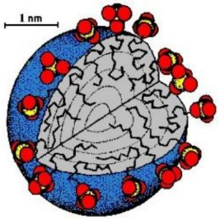
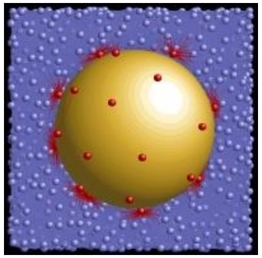
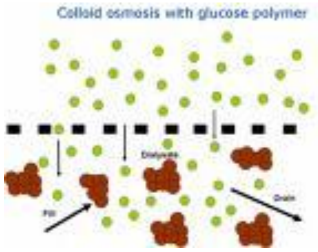
Introduction to

Colloid & Surface Chemistry



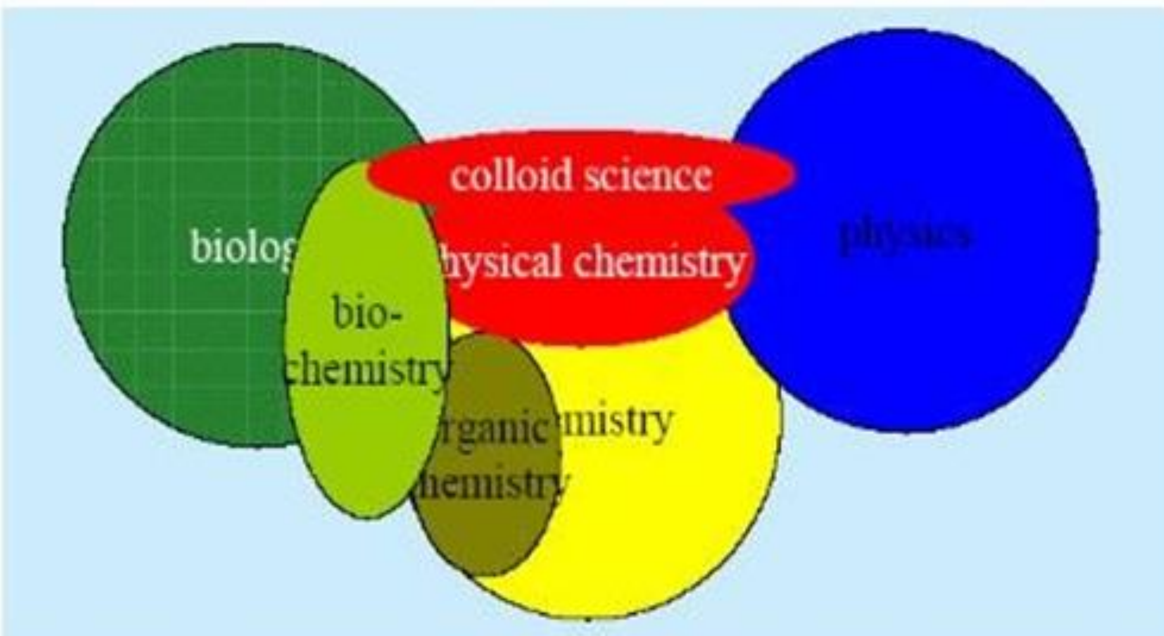




Part 1
Colloidal state

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



Examples of colloidal systems from daily life

Foams

Milk

Fog, smoke

Detergents

Aerogel

Blood

Paints

Cosmetics

Background (Old and new conceptions of colloids)

- In 1861, Thomas Graham divided soluble substances into two classes according to diffuse into water across a permeable membrane:
- He observed that crystalline substances such as sugar, urea, and sodium chloride passed through the membrane, while others like glue, gelatin and gum did not.

Thomas Graham

- He called the former **crystalloids** and the latter **colloids** (Greek, kolla = glue). Graham thought that the difference in the behavior of 'crystalloids' and 'colloids' was due to the particle size.

Crystalline

amorphous

Crystalloids:

Diffuse rapidly across vegetable or animal membranes such as salt, sugar and urea.

Colloids:

Exhibit little or no tendency to diffuse across vegetable or animal membranes such as gelatin, starch and gum.

Greek: *kola*= glue and *eiods*= like

Background (Old and new conceptions of colloids)

- According to Graham NaCl is crystalloid but it has been obtained in the colloidal state in benzene.
- Soap behaves as colloid in water and as crystalloid in alchohol

Later it was realized that (New conception):

► The difference in the rate of diffusion between crystalloids and colloids is due to the difference in the particle size

► Any substance, regardless of its nature, could be converted into a colloid by subdividing it into particles of colloidal size.

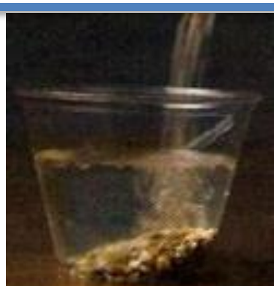
► We should speak of the colloidal state of matter as we speak of the gaseous, liquid or solid state of matter rather than to call a particular material as colloid or crystalloid

Nature of colloidal solutions (What are colloids)?

Sugar + water

True solution

1- 10 A^{o}



Sand + water

Suspension

>1000 A^{o}

Starch + water

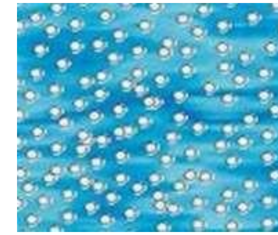
Colloidal solution

10- 1000 A^{o}

Nature of colloidal solutions (What are colloids) ?

In **a true solution** as sugar or salt in water, the solute particles are dispersed in the solvent as single molecules with diameter less than 1 nm

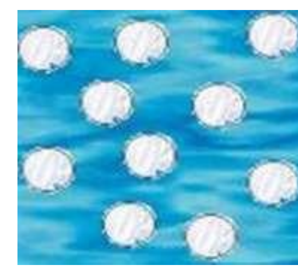
Sugar + water (true solution(



< 1 nm

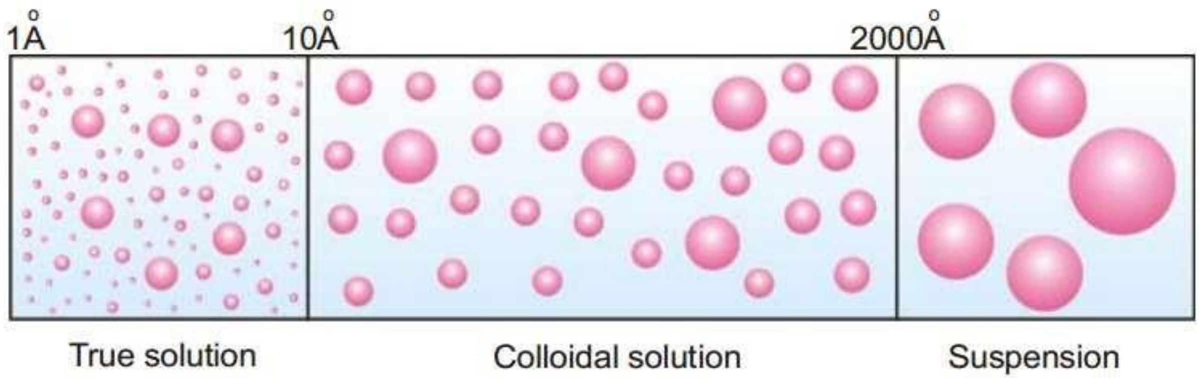
On the other hand, if **a suspension** as sand stirred into water, the dispersed particles are aggregates of millions of molecules. The diameter of these particles is of the order 1 000‹Å or more

Sand + water (suspension(



<1 000Å

The colloidal solutions or colloidal dispersions are intermediate between true solutions and suspensions. In other words, the diameter of the dispersed particles in a colloidal dispersion is more than that of the solute particles in a true solution and smaller than that of a suspension.



