Dispersion Systems

1. *The Classification of Dispersion Systems*
2. *Lyophobic Colloids*
3. *The Stability and Coagulation of Dispersion Systems*
4. *Properties of Colloids*

- **Dispersion system** is **a heterogeneous system** containing one or two substances in the form of particles spread in the medium made of another substance

Dispersion system consists of

a dispersed phase (DP) and

a dispersion medium (DM)

- The dispersed phase is a split substance
- The dispersion medium is a medium where this split substance is spread

- Dispersion means splitting
- Every substance can exist both in the form of a monolith and a split substance flour, small bubbles, small drops

To characterize the dispersion system we use the following values:

1. The transverse size of the dispersed phase:

- For spherical particles - a sphere diameter **(d)**
- For particles having a shape of a cube - edge of the cube **(ℓ)**

2. The substance splitting of a dispersed phase is characterized by **the degree of dispersion (δ)** which is opposite to the medium diameter **(d)** of the spherical particles or the medium length of the edge of the cube **(ℓ)**

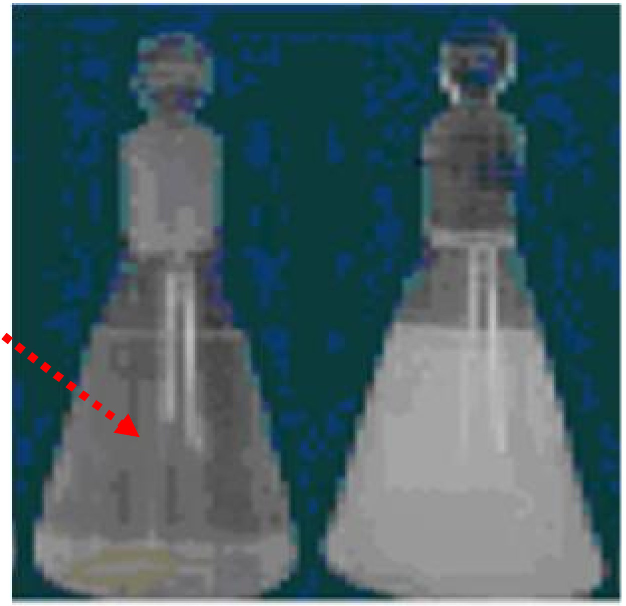
$$\delta = 1/d,\ \mathrm{m}^{-1}$$

$$\text{or } \delta = 1/\ell,\ \mathrm{m}^{-1}$$

Dispersed phase has the degree of dispersion

The degree of dispersion is greater

and the particle size is less



- Clouds, fumes, soil, clay are the examples of dispersion systems

1. The Classification of Dispersion Systems

I. **According to the dispersion degree of particles of the dispersed phase**

II. **According to the aggregative state of the phase and the medium**

III. **According to the kinetic properties of the dispersed phase**

IV. **According to the character of interaction between the dispersed phase (DP) and the dispersion medium (DM)**

I. According to the dispersion degree of particles of the dispersed phase

1. Coarsely dispersed systems

These are the systems in which the particles have the size of 10^{-7}m – 10^{-4} m

suspensions

2. Colloid-dispersed systems

The size of particles is 10^{-7}m – 10^{-9} m

The mixture is also called a colloidal solution

Colloidal particles consist of molecules, ions, or can have the form of a macromolecule

- Any substance can be obtained in the colloid state
- For example, soap in water is a colloid solution; soap in alcohol is a true solution
- Colloid solutions with liquid dispersion medium are called sols

- Biological fluids such as blood, urine, lymph, cerebrospinal fluid are also dispersion systems where different inorganic and organic salts: *phosphates, oxalates, urates, carbonates can be found in colloidal state*

3. Systems with the particle size less than 10^{-9}m are not referred to as dispersed ones

Such particles form molecular (particle diameter 10^{-10}m) and ionic (10^{-11}m) solutions known as **true solutions**

What are the basic differences between **true molecular solutions, colloidal solutions and suspensions?**

- **A true solution** is one in which the solute breaks down into its molecules or ions and is no visible even with a microscope
- **True solution** is homogeneous
- Only one phase forms in **a true solution**

- If the particle size of the solute is greater than about 10^{-7} m and the solute is insoluble in a solvent, it remains suspended in the solvent, and slowly settles down under the effect of gravity
- **Such a mixture is suspension**
- **Suspension is heterogeneous**
- **The particles are visible with a microscope**

- If the particle size is between 10^{-9}-10^{-7} m, the mixture shows deviation from a true solution
- **The colloidal particles** constitute dispersed phase and the solvent is called dispersion medium
- They do not settle out under the influence of gravity
- **The colloidal particles** are invisible with a microscope but their motions can be observed by scattering of light
- **Colloids are heterogeneous**

- Colloidal particles are larger than molecules but too small to be observed directly with a microscope; however, their shape and size can be determined by electron microscopy

- In a true solution the particles of dissolved substance are of molecular size and are thus smaller than colloidal particles

- In a coarse mixture (e.g., a suspension) the particles are much larger than colloidal particles

II. According to the aggregative state of the phase and the medium

- Depending on the aggregative state of a dispersed phase and the dispersion medium we can divide all dispersion systems into 8 types

Types of dispersion systems

Aggregative state of the DM	Type of the system	Aggregative state of the DP	Symbolic notation of the system	Examples of systems
Gas	Aerosol	Liquid Solid	L/G S/G	Mist Fumes, dust, powder
Liquid	Lyosol	Gas Liquid Solid	G/L L/L S/L	Foam Emulsions (oil, milk) Slurries, suspensions, colloid solutions
Solid	Hard sol	Gas Liquid Solid	G/S L/S S/S	Hard foams (pumice, bread) Capillary systems (liquids in porous objects, soil, ground), Hard systems (minerals, alloys, concrete)

