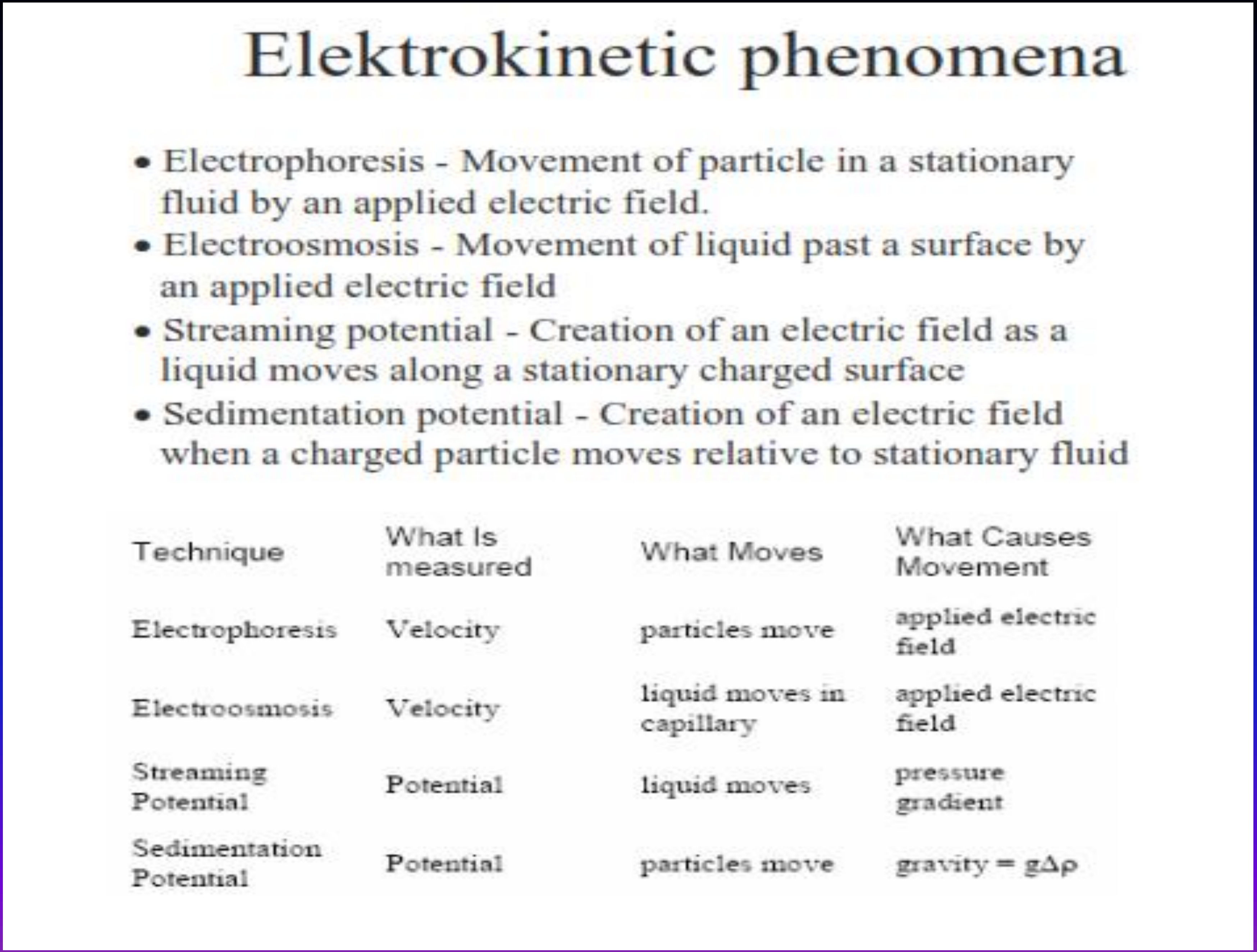
Quincke (1859) discovered other phenomenon when a liquid is pressed through a porous partition which has electrodes in both sides.

Differs from electro-osmosis in that the potential is created by forcing a liquid to flow through a bed or plug of particles.

These four phenomena are connected to the presence of an interface and hence they are very important in highly dispersed colloidal systems having a large specific surface area.

Electrokinetic phenomena

- **Electrophoresis** – a suspended, charged particle moves as a result of an applied electrical field
- **Sedimentation potential** – an electrical potential created by the movement of charged particles through a liquid by gravity
- **Electrosmosis** – a liquid flows along a charged surface when an electric field is applied parallel to the surface
- **Streaming potential** – an electric potential created when a liquid is forced to move along a charged surface



Elektrokinetic phenomena

- Electrophoresis - Movement of particle in a stationary fluid by an applied electric field.
- Electroosmosis - Movement of liquid past a surface by an applied electric field
- Streaming potential - Creation of an electric field as a liquid moves along a stationary charged surface
- Sedimentation potential - Creation of an electric field when a charged particle moves relative to stationary fluid

Technique	What Is measured	What Moves	What Causes Movement
Electrophoresis	Velocity	particles move	applied electric field
Electroosmosis	Velocity	liquid moves in capillary	applied electric field
Streaming Potential	Potential	liquid moves	pressure gradient
Sedimentation Potential	Potential	particles move	gravity = $g\Delta\rho$

Origin of Surface Charges

How these charges originate at the interface??

- Most particles in an aqueous colloidal dispersion carry an electric charge.
- There are many origins of this surface charge depending upon the nature of the particle and it's surrounding medium
- Consider the more important mechanisms

