Chapter - 1

Introduction to colloid and sol-gel chemistry
Chapter - 1
Introduction to colloid and sol-gel chemistry

1.1 Introduction

Solution is an intimate mixture of two or more chemical substances. In solution, the dissolving agent is the solvent (dispersion medium) and the substance which dissolves is the solute (dispersed phase). The state of matter of a solution may be solid, liquid or gas which are in the form of atoms, ions, or molecules.

According to Scottish chemist Thomas Graham (1861), depending on the size of solute particles, the solutions are classified as given in fig. 1.1.

![Fig. 1.1 Types of solutions](image)

1.1.1 True solutions

A true solution is a homogeneous solution in which the solute particles have diameters lesser than 1 nm i.e., the solute particles are of molecular dimensions. Such dispersed particles dissolve in solution to form a homogenous system. These do not settle down when the solution is left standing. The particles are invisible even under powerful microscopes and cannot be separated through filter paper, parchment paper or animal membranes, e.g. sodium chloride in water, sugar in water.

1.1.2 Suspensions

Suspensions consist of particles of a solid suspended in a liquid medium. Suspensions are systems with two distinct phases. The particles in suspensions are bigger than 1000 nm. The particles of a suspension are
visible to the naked eye or under a microscope. Suspensions are heterogeneous systems. They stay only for a limited period i.e. these are not stable as the particles have a tendency to settle down under the influence of gravity. The particles of a suspension can neither pass through ordinary filter paper nor through animal membranes, e.g. sand in water, oil in water.

1.1.3 Colloids

Colloids or Colloidal solutions, represent an intermediate kind of a mixture between true solution and suspension [1]. The size of a colloidal particle lies roughly between 1-1000 nm [2, 3]. Colloids are also a two-phase heterogeneous system consisting of the dispersed phase (internal or discontinuous phase) and dispersion medium (external or continuous phase). Since the dispersed phase in a colloidal system is uniformly distributed in the dispersion medium, the colloidal state appears homogenous to the naked eye or even an ordinary microscope (due to particles being invisible). However it is a heterogeneous dispersion of two immiscible phases by viewing it under an ultra-microscope, where the light reflected by colloidal particles can be seen. Colloidal particles do not settle down under gravity. Colloids can pass through ordinary filter paper but do not pass through animal membranes, e.g. a colloidal solution of gold.

Total interface area of the colloidal dispersed particles is very large due to their submicroscopic size. The huge area-to-volume ratio determines specific properties and behavior of colloids. In other words, as in the colloids the amount of dispersed particles is very large, their overall surface is very large too and by consequence the interaction of the two phases is important. Because of the wide surface of contact between the two phases, often the colloids are studied with the surface phenomena. Adsorption processes occurring on the interface between the dispersed and continuous phases exert considerable effect on the colloid physical properties, chemical reactions in the system and its stability. Surface active substances added to a colloid modify its properties.

Colloidal solutions, depending upon the nature of interactions between dispersed phase and the dispersion medium, are classified into two types as lyophilic (solvent loving) and lyophobic colloids (solvent hating).
(a) **Lyophilic colloids**: “The colloidal solution in which the particles of the dispersed phase have a great affinity for the dispersion medium, are called lyophilic colloids.” In such colloids, the dispersed phase does not precipitate easily and the colloids are quite stable. If the dispersion medium is separated from the dispersed phase, the colloids can be reconstituted by simply remixing with the dispersion medium [4]. Hence, these colloids are reversible in nature, e.g. colloids of gum, polymers in organic solvents.

(b) **Lyophobic colloids**: “The colloidal solution in which there is no affinity between particles of the dispersed phase and the dispersion medium are called lyophobic colloids.” These colloids are easily precipitated on addition of small amount of electrolytes, by heating or by shaking and therefore are not stable. Once precipitated, it is not easy to reconstitute the colloid by simple mixing with the dispersion medium. Hence these colloids are irreversible in nature, e.g. colloids of metals.

Depending upon the physical state of dispersed phase and dispersion medium whether these are solids, liquids or gases, eight types of colloidal systems are possible as given in the table 1.1 [5].