Aerosol

L/G

spray

Aerosol
S/G

smoke in air

Foam
G/L

lather

Emulsion

L/L

Milk is basically an emulsion of butterfat droplets dispersed in an aqueous solution of carbohydrates

Pumice is a volcanic rock

G/S

- The sudden release of pressure as the lava is ejected from the volcano allows dissolved gases to expand, producing tiny bubbles that get frozen into the matrix
- Pumice is distinguished from other rocks by its very low density

III.According to the kinetic properties of the dispersed phase

- Dispersion systems can be differed according to the degree of interaction of particles in the dispersed phase

- If DP particles are not connected with each other and are able to move independently in DM under the influence of thermal motion or force of gravity, such systems are called **free-dispersion systems**
- **These are sols, aerosols, rather diluted suspensions and emulsions**

- If the particles are bonded together by the intermolecular interaction forces and form spatial patterns (lattices, nets, etc), such systems are called **bound-dispersion systems**
- **These are gels, concentrated suspensions (creams, pastes) and concentrated aerosols**

IV. According to the character of interaction between DP and DM

- We should distinguish lyophilic and lyophobic systems
- Lyophilic systems are those where DP particles are very similar to those of DM
- Lyophobic systems are those with little similarity of DP and DM particles
- If water is taken as DM, then we should use the terms ‘hydrophilic and hydrophobic dispersion systems’

- The particles in a lyophilic system have a great affinity for the solvent, and are readily solvated and dispersed, even at high concentrations

- In a lyophobic system the particles resist solvation and dispersion in the solvent, and the concentration of particles is usually relatively low

- The examples of a hydrophilic system can be high-molecular compounds (HMC) like proteins, polysaccharides, nucleic acids
- The majority of dispersion systems are lyophobic (hydrophobic)

For example, sols of AgCl, $BaSO_4$ salts

2. Lyophobic colloids (sols)

- For a lyophobic colloid there is no interaction between dispersed phase and dispersion medium
- Lyophobic colloids consist of **the charged colloidal particles** and tend to stabilize by repulsion between the charged colloidal particles
- **The colloidal particles are electrically charged**
- **A colloid solution as a whole is neutral**

The obtaining of a dispersion system

- To obtain a dispersion system (including colloid solutions) we should observe three conditions:

1. **Firstly**, mutual insolubility of the dispersed phase and the dispersion medium
2. **Secondly**, the substance should be split to a certain size of DP particles
3. **Thirdly**, presence of a stabilizer

- There are two basic methods of forming a colloid: reduction of larger particles to colloidal size, and condensation of smaller particles (e.g., molecules) into colloidal particles

- Some substances are easily dispersed (in the proper solvent) to form a colloid; this spontaneous dispersion is called peptization
- A solid can be reduced to colloidal particles in a colloid mill, a mechanical device that uses a shearing force to break apart the larger particles
  - Condensation of smaller particles to form a colloid usually involves chemical reactions — typically displacement, hydrolysis, or oxidation and reduction

The obtaining of colloidal solutions by the condensation method

- At the surface of colloid particles there is **a double electric layer** formed at the interface of phases

- The necessary condition for the charge formation at the colloid particle is **the excess of one of the electrolytes** taking part in the reaction

- The excess of the electrolyte is **a stabilizer**

- It is known that if we pour together two solutions of electrolytes in equivalent amounts, there will be no colloid solution formed but there is the precipitate:

$$m\ \mathrm{BaCl_2} + m\ \mathrm{K_2SO_4} = m\ \mathrm{BaSO_4}\downarrow + 2m\ \mathrm{KCl}$$

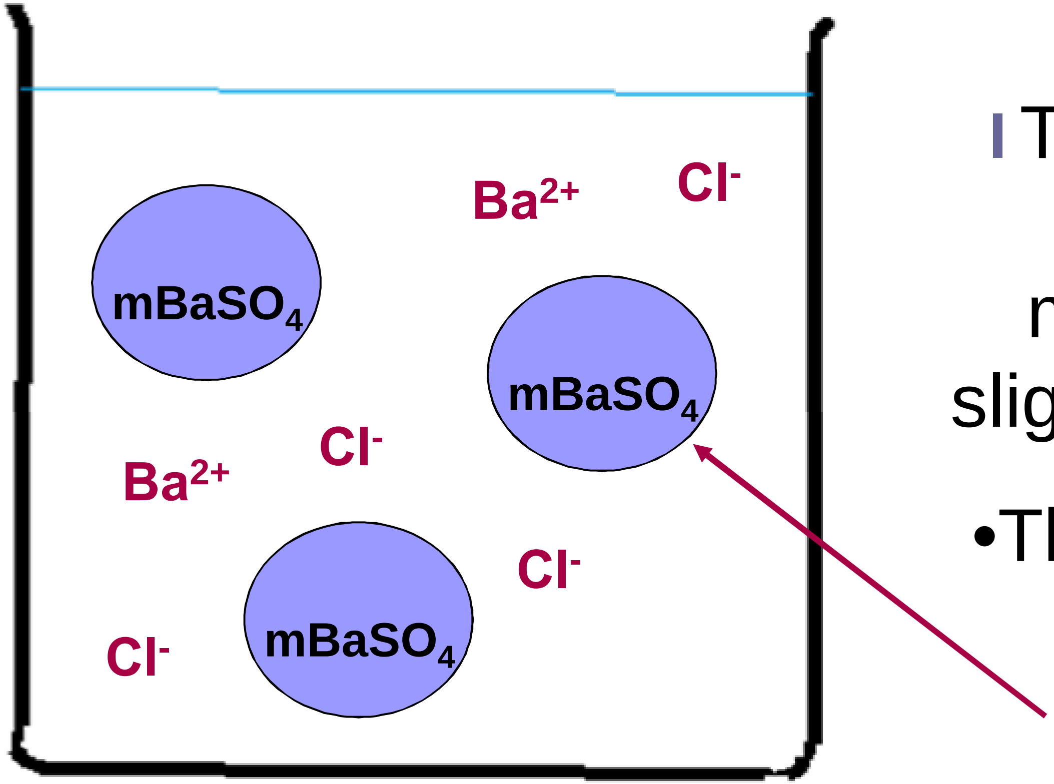
- If we have to obtain $BaSO_4$ sol, one of the electrolytes should be taken in excessive amount

