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-2H₂O
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$_2$O

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

\[ \mu_i = \mu^0 + kT \ln a \] (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