Module – 12.1

Surface Chemistry

Surface chemistry is the study of the processes that occur at the interface of two bulk phases. The bulk phases can be of the type solid – gas, solid – liquid, liquid – gas and liquid – liquid. There is no interface between gases because of their complete miscibility. The bulk phase can be solutions or pure compounds.

Sorption, which includes both absorption and adsorption, is a process in which a substance moves from one phase to be accumulated in another phase. Dyes get adsorbed as well as absorbed in the cotton fibers, i.e., sorption

Absorption and Adsorption:

In the process of absorption molecules of one phase interpenetrate uniformly among those of another phase to form a solution with the second phase.
Example: sponge in H_2O, chalk in ink etc

In adsorption, molecules of one phase are present in higher concentration at the surface of the second phase.
Example: Inert gases on charcoal

Water vapor is absorbed by calcium chloride while it is adsorbed by silica gel. In the same manner, ammonia is absorbed by water and is adsorbed by charcoal.

Adsorption:

There are several examples, which reveal that the surface of a solid has the tendency to attract and retain the molecules of the phase with which it comes into contact. These molecules remain only at the surface and do not go deeper into the bulk. The accumulation of molecular species at the surface rather than in the bulk of a solid or liquid is termed adsorption. The molecular species or substance, which concentrates or accumulates at the surface, is termed **adsorbate** and the material on the surface of which the adsorption takes place is called **adsorbent**.

Adsorption is essentially a surface phenomenon. Solids, particularly in finely divided state, have large surface area and therefore (charcoal, silica gel, alumina gel, clay, colloids, metals in finely divided state, etc.) act as good adsorbents.

Examples of adsorption:

a. If a gas like O_2, H_2, CO, Cl_2, NH_3 or SO_2 is taken in a closed vessel containing powdered charcoal, it is observed that the pressure of the gas in the enclosed vessel decreases. The gas molecules concentrate at the surface of the charcoal, i.e., gases are adsorbed at the surface.
b. In a solution of an organic dye, say methylene blue, when animal charcoal is added and the solution is well shaken, it is observed that the filtrate is colourless. The molecules of the dye, accumulate said to be on the surface of charcoal, i.e., are adsorbed.
c. Aqueous solution of raw sugar (Molasses), when passed over beds of animal charcoal, becomes colourless as the colouring substances are adsorbed by the charcoal.
d. The air becomes dry in the presence of silica gel because the water molecules get adsorbed on the surface of the gel.
   It is clear from the above examples that solid surfaces can hold the gas or liquid molecules by virtue of adsorption. The process of removing an adsorbed substance from a surface on which it is adsorbed is called desorption. I.e. it is the reverse process of adsorption.

Types of adsorption: Adsorption can be classified into two categories as described below,

1. **Depending upon the concentration:**
   In adsorption the concentration of one substance is different at the surface of the other substance as compared to adjoining bulk or interior phase.
   a. **Positive adsorption:** If the concentration of an adsorbate is more on the surface as compared to its concentration in the bulk phase then it is called positive adsorption.
      Example: H_2 on activated carbon, CH_4 on activated carbon, When a concentrated solution of KCl is shaken with animal charcoal, it shows positive adsorption.

   b. **Negative adsorption:** If the concentration of the adsorbate is less on the surface than its concentration in the bulk then it is called negative adsorption.

      Example: When a dilute solution of KCl is shaken with animal charcoal, it shows negative adsorption.

2. **Depending upon the nature of force existing between adsorbate molecule and adsorbent:**
   a. **Physical adsorption:** If the forces of attraction existing between adsorbate and adsorbent are van der Waals forces, the adsorption is called physical adsorption. This type of adsorption is also known as physisorption or van der Waals adsorption. It can be easily reversed by heating or decreasing the pressure.
   b. **Chemical adsorption:** If the forces of attraction existing between adsorbate particles and adsorbent are of a chemical nature. i.e. are almost of the same strength as chemical bonds, the adsorption is called chemical adsorption. This type of adsorption is called as chemisorption or Langmuir adsorption. This type of adsorption cannot be easily reversed.

Comparison between physisorption and chemisorptions:

Physisorption **(van der Waals adsorption)**	**Chemisorption** **(Langmuir adsorption)**
Low heat of adsorption usually in range of 20 – 40 kJ/mol	High heat of adsorption in the range of 50 – 400 kJ/mol
Forces of attraction are van der Waals forces.	Forces of attraction are chemical bond forces.
It is readily reversible	It is irreversible
It usually takes place at low temperatures and decreases with increasing temperature.	It takes place at high temperature.
It is related to the case of liquefaction of the gas.	It is not related.
It forms multimolecular layers on the adsorbent surface.	It forms monomolecular layer on the adsorbent surface.
It does not require an activation energy.	It requires high activation energy.
In case of gaseous adsorbates	In case of gaseous adsorbates

decrease of pressure on the surface causes desorption.	decrease of pressure on the surface does not cause desorption.

Assignment questions:

1. What is adsorption?

Solution:

Adsorption: In adsorption, molecules of one phase are present in higher concentration at the surface of the second phase.
Example: Inert gases on charcoal.

2. What is physisorption?

Solution:

Physical adsorption: If the forces of attraction existing between adsorbate and adsorbent are van der Waals forces, the adsorption is called physical adsorption. This type of adsorption is also known as physisorption or van der Waals adsorption. It can be easily reversed by heating or decreasing the pressure.

3. Write any two characteristics of chemisorption?

Solution:

- a) High heat of adsorption in the range of 50 – 400 kJ/mol
- b) Forces of attraction are chemical bond forces.
- c) It is irreversible
- d) It takes place at high temperature.

4. Write a note on the types of adsorption

Solution:

Types of adsorption: Adsorption can be classified into two categories as described below,

1. **Depending upon the concentration:**
   In adsorption the concentration of one substance is different at the surface of the other substance as compared to adjoining bulk or interior phase.
   a. **Positive adsorption:** If the concentration of an adsorbate is more on the surface as compared to its concentration in the bulk phase then it is called positive adsorption.
      Example: H_2 on activated carbon, CH_4 on activated carbon, When a concentrated solution of KCl is shaken with animal charcoal, it shows positive adsorption.
   b. **Negative adsorption:** If the concentration of the adsorbate is less on the surface than its concentration in the bulk then it is called negative adsorption.
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   a. **Physical adsorption:** If the forces of attraction existing between adsorbate and adsorbent are van der Waals forces, the adsorption is called physical adsorption. This type of adsorption is also known as physisorption or van der Waals adsorption. It can be easily reversed by heating or decreasing the pressure.
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5. How do you differentiate physisorption from chemisorptions?

Solution:

Physisorption **(van der Waals adsorption)**	**Chemisorption** **(Langmuir adsorption)**
Low heat of adsorption usually in range of 20 – 40 kJ/mol	High heat of adsorption in the range of 50 – 400 kJ/mol
Forces of attraction are van der Waals forces.	Forces of attraction are chemical bond forces.
It is readily reversible	It is irreversible
It usually takes place at low temperatures and decreases with increasing temperature.	It takes place at high temperature.
It is related to the case of liquefaction of the gas.	It is not related.
It forms multimolecular layers on the adsorbent surface.	It forms monomolecular layer on the adsorbent surface.
It does not require an activation energy.	It requires high activation energy.
In case of gaseous adsorbates decrease of pressure on the surface causes desorption.	In case of gaseous adsorbates decrease of pressure on the surface does not cause desorption.
It is not very specific.	It is highly specific.

