Lecture 7.
Single Equilibrium Stages (3)
[Ch. 4]

- Multicomponent Liquid–Liquid Systems
- Solid–Liquid Systems
  - Leaching
  - Crystallization
  - Liquid adsorption
- Gas–Liquid Systems
- Gas–Solid Systems
- Multiphase Systems
  - Vapor–liquid–solid system
  - Vapor–liquid–liquid system

Multicomponent Liquid–Liquid Systems

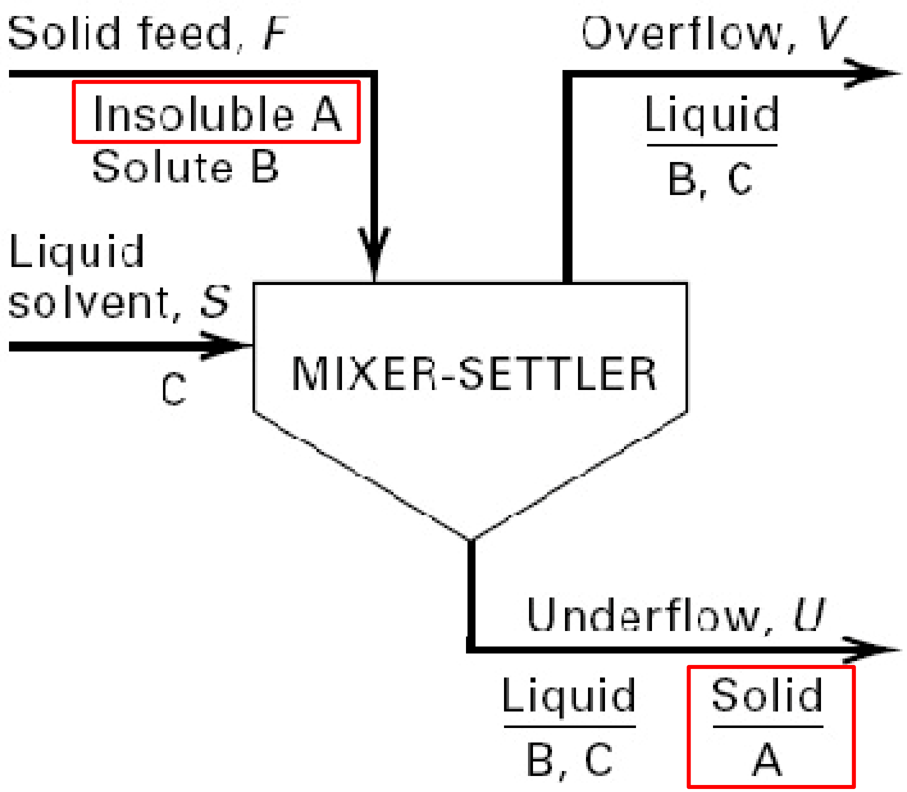
- Liquid–liquid extraction process with (1) quaternary and higher component mixtures and/or (2) two solvents
- Equilibria are very complex : no compact graphical way
  ⇒ computer–assisted algorithm using activity coefficient equations

Vapor–Liquid Equilibria	Liquid–Liquid Equilibria
Feed, F	Feed, F + solvent, S
Equilibrium vapor, V	Extract, E ($L^{(1)}$)
Equilibrium liquid, L	Raffinate, R ($L^{(2)}$)
Feed mole fraction, z_i	Mole fractions of combined F and S
Vapor mole fractions, y_i	Extract mole fractions, $x_i^{(1)}$
Liquid mole fractions, x_i	Raffinate mole fractions, $x_i^{(2)}$
K–value, K_i	Distribution coefficient, K_{Di}
$\Psi = V / F$	$\Psi = E / (F + S)$