<table>
<thead>
<tr>
<th>Table 1.1 Types of colloidal systems</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Medium / Phases</strong></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td><strong>Dispersion medium</strong></td>
</tr>
<tr>
<td>Gas</td>
</tr>
<tr>
<td>Liquid</td>
</tr>
</tbody>
</table>
1.2 Formation of Colloids

There are two basic methods for formation of colloids:
(i) Dispersion method where in the reduction of larger particles to colloidal size occurs, e.g. by mechanical subdivision of larger particles or by dissolution in the case of lyophilic sols.
(ii) Condensation method where in condensation of smaller particles (e.g., molecules) into colloidal particles occurs, e.g. from supersaturated solutions or as the product of chemical reactions.

Some substances (e.g. glue) are easily dispersed (in the proper solvent) to form a colloid; this spontaneous dispersion is called peptization. Condensation of smaller particles to form a colloid usually involves chemical reactions—typically displacement, hydrolysis, or oxidation and reduction. When a condensation method is applied, molecules (or ions) are deposited on nuclei, which may be of the same chemical species as the colloid (homogeneous nucleation) or different (heterogeneous nucleation).

1.3 Shape of colloidal particles

It is general observation that the colloidal particles acquire spherical shape. This is explained by the excess free surface energy. It is known that among the bodies of different geometrical shapes, a sphere has the smallest surface energy, and the process of sphere formation occurs spontaneously in accordance with the second law of thermodynamics. In a spherical drop all the surface molecules are indistinguishable from one another and also differ from the bulk ones in their orientation.

The excess free energy makes the colloidal solutions thermodynamically unstable. The process of lowering the excess free energy and reducing the dispersity are the fundamental characteristics of all colloidal solutions. If a colloidal solution remains unchanged in its chemical composition, but changes its free energy characteristics, then this will result in a change in colloidal properties.

1.4 Origin of charge on colloids

The origin of charges on colloidal particles arises due to friction between the colloidal particles and molecules of the dispersion medium,
preferential adsorption of ions from the solutions, dissociation of surface molecules and by the simple process of electron capture. An ionic solution adsorbs ions common to its own lattice structure e.g. AgCl particles can absorb Cl\(^-\) ions if excess of KCl solution is used for its preparation.

It is well known that most of the colloidal particles are electrically charged and will migrate in one or other direction when subjected to an electric field. It has been observed that there is a tendency for charges to accumulate at any interface between two phases, because, the relative affinities of the cations and anions for the two phases are, in general, different, one phase acquires a positive and the other a negative charge. The charge on the colloidal particle is due to the presence of an electric double layer of ions on its surface. Fig. 1.2 shows formation of electric double layer on a particle of an aqueous sol of silicon dioxide due to ionization.

![Formation of electric double layer around a particle of silicon dioxide in water](image)

This charge gives rise to a potential gradient, called as Zeta potential (\(\zeta\)) in the sol as shown schematically in Fig. 1.3.
The double layer originates either upon selective adsorption of one type of the ions of an electrolyte in a solution or owing to ionization of the surface molecules of substances. The adsorbed ions repel the ions possessing similar charge. These counter ions which compensate the particle charge, are distributed non-uniformly throughout the solution. Therefore, the potential curve drops steeper at places where there are more compensating counter ions. The potential at the outer surface of the double layer (plane AB) is still higher than that of the solution which accounts for the electrokinetic properties of the sol and is called as zeta potential.

The state of the charge on the electrolyte molecules is also determined by the pH (concentration of $H^+$ and $OH^-$ ions) of the sol. Thus a molecule having positive charge at low pH may acquire a negative charge at higher pH values and there is an intermediate pH called the isoelectric point at which the molecule will be electrically neutral [6].
1.5 Forces of interaction between colloidal particles

The stability of suspensions and emulsions against coagulation is governed by the forces between the particles. Dispersion is said to be stable when the particles are permanently free. In dispersions of fine particles in a liquid, frequent encounters between the particles occur due to Brownian movement. Such encounters may result in permanent contact or the particles become free depend upon the forces between them. The different types of forces between the particles are:

1.5.1 Van der Waals forces

If the particles don’t have a permanent dipole, fluctuations of the electron density gives rise to a temporary dipole in a particle. This temporary dipole induces a dipole in particles nearby. The temporary dipole and the induced dipole are attracted to each other. This is known as van der Waal’s force, and is always present, is short range, and is attractive. Van der Waal’s forces refer to the tendency of particles in nature to attract each other weakly if they have no charge. Van der Waals forces are always attractive between particles of the same nature. Hamaker [7] derived equations for these forces on the basis of additivity of Van der Waals energies between pairs of atoms or molecules, and assuming these energies to be proportional to the inverse sixth power of the distance.

