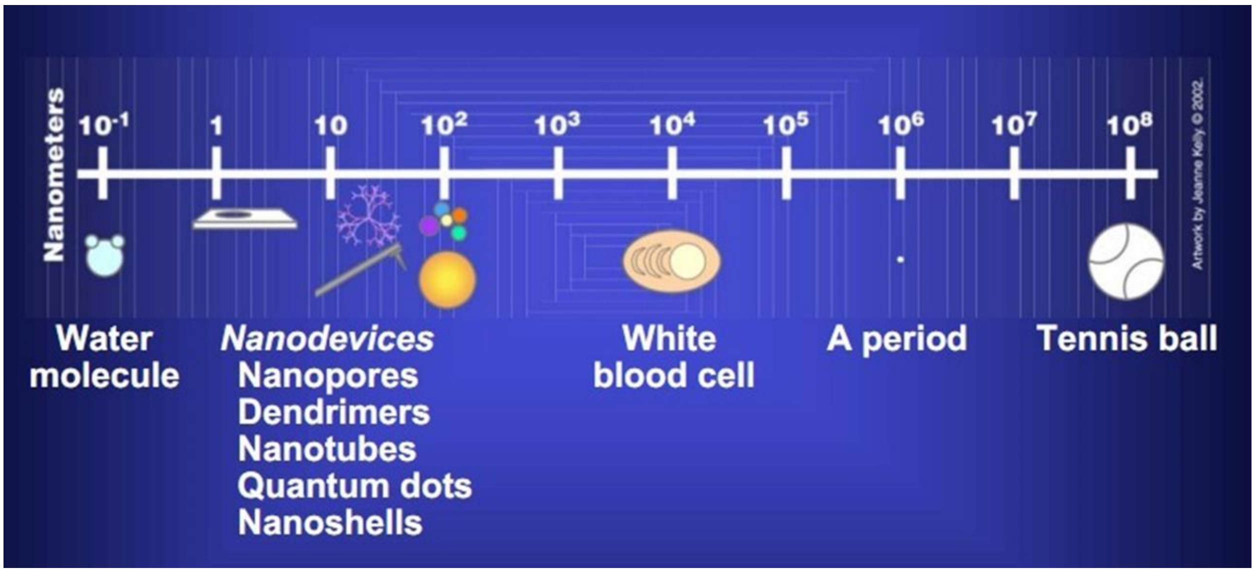
Unit-5
Nano materials and Colloidal chemistry

Introduction to Nano materials:-

- Nanomaterials are commonly defined as materials with an average grain size less than 100 nanometers
- Nanomaterials have extremely small size which having at least one dimension 100 nm
- One billion nanometers equals one meter
- The average width of a human hair is on the order of 100,000 nanometers
- A single particle of smoke is in the order of 1,000 nanometers

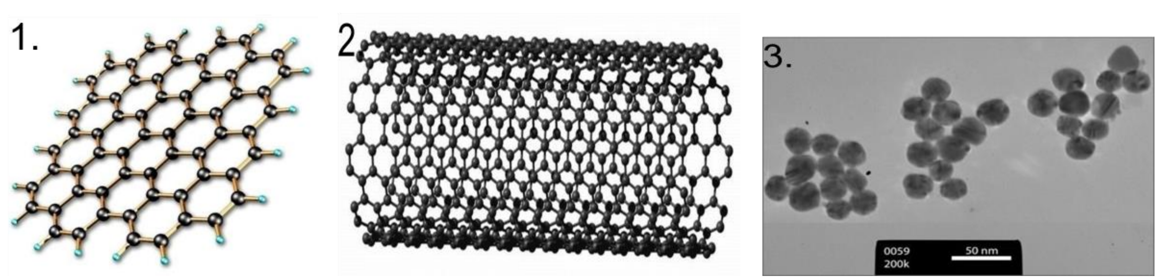
How small is1 nanometer?



Nanomaterials shapes:-

- Nanomaterials can be nanoscale in Zero dimension & **one dimension** (surface films)
- **Two dimensions** (strands or fiber)
- **Three dimensions** (particles)

They can exist in single or fused forms with spherical, tubular, and irregular shapes.



Applications of nano materials:-

MEDICINE:

- Provide new options for drug delivery and drug therapies.
- Enable drugs to be delivered to precisely the right location in the body and release drug doses on a predetermined schedule for optimal treatment.
- Attach the drug to a nanosized carrier.
- They become localized at the disease site, i.e cancer tumour.
- Then they release medicine that kills the tumour.

- Current treatment is through radiotherapy or chemotherapy.
- Nanobots can clear the blockage in arteries

NANOTECHNOLOGY IN COMPUTERS:

- The silicon transistors in your computer may be replaced by transistors based on carbon nanotubes.
- A carbon nanotube is a molecule in form of a hollow cylinder with a diameter of around a nanometer which consists of pure carbon.
- A nanorod is an upcoming technology in the displays techniques due to less consumption of electricity and less heat emission.
- Size of the microprocessors are reduced to greater extend.

NANOTECHNOLOGY IN ELECTRONICS:-

- Electrodes made from nanowires enable flat panel displays to be flexible as well as thinner than current flat panel displays.
- Nanolithography is used for fabrication of chips.
- The transistors are made of nanowires, which are assembled on glass or thin films of flexible plastic.
- E-paper, displays on sunglasses and map on car windshields.

NANOTECHNOLOGY IN MOBILE:-

- A nanotechnology concept device developed by Nokia Research Centre (NRC) and the University of Cambridge (UK).
- The Morph will be super hydrophobic making it extremely dirt repellent.
- It will be able to charge itself from available light sources using photovoltaic nanowires grass covering its surface.

NANOTECHNOLOGY IN FABRICS:-

- The properties of familiar materials are being changed by manufacturers who are adding nano-sized components to conventional materials to improve performance.
- For example, some clothing manufacturers are making water and stain repellent clothing using nano- sized whiskers in the fabric that cause water to bead up on the surface.
- In manufacturing bullet proof jackets.
- Making spill & dirt resistant, antimicrobial, antibacterial fabrics.

NANOTECHNOLOGY IN ENERGY:-

- Energy applications of nanotechnology .An important subfield of nanotechnology related to energy is nano fabrication. Nano fabrication is the process of designing and creating devices on the nano scale. Creating devices smaller than 100 nanometres opens many doors for the development of new ways to capture, store, and transfer energy.

NANO TECHNOLOGY IN TEXTILES:-

- Textiles: - The use of engineered nanofibers already makes clothes water- and stain-repellent or wrinkle-free.
- Textiles with a nanotechnological finish can be washed less frequently and at lower temperatures. Nanotechnology has been used to integrate tiny carbon particles membrane and guarantee full- surface protection from electrostatic charges for the wearer.