Solid–Liquid Systems

- Leaching (solid–liquid extraction)
  - Separation of multicomponent solid mixture by contacting the solid with a solvent that selectively dissolves some components
  - Diffusion in solids is very slow compared to diffusion in liquid
  - Complete separation of a solid phase from a liquid phase is virtually impossible
- Crystallization
  - Analogous to distillation
  - Sharp phase separation is virtually impossible
- Liquid adsorption
  - The porous solid agent selectively adsorbs certain components of the liquid mixture on its exterior and interior surface
- Membrane–separation
  - A solid membrane absorbs and transports certain species of the liquid mixture

Leaching

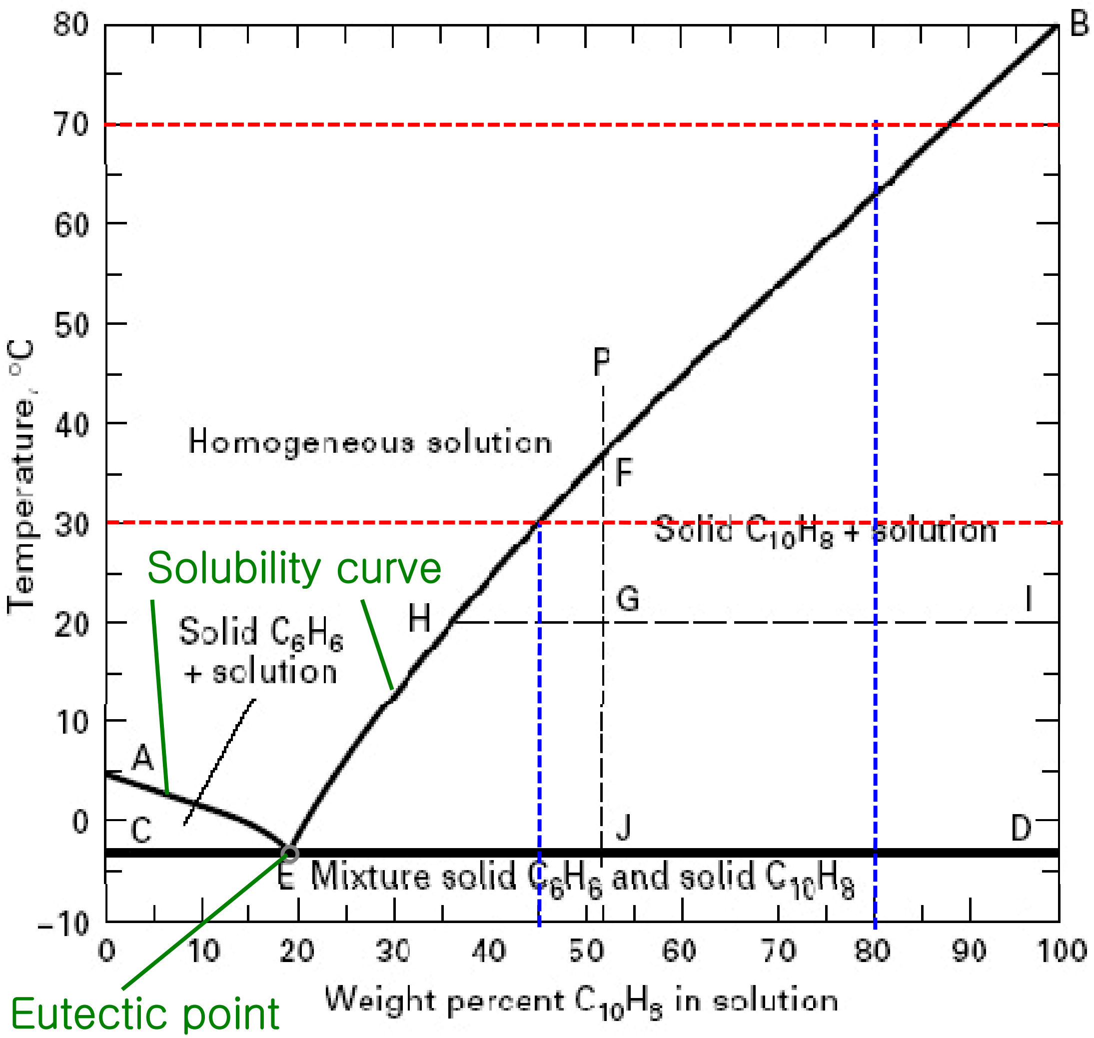


- In an ideal equilibrium leaching stage,
  - Overflow is free of solid
  - None of the solid A is dissolved
  - The composition of the underflow liquid phase is same as the composition of the overflow liquid