1.5.2 Electrostatic forces

The particles of a colloid selectively absorb ions and acquire an electric charge. All of the particles of a given colloid take on the same charge (either positive or negative) and thus are repelled by one another, due to the interaction of the electrical double layers surrounding the particles, and have surface charges and surface potentials of the same sign and magnitude.

When the surface charge is generated by the adsorption of potential determining ions, the surface potential, $\phi_0$, is determined by the activity of these ions and remains constant during interaction at least if complete adsorption equilibrium is maintained. In that case, interaction occurs at constant surface potential. The Van der Waals forces fall off as an inverse power of the separation between the particles and have a range comparable
to the particle size, whereas the electrostatic repulsion falls off as an exponential function of the distance and has a range of the order of the thickness of the electric double layer. For molecules of a simple monoatomic liquid the interaction energy between a pair of molecules is given by equation (1.1). The interaction only depends on the separation between the centers of the molecules. At large separations, \( r > \delta \) the interaction is attractive, \( u(r) < 0 \). At smaller separations, overlap of the electron orbital of the two molecules give rise to a repulsion that increases very rapidly as the separation decreases.

\[
u(r) = 4\varepsilon \left[ (\delta/r)^{12} - (\delta/r)^6 \right]
\]

--- (1.1)

Where \( \delta \) and \( \varepsilon \) give the measure of size and the strength of interaction between the molecules respectively.

![Diagram of potential energy](image)

**Fig. 1.4** Potential energy (P. E.) \( U(r) \) of two particle system as a function of distance \( r \) between them. '\( r_o \)' is equilibrium distance where the P. E. is minimum (\( U_{\text{min}} \)).

Fig. 1.4 shows the curve of potential energy of interaction against distance \( r \). At short distances, a deep potential energy minimum occurs, the
position of which decides the distance of closest approach, $r_0$. At intermediate distances the electrostatic repulsion makes the largest contribution and hence a maximum occurs in the potential energy curve, $V_m$. At larger distances, the exponential decay of the electrical double layer term causes it to fall off more rapidly than the power law of the attractive term and a second minimum appears in the curve $V_{sm}$.

1.6 Molecular kinetic and optical properties of colloids

1.6.1 Brownian movement

Brownian movement was first discovered by Robert Brown, a botanist, in 1827. He observed that pollen grains in water do not remain at the rest but move continuously and randomly. This random continuous movement (Brownian motion) was observed in colloidal sol when the sol was viewed under an ultra microscope. Brownian motion is phenomena whereby small particles suspended in a liquid tend to move in pseudo-random paths through the liquid, even if the liquid is calm. Brownian motion in colloidal sol arises due to the impact of the molecules of the dispersion medium with the colloidal particles. It has been postulated that the impact of the molecules of the dispersion medium on the colloidal particles are unequal. This leads to the zig-zag (random) motion of the colloidal particles [8] as shown in fig. 1.5. This random movement decreases as the size of the particles increases because the effect of the impact average out. When the size of the dispersed particles increases beyond the colloidal range, Brownian motion stops, i.e. no Brownian movement is observed.

Fig. 1.5 Brownian motion
The significant of Brownian movement is that

- It provides a direct demonstration of ceaseless motion of molecules as postulated by kinetic theory.
- It counters the force of gravity acting on the colloidal particles and hence helps in providing the stability to the colloidal sols by not allowing them to settle down.

The scientist who made Brownian motion famous is Albert Einstein, who brought the phenomenon to the attention of the larger physics community.

The motion is characterized by the mean displacement $\Delta x$ of the particle during time $t$. The chaotic motion of a particle occurs in a definite volume of space that grows with time. Unlike the real path of a particle, which changes its direction up to $10^{20}$ times a second, the averaged quantity, $\Delta x$ will be zero since both positive and negative displacements are equally probable. Hence, the mean square displacement $\Delta X^2$ is calculated proceeding from the statistical laws. It is given by

$$\Delta X^2 = \frac{\Delta X_1^2 + \Delta X_2^2 + \Delta X_3^2 + \ldots}{n} \quad ---- (1.2)$$

Where, $n$ is the number of particles considered and $\Delta X_i^2$ is the square of the displacement of the $i^{th}$ particle.

