



# Colloid Chemistry (general introduction to the course)

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КАЗАХСКИЙ НАЦИОНАЛЬНЫЙ УНИВЕРСИТЕТ  
имени А.Ль-ФАРАБИ

- The subject of Colloid Science
- The peculiarities of colloid systems:
- Classification of Disperse Systems
- Colloid Chemistry studies the properties of various systems (inorganic, organic, polymeric) in which at least one of the substances is in the form of particles ranging in size from about 1 nm (several molecular sizes) to 100  $\mu\text{m}$ . Particles of these sizes are called as dispersed particles.
- (Latin *dispergo* - spray, scatter).



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Colloid Science describes the features of substances in colloidal state and studies the disperse systems.

Disperse systems is characterized as an ensemble of dispersed phase particles surrounded by the dispersion medium

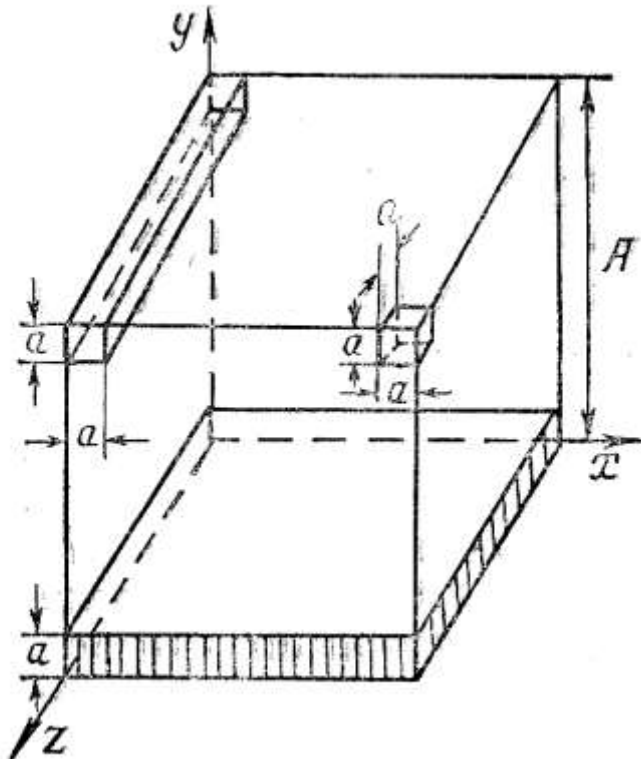
According to their sizes the colloid systems occupy the intermediate area between molecules (atoms, ions) and macroscopic objects (macrophases). The size of dispersed particles approximately equals to 1 nm – 100  $\mu\text{m}$ .



- Colloid Chemistry studies the substances in the dispersed state or **disperse systems**.
- The systems of interest in colloid chemistry include **coarse disperse systems** (with sizes of  $1\ \mu\text{m}$  or larger and with surface area less than  $1\ \text{m}^2/\text{g}$ ) and **fine disperse systems**.
- Fine disperse systems are ultramicroheterogeneous colloidal systems with fine particles down to  $1\ \text{nm}$  in diameter and with surface areas reaching  $1000\ \text{m}^2/\text{g}$  (nanosystems).



- The peculiarities of colloid systems:
- Dispersion
- Heterogeneity
- Instability (aggregative and kinetic), stabilizers.
- Degree of dispersion (Dispersion) :  $D = 1 / a$
- Specific surface area ( $s_{sp}$ ):
  - $S_{sp} = S / V$
- Free surface energy:
  - $G_s = \sigma s$



$$S_{sp} = \frac{6a^2}{a^3} = \frac{6}{a} = 6D$$



- The dispersed state and **interfacial phenomena** can not be considered separately from each other, as interfacial phenomena determine the characteristic properties of disperse systems.
- Coarse disperse systems (with sizes of  $1\ \mu\text{m}$  or larger and with **surface area less than  $1\ \text{m}^2/\text{g}$** )  
Fine disperse systems are ultramicroheterogeneous colloidal systems with fine particles down to  $1\ \text{nm}$  in diameter and with **surface areas reaching  $1000\ \text{m}^2/\text{g}$**





