2. Phase Equilibria and crystallization technique

2.1 Phase rule

- Solubility product

  K_{sp}

- Degree of freedom (F)

  P + F = C + 2

  where

  P : number of phases

  C : number of components

  Ex) NaCl + water

  Phase = 3 (solid, liquid, vapor)

  Component = 2 (NaCl, water)

  F = 2 + 2 – 3 = 1

  Transition point : NaCl, NaCl-$2H_2O$

  Phase = 4 (2 solids, liquid, vapor)

  Component = 2 (NaCl, water)

  F=2+2-4=0

  Addition of an extra-component = drowning-out

  -Eutectic system (selective crystallization)

  line BC : pure B-crystal + A/B mixture-liquid

  line AC : pure A-crystal + A/B mixture-liquid

Pure separation is possible by single step of crystallization.

Ex) gold/thallium, naphthalene/benzene, m-/p-nitrochlorobenzene, KCl/H_2O

- Compound and solid solutions (co-crystallization)
ex) NaCl/NaBr, naphthalene/beta-naphthol

Multi-step crystallization is required to purify a specified component.

2.3 The Driving force for crystallization

- Under-saturated
- Saturated
- Supersaturated = metastable, labile

- Supersaturation

$\sigma = (\mu_{ss} - \mu_{eq})/kT$

$\mu_i = \mu^0 + kT ln a_i$ (Gibbs-Duhem equation)

- Concentration driving force : $\Delta C = C_{ss} - C_{eq}$

2.4 Crystallization technique

- Suspension process
crystallization in solution depending on solubility change

ex) cooling crystallization
drowning-out crystallization
evaporation crystallization
salting-out crystallization
reaction crystallization

particulate materials :

crystal size, distribution, shape, structure, purity

- Solidification process

solidification of liquid phase below melting point

ex) melt crystallization

- purification by single step crystallization in eutectic system
- purification by multi-step crystallization (fractional crystallization)

spray drying (no purification)

- Continuous process

commodity materials produced in high tonnage

ex) slat, paraxylene, ammonium nitrate, urea, adipic acid etc

- Batch-wise process

specialty chemicals produced in low tonnage