For a spherical particle of radius $r$, the mean square displacement is directly proportional to the absolute temperature, $T$, the duration of observation, $t$ and inversely proportional to the coefficient of hydrodynamic resistance of the medium, $\omega = 6\pi\eta r$, where $\eta$ is the coefficient of viscosity.

$$\Delta X^2 = \frac{bTt}{6\pi\eta r} \quad ---- (1.3)$$

For the proportionality factor $b$ Einstein theory gives the expression:

$$b = \frac{2R}{N_A} = 2K \quad ---- (1.4)$$

where, $R$ is the molar gas constant, $N_A$ is the Avogadro constant and $k$ is the Boltzmann constant. Consequently, the final expression for the mean square displacement is:
Hence it showed that motion became more rapid and the particles moved farther in a given time interval when the temperature of the water was raised, when the viscosity of the fluid was lowered, or when the size of the particles was reduced.

1.6.2 Diffusion

Diffusion is a spontaneous, natural process leading to the transport of atomic, ionic or molecular species, across a gradient of concentration. Random walks under the ever-present thermal fluctuations let the species undergo a statistical displacement or diffusion down the concentration setup in the medium. Through the process an inhomogeneous system at local equilibriums return to its overall equilibrium by homogenization of the values of the intensive parameters. So, the phenomenon of diffusion basically involves mass transfer.

In the absence of any external fields, the chemical potential, $\mu_i$, of the substance within a phase at equilibrium is constant. If for some reason the value of $\mu_i$ vary from place to place, then the substance 'i' will tend to diffuse in such a way as to equalize the value of $\mu$ through out the phase. The driving force ($F_d$) for the diffusion process is the gradient of $\mu_i$ – larger it is, the faster is the diffusion process. For one dimensional process the force $F_d$ is given as

$$F_d = -\frac{d\mu_i}{dx} \quad ---- (1.6)$$

Further, Fick’s first law describes steady state diffusion of atomic or molecular species under their concentration gradients. The diffusion flux in one dimensional case is expressed as,

$$J = - D \left( \frac{\partial C}{\partial x} \right) \quad ---- (1.7)$$

where, $J$ is the diffusion flux (quantity of material that crosses a plane of unit area perpendicular to the diffusion direction for time unit); $D$ is the diffusion
coefficient or diffusivity of the dispersed phase; \( \frac{\partial C}{\partial x} \) is the concentration gradient in the diffusion direction.

Fick’s second law describes the diffusion under non-steady state solution, when the concentration of diffusing species is time-dependent. Within a volume element inside the medium, any accumulation or release can be accounted by the imbalance of incoming or outgoing fluxes of diffusing species and is expressed as,

\[
\frac{\partial C}{\partial t} - D \left( \frac{\partial^2 C}{\partial x^2} \right) = 0
\]

--- (1.8)

The equation being asymmetric in time flow expresses irreversibility in diffusion process.

Due to Brownian motion the colloidal particles are capable of moving (diffusing) from the regions with higher concentration to the regions with lower concentration of the dispersed phase. Because of their bigger sizes colloidal particles move slowly and diffuse at a slower rate. Since the diffusion coefficient is lower for the greater particles the concentration gradient is smaller for the colloids with finer dispersed phase. The diffusion coefficient for colloidal system:

\[
D = k_B T / (6\pi \mu r)
\]

--- (1.9)

where, \( k_B \) is Boltzmann constant (1.38×10^{-3} J/K), \( T \) is the temperature (K), \( \mu \) is the dynamic viscosity of the dispersion media (Pas) and \( r \) is the radius of the particles.

Outside force applied to the colloidal particles causes their sedimentation towards the force direction and gravity force causes the dispersed particles to sediment to the bottom. But, diffusion counteracting to any directed force prevents complete concentration of the dispersed phase at the bottom.

1.6.3 Tyndall effect and Rayleigh scattering

The optical properties of the colloidal substance are of practical importance for studying their structure, determining size and shape of the particles and also their concentration.
Although a colloidal solution appears to be homogeneous because the dispersed particles are too small too be seen, it can be distinguished from a true solution by its ability to scatter light. The scattering of light by colloidal particles is called the Tyndall effect. This effect was first observed by Tyndall in 1869. When a strong beam of light was passed through a colloidal sol placed in a dark place, then the path of beam got illuminated and this illuminated path is called Tyndall cone. Tyndall effect is not shown by true solutions because the ions or solute molecules are of such minute sizes that they cannot reflect light. Fig. 1.6 shows scattering of light by a (a) true solution and (b) colloidal dispersion. The Tyndall effect can therefore be used to distinguish between a true solution and a colloidal solution. The hazy illumination of the light beams from the headlights of a car on a dusty road is a familiar example of Tyndall effect. Blue colour of sky and seawater, twinkling of stars and visibility of tails of comets are also due to scattering of light of Tyndall effect.