- **Classification according to dispersion**
- $10^{-9} \div 10^{-7}$  m – high disperse systems or **fine disperse** systems (colloid solutions, sols).
- $10^{-6} \div 10^{-4}$  m – **coarse disperse systems** (suspensions, emulsions).
- Among the fine disperse systems there are particles with nanosizes (1-100 nm) which possess by unique physicochemical properties due to their small sizes. (Nanoscience)
- **Monodisperse and polydisperse** systems

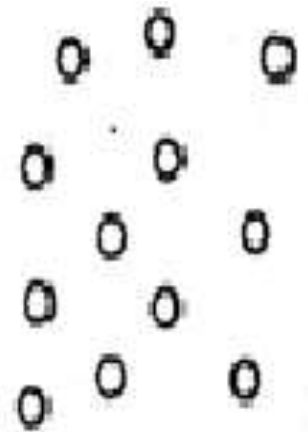
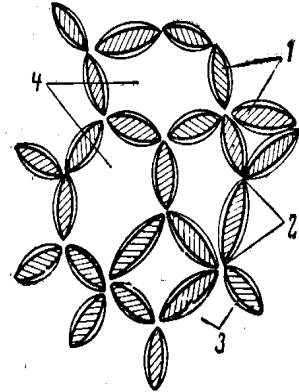


- Classification according to aggregate state of dispersed phase and dispersion medium

		Continuous phase		
		Gas	Liquid	Solid
Dispersed phase	Gas	None	Foam (shaving cream)	Solid foam (porous bodies)
	Liquid	Liquid aerosol (fog, mist)	Emulsion (cosmetic creams, mayonnaise, milk)	Capillary porous bodies, Gel (gelatin)
	Solid	Solid aerosol	Sol (paint,	Solid sol (Stained



- On structure: **Free disperse systems, structured dispersed systems**
- The fine disperse systems may be both **structured** (i.e. systems in which particles form a continuous three-dimensional network, referred to as the disperse structure),
- and **free disperse**, or unstructured (systems in which particles are separated from each other by the dispersion medium and take part in Brownian motion and diffusion).





- On degree of similarity between the dispersed
- phase and the dispersion medium (interphase interaction): *Lyophobic systems, lyophilic disperse systems.*
- High degree of similarity between the dispersed phase and the dispersion medium, and, consequently, compensation of the interactions at the interface (which usually results in very low values of interfacial free energy) is characteristic of *lyophilic disperse systems.*
-



- *These* systems, may form spontaneously and reveal complete thermodynamic stability with respect to both aggregation into a macrophase and dispersion down to particles of molecular size.
- (micellar solution of SF, polymer solution, particle of bentonite clay in aqueous solutions)
- In various *lyophobic systems* (colloidal and coarse disperse), there is a lot *less similarity* between the dispersed phase and the dispersion medium;
- (sols, emulsions, foams)
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- **History of Colloid Chemistry**
- Generally, Colloid Chemistry as an area of science has emerged due to fine disperse systems. In second half of the 19th century Italian scientist F. Selmi in the period 1845–50 noticed unusual properties of some solutions of highly dispersed solid particles distributed in a liquid dispersion medium. He had established the influence of electrolytes on stability of soles.



- in 1861 T. Graham have discovered that some substances (oxide of aluminium, silicon acid, tin acid, titanium acid, gelatin, agar) do not crystallize upon evaporation of the aqueous solution, but form jelly precipitates (gels). Their diffusion in solution is extremely slow in comparison with electrolytes - salts, acids and bases. Some of them have glueing action. The group of non-crystallizing substances T. Graham called colloids (Greek  $\alpha\epsilon\omicron\lambda\lambda\alpha$  [Kolla] - glue).
- Hence the name of the science that studies such substances is Colloid Chemistry. Dialysis, syneresis.



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- M. Faraday (1857), when the stable colloidal solutions of highly dispersed gold were obtained at first time. It is precisely these systems with a particle size of several nanometers have been the focus of many physicists and chemists of the second half of the 19th and early 20th centuries.





