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 \Rightarrow 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 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

e can grow but cannot nucleate

Point d: spontaneous nucleation of

very small crystals, that are invisible

to the naked eyes, occurs very small crystals, that are invisible to the naked eyes, occurs

• Limiting supersaturation,

 $\Delta c_{\text{limit}} = c_{\text{m}} - c_{\text{s}}$

• Kelvin equation: a relationship between solubility and crystal size

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

⁴ *s s L* ^s supersaturation,
 $\mathcal{L}_{\rm m} - \mathcal{L}_{\rm s}$

quation: a relationship between s
 $\mathcal{L}_{\rm s}$ $\left(\frac{v_s \cdot \text{molar volume of the c}}{v_{s,L} \cdot \text{interfacial tension}} \right)$
 $\mathcal{L}_{\rm s}$ $\left(\frac{v_s \cdot \text{molar volume of the c}}{v \cdot \text{number of ions/molec}} \right)$

supersaturation $\left(\frac{c}{c}\right)_m = \frac{4v_s\sigma_{s,L}}{2v_s}$, $\frac{v_s}{c_{s,L}}$: interfacial tension *v^s* : molar volume of the crystals *v* : number of ions/molecule of solute c/c_s : supersaturation ratio (=S)

• Relative supersaturation

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\nthe naked eyes, occurs

\nring supersaturation,

\nint = C_m - C_s

\nin equation: a relationship between solubility

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\ln\left(\frac{c}{c_s}\right) = \frac{4v_s \sigma_{s,L}}{vRTD_p}
$$
\ntrivial, $\frac{v_s \cdot \text{molar volume of the crystals}}{v_s \cdot \text{interfacial tension}}$

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\ntrivial terms of the crystals

\ntrivial terms of the duals

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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
	- Requres high supersaturation and is the principal mechanism in precipitation

Nucleation (2)

- 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
- dust

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bociate or grow

large enough to take on the appearance of a

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comes an embryo \rightarrow stable crystalline
nucleation
 $\sigma_{s,L}^3 N_a$
 $\left[\ln\left(\frac{c}{c_s}\right)\right]^2$ • if a cluster gets large enough to take on the appearance of a lattice structure, it becomes an embryo \rightarrow stable crystalline nucleus
	- rate of homogeneous nucleation

$$
\begin{aligned}\n\text{attice structure, it becomes an embryo} &\rightarrow \text{stable} \\
\text{ucleus} \\
\text{ate of homogeneous nucleation} \\
B^\circ &= A \exp\left[\frac{-16\pi v_s^2 \sigma_{s,L}^3 N_a}{3v^2 (RT)^3 \left[\ln\left(\frac{c}{c_s}\right)\right]^2}\right]\n\end{aligned}
$$

*B***^o :** rate of homogeneous primary nucleation, number of nuclei/cm^{3.}s

- *A* : frequency factor
- *N^a* : Avogadro's number

Nucleation (3)

- 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) **b** seent and large crystals are desired
tiated by (1) fluid shear past crystal surfaces that
tay nuclei, (2) collisions of crystals with each othe
llisions of crystals with metal surfaces (crystallize
agitator blades)
an
	- (2) and (3) mechanisms are contact nucleation: most common since they happen at the low values of relative supersatuation, s, typical of industrial applications
	- Empirical power-law function

B : rate of secondary nucleation $M_{\textit{\textbf{T}}}$: 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] **Crystal Growth (1)**

uss transfer theory of crystal growth based on equilibrius

ustal solution interface [Noyes and Whitney, 1897]
 $dm/dt = k_c A(c - c_s)$
 k_c : mass transfer coefficient
 k_c : mass transfer coefficient
 k_c :

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

- *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]

$$
k_c = \frac{D}{\delta} \qquad \frac{D : \text{ diffusivity}}{\delta : \text{ film thickness}}
$$

- 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 *c*, *s* **c**_{*i*} **c**_{*i*} **c** *c*_{*i*} **c** *c* **c** *c* **c** *c c c h* solute molecular diffusion takes place [Nernst, 1904]
 $k_c = \frac{D}{\delta}$ *c c* iim thickness
 $-$ step theory of crystal growth, diffusion-reac

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) **Crystal Growth (2)**

econd step: a first-order reaction is assumed to occur a

ystal-solution interface, in which solute molecules are

tegrated into the crystal-lattice structure (kinetic step)
 $dm/dt = k_i A(c_i - c_s)$
 $dm/dt = \frac$ Crystal Growth (2)

First-order reaction is assumed to occur at

interface, in which solute molecules are

the crystal-lattice structure (kinetic step)
 $\frac{(c-c_s)}{(c_c+c_s)^2}$

s, growth rate may **Crystal Growth (2)**

: a first-order reaction is assumed to occur

ion interface, in which solute molecules are

to the crystal-lattice structure (kinetic step)
 $\frac{A(c_i - c_s)}{1/k_c + 1/k_i}$

