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BSK1133 PHYSICAL CHEMISTRY

CHAPTER 7
SURFACE CHEMISTRY

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Description

Aims

- To study the colloidal systems.
- To study the mechanisms for adhesion between surfaces and materials.
- To describe the adsorption isotherms.
- To learn the different types of catalysts.

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Description

Expected Outcomes

- ❖ Able to describe the principles of surface– and colloid chemistry.
- ❖ Able to understand all the forces involve between adsorbent and adsorbate.
- ❖ Able to describe the adsorption isotherms, measure isotherms and make calculations in connection with these.
- ❖ Able to identify different types of catalysts.

References

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Contents

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7.1 Colloid and Crystalloid

I. Colloid

- A dispersion of the dispersed phase throughout dispersing medium.
- Colloidal particles are 1 x 10^3 pm to 1 x 10^6 pm.
- **Tyndall effect is applied to** distinguish a solution from a colloid.
- Colloidal aerosols, colloidal emulsions, colloidal foams, colloidal dispersions or hydrosols are homogenous mixtures which a dispersed phase has a certain size range.
- Colloidal suspension is referred to a solid as a dispersed phase and liquid as a dispersion medium.

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- Meanwhile, colloidal emulsion is a mixture of both dispersion medium and dispersed phase are liquid states.
- The dispersed-phase particles or droplets are affected largely by the surface chemistry present in the colloid.
- Some colloids are opaque, some are translucent and some have color.

Dispersed Phase	Dispersing Medium	Name	Example
Solid	Gas	Aerosol	Smoke
Gas	Liquid	Foam	cream
Solid	Liquid	Sol	Milk (magnesia)
Liquid	Liquid	Emulsion	Mayonnaise
Liquid	Solid	Gel	butter
Gas	Solid	Foam	Foams (plastic)
Solid	Solid	Solid sol	steel
Liquid	Gas	Aerosol	mist

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Types of Colloid:

i. Hydrophilic Colloid

- **large molecules** (proteins)
- In aqueous phase, hydrophilic parts of the molecule can interact with H_2O molecules, lead to **formation of hydrogen-bond** (are on the outside surface)

ii. Hydrophobic colloid

- **not be stable in H_2O**
- Can be **stabilized where attachment of ions on the surface due to the interaction with water**

iii. Association colloids

- Low concentration: normal strong electrolytes
- High concentration: colloid cause aggregated particles or micelles are formed.

Details:

❑Surfactants or surface active agents (soaps and synthetic detergents) form micelles when present in solution at a concentration greater than critical micellar concentration (CMC).

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Purification Methods of Colloidal Solution:

- **Dialysis**

  The removal of ions or molecules through diffusion across the membrane.

- **Electro dialysis**

  Similar as dialysis method. But, it is accelerated by application of electrical potential.

- **Ultra-filtration**

  Normally, sol particles can pass through a filter paper if the pore size of filter paper is bigger than sol particles. However, if the pore size of filter paper is smaller, then the filter paper is assume soaking in a gelatin of colloid ion solution and lastly soaking in formaldehyde. This treated filter paper may retain colloidal particles. This process is called **ultra – filtration**.

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II. Crystalloid Fluids

- Consists of a balanced of electrolyte composition
- expands total extracellular volume
- exerts a significant hydrostatic effect on capillaries that may lead to extracellular fluid accumulation, increased gastrointestinal wall edema (slow post-operative gastrointestinal recovery) and pulmonary edema.

7.2 Origin of Charge, Gels and Emulsions

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I. Origin of the Charge on Colloidal Particles

Ways of sol particles gain electrical charge:

- The dissociation or ionisation of the surface molecules in colloidal particles will be balanced by the oppositely charged ions in the sol.
- Frictional electrification where rubbing of the dispersed phase particles with dispersion medium.
- Dispersed phase will selectively adsorb ions that compatible with their lattice ions.

II. Gels

- dispersed phase is liquid and dispersing medium is solid
- Gelation is the process where coagulation of lyophilic sols and produce a semisolid jelly with encloses liquid.
- Examples:
  - ✓Elastic Gels (gelatin): show property of elasticity.
  - ✓Non-elastic gels (silica gel): rigid and fix shape.

III. Emulsions

- fine droplets of one liquid that dispersed in another liquid with mutually immiscible
- Example: milk where fat globules are dispersed in water.

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7.3 Surface Growth, Composition and Structure

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I. Surface Growth

- Terraces is a surface defect where a step between two otherwise flat layers of atoms.
- When an atom settles on a terrace, it bounces across it and might come to a step. Instead of it, the molecule may interact with several step and the interaction become strong to trap it.
- For the case that when ions deposit from solution, a strong Coulombic interaction between the arriving ions and several ions at the surface defect can offset the loss of the solvation interaction is offset by.
- However, not all defect causes in sustained surface growth.

