Naica Cave, Mexico
5 My, 50 °C

$CaSO_4 \cdot 2H_2O$

1.2 × 15 m

Growth of Single Crystals

High temperature methods

Czochralski
Stockbarger and Bridgman
Verneuil
Zone melting

Medium temperature methods

Fluxes, Ionic Liquids
Electrochemical from melts
Hydrothermal
Vapor phase transfer
Sublimation

Low temperature methods

Solution
Gel

Growth of Single Crystals

Crystallization techniques: vapor, liquid, solid phase

Single crystals

- **vital for meaningful property measurements of materials**

- **allow measurement of anisotropic phenomena (electrical, optical, magnetic, mechanical, thermal) in anisotropic crystals (symmetry lower than cubic)**

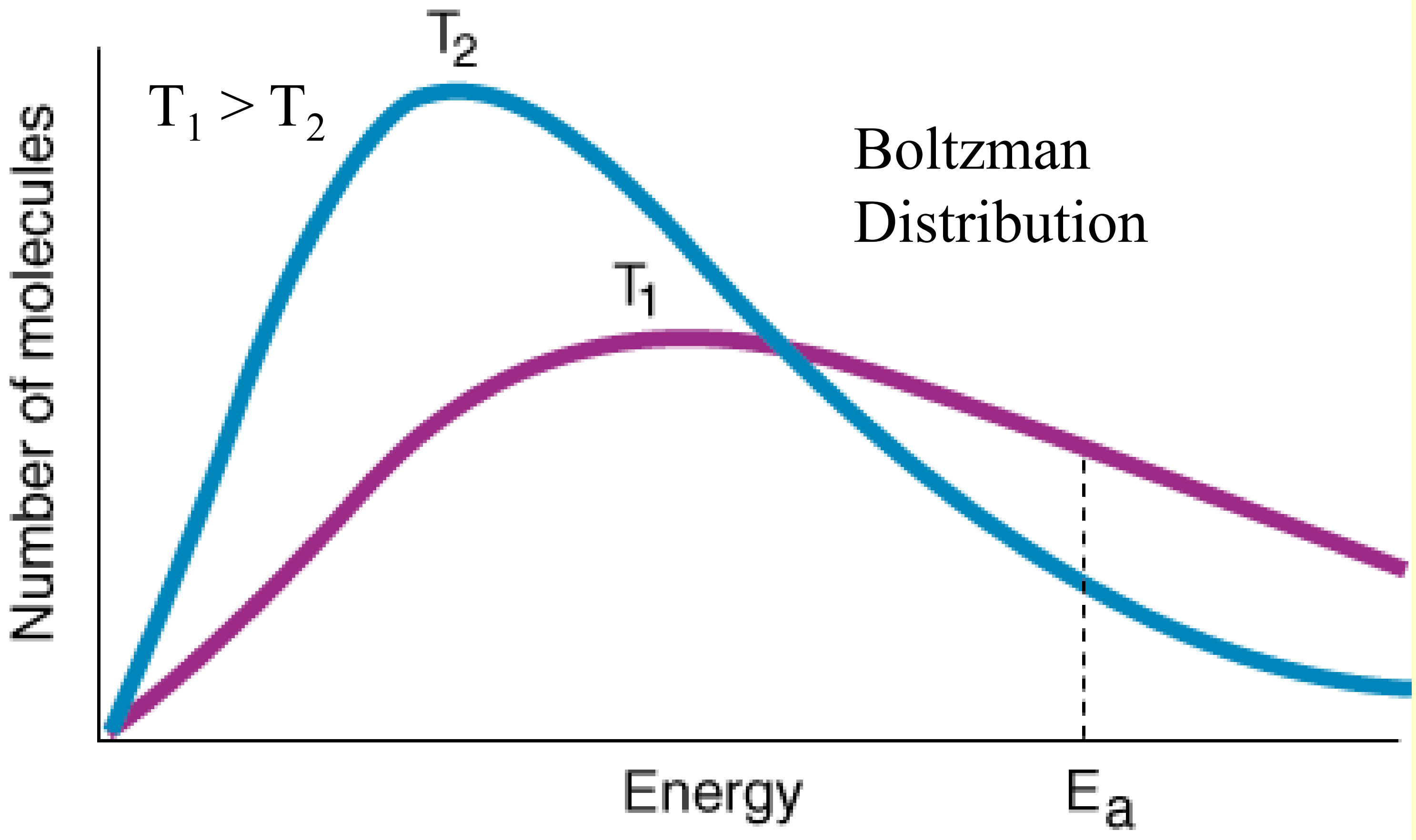
- **fabrication of devices**

$Y_3Al_5O_{12}$ (YAG = yttrium aluminum garnet) and beta-beryllium borate (BBO) for doubling and tripling the frequency of CW or pulsed laser light
SiO_2 (quartz) crystal oscillators for mass monitors
lithium niobate for photorefractive applications

Many different crystal growing techniques exist, hence one must think very carefully as to which method is the most appropriate for the material under consideration, size of crystal desired, stability in air, morphology or crystal habit required

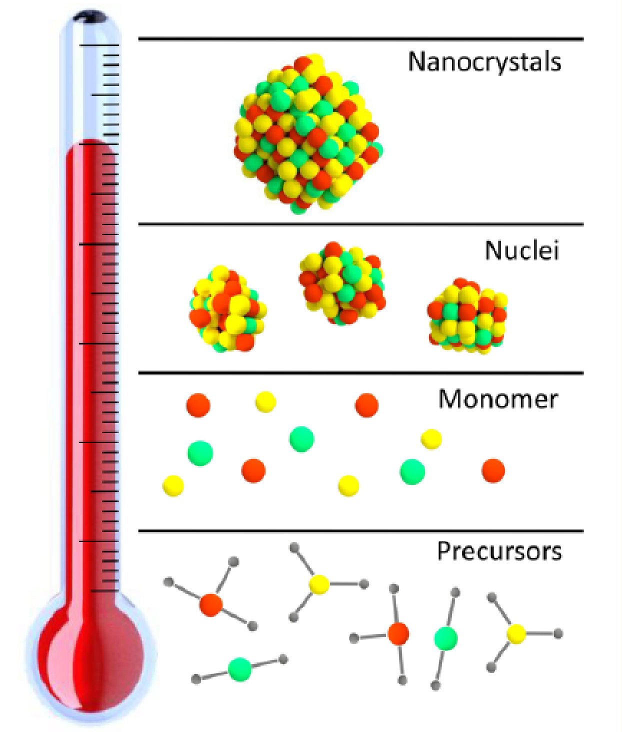
Thermodynamics and Kinetics of Crystallization

As a material cools off the average kinetic energy drops



Stages of Crystallization

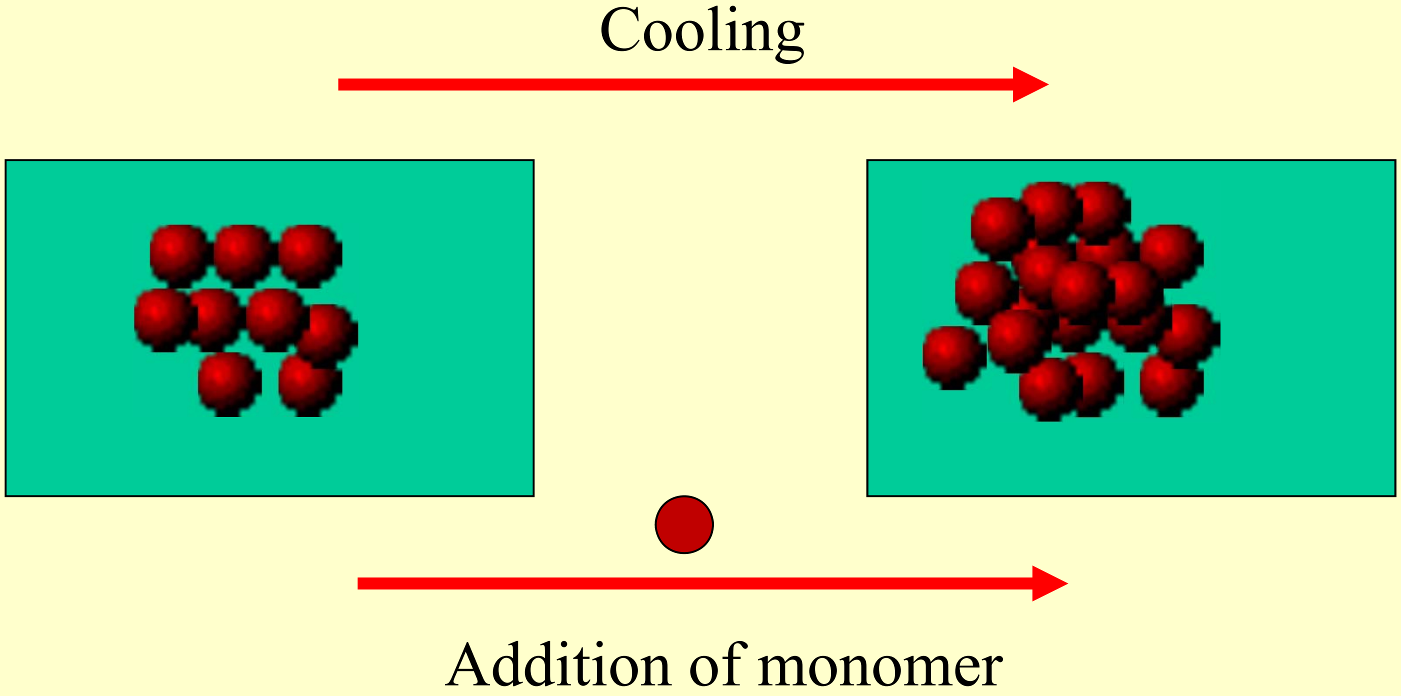
- **Nucleation – formation of nuclei of critical size**
- **Growth – diffusion of material toward the critical nuclei, depositon vs. dissolution, crystal growth**



Formation of Nuclei

Molecules are always bumping into each other – sometimes they stick

At lower kinetic energies more molecules stick together = form nuclei



Cooling

Addition of monomer

Transformation from Liquid to Solid

VOLUME

The energy of a crystalline phase is less than that of a liquid

The difference = the volume free energy ΔG_v (a negative value)

As the solid grows in size, the magnitude of the total volume free energy increases

