

# Mass Transfer-I

## Crystallization (Continue...)



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## Crystallization (Continue...)

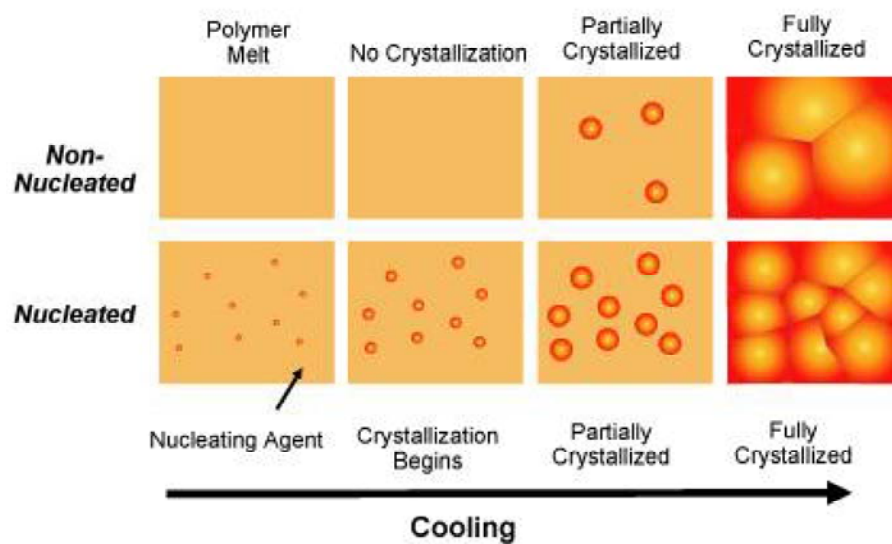
## Nucleation

- Crystallisation starts with Nucleation
- There are two types of nucleation – Primary and Secondary
- Primary relates to the birth of the crystal, where a few tens of molecules come together to start some form of ordered structure
- Secondary nucleation can only happen if there are some crystals present already. It can occur at a lower level of supersaturation than primary nucleation.
- Often, industrial crystallisers jump straight to secondary nucleation by 'seeding' the crystalliser with crystals prepared earlier

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## Cont...



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## Cont...

The factors which influence nucleation are,

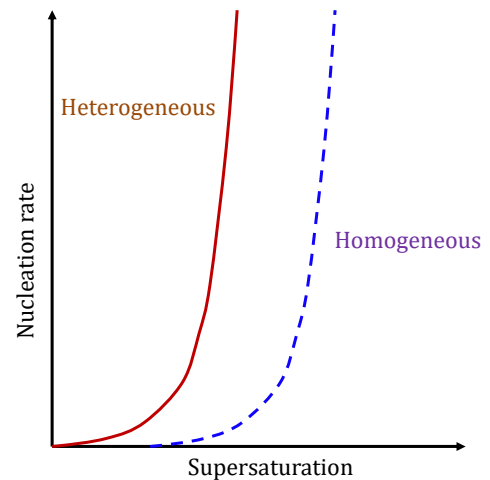
- (i) super-saturation
- (ii) it is stimulated by an input of mechanical energy—by the action of agitators and pumps
- (iii) the presence of solid particles—microscopic or macroscopic
- (iv) the effect of particle size

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## Primary Nucleation

- The birth of a new crystal is complex and involves the clustering of a few tens of molecules held together by intermolecular forces
- Homogeneous – small amounts of the new phase are formed without any help from outside
- Heterogeneous – nucleation is assisted by suspended particles of a foreign substance or by solid objects such as the wall of the container or a rod immersed in the solution – these objects catalyse the process of nucleation so it occurs at lower levels of supersaturation
- Homogenous conditions are difficult to create so heterogeneous nucleation is more normal in industrial crystallisation (if it is not seeded)



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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

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## Secondary Nucleation

- Secondary nucleation is an alternative path to primary nucleation and occurs when seed crystals are added
- Nucleation occurs at a lower supersaturation than primary when crystals are already present
- Secondary nucleation is due to:
  - Contact nucleation – crystals are created by impact with agitator or vessel wall. Nuclei are created by striking a crystal – the number created is related to the supersaturation and the energy of impact. Can occur at low supersaturation.
  - Shear nucleation – shear stresses in the boundary layer of fluid flow create new crystals/nuclei. Embryos are created and swept away that would have been incorporated into an existing crystal
- Very important in industrial crystallisers as this is the main type of crystal growth used
- Difficult to predict or model nucleation rates

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## Cont...

