Crystal Growth

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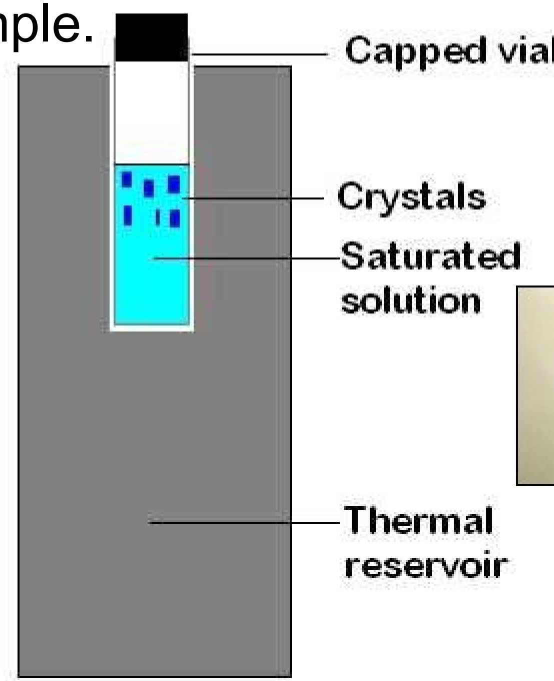
Crystal Growth

Crystallization is the process through which the atoms, molecules or ions arrange themselves in a repeating pattern. There are numerous methods to obtain crystals, any number of which may be applicable to a given compound. While sometimes it may seem that crystallization is more of an art than a science, there are several methods that generally produce crystals. For small molecules, these methods are typically based on reducing the solubility of the sample.

The solubility of most compounds decreases as the temperature is lowered thus the cooling of a saturated solution will often produce crystals. Since rapid cooling may cause the precipitation of amorphous solid or microscopic crystals, it is often wise to surround the flask with an insulating medium to slow the rate of cooling.



Crystal growth by controlled cooling

Controlled cooling

Crystal growth – theory

- Initially form a nucleus

– this is highly dependent upon the presence of

- impurities and vessel surfaces
- Growth of nucleus

– growth depends upon the presence of low

- energy surface sites such as steps

– low energy faces grow fastest

– presence of additives in solution may alter

- relative rates for different faces

Crystal growth – Practice

- Many techniques are available

– choice of method depends upon the material

- Grow from molten solid
- Grow from solution

– this can include solvents as diverse as water and molten PbO!

- Grow from vapor phase

Growth from Solution

- The most common method
- Based on precipitation from a saturated solution
- Saturation can be achieved in many ways

– cool solution

– evaporate solvent off

– add things to solvent to reduce solubility

Basic requirements – solution growth

- Pure materials
- Suitable solvent
- Glasswares
- Perforated cover
- Nylon thread for suspending seed crystals.

Solvent should be…

- High solute solubility
- High positive temperature coefficient of solute solubility
- Low volatility
- Small vapour pressure
- Low viscosity
- Less corrosion and non-toxicity

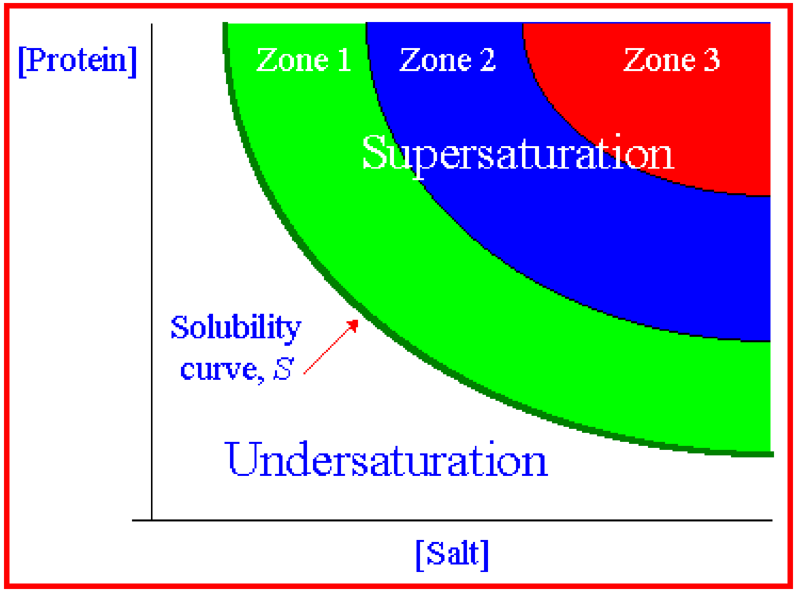
Solubility

- Solubility of the solute – dissolving the solute in the solvent at a const. Temp.

