Lecture 19.
Crystallization
[Ch. 17]

- Type of Crystallization
  - Solution crystallization
  - Melt crystallization
- Industrial Example
  - Process for production of $MgSO_4 \cdot 7H_2O$
- Crystal Geometry
  - Crystal habit
  - Sphericity

Crystallization

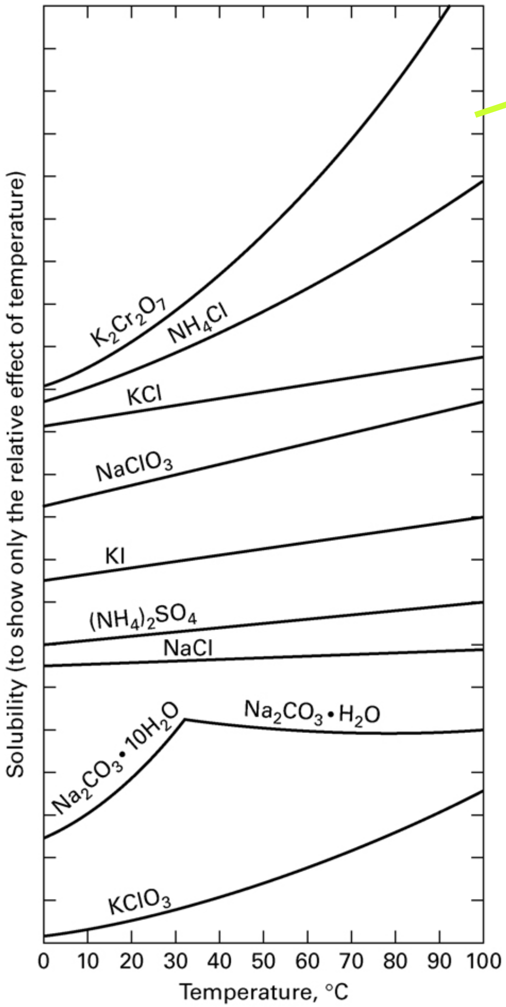
- A solid-fluid separation operation in which crystalline particles are formed from a homogeneous fluid phase
- One of the oldest separation operations : recovery of NaCl as salt crystals from seawater

- Factors for crystallization
  - Cooling the solution
  - Evaporating the solvent
  - Addition of a second solvent
    - when water is the additional solvent : watering-out
    - when an organic solvent is added to an aqueous salt solution : salting-out
    - fast crystallization called precipitation can occur

Type of Crystallization

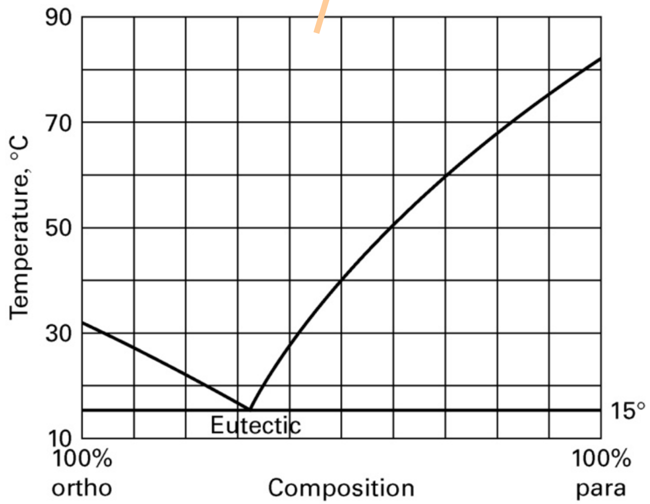
- Solubility curves

Solution crystallization
- Solute: inorganic salt → crystallized
- Solvent: water → remains in liquid phase



