**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)

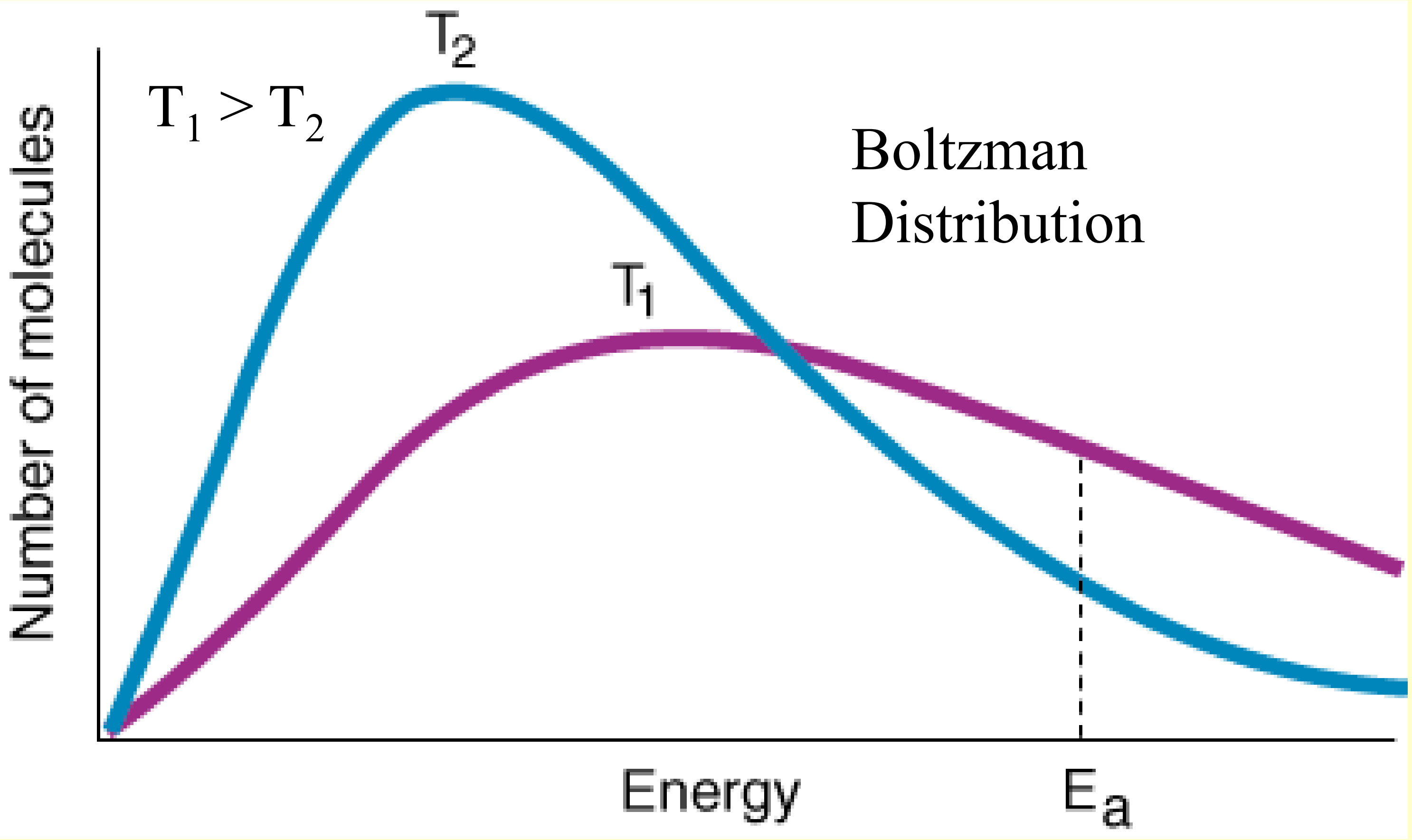
- fabrication of devices

$Y_3Al_5O_{12}$ (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

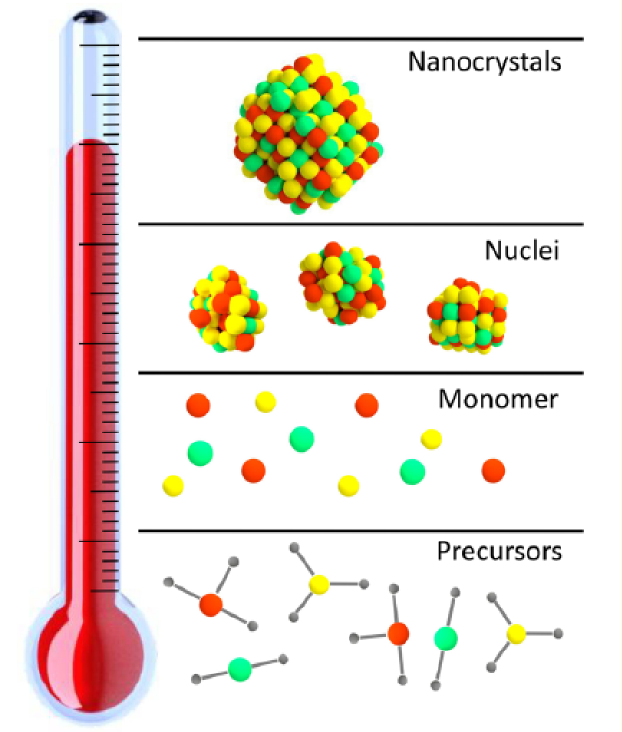
# Thermodynamics and Kinetics of Crystallization

**As