If the reaction occurs at the excess of $BaCl_2$ solution

$$(m+n)\ BaCl_2 + m\ K_2SO_4 \rightarrow m\ BaSO_4\downarrow + 2m\ KCl + n\ BaCl_2$$

- As barium chloride is a strong electrolyte, it decomposes completely into ions:

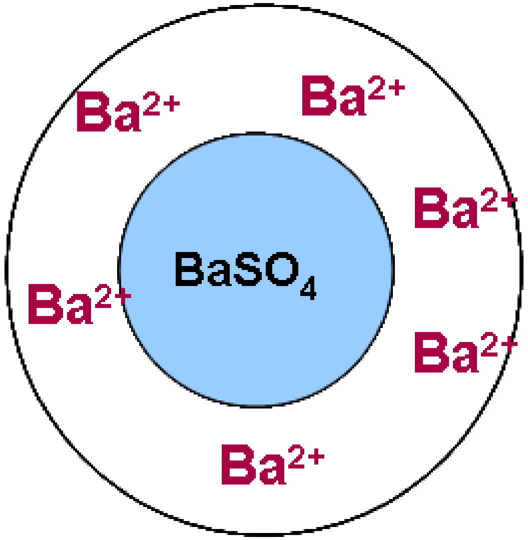
$$n\ BaCl_2 \rightarrow n\ Ba^{2+} + 2n\ Cl^-$$



- The basis of colloid particles is the microcrystals of a slightly soluble $BaSO_4$

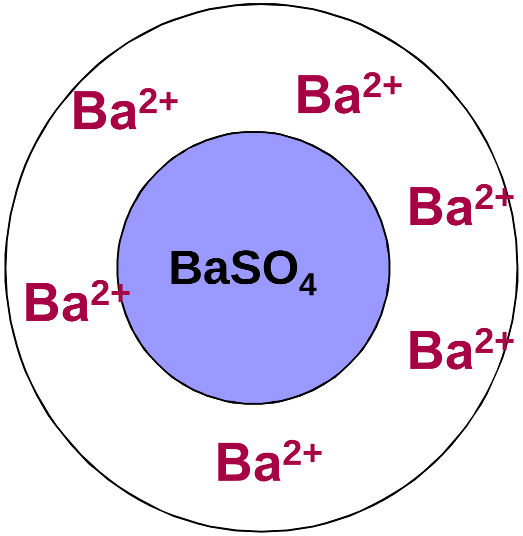
- These microcrystals are called **the aggregate**

- The surfaces of many solids present "broken bonds" which are chemically active
- A positively charged layer appears at the surface of the aggregate as a result of **selective adsorption of Ba^{2+} ions**



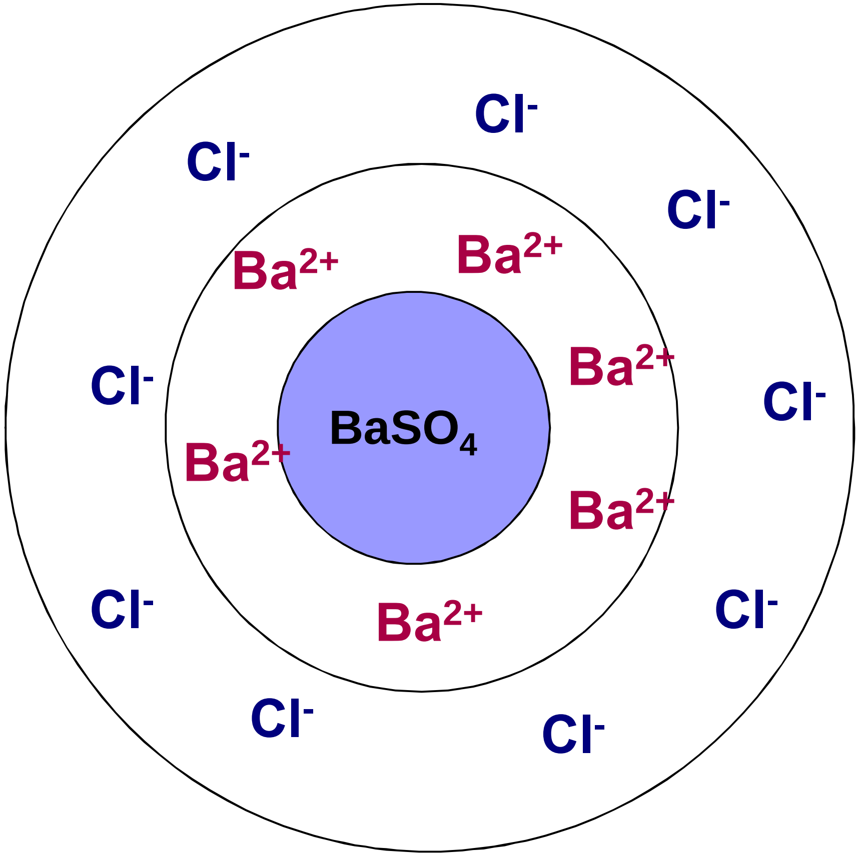
- **Selective adsorption** occurs according to **Panett-Fayance rule** which states that the lattice structure can be finished only by those ions which are a part of it
- Barium ions Ba^{2+} in this case are **potential-determining ions**

- **The aggregate** together with **the potential-determining ions** is a part of a solid phase and is called **a nucleus**

