

# Lecture 16.

## Kinetics and Mass Transfer in Crystallization

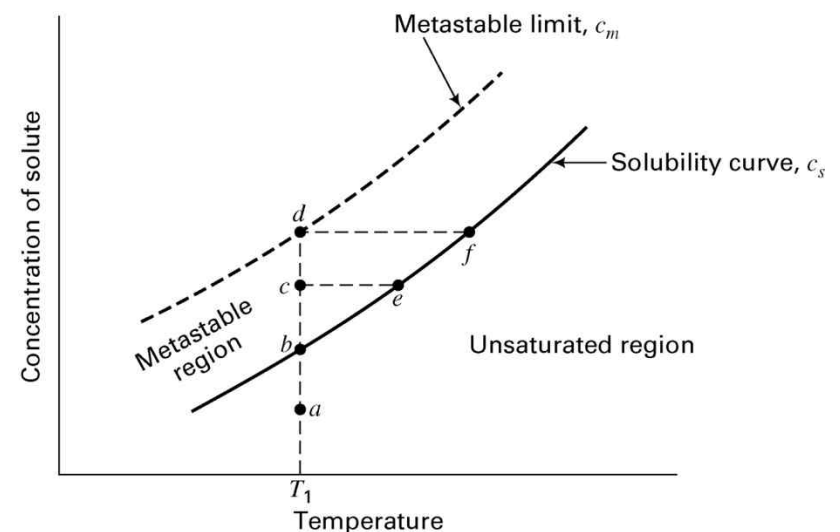
- Crystallization Kinetics
- Supersaturation
- Nucleation
  - Primary nucleation
  - Secondary nucleation
- Crystal Growth
  - Diffusion–reaction theory
  - Screw–dislocation theory

# Crystallization Kinetics

- Crystallization is a complex phenomenon involving three steps: (1) nucleation, (2) mass transfer of solute to the crystal surface, and (3) incorporation of solute into the crystal lattice  
⇒ Crystallization kinetics
- **Supersaturation** is the driving force for crystallization kinetics
- As crystal size decreases, solubility noticeably increases, making it possible to supersaturate a solution if it is cooled slowly without agitation
- The solubility of very small crystals can fall in the metastable region

Point a: the solution is undersaturated; crystals of all sizes dissolve

Point b: equilibrium between a saturated solution and crystals that can be seen by naked eyes



# Supersaturation

Point c: metastable region; crystals can grow but cannot nucleate

Point d: spontaneous nucleation of very small crystals, that are invisible to the naked eyes, occurs

- Limiting supersaturation,

$$\Delta C_{\text{limit}} = C_m - C_s$$

- Kelvin equation: a relationship between solubility and crystal size

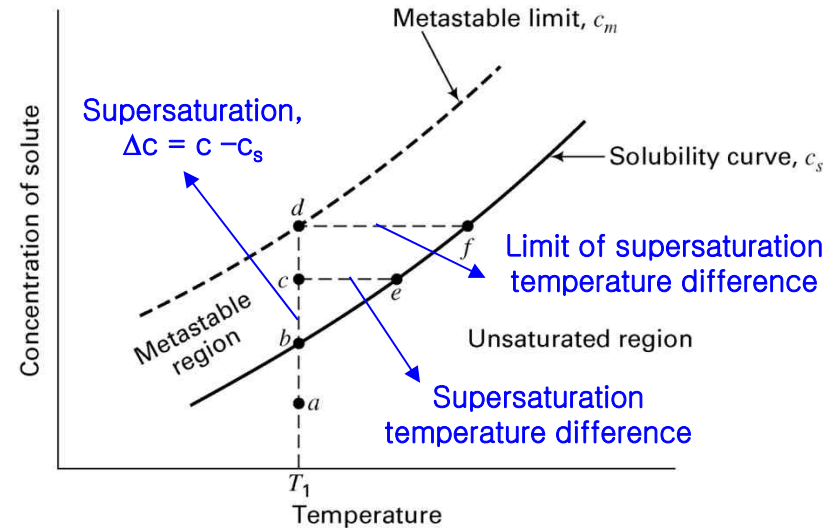
$$\ln\left(\frac{c}{c_s}\right) = \frac{4\nu_s \sigma_{s,L}}{\nu R T D_p}$$