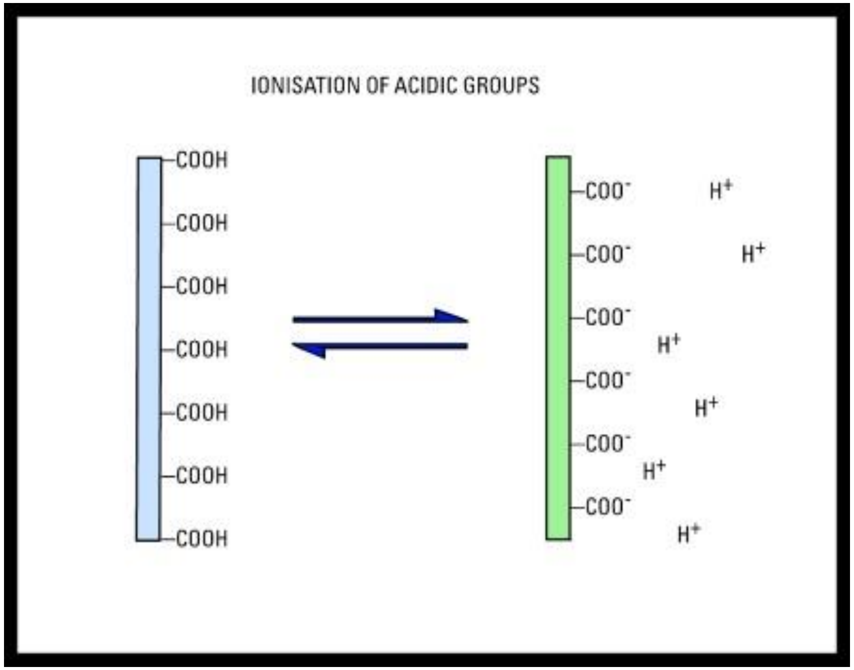
➢ Ionization of surface groups

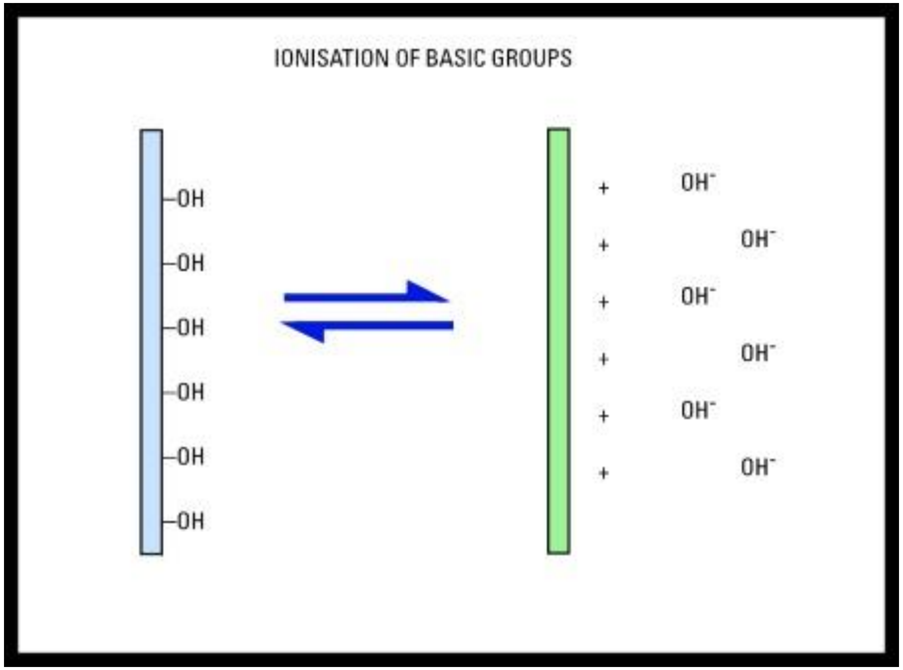
➢ Differential loss of ions

➢ Adsorption of charged species

Ionization of Surface Groups

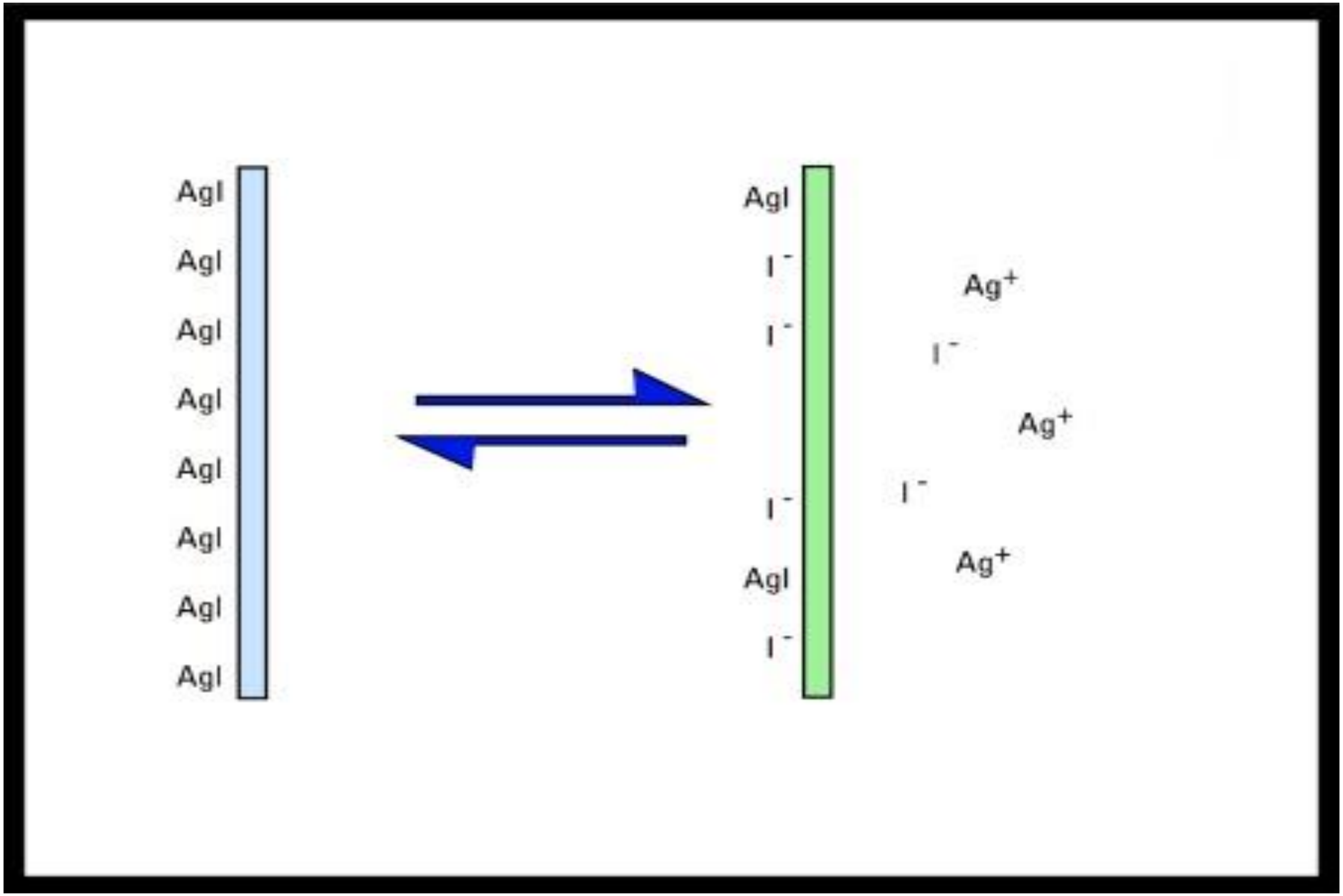
- Dissociation of any acidic groups on a particle surface will give a **negatively** charged surface
- Dissociation of any basic groups on a particle surface will give a positively charged surface
- The magnitude of the surface charge depends on the acidic or basic strengths of the surface groups and on the pH of the solution


IONISATION OF ACIDIC GROUPS
COOH
COOH
COOH
COOH
COOH
COOH
COOH
COO⁻
COO⁻
COO⁻
COO⁻
COO⁻
COO⁻
H⁺
H⁺
H⁺
H⁺
H⁺
H⁺


IONISATION OF BASIC GROUPS
OH
OH
OH
OH
OH
OH
+
+
+
+
+
+
OH⁻
OH⁻
OH⁻
OH⁻
OH⁻
OH⁻

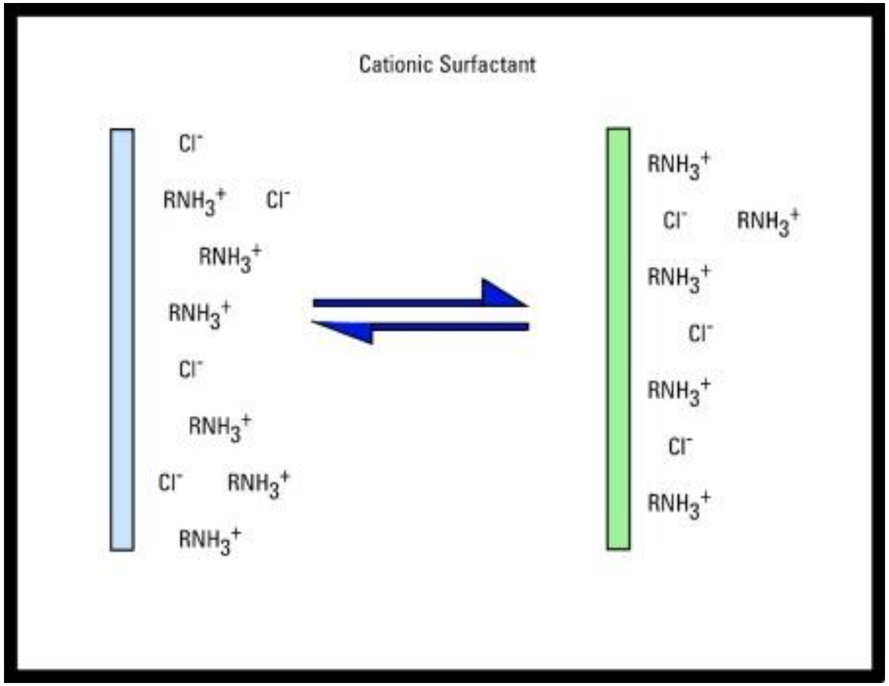
Differential loss of ions

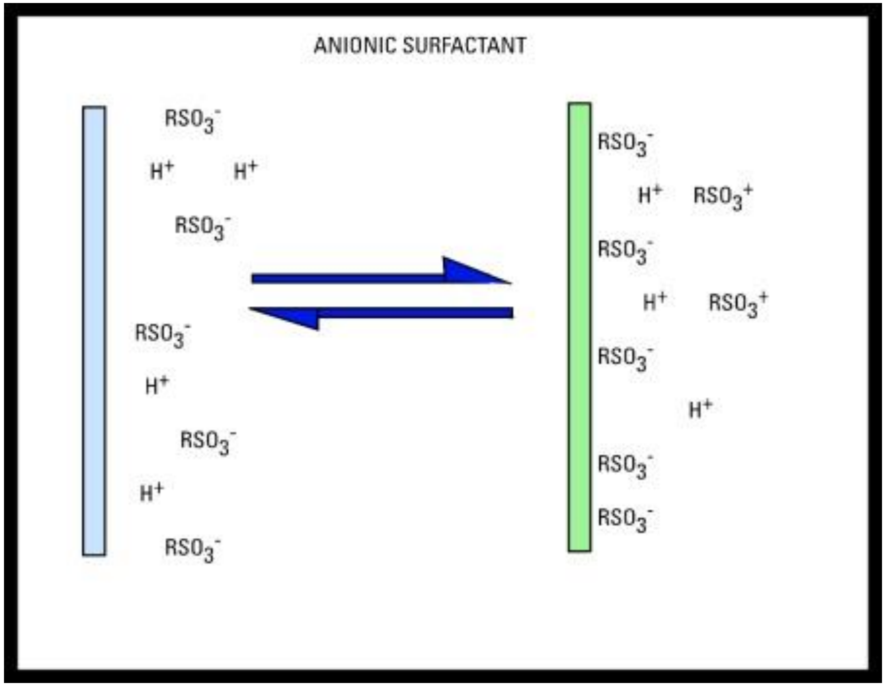
- If a crystal of AgI is placed in water, it starts to dissolve
- If equal amounts of Ag^+ and I^- ions were to dissolve, the surface would be uncharged
- In fact Ag^+ ions dissolve preferentially leaving a negatively charged surface