II. Surface Composition and Structure

- When an exposed surface is constantly bombarded with molecules gas under normal conditions, a freshly prepared surface is covered very quickly.
- The kinetic model of gases can be estimated and the expression for the collision flux:

$$Z_W = \frac{P}{(2\pi mkT)^{\frac{1}{2}}}$$

OR

$$Z_W = \frac{Z_0\left(p/Pa\right)}{\left[(T/K)\left(M/gmol^{-1}\right)\right]^{1/2}}$$

where $Z_0 = 2.63\times10^{24}m^{-2}s^{-1}$ and M: molar mass of the gas

- ✓ For air ($M \approx 29$ g mol^{-1}) at 1 atm and 25°C, the collision flux is 3×10^{27} m^{-2}s^{-1}.
- ✓ Explanation: For 1 m^2 of metal surface, has 10^{19} atoms. One atom can struck about 10^8 times/second. When a few collisions leave a molecule adsorbed to the surface, the time is very short for which a freshly prepared surface remains clean.

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7.4 Adsorption

Adsorption

$$\text{Adsorbent} + \text{Adsorbate} \xrightleftharpoons[\text{desorb}]{\text{adsorb}} \text{Adsorption Process}$$

Occur: different forces between adsorbent and adsorbate lead to attract and retain the molecules of a gas or a dissolved substance on to their surfaces with which they come in contact.

a. Basic Terms

- **Interface:** Any surface is a plane which separates any two phases in contact with each other.
- **Occlusion:** When adsorption of gases occur on the surface of metals.

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b. Surface Forces

- These atoms **posses unbalanced forces** (Van der Waal’s forces or chemical bond forces), which cause adsorption process occurs.
- Example: when a solid substance is **broken into two pieces**, two new surfaces are formed. Hence, the **number of unbalanced forces becomes more**. As a result, the tendency for adsorption become large.

i. Reversible adsorption

- **Adsorbate can be removed** from adsorbent by physical methods.

ii. Irreversible adsorption

- **Adsorbate can not be removed** from adsorbent.

  Example: Adsorption of O_2 on tungsten adsorbent.

c. Adsorption Isotherms

- At certain temperature, the relationship of pressure of the adsorbate (gas phase) and the extent of adsorption can be expressed as the following.

$$\boxed{\text{Extent of adsorption} = \frac{x}{m}}$$

where

x gram of the adsorbate is adsorbed on **m** gram of the adsorbent.

1. Freundlich Adsorption Isotherm (Gas phase)

- Freundlich adsorption isotherm: a monomolecular layer of adsorbate is forms on the surface of the adsorbent.

$$\frac{x}{m} = kp^{\frac{1}{n}} \quad \text{or} \quad \log\frac{x}{m} = \log k + \frac{1}{n}\log p \qquad (n > 1)$$

- **k** and **n** are constant at a certain temperature, adsorbent and adsorbate (gas).

- $n > 1$, indicating **the amount of the adsorbate does not increase as great as the pressure.**

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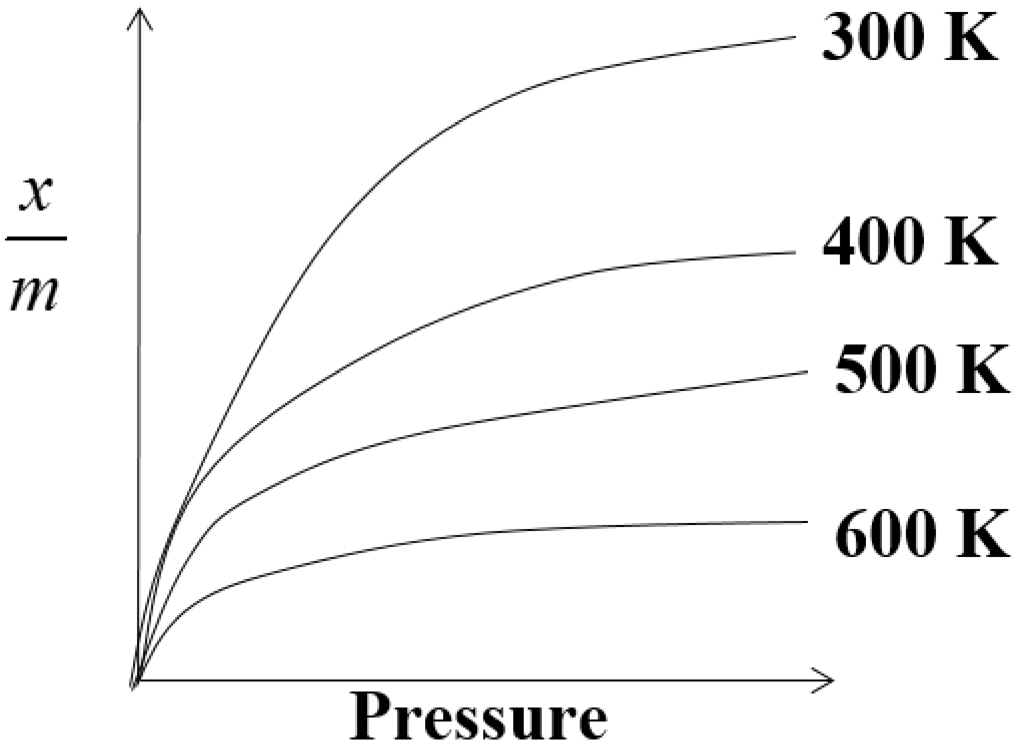