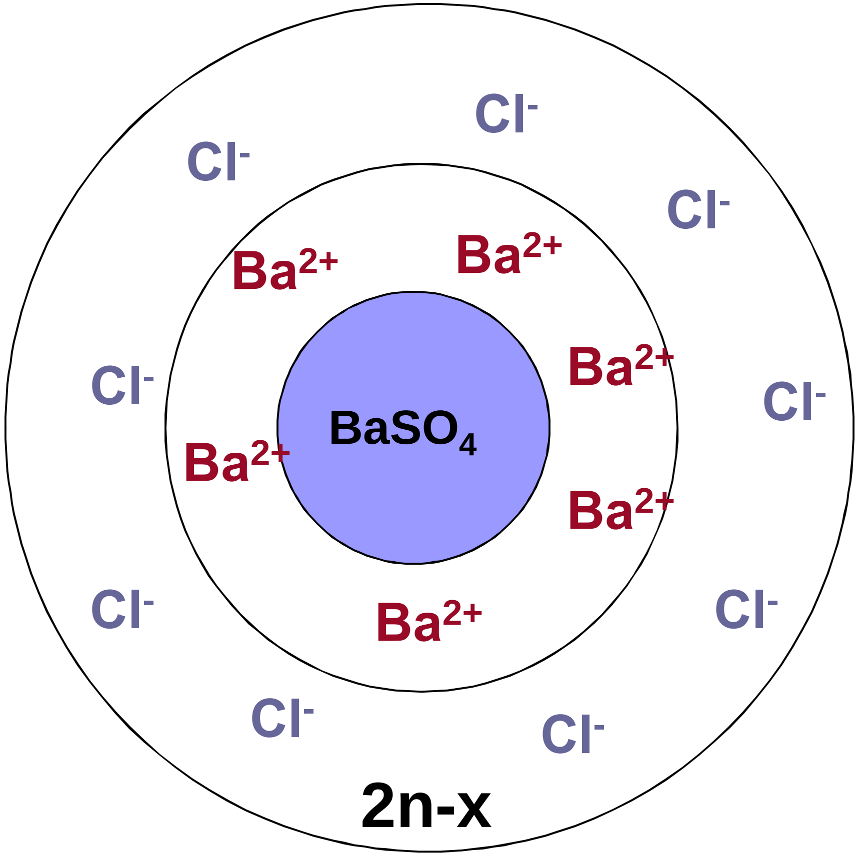


- Under the influence of electrostatic forces **2n chlorine ions Cl^-** are attracted to the nucleus

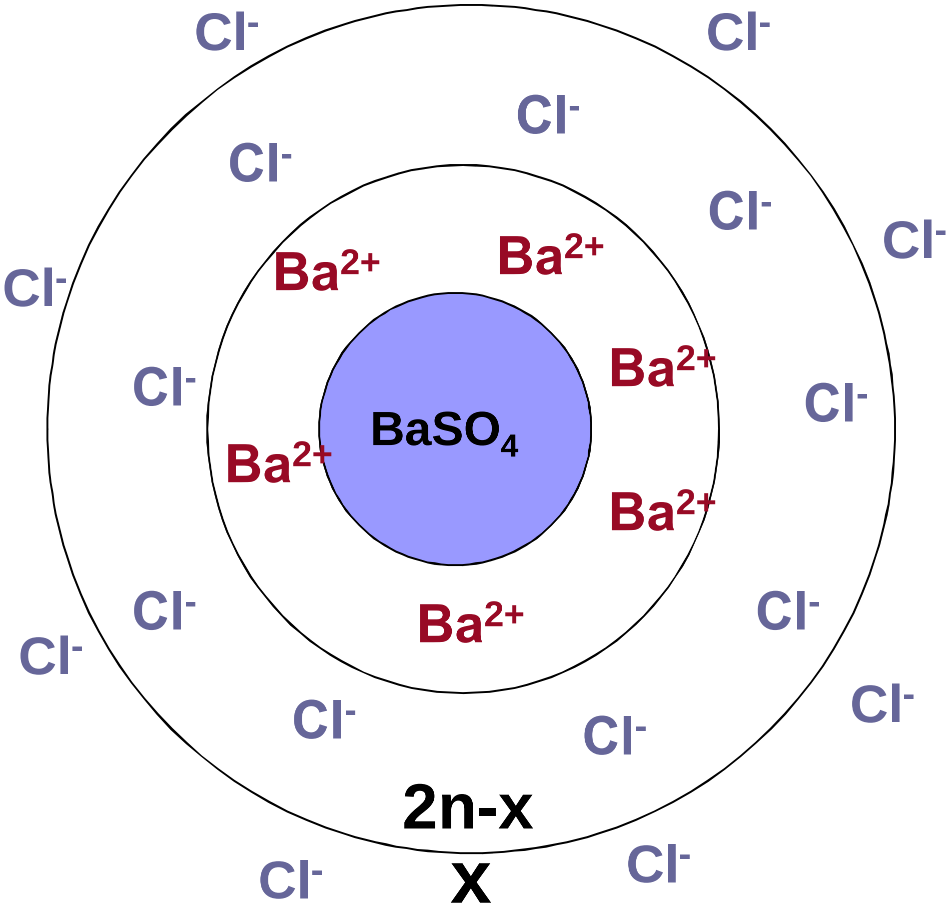
Cl^- ions are called **counterions** and they compensate the nucleus charge



- **Part of these counterions (2n-x)** is strongly attached to the nucleus and together with **potential-determining ions** Ba^{2+} form **the adsorption layer**
- **The aggregate** and **the adsorption layer** together form **a granule** which has a positive charge



- **The rest x** of chlorine counterions forms **a diffuse layer**
- **The granule** together with **the diffuse layer** forms **a micelle** which is electrically neutral



