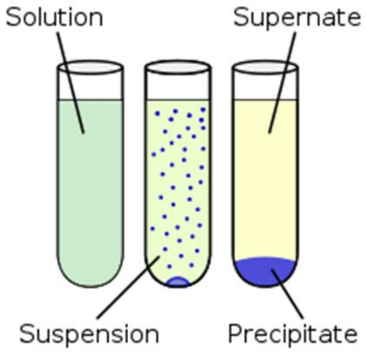
Lecture 19.
Precipitation and Melt Crystallization

- Precipitation
  - Precipitation diagrams
  - Particle growth rates
- Melt Crystallization
- Equipment for Melt Crystallization
  - Suspension crystallization
  - Layer crystallization
- Zone Melting

Precipitation (1)



- Precipitation: the formation of a solid in a solution or inside another solid during a chemical reaction or by diffusion in a solid
- Precipitation involves solutes that are only sparingly soluble
- In reactive crystallization, the precipitate is formed by changing pH, solvent concentration, or solution temperature, or by adding a reagent that reacts with the solute to produce an insoluble chemical
  - The degree of supersaturation produced by the reaction is large, causing a high degree of primary nucleation
  - Although some growth occurs as the supersaturation is depleted, precipitates generally consist of very small particles that form quickly and may be crystalline in nature, but are frequently aggregares and agglomerates
    - Aggregates: masses of crystallites that are weakly bonded together → agglomertion can follow, cemeting aggregates together

Precipitation (2)

$$\ln\left(\frac{c}{c_s}\right) = \frac{4v_s\sigma_{s,L}}{vRTD_p}$$

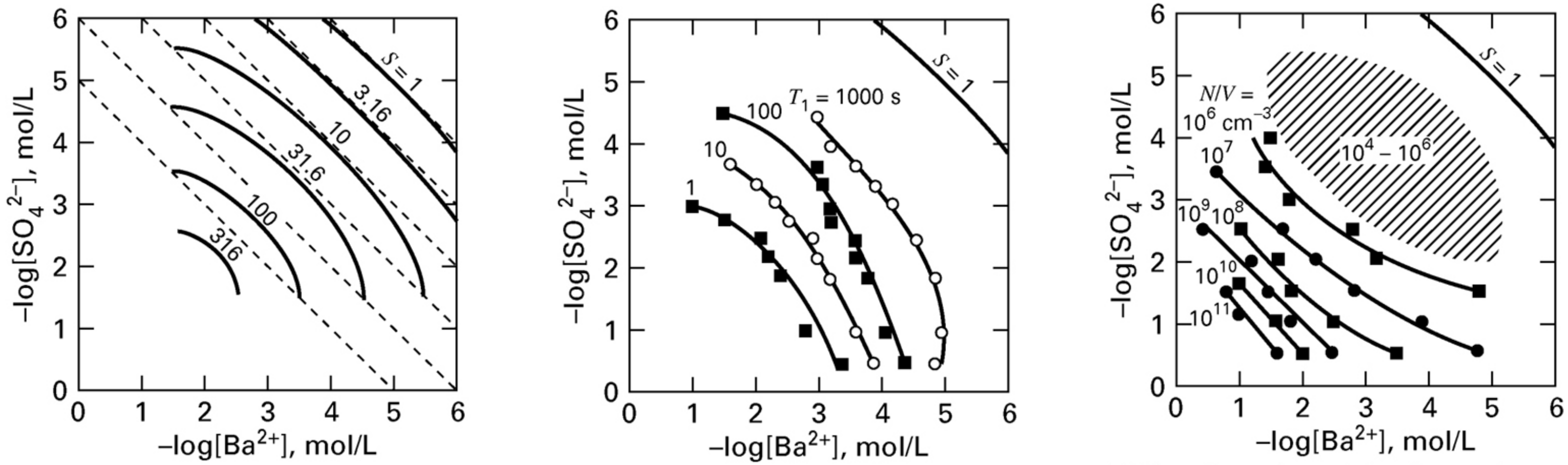
- In precipitation, particle size is related to solubility
- For precipitates formed from ionic reactions in solutions, the supersaturation ratio, S (= c/c_s) is replaced by $(\pi/K_c)^{1/v}$