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

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

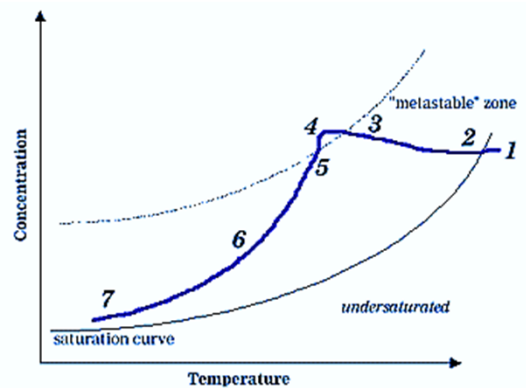
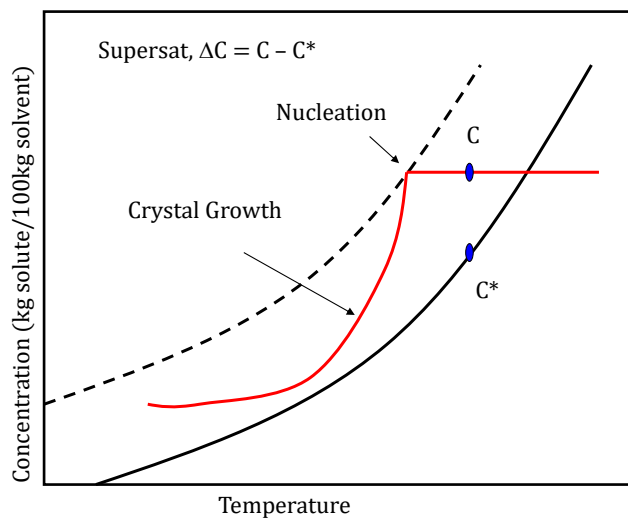
$B$  : rate of secondary nucleation  
 $M_T$  : mass of crystals per volume of magma  
 $N$  : agitation rate (e.g., rpm of an impeller)

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

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## Cont...

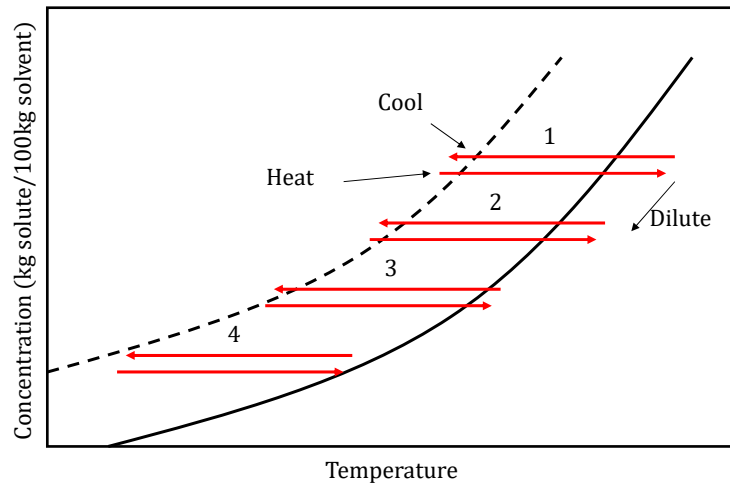


- 1 Feed location, undersaturated
- 2 Solution cools to saturation
- 3 Enter "metastable" zone, nucleation begins
- 4 Rapid nucleation
- 5 Concentration decreases with crystal growth
- 6 Crystal growth during main cooling cycle
- 7 Exit location, supersaturated

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## Determination of Metastable zone width (MSZW)



- MSZW is a function of kinetics (wider for faster cooling)

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## Crystal Growth

- Once nucleation has occurred crystal growth can happen
- The objective of crystallisation is to produce the required crystal size distribution (CSD)
- The actual CSD required depends on the process
- Crystal growth rate has proved difficult to model and empirical relationships developed from laboratory tests are generally used
- Two steps to crystal growth
  - Diffusion of solute from bulk solution to the crystal surface
  - Deposition of solute and integration into crystal lattice

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## Cont...