Review questions:

Example set:

1. Chemisorption is
    a. Multimolecular in nature
    b. Reversible
    c. Often specific and directional
    d. Not very specific

Solution: c)

2. The two phenomenon, adsorption and absorption together are known as
    a. Desorption
    b. Sorption
    c. Both a) and b)
    d. None

Solution: b)

3. Physical adsorption
    a. Is reversible
    b. decreases with temperature
    c. is exothermic
    d. All

Solution: d)

4. Which of the following is not correct about adsorption?
    a. Adsorption is a surface phenomenon
    b. Adsorption is a bulk phenomenon
    c. Adsorption is a physical phenomenon
    d. Adsorption is a chemical phenomenon

Solution: b)

5. What is absorption?

Solution: In the process of absorption molecules of one phase interpenetrate uniformly among those of another phase to form a solution with the second phase.
Example: sponge in H_2O, chalk in ink etc

6. What is chemisorption?

Solution: **Chemical adsorption:** If the forces of attraction existing between adsorbate particles and adsorbent are of a chemical nature. i.e. are almost of the same strength as chemical bonds, the adsorption is called chemical adsorption.

7. Explain types of adsorption based on concentration?

Solution: Depending upon the nature of force existing between adsorbate molecules and adsorbent:

a. **Physical adsorption:** If the forces of attraction existing between adsorbate and adsorbent are van der Waals forces, the adsorption is called physical adsorption. This type of adsorption is also known as physisorption or van der Waals adsorption. It can be easily reversed by heating or decreasing the pressure.
b. **Chemical adsorption:** If the forces of attraction existing between adsorbate particles and adsorbent are of a chemical nature. i.e. are almost of the same strength as chemical bonds, the adsorption is called chemical adsorption. This type of adsorption is called as chemisorption or Langmuir adsorption. This type of adsorption cannot be easily reversed.

Problem set:

1. Physical adsorption is characterized as ____ process
   a. Highly specific
   b. Reversible
   c. Irreversible
   d. Monolayer adsorption

Solution: b)

2. Gas masks containing activated charcoal are used to remove poisonous gases from atmosphere. They function on the principle of
   a. Adsorption
   b. Absorption
   c. Sorption
   d. All

Solution: a)

3. Chemical adsorption is ____
   a. An exothermic process
   b. An irreversible change
   c. An unilayer formation
   d. All

Solution: d)

4. Adsorption of H_2 or O_2 on activated charcoal is
    a. A physical adsorption
    b. A chemical adsorption
    c. Both physical and chemical adsorptions
    d. Neither physical nor chemical adsorption

Solution: a)

5. Distinguish between adsorption and absorption. Give examples.

Solution: Absorption and Adsorption:

In the process of absorption molecules of one phase interpenetrate uniformly among those of another phase to form a solution with the second phase.
Example: sponge in H_2O, chalk in ink etc

In adsorption, molecules of one phase are present in higher concentration at the surface of the second phase.
Example: Inert gases on charcoal.

6. Distinguish between physical adsorption and chemical adsorption

Solution:

a. **Physical adsorption:** If the forces of attraction existing between adsorbate and adsorbent are van der Waals forces, the adsorption is called physical adsorption. This type of adsorption is also known as physisorption or van der Waals adsorption. It can be easily reversed by heating or decreasing the pressure.
b. **Chemical adsorption:** If the forces of attraction existing between adsorbate particles and adsorbent are of a chemical nature. I.e. are almost of the same strength as chemical bonds, the adsorption is called chemical adsorption. This type of adsorption is called as chemisorption or Langmuir adsorption. This type of adsorption cannot be easily reversed.

Exercise questions:

1. What is the process involved in the Dewar method of separation of inert gases?
2. Why does physisorption decrease with the increase of temperature?
3. Why is adsorption always exothermic?

Solutions to exercise questions:

1. Van der Waals adsorption
2. Physisorption is exothermic in nature. Therefore, in accordance with Le-Chateliere's principle, it decreases with an increase in temperature. This means that physisorption occurs more readily at a lower temperature.
3. Adsorption is always exothermic. This statement can be explained in two ways.
    a. Adsorption leads to a decrease in the residual forces on the surface of the adsorbent. This causes a decrease in the surface energy of the adsorbent. Therefore, adsorption is an exothermic change.
    b. When a gas is adsorbed on a solid surface, its movement is restricted leading to a decrease in the entropy of the gas i.e., ΔS is negative. Now for a process to be spontaneous, ΔG should be negative. ΔH of adsorption is always negative.

Therefore, $\Delta G = \Delta H - T\Delta S$;

Since ΔS is negative, ΔH is negative to make ΔG negative $\Delta H > T\Delta S$. Hence, adsorption is always exothermic.

Module – 12.2

Factors affecting adsorption

Adsorption of gases on solids depends on the following factors:

a. Nature of the gas (adsorbate)
b. Nature of the solid (adsorbent)
c. Surface area of the solid
d. Pressure of the gas
e. Temperature

a. Nature of the adsorbate:

Since physical adsorption is non – specific, every gas (i.e. adsorbate) gets adsorbed on the surface of any solid. How much of the gas will get adsorbed depends on the nature of the gas. Under any given condition of temperature and pressure, the easily liquefiable gases such as NH_3, HCl and SO_2 are adsorbed more than the gases like H_2, N_2 and CO. The ease with which a gas can be liquefied is determined by its critical temperature, T_c. T_c is the temperature above which a gas cannot be liquefied, and however high the applied pressure may be. This implies that gases with high critical temperature values can be easily liquefied as compared to gases with low critical temperature values. The table given below illustrates the correlation between the extent of adsorption of gases on charcoal with their ease of liquefaction.

Volume of gases at N.T.P adsorbed by 1g charcoal at 288 K

Gas	H_2	N_2	CO	CH_4	CO_2	HCl	NH_3	SO_2
Volume adsorbed (cc)	4.7	8.0	9.3	16.2	48	72	181	380

Ease of Liquefaction → increases

Since chemisorption is specific in nature, a gas is chemisorbed only when it forms chemical bonds with the adsorbent. A gas which is physisorbed at a certain temperature can be chemisorbed when the temperature is increased dramatically. For e.g., at 83 K nitrogen (N_2) is physisorbed on iron surface as N_2 molecules. At room temperature there is no physisorption of N_2 on iron surface. However, at 773K nitrogen is chemisorbed on iron surface as nitrogen atoms.

b. Nature of the adsorbent:

The nature of the adsorbent has profound effect on the process of adsorption. Solids with porous structure are potentially good adsorbents. Among them, activated carbon is the most common adsorbent for gases which are easily liquefied. Activated carbon is used in gas masks to adsorb poisonous gases such as methane (CH_4).

Activated carbon is prepared from a variety of raw materials including wood, lignite, coal, bone, nut shells and petroleum residues. The new material is activated in an atmosphere of CO_2, CO, O_2 water vapor air or other selected gases at a temperature between 573 K and 1273 K. This is often followed by quenching in air or water. Adsorption on activated carbon is associated with the presence of small and uniform pores. The surface area of activated carbon is approximately 1000 m^2/g.