- Experimental studies of colloidal solutions led to the discovery of the Colloid Chemistry basics: Brownian motion and diffusion of colloidal particles (A. Einstein),
- heterogeneous nature of colloid solutions (R. Zsigmondy),
- sedimentation-equilibrium of highly dispersed systems in the gravity field (J. Perrin),
- sedimentation in a centrifuge (T. Svedberg),
- light scattering (J. Rayleigh),
- coagulation of sols with electrolytes (G. Schulze and B. Hardy).
- Investigations of the properties of colloidal solutions of various substances allowed to establish the fundamental principle of universality of the colloidal state.



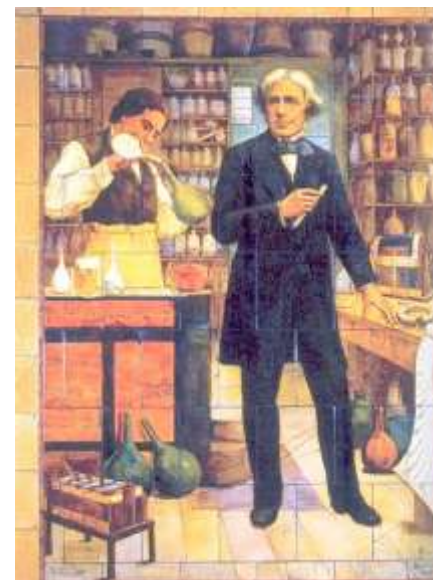
Michael Faraday  
(1791-1867)



Laboratory of M. Faraday

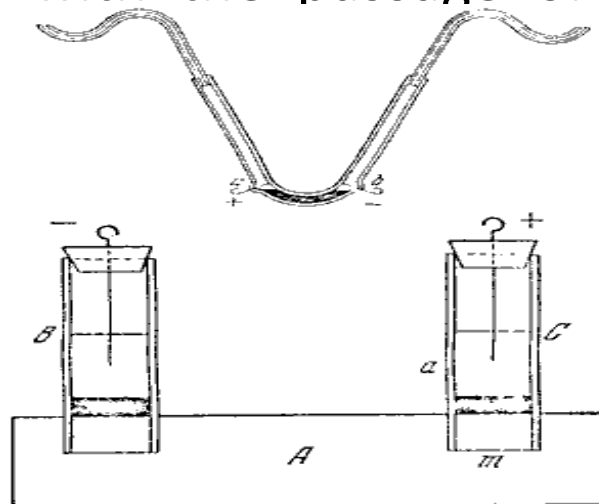


Golden sol of Faraday





- The phenomenon of adsorption from solutions (absorption of solute at the interface) was discovered in 1879 by the pharmacist T. Lovitz. Using bone coal, he developed methods for cleaning liquids from impurities. (Purification of alcohols)
- Professor of Moscow University F. Reiss, studying the electrolysis of water, discovered in 1808 electrokinetic phenomena associated with the passage of current through disperse systems.





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- In the beginning of 20<sup>th</sup> century four Nobel Prizes were in the field of colloid chemistry.
- The Austrian scientist R. Zsigmondy (1925) - "For the establishment of the heterogeneous nature of colloidal solutions and for the methods developed in this connection, which are of fundamental importance in modern colloid chemistry."



- The French physicist J. Perrin (1926) - "for work on the discrete nature of matter and in particular for the discovery of sedimentation-diffusion equilibrium."
- Swedish scientist T. Svedberg (1926) - "for work in the field of disperse systems" (primarily for the creation of an ultracentrifuge for determining the dimensions of fine dispersed particles and macromolecules).
- The American scientist I. Langmuir (1932) - "for his discoveries and research in the field of the chemistry of surface phenomena."
- It is necessary to add the Nobel Prize of the Swedish biochemist A. Tiselius (1948) - "for the study of electrophoresis and adsorption analysis, especially for the discovery of the heterogeneous nature of whey proteins."