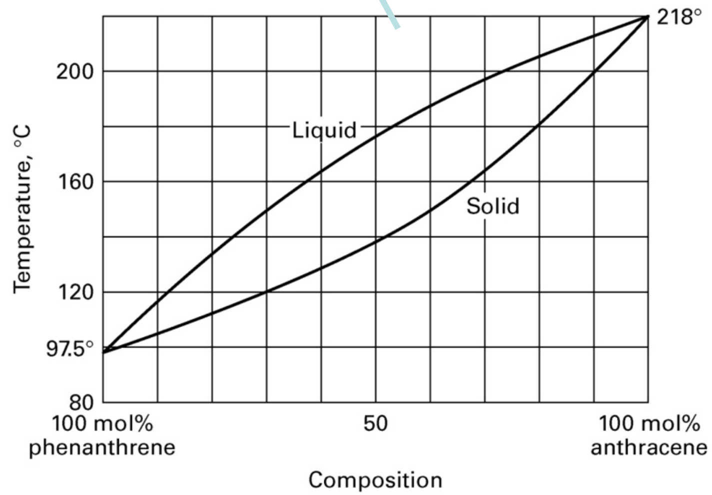
(a) Aqueous systems suitable for solution crystallization

Melt crystallization
- Eutetic point



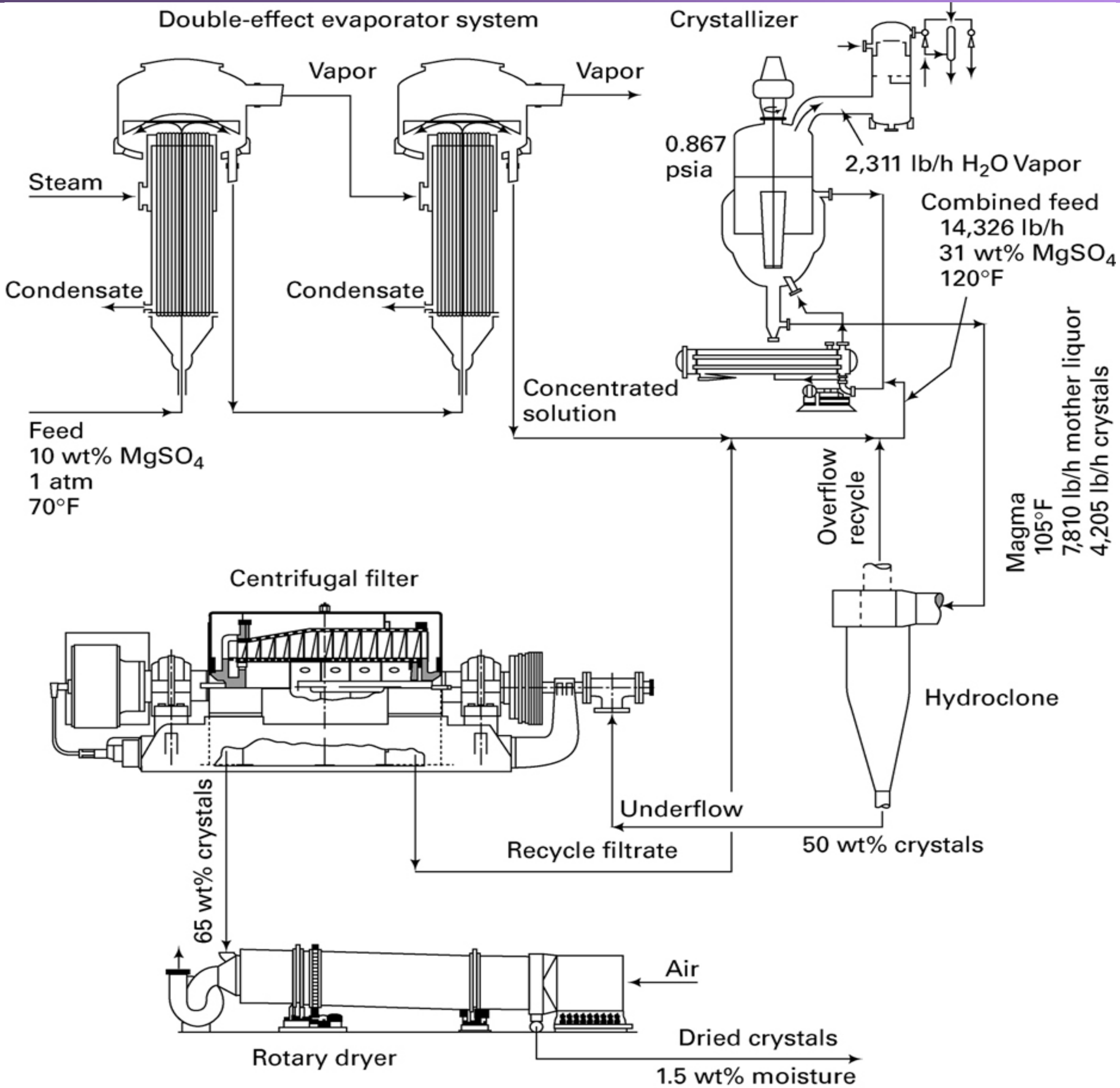
(b) Eutectic-forming system of ortho- and parachloro-nitrobenzene system suitable for melt crystallization