Apart from activated carbon, silica gel, aluminium oxide and clay are used as adsorbents. It is common knowledge that small satchets containing silica gel are used in electronic equipments such as camera to keep the lenses dry. As mentioned earlier, silica gel is used to adsorb water vapor, which is always present in the humid weather conditions.

c. Surface area of the solid adsorbent:

The extent of adsorption depends directly upon the surface area of the adsorbent, i.e. **larger the surface area of the adsorbent, greater is the extent of adsorption.**

Surface area of a powdered solid adsorbent depends upon its particle size. Smaller the particle size, greater is its surface area.

d. Pressure of the gas - Adsorption Isotherms:

The extent of adsorption of a gas on a solid generally increases with pressure. The extent of adsorption is given by x/m, (the ratio of the mass (x) of the adsorbate and the mass (m) of the adsorbent) when a dynamic equilibrium has been attained. The plot of extent of adsorption versus pressure of the gas, at a given temperature, is called the adsorption isotherm. Adsorption isotherms of different shapes have been observed in various experiments. Adsorption isotherms are usually described by different empirical equations. Here, the two most common adsorption isotherms namely, Freundlich isotherm and Langmuir isotherm will be discussed.

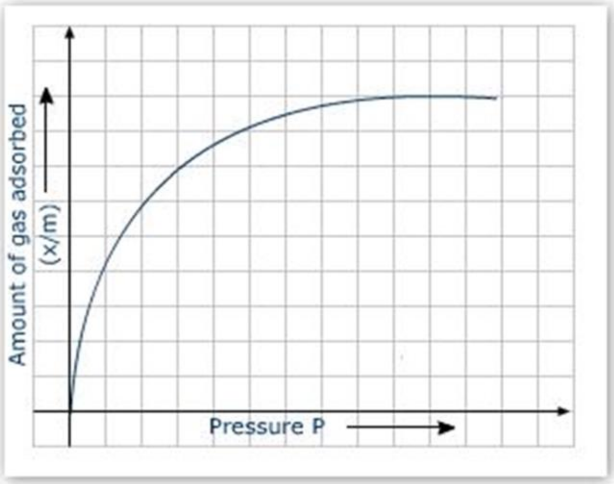
Freundlich Adsorption Isotherm:

This type of isotherm is described by the empirical equation

$$\frac{x}{m} = KP^{\frac{1}{n}} (where\ n > 1) \qquad \ldots\ldots (1)$$

Where K and n are the parameters which depend on the nature of the gas, and P is the pressure.

At equilibrium pressure, P_s, x/m reaches its maximum value, that is, no further adsorption takes place even if the pressure is increased. A saturation state has been attained. The adsorption isotherm which conforms to Freundlich equation is shown.



Freundlich adsorption isotherm

Since n is greater than one, qualitatively, it can be said that the extent of adsorption x/m does not increase rapidly with increase in pressure as shown in the above figure. Freundlich equation can be transformed into a linear form by taking the logarithms on both sides of the equation 1.

$$log\left(\frac{x}{m}\right) = log\ K + \frac{1}{n}\log P \qquad \ldots\ldots (2)$$

Hence, if the plot of log(x/m) versus log P yields a straight line, it implies that the adsorption process conforms to Freundlich isotherm. From the intercept, the parameter K is obtained, while the slope is equal to (1/n).

Langmuir Isotherm:

Langmuir adsorption isotherm is based on the following assumptions.

a. Adsorption proceeds to form only monolayers on the surface of the adsorbent.
b. All the sites available on the adsorbent surface are equivalent and the surface is perfectly uniform, that is flat.
c. The ability of a gas molecule to get adsorbed at a particular site is independent of the occupation of neighboring sites. This implies that there is no interaction between adjacent adsorbed molecules.
d. A dynamic equilibrium exists between the adsorbed molecules and the free gas molecules.

Initially, since the surface is completely free of any gas molecules, every molecule of the gas that strikes the surface of solid may get adsorbed. After some time, only those gas molecules may get adsorbed which strike the part of the surface that is not already covered. This means, that initially the rate of adsorption is high and then decreases as less surface is available for adsorption. The adsorbed gas molecules escape from the surface of the adsorbent.

A dynamic equilibrium exists between the adsorbed molecules and the free gas molecules. It implies that the adsorbed molecules also undergo desorption, probably due to thermal agitation. When the rate of adsorption equals the rate of desorption, dynamic equilibrium is established.

If q is the fraction of the total available surface covered with gas molecules, at any instant, then (1-q) is the fraction of the surface of the solid which is vacant. From kinetic theory of gases, it is known that the rate at which gas molecules collide per unit area of a surface is directly proportional to the pressure of the gas. The rate of adsorption depends on both the pressure of the gas and fraction of surface available for adsorption. Hence,

Rate of adsorption = $K_a (1 - \theta) P$ …..(3)

The rate of desorption is directly proportional to the fraction of the surface covered with gas molecules.

i.e. Rate of desorption = K_d (θ) …..(4)

At equilibrium, the rate of adsorption is equal to the rate of desorption i.e.,

$K_a (1 - \theta) P = K_d (\theta)$

$$\frac{(1-\theta)}{\theta} = \frac{K_d}{K_a P}$$

Or $\left(\frac{1}{\theta} - 1\right) = \frac{K_d}{K_a P}$ $, Then$

$$or, \theta = \frac{K_a P}{K_d + K_a P}$$

$$or, \theta = \frac{KP}{1+KP} \quad \ldots\ldots(5)$$

Where $K = \frac{K_a}{K_d}$ = constant

Now, the extent of adsorption (x/m) is proportional to the fraction of surface covered. Therefore,

$\frac{x}{m} = k\theta = \frac{kKP}{1+KP} \qquad \ldots..(6)$ where ‘k’ is a constant of proportionality.

$$or, \frac{x}{m} = \frac{\alpha P}{1+KP} \qquad \ldots..(7) \qquad (where\ \alpha = kK)$$

This is the equation which describes the Langmuir adsorption isotherm. Here ‘α’ and K are the Langmuir parameters and are characteristic of a particular system at a particular temperature.

Freundlich and Langmuir adsorption isotherms are also applicable to adsorption processes in solutions. In place of equilibrium pressures, equilibrium concentrations of the adsorbates are used and the isotherms are expressed in the forms,

$$\frac{x}{m} = Kc^{\frac{1}{n}} \quad (n > 1)(Freundlich\ isotherm)$$

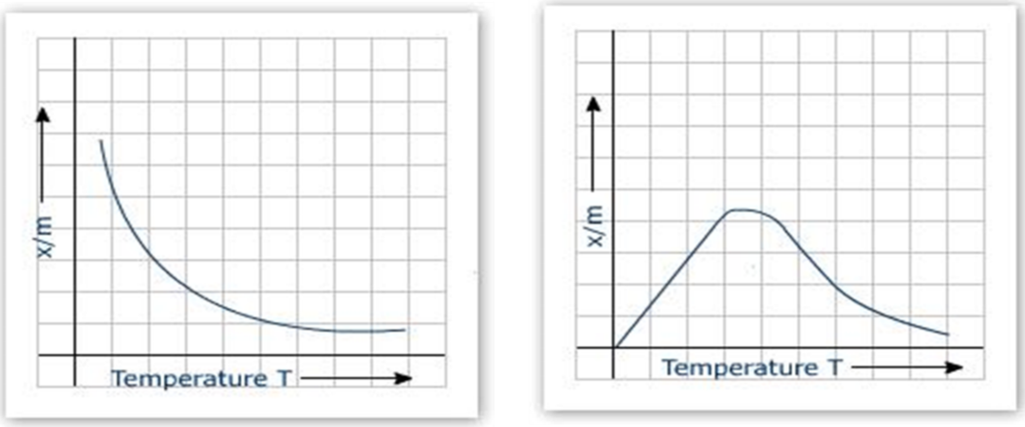
$$\frac{x}{m} = \frac{ac}{1+Kc} \qquad (Langmuir\ isotherm)$$

Where 'c' is the concentration of the solute in solution.