NANO TECHNOLOGY IN MILITARY:-

- Military By using nanotechnology, the military would be able to create sensor systems that could detect biological agents. Nanoparticles can be injected into the material on soldiers uniforms to not only make the material more durable, but also to protect soldiers from many different dangers such as high temperatures, impacts and chemicals.

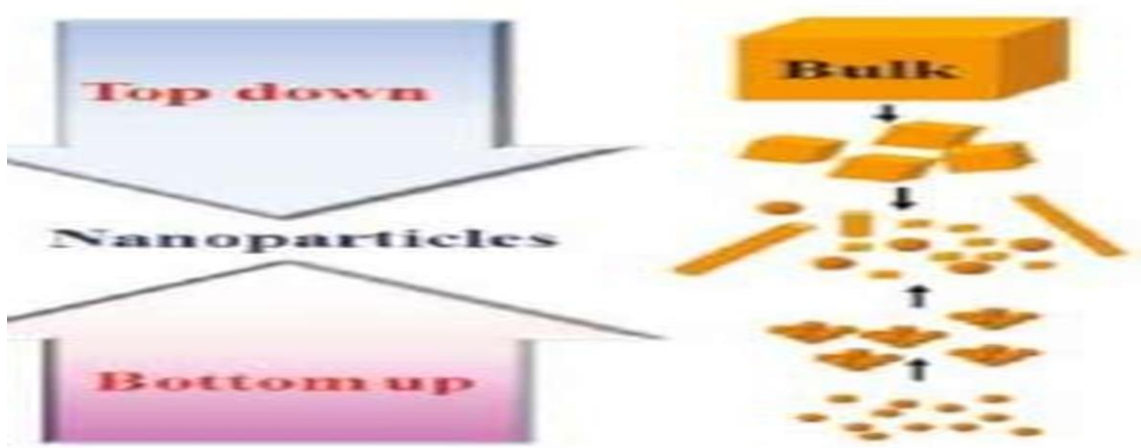
Properties of Nano materials:-

- Strength:- CNT's are the strongest and stiffest materials in terms of tensile strength and elastic module. A MWNT was tested and found tensile strength 63 giga Pascal's.
- Hardness:- The diamond is considered as hardest material. But synthesis of a super hand material by compressing SWNT to above 20 giga Pascal's at room temperature.
- Thermal conductivity:- CNT's have good thermal conductivity.
- Thermal stability:- CNT's are estimated to be up to 2800°c in vacuum and about 750°c in air of temperature stability.
- Electrical Conductivity:- CNT's have good electrical conductivity.

Chemical synthesis of nano materials: Sol-Gel method:-

Approaches:-

- **Top-down** – Breaking down matter into more basic building blocks. Frequently uses chemical or thermal methods.
- **Bottoms-up** – Building complex systems by combining simple atomic-level components.