- Solubility of the material decides the amount of the material available for crystal growth

Supersaturation

Supersaturation can be achieved by adding more of a substance (to a solution) than can normally be dissolved. This is a thermodynamically unstable state, achieved most often in protein crystallography by vapor diffusion or other slow evaporation techniques.



Zone 1 - Metastable zone.
The solution may not nucleate for a long time but this zone will sustain growth.
It is frequently necessary to add a seed crystal.

Zone 2 - Nucleation zone.
Protein crystals nucleate and grow.

Zone 3 - Precipitation zone.
Proteins do not nucleate but precipitate out of solution.

Nucleation

A phenomenon whereby a “nucleus”, such as a dust particle, a tiny seed crystal, or commonly in protein crystallography, a small protein aggregate, starts a crystallization process.

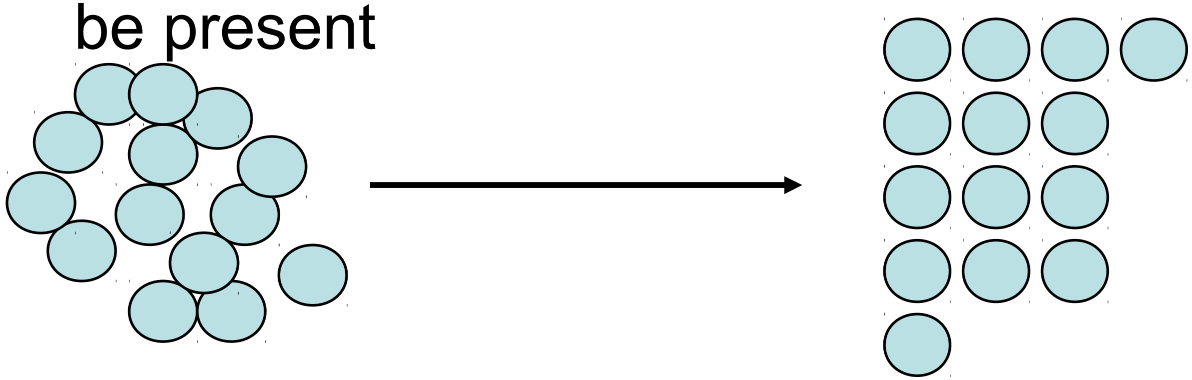
Nucleation poses a large energy barrier, which is easier to overcome at a higher level of supersaturation.

Common difficulties:

1. If supersaturation is too high, too many nuclei form, hence an overabundance of tiny crystals.
2. In supersaturated solutions that don’t experience spontaneous nucleation, crystal growth often only occurs in the presence of added nuclei or “seeds”.

Nucleation and Growth Rates Control R_c

- Nucleation, the first step…
- First process is for microscopic clusters (nuclei) of atoms or ions to form
  - Nuclei possess the beginnings of the structure of the crystal
  - Only limited diffusion is necessary
  - Thermodynamic driving force for crystallization must be present



NUCLEATION

water as example

- initiation of freezing
- formation of small nuclei -center of crystals
- homogeneous or heterogeneous
- homogeneous -water -random accumulation of water molecules
- heterogeneous -small particles present in the solution act as nuclei