Effect of temperatures on adsorption:

Generally physisorption takes place at low temperatures while chemisorptions takes place at high temperatures. At 463 K, N_2 gas undergoes physisorption on iron metal. But at 723 K iron nitride compound is formed due to chemisorption. So, as the temperature rises, physisorption may change in to chemisorptions or desorption may also take place (as in the case of inert gases on activated charcoal).

The amount of gas adsorbed by unit mass of adsorbent (i.e, $\frac{x}{m}$) changes with temperature. The process of adsorption is exothermic in nature. Hence according to Le Chatelier principle, the extent of adsorption decreases with a rise in temperature. This is very true in the case of physical adsorption. But in case of chemical adsorption the effect of temperature is complex. The amount of ($\frac{x}{m}$ value) increases first with increase in temperature, reaches a maximum and then decreases on further rising the temperature. The change in the amount of adsorption $\left(\frac{x}{m}\right)$ with temperature for physical and for chemical adsorptions are shown in the figures given below. These graphs that show the variation of $\frac{x}{m}$ with temperature are known as “adsorption isobars”. (graphs drawn at constant pressure).



a. Physical adsorption **b. Chemisorption**

Variation of $\frac{x}{m}$ with temperature (absorption isobars)

The adsorption isobars are used to distinguish physical adsorption from chemical adsorption. As can be seen from the above graphs, their shapes are different and hence physisorption and chemisorptions processes can be distinguished.

Application of adsorption:

The phenomenon of adsorption finds a number of applications. Important applications are given as follows.

1. **Production of high vacuum**
2. **In Gas masks :**
   This apparatus is used to adsorb poisonous gases (e.g. Cl_2, CO oxide of sulphur etc.) and thus purify the air for breathing.

3. **For desiccation or dehumidification:**
   These substances can be used to reduce/remove water vapours or moisture present in the air. Silica gel and alumina are used for dehumidification in electronic equipment.

4. **Removal of colouring matter from solution :**
   a. Animal charcoal removes colours of solutions by adsorbing coloured impurities.
   b. Animal charcoal is used as decolouriser in the manufacture of cane sugar.

5. Heterogeneous catalysis :

Mostly heterogeneous catalytic reactions proceed through the adsorption of gaseous reactants on solid catalyst. For example,

a. Finely powdered nickel is used for the hydrogenation of oils.
b. Finely divided vanadium pentoxide (V_2O_5) is used in the contact process for the manufacture of sulphuric acid.

6. Separation of inert gases :

Due to the difference in degree of adsorption of gases by charcoal, a mixture of inert gases can be separated by adsorption on coconut charcoal at different low temperatures.

7. Softening of hard water:

a. The hard water is made to pass through a column packed with zeolite (sodium aluminium silicate)
b. Ca^{++}, Mg^{++} ions which are responsible for hardness, get adsorbed on zeolite, exchanging sodium ions.

$$Na_2Al_2Si_2O_5 + CaCl_2 \longrightarrow CaAl_2Si_2O_8 + 2NaCl$$

c. The exhausted zeolite is regenerated with 10% of sodium chloride solution.

$$CaAl_2Si_2O_8 + 2NaCl \longrightarrow Na_2Al_2Si_2O_8 + CaCl_2$$

8. De – Ionisation of water:

a. Water can be de-ionised by removing all dissolved salts with the help of cation and anion-exchanger resins.
b. Cation-exchanger is an organic synthetic resin such as polystyrene-containing a macroanion ($R—SO^{-}_3$ etc) which has adsorbed H^+ ions.
c. A resin containing a basic group (R_3Na^+ etc.) Which has adsorbed OH^- ions acts as anion exchanger.

9. In curing diseases :

A number of drugs are adsorbed on the germs and kill them or these are adsorbed on the tissues and heat them.

10. Cleaning agents:

Soap and detergents get adsorbed on the interface and thus reduce the surface tension between dirt and cloth, subsequently the dirt is removed from the cloth.

11. Froth floatation process:

A low grade sulphide ore is concentrated by separating it from silica and other earthy matter by this method.

12. In adsorption indicators:

Surface of certain precipitates such as silver halide, have the property of adsorbing some dyes like eosin, fluorescein etc. the colour is used to detect the end point in the volumetric analysis.

13. In dyeing:

Many dyes get adsorbed on the cloth either directly or by the use of mordants.

Assignment questions:

1. Give the mathematical equation relating the pressure (P) and the extent of adsorption (x/m) of gas on a metal surface
2. Give an account of adsorption of gases by metals with examples
3. Discuss the factors that effect adsorption of gases on metals

Review questions:

Example set:

1. The extent of adsorption of a gas on a solid depends on
   a. Nature of gas
   b. Pressure of gas
   c. Temperature of the system
   d. All

Solution: d)

2. For adsorption of gas on solid surface, the plots of log x/m vs log P is linear with a slope equal to
   a. K

b. log K
c. 1n K
d. 1/n (n being integer greater than unity)

Solution: d)

3. Which of the following gases is adsorbed strongly by charcoal
    a. H_2
    b. N_2
    c. O_2
    d. NH_3

Solution: d)

4. Freundlich adsorption isotherm gives a straight line on plotting
    a. $\frac{x}{m}$ vs P
    b. log $\frac{x}{m}$ vs P
    c. log $\frac{x}{m}$ vs log P
    d. $\frac{x}{m}$ vs $\frac{1}{P}$

Solution: c)

5. Give an account of Langmuir adsorption isotherm; Freundlich isotherm

Solution:

Langmuir adsorption isotherm :The extent of adsorption (x/m) is proportional to the fraction of surface covered. Therefore,

$\frac{x}{m} = K\theta = \frac{kKP}{1+KP} \qquad \ldots..(6)$ where 'K' is a constant of prop

$$or, \frac{x}{m} = \frac{\alpha P}{1+KP} \qquad \ldots..(7) \qquad (\alpha = kK)$$

This is the equation which describes the Langmuir adsorption isotherm. Here 'α' and K are the Langmuir parameters and are characteristic of a particular system at a particular temperature.

Freundlich Adsorption Isotherm:

This type of isotherm is described by the empirical equation

$$\frac{x}{m} = KP^{\frac{1}{n}}(where\ n > 1) \qquad \ldots\ldots(1)$$

Where K and n are the parameters which depend on the nature of the gas, and P is the pressure.

6. Give the effect of temperature adsorption of gases by metals

Solution: The amount of gas adsorbed by unit mass of adsorbent (i.e, $\frac{x}{m}$) changes with temperature. The process of adsorption is exothermic in nature. Hence according to Le Chatelier principle, the extent of adsorption decreases with a rise in temperature. These graphs that show the variation of $\frac{x}{m}$ with temperature are known as "adsorption isobars".

