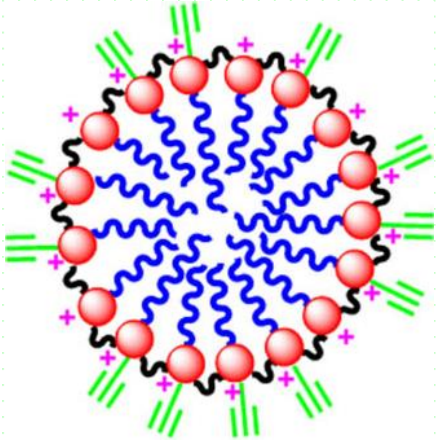


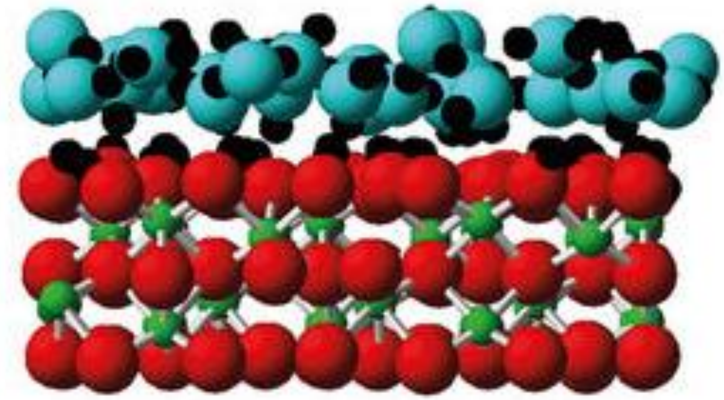
Chapter (7)

SURFACE CHEMISTRY

- Adsorption
- Colloidal dispersions

Feb. 4th, 2018

Multi-functionality of Surfaces



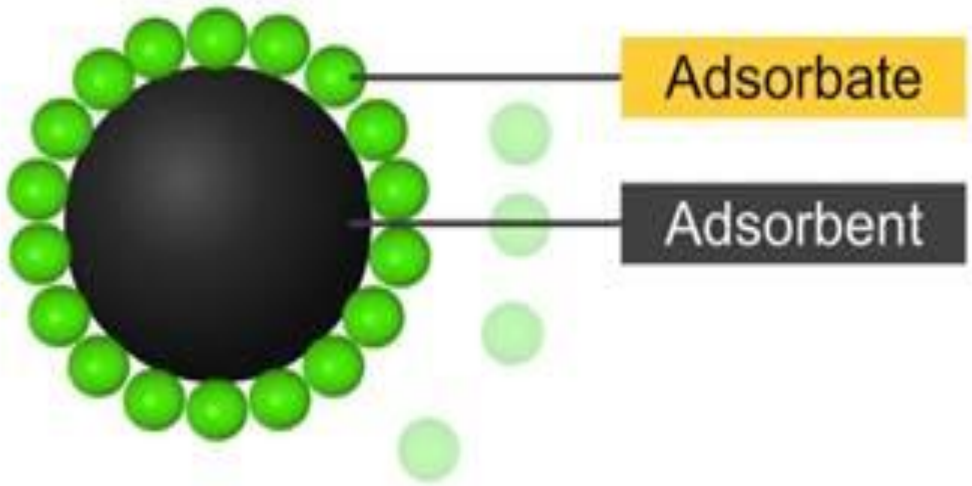
- A boundary that separates two phases is known as a surface or an interface.
- Surfaces show
- special properties that are different from those of the phases themselves.
- A surface site is differently active compared to the sites in the bulk of the material
- Multi-functionality is easily possible.

Surface Energy

- Why material accumulates at the interface is based on the excess energy associated with particles at interfaces?
  - ○ In the case of pure water and air, the water molecules at the air-water interface have higher energy than water molecules in the interior of the water phase.
  - ○ The reason that these surface molecules have higher energy is that, unlike the interior molecules, they have an unbalanced force component (on the airside of the molecule).
- Surface tension is expressed as energy per unit area (= force per length).
  - Water at 20oC = 72.7x10-3 N/m; Ethanol (Ethyl Alcohol) = 22x10-3 N/m; Mercury = 0.43 N/m (strong cohesive forces, no wetting of glass container).

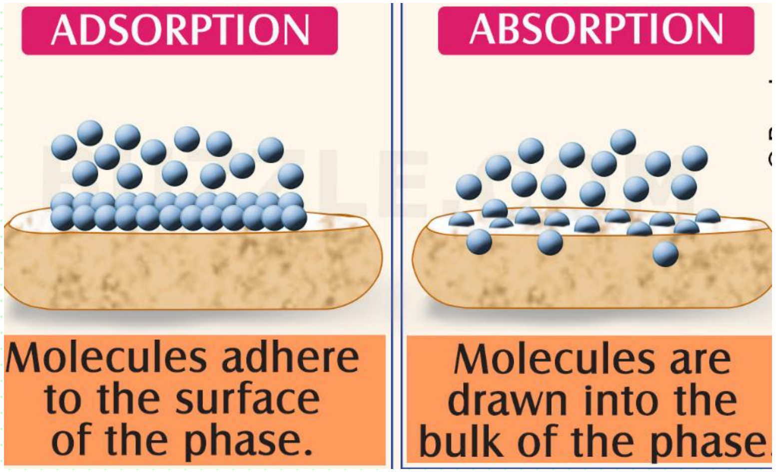
SURFACE CHEMISTRY

Adsorption



Adsorption vs. Absorption

- Absorption – a fluid phase is transferred from one medium to another (i.e. water absorbed by a sponge)
- Adsorption – certain components of a fluid (liquid or gas) phase are transferred to and held at the surface of a solid (e.g. small particles binding to a carbon bed to improve water quality – water filter)



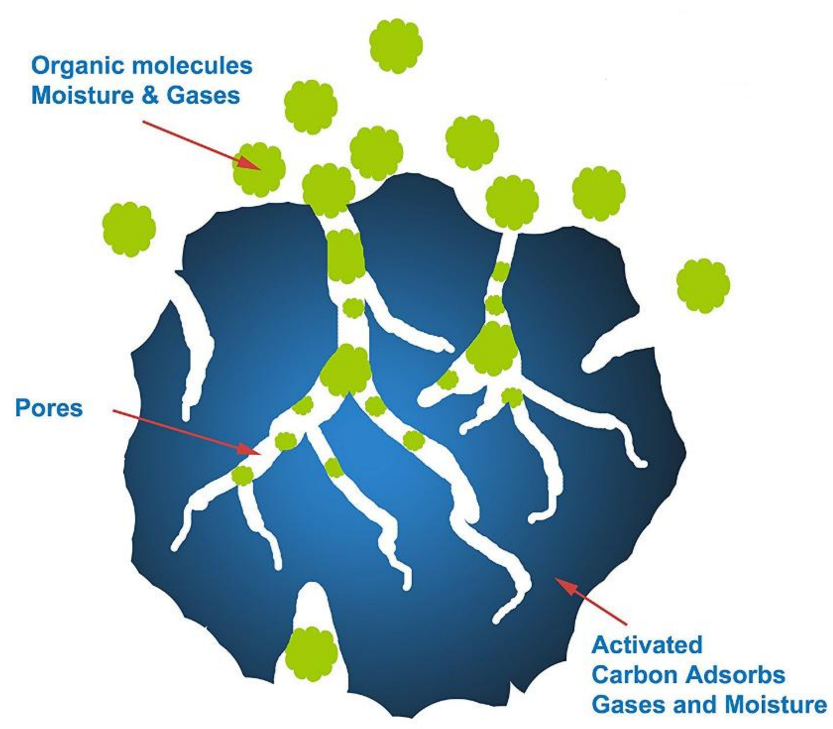
Definition: The concentration of gases, liquids or dissolved substances (adsorbate) on the surface of solids (adsorbent)

Why is Adsorption Useful?

Used in many industrial processes:

1. dehumidification
2. odor/color/taste removal
3. gas pollutant removal (H_2S)
4. water softening and deionization
5. hydrocarbon fractionation & other catalytic reactions
6. pharmaceutical purification

Adsorption Mechanism



How Activated Carbon Works

Adsorbent Materials

- Activated Carbon
- Activated Alumina
- Silica Gel
- Molecular Sieves (zeolite)

Adsorption

- Two types of adsorption:

1- **Physical adsorption**, physisorption, or van der Waals adsorption.

  - The forces are of a physical nature and the adsorption is relatively weak. The forces correspond to those considered by J. H. van der Waals in connection with his equation of state for gases.
  - The heat evolved when a mole of gas becomes physisorbed is usually small, less than 20 kJ.