Fractional melt crystallization
- Repeated melting and freezing steps



(c) Solid-solution system suitable for fractional melt crystallization

Industrial Example



- Production of $MgSO_4{\cdot}7H_2O$

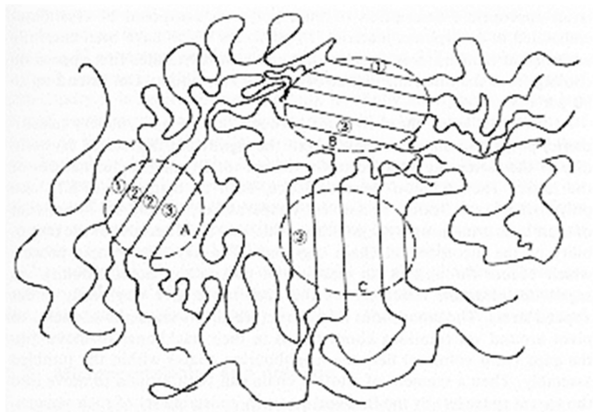
Evaporation in one or more vessels (effects) to concentrate solution

Partial separation and washing of the crystals from the resulting slurry (magma) by centrifugation or filtration

Drying the crystals to a specified moisture content

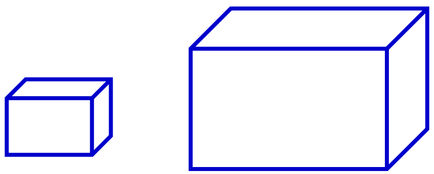
Crystal Geometry

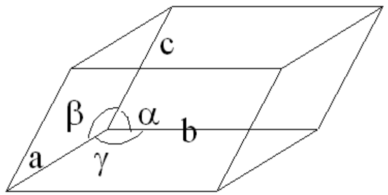
- Crystalline and amorphous states

Crystalline solid	Amorphous solid
– Regular arrangement of atoms – Physical properties depend on the direction of measurement (unless cubic in structure): anisotropic	– Irregular arrangement of atoms – Physical properties are independent of the direction of measurement: isotropic
	

Crystal Habit

- When crystals grow, they form polyhedrons with flat sides and sharp corners (if unhindered by other surfaces such as container walls and other crystals)
- Crystals are never spherical in shape
- Law of constant interfacial angles (Hauy, 1784)
  - The angles between corresponding faces of all crystals are constant, even though the crystals vary in size and in the development of the various faces
  - Crystal habit
  - The interfacial angles and lattice dimensions can be measured by X-ray crystallography





Sphericity

- Typical magmas from a crystallizer contain a distribution of crystal sizes and shapes
- Characteristic crystal dimension for irregular-shaped particle → sphericity, ψ

$$\psi = \frac{\textbf{surface area of a sphere with the same volume as the particle}}{\textbf{surface area of the particle}}$$

For a sphere, $\psi = 1$; for all other particles, $\psi < 1$

$$\left(\frac{s_p}{v_p}\right)_{\text{sphere}} = \frac{\pi D_p^2}{(\pi D_p^3/6)} = \frac{6}{D_p}$$

$$\Rightarrow \psi = \frac{6}{D_p}\left(\frac{v_p}{s_p}\right)_{\text{particle}}$$