Problem set:

1. Which is correct in case of van der Waals adsorption
   a. High temperature, low pressure
   b. Low temperature, high pressure
   c. Low temperature, low pressure
   d. High temperature, high pressure

Solution: b)

2. Which can adsorb larger volume of hydrogen gas
   a. A palladium block
   b. Finely divided palladium
   c. Broken pieces of palladium
   d. All equally adsorb

Solution: b)

3. The gases which liquefy more easily are adsorbed more readily than the permanent gases because the easily liquefiable gases have greater
   a. Van der Waals forces
   b. Molecular forces of attraction
   c. Cohesive forces

   d. All the above

Solution: d)

4. Which equation represents Langmuir adsorption
   a. $x/m = \alpha$
   b. $x/m \propto P$
   c. $x/m = 1/P$
   d. $x/m > P$

Solution: b)

5. Discuss the effect of the nature of the absorbate on adsorption

Solution:

Nature of the adsorbate:

Since physical adsorption is non – specific, every gas (i.e. adsorbate) gets adsorbed on the surface of any solid. How much of the gas will get adsorbed depends on the nature of the gas. Under any given condition of temperature and pressure, the easily liquefiable gases such as NH_3, HCl and SO_2 are adsorbed more than the gases like H_2, N_2 and CO. The ease with which a gas can be liquefied is determined by its critical temperature, T_c. T_c is the temperature above which a gas cannot be liquefied, and however high the applied pressure may be. This implies that gases with high critical temperature values can be easily liquefied as compared to gases with low critical temperature values. The table given below illustrates the correlation between the extent of adsorption of gases on charcoal with their ease of liquefaction.

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Volume adsorbed (cc)	4.7	8.0	9.3	16.2	48	72	181	380

Ease of Liquefaction → increases

Since chemisorption is specific in nature, a gas is chemisorbed only when it forms chemical bonds with the adsorbent. A gas which is physisorbed at a certain temperature can be chemisorbed when the temperature is increased dramatically. For e.g., at 83 K nitrogen (N_2) is physisorbed on iron surface as N_2 molecules. At room temperature there is no physisorption of N_2 on iron surface. However, at 773K nitrogen is chemisorbed on iron surface as nitrogen atoms.

6. Does surface area have an effect on adsorption of a gas? Explain

Solution: Surface area of the solid adsorbent:

The extent of adsorption depends directly upon the surface area of the adsorbent, i.e. **larger the surface area of the adsorbent, greater is the extent of adsorption.**

Surface area of a powdered solid adsorbent depends upon its particle size. Smaller the particle size, greater is its surface area.

Exercise questions:

1. The curve showing variation of x/m with temperature is inverted "V" shape. What is the type of adsorption?
2. Why are powdered substances more effective adsorbents than their crystalline forms?
3. Give reasons for why a finely divided substance is more effective as an adsorbent.

Solutions to exercise questions:

1. Chemisorption
2. Powdered substances are more effective adsorbents than their crystalline forms because when a substance is powdered, its surface area increases and physisorption is directly proportional to the surface area of the adsorbent.
3. Adsorption is a surface phenomenon. Therefore, adsorption is directly proportional to the surface area. A finely divided substance has a large surface area. Both physisorption and chemisorption increase with an increase in the surface area. Hence, a finely divided substance behaves as a good adsorbent.

Module – 12.3, 12.4 & 12.5

The Colloidal State

Introduction:

The foundation of colloidal chemistry was laid down by an English scientist, Thomas Graham, **in 1861**. **The credit for the various advances in this field goes to eminent scientists like** Tyndall, Hardy, Zsigmondy, N.R. Dhar, S.S. Bhatnagar and others. Thomas Graham **classified the soluble substances into two categories depending upon the rate of diffusion through animal and vegetable membranes or** parchment paper.

a. **Crystalloids:** They have higher rate of diffusion and diffused from parchment paper.

Examples: All strong acids, bases and salts and organic compounds such as sugar, urea etc.

b. **Colloids** (Greek word, kolla, meaning glue-like): They have slower rate of diffusion and can not diffuse through from parchment paper.

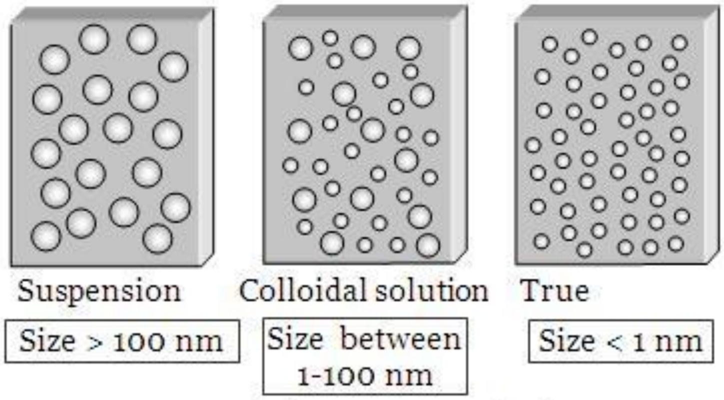
Examples: Starch, gelatin, gum, silicic acid and hemoglobin etc.

The above classification was discarded i.e., **the terms colloid does not apply to a particular class of substances but is a state of matter like solid, liquid and gas. Any substance can be brought into colloidal state. The colloidal state depends on the particle size.** It is regarded as intermediate state between true solution and suspension.

Features of the three types of solutions

Property	Suspension	Colloidal solution	True solution
Nature	Heterogeneous	Heterogeneous	Homogeneous
Particle size	> 100 nm	1 nm – 100 nm	< 1 nm
Separation by			

(i) Ordinary filtration (ii) Ultra- filtration	Possible Possible	Not possible Possible	Not possible Not possible
Settling of particles	Settle under gravity	Settle only on centrifugation	Do not settle
Appearance	Opaque	Generally transparent	Transparent
Diffusion of particles	Does not diffuse	Diffuses slowly	Diffuses rapidly



Three types solutions

Phases of colloids and their classification:

Phases of colloids: We know that a colloidal solution is of heterogeneous nature. It consists of two phases which are as follows

Internal phase or Dispersed phase (Discontinuous phase)**:** It is the component present in small proportion and is just like a solute in a solution. For example in the colloidal solution of silver in water (silver acts as a dispersed phase)

External phase or Dispersion medium (continuous phase)**:** It is generally component present in excess and is just like a solvent in a solution. For example, in the colloidal solution of silver in water. Water act as a dispersion medium.

Classification of colloids: The colloids are classified on the basis of the following criteria

a. **Classification based on the physical state of the dispersed phase and dispersion medium:** 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.

Different types of colloidal systems:

Dispersed phase	Dispersion Medium	Colloidal System	Examples
Liquid	Gas	Aerosol of liquids	Fogs, clouds, mists, fine insecticide sprays
Solid	Gas	Aerosol of solids	Smoke, volcanic dust, haze
Gas	Liquid	Foam or froth	Soap lather. Lemonade froth, foam, whipped cream, soda water
Liquid	Liquid	Emulsions	Milk, emulsified oils, medicines
Solid	Liquid	Sols	Most paints, starch in water, proteins, gold sol, arsenic sulphide sol, ink
Gas	Solid	Solid foam	Pumice stone, styrene rubber, foam rubber
Liquid	Solid	Gels	Cheese, butter, boot polish, jelly, curd
Solid	Solid	Solid sols (coloured glass)	Ruby glass, some gem stones and alloys

b. **Classification based on Nature of interaction between dispersed phase and dispersion medium:** Depending upon the nature of interactions between dispersed phase and the dispersion medium, the colloidal solutions can be classified into two types as (i) Lyophilic and (ii) Lyophobic sols.

i. **Lyophilic colloids (water loving):** “The colloidal solutions, in which the particles of the dispersed phase have a great affinity for the dispersion medium, are called **lyophilic collodis.”**

ii. **Lyophobic colloids (water heating):** "The colloidal solutions in which there is no affinity between particles of the dispersed phase and the dispersion medium are called **lyophobic colloids**."