$\nu_s$  : molar volume of the crystals  
 $\sigma_{s,L}$  : interfacial tension  
 $\nu$  : number of ions/molecule of solute  
 $c/c_s$  : supersaturation ratio (=S)

- Relative supersaturation

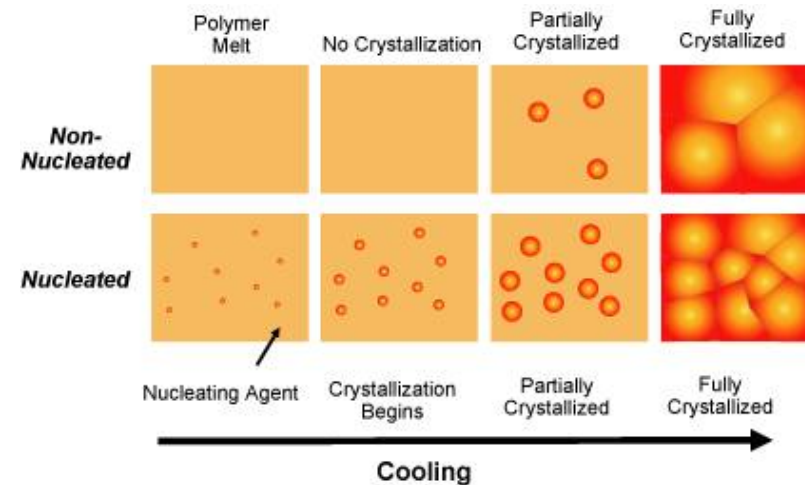
$$s = \frac{c - c_s}{c_s} = \frac{c}{c_s} - 1 = S - 1$$

In practice, s is usually less than 2%



# Nucleation (1)

- To determine volume or residence time for magma in a crystallizer, the rate of **nucleation** (birth) of crystals and their rate of growth must be established
- Relative rates of nucleation and growth are important because they determine crystal size and size distribution



- **Primary nucleation**
  - Supersaturated solution is free of crystalline surface
  - Requires high supersaturation and is the principal mechanism in precipitation

# Nucleation (2)

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- Homogeneous nucleation
  - occurs with supersaturated solutions in the absence of foreign matter, such as dust
  - molecules in the solution first associate to form a cluster, which may dissociate or grow
  - if a cluster gets large enough to take on the appearance of a lattice structure, it becomes an embryo → stable crystalline nucleus
  - rate of homogeneous nucleation

$$B^0 = A \exp \left[ \frac{-16\pi v_s^2 \sigma_{s,L}^3 N_a}{3v^2 (RT)^3 \left[ \ln \left( \frac{c}{c_s} \right) \right]^2} \right]$$

$B^0$  : rate of homogeneous primary nucleation, number of nuclei/cm<sup>3</sup>.s  
 $A$  : frequency factor  
 $N_a$  : Avogadro's number

# Nucleation (3)

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- Secondary nucleation

- Supersaturated solution contains crystals
- Key in commercial crystallizers, where crystalline surfaces are present and large crystals are desired
- Initiated by (1) fluid shear past crystal surfaces that sweeps away nuclei, (2) collisions of crystals with each other, and (3) collisions of crystals with metal surfaces (crystallizer vessel wall or agitator blades)
- (2) and (3) mechanisms are contact nucleation: most common since they happen at the low values of relative supersaturation,  $s$ , typical of industrial applications
- Empirical power-law function

$$B = k_N s^b M_T^j N^r$$

$B$  : rate of secondary nucleation

$M_T$  : mass of crystals per volume of magma

$N$  : agitation rate (e.g., rpm of an impeller)