Examples of colloidal solutions

Ink

Paint

Colloidal Gold

Nature of colloidal solutions (What are colloids) ?

True solution	Suspension	Colloidal solution
1- 10 A°	>1000 A°	10- 1000 A°
Transparent to light	Not transparent to light	Not transparent to light

Nature of colloidal solutions (What are colloids) ?

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Not influenced by the gravitational pull and remain suspended in the solvent all the time	They are influenced by the gravitational pull and settle down automatically on standing	Not influenced by the gravitational pull and remain suspended in the solvent all time

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Not influenced by the gravitational pull and remain suspended in the solvent all the time	They are influenced by the gravitational pull and settle down automatically on standing	Not influenced by the gravitational pull and remain suspended in the solvent all time
Pass through an ordinary filter paper	Retained by an ordinary filter paper	Pass through an ordinary filter paper

Colloidal particles under microscope

Light microscope

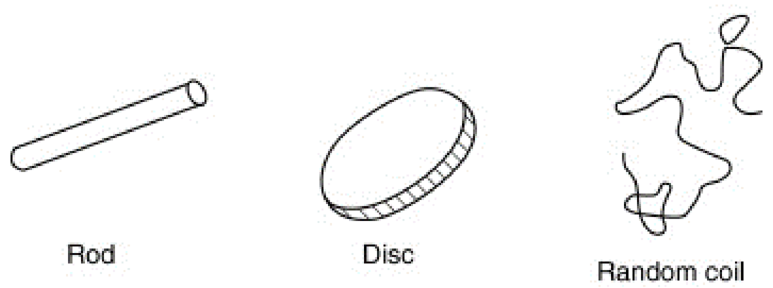
Ultra- microscope

Electron microscope

The colloidal particles are smaller than the wavelength of the visible light. Thus, they are unable to reflect light and hence cannot be seen by ordinary microscope

Note that

The colloidal particles are not necessarily corpuscular in shape. In fact, these may be rod-like, disc-like, thin films, or long filaments. For matter in the form of corpuscles, the diameter gives a measure of the particle size .



However, in other cases one of the dimensions (length, width and thickness) has to be in the colloidal range for the material to be classed as colloidal .

Thus in a broader context we can say:

“A system with at least one dimension (length, width, or thickness) of the dispersed particles in the range 10 Å to 1 000‹Å, is classed as a colloidal dispersion”

Classification of colloids

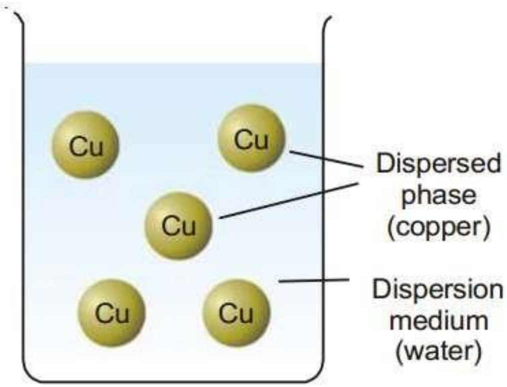
Classification is based on following criteria:

1. Physical state of dispersed phase and dispersion medium.
2. Nature of interaction between dispersed phase and dispersion medium.
3. Types of particles of the dispersed phase.

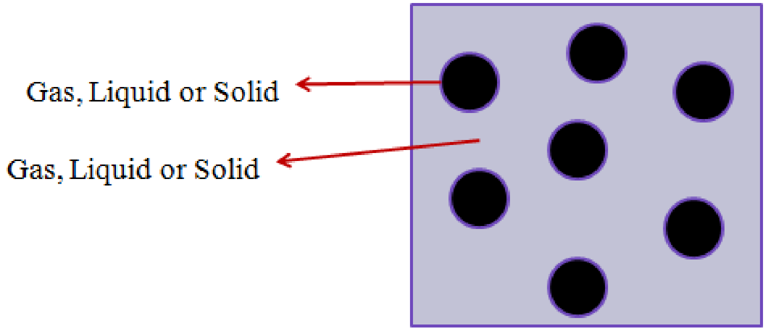
Classification based on physical state of dispersed phase and dispersion medium

Any colloidal system is made of two phases. The substance distributed as the colloidal particles is called the **Dispersed Phase** and the second continuous phase in which the colloidal particles are dispersed is called the **Dispersion Medium.**

For example, for a colloidal solution of copper in water, copper particles constitute the dispersed phase and water the dispersion medium.



Either the dispersed phase or the dispersion medium can be a gas, liquid or solid



A colloidal dispersion of one gas in another is not possible since the two gases would give a homogeneous molecular mixture. So that, there are **Eight** possible types of colloidal systems

	X								
Dispersed phase	Gas	Gas	Gas	Liquid	Liquid	Liquid	Solid	Solid	Solid
Dispersion medium	Gas	Liquid	Solid	Gas	Liquid	Solid	Gas	Liquid	Solid

1 Foam

Dispersed phase: Gas **Dispersion medium: Liquid**

Examples

Whipped cream

Shaving cream

Soda water

Soap Solution

2 Solid Foam

Dispersed phase: Gas **Dispersion medium: Solid**

Examples

Cork stoppers

Pumice stone

Foam rubber

Marshmallow

3 **Aerosol**

Dispersed phase: Liquid **Dispersion medium: Gas**

Examples

Cloud

Aerosol spray

Mist

Fog

4 **Emulsion**

Dispersed phase: Liquid **Dispersion medium: Liquid**

Examples

Milk

Hair cream

Mayonnaise

Emulsified water

5 Solid Emulsion (Gel)

Dispersed phase: Liquid

Dispersion medium: Solid

Examples

Butter

Cheese

Jelly

Boot Polish

6 Smoke

Dispersed phase: Solid **Dispersion medium:** Gas

Examples

7 Sol (Colloidal Solutions)

Dispersed phase: Solid
Dispersion medium: Liquid

Examples


Ink


Paint

Colloidal Gold

8 Solid Sol

Dispersed phase: Solid

Dispersion medium: Solid

Examples


Colored Glass



Metal Alloys

Classification of colloids

Classification is based on following criteria:

1. Physical state of dispersed phase and dispersion medium.
2. Nature of interaction between dispersed phase and dispersion medium.
3. Types of particles of the dispersed phase.

Classification based on nature of interaction

Solid dispersed in liquid (Sols(

Lyophilic (solvent-loving) **and Lyophobic** (solvent-hating) **sols**

Lyophilic sols: are those in which the dispersed phase exhibits a definite affinity for the medium or the solvent.

The examples of Lyophilic sols are dispersions of starch, gum, and protein in water.

Lyophobic sols: are those in which the dispersed phase has no attraction for the medium or the solvent.

The examples of Lyophobic sols are dispersion of gold, iron (III) hydroxide and sulphur in water.

