

Crystal Growth

“Crystal growth is achieved by the slow dehydration of the water of solvation from the sample in a controlled manner that prevents precipitation and takes the sample out of solution and into a crystalline state.”

Crystal growth consists of two steps :

Nucleation and Growth

Solution → Nucleation → Solid State → Crystal or Precipitation

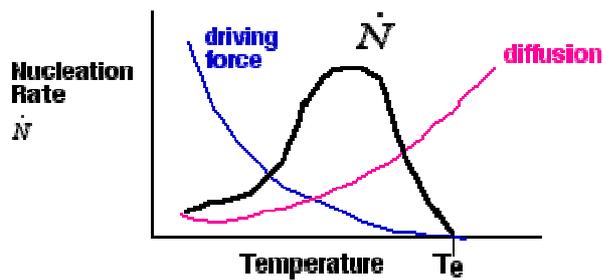
Nucleation, the initial process that occurs in the formation of a crystal from a solution, a liquid, or a vapour, in which a small number of ions, atoms, or molecules become arranged in a pattern characteristic of a crystalline solid, forming a site upon which additional particles are deposited as the crystal grows.

Nucleation processes are classed as heterogeneous or homogeneous. In the former, the surface of some different substance, such as a dust particle or the wall of the container, acts as the centre upon which the first atoms, ions, or molecules of the crystal become properly oriented; in the latter, a few particles come into contact in the course of their random movement through the bulk of the medium. Heterogeneous nucleation is more common, but the homogeneous mechanism becomes more likely as the degree of supersaturation or supercooling increases.

Nucleation depends on:

- liquid phase instability
 - driving force toward equilibrium
 - increases as we move to lower temperatures
- diffusion of atoms into clusters
 - increases at higher temperatures

combine these two terms (multiplication) to determine the total nucleation rate (\dot{N})



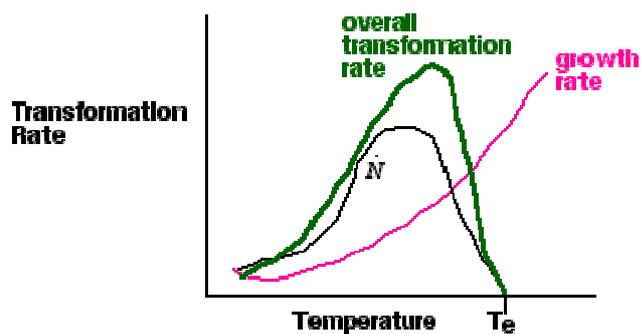
The maximum rate of nucleation is at some $T < T_e$

Growth:

growth of the phase is diffusion controlled => increases with temperature

Transformation rate:

Total rate of forming solid is product of nucleation rate and growth rate



Where T_e is eutectic temperature.

If nucleation rates are slow and growth is rapid large crystals will result.

If nucleation is rapid, relative to growth, small crystals or even polycrystalline samples will result.

For rapid growth rates diffusion coefficients must be large, hence crystal growth typically occurs via formation of a solid from another state of matter:

- (a) Liquid (Melt) to Solid (Freezing)
- (b) Gas (Vapor) to Solid (Condensation)
- (c) Solution to Solid (Precipitation)

Variables that effect crystallization

(i) Precipitants: Ionic compounds (salts)

Organic compounds (Polyethylene Glycol)

(ii) Sample: Concentration, Buffer

(iii) Environment: Temperature, pH, Magnetic fields, Gravity

(iv) Methods: Surface area, Volume

Several techniques are used separately or in combination to induce nucleation of the solid phase at a slow and controlled rate :

(a) Slow Cooling of Melts

(b) Temperature Gradients

(c) Introduction of Seed Crystals

Summary Crystal Growth Methods

(1) Slow Cooling of the Melt

Simple method for growing crystals of congruently melting compounds, when used in conjunction with low melting fluxes can be used to grow crystals at low temperature.

(2) Czochralski Method

Useful for growing large crystals of congruently melting compounds from a seed crystal

(3) Zone Melting

Excellent for producing high quality pure crystals, or purifying crystals grown via another technique.

(4) Chemical Vapor Transport

Useful (primarily research) tool for growing crystals from powders, using a reactive transport gas.

Prepare any one method in detail

Crystal Growth Methods (Detailed)

(1) Slow cooling of the melt

With **congruently melting materials (those which maintain the same composition on melting)** one simply melts a mixture of the desired composition then cools slowly (typically 2-10 °C/hr) through the melting point.

With incongruently melting materials, knowledge of the phase diagram is needed.

Often times the phase diagram is not known, consequently there is no guarantee that crystals will have the intended stoichiometry.

Molten salt fluxes are often used to facilitate crystal growth in systems where melting points are very high and/or incongruent melting occurs.

Crystals grown in this way are often rather small, thus this method is frequently used in research, but usually not appropriate for applications where large xtals are needed.

(2) Czochralski Method

A seed crystal is attached to a rod, which is rotated slowly.

The seed crystal is dipped into a melt held at a temperature slightly above the melting point.

A temperature gradient is set up by cooling the rod and slowly withdrawing it from the melt (the surrounding atmosphere is cooler than the melt)

Decreasing the speed with which the crystal is pulled from the melt, increases the quality of the crystals (fewer defects) but decreases the growth rate.

The advantage of the Czochralski method is that large single crystals can be grown, thus it used extensively in the semiconductor industry.

In general this method is not suitable for incongruently melting compounds, and of course the need for a seed crystal of the same composition limits its use as tool for exploratory synthetic research.