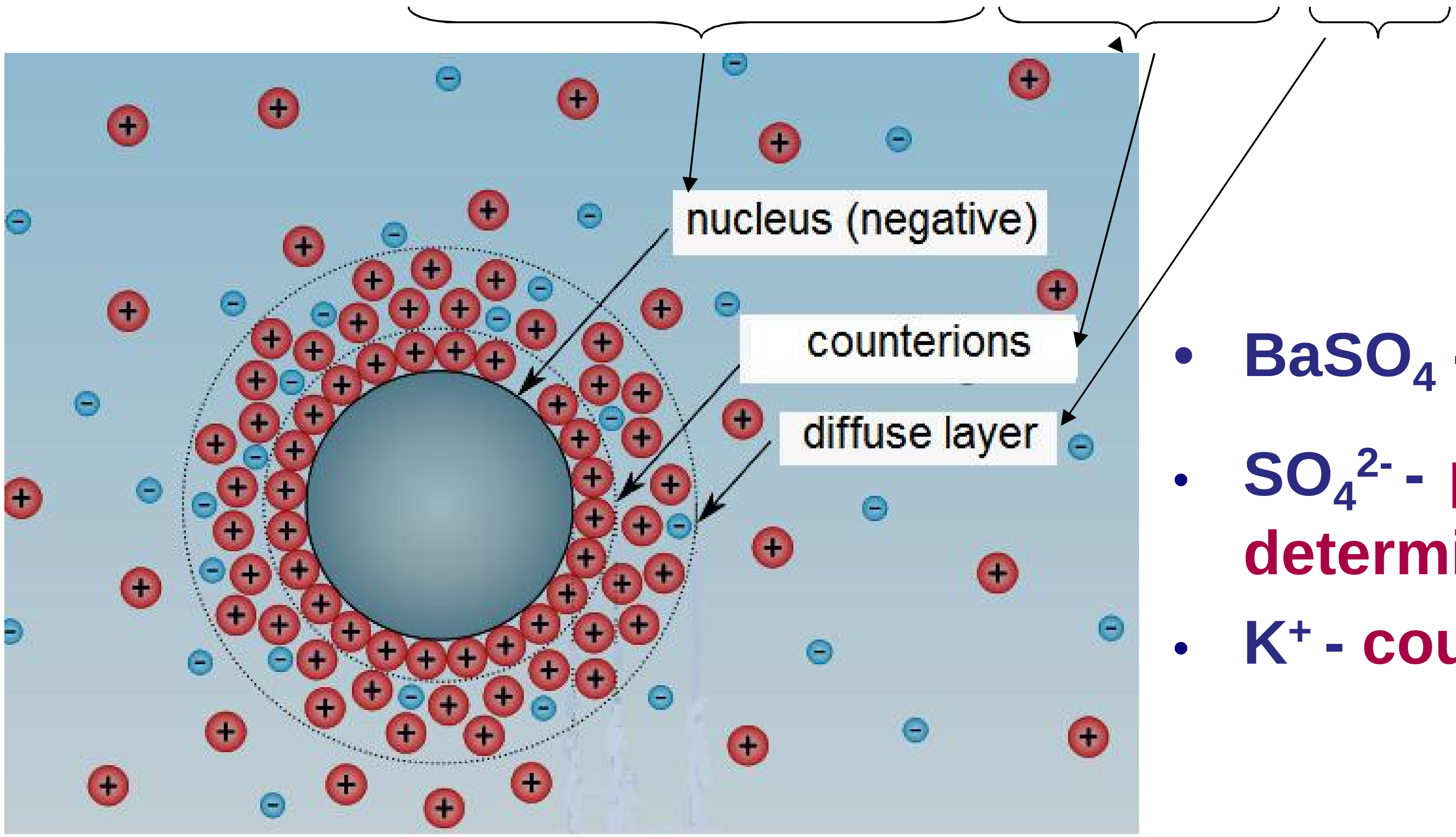
The micelle scheme

$$\left\{\underbrace{\mathrlap{\overbrace{\phantom{[mBaSO_4]\cdot nBa^{2+}}}^{\text{nucleus}}}\underbrace{[mBaSO_4]}_{\text{aggregate}}\cdot\underbrace{nBa^{2+}\,(2n-x)Cl^-}_{\text{adsorption layer}}}_{\text{Granule}}\right\}^{x+}\cdot\underbrace{xCl^-}_{\text{diffuse layer}}$$

- In the case when the solution of potassium sulfate K_2SO_4 is taken in excess amount, the micelle scheme will be different:

$$\{[mBaSO_4]\cdot nSO_4^{2-}\cdot(2n-x)K^+\}^{x-}\cdot xK^+$$

$$\underbrace{\{[mBaSO_4]\cdot nSO_4^{2-}\cdot}\ \underbrace{(2n-x)K^+\}}{}^{x-}\cdot \underbrace{xK^+}$$



- **$BaSO_4$ - aggregate**
- **SO_4^{2-} - potential-determining ions**
- **K^+ - counterions**