AgI
AgI
AgI
AgI
AgI
AgI
AgI
AgI
AgI
I⁻
I⁻
I⁻
AgI
I⁻
Ag⁺
I⁻
Ag⁺
I⁻
Ag⁺

Adsorption of charged species (ions or ionic surfactants)

- **Surfactant ions may be specifically adsorbed onto the surface of a particle.**
- **Cationic surfactants would lead to a positively charged surface.**
- **Anionic surfactants would lead to a negatively charged surface.**


Cationic Surfactant
Cl^-
RNH_3^+ Cl^-
RNH_3^+
RNH_3^+
Cl^-
RNH_3^+
Cl^- RNH_3^+
RNH_3^+
RNH_3^+
Cl^- RNH_3^+
RNH_3^+
Cl^-
RNH_3^+
Cl^-
RNH_3^+


ANIONIC SURFACTANT
RSO_3^-
H^+ H^+
RSO_3^-
RSO_3^-
H^+
RSO_3^-
H^+
RSO_3^-
RSO_3^-
H^+ RSO_3^+
RSO_3^-
H^+ RSO_3^+
RSO_3^-
H^+
RSO_3^-
RSO_3^-

- Surface charge of colloidal particle **is controlled by** the charge of ion present in excess in the medium.
- **Examples; 1)** $AgNo_3 + NaI \rightarrow AgI + NaNo_3$

a) silver iodide in a solution with excess iodide → Particles acquire - ve charge & vice versa. if excess Ag the charge will be +ve since the conc. Of Ag and I determine the electric potential

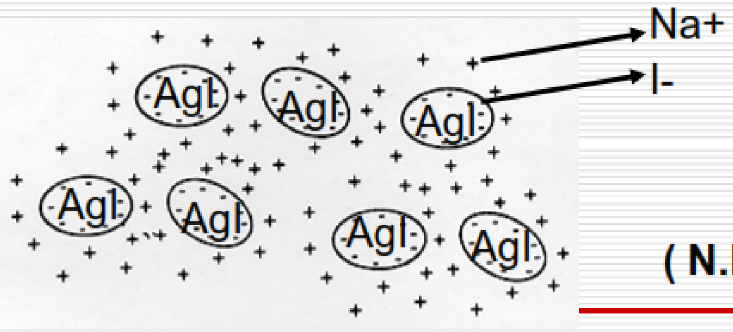
b) Aluminum hydroxide in a solution with excess hydroxide → particles acquire – ve charge & vice versa.

Potential determining ions: ions whose conc. determine the electric potential at the particle surface (e.g. Ag^+ , I^-, H^+, OH^-)

- **Example;**

$AgNO_3 + NaI \rightarrow AgI + NaNO_3$

•At xs NaI :



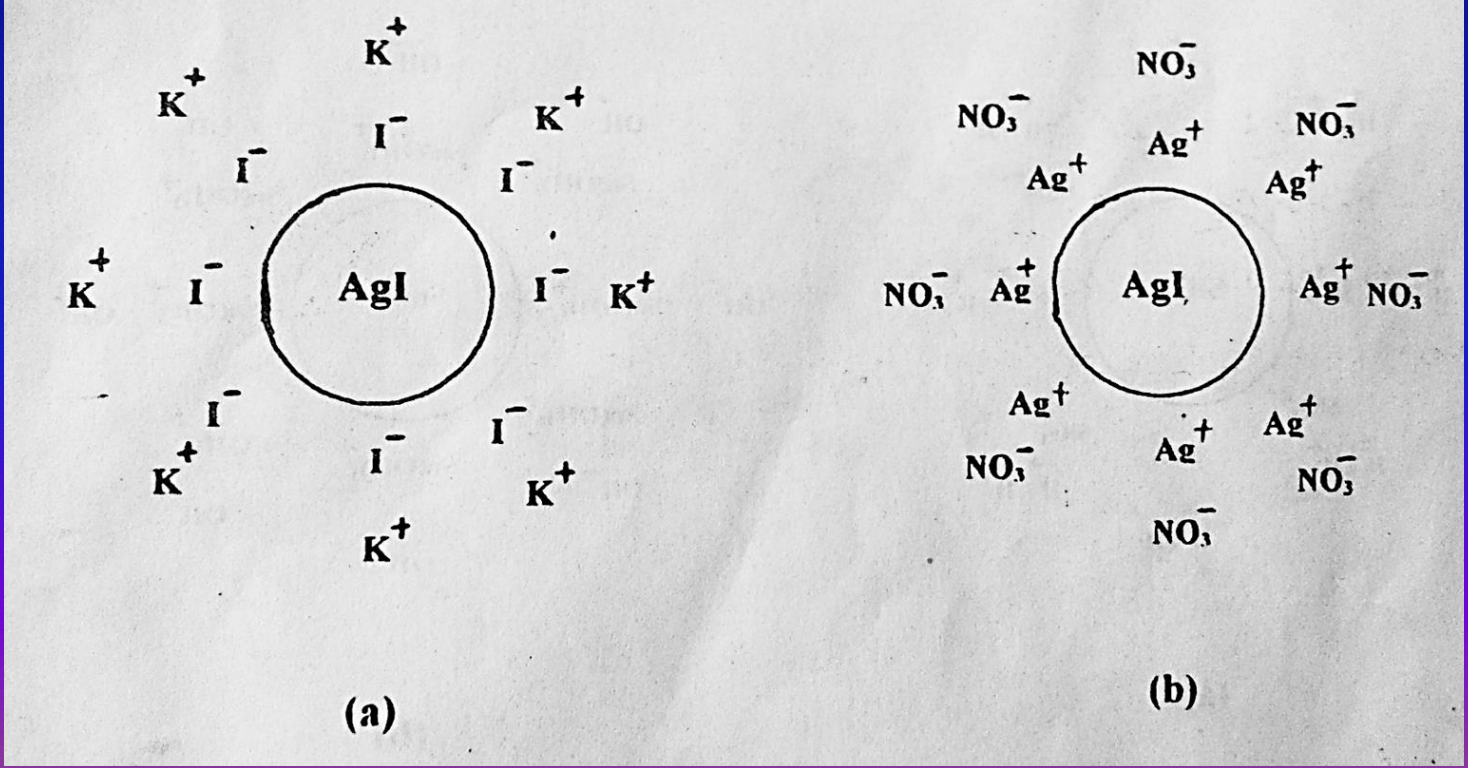
(N.B. Vice versa if xs AgNO3)

- Silver iodide sols can be prepared by the reaction,
  - AgNo3 + Nal---- Agl + NaNo3
- In the bulk of AgI particles ⇨ 1 : 1 ratio of Ag+ and I-