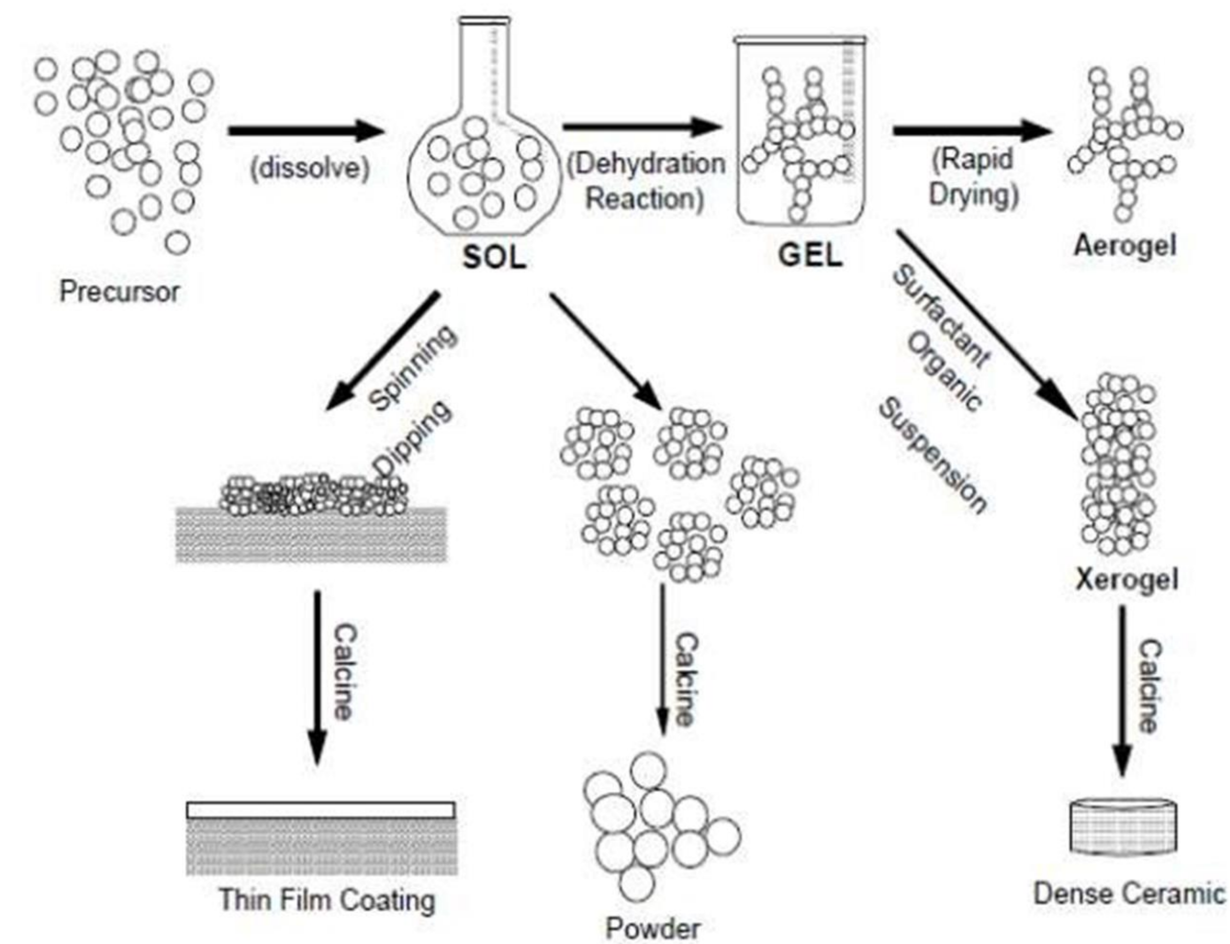
Methods for creating nanostructures:-

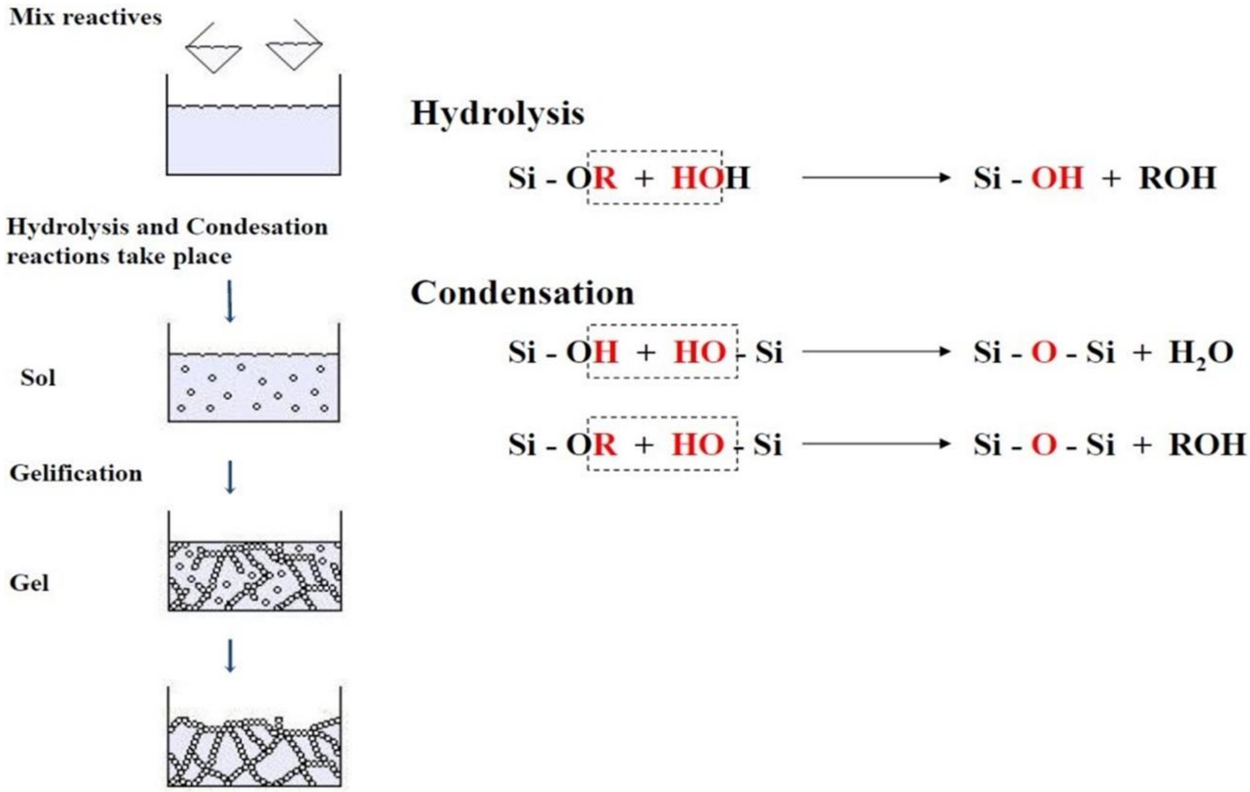
- Mechanical grinding: Example of (Top-down) method
- Wet Chemical: Example of both (Top-down) & (bottom up) [Sol-Gel process]

Sol-Gel process:-

- The sol-gel process is very long known since the late 1800s. The versatility of the technique has been rediscovered in the early 1970s when glasses where produced without high temperature melting processes.
  Sol-gel is a chemical solution process used to make ceramic and glass materials in the form of thin films, fibers, or powders.
- A sol is a colloidal (the dispersed phase is so small that gravitational forces do not exist; only Vander Waals forces and surface charges are present) or molecular suspension of solid particles of ions in a solvent.

- A gel is a semi-rigid mass that forms when the solvent from the sol begins to evaporate and the particles or ions left behind begin to join together in a continuous network
- The sol-gel process is a wet-chemical technique that uses either a chemical solution (sol short for solution) or colloidal particles (sol for nanoscale particle) to produce an integrated network (gel).
- Metal alkoxides and metal chlorides are typical precursors. They undergo **hydrolysis and polycondensation reactions** to form a colloid, a system composed of Nanoparticles dispersed in a solvent. The sol evolves then towards the formation of an inorganic continuous network containing a liquid phase (gel).
- Formation of a metal oxide involves connecting the metal centers with oxo (M-O-M) or hydroxo (M-OH-M) bridges, therefore generating **metal-oxo or metal-hydroxo polymers** in solution.
- After a drying process, the liquid phase is removed from the gel. Then, a thermal treatment **(calcination)** may be performed in order to favour further polycondensation and enhance mechanical properties.





1 – General mechanisms in the metal-organic route

Based on the growth of **metal oxo polymers** in a solvent

- inorganic step polymerization reactions through hydrolysis and condensation of metal alkoxides $M(OR)_Z$, where M = Si, Ti, Zr, Al, Sn, Ce…, OR is an alkoxy group and Z is the valence or the oxidation state of the metal
- first step : hydroxylation upon the **hydrolysis** of alkoxy groups :

$$M\text{-}OR + H_2O \rightarrow M\text{-}OH + ROH$$

- second step : polycondensation process leading to the formation of branched oligomers and polymers with a metal oxo based skeleton and reactive residual hydroxo and alkoxy groups ; 2 competitive mechanisms :

■ **oxolation** : formation of oxygen bridges :

$$M\text{-}OH \; + \; XO\text{-}M \; \rightarrow \; M\text{-}O\text{-}M \; + \; XOH$$

where X = H, generally when **hydrolysis ratio h** = $H_2O/M >> 2$
or X = R, when h = $H_2O/M < 2$

■ **olation** : formation of hydroxo bridges when the coordination of the metallic center is not fully satisfied (N - Z > 0) :

$$M\text{-}OH \; + \; HO\text{-}M \; \rightarrow \; M\text{-}(OH)_2\text{-}M \quad \text{where } X = H \text{ or } R$$

The kinetics of olation are usually faster than those of oxolation

➢ formation of a metal oxo macromolecular network :

■ a **sol** where the polymerized structures do not reach macroscopic sizes

■ a **gel** when the recombination of the metal oxo polymers can produce bushy structures which invade the whole volume inside which the solvent, reaction by-products and free polymers are trapped

■ a **precipitate** when the reactions produce dense rather than bushy structures

Advantages of Sol-Gel Processes:-

In general:

- Able to get uniform & small sized powder
- Can get at low temperature high density glass, without high temperature re-crystallization
- Can get new compositions of glass
- New microstructure and composition
- Easy to do coating for films
- Can get objects or films with special porosity
- Can get metal (inorganic) – organic composites
- Can coat onto large area or complex shape objects
- Can get fibers
- High uniformity, multicomponent systems