The volume free energy ΔG_v drives crystallization

SURFACE

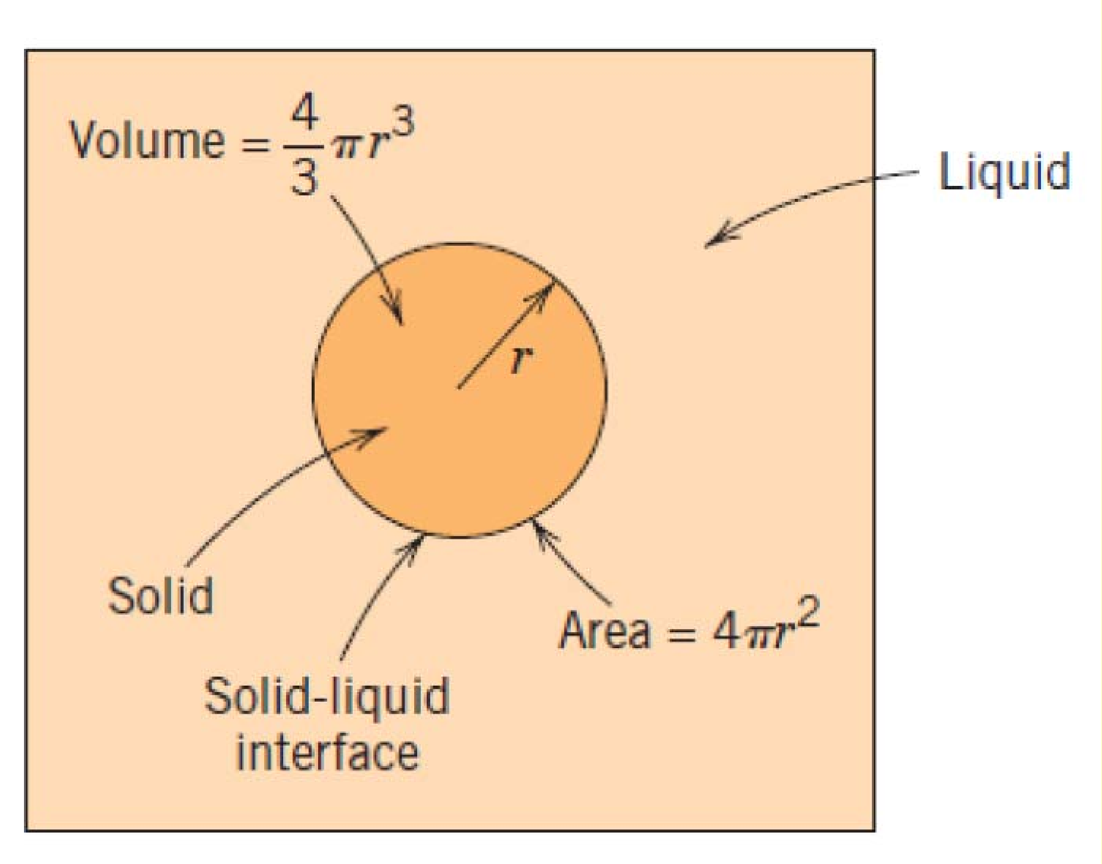
When solids form in a liquid there is an interface created

The surface free energy, γ_{SL} = the solid/liquid interfacial energy associated with this interface (changed in different solvents)

As the solid grows, the total surface free energy increases (a positive value)

The surface free energy hinders crystallization

Transformation from Liquid to Solid



Thermodynamics of Nucleation

The driving force = the supersaturated solution is not stable in energy.
The total change in free energy for the nucleating system is the sum of the two factors.
For spherical nuclei

$$\Delta G_T = \frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma_{SL}$$

The volume free energy goes up with the cube of the radius

The surface free energy goes up with the square of the radius

ΔG_T has a maximum at a critical radius – critical free energy ΔG_N

If just a few molecules stick together, they will redissolve
If enough molecules stick together, the embryo will grow

Volume Free Energy

$$\Delta G_V = -\frac{RT \ln S}{V_m}$$

ΔG_V – the free energy change between the ‘monomer’ in solution and in a unit volume of bulk crystal

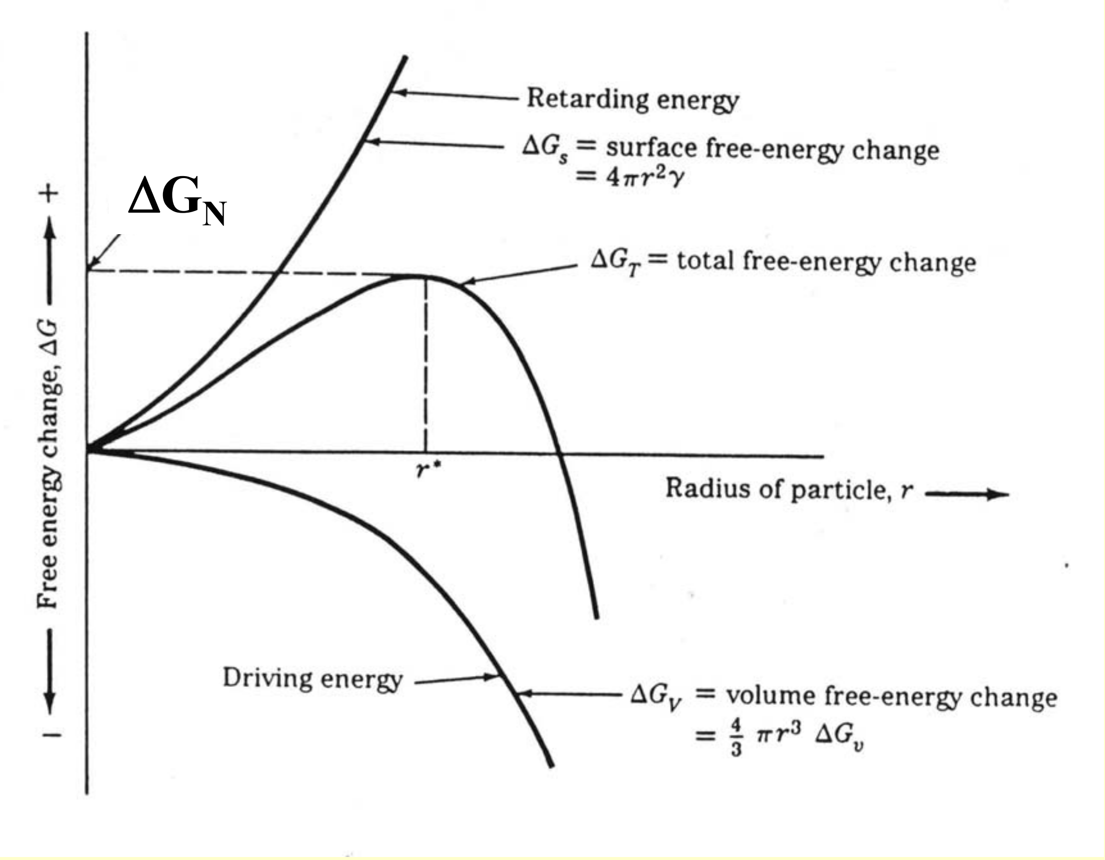
S – supersaturation = the quotient of the actual concentration [M] and the concentration of the respective species at equilibrium with the flat crystal surface $[M_\propto]$, indicates how far away from equilibrium the system is:

$$S = \frac{[M]}{[M_\infty]}$$

V_m – molar volume of the monomer composing the bulk crystal

Nucleation

ΔG



r: radius of spherical nuclei

r*: critical radius

(r>r* seed grows by itself)

ΔG_T: total free energy change

ΔG_s: surface free energy change

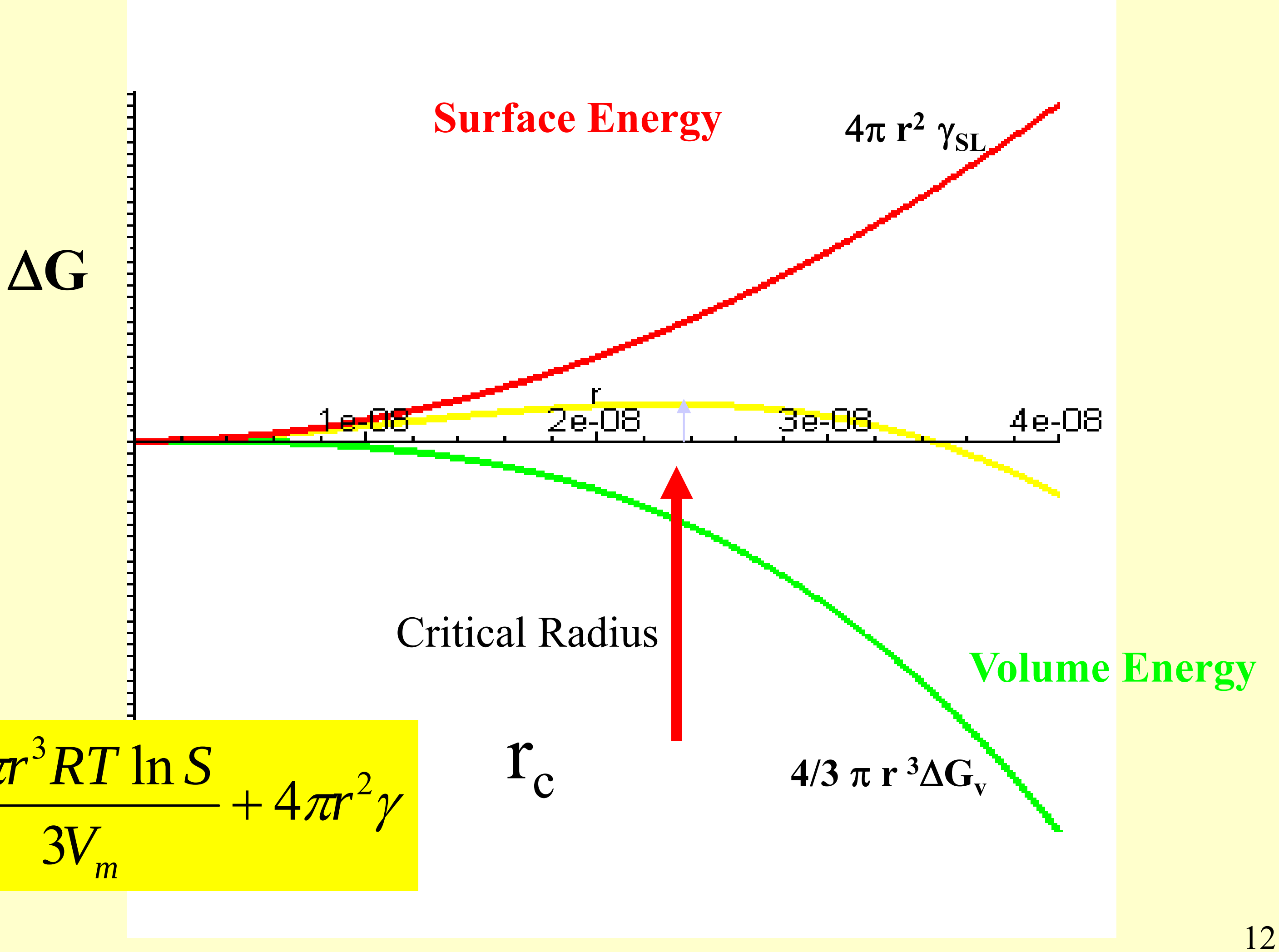
ΔG_v: volume free energy change

ΔG_N: critical free energy change

(activation energy to nucleation)

$$\Delta G_T = 4\pi r^2\gamma_{SL} + 4/3\pi r^3\Delta G_V$$

Total Free Energy of a Solid-Liquid System



$$\Delta G_T = -\frac{4\pi r^3 RT \ln S}{3V_m} + 4\pi r^2 \gamma$$

Supersaturated Solutions

If the liquid is just at the freezing point, only a few molecules stick, because they have comparatively high energy.

As the liquid is cooled, more molecules can form into nuclei.