a material cools off the average kinetic energy drops**



# Stages of Crystallization

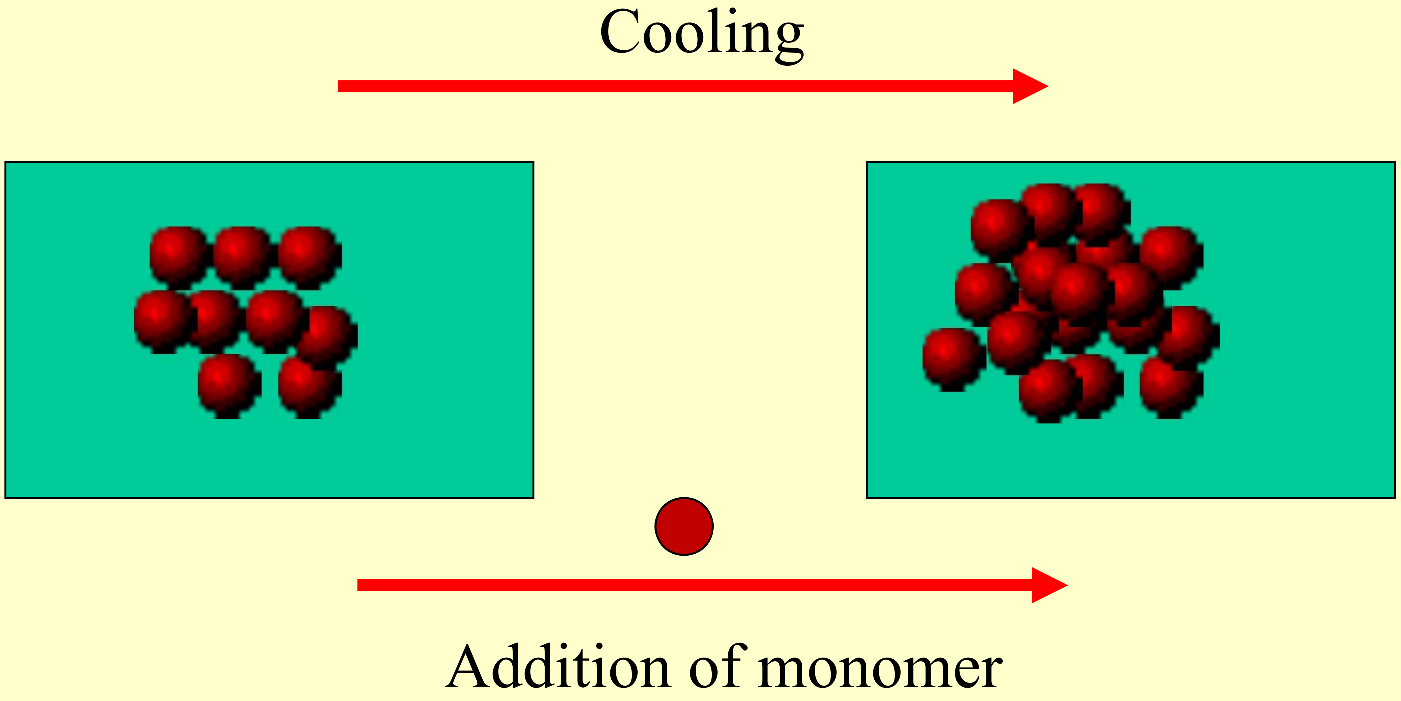
- **Nucleation – formation of nuclei of critical size**
- **Growth – diffusion of material toward the critical nuclei, depositon vs. dissolution, crystal growth**