The theory of light scattering was developed by Lord Rayleigh for spherical non-conducting particles that do not absorb light. This scattering results from the interaction of light with inhomogenities in solid, liquid, or gaseous materials. The actual entities that causes scattering, called scattering center, can be as small as single large molecules arranged in a non-uniform way. However, scattering becomes more effective when the size of scattering center is similar to wavelength of incident light. When a light wave passes through a medium containing non-conducting particles, the time varying electromagnetic field polarizes them. The so formed dipoles become source of light emission. In a homogeneous medium, the light
emitted by all the dipoles propagates only in the initial direction due to interference. On the other hand, if the medium containing heterogeneities with a different refractive index, as in colloidal systems with density fluctuations, the value of the dipole moment at these nodes becomes different and dipole emit non-compensated radiation in the form of scattered light. According to Rayleigh, the intensity of the scattered light, \( I \), is given by the equation:

\[
I = I_0 \frac{24 \pi^3 v^2}{\lambda^4} \left( \frac{n_1^2 - n_0^2}{n_1^2 + 2n_0^2} \right) \quad ---- (1.10)
\]

Where, \( n \) and \( n_0 \) are refractive indices of the dispersed phase and the dispersing medium; \( \lambda \) is the wavelength; \( v \) is the volume of the particle and \( \nu \) is the particle concentration.

1.7 Coagulation of colloidal particles

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 perikinetich aggregation, if by hydrodynamic motion (i.e. convection or sedimentation), the process is called orthokinetic aggregation.

Coagulation causes the destabilization of colloids by neutralizing the electric charge of the dispersed phase particles, which results in aggregation of the colloidal particles. The purpose of most coagulant chemicals is to neutralize the negative charges on the turbidity particles to prevent those
particles from repelling each other. The amount of coagulant which should be added to the water will depend on the zeta potential, a measurement of the magnitude of electrical charge surrounding the colloidal particles. It is the amount of repulsive force which keeps the particles in the water. If the zeta potential is large, then more coagulants will be needed. Coagulants tend to be positively charged. Due to their positive charge, they are attracted to the negative particles in the water. The combination of positive and negative charge results in a neutral, or lack, of charge. As a result, the particles no longer repel each other.

1.8 Sedimentation of colloidal particles

Sedimentation is the settling of suspended particles under the action of gravity or a centrifugal field. If the concentration of particles is high and interparticle forces are strong enough, the process of sedimentation may be better described as compaction of the particle structure with pressing out of the liquid. This particular kind of settling is also called subsidence.

The rate of sedimentation can be greatly increased using high speed ultra centrifuge. The force of gravity, F, is directly proportional to the effective mass, \((m-m_0)\), of the particle. Then, \(F = g (m-m_0)\) where \(m\) is the mass of the particle, \(m_0\) is mass of the dispersing medium in the volume of the particle and \(g\) is the acceleration due to gravity. Sedimentation also depends on the radius of the particle, \(r\), which is given by the equation:

\[
r = \left[ \frac{9\eta h}{2t(d-d_0)g} \right]^{1/2} \quad ---- (1.11)
\]

where \(\eta\), is the viscosity of the medium, \(h\) is height, \(t\) is the time for setting (sedimentation time), \(d\) is the density of the particle and \(d_0\) is the density of the medium. Hence, a growth in dispersity is followed by a sharp decrease in the setting speed and for colloidal particles the setting time is months and years. The following table gives the settling time of a sand particle in water to a depth of 10 cm.

<table>
<thead>
<tr>
<th>Radius (µm)</th>
<th>50</th>
<th>10</th>
<th>5</th>
<th>1</th>
<th>0.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time</td>
<td>12 Sec</td>
<td>5 min</td>
<td>20 min</td>
<td>8.3 hrs</td>
<td>&gt; 1 month</td>
</tr>
</tbody>
</table>
1.9 Sol-Gel Processing

Sol-gel synthesis encompasses a wide range of organic, inorganic and organic-inorganic porous materials which share a common preparation strategy. Generally, the sol-gel process involves the evolution of inorganic networks through the formation of a colloidal suspension (sol) and gelation of the sol to form a network in a continuous liquid phase (gel). The sol-gel process always consists in selecting the precursor of the required material, water and catalysts.