The constants  $k_N$ ,  $b$ ,  $j$ , and  $r$  are determined from experiments

# Crystal Growth (1)

- Mass transfer theory of crystal growth based on equilibrium at the crystal solution interface [Noyes and Whitney, 1897]

$$dm/dt = k_c A(c - c_s)$$

$dm/dt$  : rate of mass deposited on the crystal surface

$k_c$  : mass-transfer coefficient

$A$  : surface area of the crystal

$c$  : mass solute concentration in the bulk supersaturated solution

$c_s$  : solute mass concentration in the solution at saturation

- Thin, stagnant film of solution adjacent to the crystal face through which solute molecular diffusion takes place [Nernst, 1904]

$$k_c = \frac{D}{\delta}$$

$D$  : diffusivity

$\delta$  : film thickness

- Two-step theory of crystal growth, diffusion-reaction theory [Valeton, 1924]
  - First step: mass transfer of solute from the bulk of the solution to the crystal-solution interface occurs

$$dm/dt = k_c A(c - c_i)$$

$c_i$  : supersaturated concentration at the interface

# Crystal Growth (2)

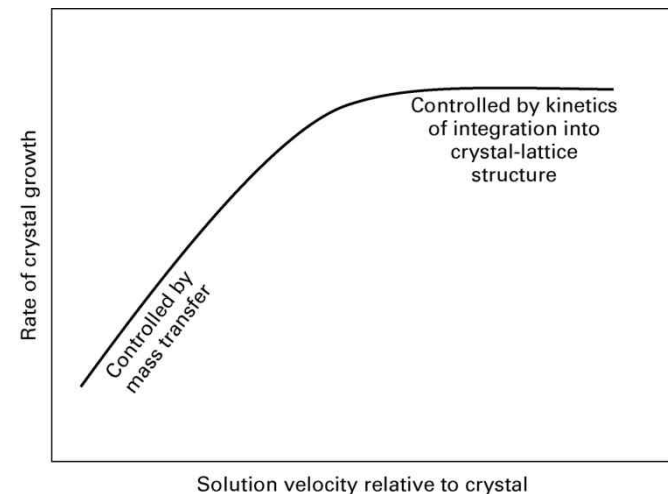
- Second step: a first-order reaction is assumed to occur at the crystal-solution interface, in which solute molecules are integrated into the crystal-lattice structure (kinetic step)