When the nucleus is big enough (because of undercooling) the supercooled liquid suddenly changes to a solid.

Nucleation - Critical Radius r_c

$$\Delta G_T = -\frac{4\pi r^3 RT \ln S}{3V_m} + 4\pi r^2 \gamma \longrightarrow \frac{d(\Delta G_T)}{dr} = 0$$

r_c critical nuclei radius is:

$$r_c = -\frac{2\gamma_{SL}}{\Delta G_V} = \frac{2\gamma_{SL} V_m}{RT \ln S}$$

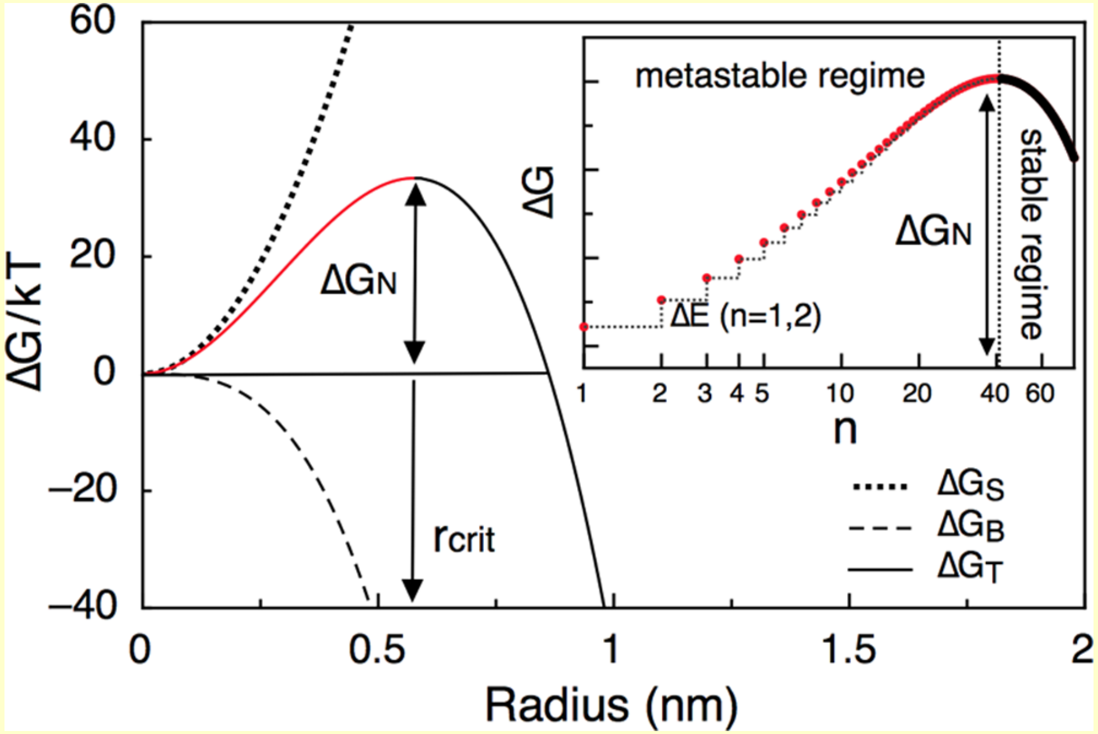
S = supersaturation

At larger supersaturation, the critical radius of nuclei is smaller

Nucleation - Critical Free Energy ΔG_N

$$\Delta G_N = \frac{16\pi\gamma_{SL}^3 V_m^2}{3\left(RT\ln S\right)^2}$$

The free energy necessary to form stable nuclei
Thermodynamic barrier to nucleation



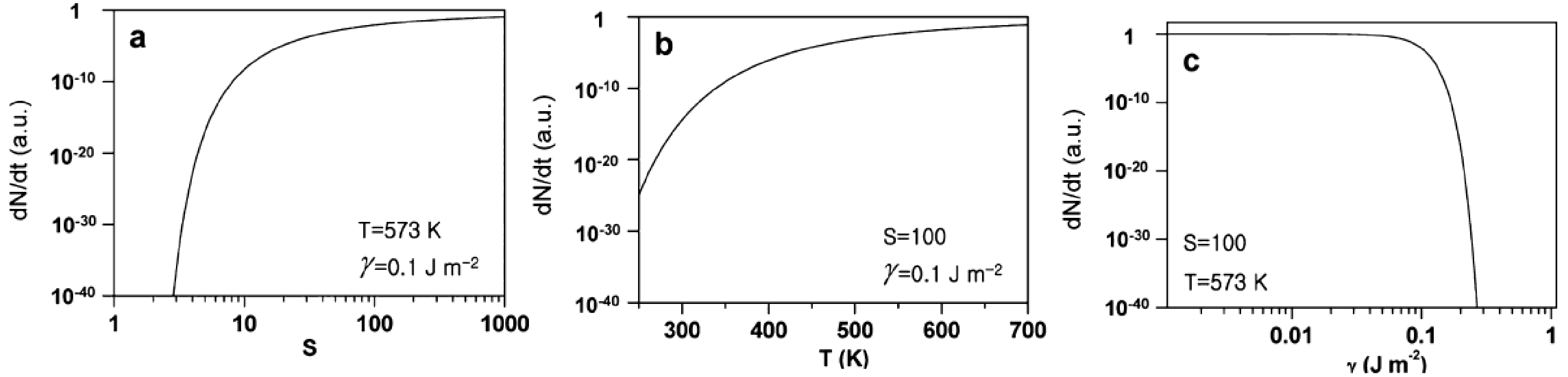
Rate of Nucleation

ΔG_N – the free energy barrier to nucleation
S – supersaturation
V_m – molar volume of the bulk crystal

Arrhenius equation

$$\frac{d[N]}{dt} = A\exp\left(-\frac{\Delta G_N}{kT}\right) = A\exp\left(-\frac{16\pi\gamma_{SL}^3 V_m^2}{3k^3T^3N_A^2(\ln S)^2}\right)$$

Nucleation Rate



$$\frac{d[N]}{dt} = A\exp\left(-\frac{\Delta G_N}{kT}\right) = A\exp\left(-\frac{16\pi\gamma_{SL}^3 V_m^2}{3k^3T^3N_A^2(\ln S)^2}\right)$$

$V_m = 3.29 \times 10^{-5}$ m^3 mol^{-1} (the value for CdSe)

Homogeneous Nucleation

The process of solid formation from liquid phase = homogeneous nucleation

It only occurs if the material is very pure

The size of the critical radius is:

$$r_c = -\frac{2\gamma_{SL}}{\Delta G_V} = \frac{2\gamma_{SL} V_m}{RT \ln S}$$

Metal crystallization from melts

ΔT is the undercooling

Metals often experience undercooling of 50 to 500 ºC

$$r^* = \frac{2\gamma_{SL} T_m}{\Delta H_f \Delta T}$$

Heterogeneous Nucleation

Homogeneous nucleation usually only occurs under very clean conditions

Impurities provide a “seed” for nucleation

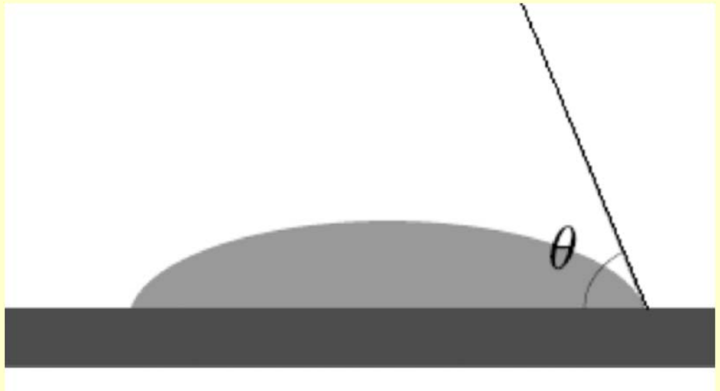
Solidification can start on a wall

It’s like cloud seeding, or water condensing on the side of a glass

Adding impurities on purpose = inoculation

$$\Delta G_N^{hetero} = \phi\, \Delta G_N^{homo}$$

$$\phi = \frac{(2 + \cos\theta)(1 - \cos\theta)^2}{4}$$

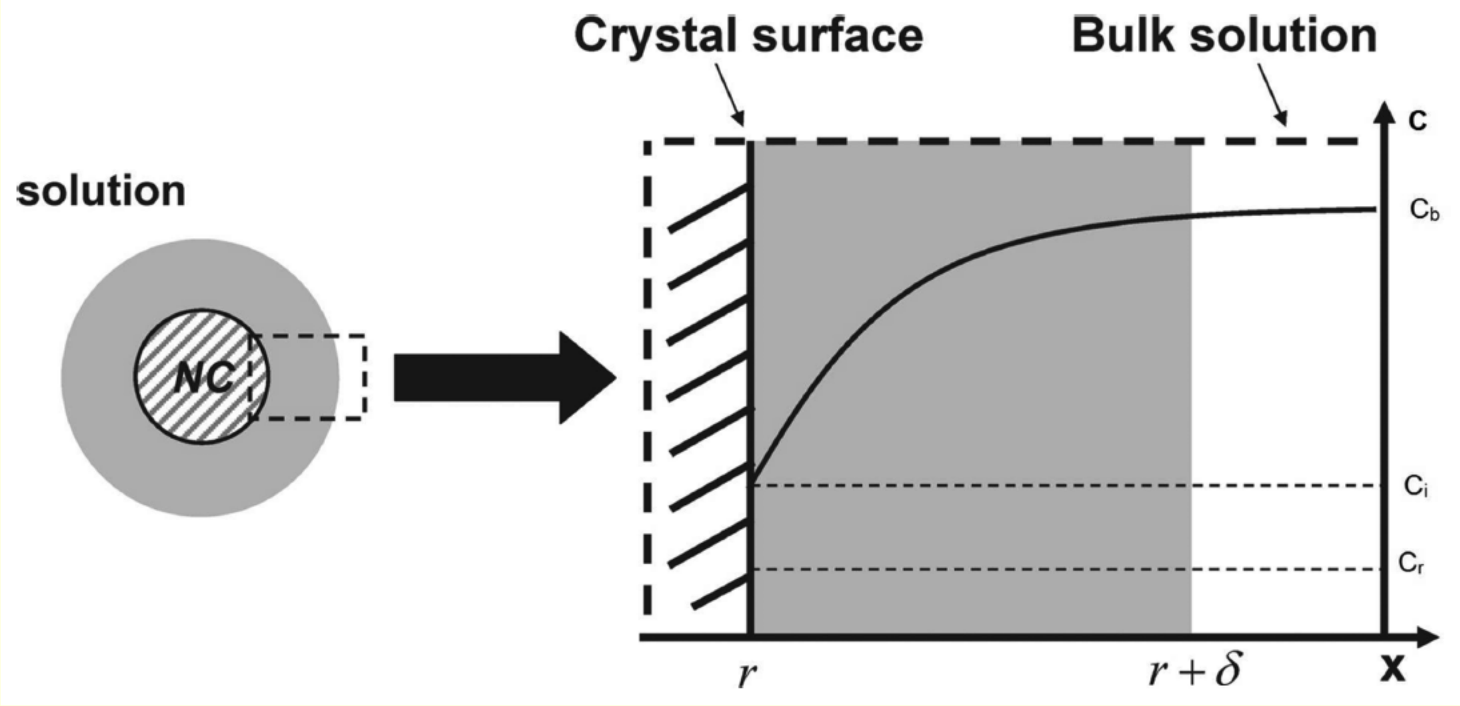


Growth

Growth = monomer diffusion + surface reaction

the growth rate of spherical particles (dr/dt) depends on:

- **the flux of the monomers to the particles (J)**
- **the rate of surface reaction (k)**



Growth

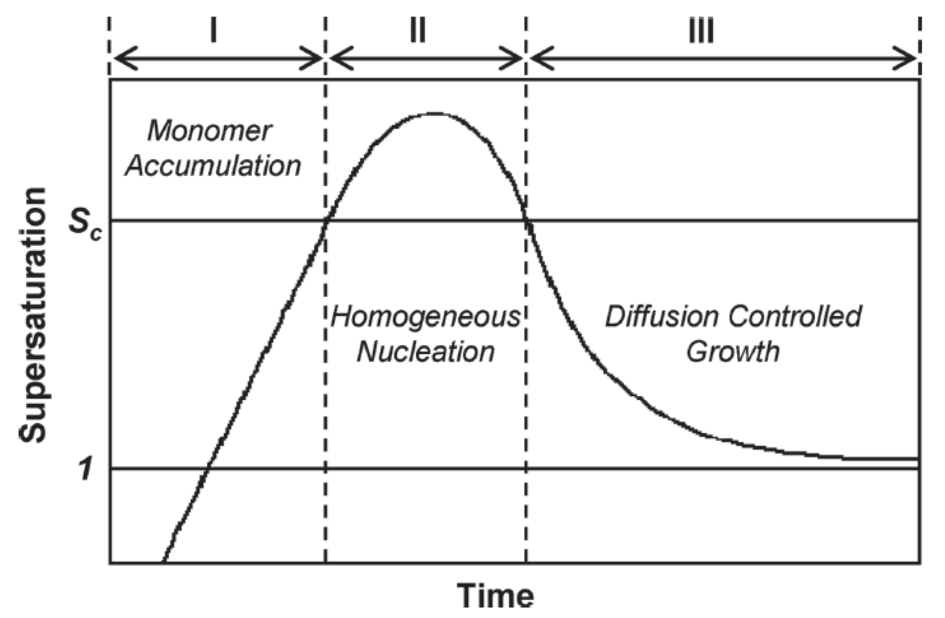
Growth by diffusion
the growth rate of spherical particles (dr/dt)

$$J = \frac{4\pi r^2}{V_m}\frac{dr}{dt} \qquad J = 4\pi x^2 D\frac{dC}{dx}$$

$$\int_{r}^{r+\delta}\frac{dx}{x^2} = \frac{4\pi D}{J}\int_{C_s}^{C_\delta} dC$$

$$J = 4\pi D\frac{r(r+\delta)}{\delta}\left[C_\delta - C_s\right]$$

La Mer Mechanism

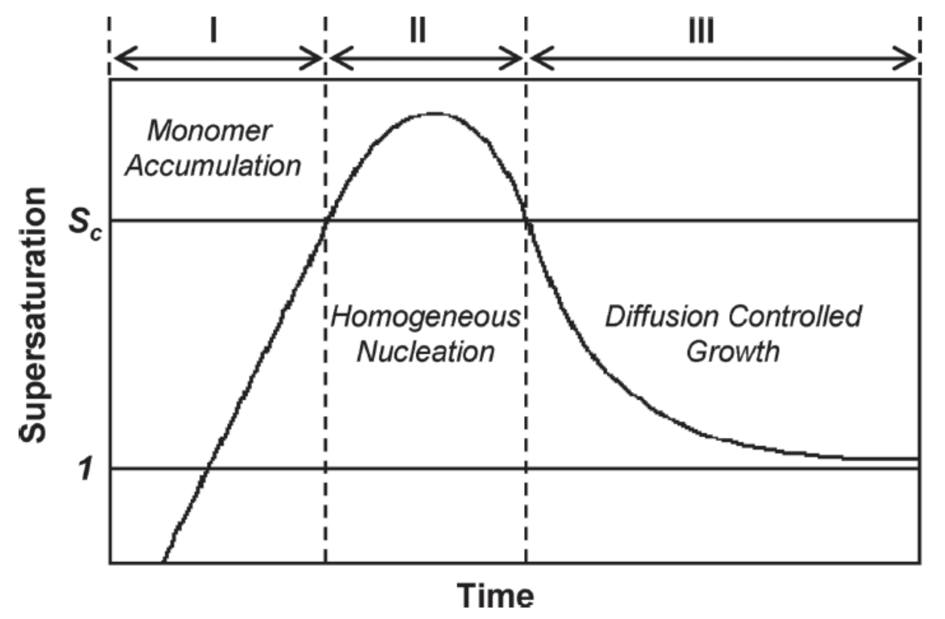


3 Separate stages:

- Monomer formation
- Burst nucleation
- Growth by diffusion

Monomer formation - concentration of monomer increases to a critical value
Burst nucleation - many nuclei are generated at the same time
Growth - the nuclei grow without additional nucleation, all of the particles nucleate simultaneously, their growth histories are the same

Control of the size distribution of the ensemble of particles during growth - synthesis of monodisperse nanocrystals



Stage I - The concentration of "monomer", (the minimum subunit of bulk crystal) constantly increases with time, precipitation does not occur even under supersaturated conditions (S > 1), the energy barrier for spontaneous homogeneous nucleation is too high.

Stage II - Nucleation occurs, the degree of supersaturation is high enough to overcome the energy barrier for nucleation, the formation and accumulation of stable nuclei. The rate of monomer consumption exceeds the rate of monomer supply, the monomer concentration decreases until it reaches the level at which the nucleation rate is zero.

Stage III - The growth stage, nucleation stopped, the particles keep growing as long as the solution is supersaturated by diffusion of monomer towards crystals

Growth and Solidification - Grain Size

Solidification caused by homogeneous nucleation occurs suddenly, and only produces a few grains

In heterogeneous nucleation, solidification occurs on many “seeds”, so the grains are smaller, and more uniform

If a melt is cooled slowly, and the temperature is the same throughout, solidification occurs with equal probability everywhere in the melt.

Metals are usually cooled from the container walls – so solidification starts on the walls

Nucleation vs. Crystal Growth (solution or melt)

Undercooling – cooling below the melting point

relations between undercooling, nucleation rate and growth rate of the nuclei

large undercooling:	**many small nuclei** **(spontaneous nucleation)** **growth rate small**
small undercooling:	**few (evtl. small) nuclei** **growth rate high**

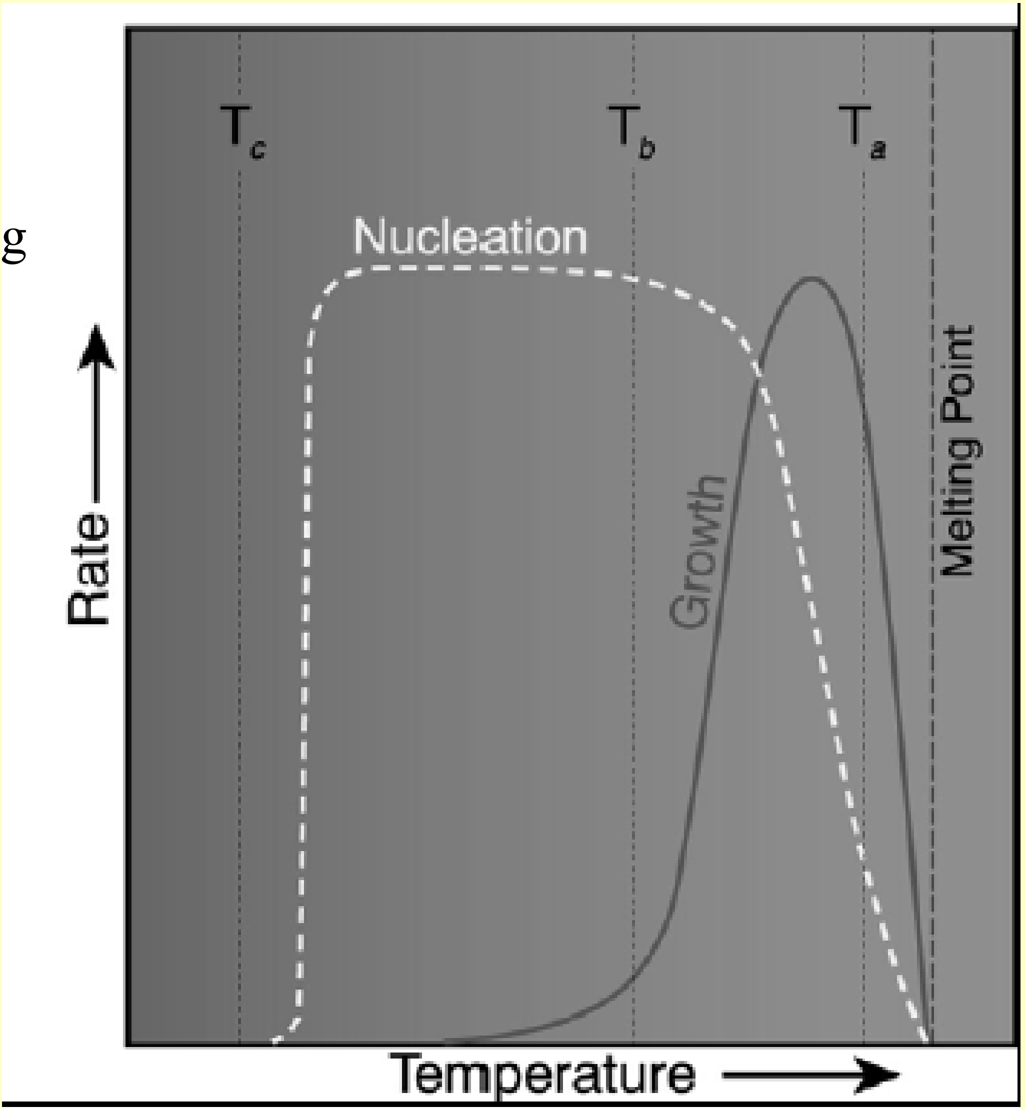
Nucleation vs. Crystal Growth

Rate of nucleation
Rate of growth

T_a = small undercooling, slow cooling rate
Fast growth, slow nucleation = Few coarse crystals

T_b = larger undercooling, rapid cooling rate
Rapid nucleation, slow growth = many fine-grained crystals

T_c = very rapid cooling
Nearly no nucleation = glass



Heat of Fusion

When the liquid solidifies, energy must be removed.