Distinction between lyophilic and lyophobic sols:

Property	Lyophilic sols (suspensoid)	Lyophobic sols (Emulsoid)
Surface tension	Lower than that of the medium	Same as that of the medium
Viscosity	Much higher than that of the medium	Same as that of the medium
Reversibility	Reversible	Irreversible
Stability	More stable	Less stable
Visibility	Particles can't be detected even under ultramicroscope	Particles can be detected under ultramicroscope.
Migration	Particles may migrate in either direction or do not migrate in an electric field because do not carry any charge.	Particles migrate either towards cathode or anode in an electric field because they carry charge.
Action of electrolyte	Addition of smaller quantity of electrolyte has little effect	Coagulation takes place
Hydration	Extensive hydration takes place	No hydration
Examples	Gum, gelatin, starch, proteins, rubber etc.	Metals like Ag and Au, hydroxides like $Al(OH_3)$, $Fe(OH)_3$ metal sulphides like AS_2S_3 etc.

c. **Classification based on types of particle of dispersed phase:** Depending upon the type of the particles of the dispersed phase, the colloids also can be classified.

i. **Multimolecular colloids:** When on dissolution, atoms or smaller molecules of substances (having diameter less than 1nm) aggregate together to form particles of colloidal dimensions, the particles thus formed are called **multimolecular colloids**.

In these sols the dispersed phase consists of aggregates of atoms or molecules with molecular size less than 1 nm.

For example, sols of gold atoms and sulphur molecules. In these colloids, the particles are held together by **van der Waal's forces.** They have usually **lyophilic character.**

ii. **Macromolecular colloids:** These are the substances having big size molecules (called macromolecules) which on dissolution form particles of the size in the colloidal range. Such substances are called **macromolecular colloids**. These macromolecules forming the dispersed phase are generally **polymers** having very high molecular masses.

Naturally occurring macromolecules are starch, cellulose, proteins, enzymes, gelatin etc. Artificial macromolecules are synthetic polymers such as nylon, polythene, plastics, polystyrene etc.

They have usually **lyophobic character.**

iii. **Associated colloids:** These are the substances which on dissolved in a medium behave as normal electrolytes at low concentration but behave, as colloidal particles at higher concentration due to the formation of aggregated particles. The particles aggregates thus formed are called **micelles.**

Their molecules contain both **lyophilic** and **lyophobic** groups.

Properties of Colloidal Sols:

Heterogeneous nature:

Colloidal sols are biphasic in nature. It consists of the dispersed phase and the dispersion medium. In the colloidal solution, each particle is contained within its own surface boundary and therefore has a separate existence from the dispersion medium.

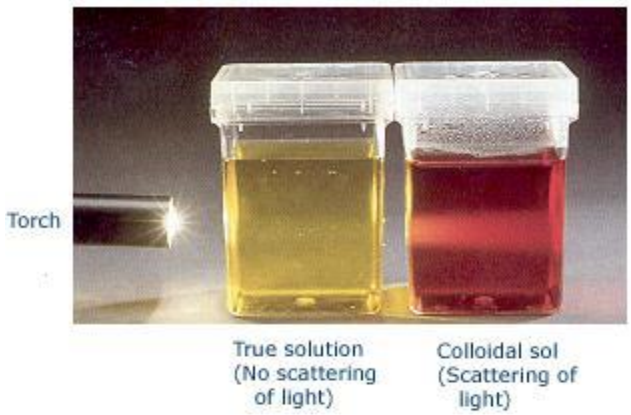
Colligative properties:

Colloidal particles have high average molecular masses. Therefore the mole fraction of the dispersed phase is very low. Hence, in colloidal solutions the relative lowering of vapor pressure, elevation in boiling point, depression in freezing point and osmotic pressure is very low.

Optical properties:

Although a colloidal solution appears to be homogenous 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 sized particles is called the Tyndall effect. This effect was first observed by Tyndall in 1869. A strong beam of light was passed through a colloidal sol placed in a dark place. The path of the beam got illuminated. The illuminated path of the beam is called Tyndall cone.

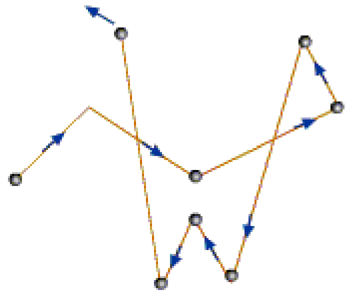


Demonstration of Tyndall effect

Mechanical Properties:

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 rest but move about continuously and randomly. This random continuous movement (Brownian motion) was observed in colloidal sol when the sol was viewed under a ultra microscope. Brownian motion in colloidal sols 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 dispersion medium on the colloidal particles are unequal. This leads to the zig-zag (random) motion of the colloidal particles.



Zig-zag or Brownian motion

This random movement decreases as the size of the particles increases because the effect of the impacts average out. When the size of the dispersed particles increases beyond the colloidal range, Brownian motion stops, i.e., no Brownian movement is observed.

The significance of Brownian movement is that

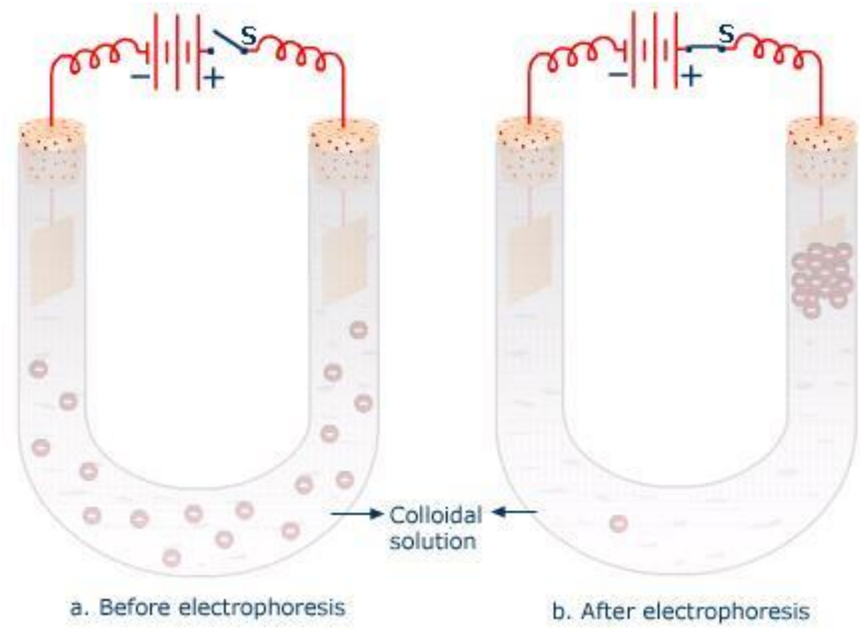
a. It provides a direct demonstration of ceaseless motion of molecules as postulated by kinetic theory.
b. It counters the force of gravity acting on colloidal particles and hence helps in providing stability to colloidal sols by not allowing them to settle down.

Electrical Properties:

Electrophoresis:

The colloidal particles are electrically charged and they carry a charge, that is, either the colloids are negatively charged or positively charged. The dispersion medium has an equal and opposite charge making the system neutral as a whole. Since the colloids carry charge, they repel each other and do not combine to form bigger aggregates. This is the reason why a sol is stable. The existence of charge on the colloidal particles is inferred from the observation that the colloidal particles move either towards the cathode or anode when the colloidal sol is placed in an electric field. This phenomenon of colloidal charged particles moving towards the oppositely charged electrodes in the presence of an electric field is called electrophoresis.