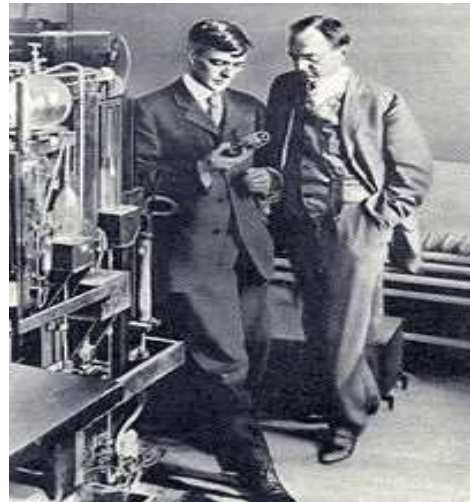
R. Zsigmondy  
(1865 - 1929)



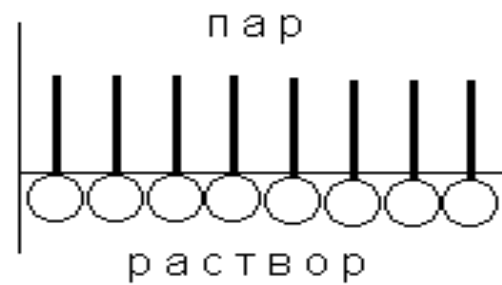
J. Perrin (1870-  
1942)



T. Svedberg  
(1870-1971)



I. Langmuir (1881-  
1957)





- P.A. Rehbinder - adsorption of surfactants leads to a decrease in the strength of crystals and other solids.
- B.V. Deryaguin - property of thin films "disjoining pressure".
- Modern colloidal chemistry has great practical importance (oil production, flotation, production of building materials, formulation of cosmetics and medicines).
- New ideas are based on the fact that highly dispersed particles (droplets of microemulsions, surfactant micelles, thin films) can serve as microreactors, the properties of the ultradisperse systems are studied, i.e. nanosystems.



- Preparation of disperse systems and their degradation.
- Optical properties of colloid systems. Rayleigh equation. Ultramicroscopy.
- Molecular-kinetic properties of disperse systems.
- Brownian motion. Diffusion. Sedimentation of coarse disperse systems.



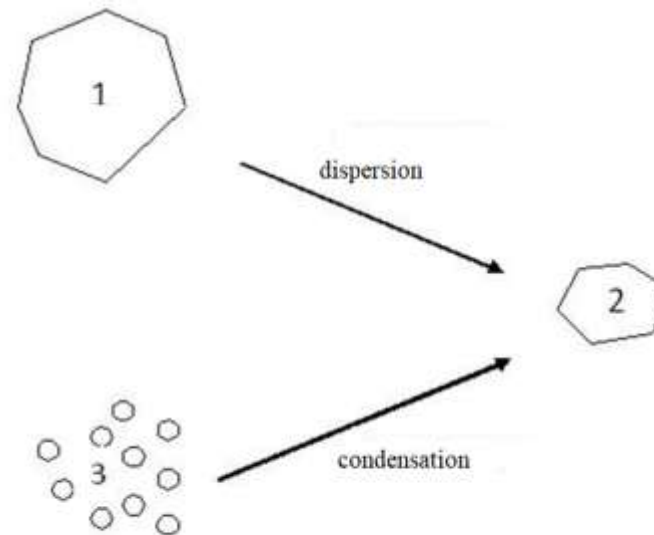


- Dispersion methods:

- Colloidal mills.
- Ultrasound treatment
- Electric dispersion
- Peptization

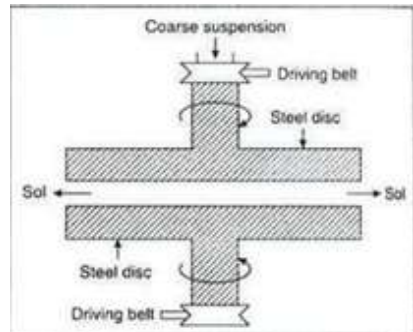
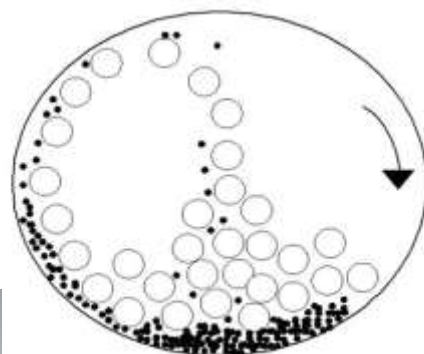
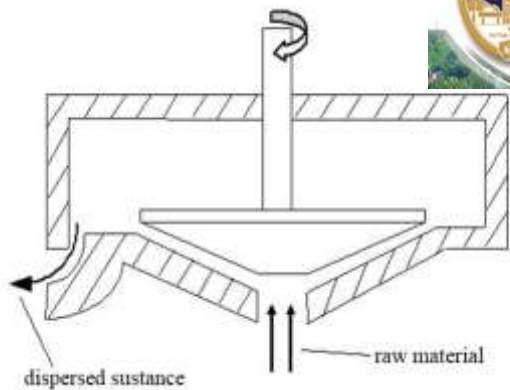
- Condensation method:

- Physical condensation
- (solvent displacement, condensation from vapours)
- Chemical condensation





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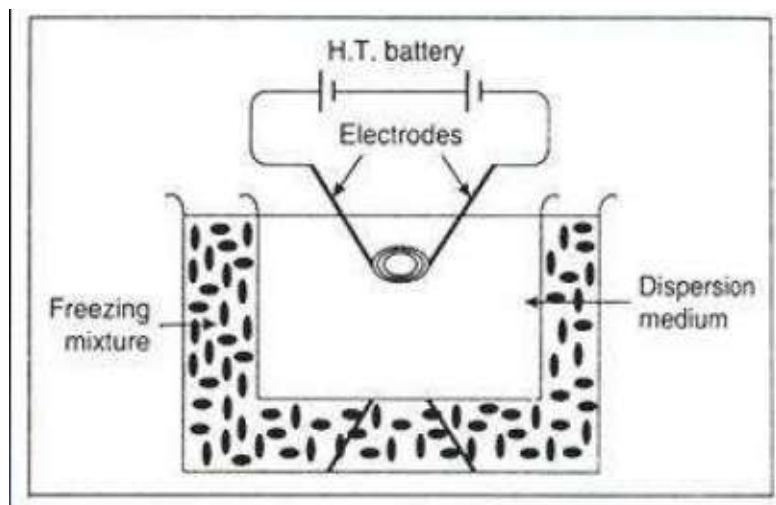
- The sound waves of high frequency are usually called **ultrasonic** waves. Ultrasonic waves are passed through the solution containing larger particles. They break down to form colloidal solution.





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- The dispersion of a precipitated material into colloidal solution by the action of an electrolyte in solution is termed as **peptisation**. The electrolyte used is called a peptizing agent.
- (Silver chloride can be converted into a sol by adding hydrochloric acid; Ferric hydroxide yields a sol by adding ferric chloride)



- Bredig arch method
- In this method two metallic wires functioning as electrodes are immersed into water, then on both ends of wires is given a strong enough electric current to be evaporated and then it is dispersed into water to form a metallic sol.

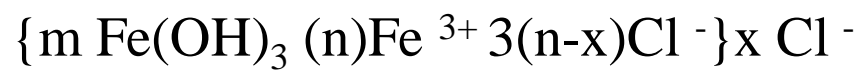
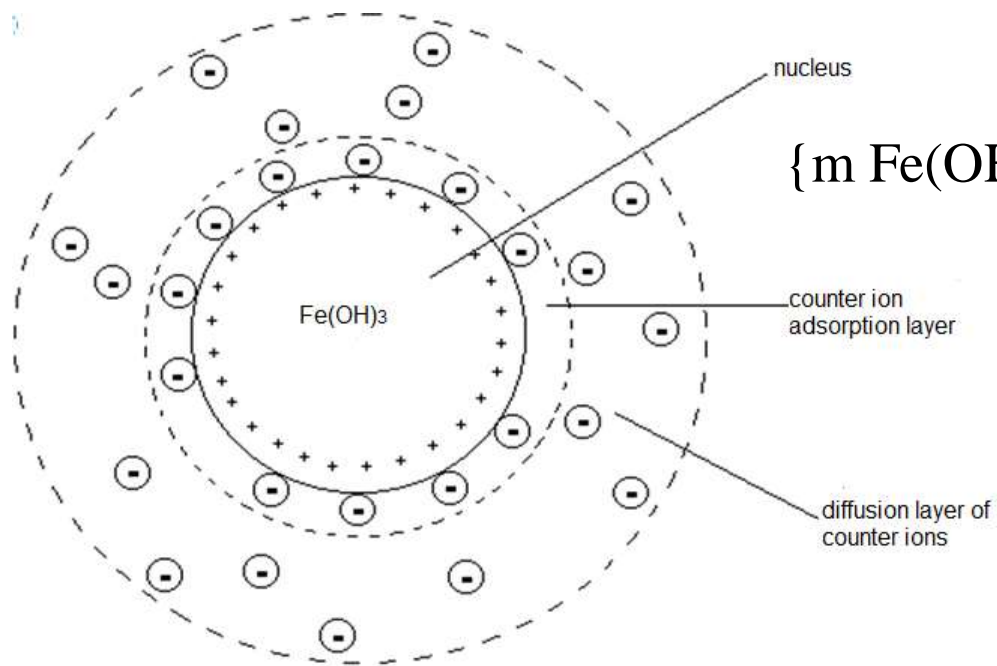