π : ionic concentration product for the reaction
K_c : (equilibrium) solubility product
v : sum of the cations and anions that form the precipitated compound

- When a reagent is added to a solution to form a sparingly soluble compound, a high supersaturation, which depends on the ionic concentrations in solution, develops
- Precipitation does not take place immediately after development of a large supersaturation because of the slow growth of very small particles
- After a period of time (the induction period, T_1), visible precipitation begins. This period depends on initial ion concentrations and the supersaturation ratio

Precipitation (3)

- Precipitation diagrams for $BaSO_4$



(a) Extent of supersaturation (b) Induction period (c) Number of particles formed

- The number of particles formed per unit volume of solution, N/V, also depends on initial concentrations of anion and cation and, therefore, on the supersaturation at high ion concentrations
  - The number of particles formed also depends on particle growth rate, which may be controlled by mass transfer of ions to a particle surface and/or integration of ions into the particle crystalline lattice (surface reaction)

Precipitation (4)

- Particle growth rates during precipitation
  - Linear rate law, $G = k_1 s$
    : often applies for G > 10 nm/s; indicates mass-transfer control or surface-adsorption control, where the latter depends on more strongly on temperature
  - Parabolic rate law, $G = k_2 s^2$
    : G may be < 10 nm/s, applies to screw-dislocation-controlled growth
  - Exponential rate law, $G = k_3 f\{s\}$
    : f{s} can involve a complex exponential, log, and/or power-law dependency; corresponds to growth control by surface nucleation
  - When growth is rapid, co-precipitation of soluble electrolytes may occur by entrapment, making it difficult to obtain a pure precipitate

Precipitation (5)

- Because a precipitate is formed at considerable supersaturation, resulting particle shapes may be far from what corresponds to a minimum Gibbs energy, which depends on the particle surface area and interfacial tension
- If precipitate and mother liquor are allowed to age, then precipitate particle sizes and shapes tend toward equilibrium values by:

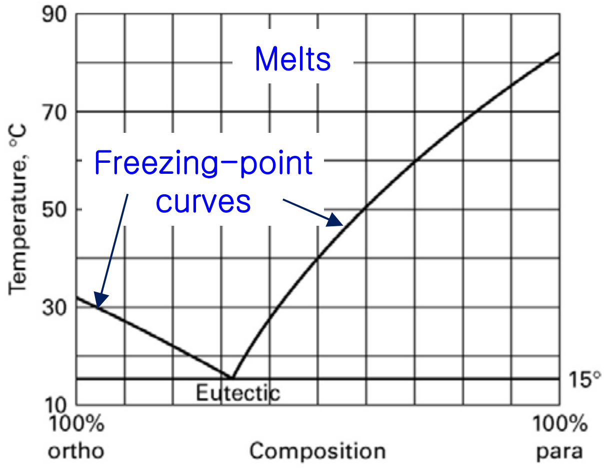
  (1) flocculaiton and sintering of fine particles

  (2) ion transport over the surface

  (3) ripening by dissolution and redeposition
- Ripening can result in the release of co-precipitates, thus increasing precipitate purity
- Small particles produced in abundance during precipitation have a tendency to cluster together by interparticle collisions, variously referred to as agglomeration, aggregation, and flocculation