- The granule charge is determined by the charge of potential-determining ions

$$\{[mBaSO_4]\cdot nSO_4^{2-}\cdot (2n–x)K^+\}^{x-}\cdot xK^+$$

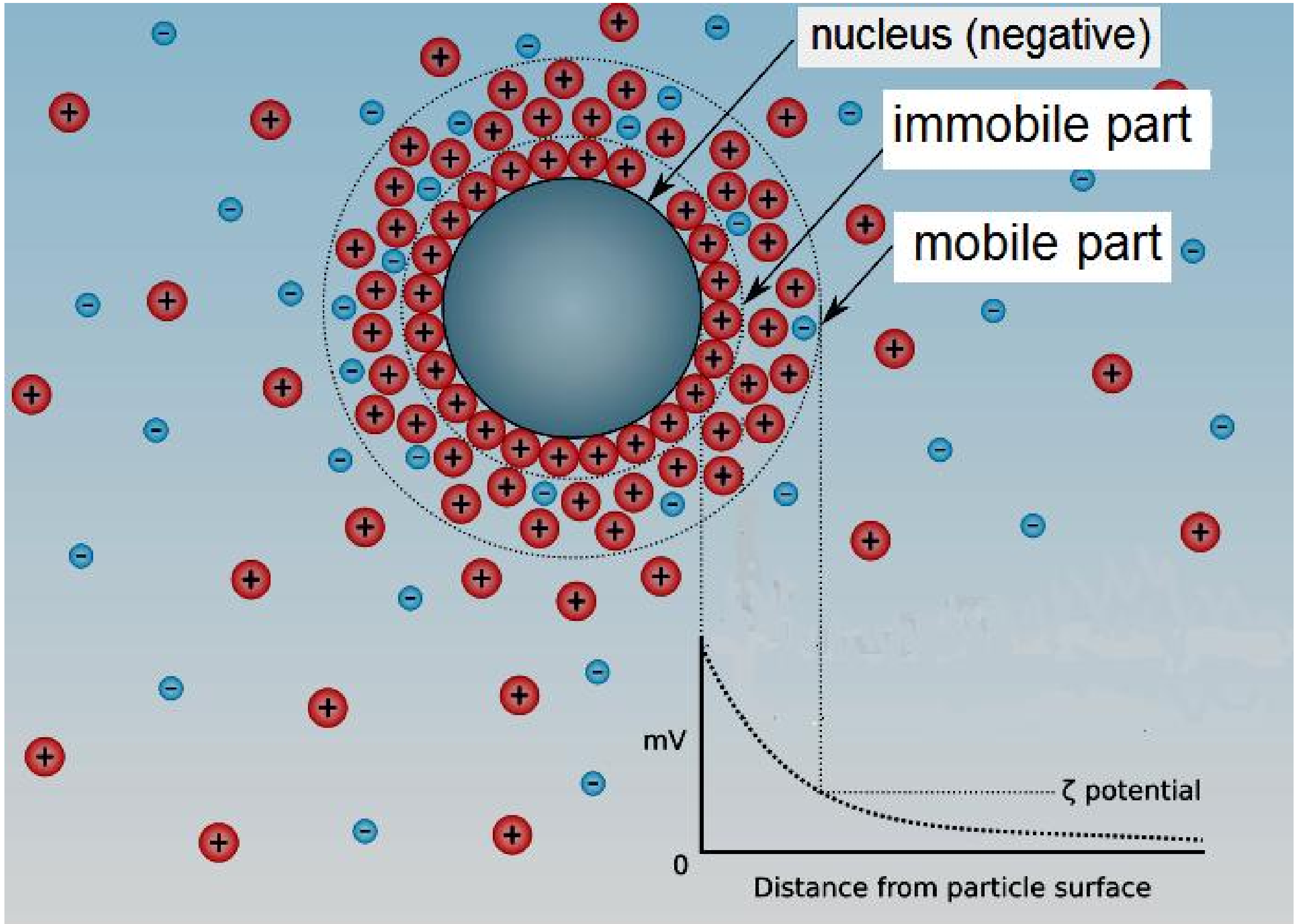
SO_4^{2-} - potential-determining ions (K_2SO_4 is taken in excess amount)

- The granule becomes neutral if all the counterions from the diffuse layer transfer to the adsorption layer

$$\{[mBaSO_4]\cdot nSO_4^{2-}\cdot 2nK^+\}^0$$

- All of the particles of a given colloid take on the same charge (either positive or negative) and thus are repelled by one another
- If an electric potential is applied to a colloid, the charged colloidal particles move toward the oppositely charged electrode; this migration is called electrophoresis
- If the charge on the particles is neutral, they may precipitate out

The potential drop between the mobile (the diffuse layer) and immobile (the adsorption layer) parts of the double electric layer is called electrokinetic potential or ξ zeta potential



- Electrokinetic potential or ξ zeta potential is calculated using the formula

$$x = \frac{V \cdot K \cdot \pi \cdot \eta}{H \cdot \varepsilon}$$

Where:

K is the coefficient, the value of which depends on the form of particles: K=4 for cylindrical, K=6 for spherical;

V is the linear speed of particle transfer, m/sec;

η is the viscosity of the medium, Newton·sec/m^2;

H is the electric field intensity (potential gradient), V/m;

ε is the relative dielectric permittivity of the medium.

- ξ -potential depends on the blurring degree of diffuse layer,

  electrolyte concentration and

  ion charges

- Maximum potential drop between the solid surface and all other counterions is called thermodynamic potential E
- The value of thermodynamic potential is 30-100 mV

3. The stability and coagulation of dispersion systems

Stability of a dispersion system is
the constancy of this system in time,
first of all **the constancy of dispersion**
and the constancy of even particle distribution of dispersed phase in the medium

- We should distinguish two kinds of stability of dispersion systems:

sedimentation (kinetic) and aggregative

- **Sedimentation stability** is the ability of particles of a dispersed phase to remain in the suspension state
  - This ability depends on