$$dm/dt = k_i A(c_i - c_s)$$



$$dm/dt = \frac{A(c - c_s)}{1/k_c + 1/k_i}$$

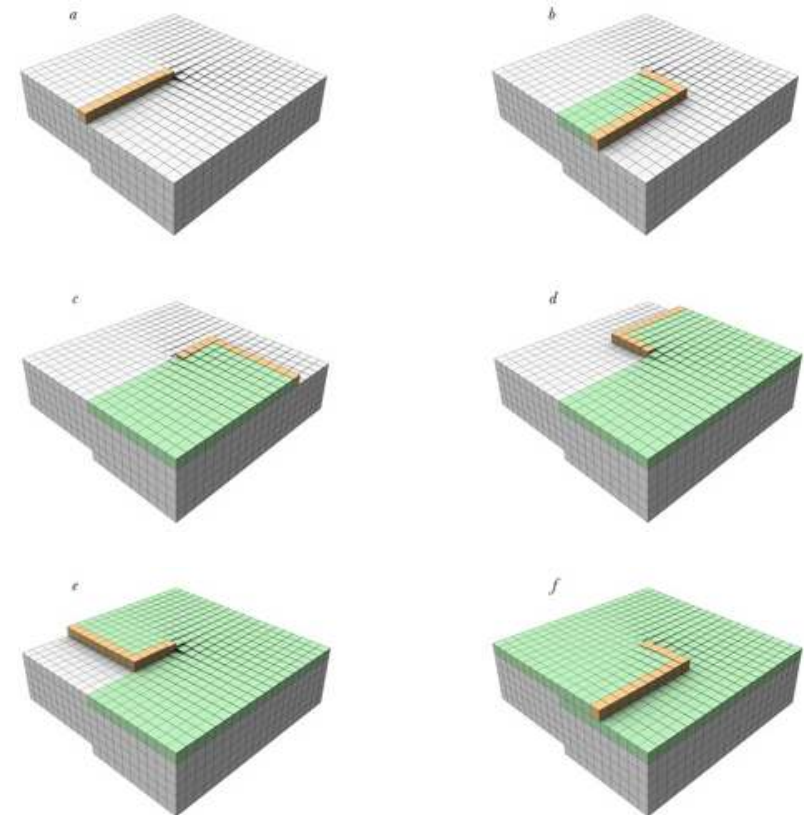
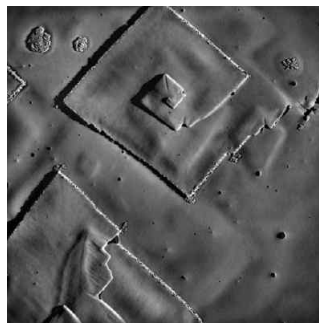
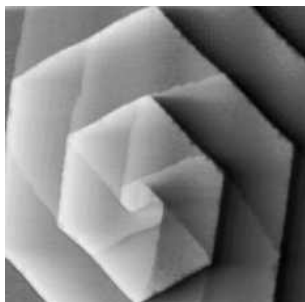
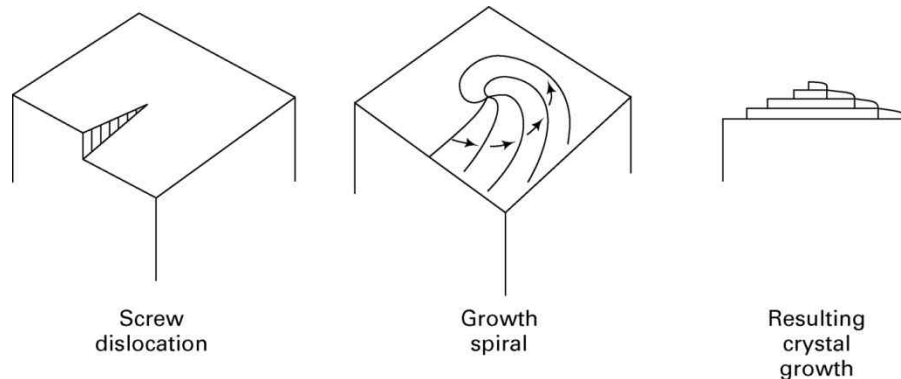
- At low velocities, growth rate may be controlled by the first step (mass transfer)
- The second step (kinetics) is important when solution velocity past the crystal surface is high:  $k_c > k_i$
- The mass-transfer coefficient,  $k_c$ , for the first step is independent of the crystallization process
- The kinetic coefficient,  $k_i$ , is unique to the crystallization process





# Crystal Growth (3)

- Screw-dislocation theory
  - a dislocation is an imperfection in the crystal structure
  - predicts a growth rate proportional to  $(c_i - c_s)^2$  at low supersaturation and to  $(c_i - c_s)$  at high supersaturation



# Crystal Growth (4)

- Although crystals do not grow as spheres, an equation can be derived for the diameter of a spherical crystal

$$dm/dt = K_c A(c - c_s) \quad K_c : \text{overall mass-transfer coefficient}$$

$$\frac{dD_p}{dt} = \frac{2K_c(c - c_s)}{\rho} = \frac{2K_c(\Delta c)}{\rho} \quad \left. \vphantom{\frac{dD_p}{dt}} \right\} A = \pi D_p^2 \text{ and } m = \frac{\pi D_p^3}{6} \rho$$

If growth rate is controlled by  $k_i$ , which is assumed to be independent of  $D_p$

$$\frac{\Delta D_p}{\Delta t} = \frac{2k_i(\Delta c)}{\rho} \quad \text{Crystal-size increase is linear in time for a constant supersaturation}$$

If growth rate is controlled by  $k_c$  at a low velocity

$$K_c = k_c = 2D/D_p \quad D : \text{solute diffusivity}$$

$$\rightarrow \frac{dD_p}{dt} = \frac{4D(\Delta c)}{D_p \rho}$$

# Crystal Growth (5)

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Integrating from  $D_{p_0}$  to  $D_p$

$$\frac{D_p^2 - D_{p_0}^2}{2} = \frac{4D(\Delta c)}{\rho} t$$

If  $D_{p_0} \ll D_p$ ,

$$D_p = \left( \frac{8D(\Delta c)t}{\rho} \right)^{1/2}$$

In this case, the increase in crystal diameter slows with time

At higher solution velocities where  $k_c$  still controls,

$$K_c = k_c = C_1 / D_p^{1/2}$$

For this case, the increase in crystal diameter also slows with time, but not as rapidly as predicted in the previous case