- Applications
  - Separation of metal from ore using acid
  - Separation of soybean oil from soybean using hexane

Crystallization

- Crystallization of naphthalene ($C_{10}H_8$) in benzene (C_6H_6)



8,000 kg/h liquid solution of 80 wt% naphthalene and 20 wt% benzene at 70℃ is cooled to 30℃ → forming naphthalene crystals

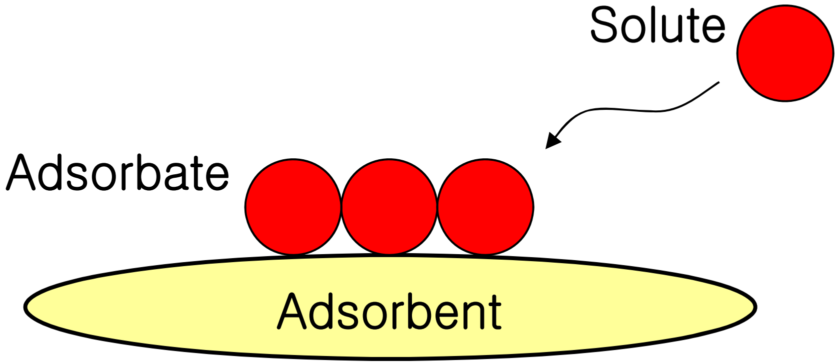
At 30℃, the solubility of naphthalene is 45 wt%.
By the inverse-lever-arm rule,

$$\frac{\text{kg naphthalene crystals}}{\text{kg original mixture}}$$

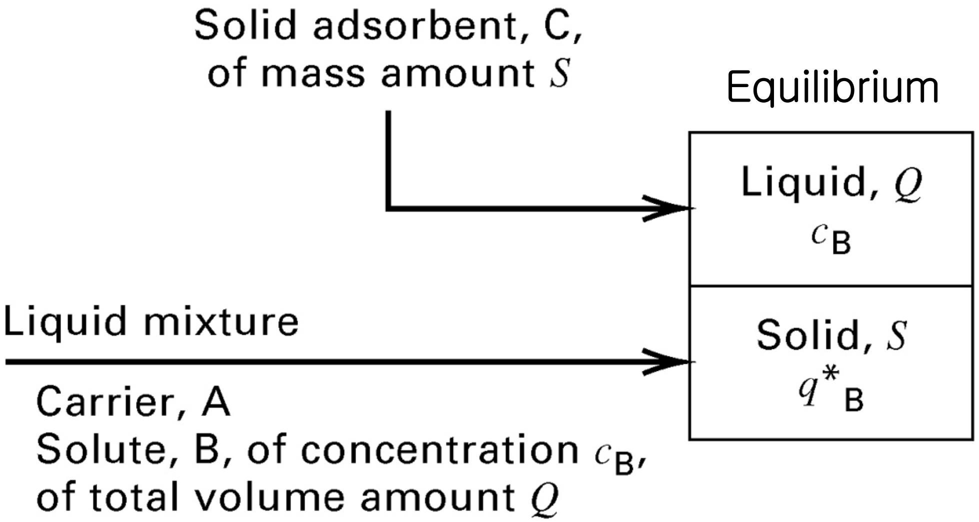
$$= (80 - 45)/(100 - 45) = 0.636$$

Flow rate of crystals
= 0.636 × 8,000 = 5,090 kg/h
Mother liquor (remaining liquid)
= 2,910 kg/h