In planar growth the energy is conducted into the solid and out through the walls of the container

If the melt is not well inoculated

Solidification starts on the walls

The surrounding liquid is supercooled, so the solid quickly grows

All heat that is evolved is hard to conduct away

Some of it is absorbed by the surrounding liquid which then heats up

Growth of Single Crystals

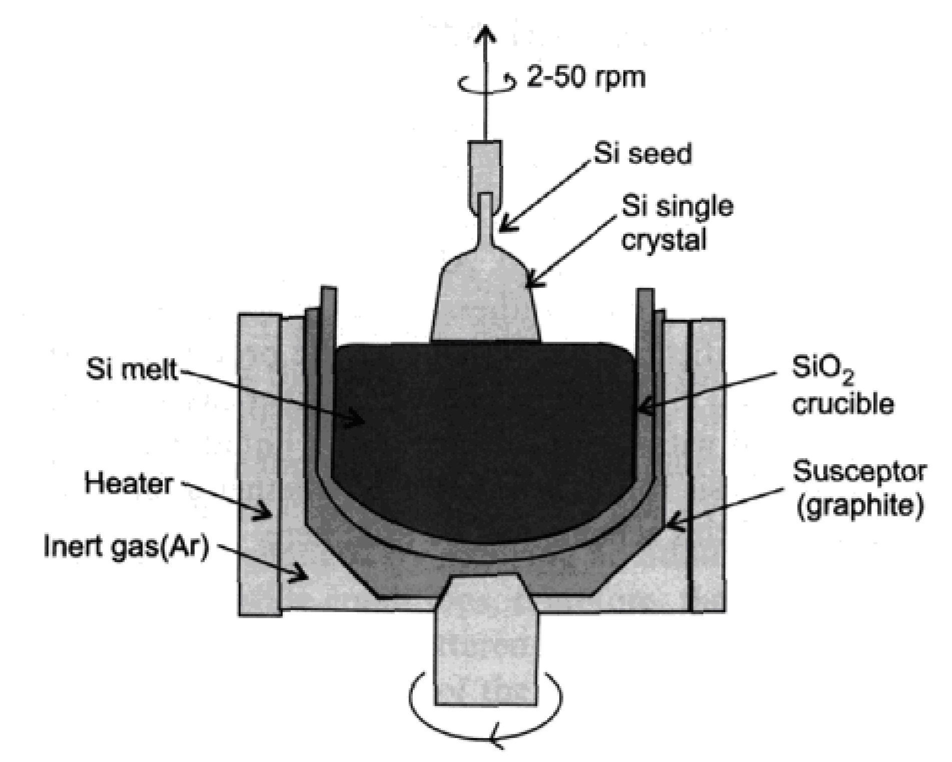
CZOCHRALSKI or KYROPOULOS METHOD

1917
Crystal pulling technique
Single crystal growth from the melt precursor(s)
Crystal seed placed in contact with surface of melt
Temperature of melt held just above melting point = highest viscosity, lowest vapor pressure
Seed gradually pulled out of the melt, 1 mm per hour
Melt solidifies on surface of seed
Melt and seed usually rotated counterclockwise with respect to each other to maintain constant temperature and to facilitate uniformity of the melt during crystal growth, 10 rpm
Produces higher quality crystals, less defects
Inert atmosphere, often under pressure around growing crystal and melt to prevent any materials loss

Jan Czochralski
(1885 – 1953)

Growth of Single Crystals

CZOCHRALSKI or KYROPOULOS METHOD



Diam 300 mm
Length 2 m
Weight 265 kg

Growth of Single Crystals

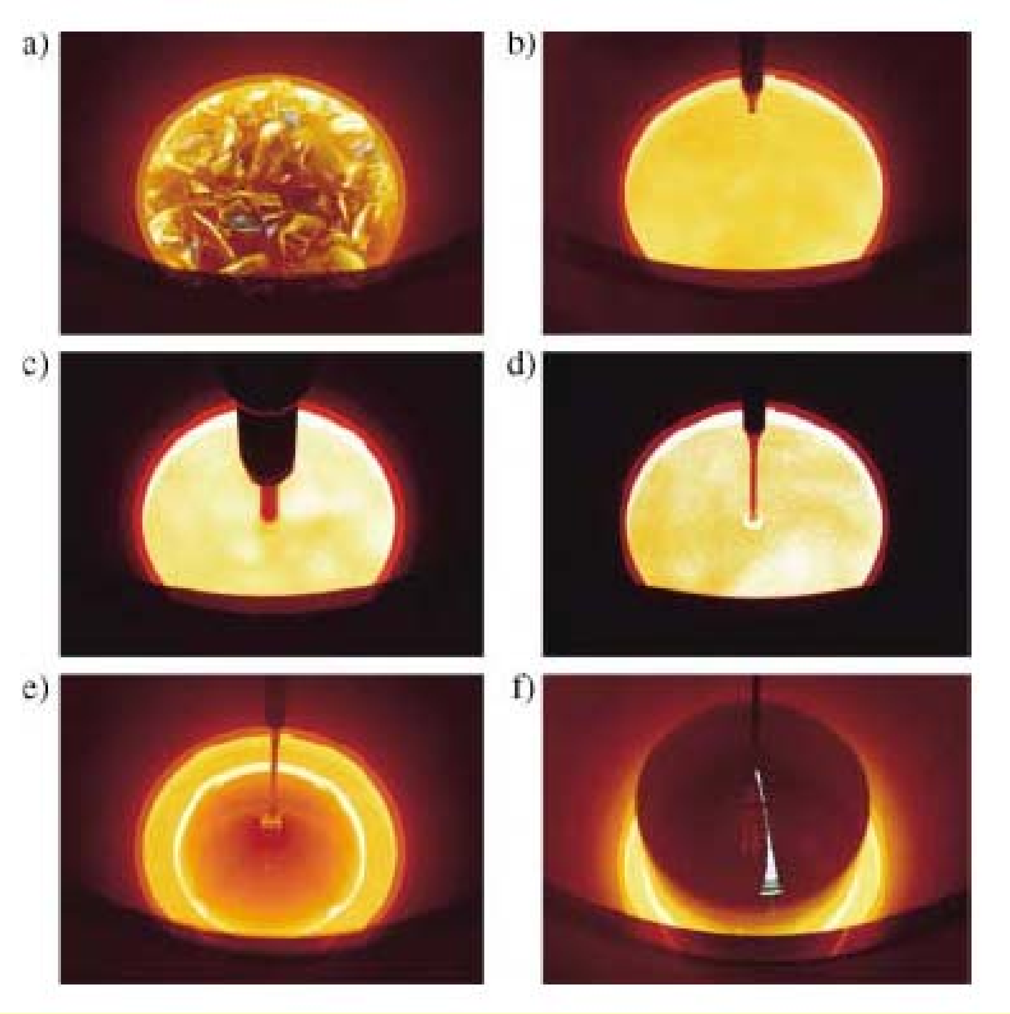
Growing bimetallic crystals like GaAs

Layer of molten inert oxide like B_2O_3 spread on to the molten feed material to prevent preferential volatilization of the more volatile component of the bimetal
critical for maintaining precise stoichiometry
for example $Ga_{1+x}As$ and $GaAs_{1+x}$ which are respectively rich in Ga and As, become p-doped and n-doped

Growth of Single Crystals

The Czochralski crystal pulling technique for growing large single crystals in the form of a rod
subsequently cut and polished for various applications

Si
Ge
GaAs
$LiNbO_3$
$SrTiO_3$
$NdCa(NbO_3)_2$



Six steps in the CZ growth of a silicon single crystal:

a) Evacuation and heating of the polycrystalline silicon (“pumping”)

b) Setting the temperature of the Si melt just above 1414 ºC (“melting”)

c) Dipping the thin Si seed crystal into the homogeneous Si melt (“dipping”)

d) Initiating crystallization at the neck of the thin Si seed (“necking”)

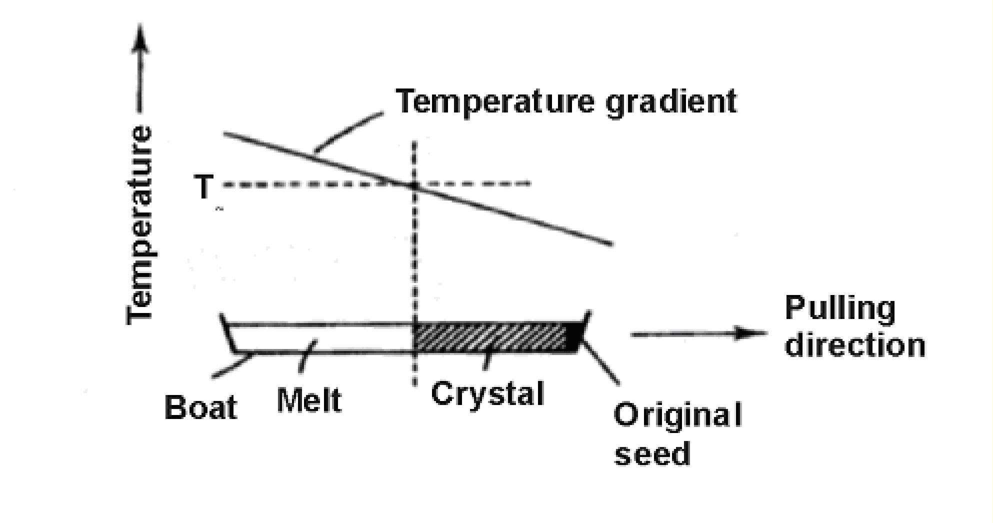
e) Adjustment of the shoulder of the desired single crystal diameter (“shoulder”; four positions which portray the fourfold drawing axis [100] are visible at the hot, light marginal zone of the single crystal)

f) Growing phase of the single crystal with constant diameter (“body”).

Growth of Single Crystals

STOCKBARGER AND BRIDGMAN METHODS

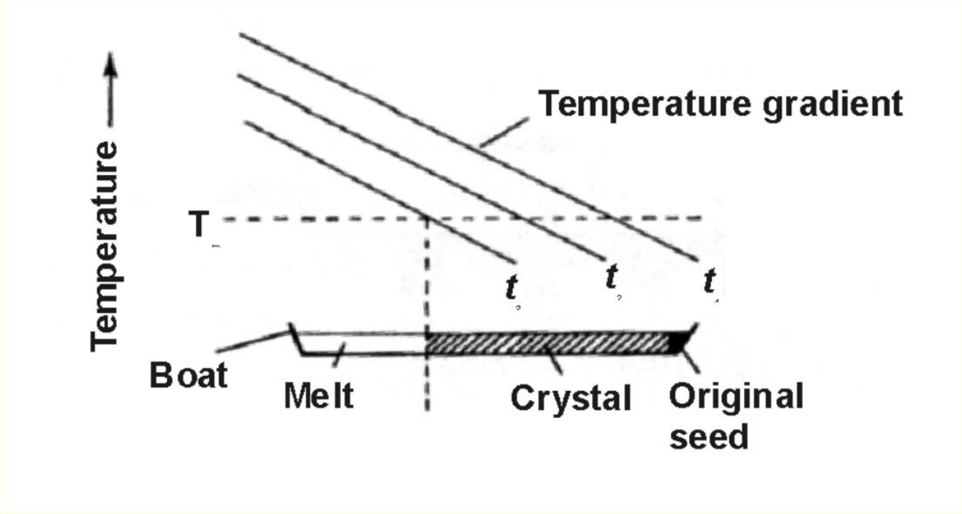
Stockbarger method is based on a crystal growing from the melt, involves the relative displacement of melt and a temperature gradient furnace, fixed gradient and a moving melt/crystal