Solid dispersed in liquid (Sols(

Lyophilic (solvent-loving) **and Lyophobic** (solvent-hating) **sols**

- The affinity or attraction of the sol particles for the medium, in a lyophilic sol, is due to hydrogen bonding with water .
- If the dispersed phase is a protein (as in egg) hydrogen bonding takes place between water molecules and the amino groups ($-NH-$, $-NH_2$) of the protein molecule.
- In a dispersion of starch in water, hydrogen bonding occurs between water molecules and the – OH groups of the starch molecule.
- There are no similar forces of attraction when sulphur or gold is dispersed in water.

Differences between lyophilic and lyophobic sols

Lyophilic Sols	Lyophobic Sols
1. Prepared by direct mixing with dispersion medium.	**1.** Not prepared by direct mixing with the medium.
2. Little or no charge on particles.	**2.** Particles carry positive or negative charge.
3. Particles generally solvated.	**3.** No solvation of particles.
4. Viscosity higher than dispersion medium; set to a gel.	**4.** Viscosity almost the same as of medium; do not set to a gel.

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5. Precipitated by high concentration of electrolytes.	**5.** Precipitated by low concentration of electrolytes.
6. Reversible.	**6.** Irrerversible.
7. Do not exhibit Tyndall effect.	**7.** Exhibit Tyndall effect.
8. Particles migrate to anode or cathode, or not at all.	**8.** Particles migrate to either anode or cathode.

Preparation of sols

<u>Lyophilic sols</u> may be prepared by simply warming the solid with the liquid dispersion medium e.g., starch with water.

Preparation of sols

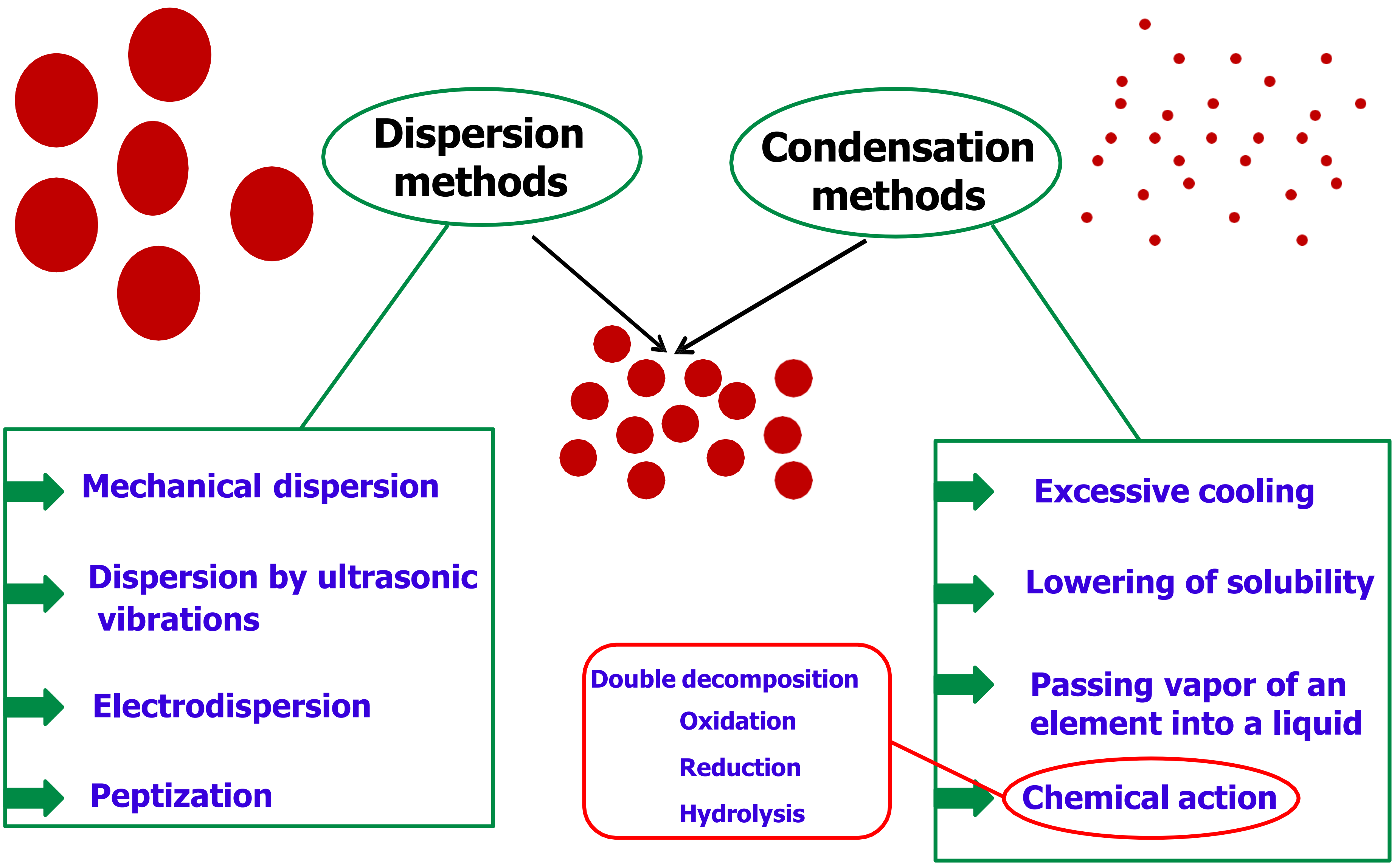
Lyophobic sols

Have to be prepared by special methods. These methods fall into two categories :

Dispersion Methods: in which larger macro-sized particles are broken down to colloidal size.

Aggregation (Condensation) Methods: in which colloidal size particles are built up by aggregating single ions or molecules of true solution

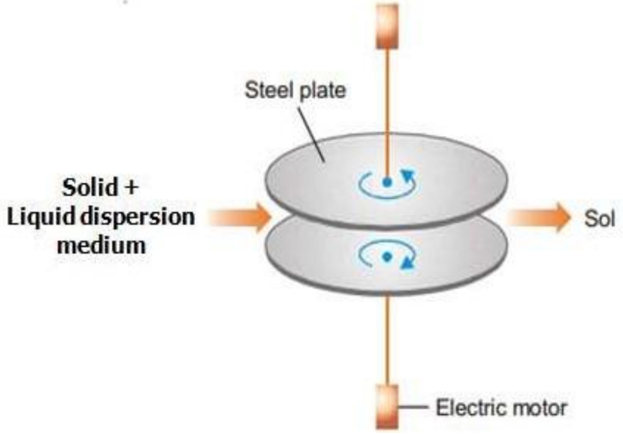
Preparation of colloidal solutions



A- Dispersion Methods

-1Mechanical dispersion using colloid mill

- The solid along with the liquid dispersion medium is fed into a Colloid disk mill.
- The mill consists of two steel plates nearly touching each other and rotating in opposite directions with high speed.
- The solid particles are ground down to colloidal size and are then dispersed in the liquid to give the sol.
- Colloidal graphite and printing inks are made by this method.