Characterization:
THE SCANNING ELECTRON MICROSCOPE:-

- The surface morphology, homogeneity and size of the deposited film can be studied by SEM.
- If is most versatile and commonly used instrument technique to study the surface and particle size

PRINCIPLE:

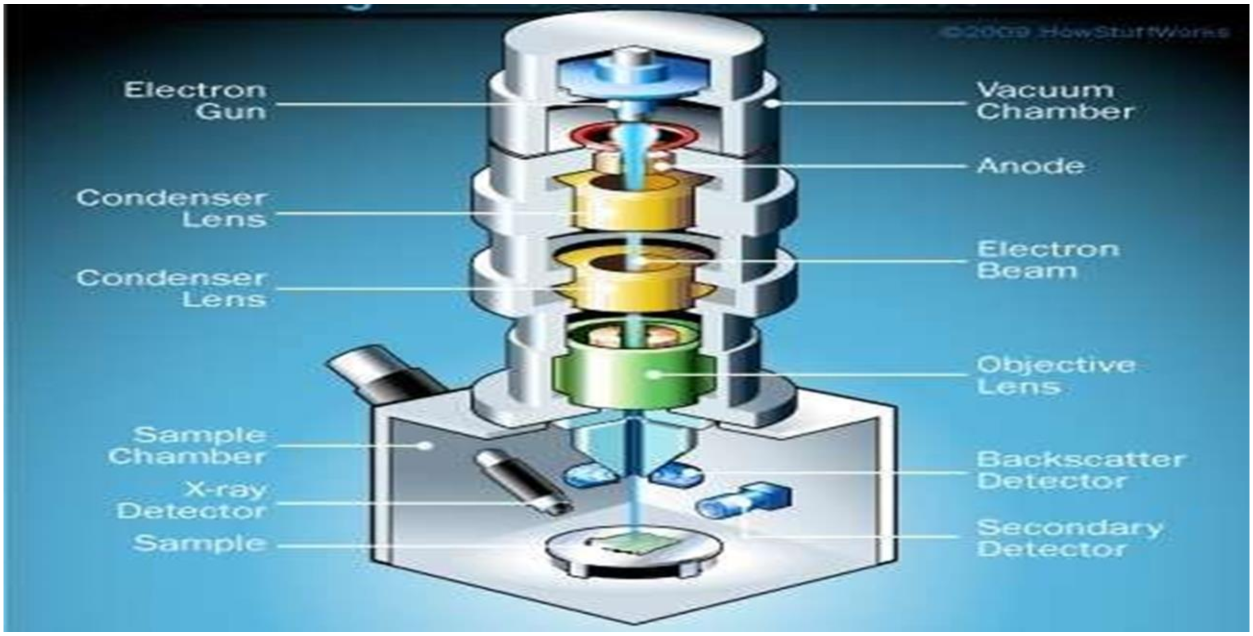
➢ The basic principle is that a beam of electrons is generated by a suitable source, typically a tungsten filament or a field emission gun.

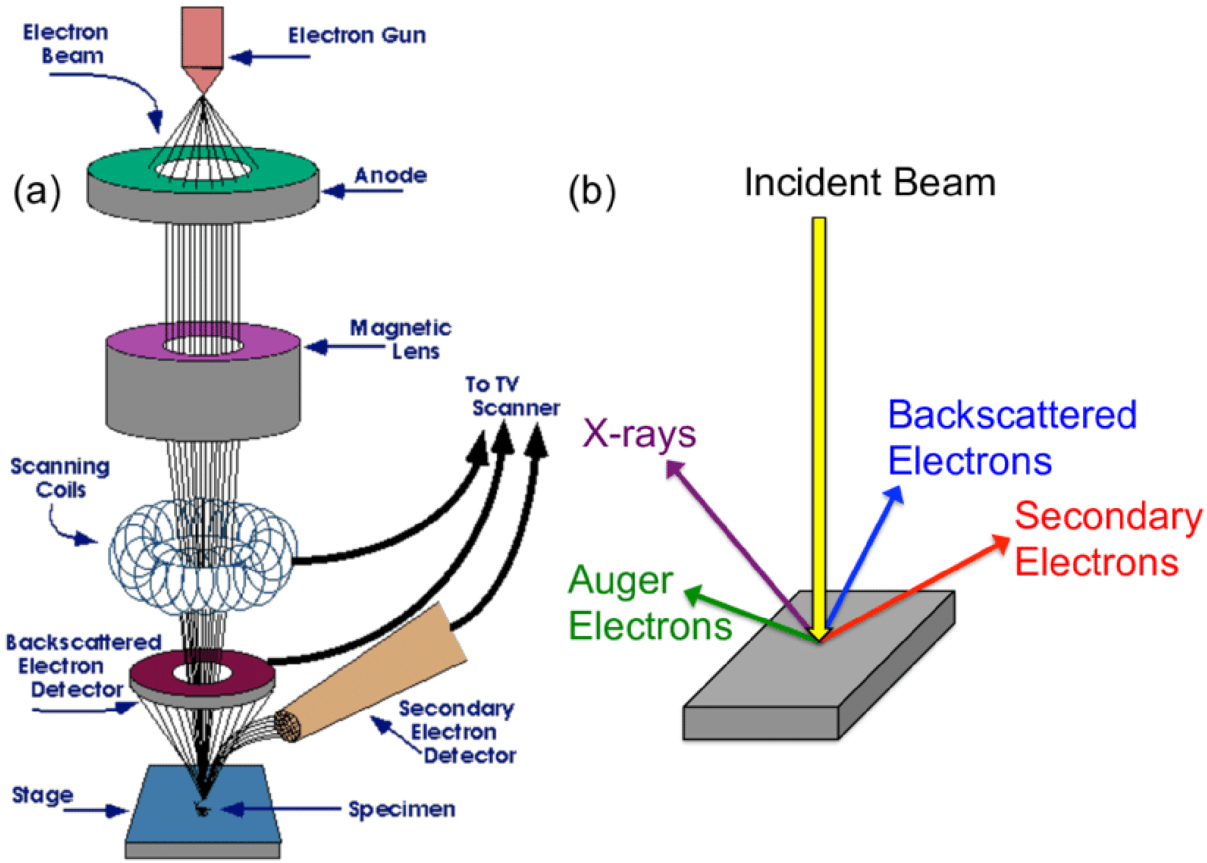
- The electron beam is accelerated through a high voltage (e.g.: 20 kV) and pass through a system of apertures and electromagnetic lenses to produce a thin beam of electrons.
- Then the beam scans the surface of the specimen. Electrons are emitted from the specimen by the action of the scanning beam and collected by a suitably-positioned detector.