2- **Chemisorption:**

- First considered in 1916 by the American chemist *Irving Langmuir* (1881-1957), the adsorbed molecules are held to the surface by covalent forces of the same general type as those occurring between atoms in molecules.

- The heat evolved per mole for this type is usually comparable to that evolved in chemical bonding, namely 100 to 500 kJ/mol.

- An important consequence of chemisorption is that after a surface has become covered with a single layer of adsorbed molecules, it is saturated; additional adsorption can occur only on the layer already present, and this is generally weak.

Chemisorption:

- Langmuir thus emphasized that chemisorption involves the formation of a unimolecular layer.
- It was suggested by Taylor (1890—1974) that chemisorption is frequently associated with an appreciable activation energy and may therefore be a relatively slow process.
- For this reason chemisorption is often referred to as activated adsorption.
- By contrast, van der Waals adsorption requires *no activation energy* and therefore occurs more rapidly than chemisorption.

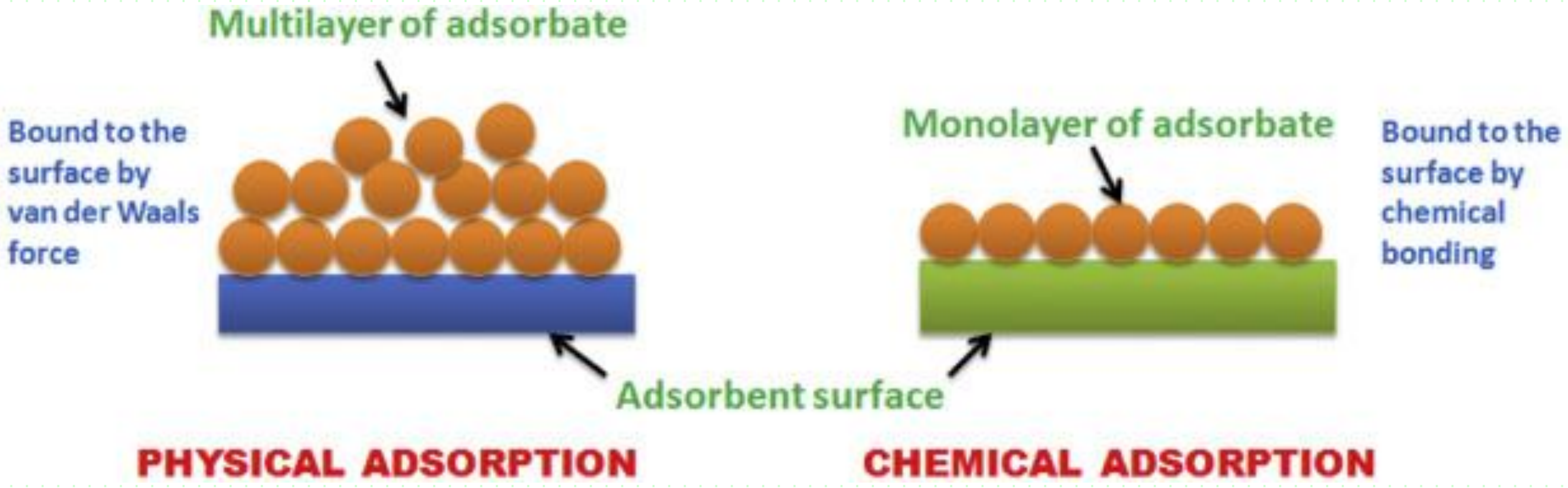
Adsorption Types

Physical Adsorption

- result of intermolecular forces causing preferential binding of certain substances to certain adsorbents
- reversible by addition of heat (via steam, hot inert gas, oven)
- Attachment to the outer layer of adsorbent material

Chemisorption

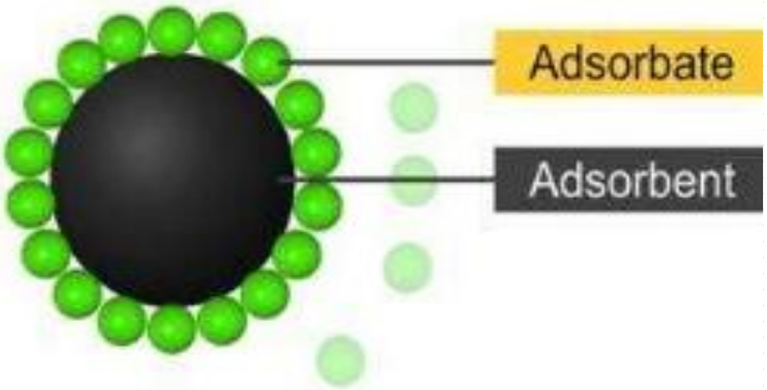
- result of chemical interaction
- large amount heat released
- irreversible
- mainly found in catalysis



Adsorption Isotherms

- Models describing equilibrium between the gaseous and the adsorbed phases at a given fixed temperature
- Can also be used for adsorption of solutes from liquid phase.
- Simplest model is that based on Irving Langmuir’s proposals, 1918
- *ISOTHERM is an equation that relates the amount of a substance attached to a surface to its concentration in the gas phase or in solution, at a fixed temperature, is known as an adsorption isotherm.*

The Langmuir Isotherm



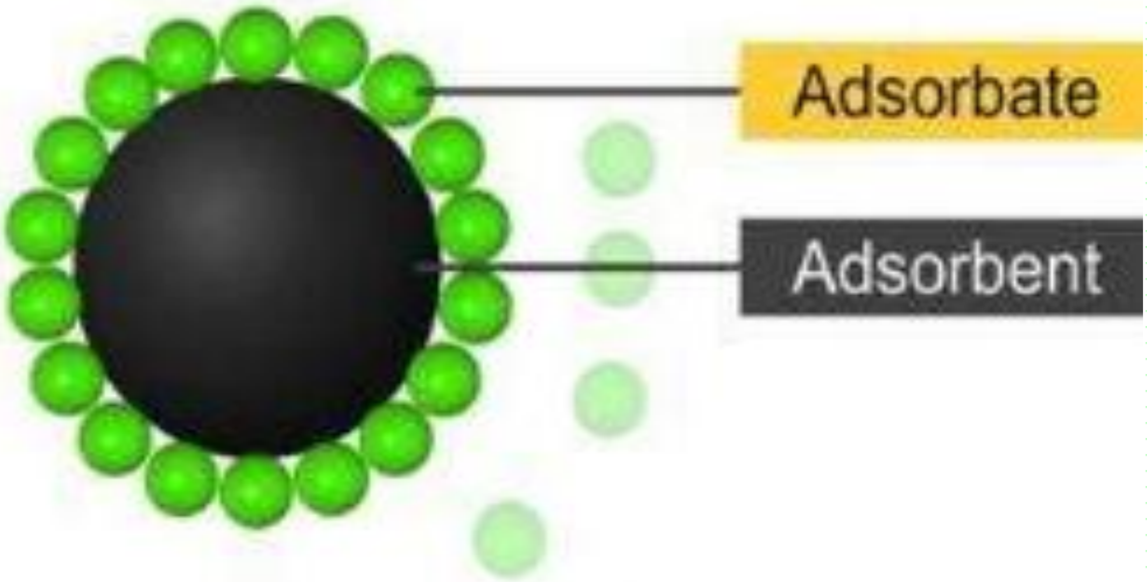
- The basis of the derivation of the Langmuir isotherm is that all parts of the surface behave in exactly the same way as far as adsorption is concerned.

- Suppose that, after equilibrium is established, a
  - Fraction **"θ"** of the surface is covered by adsorbed molecules; a
  - Fraction "**1 –θ**" will not be covered.