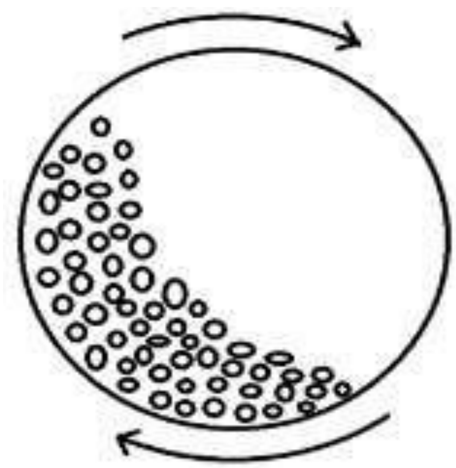


Disk mill

A- Dispersion Methods

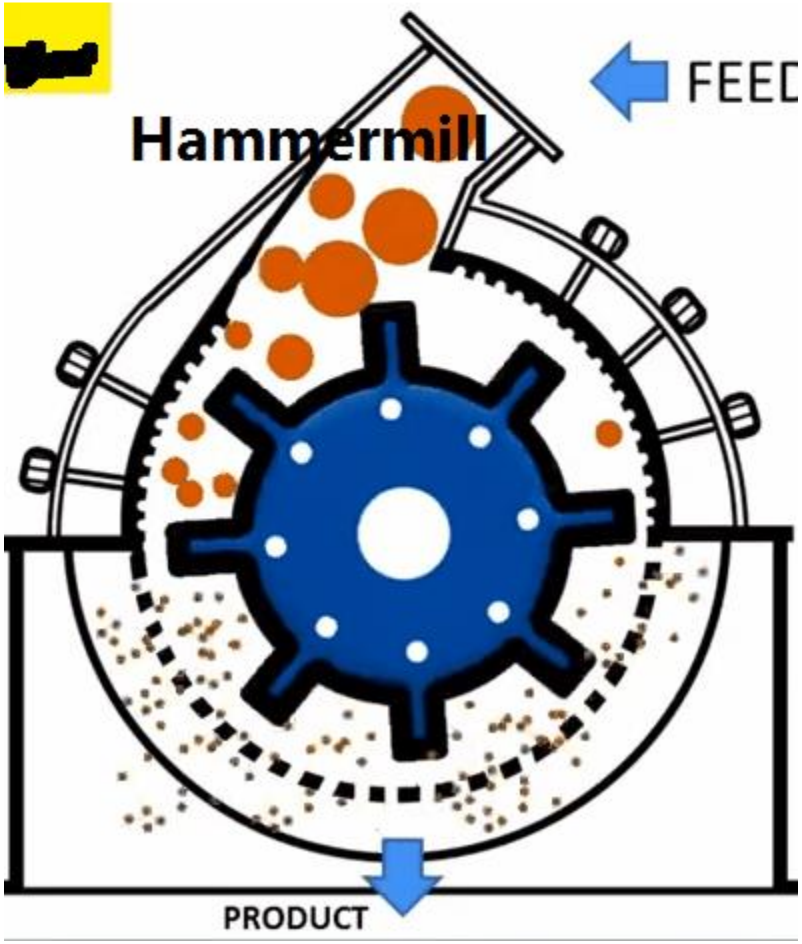
-1Mechanical dispersion using colloid mill

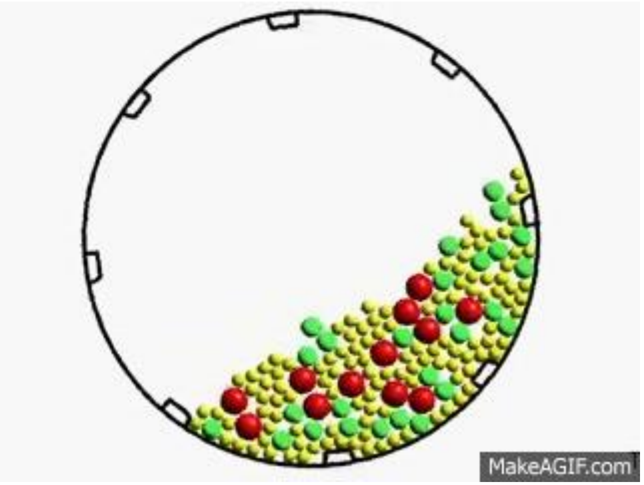
- A colloidal ball mill can also employed to obtain a colloidal solution from suspension .
- Due to the high speed rotation of the mill the coarse particles roll over one another to form fine particles of the colloidal size.