- 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

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<https://www.cheric.org/files/education/cyberlecture/d201501/d201501-1601.pdf>

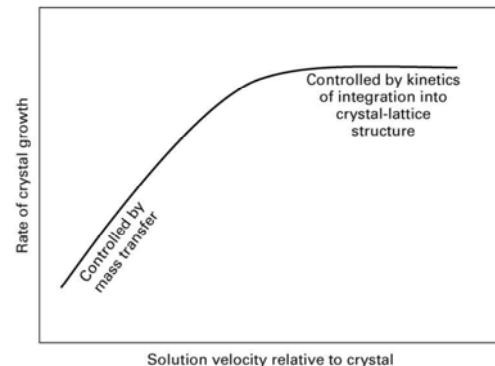
## Cont...

- 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)

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

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

- 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



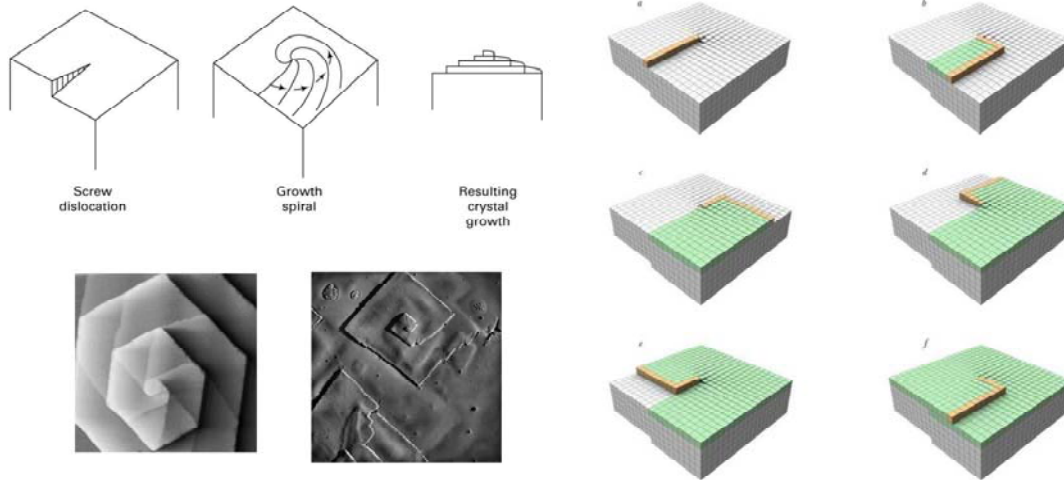
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<https://www.cheric.org/files/education/cyberlecture/d201501/d201501-1601.pdf>

## 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



<https://www.cheric.org/files/education/cyberlecture/d201501/d201501-1601.pdf>

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## Cont...

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

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

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

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

$$\frac{\Delta D_p}{\Delta t} = \frac{2k_i (\Delta c)}{\rho}$$

Crystal-size increase is linear in time for a constant supersaturation

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

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

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

<https://www.cheric.org/files/education/cyberlecture/d201501/d201501-1601.pdf>

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## Cont...