Electrophoresis is carried out by placing the colloidal solution in a U tube which is fitted with platinum electrodes.



Apparatus for electrophoresis

When electric current is passed, the charged colloidal particles move towards the oppositely charged electrode. A colloidal sol of sS_2S_3, which is negatively charged will move towards the anode when placed in an electric field.

Emulsion:

“The colloidal systems in which one liquid are dispersed in another liquid is called emulsions the two liquids otherwise being mutually immiscible.”

or

“Emulsion are the colloidal solutions in which both the dispersed phase and the dispersion medium are liquids.”

A good example of an emulsion is milk in which fat globules are dispersed in water. The size of the emulsified globules is generally of the order of 10^{-6} m. Emulsions resemble lyophobic sols in some properties.

a. **Types of Emulsion :** Depending upon the nature of the dispersed phase, the emulsions are classified as;
b. **Oil-in-water emulsions** (O/W)**:** The emulsion in which oil is present as the dispersed phase and water as the dispersion medium **(continuous phase)** is called an oil-in-water emulsion. Ex: Milk
c. Water-in-oil emulsion **(W/O)**: The emulsion in which water forms the dispersed phase, and the oil acts as the dispersion medium is called a water-in-oil emulsion. These emulsions are also termed **oil emulsions. Ex: Butter** and **cold cream**

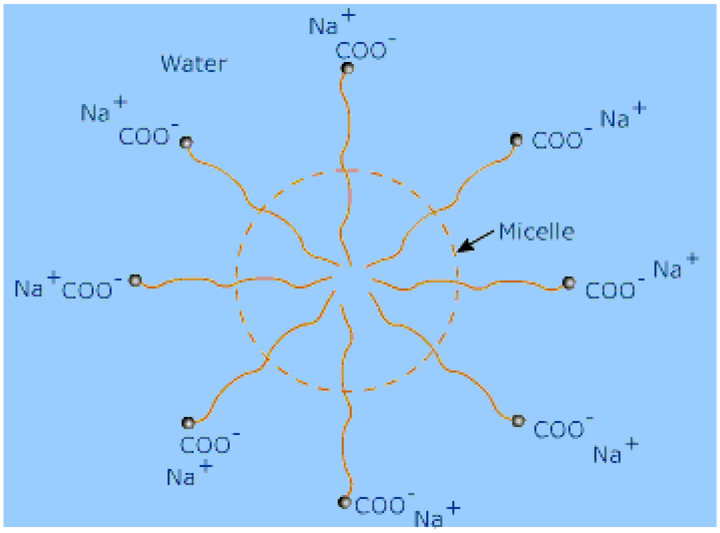
Micelles:

Micelles have both a lyophilic and lyophobic parts. Micelles may consist of more than 100 molecules.Certain substances behave as strong electrolytes at low concentration but at higher concentrations these substances exhibit colloidal characteristics due to the formation of aggregated particles. These aggregated particles are called micelles. **Micelles are called associated colloids.** The formation of micelles takes place only above a particular temperature called **Kraft Temperature (T_k)** and above a particular concentration called the **Critical micelle concentration (CMC).** On dilution, these colloids revert back to individual ions. Surface active molecules such as soaps and synthetic detergents form associated colloids in water. For soaps, the CMC is about 10^{-4} to 10^{-3} mol L^{-1}.

Mechanism of Micelle Formation:

Micelles are formed by specific molecules which have lyophilic as well as lyophobic ends. Ordinary soap which contains sodium stearate ($C_{17}H_{35}COONa$) forms micelle in water. The stearate ion has a long hydrocarbon end that is hydrophobic (because it is nonpolar) and a polar carboxyl group (COO^-) that is hydrophilic.

When the concentration of sodium stearate is below its CMC, then it behaves as a normal electrolyte and ionizes to give Na^+ and $C_{17}H_{35}COO^-$ ions. As the concentration exceeds the CMC, the hydrophobic end starts receding away from the solvent and approach each other. However, the polar COO^- part interacts with water. This leads to the formation of a cluster having the dimensions of a colloid particles. In each cluster a large number of stearate groups clump together in a spherical manner such that the hydrocarbon parts interact with one another and the COO^- groups remains projected in water to the surface.



Aggregation of $RCOO^-$ ions to form a micelle

Assignment questions:

1. What are “colloids”? Give the difference between “colloidal solution” and “true solution”?
2. In how many ways are colloids classified? Give a brief explanation of each.
3. Explain tyndall effect, Brownain movement

Example set:

1. The colloidal system of a solid dispersed in a liquid medium is called
    a. Aerosol
    b. Sol
    c. Gel
    d. Foam

Solution: b)

2. The number of phases that can be present in a simple colloidal solution is
    a. 2
    b. 4
    c. 3
    d. 1

Solution: a)

3. An emulsion is a colloidal solution consisting of
    a. Solids only
    b. Liquids only
    c. A number of components always
    d. One solid and one liquid only

Solution: b)

4. Milk is
    a. Fat dispersed in water
    b. Water dispersed in fat
    c. Water dispersed in oil
    d. A homogeneous solution only and not a colloid.

Solution: a)

5. In Brownian movement or motion the paths of the dispersed phase particles are
    a. Linear

b. Zig – Zag
c. Uncertain
d. Circular

Solution: b)

6. What are lyophilic, lyophobic colloids? Give examples

Solution:

Distinction between lyophilic and lyophobic sols:

Property	Lyophilic sols (suspensoid)	Lyophobic sols (Emulsoid)
Surface tension	Lower than that of the medium	Same as that of the medium
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Hydration	Extensive hydration takes place	No hydration
Examples	Gum, gelatin, starch, proteins, rubber etc.	Metals like Ag and Au, hydroxides like $Al(OH_3)$, $Fe(OH)_3$ metal sulphides like AS_2S_3 etc.

7. How are emulsions classified? Give two examples of each.

Solution:

Types of Emulsion : Depending upon the nature of the dispersed phase, the emulsions are classified as;

a. **Oil-in-water emulsions** (O/W)**:** The emulsion in which oil is present as the dispersed phase and water as the dispersion medium **(continuous phase)** is called an oil-in-water emulsion. Ex: Milk
b. Water-in-oil emulsion **(W/O)**: The emulsion in which water forms the dispersed phase, and the oil acts as the dispersion medium is called a water-in-oil emulsion. These emulsions are also termed **oil emulsions. Ex: Butter** and **cold cream**

Problem set:

1. The size of the colloidal particles is in the range od
   a. $10^{-7} – 10^{-9}$ pm
   b. $10^{-9} – 10^{-11}$ m
   c. $10^{-5} – 10^{-7}$ cm
   d. $10^{-2} – 10^{-3}$ nm

Solution: c)

2. Which of the following forms a colloidal solution in water
   a. NaCl
   b. Gelatin
   c. Starch
   d. Both b) and c)

Solution: d)

3. Cloud is _________ type of a colloidal.
   a. Liquid in gas.
   b. Gas in a liquid.
   c. Liquid in liquid.
   d. Liquid in solid.