CONSTRUCTION:

Basic components are as following:

- Electron gun (Filament)
- Condenser lenses
- Objective Aperture
- Scan coils
- Chamber
- Detectors
- Computer hardware and software





HOW THE SEM WORKS:-

- The SEM uses electrons instead of light to form an image.
- A beam of electrons is produced at the top of the microscope by heating of a metallic filament.
- The electron beam follows a vertical path through the column of the microscope. It makes its way through electromagnetic lenses which focus and direct the beam down towards the sample.
- Once it hits the sample, other electrons (backscattered or secondary) are ejected from the sample.
- Detectors collect the secondary or backscattered electrons, and convert them to a signal that is sent to a viewing screen similar to the one in an ordinary television, producing an image.

CHARACTERISTIC INFORMATION: SEM

- Topography: The surface features of an object or "how it looks", its texture; direct relation between these features and materials properties
- Morphology: The shape and size of the particles making up the object; direct relation between these structures and materials properties

- Composition: The elements and compounds that the object is composed of and the relative amounts of them; direct relationship between composition and materials properties
- Crystallographic Information: How the atoms are arranged in the object; direct relation between these arrangements and material properties.

ADVANTAGES:-

- Advantages of a Scanning Electron Microscope include its wide-array of applications, the detailed three-dimensional and topographical imaging and the versatile information garnered from different detectors.
- SEMs are also easy to operate with the proper training and advances in computer technology and associated software make operation user-friendly.
- Although all samples must be prepared before placed in the vacuum chamber, Most SEM samples require minimal preparation actions.

DISADVANTAGES:-

- The disadvantages of a Scanning Electron Microscope start with the size and cost.
- SEMs are expensive, large and must be housed in an area free of any possible electric, magnetic or vibration interference.
- Maintenance involves keeping a steady voltage, currents to electromagnetic coils and circulation of cool water.
- SEMs are limited to solid, inorganic samples small enough to fit inside the vacuum chamber that can handle moderate vacuum pressure.

APPLICATIONS:-

- SEMs have a variety of applications in a number of scientific and industry-related fields, especially where characterizations of solid materials is beneficial.
- In addition to topographical, morphological and compositional information, a Scanning Electron Microscope can detect and analyze surface fractures, provide information in microstructures, examine surface contaminations, reveal spatial variations in chemical compositions, provide qualitative chemical analyses and identify crystalline structures.
- In addition, SEMs have practical industrial and technological applications such as semiconductor inspection, production line of miniscule products and assembly of microchips for computers.
- SEMs can be as essential research tool in fields such as life science, biology, gemology, medical and forensic science, and metallurgy.

TRANSMISSION ELECTRON MICROSCOPE:-

Microscopes are used to see objects that cannot be seen by naked eyes. The range can be between mm to nm. There are three main microscopic techniques:

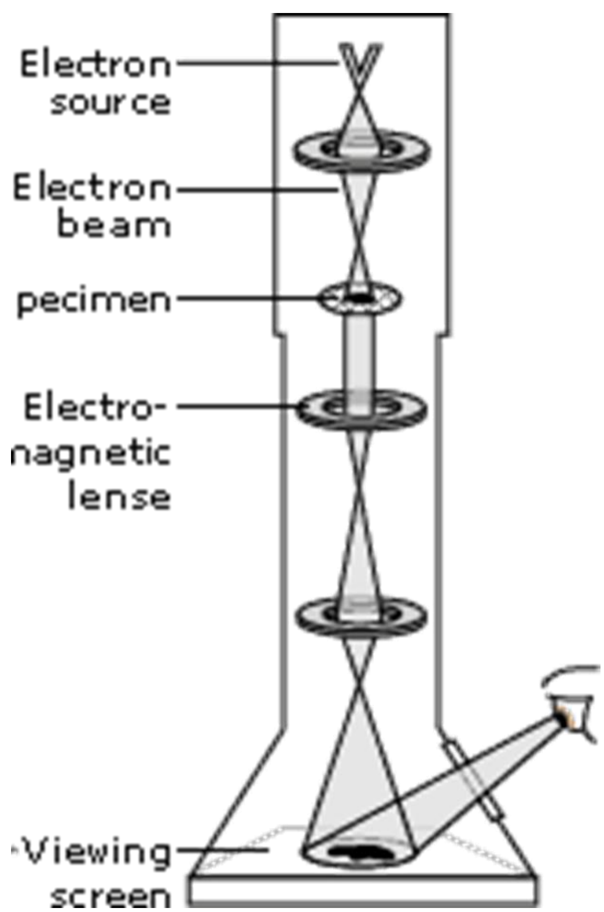
- Optical Microscopy
- Scanning Probe Microscopy
- Electron Microscopy

Transmission electron microscopy (TEM) is a microscopy technique where a beam of electrons is transmitted through a ultra thin specimen. An image is formed from the interaction of the electrons transmitted through the specimen; the image is magnified and focused onto an imaging device, such as a fluorescent screen, on a layer of photographic film, or to be detected by a sensor such as a CCD camera.

Principle:-

- TEM operates on the same basic principle as the light microscope but uses electrons instead of light.
- Since light microscope is limited by the wave length of light.
- TEM use electrons as a light source and their much lower wave length make it possible to get a resolution a 100 times better than with a light microscope.
- In TEM, on electron beam with energy of lower or more is allowed to go through a thin specimen.
- Scattering occurs when the electron beam interacts with matter.
- Scattering may be of no energy change (Elastic) or energy change (Inelastic).
- Elastic scattering can be in the forms of rings in the case of Poly crystalline materials.
- High resolution TEM is one of the most powerful tools of nano science.
- Interaction of electron with the sample produces elastic or inelastic scattering.
- Most of the studies are done with the elastically scattered electrons which from the bright image.

Instrumentation:



Construction:

- Electron gun
- Condenser lens
- Specimen
- Objective lens
- Projector lens
- Fluorescent screen.

Applications:

1. In medicine as a diagnostic fuel.

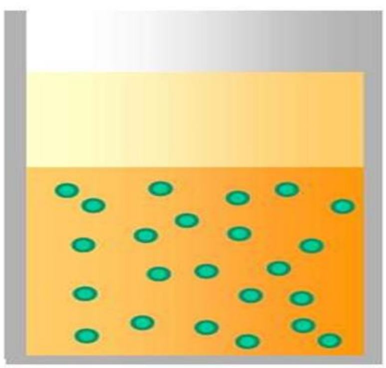
2. Cancer research studies of tumor cell ultra stmeture.

3. Toxicology-To study the impacts of environmental pollutions on the different levels of biological organization.

Colloidal chemistry

Introduction of colloids:-

- A colloid is a substance microscopically dispersed throughout another substance.
- The word colloid comes from a Greek word '**kolla**', which means glue thus colloidal particles are glue like substances.
- These particles pass through a filter paper but not through a semipermeable membrane. Colloids can be made settle by the process of centrifugation.