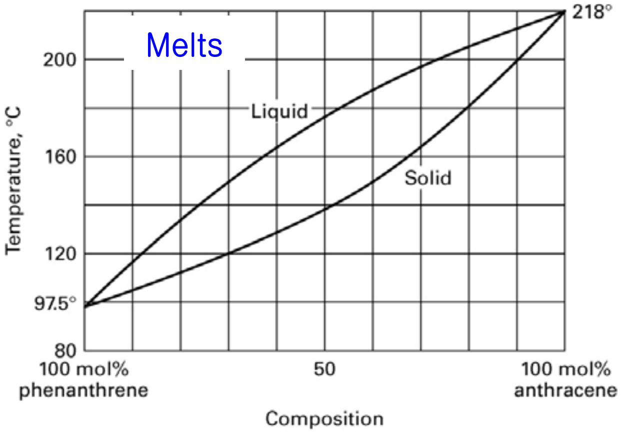
Melt Crystallization

- Eutectic–forming systems consist of compounds that cannot substitute for each other in the crystal lattice, so the eutectic mixture consists of two different solid phases (e.g. ortho–chloronitrobenzene and para–chloronitrobenzene)



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

- Solid–solution–forming systems consist of compounds so nearly alike in structure that they can substitute for each other in the crystal lattice to form a single crystalline phase over a wide range of composition (e.g. phenanthrene and anthracene)



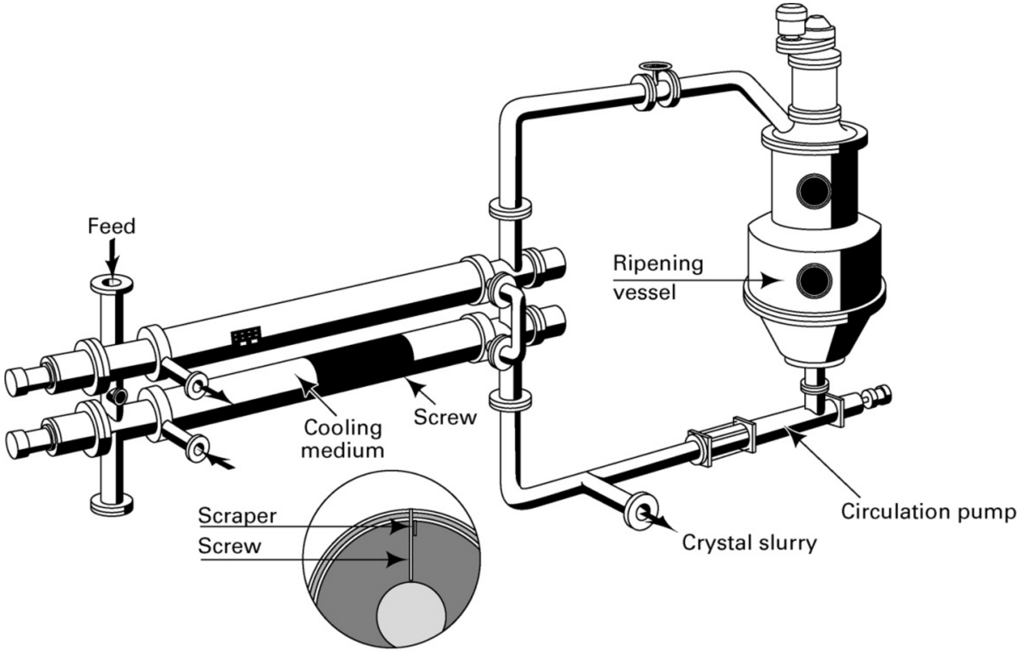
(c) Solid-solution system suitable for fractional melt crystallization

- Theoretically, melt crystallization of eutectic–forming systems, like solution crystallization of such systems, can produce pure crystals

Equipment for Melt Crystallization (1)

- Suspension crystallization: crystals of a desired size distribution are grown slowly in a suspension by subcooling a seeded-feed melt
  - The remaining melt must be separated from the crystals by centrifugation, filtration, and/or settling