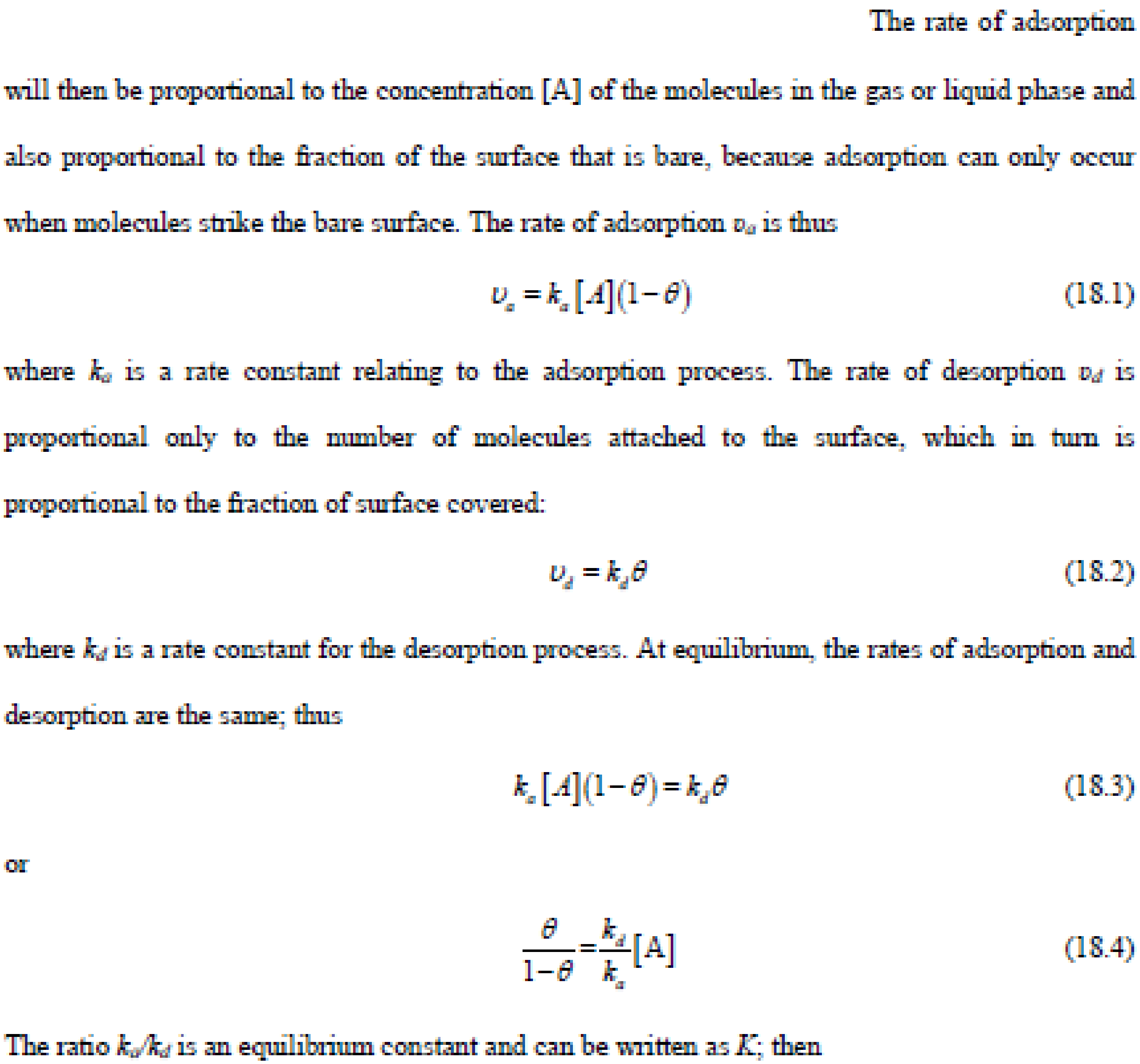
- The rate of adsorption will then be proportional to the concentration [A] of the molecules in the gas or liquid phase and also proportional to the fraction of the surface that is bare, because adsorption can only occur when molecules strike the bare surface.

Langmuir Isotherm: Assumptions

1. Adsorption proceeds to monolayer formation only.
2. All sites are equivalent and the surface is uniform.
3. Molecule adsorption is independent of occupation of neighbouring sites.



Derivation Langmuir Isotherm-1



The rate of adsorption will then be proportional to the concentration [A] of the molecules in the gas or liquid phase and also proportional to the fraction of the surface that is bare, because adsorption can only occur when molecules strike the bare surface. The rate of adsorption υ_a is thus

$$\upsilon_a = k_a[A](1-\theta) \qquad (18.1)$$

where k_a is a rate constant relating to the adsorption process. The rate of desorption υ_d is proportional only to the number of molecules attached to the surface, which in turn is proportional to the fraction of surface covered:

$$\upsilon_d = k_d\theta \qquad (18.2)$$

where k_d is a rate constant for the desorption process. At equilibrium, the rates of adsorption and desorption are the same; thus

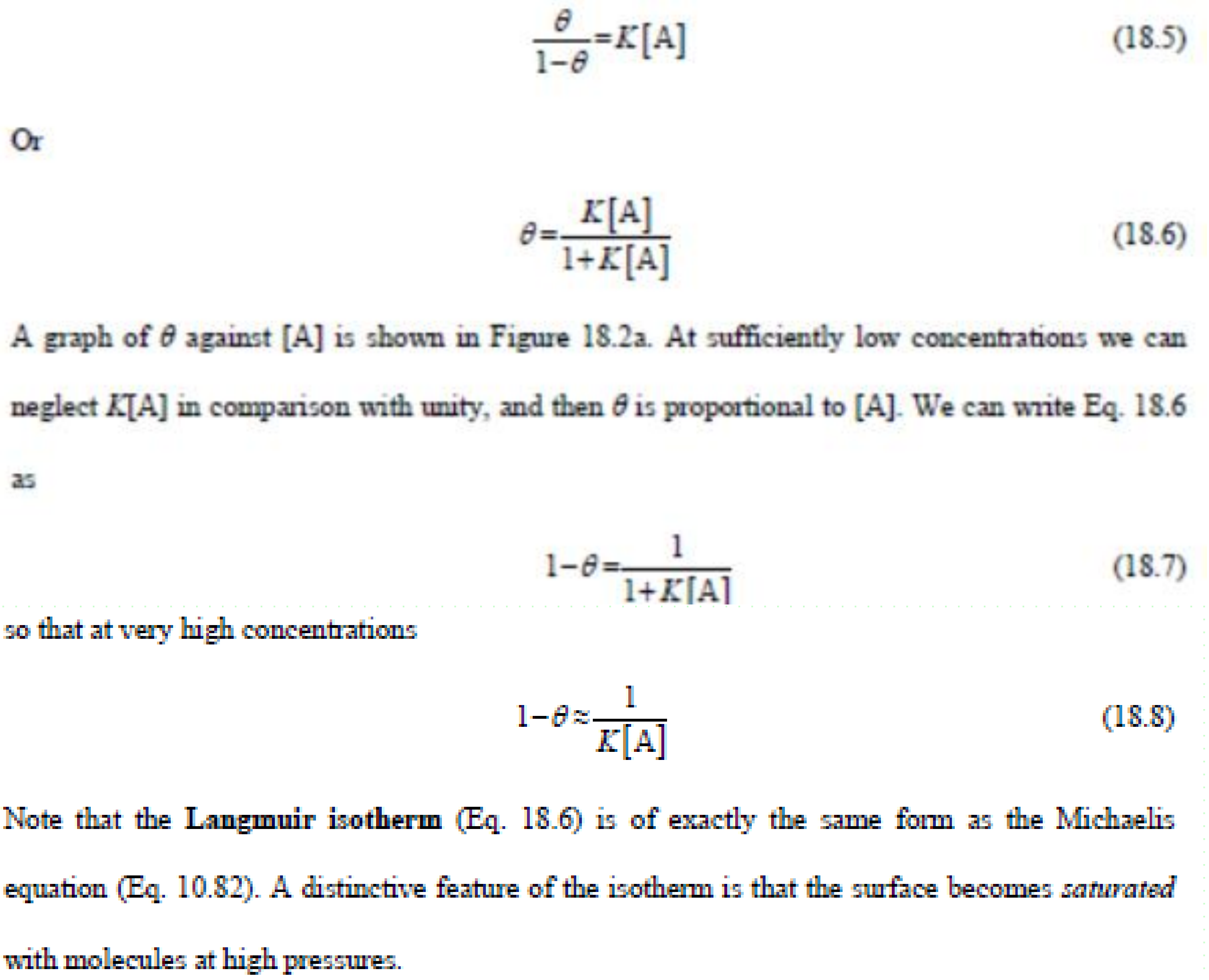
$$k_a[A](1-\theta) = k_d\theta \qquad (18.3)$$

or

$$\frac{\theta}{1-\theta} = \frac{k_a}{k_d}[\mathrm{A}] \qquad (18.4)$$

The ratio k_a/k_d is an equilibrium constant and can be written as K; then

Derivation Langmuir Isotherm-2



$$\frac{\theta}{1-\theta}=K[\mathrm{A}] \qquad (18.5)$$

Or

$$\theta=\frac{K[\mathrm{A}]}{1+K[\mathrm{A}]} \qquad (18.6)$$

A graph of θ against [A] is shown in Figure 18.2a. At sufficiently low concentrations we can neglect K[A] in comparison with unity, and then θ is proportional to [A]. We can write Eq. 18.6 as

$$1-\theta=\frac{1}{1+K[\mathrm{A}]} \qquad (18.7)$$

so that at very high concentrations

$$1-\theta\approx\frac{1}{K[\mathrm{A}]} \qquad (18.8)$$

Note that the **Langmuir isotherm** (Eq. 18.6) is of exactly the same form as the Michaelis equation (Eq. 10.82). A distinctive feature of the isotherm is that the surface becomes *saturated* with molecules at high pressures.