the dispersion degree of particles,

dispersed phase viscosity,

differences in the density of the dispersed phase and the dispersion medium,

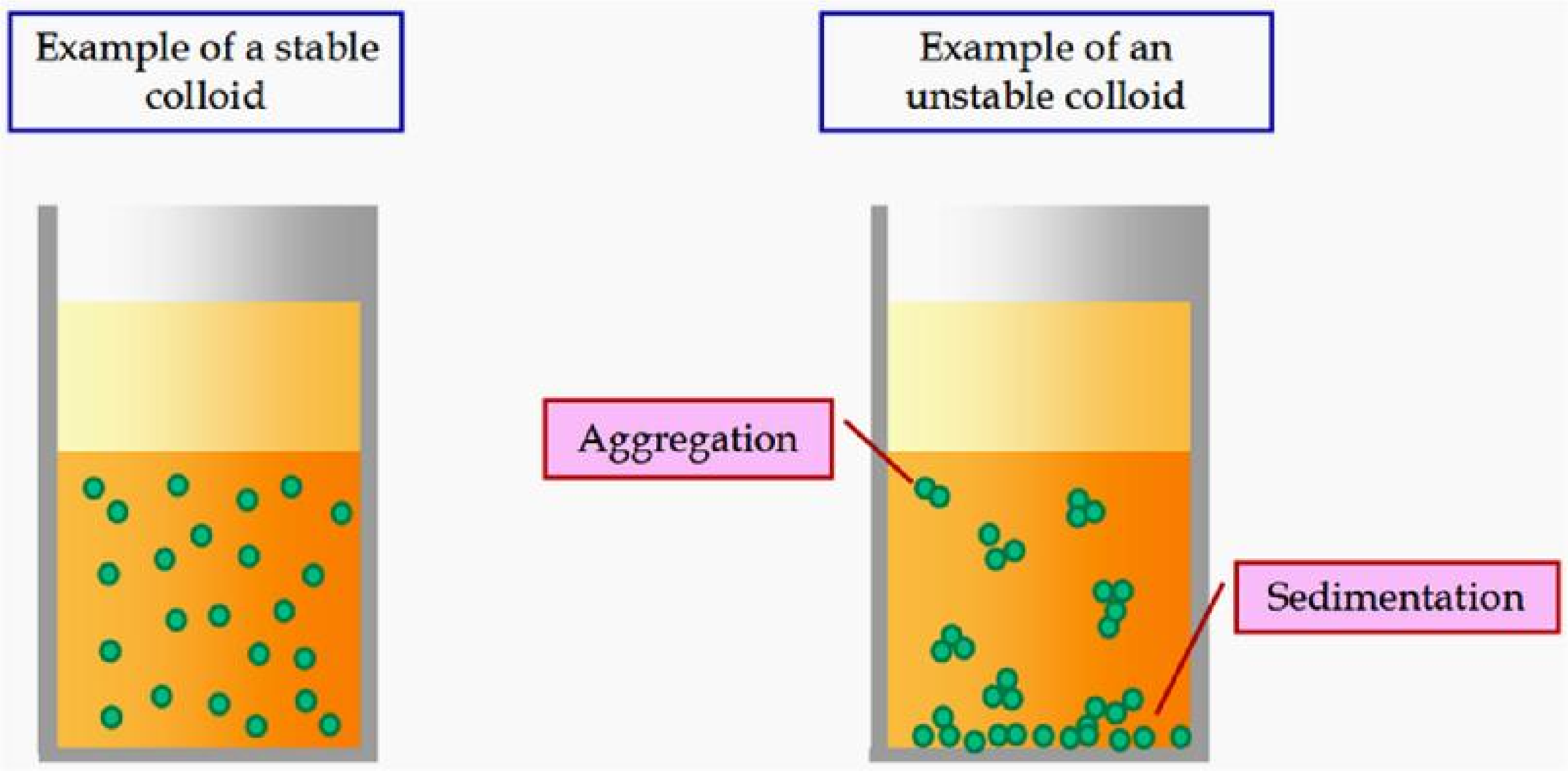
temperature

- Kinetic (sedimentation) stability of the sol is the higher when
- the smaller is the particle size,
- the closer are the values of phase density and medium
- and the higher is the dispersion medium viscosity
- while the dispersion degree of particles is the most influential characteristic

- **Aggregative stability** characterizes the ability of particles from dispersed phase to show resistances to their adhesion and in this way to keep a definite degree of dispersion

- The main factors of aggregative stability of dispersion systems are the following: particles have an ionic shell, i.e. double electric layer,
- the diffuse layer of counterions and also their solvation (hydrated) sphere
- The loss of aggregative stability leads to coagulation

- **Coagulation** is the process of joining of colloid particles and forming of greater aggregates which leads to their precipitation under the influence of the forces of gravity followed by further phase division



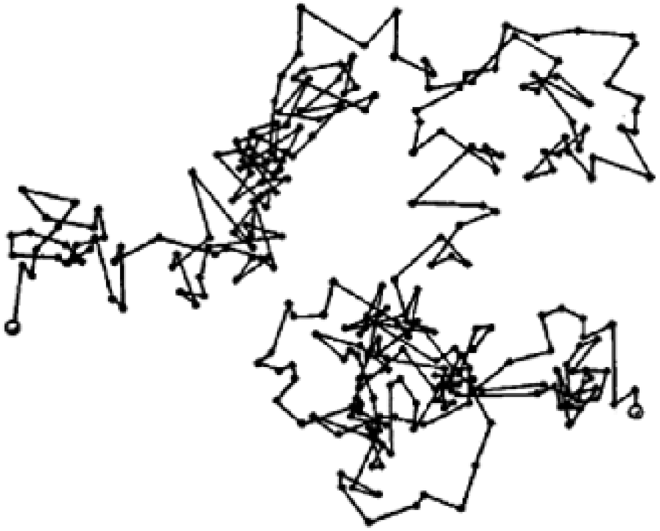
- **Coagulation can be caused by different factors:** change in temperature, action of light, mechanical influence, irradiation, the increase in sol concentration, adding of electrolytes

4. Properties of Colloids

1. Colloids are heterogeneous
2. The solute particles are invisible but their motions can be observed by scattering of light
3. The colloidal particles cannot be separated by filtration
4. Colloidal particles diffuse slowly because of their large sizes
5. Colligalive properties are not appreciable
6. Brownian movement
7. Optical properties

Brownian movement

- When an ultramicroscope is used to examine a colloid, the colloidal particles appear as tiny points of light in constant motion; this motion, called Brownian movement, helps keep the particles in colloidal state



These particles are in constant irregular motion

- **Brownian movement** - it is named for the botanist Robert Brown who observed (1827) the movement of plant spores floating in water

- The effect, being independent of all external factors, is ascribed to the thermal motion of the molecules of the fluid
  - The intensity of Brownian movement increases with the temperature of the medium and with the reduction of its viscosity and the particle size