Two-stage, scraped-wall melt crystallizer

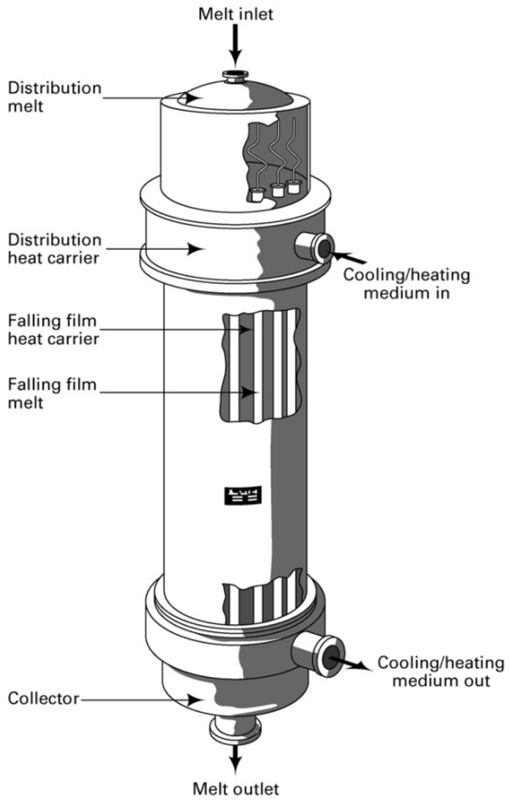


- A cooling medium is used to control the surface temperatures of the two scraped-wall units, causing crystals to grow, which are subsequently scraped off by screws. The melt mixture is circulated through a ripening vessel

Equipment for Melt Crystallization (2)

- Layer crystallization: crystals of uncontrolled size are grown rapidly on a cooled surface, wherein subcooling is supplied through the crystallized layer; the remaining melt or residual liquid is drained from the solid layer, followed by melting of the solid

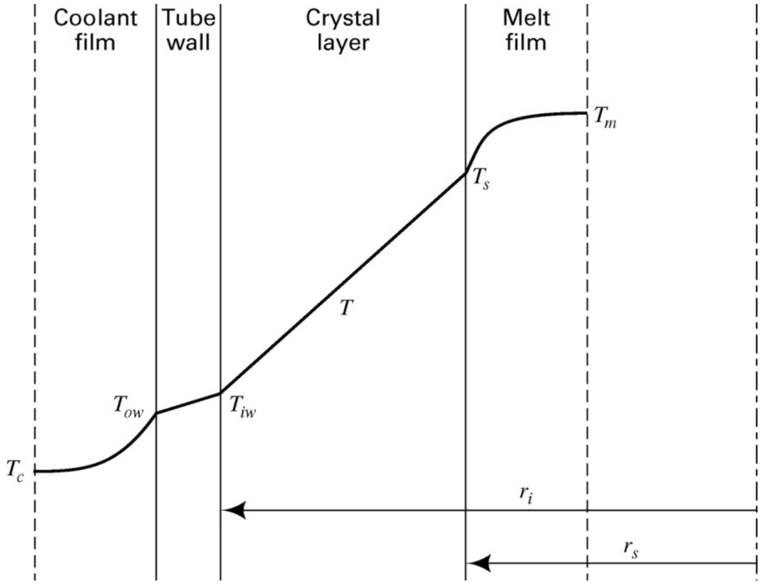
Sulzer falling-film melt crystallizer



- The feed melt flows as a film down the inside of the tubes over a crystal layer that forms and grows by progressive freezing because the wall of the tube is cooled from the outside
- When a predetermined crystal-layer thickness, typically 5–20 mm, is reached, the feed is stopped and the tubes are warmed to cause partial melting (sweating) to remove impurities that may be bonded to the crystal layer → followed by complete melting of the remaining layer, which is of high purity

Equipment for Melt Crystallization (3)

- Heat transfer in falling-film melt crystallizer
  - Heat is transferred from the melt to the coolant, causing the melt to form a crystal layer at the inside tube wall
  - As melt and coolant flow down the tube, their temperatures decrease and increase, respectively
  - The thickness of the crystal layer increases with time, with the latent heat of fusion transferred from the crystal-melt interface to the coolant



- For a eutectic-forming, binary melt, only one component crystallizes, although small amounts of the other component may be trapped in the crystal layer, particularly if the rate of crystal formation is too rapid