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d by the fi interface, in which solute m

the crystal-lattice structure (
 $-c_s$)
 $\frac{(c-c_s)}{c+1/k_i}$

s, growth rate may **Crystal Growth (2)**

and step: a first-order reaction is assumed to occurred into the crystal-lattice structure (kinetic step)
 $\frac{d\mathbf{m}}{dt} = k_i A(c_i - c_s)$
 $\frac{d\mathbf{m}}{dt} = \frac{A(c - c_s)}{1/k_c + 1/k_i}$

w velocities, growth rate ma

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

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

- 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 surfac is high: $k_c > k_i$
- The mass-transfer coefficient, $k_{\rm c}$, 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 proprotional 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 **h** (4)
res, an equation can be
crystal
 $\frac{\pi D_p^2}{\pi D_p^2}$ and $m = \frac{\pi D_p^3}{6} \rho$
assumed to be independent **A Define A**
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cal crystal
 $A = \pi D_p^2$ and $m = \frac{\pi D_p^3}{6} \rho$

is assumed to be independent **Crowth (4)**

grow as spheres, an equation can be

f a spherical crystal
 $\frac{(\Delta c)}{c}$ $A = \pi D_p^2$ and $m = \frac{\pi D_p^3}{6} \rho$
 γ k_i, which is assumed to be independent **²***K c ^c* ^D

Crystal Growth (4)
\nthough crystals do not grow as spheres, an equation can be
\n
$$
dm/dt = K_cA(c-c_s)
$$
 K_c overall mass-transfer coefficient
\n $\frac{dD_p}{dt} = \frac{2K_c(c-c_s)}{\rho} = \frac{2K_c(\Delta c)}{\rho} = \frac{2K_c(\Delta c)}{\rho} = \frac{2K_c(\Delta c)}{\rho}$ and $m = \frac{\pi D_p^3}{6}\rho$
\ngrowth rate is controlled by k_i , which is assumed to be independent
\n $\frac{\Delta D_p}{\Delta t} = \frac{2k_i(\Delta c)}{\rho}$ Crystal-size increase is linear in time
\nfor a constant supersaturation
\ngrowth rate is controlled by k_c at a low velocity
\n $K_c = k_c = 2D/D_p$ D : soluble diffusivity
\n $\frac{dD_p}{dt} = \frac{4D(\Delta c)}{D_p\rho}$

If growth rate is controlled by k_i , which is assumed to be independent of D_p orth rate is controlled by k_i , which is assumed to be
 $\frac{p}{\rho} = \frac{2k_i(\Delta c)}{\rho}$ Crystal-size increase is linear in

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\frac{\Delta D_p}{\Delta t} = \frac{2k_i(\Delta c)}{\rho}
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If growth rate is controlled by k_c at a low velocity

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K_c = k_c = 2D/D_p
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\frac{dD_p}{dt} = \frac{4D(\Delta c)}{D_p \rho}
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Crystal Growth (5) $\begin{CD} {\displaystyle\int\limits_{\mathbb{R}}\mathbf{y}\mathbf{y}\mathbf{y}\mathbf{y}\mathbf{y}}\mathbf{y}\left(\mathbf{y}\right) \left(\math$ **Crystal Growth (5)**
 *D*_{*p*} *D*_{*p*} *D*_{*p*} $D_{p}^2 - D_{p_a}^2 = \frac{4D(\Delta c)}{\rho}t$
 $D_{p_0} \ll D_{p}$, **Crystal Growth (5)**
 $\frac{4D(\Delta c)}{\rho}t$
 $\frac{(\Delta c)t}{\rho}$ ^{1/2} In this case, the increase in crys

diameter slows with time

ution velocities where k_c still controls,

Integrating from D_{po} to D_p

Crystal Growth
egrating from D_{po} to D_p

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

Crystal Growth (5)
Integrating from D _{po} to D _p
$\frac{D_p^2 - D_{p_o}^2}{2} = \frac{4D(\Delta c)}{\rho}t$
If D _{po} & 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,

 ρ diameter slows with time that ρ $\left(\frac{8D(\Delta c)t}{\Delta c}\right)^{1/2}$ In this case, the increase in crystal to D_p
 $\frac{\Delta c}{t}$

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diameter slows with **Crystal Growth (5)**

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

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= $\left(\frac{8D(\Delta c)t}{\rho}\right)^{1/2}$ In this case, the increase in crystal

diameter slows with time

ner solution velocities where k_c still

At higher solution velocities where k_c still controls,

$$
\boldsymbol{K}_c = \boldsymbol{k}_c = \boldsymbol{C}_1 / \boldsymbol{D}_p^{1/2}
$$

 $\frac{D_p^2 - D_{p_s}^2}{2} = \frac{4D(\Delta c)}{\rho}t$
 $D_{\rho o} \ll D_{\rho}$,
 $D_p = \left(\frac{8D(\Delta c)t}{\rho}\right)^{1/2}$ In this case, the increase in cryst

diameter slows with time

higher solution velocities where k_c still controls,
 $K_c = k_c = C_1/D_p^{1/2}$

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