- **Precursor**: It is the precursor that, by its chemistry, leads the reaction towards the formation of colloidal particles. The precursors for synthesizing these colloids consist of a metal or metalloid element surrounded by various reactive ligands. Alkoxides are most popular because they react readily with water. For example Tetraethoxysilane (TEOS), Tetramethoxysilane (TMOS). Also, the inorganic precursor Sodium silicate (Na$_2$SiO$_3$) is also used in sol-gel processing.

- **Water**: The complete hydrolysis and polycondensation of the precursor takes place in presence of water only. Further, water is a side product of condensation and, hence, its excess should promote the reverse reaction, i.e., the hydrolysis of siloxane bonds.

- **Catalyst**: The kinetics of the reaction are impractically slow at room temperature, often requiring several days to reach completion. For this reason acid or base acatlysts are added to the formulation. The amount and type of catalyst used play key role in the microstructural, physical and optical properties of final product. Catalysts promote the hydrolysis of the precursors and render it more complete. Various mineral and carboxylic acids can be applied in the sol-gel synthesis.

Sol-Gel processing designates a type of solid materials synthesis procedure, performed in a liquid and at low temperature (typically $T < 100 \, ^\circ C$). The solid is formed as the result of a polymerization process which involves the establishment of M-OH-M or M-O-M bridges between the metallic atoms M of the precursor molecules. Such transformations are the equivalent of the polymerization process well-known to occur in organic chemistry and which consists of the establishment of direct bonds between
the carbon atoms of organic precursors. Regarding inorganic gels, that is to say mostly oxides, independent solid colloidal particles (i.e., nanoparticles with a size below a micrometer) are often formed, in a first step of the process. Each colloidal particle has a more or less densely crosslinked internal structure, as illustrated in fig. 1.7 a. It is usually easy to maintain such particles in a dispersed state in the solvent, in which case a colloidal suspension also termed a sol is obtained. In a second step, these colloidal particles can be made to link with each other, while they are still in the solvent, so as to build a three-dimensional open grid, termed a gel (fig. 1.7 b). The transformation of a sol to a gel constitutes the gelation process [9].

![Fig. 1.7 The sol-gel process, (a) sol, (b) gel](image)

The general hydrolysis and condensation reactions are given below:

**Hydrolysis:**

\[
\equiv M - X + H_2O \rightarrow \equiv M - OH + HX \hspace{1cm} (1.12)
\]

M = metal or Si; X = reactive ligand like halogen, OR, NR$_2$, acylate

**Condensation:**

**Alcohol condensation**

\[
\equiv M - OH + X-M \equiv \rightarrow \equiv M-O- M \equiv + HX \hspace{1cm} (1.13)
\]

**Water condensation**

\[
\equiv M - OH + HO-M \equiv \rightarrow \equiv M-O- M \equiv + H_2O \hspace{1cm} (1.14)
\]
1.9.1 Sol

A sol is a dispersion of colloidal particles suspended in Brownian motion within a fluid matrix. Suspension of particles of linear dimensions between 1nm (10 Å) and 1µm (10^4 Å) are called colloids [10]. The particles in this proper size range can be divided into three categories. They can be either composed of subdivided parts of bulk mater (e.g. small particles of alumina), or real macromolecules that are big enough to be colloidal (such as proteins), or of small particles that can be considered both macromolecules and as tiny parts of macroscopic matter (e.g. lacy particles). In the case of subdivided parts of bulk material, there are two thermodynamic phases and the sol is considered as lyophobic, or hydrophobic if water is the main solvent used.

1.9.2 Gelation

Gelation occurs when links form between silica sol particles, produced by hydrolysis and condensation reactions, to such an extent that a giant spanning cluster reaches across the containing vessel. At this point, although the mixture has a high viscosity so that it does not pour when the vessel is tipped. Many sol particles are still present as such, entrapped and entangled in the spanning cluster. This initial gel has a high viscosity but low elasticity. There is no exotherm or endotherm, nor any discrete chemical change at the gel point, only the sudden viscosity increase as shown in fig. 1.8.

![Fig. 1.8 Change in viscosity and elasticity of the sol with time](image-url)
Following gelation, further cross-linking and chemical inclusion of isolated sol particles into the spanning cluster continues, leading to an increase in the elasticity of the sample. Precise definition of the term “gelpoint” is the time interval starting from the moment of sol preparation to the moment no more fluidity of the sol [11].