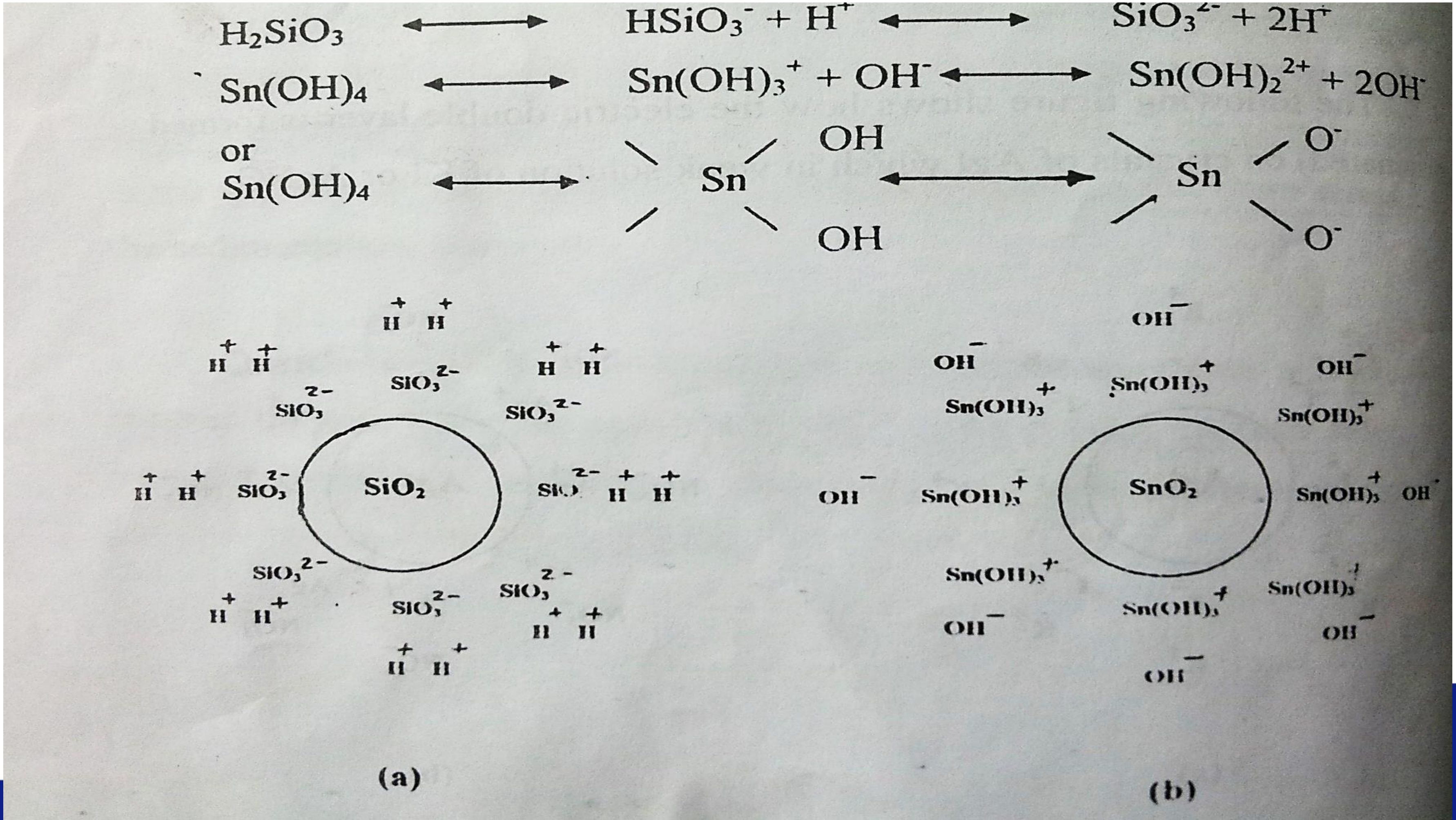
- If the reaction is carried out with an excess silver nitrate, there will be more Ag+ than l- ions in the surface of the particles ⇨ The particles will thus be positively charged and the counterions surrounding them will be No3-.
- The combination of the positively charged surface and the atmosphere of counter ions surrounding it is called the electric double layer.
- If the reaction is carried out with an excess NaI, there will be more l- than Ag+ ions in the surface of the particles ⇨ The particles will thus be negatively charged and the counter ions surrounding them will be Na+.

The electric double layer originated on AgI crystals in weak solution of KI and $AgNO_3$

In a) Iodide ions (potential-determining ions) complete the construction of the crystal lattice of AgI and thus charge it with –ve where K+ is (counterions) are in the solution near the interface. The total complex is electroneutral. (in b,??)



The origin of an electrical charge owing to the ionization (dissociation) of the surface groups can be explained in SiO_2 or SnO_2 particles in water. (the entire complex is neutral).



$$H_2SiO_3 \longleftrightarrow HSiO_3^- + H^+ \longleftrightarrow SiO_3^{2-} + 2H^+$$

$$Sn(OH)_4 \longleftrightarrow Sn(OH)_3^+ + OH^- \longleftrightarrow Sn(OH)_2^{2+} + 2OH^-$$

or

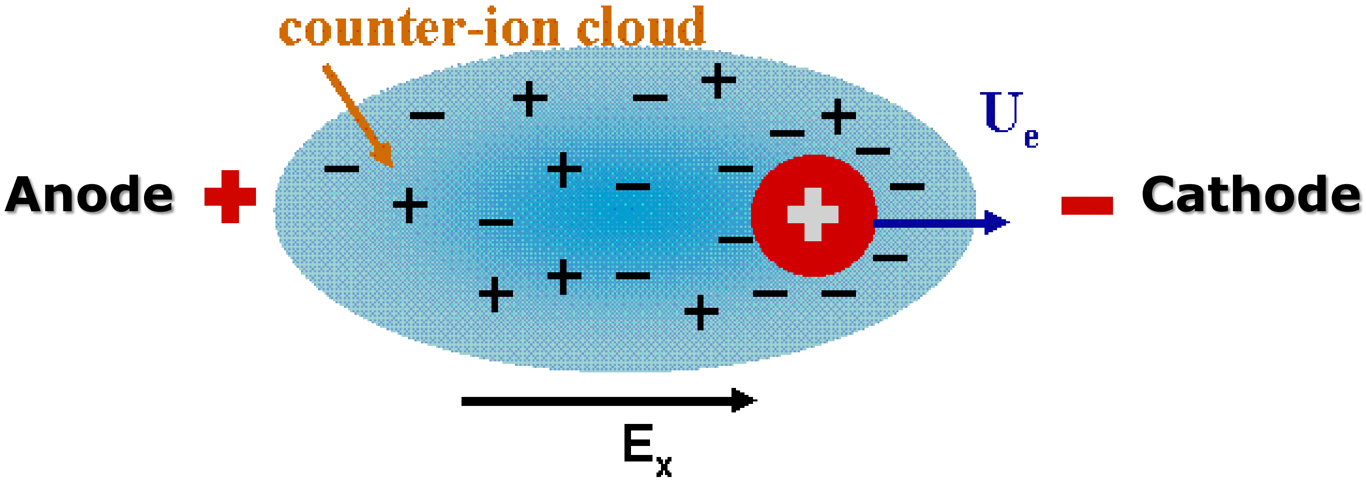
$Sn(OH)_4 \longleftrightarrow$

(a)

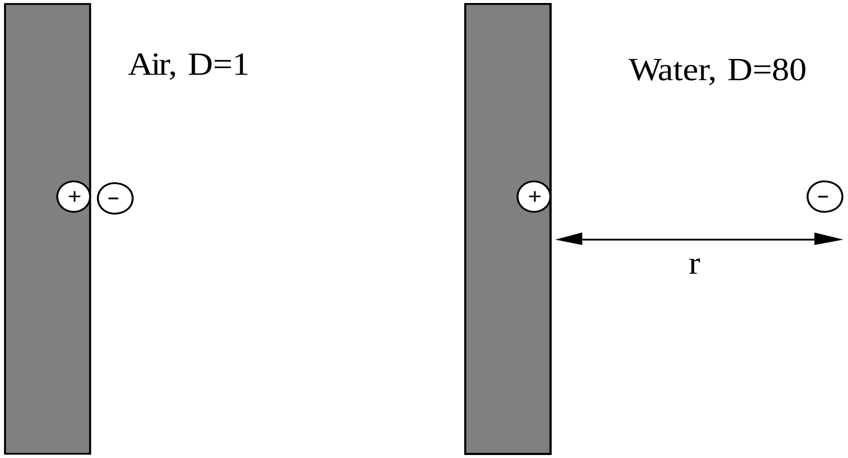
(b)

- Electrophoresis is the most known Electrokinetic phenomena. If an electric potential is applied to a colloid carrying an EDL, a phenomenon similar to electrolysis occurs. If the dispersed phase is + ve charged the particles move along with their potential determining ions towards the cathode (–ve), while the negatively charged counterions move to the anode (+ ve).

- Only part of counterions moves to electrode having the same sign. The other part is bound strongly to the solid particles via strong electric and adsorption forces and is forced to move together with the particles.