- Integrating from  $D_{po}$  to  $D_p$

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

- If  $D_{po} \ll D_p$ ,

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

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

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<https://www.cheric.org/files/education/cyberlecture/d201501/d201501-1601.pdf>

## Supersaturation and Crystal Growth

- For low supersaturation primary nucleation is not widespread. Secondary nucleation on existing crystals is more likely. Result is small numbers of large crystals
- For high supersaturation primary nucleation is widespread. This results in many crystals of small size.
- Slow cooling with low supersaturation creates large crystals
- Fast cooling from high supersaturation creates small crystals
- Agitation reduces crystal size by creating more dispersed nucleation
- Rate of cooling can affect purity of product - see handout on slow cooling v rapid cooling

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## Impurities and Crystal Growth

- Impurities can prevent crystal growth
- If concentration of impurities is high enough crystals will not grow
- Should not be an issue in the pharmaceutical industry
- For example, the production of non crystalline sweets such as lollipops (sugar crystals give an unwanted grainy texture)
  - Addition of acid breaks sucrose into fructose and glucose
  - This makes it difficult for sucrose crystals to form because the impurities damage the structure
  - Addition of other sugars creates the same result

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## Seeding

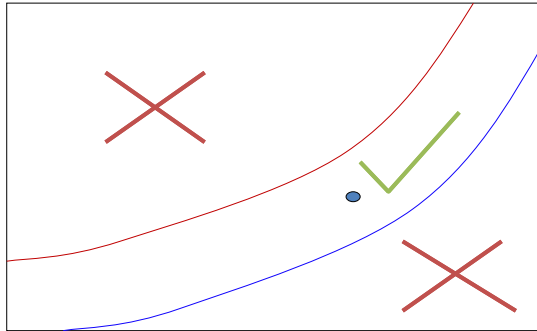
- The type or quality of seed used can influence the crystallisation process
- Good seed results in a good crystallisation, i.e. a particle size distribution that does not include fines
- Bad seed can increase the amount of fines produced
- Good and Bad can be defined by the seed crystal size
- Source of seed can be
  - Material left from the last batch (no tight control on particle size)
  - Specially prepared material or material from a good batch (tight particle size distribution)

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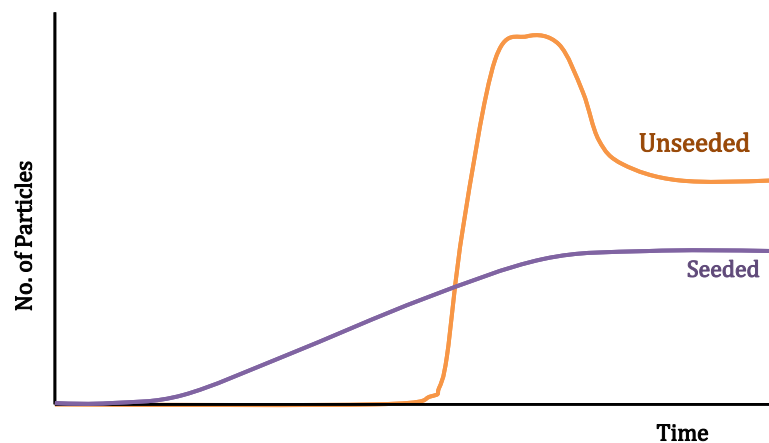
## When to Seed?

- Seed can be added dry to the crystalliser
- Allow time for dispersion throughout the crystalliser – this can take several hours
- Never seed to the right of the solubility curve – the solution is not yet ready
- Never seed to the left of the solubility curve – nucleation is already happening
- Seed half way between the two



## Seeded vs Unseeded

- With unseeded nucleation does not occur till later when supersaturation is higher. High rate of nucleation follows.



## Seeding – advantages, disadvantages

- Advantages include
  - Point of nucleation from batch to batch is repeatable
  - Reduces the number of fines
  - Improves predictability of scale up
  - Can prevent polymorphism
- Disadvantages
  - Experience has shown that not any seed will do, good quality seed is needed
  - Extra addition point on vessel or hand hole is usually opened to manually add seed which could create health and safety issues

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## References



ETH

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Swiss Federal Institute of Technology Zürich

Mass Transfer

Theories for Mass Transfer Coefficients

Lecture 9, 15.11.2017, Dr. K. Wegner

CHEMICAL ENGINEERING AND CHEMICAL PROCESS TECHNOLOGY – Vol. II - Mass Transfer Operations: Absorption  
And Extraction - José Coca, Salvador Ordóñez and Eva DíazMASS TRANSFER OPERATIONS: ABSORPTION AND  
EXTRACTION

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