Fig. 1.9 depicts the bond formation between two colloidal silica particles while gelation takes place.

The kind of inorganic network formed by the condensation reactions not only depends on the absolute rates of the individual reactions but also on the relative rate of hydrolysis and condensation reactions as illustrated in fig. 1.10 [12].

Acidic conditions (pH 2–5) favor hydrolysis, and condensation is the rate-determining step. A great number of monomers or small oligomers with reactive Si–OH groups are simultaneously formed. Under these conditions, reactions at terminal silicon atoms are favored, and chains with few branches are formed. This results in polymer like networks with small pores.

Hydrolysis is the rate-determining step under basic conditions, which favor reaction at central silicon atoms of an oligomer. The resulting network has a particulate character with large particles and large pores (“colloidal” gels). Hydrolyzed species are immediately consumed because of the faster condensation reaction. Condensation of clusters with each other is relatively
unfavorable. Therefore, the clusters mainly grow by the condensation of monomers.

![Graph showing dependence of relative hydrolysis and condensation reaction on pH](image)

**Fig. 1.10 Dependence of the relative hydrolysis and condensation reaction on the pH of the sol**

1.9.3 Gel

A gel is a porous 3-dimensionally interconnected semi-solid network that expands in a stable fashion throughout a liquid medium and is only limited by the size of the container. The nature of gels depends on the coexistence between the solid network and the liquid medium. The liquid is present between the mesh of the solid network that composes the gel; it does not flow out spontaneously and is in thermodynamic equilibrium with the solid network. A gel is a soft material that can be easily cut with a knife. Finally, removal of the liquid phase leads to the xerogel or aerogel which depends upon the drying conditions of the gel.

1.10 Types of gel

Depending on the way of formation of gel network, the gels are classified as colloidal and polymeric gels.

1.10.1 Colloidal gel: Systems containing colloidal particles (1-1000 nm) upon aggregation and condensation are linked into a three-dimensional network
surrounded by liquid phase are termed as colloidal gels. Theses gels are formed from sol particles and are also known as corpuscular gel.

1.10.2 Polymeric gel: These are considered as suspensions of highly branched macromolecules in which individual particles cannot be distinguished. If the solid network is made up of sub-colloidal chemical units then the gel is polymeric. A polymer, as defined by the Flory is a group of molecules whose structure can be generated through repetition of one or a few elementary units [13]. The solubility of these macromolecules in a water-alcohol acid medium prevents the transformation of these chains into individual particles. They are directly formed gels from rather linear polymer formed from a precursor solution, without the intermediate occurrence of individual particles.

Further depending on the fluid present in the pores of gels, they are classified as given in the table 1.3.

<table>
<thead>
<tr>
<th>Fluid</th>
<th>Gel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>Hydrogel / Aquagel</td>
</tr>
<tr>
<td>Alcohol</td>
<td>Alcogel</td>
</tr>
<tr>
<td>Air</td>
<td>Aerogel</td>
</tr>
</tbody>
</table>

1.11 Advantages of sol-gel processing

Sol–gel synthesis is one of the pursuits of modern materials science. This method is widely used in practice owing to the large number of advantages over the traditional synthesis of materials from powders. These advantages are as follows [14]:

(i) the simplicity of purification of initial metal alkoxides (in the case of synthesis of xerogels by hydrolysis and polycondensation of alkoxides),

(ii) a high degree of homogeneity in a multicomponent system,

(iii) a considerable decrease in the expenditure of energy upon sintering of colloidal particles due to their high surface energy,
(iv) the possibility of producing noncrystalline systems whose synthesis by traditional methods leads to the phase separation or crystallization,

(v) the possibility of retaining the shape and volume from the pouring of a liquid sol to the preparation of a final product, and

(vi) a sufficiently large amount of information in the field of preparation technology.

Due to possibility of obtaining high surface area solids with homogeneous compositions and controlled porosity, sol-gel methods have been widely employed for the synthesis of micro and mesoporous materials.

There are three strategies that enable to control the pore size:

- Solvent-templating of the silica framework (Aerogel, Xerogel)
- The preparation of hybrid organic-inorganic membranes followed by the extraction of the organic constituents that serves as micropore templates.
- Surface derivatization of preformed pore networks with well-defined molecular species.
References