Equipment for Melt Crystallization (4)

- If mass transfer of the crystallizing component from the melt film to the phase interface is rapid, the interface temperature will correspond to the melt-film composition at that vertical location
- Model for rate of increase of crystal-layer thickness with time
  - At a particular vertical location, $T_s \approx T_m$ and $T_{iw} \approx T_c$

(the rate of heat released by freezing, ΔH_f) = (the rate of heat conduction through the crystal layer)

$$\Delta H_f \frac{dm}{dt} = -A\rho_c(\Delta H_f)\frac{dr_s}{dt} = \frac{k_c A(T_m - T_c)}{r_i - r_s}$$

Integration with an initial condition $r_s = r_i$ at $t = 0$

$$\frac{(r_i - r_s)^2}{2} = \frac{k_c(T_m - T_c)t}{\rho_c \Delta H_f}$$

$$(r_i - r_s) = \sqrt{\frac{2k_c(T_m - T_c)t}{\rho_c \Delta H_f}}$$

Crystal-layer thickness

Crystal layer grows as the $\sqrt{t}$

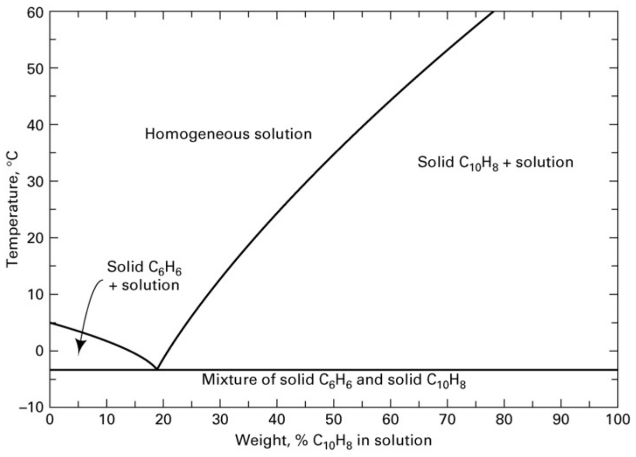
Equipment for Melt Crystallization (5)

- For a cylindrical–tube wall, where r_i = inside radius of the tube

$$\underbrace{\frac{1}{4}(r_i - r_s)^2 - \frac{r_s^2}{2}\ln\left(\frac{r_i}{r_s}\right)}_{\displaystyle \Downarrow \atop \displaystyle \frac{(r_i - r_s)^2}{2}} = \frac{k_c(T_m - T_c)t}{\rho_c \Delta H_f}$$

As the value or r_s approaches the value of r_i

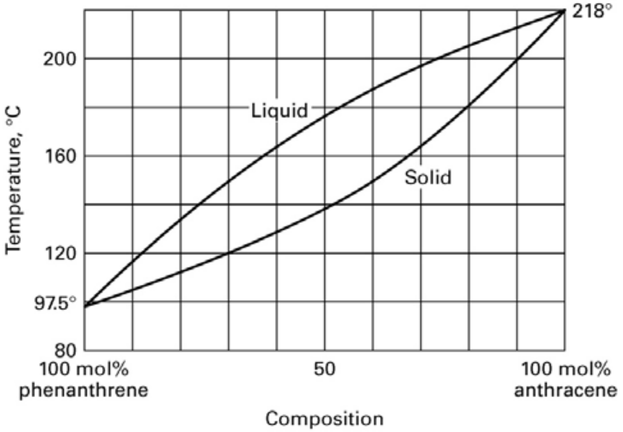
- The melt temperature at any elevation will be the temperature corresponding to the solubility curve for the melt composition at that elevation
- The eutectic point represents the theoretical concentration limit for any melt crystallization process. Higher concentrations of impurities generally inhibit growth and can affect the crystal purity



Zone Melting (1)