- A decrease in adsorption when the temperature is increase.
- These curves approach to saturate at high pressure.
- Freundlich isotherm is not obeyed at high pressure.

2. Freundlich Adsorption Isotherm (not applicable for high pressure)

- At low pressure which $\frac{1}{n} = 1$, hence $\frac{x}{m}$ = kp. Therefore, $\boldsymbol{\frac{x}{m}}$ **α** $\boldsymbol{p}$. It is varies linearly with pressure.
- At high pressure which $\frac{1}{n} = 0$, hence $\frac{x}{m}$ = constant. Therefore, the extent of adsorption is independent to pressure.
- $\frac{x}{m}$ depends on pressure, which is raised to powers $\frac{x}{m}$ α $p^{\frac{1}{n}}$ at moderate pressure,

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3. Langmuir Adsorption Isotherm

- ○ **Irving Langmuir (1916)** related the adsorption isotherm to **kinetic theory of gases.**
- ○ Only an unimolecular layer of the adsorbate.
- ○ Adsorption consists of:
  - ✓The rate of condensation (refer to uncovered surface): At the beginning, the rate is very high.

    After certain time, the rate is decreased cause many covered surfaces are present.
  - ✓The rate of evaporation (refer to covered surface): increase rapidly as more covered surfaces are present.
  - ✓ Finally, an equilibrium is achieved.

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Formula

The Langmuir isotherm

- relation between the fractional coverage and partial pressure of the adsorbate:

$$\theta = \frac{KP}{1+KP}$$

θ = the number of covered surface by adsorbate
P = pressure
K = equilibrium constant

What will happen to the equilibrium constant at low and high pressure?

- ✓ At lower pressure, $\theta = KP$.
- ✓ At high pressure, $\theta = \frac{KP}{KP} = 1$

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l. Application of Adsorption

- High vacuum region can be produced
- Gas masks
- Desiccation or dehumidification
- Removal of pollutants from solution
- Catalysis
- Separation (inert gases)
- Chromatographic analysis

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7.5 Catalysis

Catalysis

Catalyst - a substance which can alter the rate of a chemical reaction only.

Types:

i. **Homogeneous catalysis**: reactants and the catalyst are in the same physical state.

Hydrolysis of ester:

$$CH_3COOCH_2CH_3(l) + H_2O(l) \overset{\textbf{HCl (l)}}{\rightleftharpoons} CH_3COOH(l) + CH_3CH_2OH(l)$$

ii. **Heterogeneous catalysis**: reactants and catalyst are in different physical state.

Haber's Process:

$$N_2\ (g) + 3H_3\ (g) \overset{\textbf{Fe(s)}}{\rightleftharpoons} 2NH_3\ (g)$$

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Positive catalysis: enhance the reaction rate

$$2KClO_3\ (s) \xrightarrow{MnO_2(s)} 2KCl\ (s) + 3O_2\ (g)$$

Negative catalysis: decrease the reaction rate

$$Na_2SO_3\ (s) + O_2\ (g) \xrightarrow{C_2H_5OH(l)} Na_2SO_4\ (s)$$

Auto-catalysis: form as one of the products in the reaction and will aid in the reaction rate.

$$2KMnO_4 + 5H_2C_2O_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4\text{(autocatalyst)} + 10CO_2 + 8H_2O$$

Induced catalysis: as one of the reactants, but unlikely happen under certain condition.

$$Na_3AsO_3 + Na_2SO_3\text{(induced catalyst)} \longrightarrow Na_3AsO_4\text{(sodium arsenate)} + Na_2SO_4$$

Conclusion

- ❖ Tyndall effect is applied to distinguish a solution from a colloid.
- ❖ Different forces between adsorbate and adsorbent result in an adsorption process.
- ❖ Catalyst is used to alter the reaction rate of a process.

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