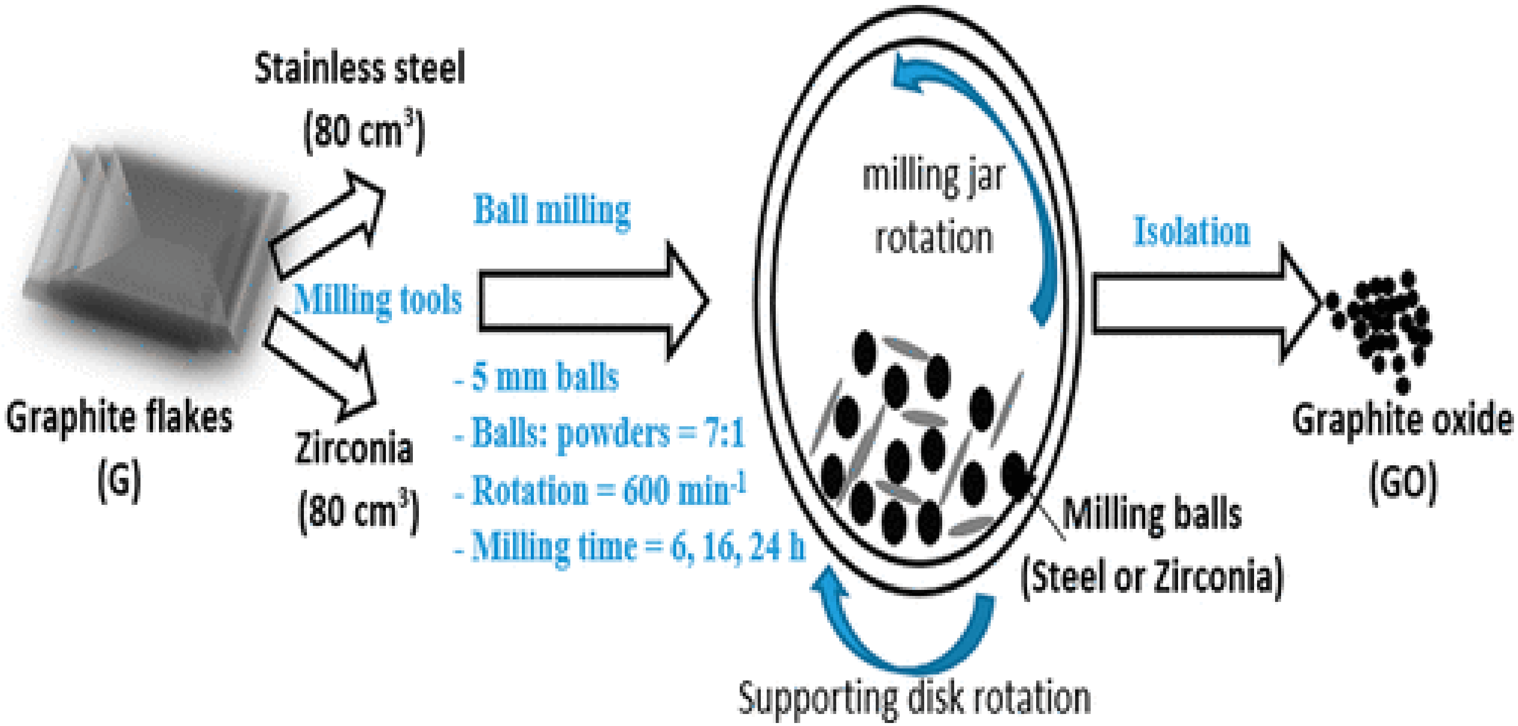
Ball mill

1- Mechanical dispersion using colloid mill





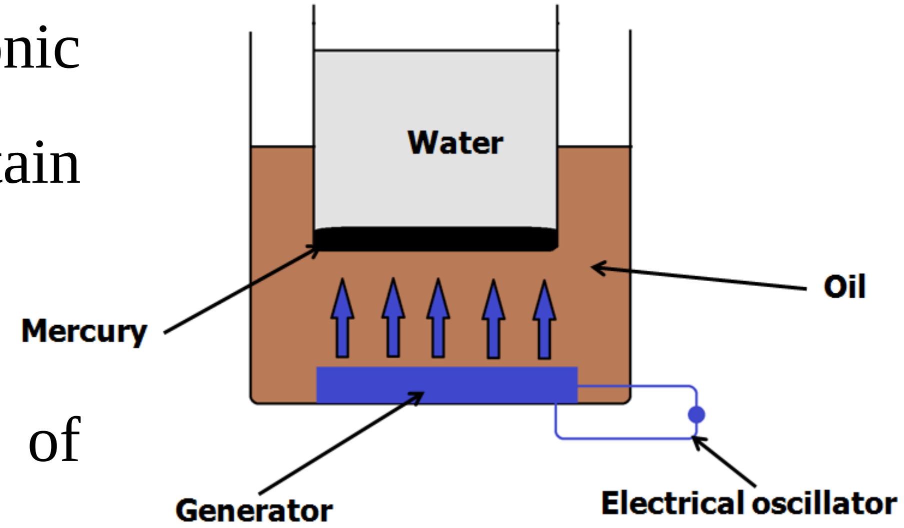
-1Mechanical dispersion using colloid mill



Ref: Sustainable Synthesis of High-Surface-Area Graphite Oxide via Dry Ball Milling, Alaa El Din Mahmoud, Achim Stolle, and Michael Stelter, *ACS Sustainable Chem. Eng.* 2018, 6, 5, 6358–6369.

-2Dispersion by ultrasonic vibrations

- In this case, the transformation of coarse particles to the colloidal size is carried out using the ultrasonic vibrations produced by a certain generator.

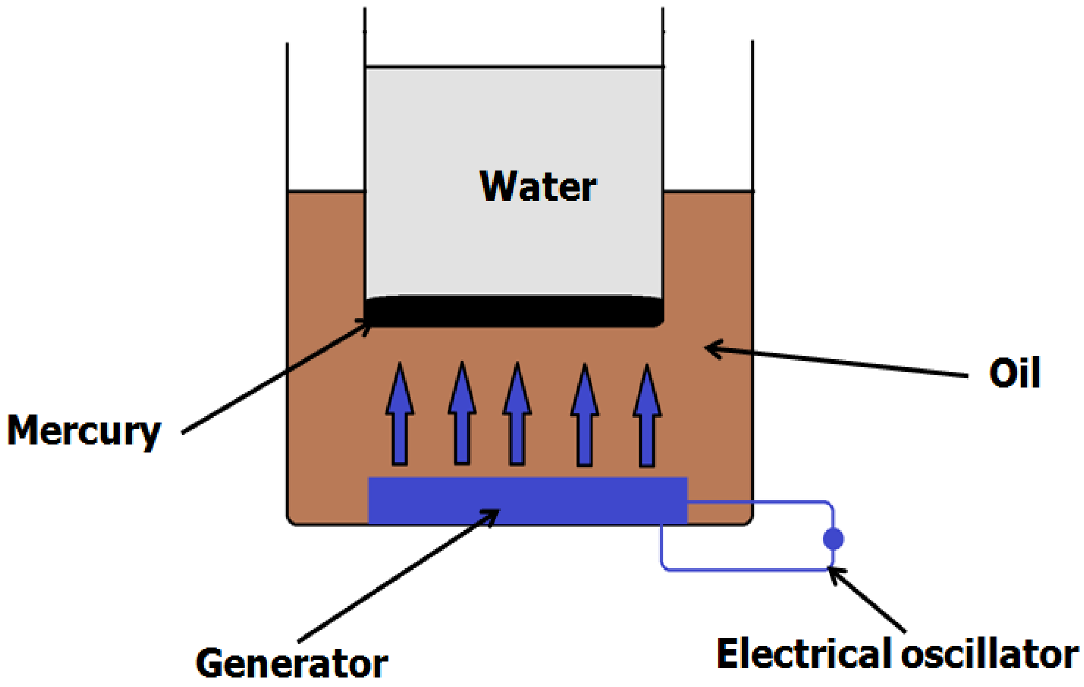


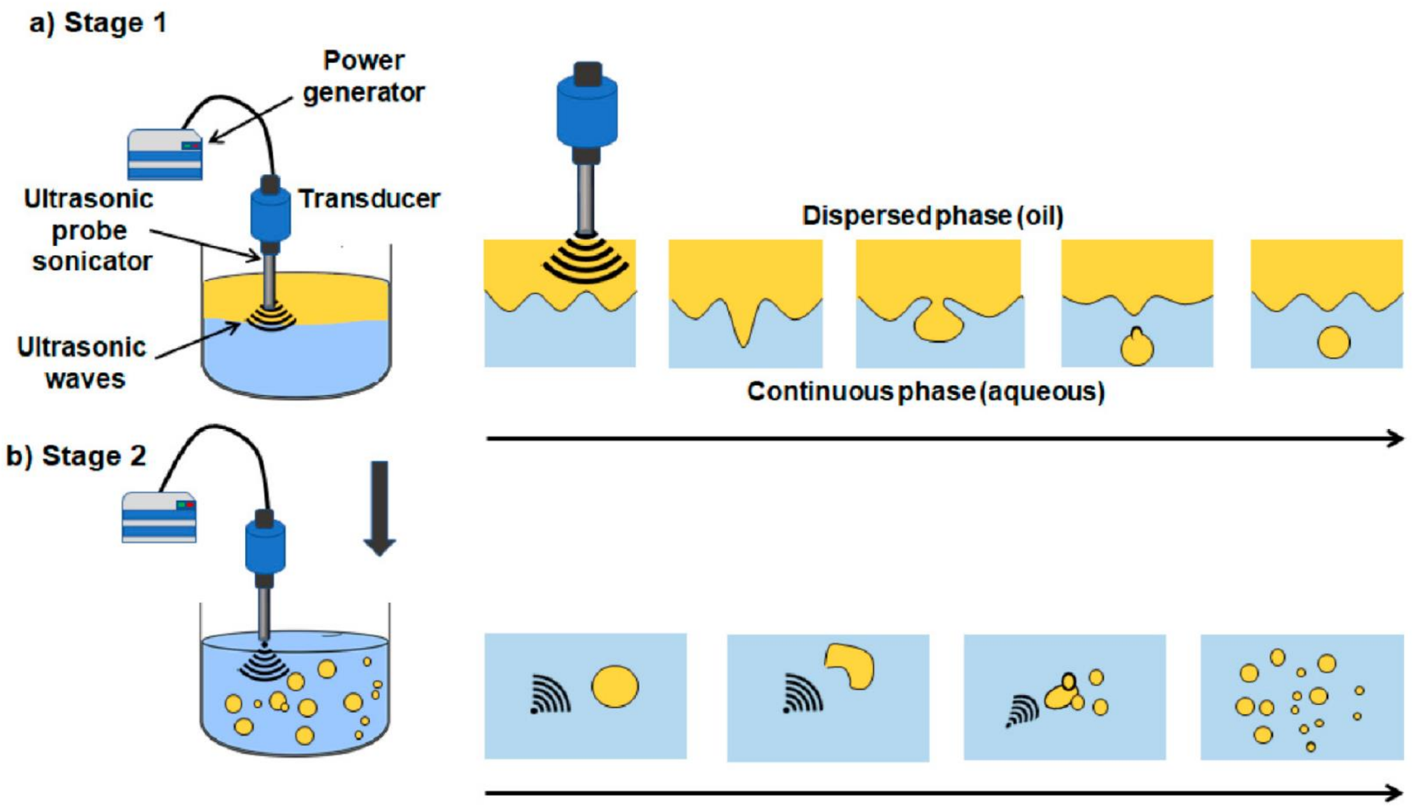
- The figure shows the formation of colloidal solution of mercury in water.