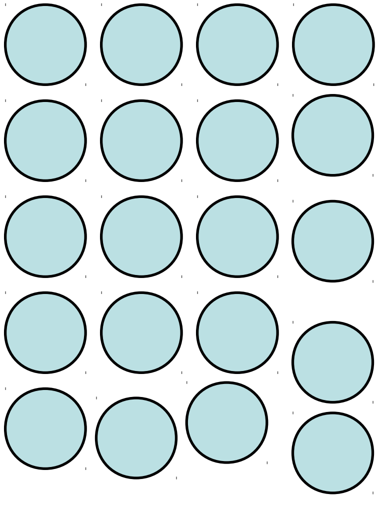
Crystal Growth

water as example

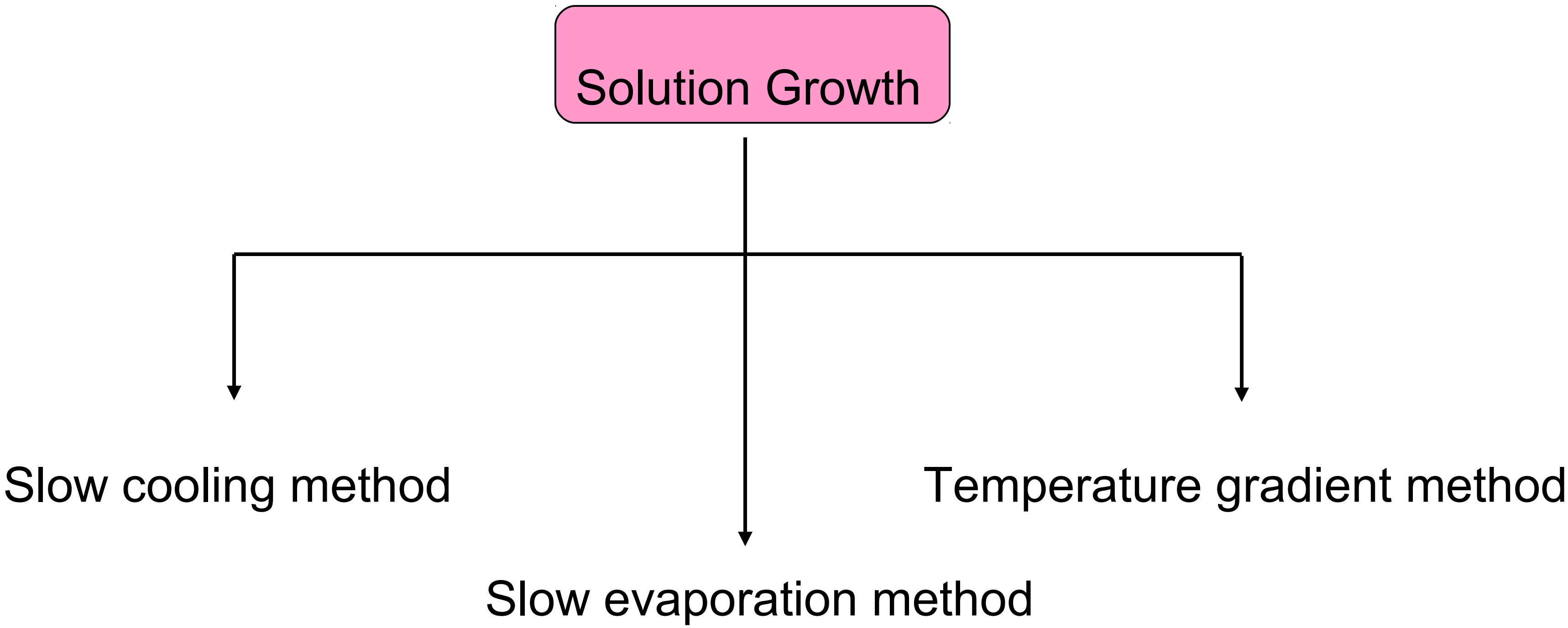
- can only occur after nuclei are formed
- exceed the crystal size
- function of :
  - rate at which the water molecules reacts at the crystal surface
  - diffusion rate of water molecules from the unfrozen solution to the crystal surface
  - rate heat is removed

Growth of crystals from nuclei

- Growth processes then enlarge existing nuclei
- Smallest nuclei often redissolve
- Larger nuclei can get larger
- Thermodynamics favors the
- formation of larger nuclei



Methods of Crystallization – Low temperature solution growth

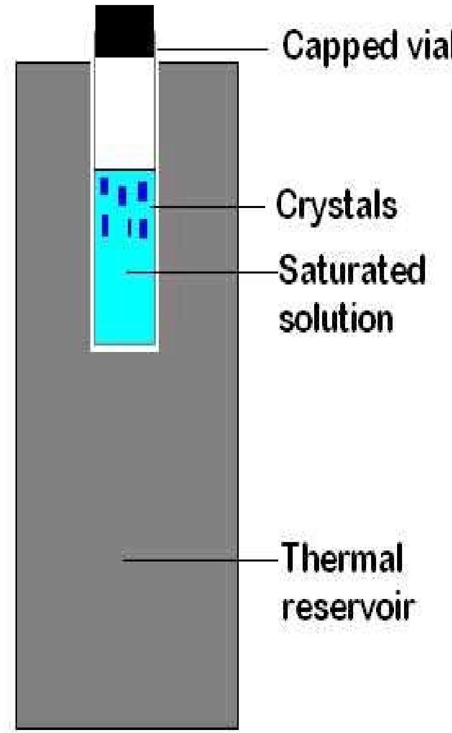


Slow cooling method

- Supersaturated solution
- Systematic cooling
- Solubility – High in higher temperature
  Low in lower temperature
- Reduce the temperature – excess amount of solute (substance) gets crystallized
- 45-75°C

Slow evaporation method

- Supersaturated solution
- Constant temperature
  - Temperature stabilization - ±0.005°C
  - Rates of evaporation – few mm^3/hr
- Solubility – High in large amount of solvent
  Low in small amount of solvent
- Evaporation of solvent – excess amount of solute (substance) gets crystallized



Crystal growth by controlled cooling

Temperature gradient method

- Transport of the materials from hot (Source) to cold region

Advantage

Crystal grows at fixed temperature

Insensitive to changes in temperature

Economy of solvent and solute