Langmuir Isotherm

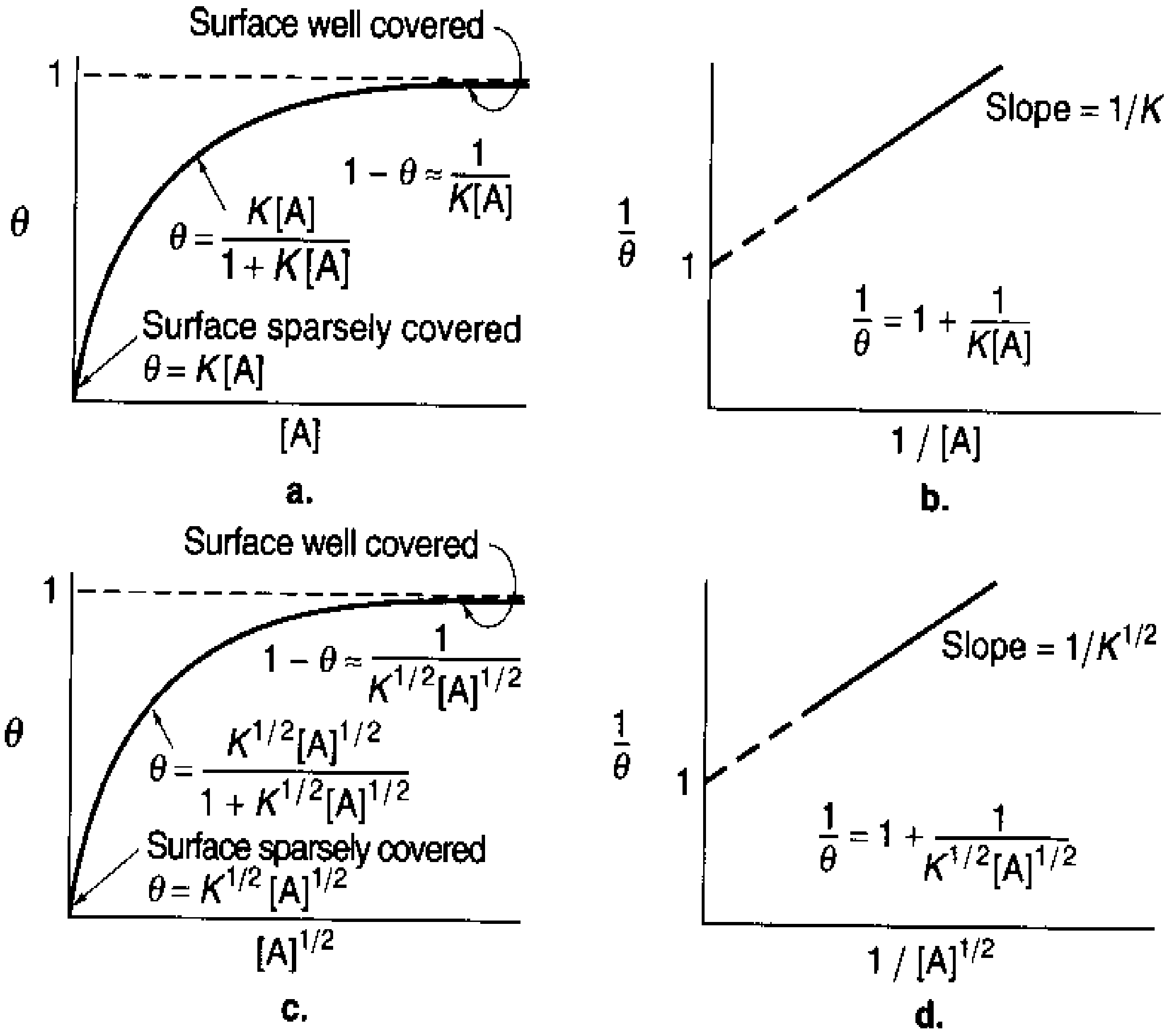
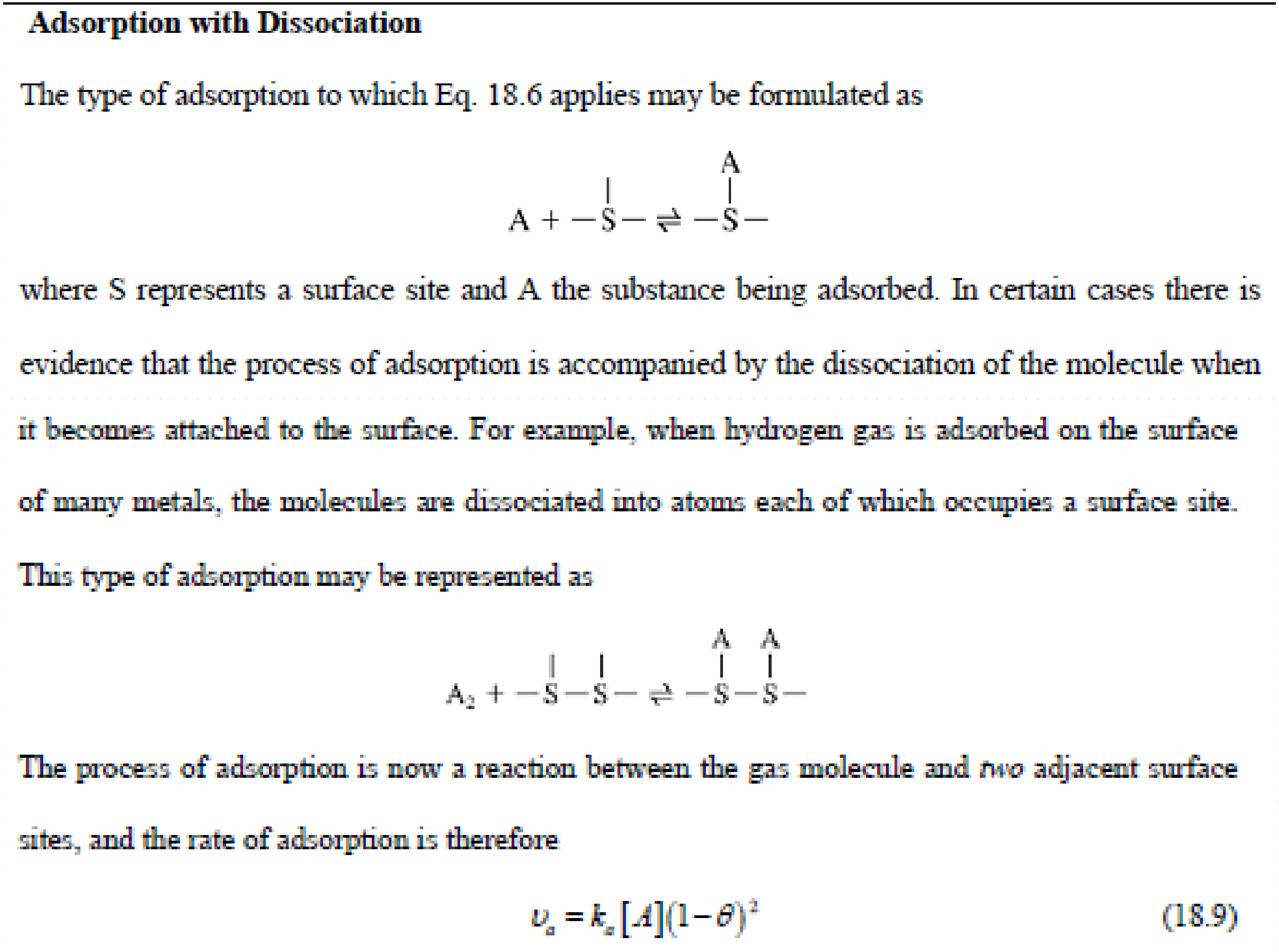


FIGURE 18.2
(a) Schematic plots of θ (fraction of surface covered) against [A] for a system obeying the Langmuir adsorption isotherm, without dissociation. (b) Reciprocal Langmuir plots. (c) Langmuir plots for the case of adsorption with dissociation. (d) Reciprocal Langmuir plots for adsorption with dissociation.