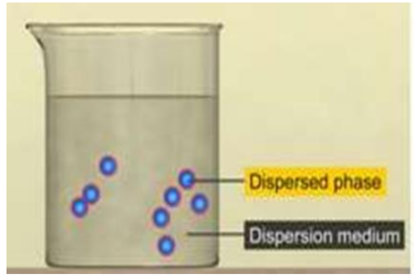
The colloidal system consists of two phases.

1. A dispersed phase (A discontinuous phase)

2. A dispersion medium (A continuous phase)

- The dispersed-phase particles have a diameter of between approximately **1nm – 100nm.**

- Such particles are normally invisible in an optical, though their presence can be confirmed with the use of an **ultra microscope or an electron microscope.**



Comparison of the Properties of Solutions, Colloids, and Suspensions:

Property	True Solution	Colloid	Suspension
Particle Size	Less than 1 nm	1 to 100 nm	More than 100 nm
Appearance	Clear	Cloudy	Cloudy
Homogeneity	Homogeneous	Homogeneous or Heterogeneous	Heterogeneous
Transparency	Transparent but often colored	Often translucent and opaque but can be transparent	Often opaque but can be translucent
Separation	Does not separate	Can be separated	Separates or settles
Filterability	Passes through filter paper	Passes through filter paper	Particles do not pass through filter paper

CLASSIFICATION OF COLLOIDS:-

- Based on physical state of dispersed phase a dispersion medium.
- Based on nature of interaction between dispersed phase and dispersion medium.
- Based on molecular size in the dispersed phase.
- Based on appearance of colloids.
- Based on electric charge on dispersion phase.

Based on physical state of dispersed phase and dispersion medium:

Dispersed Phase	Dispersion Medium	Name	Examples
Solid	Solid	Solid-Sol	Alloys, Cranberry glass
Solid	Liquid	Sol	Ink, Blood
Solid	Gas	Aerosol	Smoke, Ice cloud
Liquid	Solid	Gel	Jelly, Curd
Liquid	Liquid	Emulsion	Milk, Cream
Liquid	Gas	Liquid aerosol	Cloud, Fog
Gas	Solid	Solid form	Aerogel, Pumice stone
Gas	Liquid	Foam	Shaving cream
Gas	Gas	None	All gases are miscible

BASED ON NATURE OF INTERACTION BETWEEN DISPERSED PHASE AND DISPERSION MEDIUM:

LYOPHILIC COLLOIDS:

- Colloidal solution in which the dispersed phase has a great affinity for the dispersion medium.
- They are also termed as intrinsic colloids.
- Such substances have tendency to pass into colloidal solution when brought in contact with dispersion medium.
- If the dispersion medium is water, they are called hydrophilic or emulsoids.
- The lyophilic colloids are generally self- stabilized.
- Reversible in nature and are heavily hydrated.
- Example of lyophilic colloids is starch, gelatin, rubber, protein etc.

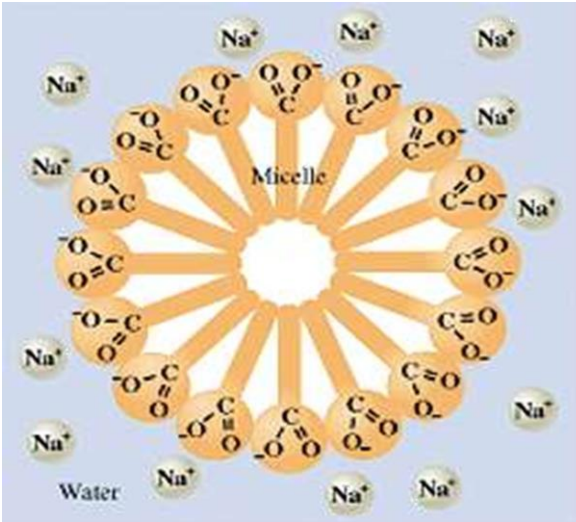
LYOPHOBIC COLLOIDS:

- Colloidal solutions in which the dispersed phase has no affinity to the dispersion medium.
- These are also referred as extrinsic colloids.

- Such substances have no tendency to pass into colloidal solution when brought in contact with dispersion medium.
- The lyophobic colloids are relatively unstable.
- They are irreversible by nature and are stabilized by adding small amount of electrolyte.
- They are poorly hydrated.
- If the dispersion medium is water, the lyophobic colloids are called hyrophobic or suspenoids.
- Examples: sols of metals like Au, Ag, sols of metal hydroxides and sols of metal sulphides.

Micelle:-

- These colloids behave as normal electrolytes at low concentrations but behave as colloids at higher concentrations.
- These associated colloids are also referred to as micelles.
- Sodium stearate ($C_{18}H_{35}NaO_2$) behaves as electrolyte in dilute solution but colloid in higher concentrations.
- Examples: Soaps, higher alkyl sulphonates, polythene oxide.

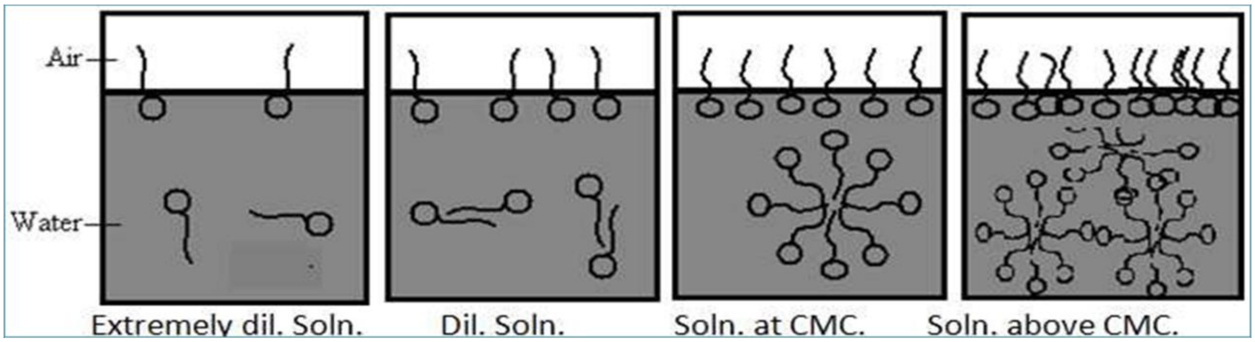


HOW DOES SOAP WORK?