- Ultrasonic vibrations spread through the oil and hit the vessel having mercury under water .

-2Dispersion by ultrasonic vibrations

- The ultrasonic vibrations travels through the walls of the mercury container and produce clouds of mercury which form the mercury sol.





Schematic representation of ultrasonic emulsification.

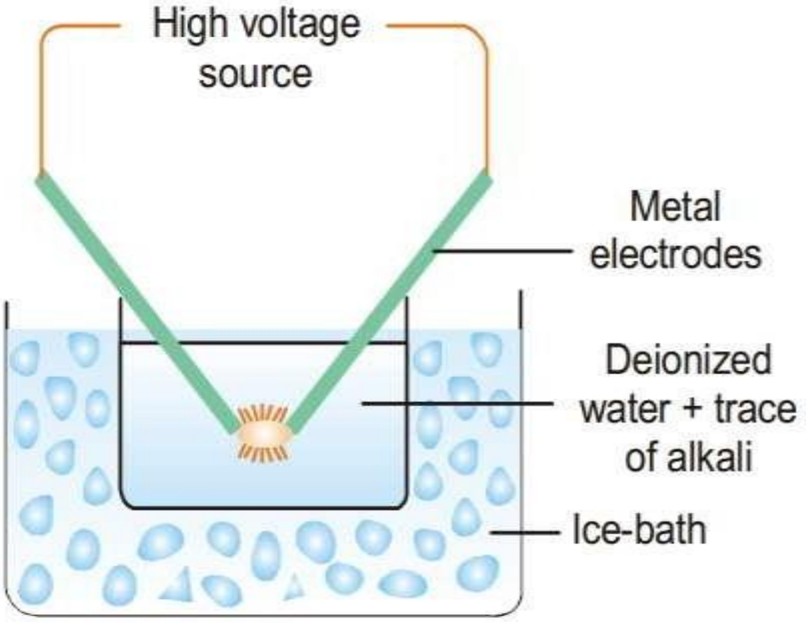
(a) The shear forces generated during acoustic cavitation near the interface between the aqueous phase and oil phase promote the eruption of large oil drops (dispersed phase) in the continuous aqueous phase.

(b) The oil droplets formed in the first stage are reduced to smaller droplets as a consequence of the shock waves generated during cavitation

(adapted from Perdih et al., 2019 and Plüisch and Wittemann, 2016).

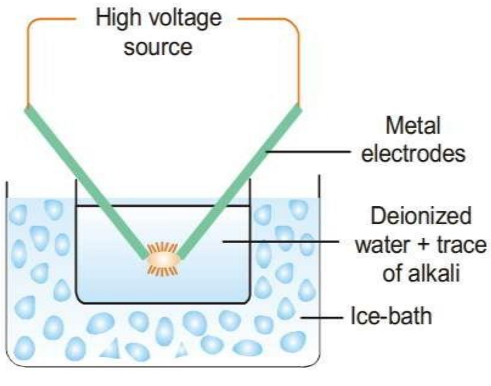
-3Bredig's Arc Method (electrical disintegration)

- It is used for preparing hydrosols of metals e.g., silver, gold and platinum .
- An arc is struck between the two metal electrodes held close together in de- ionized water with trace of alkali .
- The water is kept cold by immersing the container in ice/water bath.
- The intense heat of the spark across the electrodes vaporizes some of the metal and the vapor condenses under water.