Liquid Adsorption



- The maximum extent of adsorption occurs at equilibrium.



c_B: concentration of solute in the carrier liquid, mol/volume

q_B: concentration of adsorbate, mol/mass

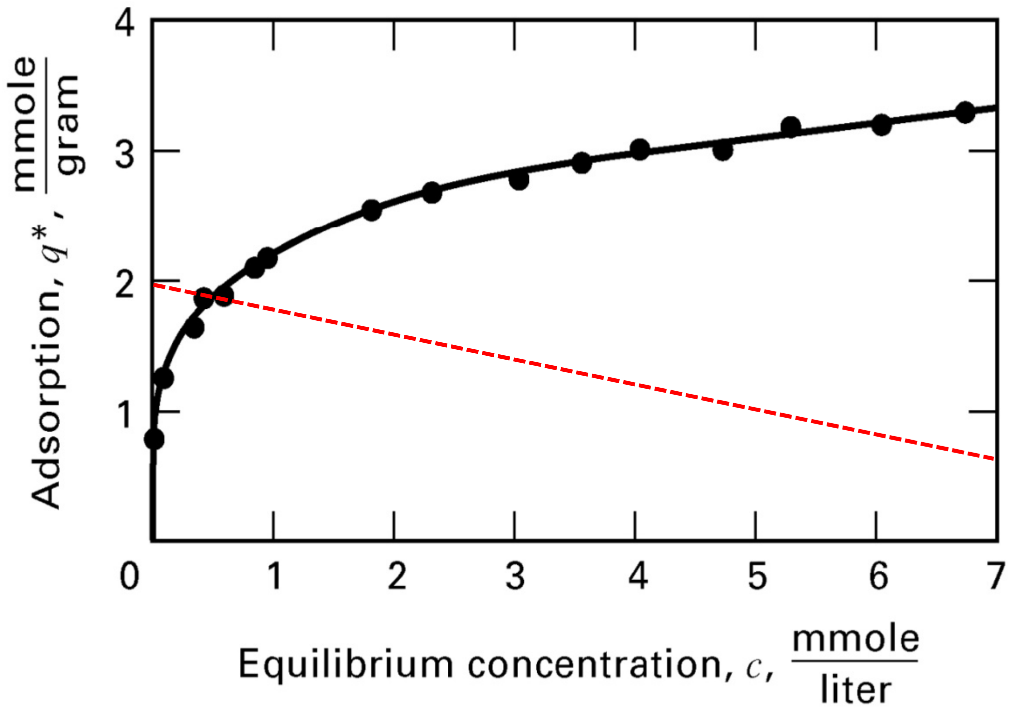
Q: volume of liquid

S: mass of adsorbent

$$c_B^{(F)} Q = c_B Q + q_B^* S \quad \rightarrow \quad q_B^* = -\frac{Q}{S} c_B + c_B^{(F)} \frac{Q}{S}$$

[Example] Adsorption of Phenol on Activated Carbon

One liter of an aqueous solution containing 0.010 mol of phenol is brought to equilibrium at 20℃ with 5 g of activated carbon. Determine the percent adsorption of the phenol and equilibrium concentration of phenol on carbon.



$c^{(F)}$ = 10 mmol/L, Q = 1 L, S = 5 g

$$q_B^* = -\frac{Q}{S}c_B + c_B^{(F)}\frac{Q}{S}$$

$$= -\left(\frac{1}{5}\right)c_B + 10\left(\frac{1}{5}\right) = -0.2c_B + 2$$

q_B^*= 1.9 mmol/g, c_B= 0.57 mmol/L

The percent adsorption of phenol

$$\frac{c_B^{(F)} - c_B}{c_B^{(F)}} = \frac{10 - 0.57}{10} = 0.94 \text{ or } 94\%$$