- When greasy dirt is mixed with soapy water, the soap molecules arrange themselves into tiny clusters called micelles.
- The water-loving (hydrophilic) part of the soap molecules sticks to the water and points outwards, forming the outer surface of the micelle.
- The oil-loving (hydrophobic) parts stick to the oil and trap oil in the center where it can't come into contact with the water. With the oil tucked safely in the center, the

Micelle formation

- The process of forming micelle is known as micellization.
- Typical micelle is Spherical in structure which contain 50-100 monomers
- Number of monomers to form micelle is called as aggregation number



Process of Micellization:

SAA bulk Concentration

⇩

Surface excess

⇩

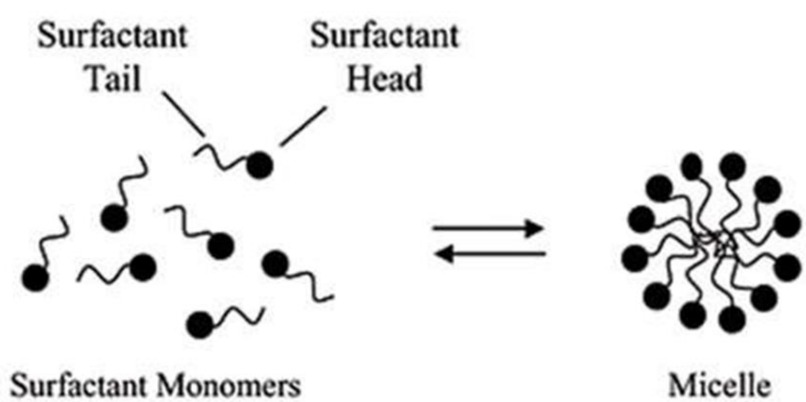
Surface saturated with SAA

⇩

Excess in the bulk

⇩

Micelles (colloidal aggregates)



Synthesis of colloids:-

- **Condensation Method*:-*** In condensation method, the smaller particles of the dispersed phase are aggregated to form larger particles of colloidal dimensions.

Some important condensation methods are described below:

a) Solutions of substances like mercury and sulphur are prepared by passing their vapours through cold water containing a suitable stabilizer such as ammonium salt or citrate.

b)By excessive cooling: A colloidal solution of ice in an organic solvent like ether or chloroform can be prepared by freezing a solution of water in solvent. The molecules of water which can no longer be held in solution separately combine to form particles of colloidal size.

c) By exchange of solvent: Colloidal solution of certain substances such as sulphur, phosphorus which are soluble in alcohol but insoluble in water can be prepared by pouring their alcoholic solution in excess of water. For example alcoholic solution of sulphur on pouring into water gives milky colloidal solution of sulphur.

d) Chemical methods: Colloids can be prepared by following chemicals methods..

1) Oxidation: Addition of oxygen and removal of hydrogen is called oxidation.

For example: Colloidal solution of sulphur can be prepared by oxidizing an aqueous solution of H2S with a suitable oxidizing agent such as bromine water.

$$H_2S + Br_2 \rightarrow 2HBr + S$$

$$2H_2S + SO_2 \rightarrow 2H_2O + 3S$$

2) Reduction: Addition of hydrogen and removal of oxygen is called reduction.

For example: Gold sol can be obtained by reducing a dilute aqueous solution of gold with stannous chloride.

$$2AuCl_3 + 3SnCl_2 \rightarrow 3SnCl_4 + 2Au$$

3) Hydrolysis: It is the breakdown of water. Sols of ferric hydroxide and aluminium hydroxide can be prepared by boiling the aqueous solution of the corresponding chlorides. For example.

$$FeCl3 + 3H_2S \rightarrow Fe(OH)3 + 3HCl$$

4) Double Decomposition: The sols of inorganic insoluble salts such as arsenous sulphide, silver halide etc may be prepared by using double decomposition reaction.

For example: Arsenous sulphide sol can be prepared by passing H2S gas through a dilute aqueous solution of arsenous oxide.

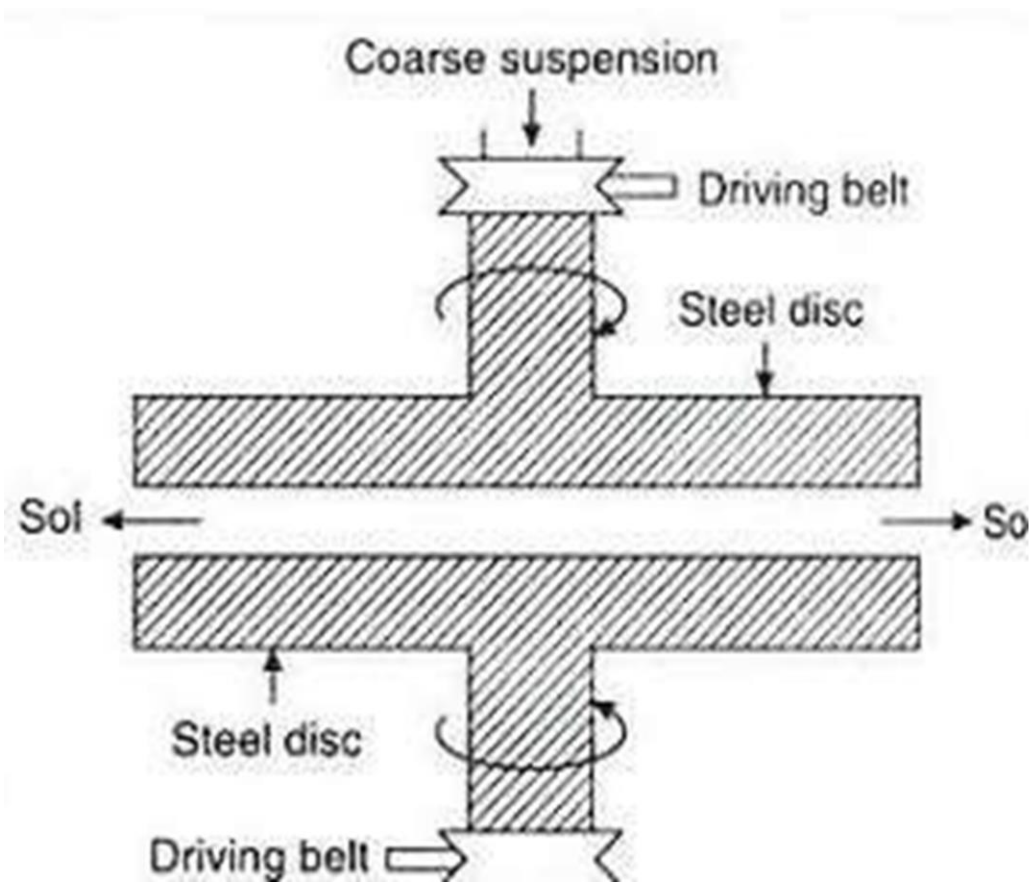
$$As_2O_3 + 3H_2S \rightarrow As_2S_3(OH)_3 + 3H_2O$$