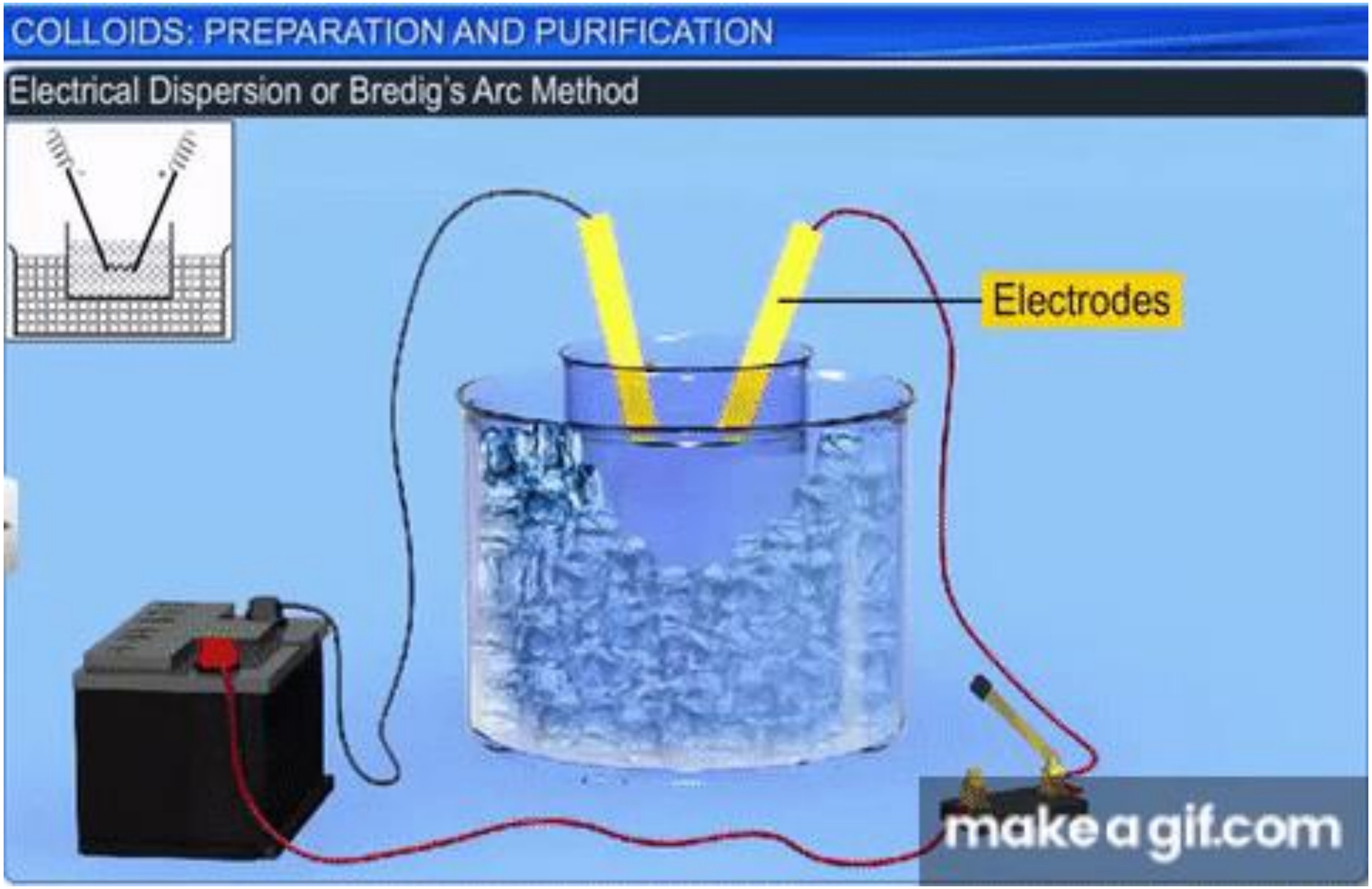


-3Bredig's Arc Method

- Thus the atoms of the metal present in the vapour aggregate to form colloidal particles in water .
- Since the metal has been ultimately converted into sol particles (via metal vapour), this method has been treated as of dispersion method also.
- Non-metal sols can be made by suspending coarse particles of the substance in the dispersion medium and striking an arc between iron electrodes.
- This method is not suitable when the dispersion medium is an organic liquid as considerable charring occurs.



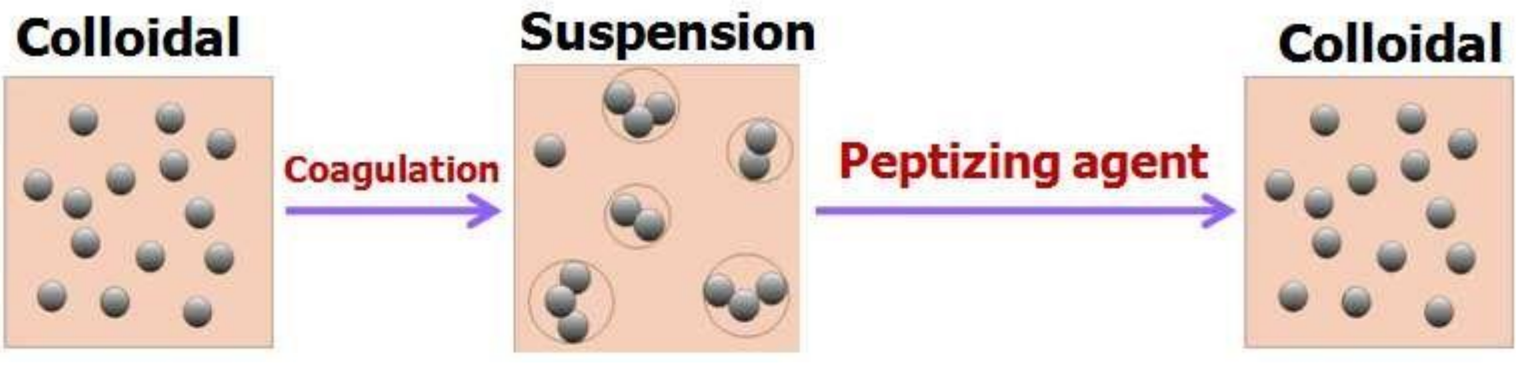
3- Bredig's Arc Method



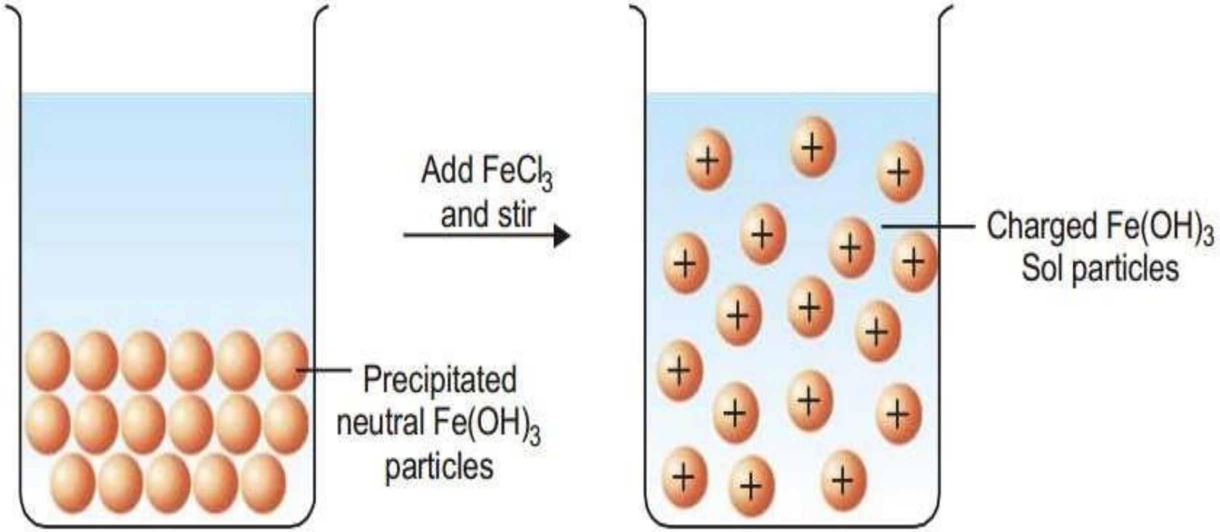
-4Peptization

- Some freshly precipitated ionic solids are dispersed into colloidal solution in water by the addition of small quantities of electrolytes, particularly those containing a common ion .

- The precipitate particles adsorbs the common ions to be electrically charged particles, then split from each other to form colloidal solution.



Sol of ferric hydroxide is obtained by stirring fresh precipitate of ferric hydroxide with a small amount of $FeCl_3$

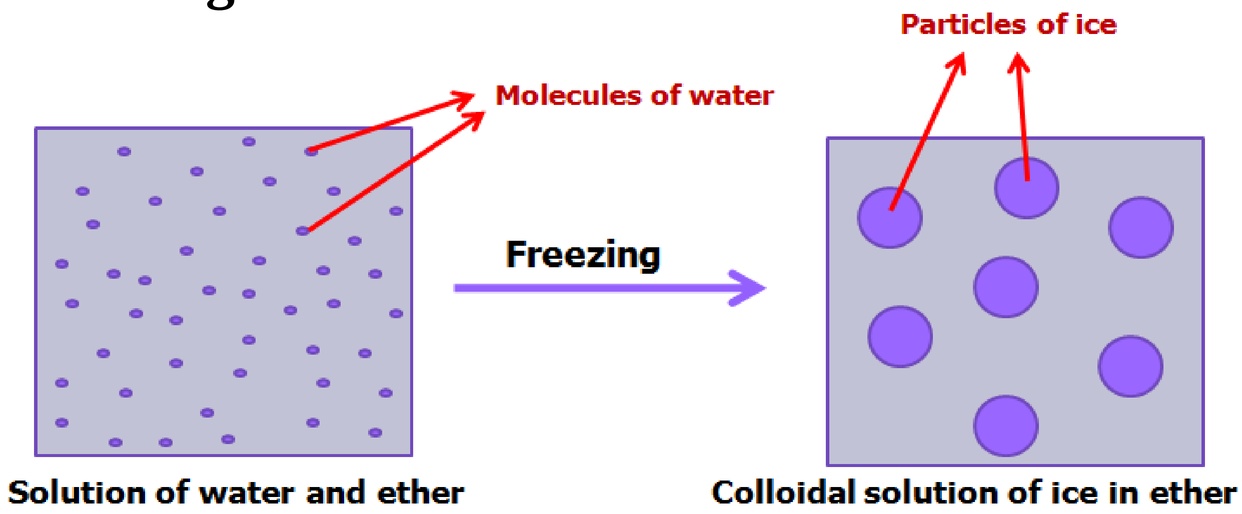


- The transformation of a precipitated material to colloidal solution by the action of an electrolyte in solution, is termed **peptization** which is the reverse of **coagulation** and the electrolyte used is called a peptizing agent.
- Another examples of preparation of sols by peptization is silver chloride, AgCl which can be converted into a sol by adding hydrochloric acid