Growth of Single Crystals

STOCKBARGER AND BRIDGMAN METHODS

Bridgman method is again based on crystal growth from a melt, but now a temperature gradient furnace is gradually cooled and crystallization begins at the cooler end, fixed crystal and changing temperature gradient



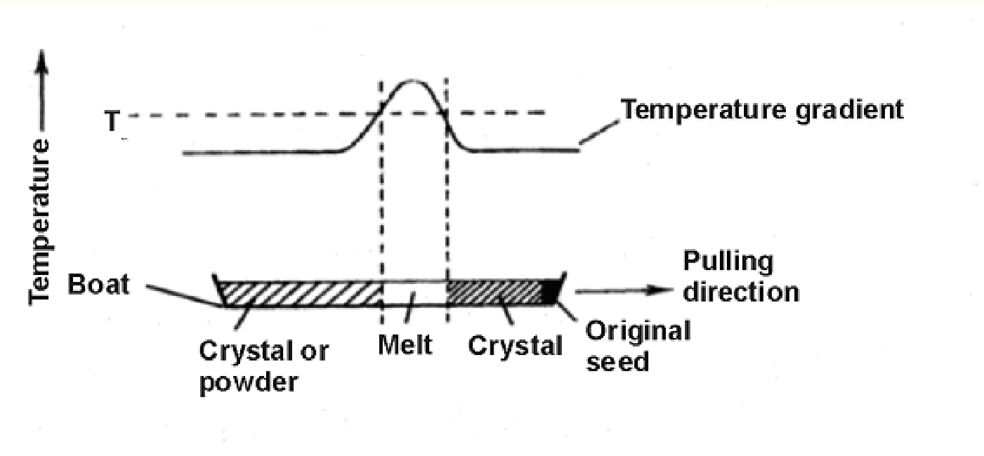
Both methods are founded on the controlled solidification of a stoichiometric melt of the material to be crystallized
Enables oriented solidification
Melt passes through a temperature gradient
Crystallization occurs at the cooler end
Both methods benefit from seed crystals and controlled atmospheres (sealed containers)

crystal	mp (^oC)	velocity of grad.	container material
Al_2O_3	2037	2-8 mm h^{-1}	Mo
$FeAl_2O_4$	1790	5-10	Ir
Cu	1083	6-60	graphite
AgBr	434	1-5	Pyrex
Ar (!)	-189	0.5-1.5	Mylar

Zone Melting

Purification of solids
Crystal growth

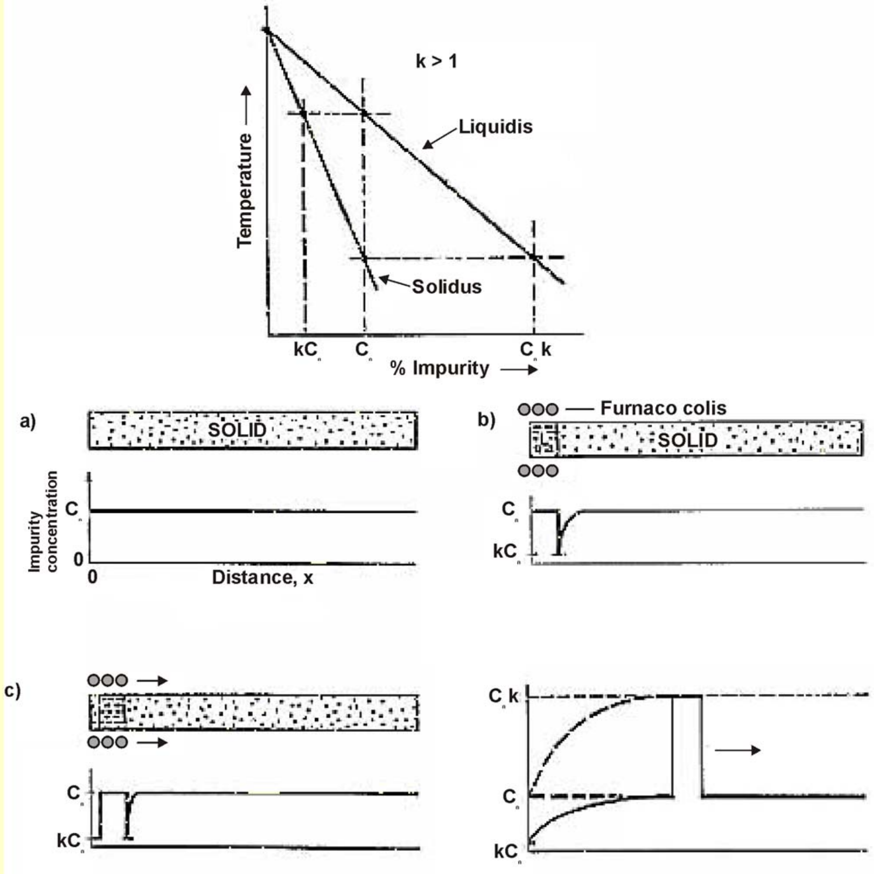
Thermal profile furnace, RF, arc, electron beam heating
Material contained in a boat (must be inert to the melt)
Only a small region of the charge is melted at any one time
Initially part of the melt is in contact with the seed
Boat containing sample pulled at a controlled velocity through the thermal profile furnace - zone of material melted
Oriented solidification of crystal occurs on the seed



Zone Melting

Zone refining methods for purifying solids
Partitioning of impurities occurs between melt and the crystal
Impurities concentrate in liquid more than the solid phase, swept out of crystal by moving the liquid zone

Used for purifying materials like W, Si, Ge to ppb level of impurities, often required for device applications



Zone Melting

- a small slice of the sample is molten and moved continuously along the sample

- impurities normally dissolve preferably in the melt (!! icebergs in salt water don‘t contain any salt !!)

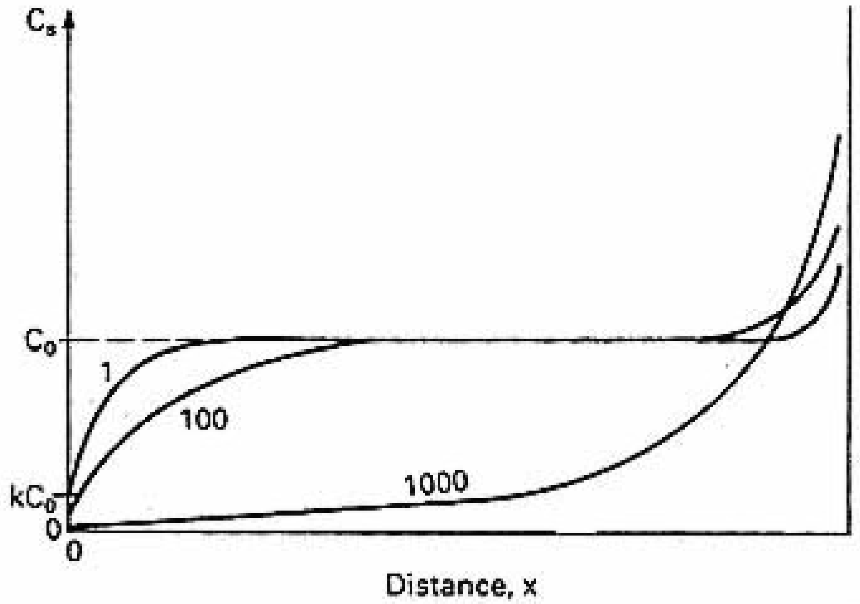
- segregation coefficient k:

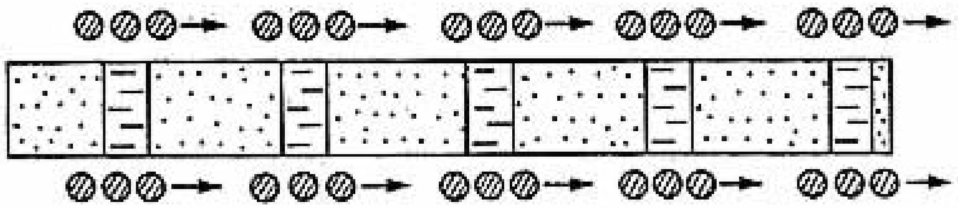
$$k = c_{solid}/c_{liquid}$$

(c: concentration of an impurity)

only impurities with k < 1 can be removed by zone melting !!

Zone Melting



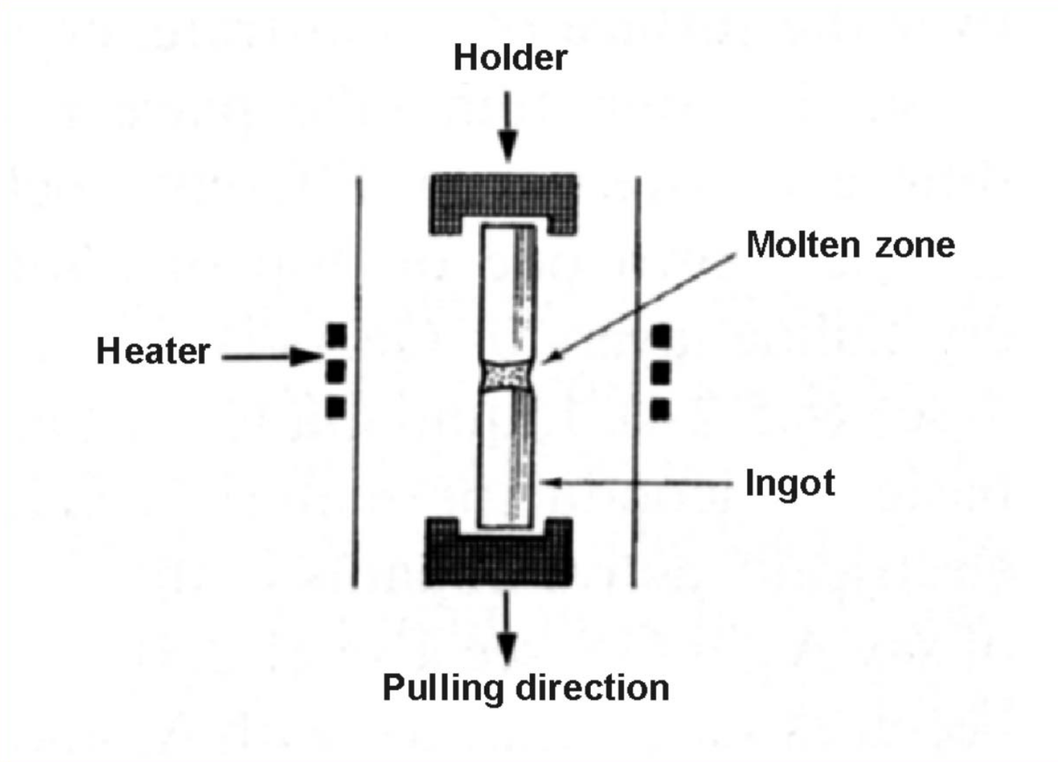


A multi-heater arrangement gives much faster zone refining

Zone Melting

FLOATING ZONE METHOD

Molten zone is confined by surface tension between a polycrystalline ingot and a single-crystal seed



Verneuil Fusion Flame Method

1902 - French chemist Auguste Verneuil

the first commercially successful method of manufacturing synthetic gemstones - ruby, sapphire, diamond simulants rutile and strontium titanate