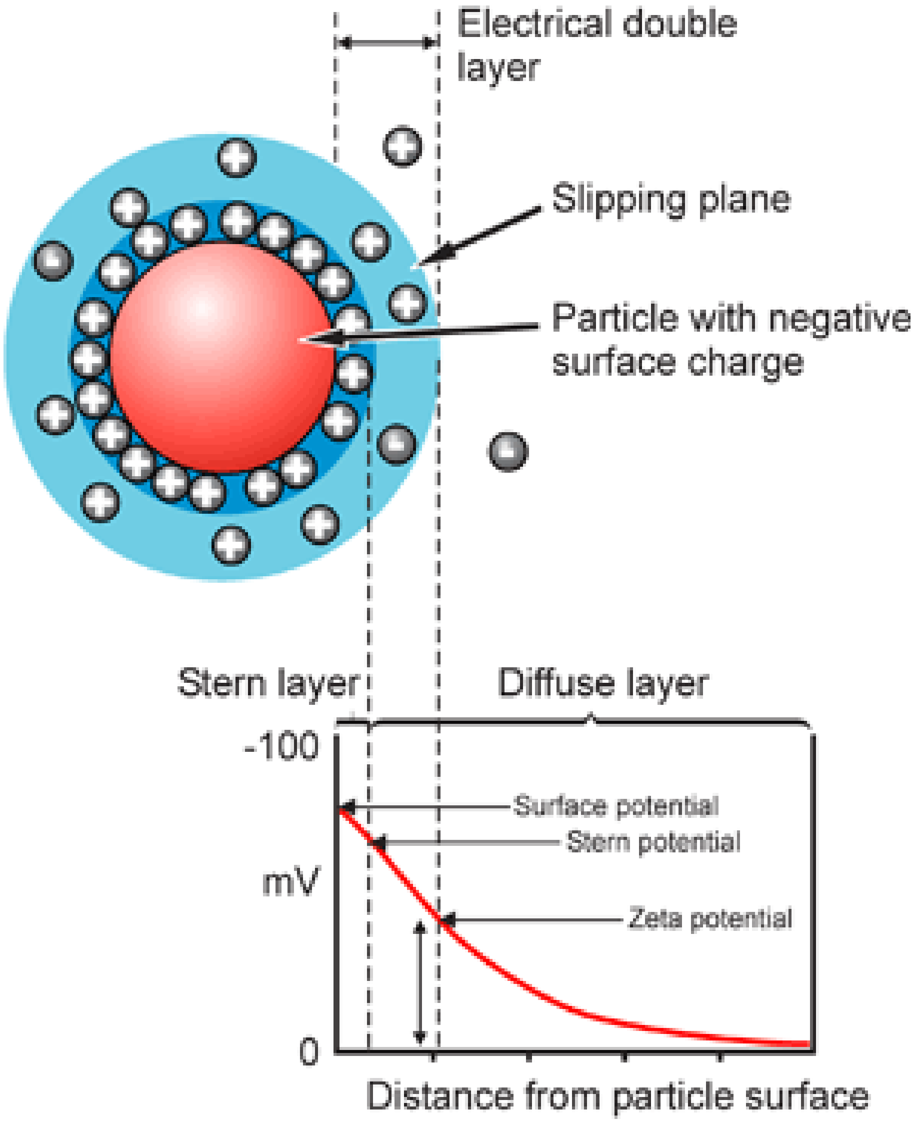


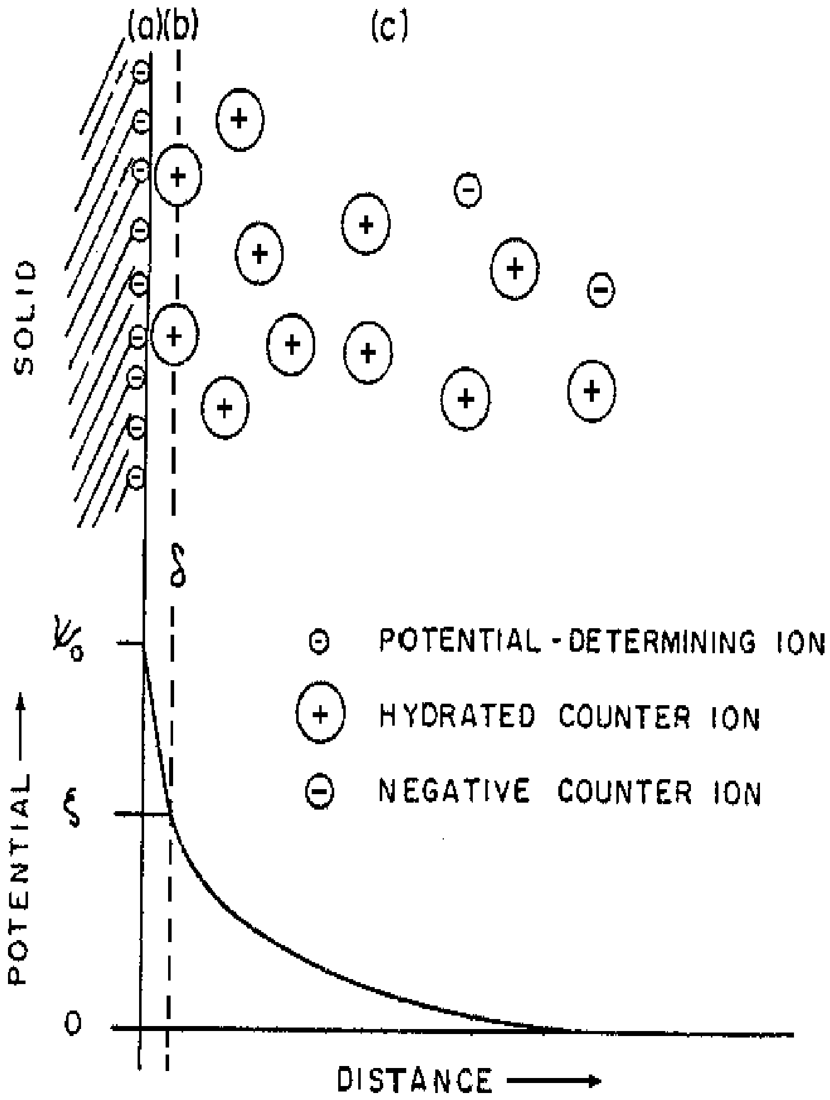
Structure of The electrical double layer (EDL)



D or (ε) is the static dielectric constant: dielectric constant, it is property of an electrical insulating material (a dielectric) equal to the ratio of the capacitance of a capacitor filled with the given material to the capacitance of an identical capacitor in a vacuum without the dielectric material.

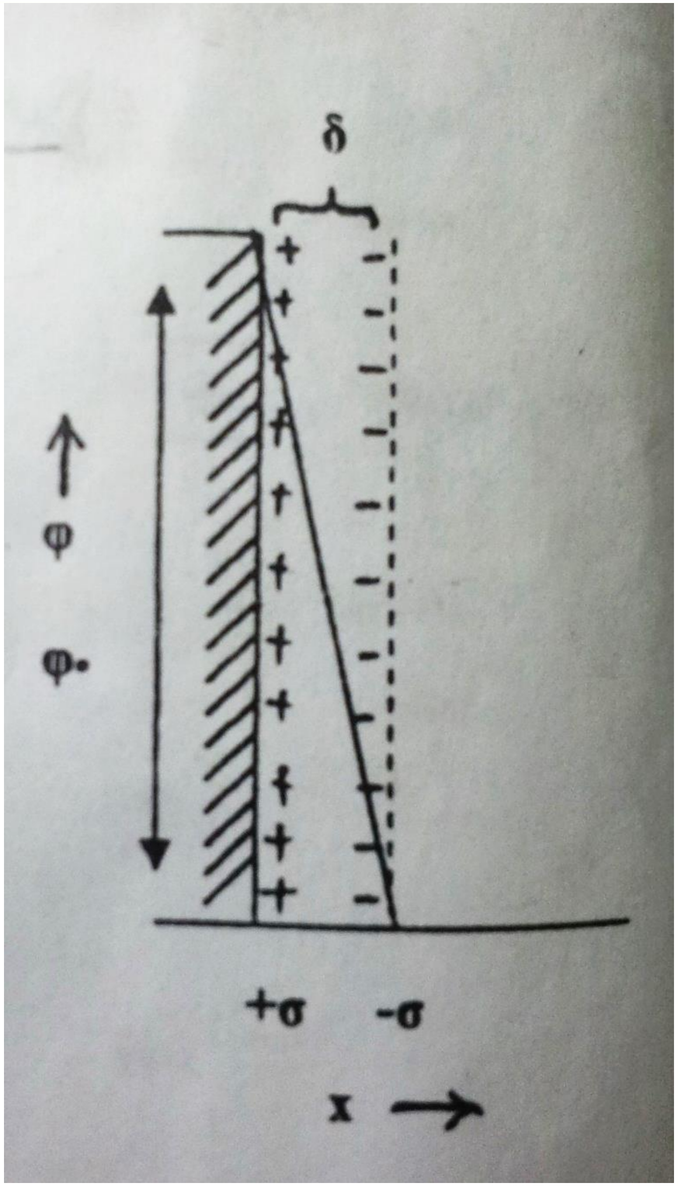
- **Development of a net charge at the particle surface affects the distribution of ions in the surrounding interfacial region, resulting in an increased concentration of counter ions (ions of opposite charge to that of the particle) close to the surface.**
- **An electrical double layer exists around each particle.**
- **The liquid layer surrounding the particle exists as two parts; an inner region (Stern layer) where the ions are strongly bound and an outer (diffuse) region where they are less firmly associated**
- **Within this diffuse layer is a imaginary boundary known as the slipping plane, within which the particle acts as a single entity**
- **The potential at this boundary is known as the Zeta Potential**


Electrical double layer
Slipping plane
Particle with negative surface charge
Stern layer
Diffuse layer
-100
mV
0
Surface potential
Stern potential
Zeta potential
Distance from particle surface


(a)(b)
(c)
SOLID
δ
ψ_0
ξ
POTENTIAL
0
DISTANCE
⊖ POTENTIAL - DETERMINING ION
⊕ HYDRATED COUNTER ION
⊖ NEGATIVE COUNTER ION

Helmholtz-Perrin theory

- The EDL is flat condenser
- Two plates with opposite charges with very close distance from the solid wall.
- The potential falls very sharply along the straight line.
- The surface charge density **$(\sigma) = (\varepsilon/4\pi\delta)\ \phi^0$**
- ε is dielectric constant of the medium between the plates, ϕ^0 is potential difference between the phases, δ is distance between plates.