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- *Physical condensation methods.*
- *Method of physical state change.*
- The base of this method for dispersed particles obtaining is the separation of the new phase particles from vapour (at condensation) or from a liquid (at crystallization).
- A necessary condition for physical condensation is the deviation of an initial homogeneous system (vapour or liquid) from the state at some particular temperature or pressure. Colloidal solutions of sulphur are obtained by passing their vapour through cold water containing a stabiliser.
- *Method of solvent replacement.* If a solution of sulphur or phosphorus in alcohol is poured into water, a colloidal solution of sulphur or phosphorus is obtained due to low solubility in water.



- *Chemical condensation methods.* The chemical methods involve chemical reaction in a medium in which the dispersed phase is sparingly soluble.
- $\text{HAuCl}_4 + 2\text{K}_2\text{CO}_3 + \text{H}_2\text{O} = \text{Au}(\text{OH})_3 + 2\text{CO}_2 + 4\text{KCl}$
- $2\text{Au}(\text{OH})_3 + \text{K}_2\text{CO}_3 = 2\text{KAuO}_2 + 3\text{H}_2\text{O} + \text{CO}_2$
- $2\text{KAuO}_2 + 3\text{HCOH} + \text{K}_2\text{CO}_3 = 2\text{Au} + 3\text{HCOOK} + \text{KHCO}_3 + \text{H}_2\text{O}$
- 
- Another example is preparation of Prussian blue solution and formation a ferric hydroxide sol:
- $4\text{FeCl}_3 + 3\text{K}_4[\text{Fe}(\text{CN})_6] = \text{Fe}_4[\text{Fe}(\text{CN})_6]_3 + 12\text{KCl}$
- $\text{FeCl}_3 + 3\text{H}_2\text{O} = \text{Fe}(\text{OH})_3 + 3\text{HCl}$

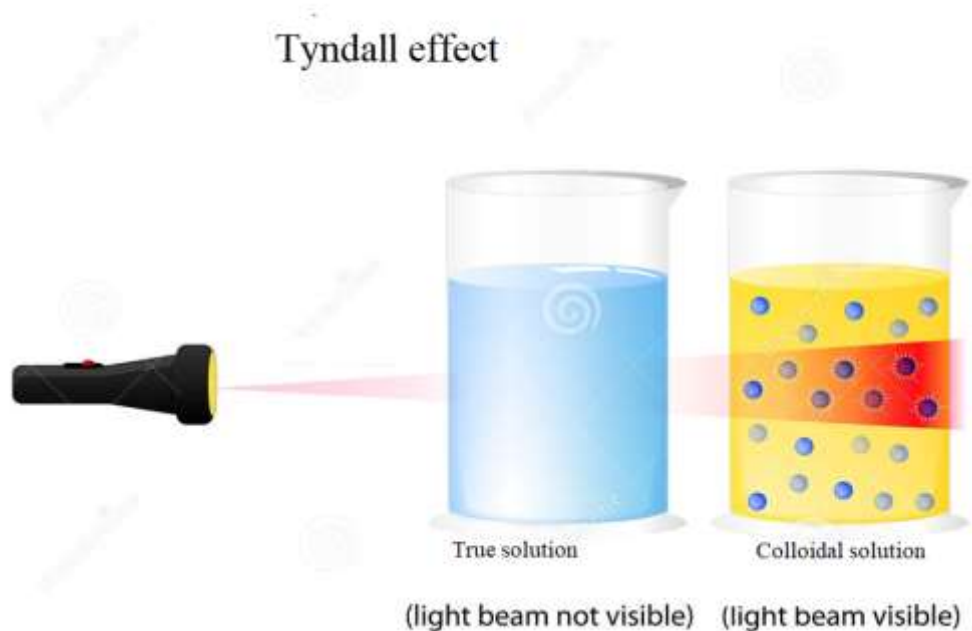






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- Optical properties of colloid systems.
- Rayleigh equation.
- Ultramicroscopy.