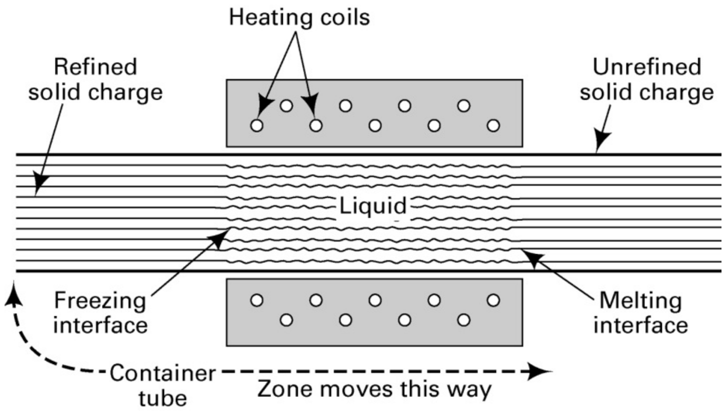
- When melt consists of two components that form a solid solution, liquid and solid phases at equilibrium contain both components

  ⇒ multiple stages of crystallization are required to obtain products of high purity



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

- Zone melting: a method of purifying crystals, in which a narrow region of a crystal is molten, and this molten zone is moved along the crystal
  - The molten region melts impure solid at its forward edge and leaves a wake of purer material solidified behind it as it moves through the slab
  - The impurities concentrate in the melt, and are moved to one end of the slab



Zone Melting (2)

- The slab cab be arranged horizontally or vertically, with the latter preferred because it takes advantage of the density difference between crystals and melt
- Solid–liquid equilibrium distribution coefficient

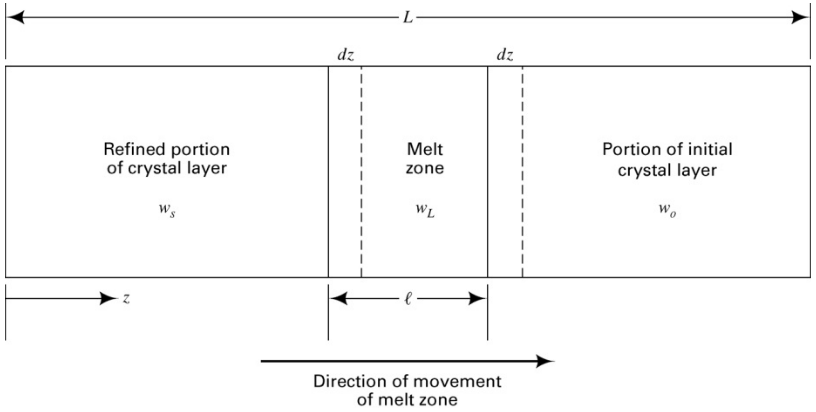
$$K_i = \frac{\textbf{concentration of impurity, } \boldsymbol{i}\textbf{, in the solid phase}}{\textbf{concentration of impurity, } \boldsymbol{i}\textbf{, in the melt phase}}$$

  - When $K_i > 1$, impurities raise melting points and concentrate in the solid phase
  - When $K_i < 1$, impurities lower melting points and concentrate in the melt
  - When $K_i \to 1$, purification by zone melting becomes very difficult

- Ideal zone–melting model

  Mass balance on the impurity for a dz melt–zone movement

(mas of impurity added to melt zone)
– (mass of impurity removed from melt zone)
= (increase in mass of impurity in the melt zone)



Zone Melting (3)

$$w_o \rho_c A_c dz - w_s \rho_c A_c dz = \rho_L A_c l dw_L$$

$$K = w_s / w_L$$

➡ $$dw_L = dw_s / K$$

$$\frac{K}{l}\int_0^z dz = \int_{Kw_o}^{w_s} \frac{dw_s}{w_o - w_s}$$ ⬅ assuming $\rho_L = \rho_c$

Integration for z/l = 0 to z/l = L/l −1

$$\frac{w_s}{w_o} = 1 - (1 - K)\exp(-Kz/l)$$