Helmholtz-Perrin theory

- The potentials falls with distance (x) from the surface and the total potential jump of EDL = the jump in potential between the solid phase and the solution.
- **The shortcomings of this theory is:**
- 1- the thickness of EDL is very small.
- 2- slipping plane is not defined. (it should be in the liquid phase away from the interface).
- 3- the Electrokinetic potential = the total potential jump (but as a rule **Electrokinetic potential is < total potential jump** (dose not depend on indifferent electrolytes which do not contain ions that can complete the construction of the crystal lattice of the sol, but can greatly affect the zeta-potential..
- 4- Therefore, this theory of the flat EDL **is not enough** for explaining the Electrokinetic phenomena.

Gouy-Chapman theory

- Counterions cannot concentrate only at interface as a monoionic layer but are scattered in the liquid phase at a certain distance.
- Electric filed of the solid phase attracts an equivalent amount of oppositely charges ions as close as possible to the wall and by the thermal motion of the ions where counterions scatter in the liquid.
- As distance from the interface increases, the potential decreases and the counterions scatter more and more and their concentration = that in the bulk liquid.
- This is called **diffused counterions** layer and a **dynamic equilibrium** exists between ions in the **EDL** and the **bulk**.

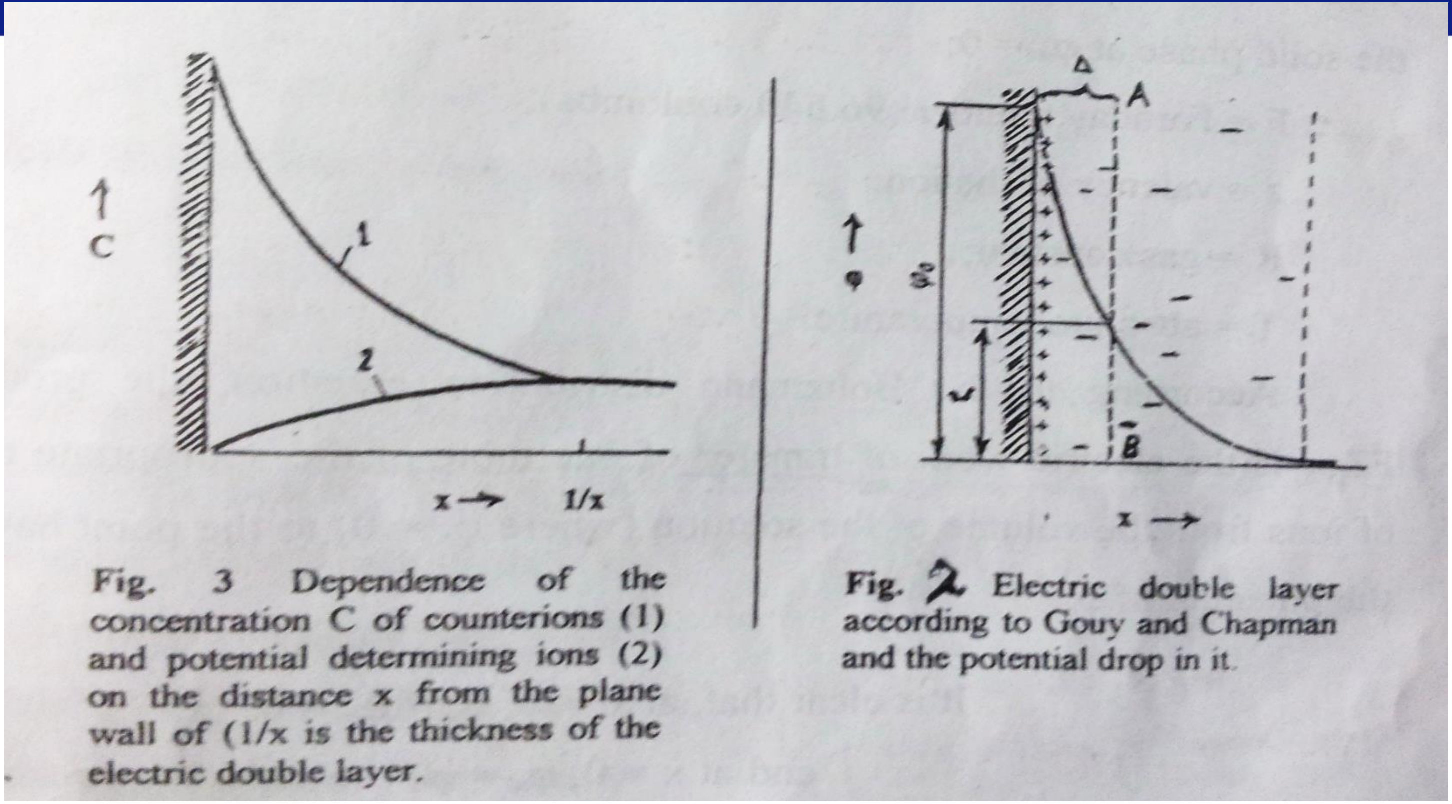


Fig. 3 Dependence of the concentration C of counterions (1) and potential determining ions (2) on the distance x from the plane wall of (1/x is the thickness of the electric double layer.

Fig. 2 Electric double layer according to Gouy and Chapman and the potential drop in it.

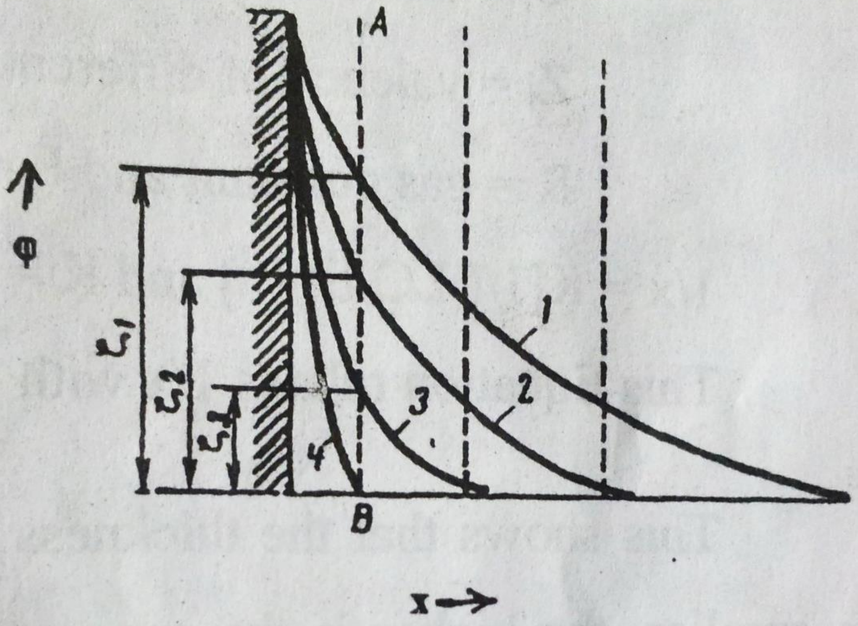
- Distribution of potential-determining ions (2) and counterions (1) is shown in Figure 3. Figure 2 shows that the potential drop as a curve because the counterions distributed not uniformly which compensate the wall charges.
- Slipping plane AB lies in the liquid at a small distance Δ away from the interface where the potential does not drop to that of liquid, the different between it and that in the liquid = charge of this part of the diffused layer.
- We call this Electrokinetic potential (ζ-potential)

- **Zeta potential is an abbreviation for electrokinetic potential in colloidal systems. In the colloidal chemistry literature, it is usually denoted using the Greek letter zeta, hence *ζ-potential*. From a theoretical viewpoint, zeta potential is electric potential in the interfacial double layer (EDL) at the location of the slipping plane versus a point in the bulk fluid away from the interface.**
- **In other words,** ζ-potential is part of the total potential jump ϕ^0 and is differ from zero but not equal to the total potential jump.

- Gouy-Chapman theory explain the effect of different factors on both the total potential jump and ζ-potential:

Indifferent electrolytes do not contain ions which are able to complete the construction of the crystal lattice of the colloidal particles

- **Example: Effect of Addition of indifferent electrolyte to the system on both potentials:**
- **As seen in the Fig. on the right, total potential jump do not change.**
- ζ-potential is greatly affected: ??? By increasing the conc. of added electrolyte, the thickness of the **diffused layer** decreases and it said to be contracted. At higher conc. (C4), the diffused layer shrinks to **monoionic** layer then the EDL becomes the **Helmholtz-Perrin** layer and **ζ-potential = zero** since the layer will be closer to the wall than the slipping plane (AB).