When a beam of light is directed at a colloidal solution or dispersion, some of the light may be absorbed (colour is produced when light of certain wavelengths is selectively absorbed), some is **scattered** and the remainder is transmitted undisturbed through the sample.

Light scattering results from the electric field associated with the incident light inducing periodic oscillations of the electron clouds of the atoms of the material in question - these



## Rayleigh equation

$$I_{sc} = I_0 24 \pi^3 \left( \frac{n_1^2 - n_0^2}{n_1^2 + 2n_0^2} \right)^2 \frac{v \nu^2}{\lambda^4}$$

$I_0$  and  $I_{sc}$  – intensity of incident and scattering light,

$n_1$  and  $n_0$  - coefficients of refraction of dispersed phase and dispersion medium;

$v$ -partial concentration of particles;

$\nu$ -volume of dispersed phase particles;  $\lambda$ -length of wave of incident light.

$d \approx 0,1 \lambda$  term of the Rayleigh equation.

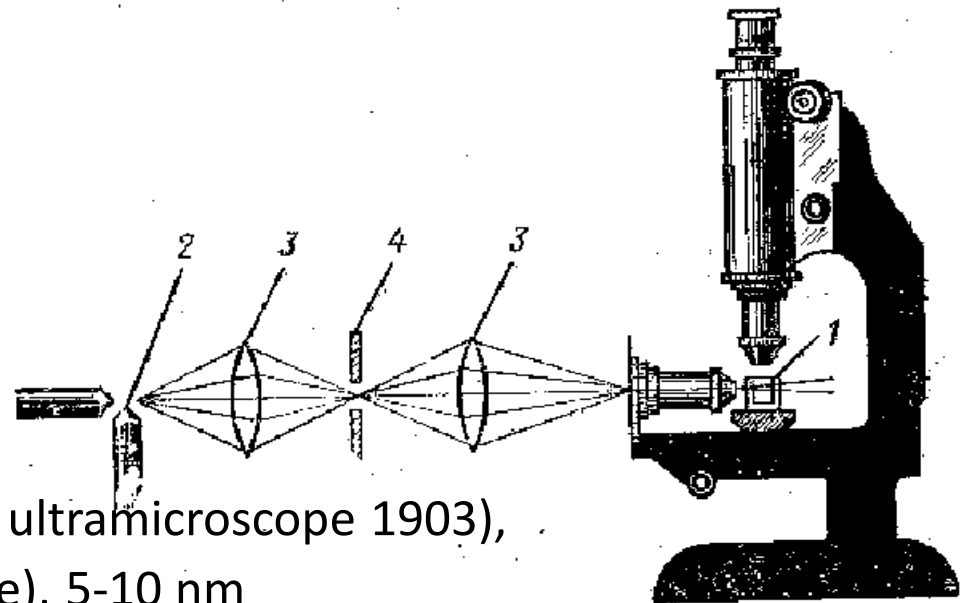


## • Ultramicroscopy

- 1- colloidal solution
- 2 – light source
- 3 – lens
- 4 – diaphragm

- Siedentopf and Zsigmondy (slit ultramicroscope 1903),
- Derjaguin (flow ultramicroscope), 5-10 nm

- Ultramicroscopy is an extremely useful technique for studying colloidal dispersions and obtaining information concerning average size, polydispersity, asymmetry of particles, molecular-kinetic properties.





- References:

1. Duncan J. Show. Introduction to colloid and surface chemistry 4th, 2003 - 306 p.
2. Shchukin E.D., Pertsov A.V., Amelina E.A., Zelenev A.Z. Colloid and surface chemistry. Elsevier, 2001 747 p.
3. Сумм Б.Д. Основы коллоидной химии. М., Изд-во центр «Академия», 2007, 238 с.
4. Фридрихсберг. Курс коллоидной химии. Л.: Химия, 1984, 368с.

- *Thank you for your attention!*