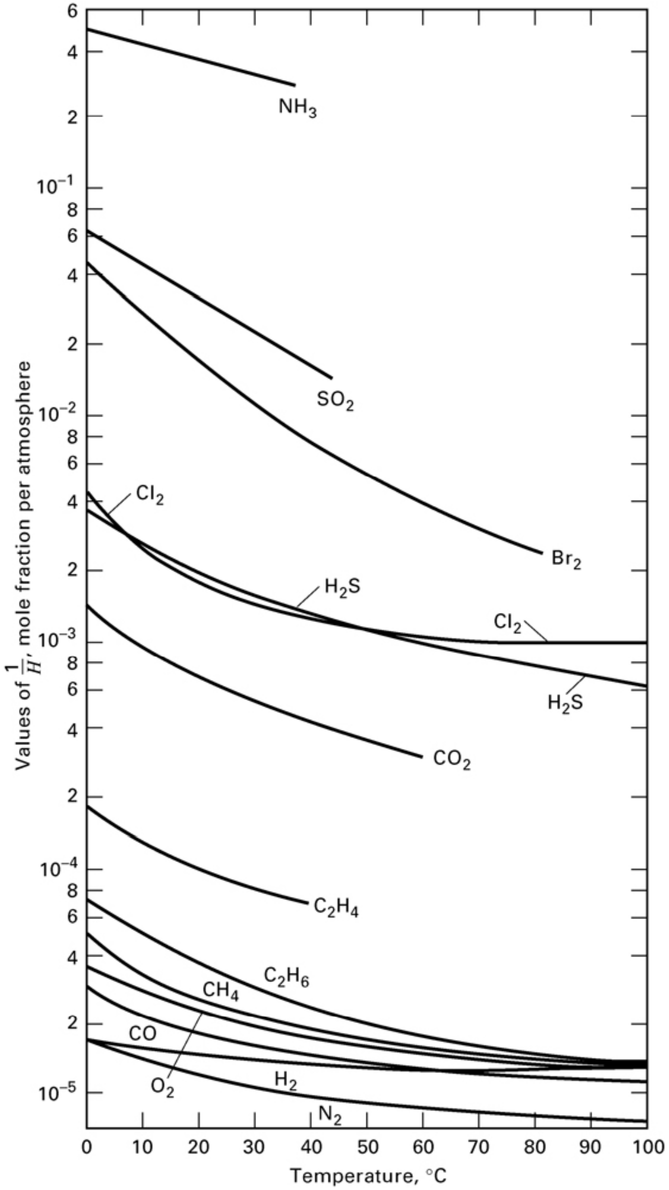
Gas–Liquid Systems

- Vapor : a mixture of species, most or all of which are condensable
- Gas : a mixture for which the temperature is above the critical temperature of most or all of the species

  → the components of a gas mixture are not easily condensed to a liquid

Estimation of the solubility in water by applying Henry's law

$$x_i = \left(\frac{1}{H_i}\right) y_i P$$

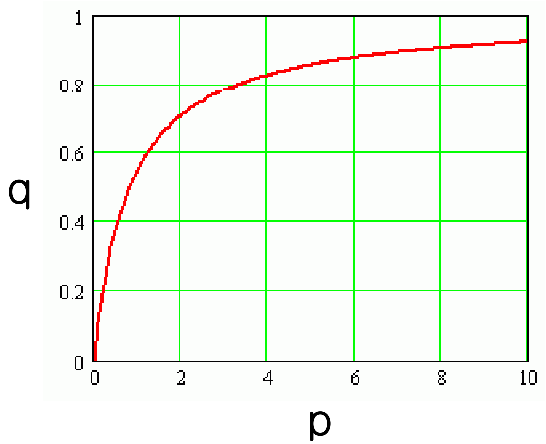


Gas–Solid Systems

- Sublimation & desublimation
  - Sublimation: a solid vaporizes into a gas phase without passing through a liquid state
  - Desublimation: one or more components (solutes) in the gas phase are condensed to a solid phase without passing through a liquid state