Effect of indifferent electrolyte on both the thickness of the electric double layer and the electrokinitic potential
$C_4 > C_3 > C_2 > C_1$
C = concentration of the electrolyte.

- The thickness of the EDL given by Gouy-Chapman is:

$$1/X = K\,[1/(C_iZ_i^2)^{1/2}]$$

C_i = bulk conc. of ions, Z_i = ion valency, K = constant

- This shows that 1/x or ζ-potential decreases by increasing both the Ci and Zi of the ions.
- It was found that size and polarizability of ions can also affect the compression of the EDL.

Shortcoming of the theory:

1- The measured capacity of the EDL is 10 times higher than the calculated one because the theory does not take the dimension of the ions into account and regard them as just point charges.

2- It does not explain the reversal of the sign of the ζ-potential when polyvalent ions of opposite sign are added to the sol??.

3- Does no explain effect of counterions of same valency on the EDL. The effect of ions of the same valency on the EDL grows with the ionic radius.

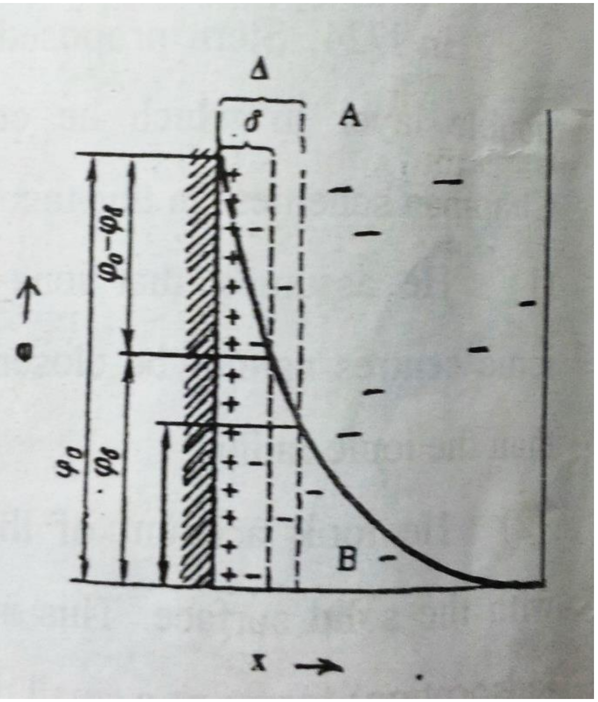
Stern Theory

- He combined both theories and proposed:

1- ions have finite dimensions (no distance smaller than ionic radius to the solid surface.

2- takes into account the specific non-electric interaction of ions with the wall surface, i.e. adsorption forces.

- The first layer of counterions is attracted to the wall by both electrostatic and adsorption forces at a very close distance with one-two molecules thickness (δ) is called Stern Layer. The remaining ions form the diffused part of the EDL as proposed by Gouy-chapman.
- The slipping plane (AB) is considered to be in the diffused layer (Gouy layer).
- When electrolyte is added the diffused layer will contract and the EDL become closer to the Helmholtz-Perrin layer. If the system is diluted the diffused layer expands and z-potential grows



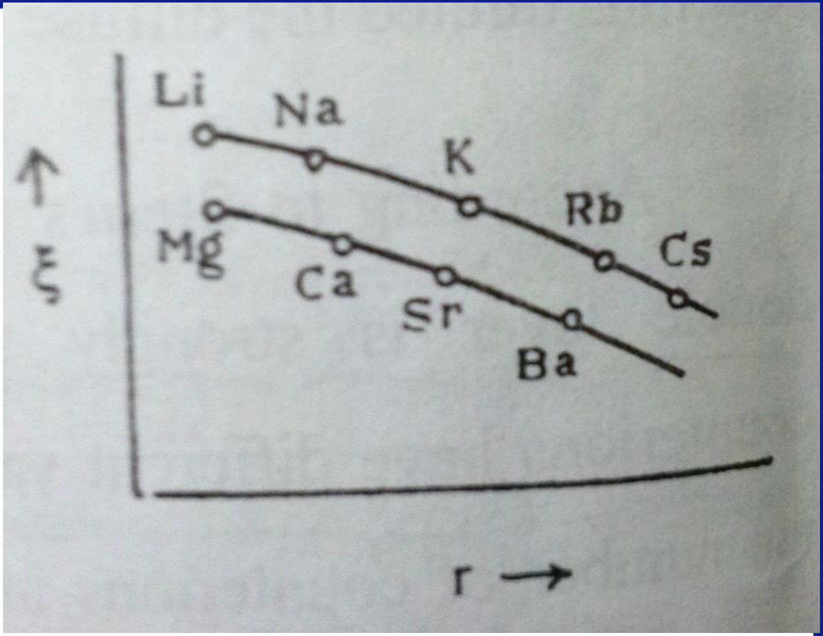
Stern Theory

(nature of counterions and the EDL)

- If counterions have different valences, the thickness of the diffuse layer and no. of counterions in the stern layer (adsorbed layer) are determined by the **ionic valency** hence depend on electrostatic forces. So the grater is the valancy, the thinner is the EDL and smaller ζ-potential.
- If the counterions have the same valances, thickness and ζ-potential are determined by **polarizability and hydration of the ions i.e., their true size**.
- The great polarizability of ions reduced the EDL thickness as a result of additional forces originate between the solid and the induced dipole.
- polarization of anions are grater than that of cations since the anions have larger radii
- Ionic hydration decreases by increasing true ionic radius. So, the decreases in hydration will promote the shrinking of the EDL where the hydrated membrane reduces the electrostatic interaction near the wall.

Stern Theory

- This explains the increasing ability of ions of larger radius to compress the EDL and reduce the ζ-potential as seen in the –ve clay sol in Fig. with added Li to Cs or F to I, and bivalent counterions.
- Polyvalent ions enter the adsorbed layer by (strong electrostatic and adsorption forces) + polarizability. Then the ions adsorbed in great amount and can finally **reverse the charge of the solid surface**.
- Polyvalent ions of Al^{3+} and Th^{4+} are used for recharging the –ve ζ-potential to +ve sign.



Effect of different factors on ζ-potential

1- Effect of indifferent electrolytes

- These electrolytes affects only the ζ-potential by increasing the conc. Of counterions and hence shrining the EDL.
- A) when the electrolyte has one ion similar to the counterions: increasing the conc. Of such ions leads to decrease in EDL thickness and becomes equal to the Strern layer. The ζ-potential becomes zero which corresponds to the state called (isoelectric point) of the system.
- B) when the electrolyte does not has ions similar to the counterions: the counterions only exchanged for an equivalent amount of the added ions of the same sign when there is no specific adsorption then this exchange is affected by the ionic valency only.
- Ion exchange follows the ratio:

$$g_1/g_2 = C_1/C_2$$

G1,2is conc. of ions 1 and 2 in EDL; and c1,c2 is conc. in the bulk.

- If the valency is not the same the exchange equilibrium is shifted to the ions of higher valency.

Effect of different factors on ζ-potential

1- Effect of indifferent electrolytes

$$g_1/g_2 = f\ (C_1/C_2)$$

- When specific adsorption is considered the coefficient *f* is added to the equation which depends on the adsorption potential of the ions θ1 and θ2.
- When adsorption potential is high, ions with opposite sign to the solid sol can cause reversal of its charge.
- If the valency is not the same the exchange equilibrium is shifted to the ions of higher valency.