  - The kinetic stability with the increase in temperature increases too in the result of intensification of Brownian motion

Optical properties of colloid solutions

- Light diffusion (Tindal’s effect)
- Opalescence

- One property of colloid systems that distinguishes them from true solutions is that colloidal particles scatter light

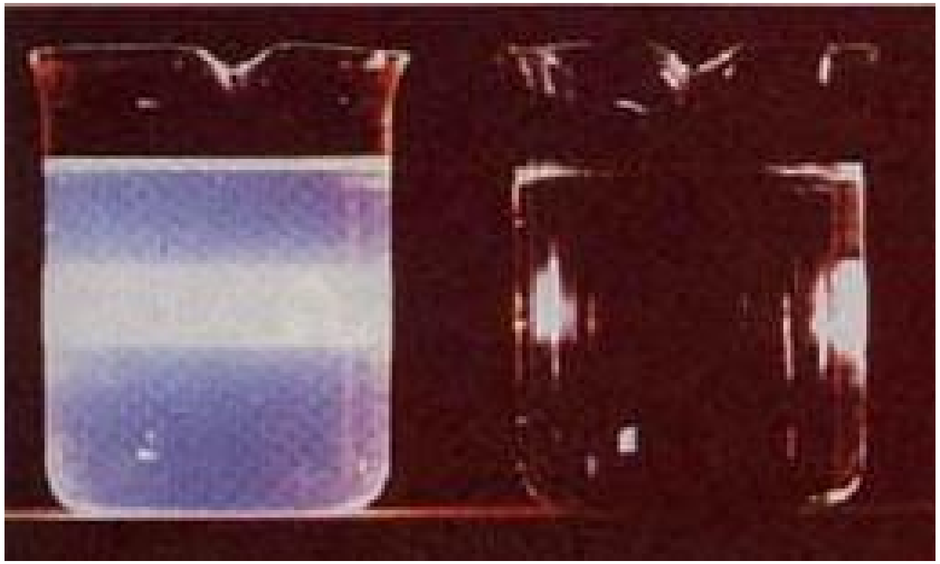
- If a beam of light passes through a colloid, the light is reflected (scattered) by the colloidal particles and the path of the light can therefore be observed

- When a beam of light passes through a true solution (e.g., salt in water) there is so little scattering of the light that the path of the light cannot be seen and the small amount of scattered light cannot be detected except by very sensitive instruments

- **The scattering of light by colloids, known as the Tyndall effect, was first explained by the British physicist John Tyndall**

- The Tyndall effect, also known as Tyndall scattering, is light scattering by particles in a colloid or particles in a fine suspension
- Under the Tyndall effect, the longer-wavelength light is more transmitted while the shorter-wavelength light is more reflected via scattering
  - The Tyndall effect is seen when light-scattering particulate-matter is dispersed in an otherwise light-transmitting medium, when the cross-section of an individual particulate is the range of roughly between 40 and 900 nanometers, i.e., somewhat below or near the wavelength of visible light (400–750 nanometers)

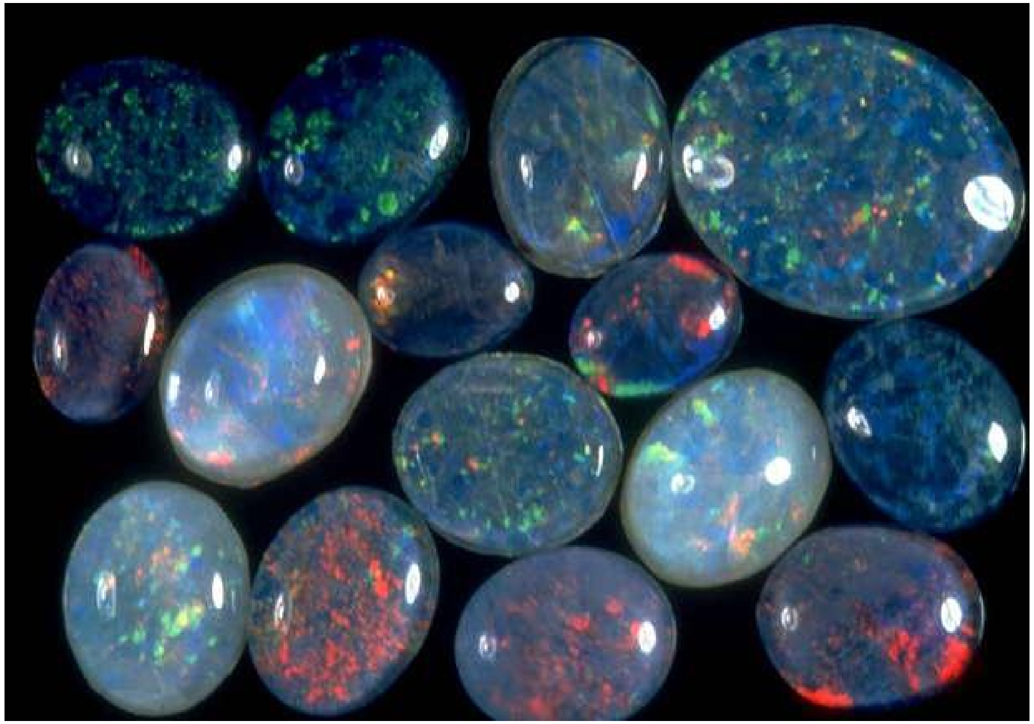
- A collimated beam of light passing through a solution composed of ordinary molecules tends retain its shape
- When such a beam is directed through a colloidal dispersion, it spreads out (left container)→



Opalescence

- Flour suspended in water appears to be blue because only scattered light reaches the viewer and blue light is scattered by the flour particles more strongly than red

Opalescence



- Opal consists of droplets of liquid water dispersed in a silica (SiO_2) matrix

- The Tyndall effect in opalescent glass: It appears blue from the side, but orange light shines through


ALLDAY.RU