Adsorption with Dissociation



Adsorption with Dissociation

The type of adsorption to which Eq. 18.6 applies may be formulated as

$$A + -\overset{|}{S}- \rightleftharpoons -\overset{\overset{A}{|}}{S}-$$

where S represents a surface site and A the substance being adsorbed. In certain cases there is evidence that the process of adsorption is accompanied by the dissociation of the molecule when it becomes attached to the surface. For example, when hydrogen gas is adsorbed on the surface of many metals, the molecules are dissociated into atoms each of which occupies a surface site. This type of adsorption may be represented as

$$A_2 + -\overset{|}{S}-\overset{|}{S}- \rightleftharpoons -\overset{\overset{A}{|}}{S}-\overset{\overset{A}{|}}{S}-$$

The process of adsorption is now a reaction between the gas molecule and *two* adjacent surface sites, and the rate of adsorption is therefore

$$\upsilon_a = k_a[A](1-\theta)^2 \qquad (18.9)$$

Adsorption with Dissociation

The desorption process involves reaction between *two* adsorbed atoms, and the rate is therefore proportional to the square of the fraction of surface covered,

$$\upsilon_d = k_d \theta^2 \tag{18.10}$$

At equilibrium the rates are equal, and therefore,

$$\frac{\theta}{1-\theta} = \left(\frac{k_a}{k_d} [\mathrm{A}] \right)^{1/2} \tag{18.11}$$

$$= K^{1/2} [\mathrm{A}]^{1/2} \tag{18.12}$$

where K is equal to k_a/k_d. This equation can be written as

$$\theta = \frac{K^{1/2}[\mathrm{A}]^{1/2}}{1 + K^{1/2}[\mathrm{A}]^{1/2}} \tag{18.13}$$

A plot of θ against $[\mathrm{A}]^{1/2}$ is shown in Figure 18.2c. When the concentration is very small, $K^{1/2}[\mathrm{A}]^{1/2}$ is much smaller than unity, and θ is then proportional to $[\mathrm{A}]^{1/2}$. Equation 18.13 may be written as

$$1 - \theta = \frac{1}{1 + K^{1/2}[\mathrm{A}]^{1/2}} \tag{18.14}$$

so that at high concentrations, when $K^{1/2}[\mathrm{A}]^{1/2} \quad 1$,

$$1 - \theta = \frac{1}{K^{1/2}[\mathrm{A}]^{1/2}} \tag{18.15}$$

Thermodynamics of Adsorption

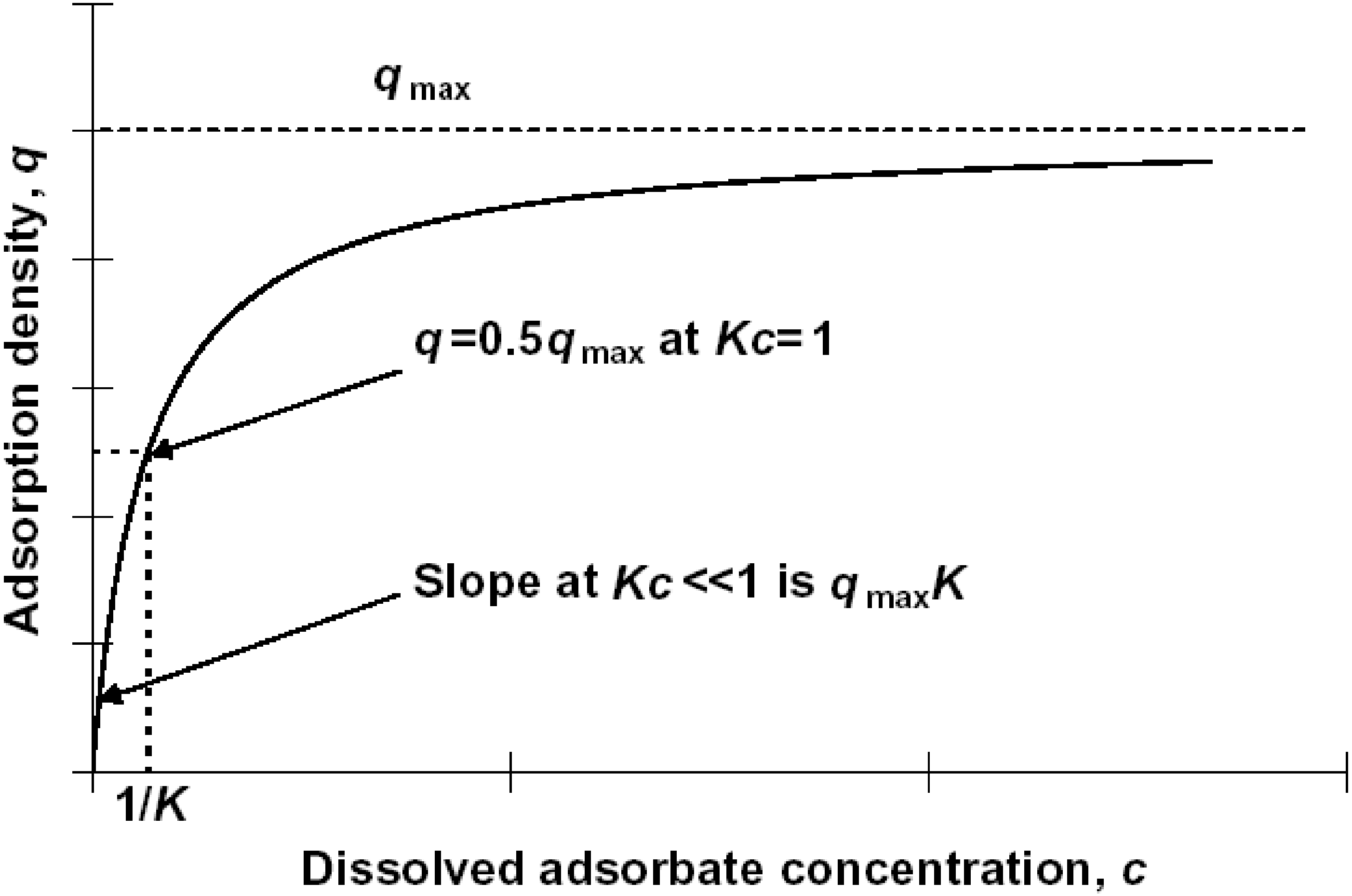
- A considerable number of measurements have been made of the enthalpy and entropy changes that occur on adsorption and desorption.
- As we have seen, van der Waals adsorption and chemisorption can be distinguished by the magnitudes of the enthalpy changes.
- Heat is always liberated on adsorption, and the enthalpy of adsorption is therefore always negative.
- The reason that enthalpies of adsorption must be negative is that the adsorption process inevitably involves a decrease in entropy.
- This is because a molecule in the gas phase or in solution has more freedom of motion than one that is attached to a surface. In view of the thermodynamic relationship:

$$\Delta G = \Delta H - T\Delta S \qquad (18.26)$$

Chemical Reactions on Surfaces

- An important concept in connection with surface reactions is the molecularity, which is the number of reactant molecules that come together during the course of reaction; we do not count the surface sites.
- Molecularity of a surface reaction is deduced from the kinetics on the basis of the experimental results and of theoretical considerations.
- Reactions involving a single reacting substance are usually unimolecular, e.g. Surface-catalyzed ammonia decomposition.
- Kinetics of acetaldehyde decomposition of on various surfaces can only be interpreted on the hypothesis that two acetaldehyde molecules, adsorbed on neighboring surface sites, undergo a bimolecular reaction. Reactions involving two reacting substances are usually bimolecular.
- When reactant molecules are dissociated on the surface, the reaction may involve interaction between an atom or radical and a molecule; for example, the exchange reaction between ammonia and deuterium on iron is a bimolecular interaction between a deuterium atom and an ammonia molecule.

Shape of Langmuir Isotherm



SURFACE CHEMISTRY

Part B

Colloidal Systems

Based on particle size,
solid-liquid systems
are classified as:

1- Suspension
2- Colloidal dispersion
3- True solution

Colloidal Systems

- In a true solution, such as one of sugar or salt in water, the solute particles consist of individual **molecules or ions.**

- At the other extreme there are suspensions, in which the **particles** contain more than one molecule and are large enough to be seen by the eye or at least under a microscope.

- Between these extremes are to be found the **colloidal dispersions**, in which the particles may contain **more than one molecule but are not large enough** to be seen in a microscope

- Size of **colloidal dispersions range from 5-200 nm** - Typical of the diameters of certain **macromolecules**, such as starch and proteins.

What is Colloid

- A **colloid** is a type of mixture that appears to be a solution but it is actually a mechanical mixture.

- A colloidal system consists of **two separate phases**: a dispersed phase (internal phase) and a continuous phase (dispersion medium).

- In a colloid, the ***dispersed phase*** is made of tiny particles or droplets that are distributed evenly throughout the ***continuous phase***.