- **Dispersion (or) Disintegration method:-**This technique is a direct method and consists of finely pulversing substance to be dispersed in the medium which is to constitute the dispersion phase. The important dispersion methods are

A) Mechanical dispersion:

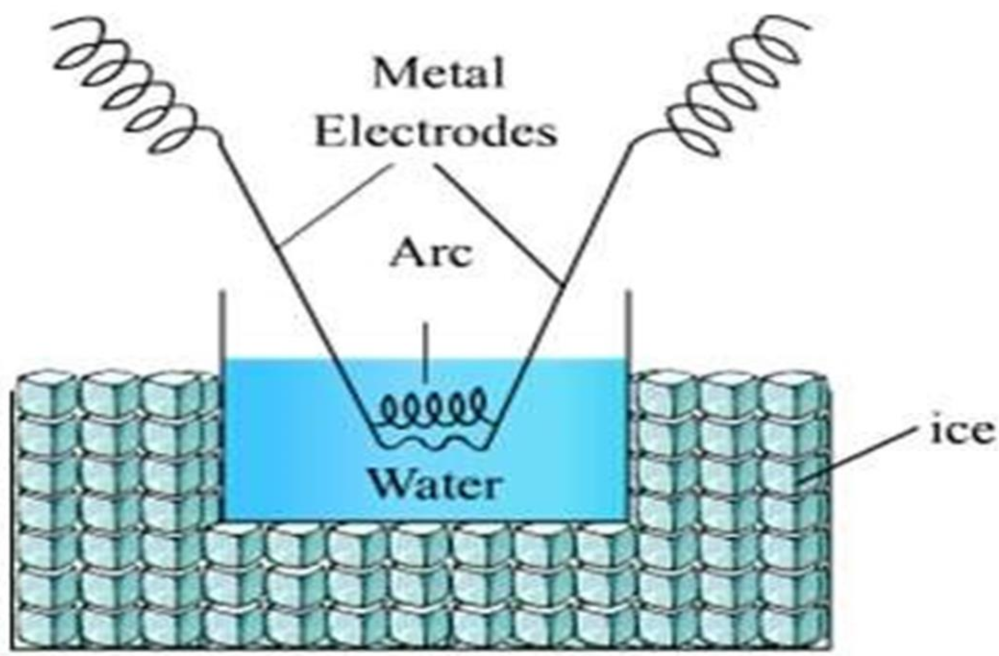
In this method,

- The substance is first ground to coarse particles.
- It is then mixed with the dispersion medium to get a suspension.
- The suspension is then grinded in colloidal mill.
- It consists of two metallic discs nearly touching each other and rotating in opposite directions at a very high speed about 7000 revolution per minute.
- The space between the discs of the mill is so adjusted that coarse suspension is subjected to great shearing force giving rise to particles of colloidal size. Colloidal solutions of black ink, paints, varnishes, dyes etc. are obtained by this method.



(B) By electrical dispersion or Bredig's arc method:

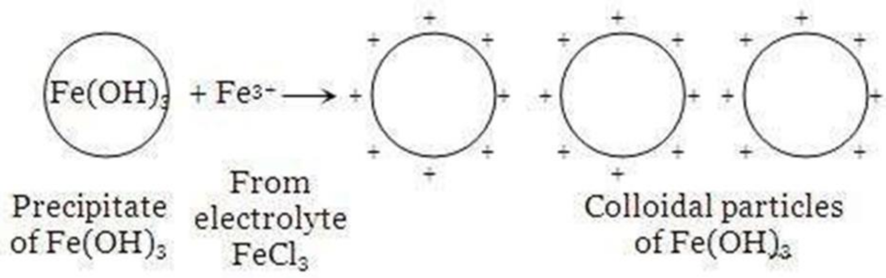
- This method is used to prepare sols of platinum, silver, copper or gold.
- The metal whose sol is to be prepared is made as two electrodes which immerge in dispersion medium such as water etc.
- The dispersion medium is kept cooled by ice.
- An electric arc is struck between the electrodes.
- The tremendous heat generated by this method gives colloidal solution.
- The colloidal solution prepared is stabilized by adding a small amount of KOH to it.



Bredig's arc method

C) By peptisation:

- The process of converting a freshly prepared precipitate into colloidal form by the addition of suitable electrolyte is called peptisation.
- Cause of peptisation is the adsorption of the ions of the electrolyte by the particles of the precipitate.
- The electrolyte used for this purpose is called peptizing agent or stabilizing agent.
- Important peptizing agents are sugar, gum, gelatin and electrolytes.



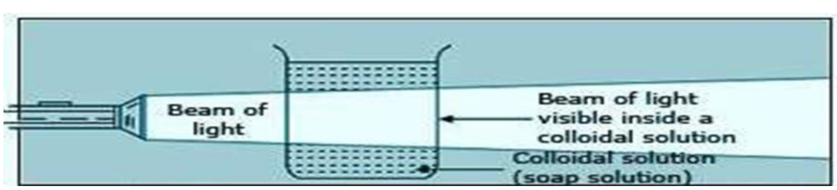
PHYSICAL PROPERTIES OF COLLOIDS:

- Heterogeneity: Colloidal solutions consist of two phases-dispersed phase and dispersion medium.
- Visibility of dispersed particles: The dispersed particles present in them are not visible to the naked eye and they appear homogenous.
- Filterability: The colloidal particles pass through an ordinary filter paper. However, they can be retained by animal membranes, cellophane membrane and ultra filters.
- Stability: Lyophilic sols in general and lyophobic sols in the absence of substantial concentrations of electrolytes are quite stable.
- Color: The color of a colloidal solution depends upon the size of colloidal particles present in it. Larger particles absorb the light of longer wavelength and therefore transmit light of shorter wavelength.

OPTICAL PROPERTIES OFCOLLOIDS: TYNDALL EFFECT

- When an intense converging beam of light is passed through a colloidal solution kept in dark, the path of the beam gets illuminated with a bluish light.
- This phenomenon is called Tyndall effect and the illuminated path is known as **Tyndall cone**.
- The Tyndall effect is due to the scattering of light by colloidal particles.
- Tyndall effect is not exhibited by true solutions. This is because the particles present in a true solution are too small to scatter light.

Tyndall effect can be used to distinguish a colloidal solution from a true solution. The phenomenon has also been used to devise an instrument known as ultra microscope. The instrument is used for the detection of the particles of colloidal dimensions.



Applications:-

1. Rubber plating

2. Sewage disposal

3. Smoke screen.

4. Purification of water

5. Cleaning action of soap

6. In medicines.

7. Formation of delta

8. Artificial rains.

9. Photography.