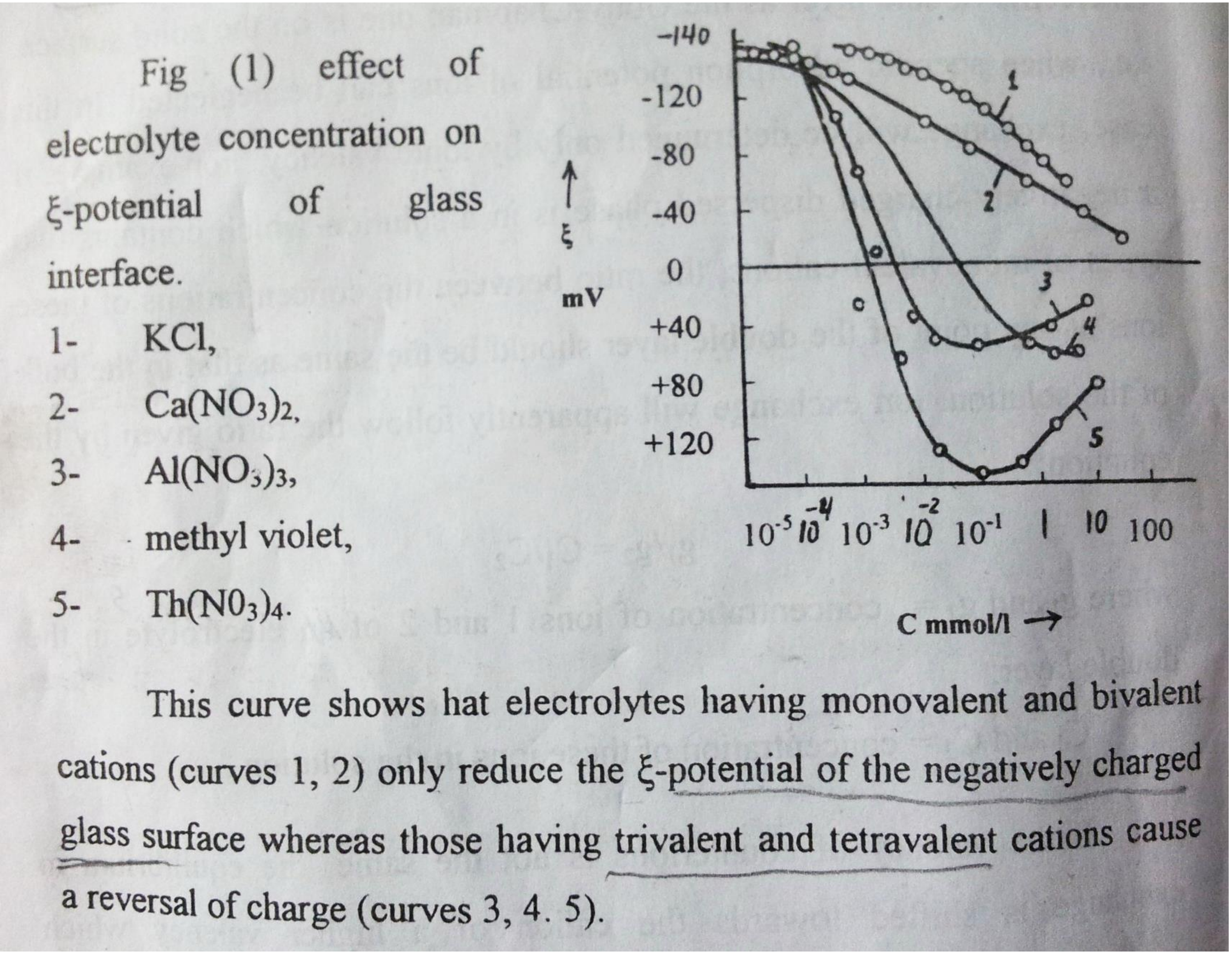


Fig (1) effect of electrolyte concentration on ξ-potential of glass interface.

1- KCl,

2- $Ca(NO_3)_2$,

3- $Al(NO_3)_3$,

4- methyl violet,

5- $Th(NO_3)_4$.

This curve shows hat electrolytes having monovalent and bivalent cations (curves 1, 2) only reduce the ξ-potential of the negatively charged glass surface whereas those having trivalent and tetravalent cations cause a reversal of charge (curves 3, 4. 5).

Effect of different factors on ζ-potential

2- Effect of non-indifferent electrolytes

- Ions of such electrolyte are capable of completing the construction of the crystal lattice of the sol.
- The potential-determining ion of the electrolyte can raise the surface potential ϕ^0 whereas the other ions with the same sign as counterions can compress the EDL.
- The first effect is mainly exhibited at low conc. Of non-indifferent electrolyte. The second prevails at high conc. when the construction of the crystal lattice is completed.
- Therefore, when an increasing conc. Of non-indifferent electrolyte is added the z-potential first grows, reaching the maximum then drops as in the following figure

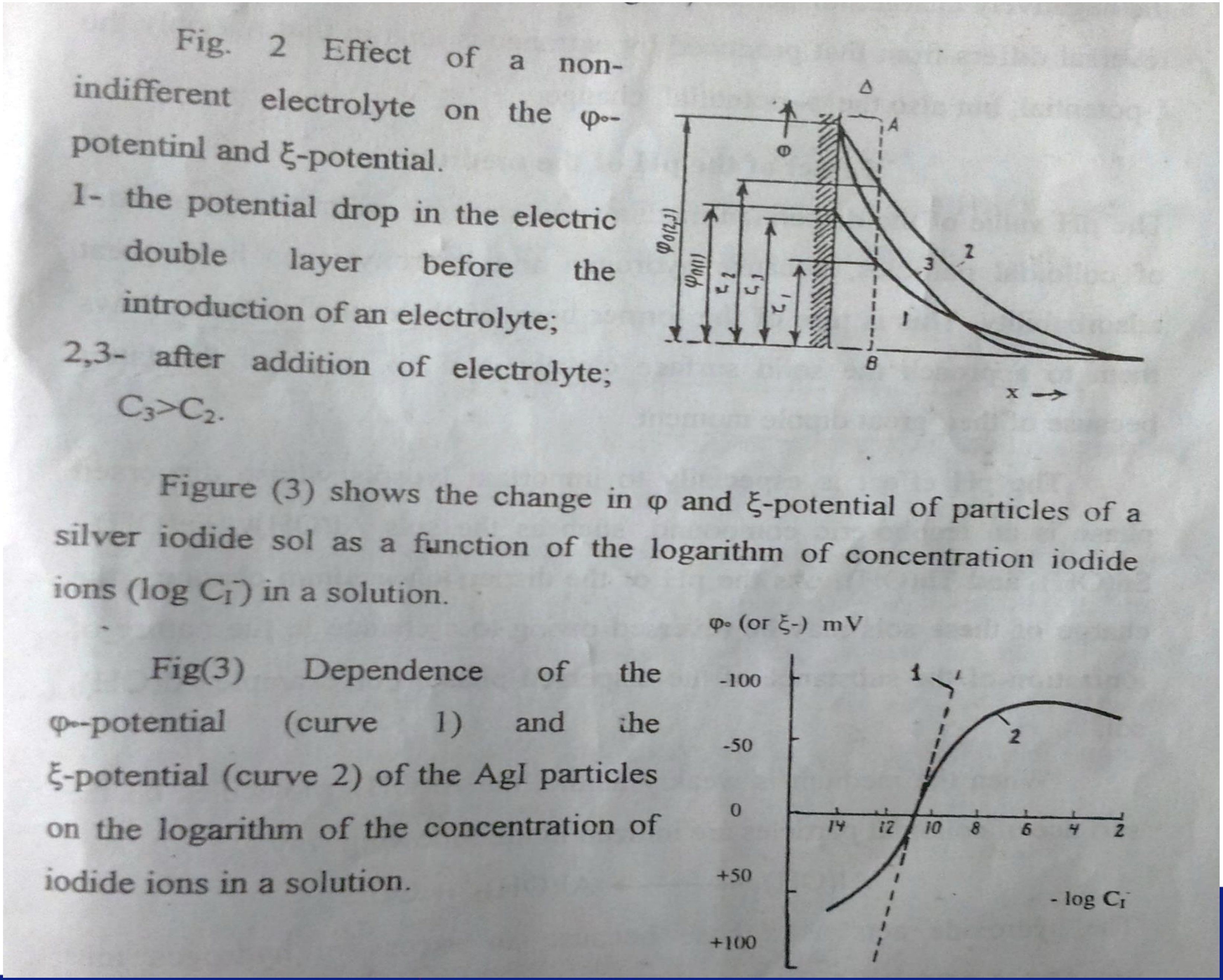


Fig. 2 Effect of a non-indifferent electrolyte on the $\varphi_\circ$-potentinl and ξ-potential.

1- the potential drop in the electric double layer before the introduction of an electrolyte;

2,3- after addition of electrolyte; $C_3>C_2$.

Figure (3) shows the change in φ and ξ-potential of particles of a silver iodide sol as a function of the logarithm of concentration iodide ions (log C_{I^-}) in a solution.

Fig(3) Dependence of the $\varphi_\circ$-potential (curve 1) and the ξ-potential (curve 2) of the AgI particles on the logarithm of the concentration of iodide ions in a solution.

Effect of different factors on ζ-potential

2- Effect of non-indifferent electrolytes

- In Fig 3, addition of KI (non-indifferent electrolyte) to the positively charged AgI sol which stabilized by AgNO3.
- First the potential-determining ions in the sol are Ag^+ and the counterions are NO_3^-. After the addition of KI in excess the potential determining ions will be I- and the counterions are K^+ and the sol becomes negatively charged.
- $AgNO_3$ in the dispersion medium will react with KI to form more negatively charged AgI sol.
- In this case both the total potential and z-potential have changed.

- Effect of the pH study it on (page 82-83): which is important.