Properties of Colloids

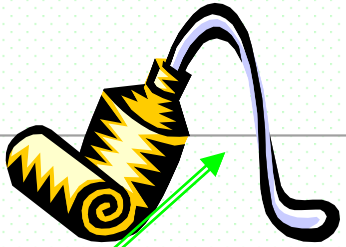
- The essential properties of colloidal systems are due to the fact that the **ratio of surface area to volume** is very large.

- A true solution is a one-phase system, but a colloidal dispersion behaves as a two-phase system, since for each particle there is a definite **surface of separation** between it and the medium in which the particles are dispersed (the dispersion medium).

- At this surface certain characteristic properties, such as **adsorption and electric potential** become evident, since the total surface area in a colloidal dispersion can be very large.

Colloidal Systems

Classification based on physical state of dispersed phase and dispersion medium



Dispersed phase	**Dispersion medium**	**Type of colloid**	**Examples**
Solid	Solid	Solid Sol	Colored glasses, gem stones
Solid	Liquid	Sol	Paints, tooth paste, cell fluids
Solid	Gas	Aerosol (S)	Smoke, dust
Liquid	Solid	Gel	Cheese butter, jelly
Liquid	Liquid	Emulsion	Milk, hair cream
Liquid	Gas	Aerosol (L)	Fog, mist, cloud, insecticide spray
Gas	Solid	Solid Sol	Pumice stone, foam rubber
Gas	Liquid	Foam	Froth, fire extinguisher, soap-lather

Areas of Science and Technology in which particles in the colloidal size range are regularly encountered

Analytical chemistry :

adsorption indicators, ion exchange, nephelometry, precipitate filterability, chromatography, and decolorization

Physical chemistry :

nucleation; superheating, supercooling and supersaturation; and liquid crystals

Biochemistry and molecular biology :

electrophoresis; osmotic and Donnan equilibria and other membrane phenomena; viruses, nucleic acids, and proteins; and hematology

Chemical manufacturing :

catalysis, soaps and detergent, paints, adhesives, ink; paper and paper coating; pigment; thickening agents; lubricants

Areas of Science and Technology in which particles in the colloidal size range are regularly encountered

Environmental science_:

aerosols, fog and smog, foams, water purification and sewage treatment; cloud seeding; clean rooms

Materials science_ :

powder metallurgy, alloys, ceramics, cement, fibers, and particles of all sorts

Petroleum science, geology and soil science_:

oil retrieval, emulsification, soil porosity, floatation, and ore enrichment

Household and consumer products_ :

milk and dairy products, beer, water proofing, cosmetics, and encapsulated products

SOLS: Lyophobic and Lyophilic

Colloidal dispersions of **solids in liquids (i.e., sols)** can be roughly divided into two types:

1. Lyophobic Sols. These can be called hydrophobic sols if the dispersion medium is water. The term **hydrophobic** refers to water-repellent surfaces.

Since there is low affinity for the solvent, lyophobic sols are relatively unstable.

2. Lyophilic (liquid-loving) Sols. These are sols in which there is a strong affinity between the disperse phase and the molecules comprising the dispersion medium.

These sols are much more stable, and they behave much more like true solutions.

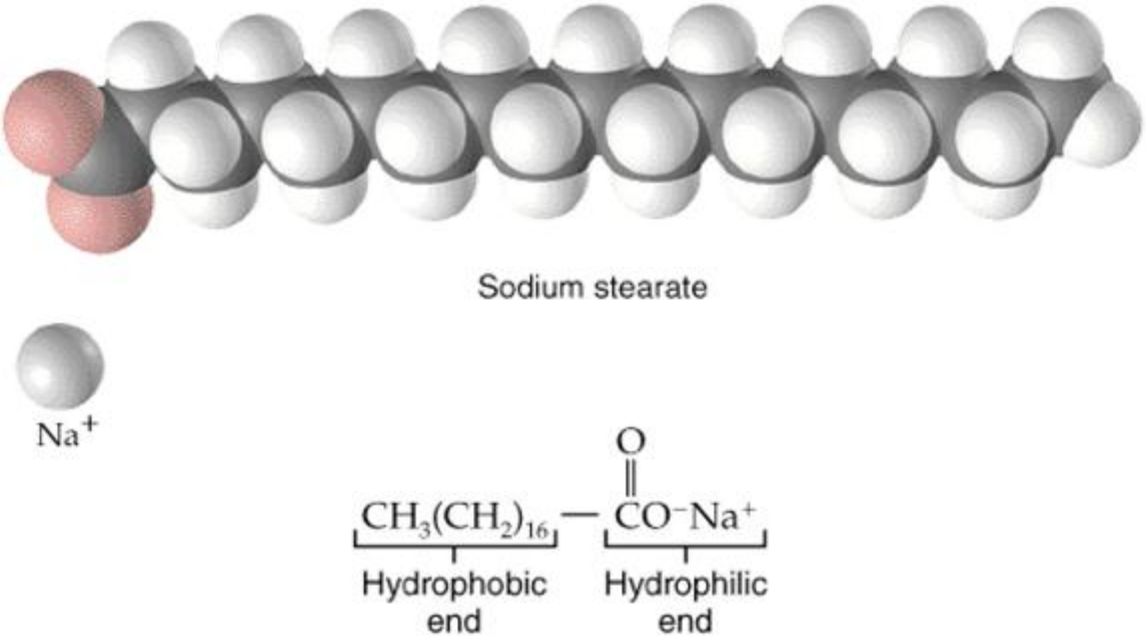
Emulsions

- **Emulsion** is a colloidal dispersion of a liquid in a liquid.
- Good Examples of emulsions are milk and butter.
  - An emulsifying agent is essential for the formation of an emulsion and for maintaining the emulsion's stability.
  - Oils and greases are not soluble in water. However, they readily form a colloidal dispersion if soap or detergent is added to the water.

Emulsions

- Soaps and detergents are **emulsifying agents**.
- One end of a large soap or detergent molecule is polar and is attracted to water molecules.
- The other end of the soap or detergent molecule is non-polar and is soluble in oil or grease.

Emulsifiers thus allow the formation of colloidal dispersions between liquids that do not ordinarily mix.


Sodium stearate

$$\underbrace{CH_3(CH_2)_{16}}_{\text{Hydrophobic end}}-\underbrace{\overset{\overset{O}{\|}}{C}O^-Na^+}_{\text{Hydrophilic end}}$$

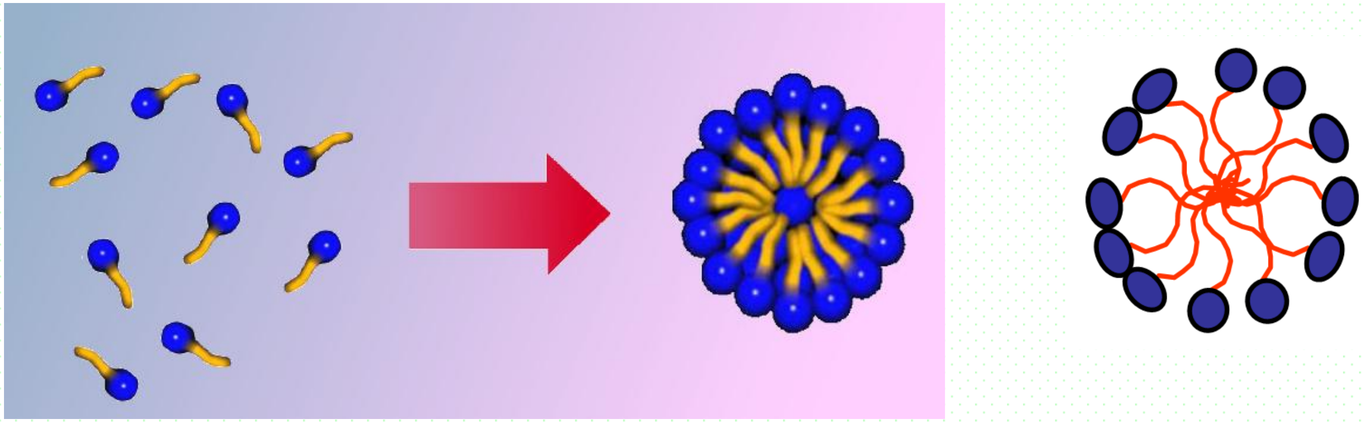
Emulsifiers

Preparation of Colloidal dispersions

Colloidal dispersions are prepared in a variety of ways.

A colloidal solution of **starch**, for example, is easily prepared by introducing starch into boiling water.

Intrinsic colloids are usually **lyophilic,** and they are usually either macromolecules (such as proteins) or long-chain molecules with polar end groups, which tend to aggregate and form particles of colloidal size, known as micelles; soaps and other detergents are of this type.



