Lecture 32

Thermodynamics of Interfaces

Adsorption

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Topics to Discuss

- Adsorption
  - Gibb's adsorption equation
  - Langmuir adsorption isotherm
  - Classifications of adsorption
  - Applications of adsorption

Adsorption

- When a substance is present at a higher concentration at the surface of a solid or liquid phase than in the bulk of that phase, the substance is said to be **adsorbed** on the surface of that phase.
- Resulted from the deposition of a vapour or liquid substance on to a phase.
- The bond formed between the adsorbed substance and the phase is **too weak to penetrate** more on the bulk, or the particles of the substance are of **larger in size** to force their way into the adsorbed phase.

Gibb's adsorption equation

- The concentration of a solute that can be adsorbed on to a solid or liquid phase

$$\Gamma_k = -\frac{c_k}{RT}\left(\frac{d\gamma}{dc_k}\right)$$

Γ_k = excess concentration of solute k per m^2 of substance
c_k = concentration of the solute at the bulk
γ = interfacial energy

- ☐ For a solute to be adsorbed at an interface, **($d\gamma/dc$) term must be negative** i.e., the interfacial tension must be reduced due to the addition of k.

- **The equation is applied only to dilute solutions.**
- **For ideal solutions, c_k can be replaced by X_k while for real solutions, c_k is replaced by a_k.**

Langmuir adsorption isotherm

- Adsorption of gas molecules occur on solid surfaces in layers of only one molecular thick (monolayers) and follow the rule

$$\theta = \frac{kp}{kp + k'}$$

θ = fraction of total adsorption site filled with gas molecules
p = partial pressure of gas
k and k' = constants

Classification of Adsorption

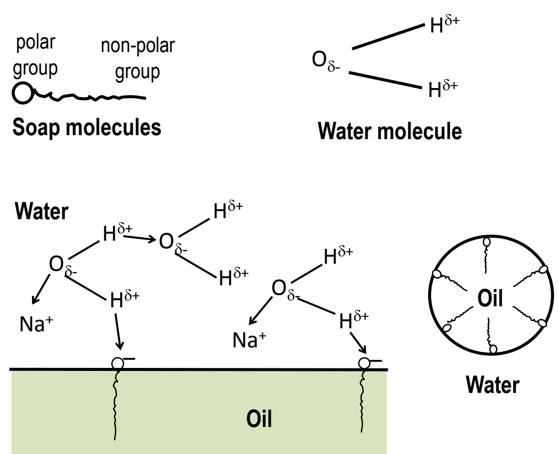
Physical adsorption	Chemical adsorption
• gas molecules adsorbed in more than one molecule in thickness. • dominant at lower temperatures. • gas molecules are held by a weak van der Waals bond • can easily be overcome by thermal agitation. • does not obey Langmuir isotherm	• the adsorbed layer is one molecule thick • dominant at higher temperatures. • the gas molecules are held by strong true chemical bonds. • obeys Langmuir isotherm • kinetics of this type of adsorption follows the Arrhenius type of rate equation: rate = exp (-E/RT)

Example: Adsorption of hydrogen

- Hydrogen molecules physically adsorbed on metallic surfaces below -200 C
- During heating, they desorb until about -100 C, where chemisorption takes over

Application of Adsorption

Cutting Fluid



- Cutting fluid is a mixture of mineral oil and water.
- **Emulsifier** added to lower surface tension between oil and water.
- Intimate mixture of small droplets of oil dispersed in water formed.

Common emulsifier:

Sodium stearate
$CH_3\,(CH_2)_{16}\,.\,COONa$

Froth Flotation Process

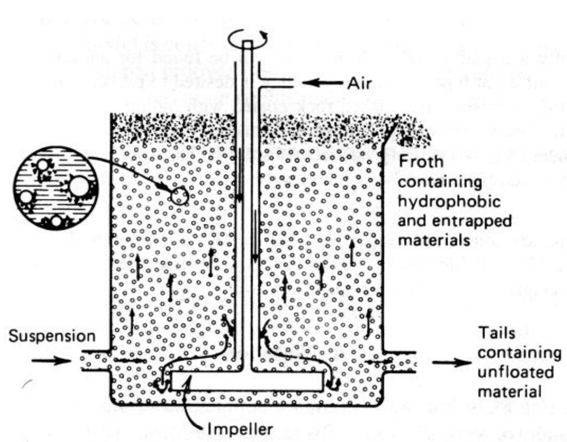
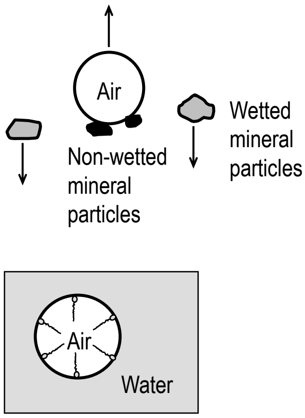


FIGURE 9.10
Schematic diagram of a froth flotation cell.

- Ore minerals always associated with valueless gangue mineral.
- To improve the concentration of value minerals, mineral concentration processes, such as **froth flotation**, are used.



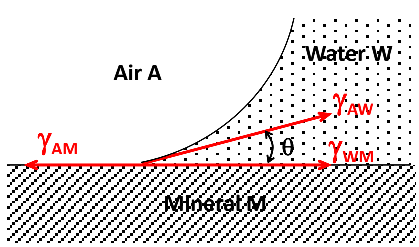
- Froth flotation is a mineral dressing process.
- Mineral particles wetted by water sink, while

  mineral particles non-wetted by water become attached to air bubble and float.
- **Frothers** added to lower the interfacial tension of air-water interface to form stable air bubble.

Common frother:

Pine oil ($C_{10}H_{17}OH$)

- The wettability of mineral particles is also important for separation of minerals.



$$\gamma_{AM} = \gamma_{AW}\cos\theta + \gamma_{WM}$$

- Condition for a mineral to be non-wetted by the water:

$$\theta > 90° \quad \text{and} \quad \gamma_{AM} < \gamma_{WM}$$

$\theta > 90°$ and $\gamma_{AM} < \gamma_{WM}$

- To lower γ_{AM}, **collectors** are added (which absorbs at the mineral/air interface).

  Example : Potassium Ethyl Xanthate (for PbS-SiO_2 system)

- **Water wets both galena and silica, but if a small quantity of the collector is added, the contact angle is raised from 0 to 60° on the galena, whereas the contact angle on the silica remains almost zero.**
  - The polar group of this xanthate molecule attracts the Pb^{++} of galena and form lead xanthate which exists on the galena surface and raises its contact angle and lowers γ_{AM}.
  - On the other hand, the non-polar ethyl group faces outwards the galena (or towards water) and is less attracted to water and raised the value of γ_{WM}.
  - Xanthate molecules have no action on silica which remains wetted by water and sinks.

Next Class

Lecture 33

Statistical Thermodynamics

Microstate, macrostate and entropy