B- Aggregation Methods

The more important aggregation methods are:

-1Extensive cooling



- The colloidal solution of ice in an organic solvent like ether is obtained by freezing a solution of water in the solvent .
- As a result of the sudden freezing of the solution, the molecules of water held together to form particles in the colloidal size dispersed in the organic solvent (ether(

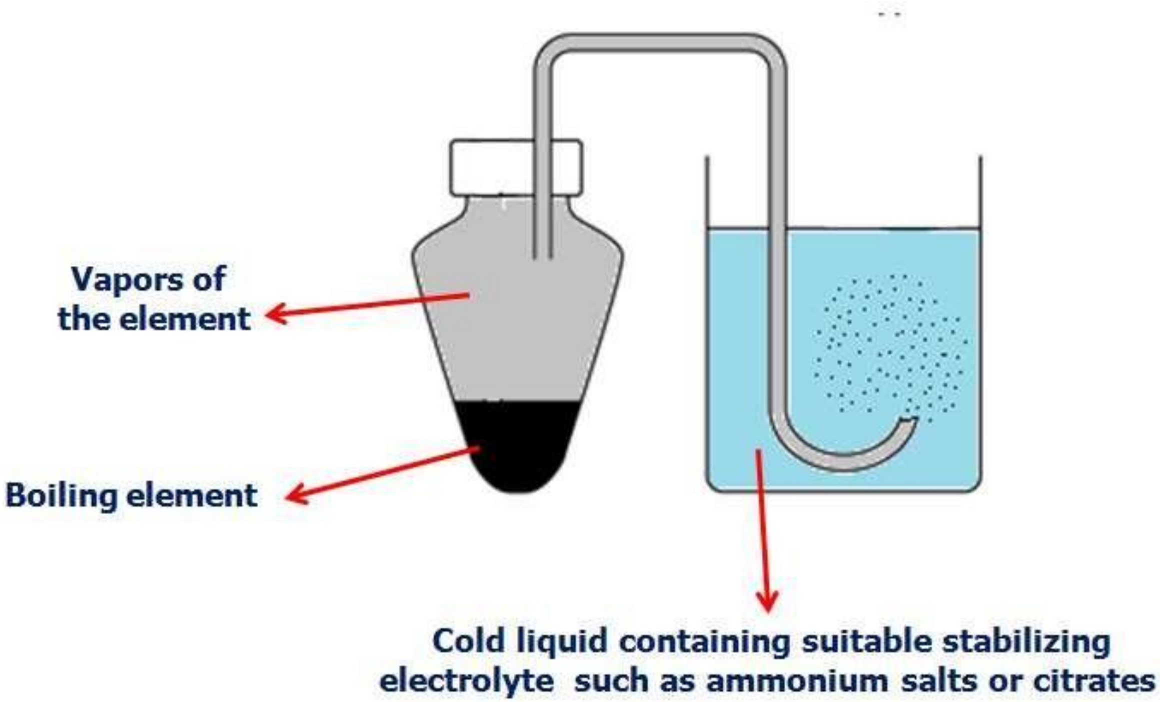
-2Lowering of solubility by exchange of solvent

- Substances like **sulphur**, **phosphorous**, etc., which are more soluble in alcohol than in water give a hydrosol by pouring a small amount of their alcoholic solution in excess of water .

- By the transference from alcohol to water, the substance is transformed from the **molecular state (true solution)** to the **colloidal state** by the coagulation of molecules together to form particles in the colloidal range.

- Phenolphthalein indicator, for example, is soluble in alcohol and not in water, so that, it is supplied to laboratory as alcoholic solution. If water is added to this solution, a milky liquid of colloidal phenolphthalein in water is produced.

-3Passing vapor of an element into a liquid



- If the vapors of a boiling element are conducted into a cold liquid, condensation takes place. Sometimes, this condensation resulted in the formation of a stable sol .
- Mercury and sulphur sols can be prepared by this method.

-4Chemical action

a- Double decomposition

- An arsenic sulphide (As_2S_3) sol is prepared by passing a slow stream of hydrogen sulphide gas through a cold solution of arsenious oxide (As_2O_3).

$$As_2O_3 + 3\,H_2S \rightarrow As_2S_{3(\text{yellow sol})} + 3\,H_2O$$

- This is continued till the yellow colour of the sol attains maximum intensity.

-4Chemical action

b- Reduction

Silver sols and gold sols can be obtained by treating dilute solutions of silver nitrate or gold chloride with suitable reducing agents

$$AgNO_3 \xrightarrow{\text{Reducing agent}} \text{Ag sol}$$

$$AuCl_3 \xrightarrow{\text{Reducing agent}} \text{Au sol}$$

Reducing agents could be organic reducing agents like tannic acid or formaldehyde or others.

c- Oxidation

A sol of sulphur is produced by passing hydrogen sulphide into a solution of sulphur dioxide.

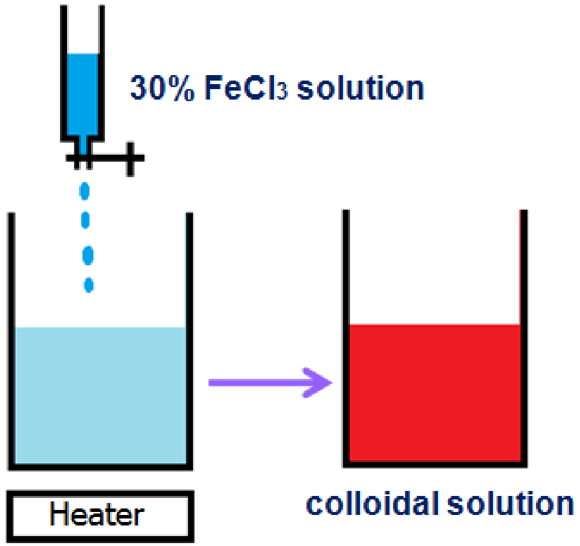
$$2H_2S + SO_2 \longrightarrow 2H_2O + S\downarrow$$

Or exploring H_2S to air for a long time

$$H_2S + O \rightarrow H_2O + S$$

d- Hydrolysis

- Sols of the hydroxides of **iron**, **chromium** and **aluminium** are readily prepared by the hydrolysis of salts of the respective metals .



- In order to obtain a red sol of ferric hydroxide, a few drops of 30% ferric chloride solution is added to a large volume of almost boiling water and stirred with a glass rod.

$$FeCl_3 + 3H_2O \longrightarrow \underset{\text{red sol}}{Fe(OH)_3} + 3HCl$$

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:

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

Condensation method

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

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).

Condensation method

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.