(3) Zone Melting

A polycrystalline specimen is prepared, typically in the shape of a cylinder and placed into a crucible, with a seed crystal near the top of the crucible.

The sample cylinder is placed in a furnace with a very narrow hot zone (sometimes this is done using halogen lamps as heat sources).

The portion of the cylinder containing the seed crystal is heated to the melting point, and the rest of the cylinder is slowly pulled through the hot zone.

Zone melting setups are modifications of either the Bridgman or Stockbarger methods of crystal growth.

Bridgman - Hot zone moves, crucible stationary

Stockbarger - Crucible moves, hot zone stationary

An advantage of the zone melting technique is that impurities tend to be concentrated in the melted portion of the sample. Consequently, this process sweeps them out of the sample and concentrates them at the end of the crystal boule, which is then cut off and discarded. Thus this method is sometimes used to purify semiconductor crystals.

(4) Chemical Vapor Transport

A polycrystalline sample, A, and a transporting species, B, are sealed together inside a tube.

Upon heating the transporting species reacts with the sample to produce a gaseous species AB.

When AB reaches the other end of the tube, which is held at a different temperature, it decomposes and redeposits A.

If formation of AB is endothermic (rxn \leftarrow , as T \downarrow)

A (powder) + B (g) \rightarrow AB (g) (hot end)

AB (g) \rightarrow A (xtal) + B (g) (cold end)

If formation of AB is exothermic (rxn \rightarrow , as T \downarrow)

$A \text{ (powder)} + B \text{ (g)} \rightarrow AB \text{ (g)} \text{ (cold end)}$

$AB \text{ (g)} \rightarrow A \text{ (xtal)} + B \text{ (g)} \text{ (hot end)}$

Typical transporting agents include:

$I_2, Br_2, Cl_2, HCl, NH_4Cl, H_2, H_2O, TeCl_4, AlCl_3, CO, S_2$

Temperature gradient is typically created and controlled using a two-zone furnace.

Tubes are usually SiO_2 , unless reactive, in which case metal tubes (Pt, Au, Nb, Ta, W) are used.

Examples :

$Fe_3O_4 \text{ (s)} + 8HCl \text{ (g)} \rightarrow FeCl_2 \text{ (g)} + FeCl_3 \text{ (g)} + 4H_2O$
(Endothermic)

$ZrNCl \text{ (s)} + 3HCl \text{ (g)} \rightarrow ZrCl_4 \text{ (g)} + NH_3 \text{ (g)}$ (Exothermic)

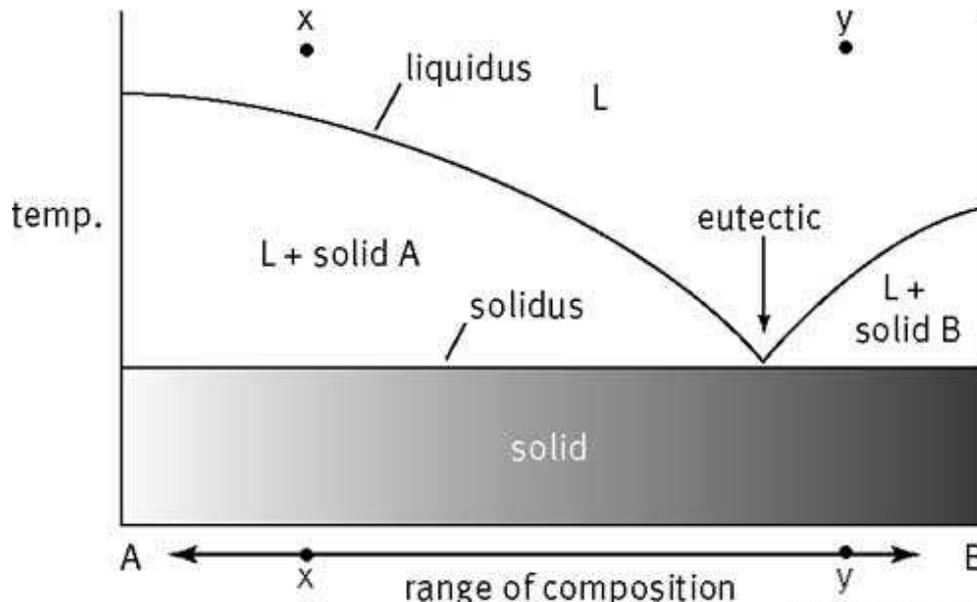
Chemical Vapor Transport is a good method of growing high quality crystals from powders. However, growth rates are usually quite slow (mg/hr) which makes this approach more attractive for research than for industrial applications.

Eutectic Temperature (Read only)

It is the lowest possible temperature of solidification for any mixture of specified constituents, especially of an alloy whose melting point is lower than that of any other alloy composed of the same constituents in different proportions.

At eutectic temp, the proportion of constituents in an alloy or any other mixture yields the lowest possible complete melting point. In all other proportions the mixture will not have a uniform melting point; some of the mixture will remain solid and some liquid.

At the eutectic, the **solidus** and **liquidus** temperatures are the same.



Substance X consists of two components, A and B (approximately 80% A and 20% B).

Above the **liquidus (the temperature at which the first solid begins to form)** both components are liquid.

As the temperature drops to the liquidus, component A starts to solidify, and the remaining liquid becomes less rich in component A and more rich in component B.

When the temperature has dropped to the solidus, which is the same as the eutectic temperature, solid B starts to form as well.

Below the solidus, the entire mixture is solid.

A liquid of composition Y (consisting of approximately 80% B and 20% A) would cool in a similar manner, but with solid B forming first. A mixture of eutectic proportions is always either entirely solid or entirely liquid.