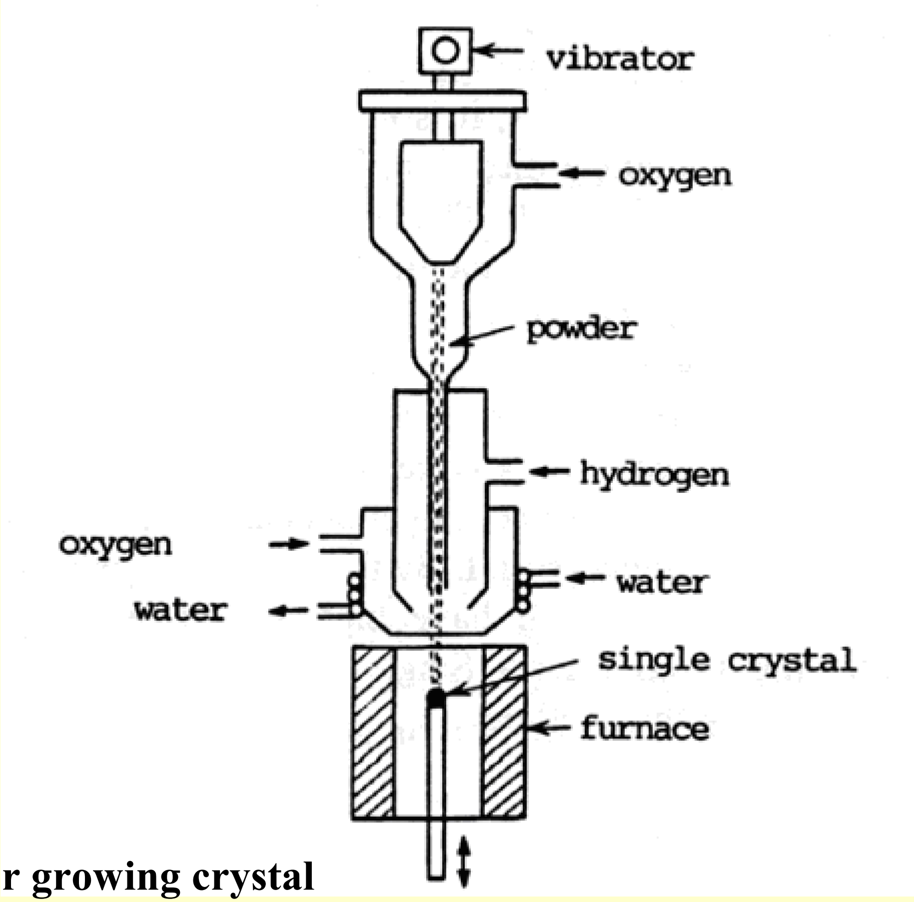
Verneuil Fusion Flame Method

Useful for growing crystals
of extremely high melting metal oxides
Examples include:

Ruby from Cr^{3+}/Al_2O_3 powder

Sapphire from Cr_2^{6+}/Al_2O_3 powder

Spinel, CoO, ferrites



Starting material fine powder
Passed through O_2/H_2 flame or plasma torch
Melting of the powder occurs in the flame
Molten droplets fall onto the surface of a seed or growing crystal
Controlled crystal growth

Lowered 10 mm/hour

THE FLUX METHOD

Material dissolved in a suitable flux = solvent (metals, fluorides, oxides), lower melting point than the pure solute

Single crystals grown from supersaturated solution

Suitable for materials which:

◆ vaporize or dissociate at temperatures above their mp

◆ there are no suitable containers at elevated temperatures

Material	**Flux**
As	**Ga**
B	**Pt**
Si, Ge	**Pb, Zn, Sn**
GaAs, GaP	**Pb, Zn, Sn**
$BaTiO_3$	**KF**
ZnO	PbF_2
ZnS	SnF_2
$MgFe_2O_4$	**NaF**
Co_3O_4	B_2O_3 – PbO
Fe_2O_3	$Na_2B_4O_7$
TiO_2	$Na_2B_4O_7 – B_2O_3$

THE FLUX METHOD

AlF_3

2.0 g of AlF_3, 25.0 g of $PbCl_2$, 2.5 g PbF_2

24 h at 1200 K, cooled at 4 deg h^{-1} down to 723 K

thick platelets and small cubes

THE SOLUTION METHOD

Suitable for materials with a reasonable solubility in the selected solvent: water, organic solvents, $NH_3(l)$, HF, $SO_2(l)$

Nucleation homogeneous
heterogeneous

Dilute solution, solvent with low solubility for given solute
Supersaturated solution, seed crystals
Single crystals grown at constant supersaturation

Techniques:

- **slow evaporation**
- **slow cooling**
- **vapor diffusion**
- **solvent diffusion**
- **reactant diffusion**
- **recirculation, thermal differential, convection**
- **cocrystallants ($OPPh_3$ for organic proton donors)**
- **counterion, similar size of cation and anion least soluble**
- **ionization of neutral compounds, protonation/deprotonation, hydrogen bonding**

Rochelle salt: *d*-$NaKC_4H_4O_6.4H_2O$ (tartrate)
KDP
alum

KDP crystals (KH_2PO_4)

grown from supersaturated solution

crystal seed

slow cooling

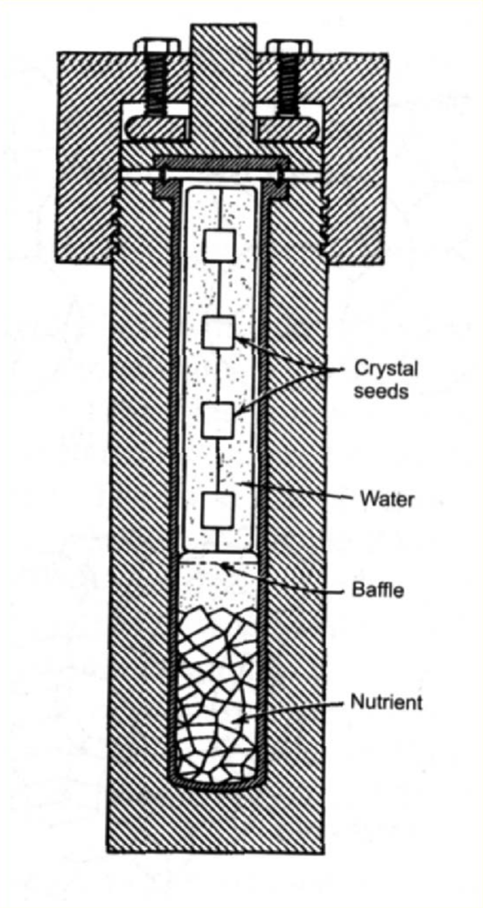
a frequency converter - converts the infrared light at 1053 nm into the ultraviolet at 351 nm

Hydrothermal Synthesis

1957 - Bell Labs

Water medium
High temperature growth, above normal boiling point
Water acts as a pressure transmitting agent
Water functions as solubilizing phase
Often a mineralizing agent is added to assist with the transport of reactants and crystal growth
Speeds up chemical reactions between solids
Crystal growth hydrothermally involves:

Temperature gradient reactor = autoclave (a bomb !!)
Dissolution of reactants at one end
Transport with help of mineralizer to seed at the other end
Crystallization at the other end



Hydrothermal Synthesis

Useful technique for the synthesis and crystal growth of phases that are unstable in a high temperature preparation in the absence of water
materials with low solubility in water below 100 ^{o}C

Some materials have negative solubility coefficients,
crystals can grow at the hotter end in a temperature gradient hyrdothermal reactor
Example: α-$AlPO_4$ (Berlinite) important for its high piezoelectric coefficient (larger than α-quartz with which it is isoelectronic) used as a high frequency oscillator

Hydrothermal growth of quartz crystals

Water medium, nutrients 400 ^{o}C, seed 360 ^{o}C, pressure 1.7 kbar
Mineralizer 1M NaOH

Uses of single crystal quartz: Radar, sonar, piezoelectric transducers, monochromators, XRD
Annual global production hundreds of tons of quartz crystals

Hydrothermal Synthesis

Hydrothermal crystal growth is also suitable for growing single crystals of:

Ruby: Cr^{3+}/Al_2O_3
Corundum: α-Al_2O_3
Sapphire: Cr_2^{6+}/Al_2O_3
Emerald: $Cr^{3+}/Be_3Al_2Si_6O_{18}$
Berlinite: α-$AlPO_4$
Metals: Au, Ag, Pt, Co, Ni, Tl, As

Role of the mineralizer:

Control of crystal growth rate:
choice of mineralizer, temperature and pressure
Solubility of quartz in water is important

HYDROTHERMAL SYNTHESIS

$SiO_2 + 2H_2O \leftrightarrow Si(OH)_4$

0.3 wt% even at supercritical temperatures >374 ^oC

A mineralizer is a complexing agent (not too stable) for the reactants/precursors that need to be solublized (not too much) and transported to the growing crystal

Some mineralizing reactions:

NaOH mineralizer, dissolving reaction, 1.3-2.0 kbar

$3SiO_2 + 6OH^- \leftrightarrow Si_3O_9^{6-} + 3H_2O$

Na_2CO_3 mineralizer, dissolving reaction, 0.7-1.3 kbar

$SiO_2 + 2OH^- \leftrightarrow SiO_3^{2-} + H_2O$

$CO_3^{2-} + H_2O \leftrightarrow HCO_3^- + OH^-$

NaOH creates growth rates about 2x greater than with Na_2CO_3 because of different concentrations of hydroxide mineralizer

HYDROTHERMAL SYNTHESIS

Examples of hydrothermal crystal growth and mineralizers

Berlinite α-$AlPO_4$
Powdered $AlPO_4$ cool end of reactor
negative solubility coefficient!!!
H_3PO_4/H_2O mineralizer, $AlPO_4$ seed crystal at hot end

Emeralds $Cr^{3+}/Be_3Al_2Si_6O_{18}$
SiO_2 powder at hot end 600 °C, NH_4Cl or HCl/H_2O mineralizer, 0.7-1.4 kbar, cool central region for seed, 500 °C, $Al_2O_3/BeO/Cr^{3+}$ dopant powder mixture at other hot end 600 °C

$6SiO_2 + Al_2O_3 + 3BeO \rightarrow Be_3Al_2Si_6O_{18}$

Beryl contains $Si_6O_{18}^{12-}$ six rings

HYDROTHERMAL SYNTHESIS

Metal crystals
Metal powder at cool end 480 °C, Mineralizer 10M HI/I_2
Metal seed at hot end 500 °C.
Dissolving reaction that also transports Au to the seed crystal:

$$Au + 3/2I_2 + I^- \leftrightarrow AuI_4^-$$

Metal crystals grown this way include Au, Ag, Pt, Co, Ni, Tl, As at 480-500 °C

Diamonds

$$Ni + C + H_2O \xrightarrow{800\ °C,\ 140\ MPa} \text{diamond}$$

HYDROTHERMAL SYNTHESIS

Carbon films on SiC fibers

$$SiC + 2\ H_2O \xrightarrow[300\text{-}600°C]{100\ MPa} C + 2\ H_2 + SiO_2$$

Zeolites

$Al(OH)_3$, SiO_2, NaOH, template

$M_{x/n}\ [(AlO_2)_x(SiO_2)_y].\ {}_mH_2O$

HYDROTHERMAL SYNTHESIS

necessitates knowledge of what is going on in an autoclave under different degrees of filling and temperature