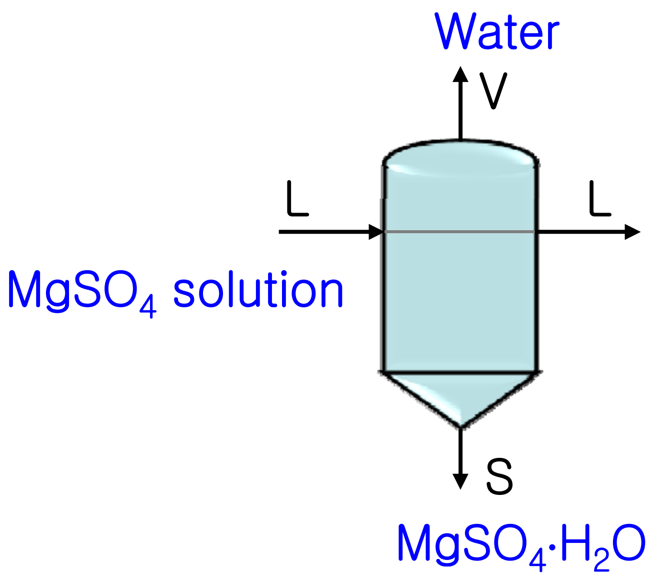
- Gas adsorption
  - One or more components of a gas mixture can be adsorbed on the surface of a solid adsorbent
  - Adsorption isotherm: (partial pressure of solute in the gas) *vs.* (concentration of adsorbate in the solid)

Adsorption isotherm



Vapor–Liquid–Solid Systems

- Example: vacuum evaporative crystallizer
  - The system pressure can be approximated by applying Raoult's law to the water in the liquid $P = P^s_{H_2O} x_{H_2O}$



A 5,000 lb batch of 20 wt% aqueous $MgSO_4$ solution is fed to a vacuum, evaporative crystallizer operating at 160°F. At this temperature, the stable solid phase is the monohydrate, with a $MgSO_4$ solubility of 36 wt%. 75% of the water is evaporated.

Pounds of water evaporated ?

Feed solution: 0.2 x 5,000 = 1,000 lb $MgSO_4$

5,000 – 1,000 = 4,000 lb H_2O

Water evaporated: 0.75 x 4,000 = 3,000 lb H_2O

Vapor–Liquid–Liquid Systems

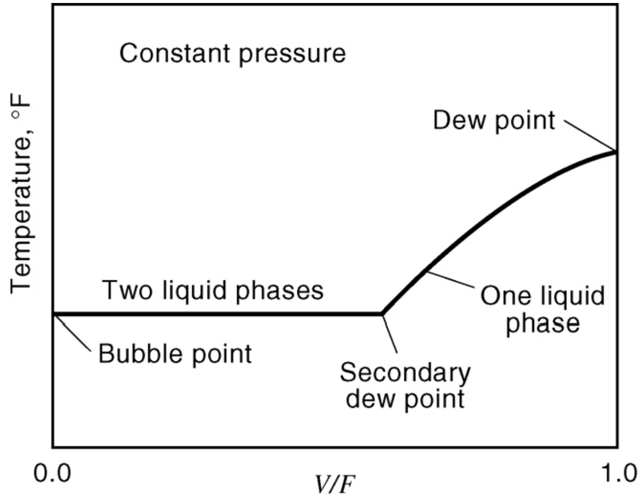
- Example: mixture containing water and hydrocarbons
  $\rightarrow$ vapor phase, two liquid phases (HC-rich & water-rich)
- If the solubilities of water in the liquid HC phase and HCs in the water phase are negligible, and the liquid HC phase obeys Raoult's law

$$P = P^s_{H_2O} + \sum_{HCs} P^s_i x^{(1)}_i$$

More general cases,

$$P = P^s_{H_2O} + P\sum_{HCs} K_i x^{(1)}_i$$

Only one HC species present



More than one HC species present