Solution: b)

4. Tyndall effect in colloidal solution is due to
    a. Absorption of light
    b. Scattering of light
    c. Reflection of light
    d. Presence of electrically charged particles

Solution: b)

5. Lyophilic sols are more stable than lyophobic sols because
    a. The colloidal particles have positive charge
    b. The colloidal particles have negative charge
    c. The colloidal particles are solvated
    d. There are strong electrostatic repulsions

Solution: c)

6. What is a micelle? Give one example and the mechanism of its formation.

Solution:

Micelles:

Micelles have both a lyophilic and lyophobic parts. Micelles may consist of more than 100 molecules.Certain substances behave as strong electrolytes at low concentration but at higher concentrations these substances exhibit colloidal characteristics due to the formation of aggregated particles. These aggregated particles are called micelles. **Micelles are called associated colloids.** The formation of micelles takes place only above a particular temperature called **Kraft Temperature (T_k)** and above a particular concentration called the **Critical micelle concentration (CMC).** On dilution, these colloids revert back to individual ions. Surface active molecules such as soaps and synthetic detergents form associated colloids in water. For soaps, the CMC is about 10^{-4} to 10^{-3} mol L^{-1}.

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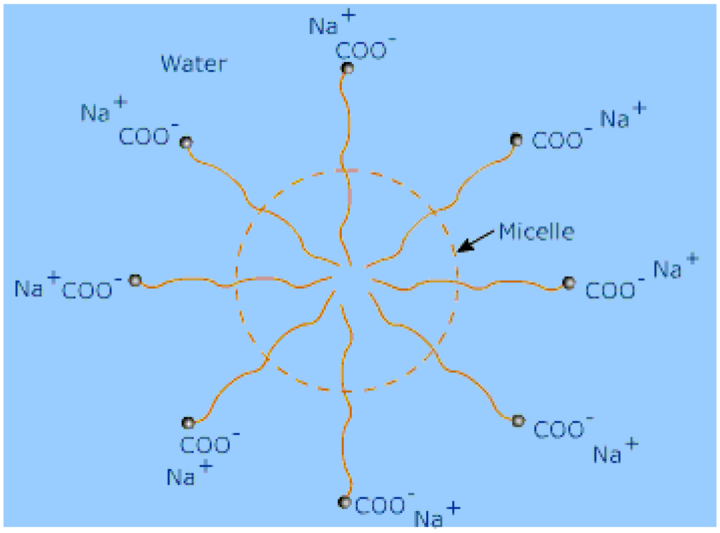

Aggregation of $RCOO^-$ ions to form a micelle

7. Explain electrophoresis

Solution: **Electrophoresis:**

The colloidal particles are electrically charged and they carry a charge, that is, either the colloids are negatively charged or positively charged. The dispersion medium has an equal and opposite charge making the system neutral as a whole. Since the colloids carry charge, they repel each other and do not combine to form bigger aggregates. This is the reason why a sol is stable. The existence of charge on the colloidal particles is inferred from the observation that the colloidal particles move either towards the cathode or anode when the colloidal sol is placed in an electric field. This phenomenon of colloidal charged particles moving towards the oppositely charged electrodes in the presence of an electric field is called electrophoresis.

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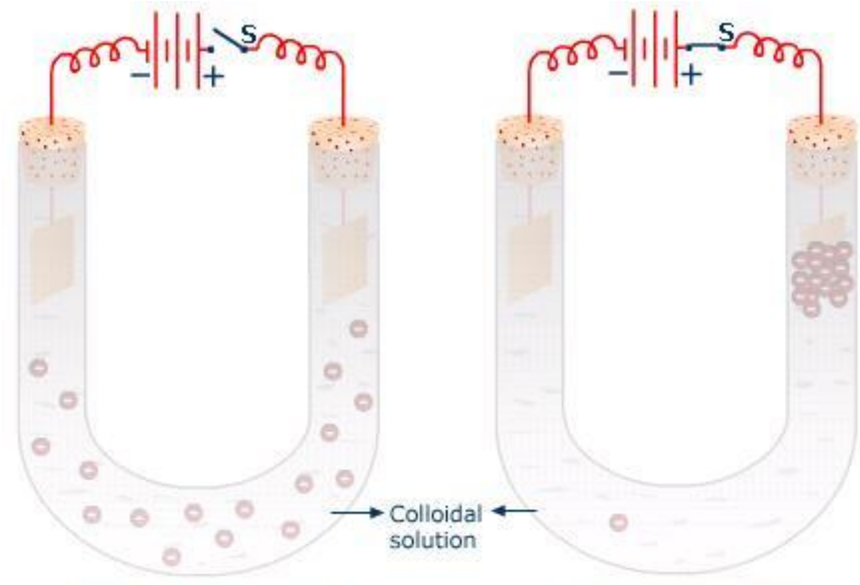

a. Before electrophoresis

b. After electrophoresis

Apparatus for electrophoresis

When electric current is passed, the charged colloidal particles move towards the oppositely charged electrode. A colloidal sol of AS_2S_3, which is negatively charged will move towards the anode when placed in an electric field.

Exercise questions:

1. Comment on the statement that “colloid is not a substance but a state of substance”. Justify your comment.
2. Action of soap is due to emulsification and micelle formation. Comment.
3. Why hydrophobic sols are easily coagulated?
4. Explain what is observed in the following processes
   a. When a beam of light is passed through a colloidal sol.
   b. An electrolyte, NaCl is added to hydrated ferric oxide sol.
   c. Electric current is passed through a colloidal sol? specify

Solutions to exercise questions:

1. Common salt (a typical crystalloid in an aqueous medium) behaves as a colloid in a benzene medium. Hence, we can say that a colloidal substance does not represent a separate class of substances. When the size of the solute particle lies between 1 nm and 1000 nm, it behaves as a colloid.

   Hence, we can say that colloid is not a substance but a state of the substance which is dependent on the size of the particle. A colloidal state is intermediate between a true solution and a suspension.

2. The cleansing action of soap is due to emulsification and micelle formation. Soaps are basically sodium and potassium salts of long chain fatty acids, $R\text{-}COO^{-}Na^{+}$. The end of the molecule to which the sodium is attached is polar in nature, while the alkyl-end is non-polar. Thus, a soap molecule contains a hydrophilic (polar) and a hydrophobic (non – polar) part.

   When soap is added to water containing dirt, the soap molecules surround the dirt particles in such a manner that their hydrophobic parts get attached to the dirt molecule and the hydrophilic parts point away from the dirt molecule. This is known as micelle formation. Thus, we can say that the polar group dissolves in water while the non-polar group dissolves in the dirt particle. Now, as these micelles are negatively charged, they do not coalesce and a stable emulsion is formed.

3. The stability of hydrophilic sols depends on two things. The presence of a charge and the salvation of colloidal particles. On the other hand, the stability of hydrophobic sols is only because of the presence of a charge. Therefore, the

latter are much less stable than the former. If the charge of hydrophobic sols is removed (by addition of electrolytes), then the particles present in them come closer and form aggregates, leading to precipitation

4. a. When a beam of light is passed through a colloidal solution, then scattering of light is observed. This is known as the Tyndall effect. This scattering of light illuminates the path of the beam in the colloidal solution.

   b. When NaCl is added to ferric oxide sol, it dissociates to give Na^+ and Cl^- ions. Particles of ferric oxide sol are positively charged. Thus, they get coagulated in the presence of negatively charged Cl^- ions.

   c. The colloidal particles are charged and carry either a positive or negative charge. The dispersion medium carries an equal and opposite charge. This makes the whole system neutral. Under the influence of an electric current, the colloidal particles move towards the oppositely charged electrode. When they come in contact with the electrode, they lose their charge and coagulate.