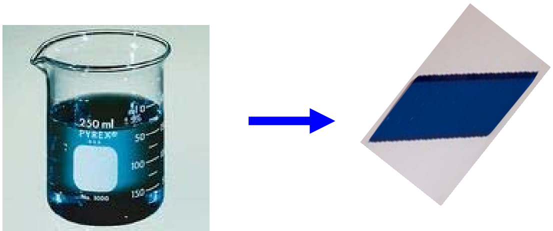
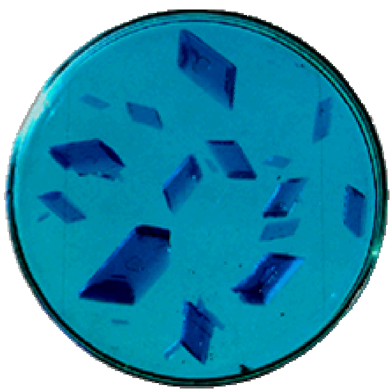
Growth and assessment of single crystals



http://www.nott.ac.uk/~pczajb2/growcrys.htm

Outline

1. Common crystal growth methods from solution
2. Less usual crystal growth methods from solution
3. Other methods of crystal growth
4. Evaluation of crystal quality
5. Crystal mounting



1.

Common crystal growth methods from solution

Aims of crystal growth

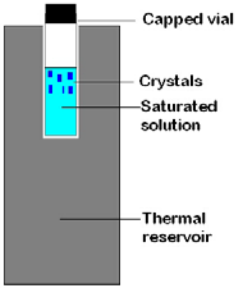
- produce relatively large crystals
- mean dimension *ca*. 0.1 - 0.4 mm
- yield need not be high (*cf*. for purification)
- in general, grow crystals S L O W L Y

Common crystal growth methods from solution

(a) single solvent

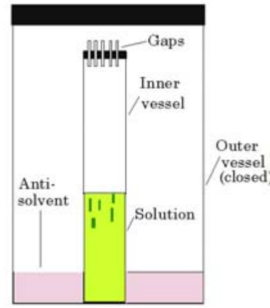
- dissolve solute, reduce volume by evaporation
- use hot solvent and allow to cool
- dissolve then cool solution below RT
- solubility generally decreases with *T*

Crystal growth by controlled cooling



Vapour diffusion = isothermal distillation

- allow vapour of anti-solvent to diffuse into a solution



Common crystal growth methods from solution

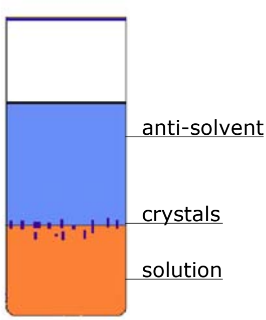
(b) mixed solvent systems

- solvents (“good”) and anti-solvents (“bad”)
- mix solvents to obtain intermediate solubility
- layer anti-solvent on top of solution and allow to mix slowly = layering or solvent diffusion

2.

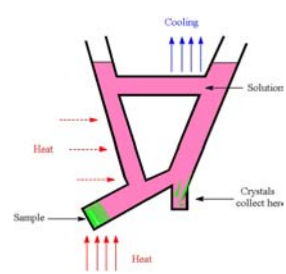
Less usual crystal growth methods from solution

Solvent diffusion

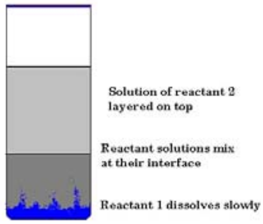


Convection

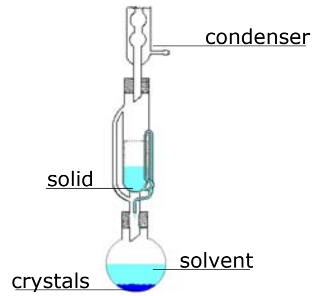
- temperature gradients
- cold surface
- window
- special equipment



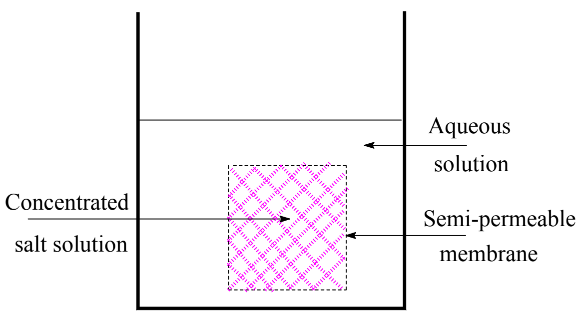
Crystal growth controlled by both dissolution and mixing



Soxhlet extraction



Osmosis



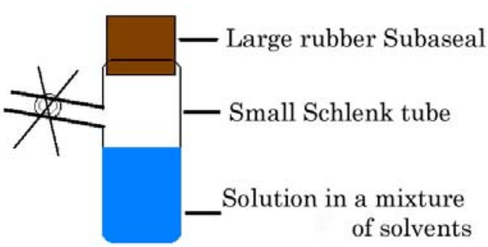
Seed crystals

- good quality crystals, but too small
- use a small number of these as seeds
- use a warm saturated solution of your compound
- allow this to cool
- the seed may grow into a larger single crystal

NMR tubes

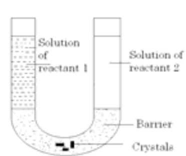
- a clean NMR tube is an excellent environment
- “sealed” but allows very slow evaporation of solvent

Selective removal of a less volatile solvent



Reactant diffusion

- combine synthesis and crystal growth
- slow reaction to avoid small/low-quality crystals
- slow addition of one of the reactants
- control the rate at which reactant solutions mix
- can use a semi-permeable barrier (sinter,liquid,etc)