Preparation of Colloidal dispersions

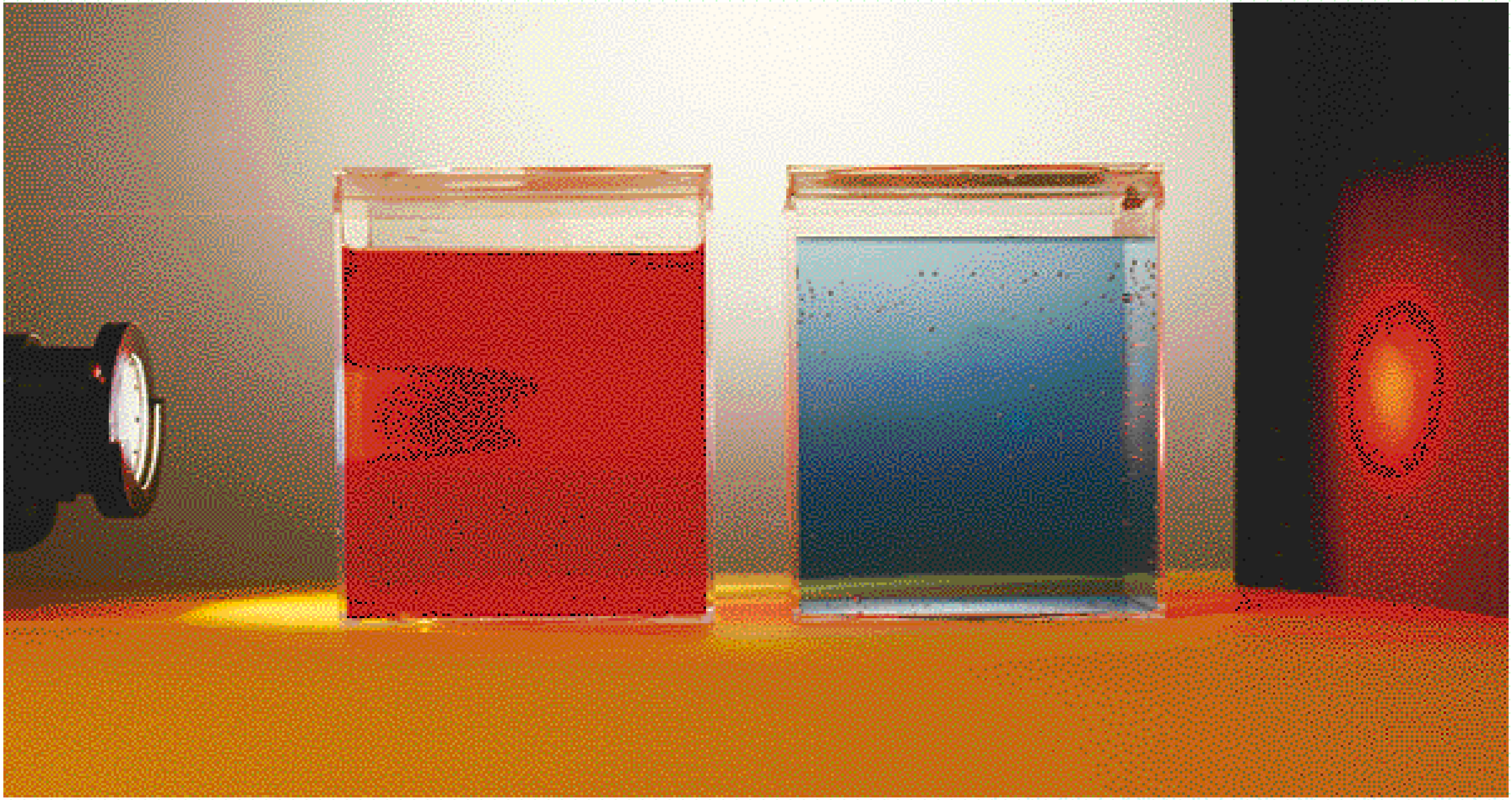
- **Extrinsic colloids**, on the other hand, do not form colloidal dispersions readily, and special methods have to be used; **lyophobic colloids** are frequently of this kind. The methods used fall into two classes:

1. **Condensation Methods**. The materials are initially in true solution. Chemical reactions are used to produce the sol.
2. **Dispersion Methods**. Material originally in massive form is disintegrated into particles of colloidal dimensions.

Light Scattering by Colloidal Particles

- Although by definition colloidal particles are too small to be seen in the microscope, they can be detected by optical means.
- When light passes through a medium that contains no particles larger than about 1 nm diameter, the path of light cannot be detected and the medium is said to be optically clear
- When colloidal particles are present, however, some of the light is scattered, and the incident beam passes through with weakened intensity.
- This is known as the **Tyndall effect**; the path of light through the medium, made visible as a result of the scattering, is known as the **Tyndall beam.**
- The type of apparatus used in a light-scattering experiment is shown schematically in **Figure 18.13**.

- Tyndall effect: ability of a Colloid to scatter light. The beam of light can be seen through the colloid.



Tyndall effect

Tyndall effect

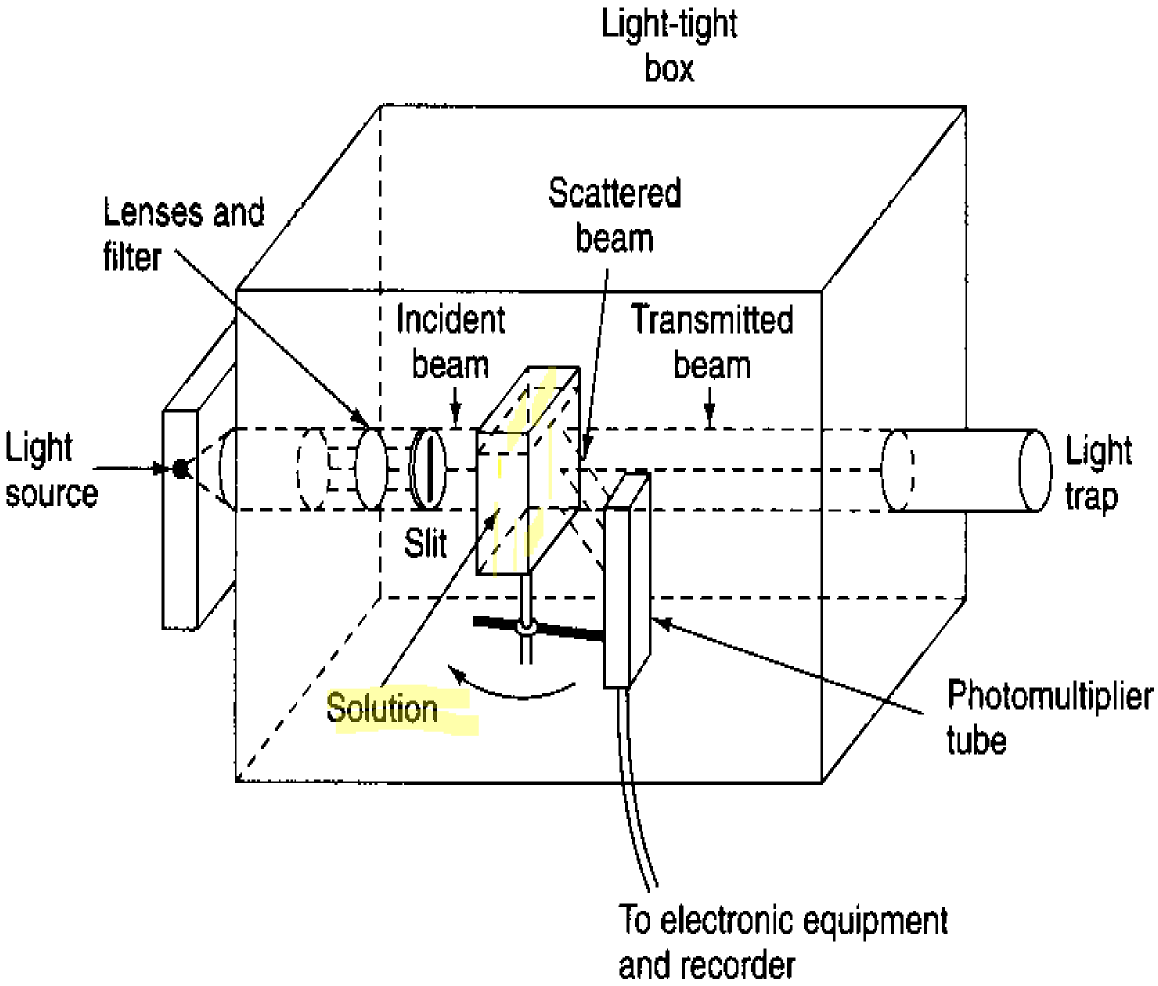
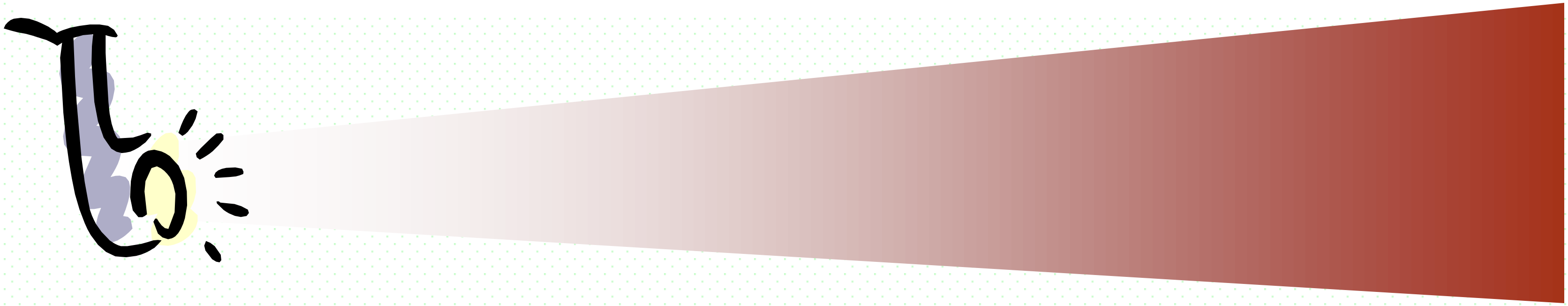