Pressure, volume, temperature tables of dense fluids like water

Critical point of water: 374.2 ^{o}C, 218.3 bar

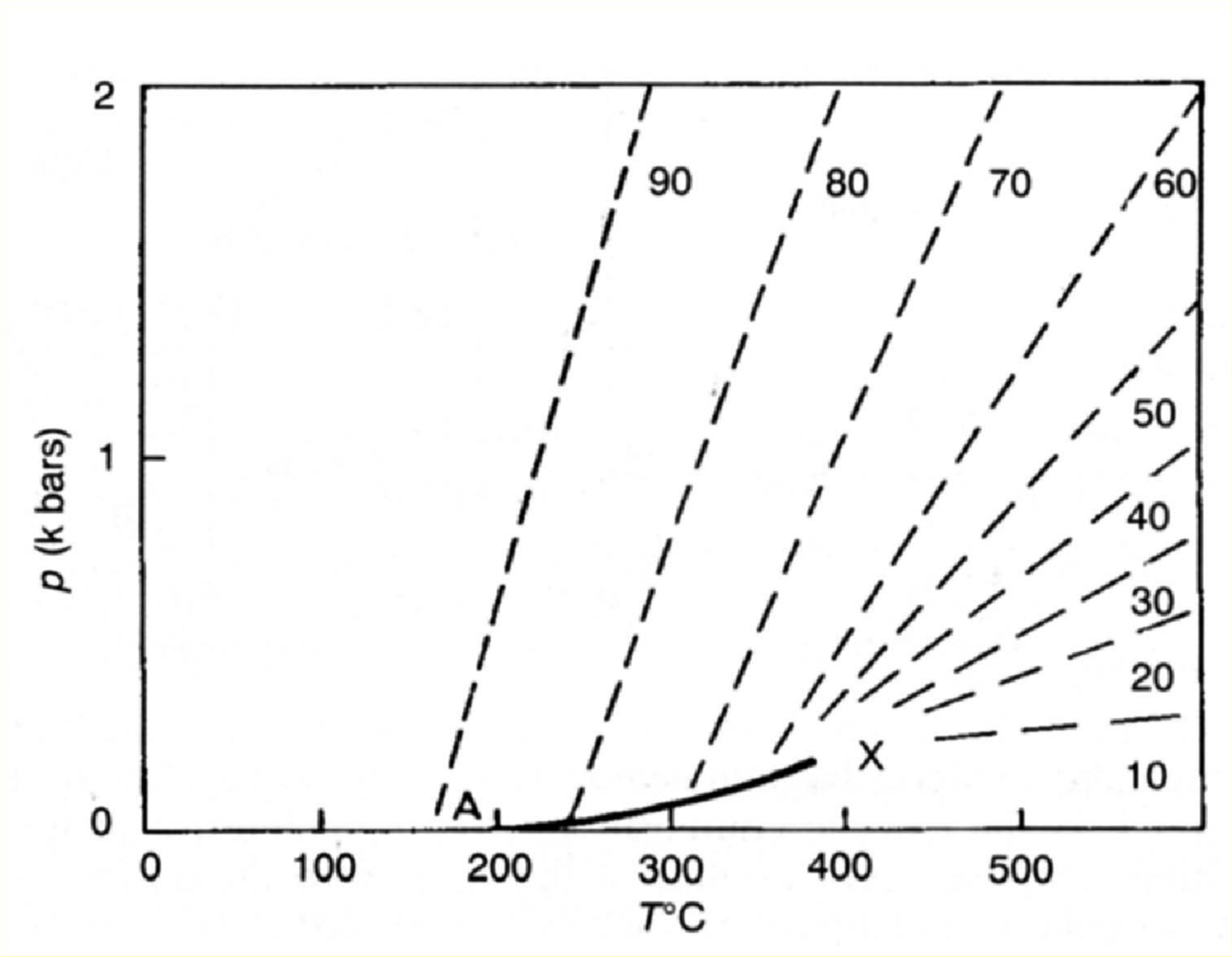
Density of liquid water decreases with T
Density of water vapor increases with T

Density of gas and liquid water the same 0.32 gcm^{-3}, at the critical point

Liquid level in autoclave rises for > 32% volume filling
Autoclave filled at 250 ^{o}C for > 32% volume filling

For 32% volume filling liquid level remains unchanged and becomes fluid at critical temperature

HYDROTHERMAL SYNTHESIS



HYDROTHERMAL SYNTHESIS

Tables of pressure versus temperature for different initial volume filling of autoclave must be consulted to establish a particular set of reaction conditions for a hydrothermal synthesis or crystallization

Safety: if this is not done correctly, with proper protection equipment in place, you can have an autoclave explosion that can kill!!!

BULK-MATERIAL DISSOLUTION TECHNIQUE

large zeolite crystals: up to 3 mm, SOD, MFI, ANA,CAN, JBW

autoclave, PTFE liner

quartz tube (SiO_2)	**TPAOH, HF, H_2O**	**200 °C, 25-50 days**
ceramic tube (SiO_2, Al_2O_3)	**NaOH, H_2O**	**100-200 °C, 7-20 days**

Small surface area, low dissolution rate, saturation concentration maintained, only a few nuclei are produced at the beginning, no large crystals formed in the stirred reactions, concentration gradients

DECOMPLEXATION CRYSTALLIZATION

crystallization under ambient conditions, low temperature and pressure, provides kinetic products, control of crystal size and morphology, habit

AgX, X = Cl, Br, I
MX, M = H, Na, K, NH_4

$AgI + HI \rightleftharpoons H^+ + [AgI_2]^-$ aqueous solution
overlayer absolute ethanol, HI diffusion, decomplexation of AgI, hexagonal plates 5 mm

$AgX + 2\ NH_3 \rightleftharpoons [Ag(NH_3)_2]^+ + X^-$
X = Cl, Br, slow evaporation (3-5 days), AgX crystals

$AgI + KI \rightleftarrows K^+ + [AgI_2]^-$

© concentration gives $K[AgI_2]$ crystals
© dilution by slow diffusion gives 20 mm AgI crystals
© warming gives AgI crystals (inverse temperature dependence of AgI solubility in KI)

$CuCl + HCl \rightleftarrows H^+ + [CuCl_2]^- \rightleftarrows CuCl$

$HgI_2 + KI \rightleftarrows [HgI_3]^- \rightleftarrows [HgI_4]^{2-} \rightleftarrows HgI_2$

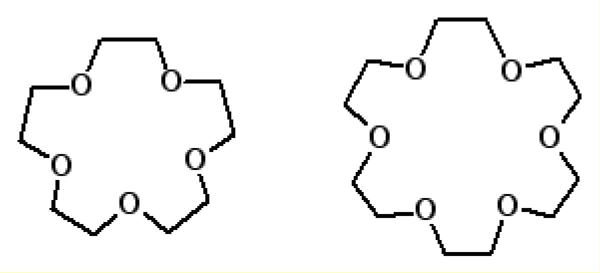
PbO + hot KOH solution, slow cooling provides PbO as 2 mm yellow needles and 1 mm red blocks

COMPLEXATION-MEDIATED CRYSTALLIZATION

Salts with high lattice energy
fluorides, carbonates, acetates

Solubilized in organic solvents by crown ethers
Crystallization provides uncomplexed salts

$NaOOCCH_3.3H_2O$ dissolves in cyclohexane with 15-crown-5
prismatic crystals



COMPLEXATION-MEDIATED REACTION CRYSTALLIZATION

Two soluble salts react to produce an insoluble phase

- **© aqueous solutions**
- **© nonaqueous solvents**

$CaCO_3$	**calcite**	**TD stable phase at room temp., in H_2O**
	vaterite	**kinetic product**
	aragonite	**TD stable at high temperature**

$CaCl_2$ (in MeOH) + $NaHCO_3$ (in MeOH, 18-crown-6)
microcrystalline calcite
upon aging converts to nanocrystalline vaterite, surface stabilization by surface chelatation

THE GEL METHOD

Large single crystals

- **hydrogels: silicagel (water glass), polyvinyl alcohol, gelatin, agar**

Silicate gel
Impregnation with metal or ligand, setting the gel = condensation, crosslinking, pH control of the condensation rate
Layered with the solution of ligand or metal
Slow diffusion, xtal growth

$CuSO_4 + [NH_3OH]Cl \longrightarrow Cu$
$Pb(OAc)_2 + Zn \longrightarrow Pb + Zn(OAc)_2$
$Pb(OAc)_2 + KI \longrightarrow PbI_2 + 2\ KOAc$
Liesegang rings, agates
$RbSnBr_3$, $CsSb_2I_5$ semiconductors

THE GEL METHOD

◆ nonaqueous gels

PEO (MW = 100 000) in 1,2-dichloroethane + MeOH, EtOH, PrOH, DMF, CH_3CN, DMSO

Impregnation with metal or ligand

Layered with the solution of ligand or metal

Slow diffusion, crystal growth

U-tube, counter-diffusion

Concentration programming, increasing concentrations

Ostwald rippening = larger xtals grow, smaller dissolve

ELECTROCHEMICAL REDUCTIVE SYNTHESIS, CRYSTAL GROWTH

Molten mixtures of precursors, product crystallizes from melt

Melt electrochemistry: Electrochemical reduction

$CaTi(IV)O_3$ (perovskite)/$CaCl_2$ (850 °C) → $CaTi(III)_2O_4$ (spinel)

$Na_2Mo(VI)O_4/Mo(VI)O_3$ (675 °C) → $Mo(IV)O_2$ (large crystals)

$Li_2B_4O_7/LiF/Ta(V)_2O_5$ (950 °C) → $Ta(II)B_2$

$Na_2B_4O_7/NaF/V(V)_2O_5/Fe(III)_2O_3$ (850 °C) → $Fe(II)V(III)_2O_4$ (spinel)

Na_2CrO_4/Na_2SiF_6 (T °C) → Cr_3Si

$Na_2Ge_2O_5/NaF/NiO$ → Ni_2Ge

ELECTROCHEMICAL REDUCTIVE SYNTHESIS, CRYSTAL GROWTH

Phosphates → phosphides
Carbonates → carbides
Borates → borides
Sulfates → sulfides
Silicates → silicides
Germanates → germides

Synthesis of Amorphous Materials

Quenching of molten mixture of metal oxide with a glass former
(P_2O_5, V_2O_5, Bi_2O_3, SiO_2, CaO, …), large cooling rates required ($>10^7$ K s^{-1})

Ion beam sputtering

Thermal evaporation

Thermal decomposition of organometallic precursors ($Fe(CO)_5$, …)
Cr_2O_3, MnO_2, PbO_2, V_2O_5, Fe_2O_3

Sonochemical decomposition of organometallic precursors
($Fe(CO)_5$, $M(acac)_n$,…

Precipitation on metal hydroxides, transformation to hydrous oxides

MW heating of metal salt solution
Cr_2O_3, Fe_2O_3