Crystallisation from gels

- can grow high-quality crystals in microgravity
- avoids sedimentation, convection, rapid mixing
- gels allow this to be achieved terrestrially
- can grow crystals of poorly soluble compounds
- mostly used with aqueous systems
- but can condition gels for use with organic solvents

Other methods

(a) sublimation: solid → gas → solid

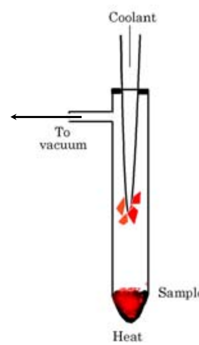
- enough vapour pressure below T(dec)
- normally use heat/low pressure/cold finger
- useful for growing solvent-free crystals

Zeolites and other network structures

- cannot be recrystallised
- must be grown from the reaction mixture
- use fine tuning of the reaction conditions:

proportions of reagents	mixing regime
concentrations of reagents	temperature
atmosphere	template molecule
pressure	reaction time

Sublimation

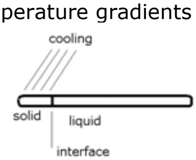


3.

Other methods of crystal growth

Growth from pure liquids and gases

- very small molecules must be cooled
- melts tend to give aggregates on cooling
- involves accurate temperature control
- use of seed crystals
- exploit temperature gradients



- at high temperatures = zone refining techniques

Solid state synthesis

- involves heating two or more solids together
- typically at about 3/4 of the lowest melting point
- may use vacuum, or a reactive or inert atmosphere
- variation of synthetic conditions:

temperature	proportions	atmosphere
pressure	container	flux

- methodology dependent on the system under study
- growth on metal foils exploits grain boundaries
- use of (pre-)reactant to remove oxide film

Optical microscopy

Need:

- a microscope
- a polarising attachment
- up to x40 magnification
- a good depth of field
- a strong light source

4.

Evaluation of crystal quality

Optical microscopy

STEP ONE:

- look at the crystals in normal light
- do they have reasonable shapes?
- reject ones which are curved, deformed,
  non-singular or have re-entrant angles
- the adequate size will depend on chemical content
  $0.1 \times 0.1 \times 0.1$ mm^3 may too small for organics
  but ideal for an osmium cluster

Evaluation

- are crystals suitable for data collection?
- need a rapid assessment procedure
- can save large amounts of (diffractometer) time
- but make sure not to damage your crystals
- apply all the tests *optimistically*
- only clearly unsuitable crystals should be rejected
- always give crystals the benefit of the doubt

Optical microscopy

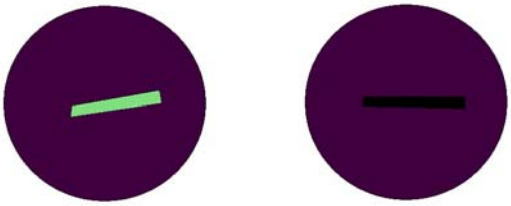
STEP TWO:

- with the analyser in …
- most crystals will transmit polarised light
- exceptions for some high-symmetry crystals

STEP THREE:

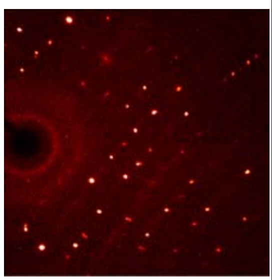
- if a crystal transmits polarised light, turn the stage
- the crystal turns dark then light again (every 90^o)
- this extinction indicates crystal quality
- it must be complete through the crystal, and sharp

Optical extinction



Diffractometry

Ultimate test of crystal quality



Reflections must

- be of adequate intensity
- have a good shape
  - not split or streaked
- form a rational lattice
- index to give a unit cell

5.

Crystal mounting

Crystal mounting

For stable crystals:

- glue crystal securely onto a glass or quartz fibre
- glue this fibre into a metal pip
- insert the pip into the well of a goniometer head
- place the goniometer head on the diffractometer

- for small crystals, use a two-stage fibre
- in all cases crystal movement must be avoided

Crystal mounting

For less stable crystals:

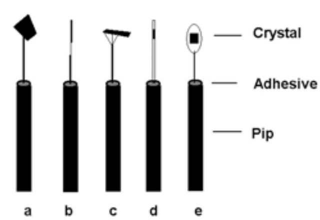
seal crystals into glass capillary

coat with inert adhesive

better to use inert oil and low temperature

- transfer crystal into the oil (e.g., from Schlenk)
- examine crystal under the oil
- transfer lightly coated crystal to fibre
- flash cool crystal/oil on diffractometer
- oil hardens, protects and attaches crystal
- now well established and routine

Crystal mounting



Some ways to mount crystals: a) on a glass fibre; b) on a "two-stage" fibre; c) on a fibre topped with several lengths of glass wool; d) within a capillary tube; e) in a solvent loop.

Crystal growing hints and tips

- Peter G. Jones, *Chemistry in Britain*, 1981, 222-225
- H.E. Buckley, "Crystal Growth", Wiley (London), 1951
- T. Köttke & D. Stalke, *J. Appl. Cryst.* 1993, **26**, 615
- Almost any text on crystal structure determination
- The related chemical literature

http://laue.chem.ncsu.edu/web/GrowXtal.html

http://www.cryst.chem.uu.nl/lutz/growing/gel.html

http://www.geocities.com/shajan89/gel1.htm

http://www.cryst.chem.uu.nl/lutz/growing/reading.html

http://www.cryst.chem.uu.nl/growing.html

http://www.nott.ac.uk/~pczajb2/growcrys.htm