FIGURE 18.13
Schematic diagram of the type of apparatus used in a light-scattering experiment.



Electrical Properties of Colloidal Systems: Sols

- When two electrodes are placed in a sol and an electric potential is applied across them, the particles in general move in one direction or another.
  - This migration of colloidal particles in an electric field is called **electrophoresis.** The motion occurs as a result of zeta potential.

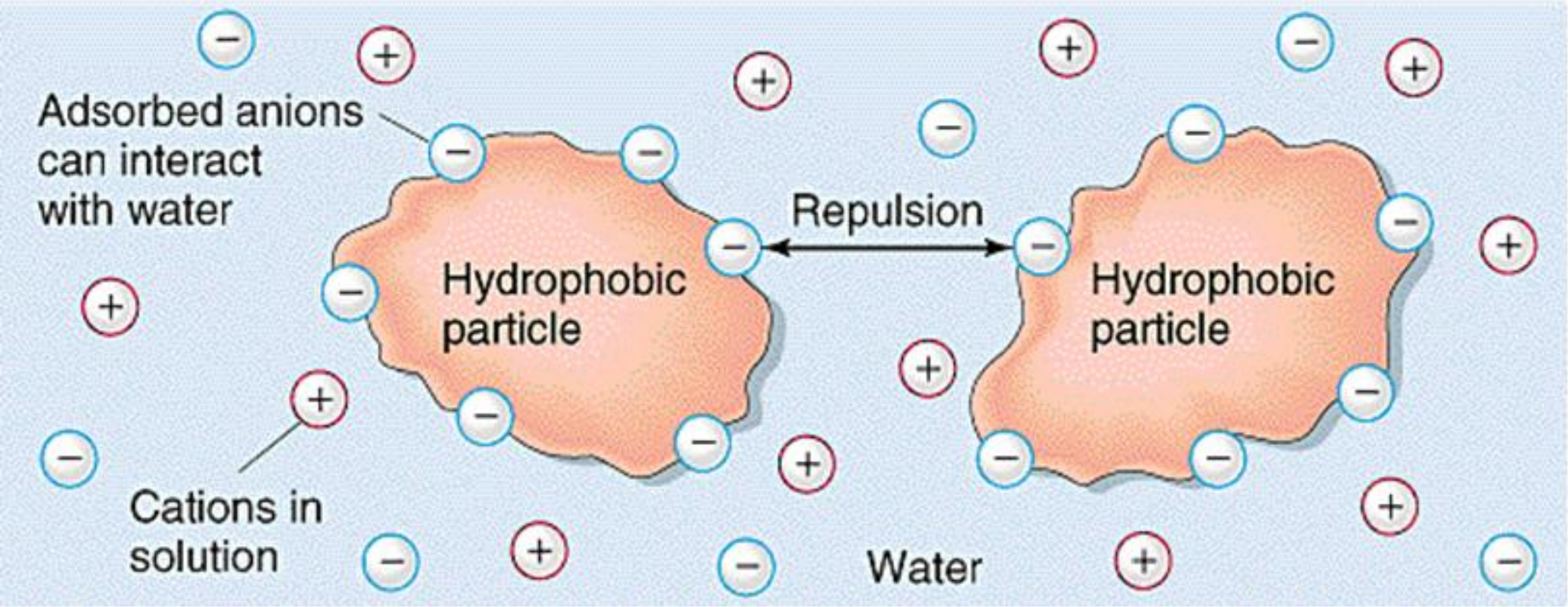
- Both lyophobic and lyophilic sols undergo **electrophoresis.**

- The electric double layer and the potential are important for colloids in other ways.

- The stability of a hydrophobic sol is highly dependent on the charges on the surface of the particles

Electrical Properties of Colloidal Systems: Sols

- repulsion between particles carrying the same charges prevents them from approaching one another and forming larger particles that will precipitate out.



Electrical Properties of Colloidal Systems: Sols

The charges at the surface of colloidal particles are influenced to a considerable extent by ***the adsorption of ions***.

Examples:

1. **Ag+ solution + excess NaI solution →**
   silver iodide sol (particles –ve charge)

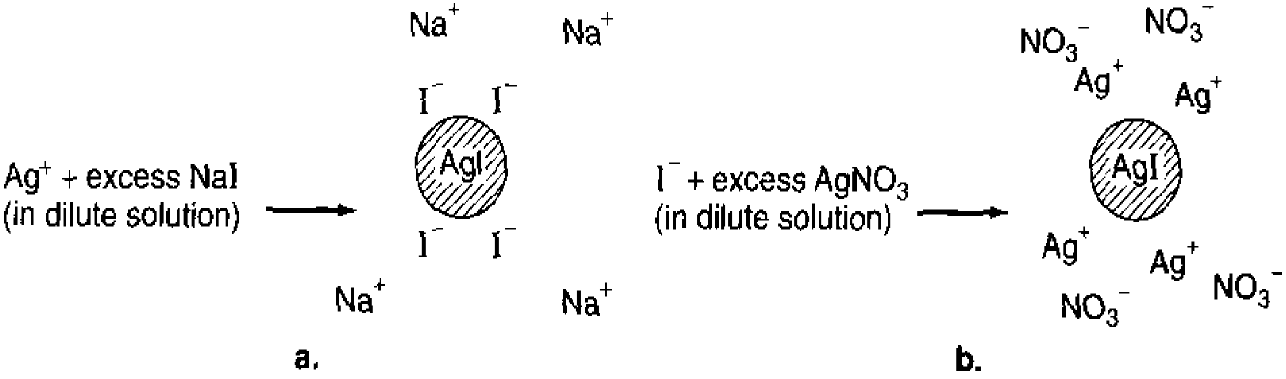
I- ions adsorbed on surface of AgI (Figure 18.14a)
Na+ ions in solution form a +ve charged atmosphere.

Electrical Properties of Colloidal Systems: Sols

**2. iodide (I-) solution + excess AgNO3 solution →
AgI sol (particles +ve charge)**

Ag+ ions are adsorbed on surface of AgI (Figure 18.14b)
NO3- ions in solution form a -ve charged atmosphere.

FIGURE 18.14
Silver iodide sols. (a) The particles are formed in the presence of excess iodide ions, which become adsorbed. (b) The particles are formed in the presence of excess silver ions, which are adsorbed.



- **Protein molecules** in general bear positive or negative charges because of the ionizations of COOH, NH3+, OH- and other groups.

1. At low pH values the protein bears a net +ve charge because groups like NH3+ are present.

2. At high pH values negative groups like COO- and O- are present so the molecule has a net -ve charge.
3. At some intermediate pH (the isoionic or isoelectric point) , the protein does not migrate in an electric field.

- **Added electrolytes** influence the stability of colloidal particles by affecting their charges.

REFERENCES

1. Atkins, P. and de Paula, . ”Physical Chemistry”, 10^{th} edition, Oxford University Press, London, 2014.
2. Keith J. Laidler , John H. Meiser , Bryan C. Sanctuary. “Physical Chemistry”, 4th edition, Houghton Mifflin, 2002.