# 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 $\Delta G_v$ (a negative value)**

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

**The volume free energy $\Delta G_v$ drives crystallization**

**SURFACE**

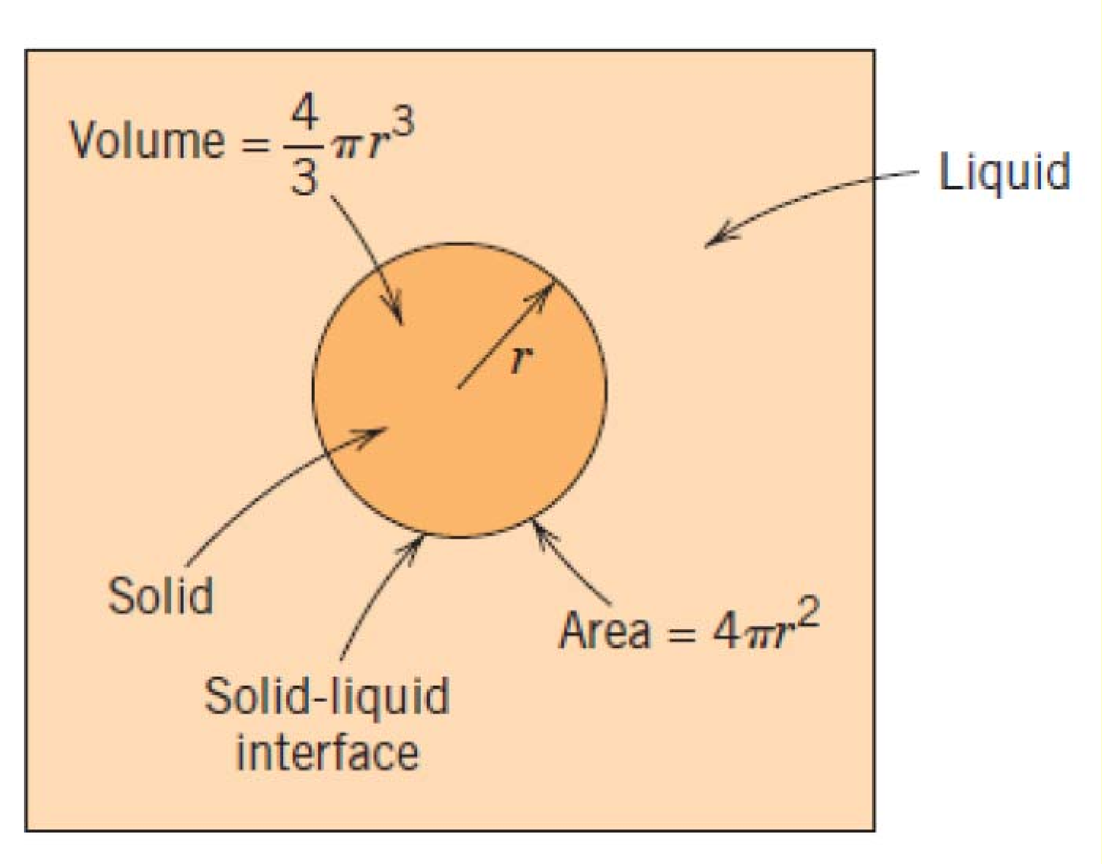
**When solids form in a liquid there is an interface created**

**The surface free energy, $\gamma_{SL}$ = 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**

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

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

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

**$\Delta G_T$ has a maximum at a critical radius – critical free energy $\Delta G_N$**

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

# Volume Free Energy

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

**$\Delta G_V$ – the free energy change between the ‘monomer’ in solution and in a unit volume of bulk crystal**

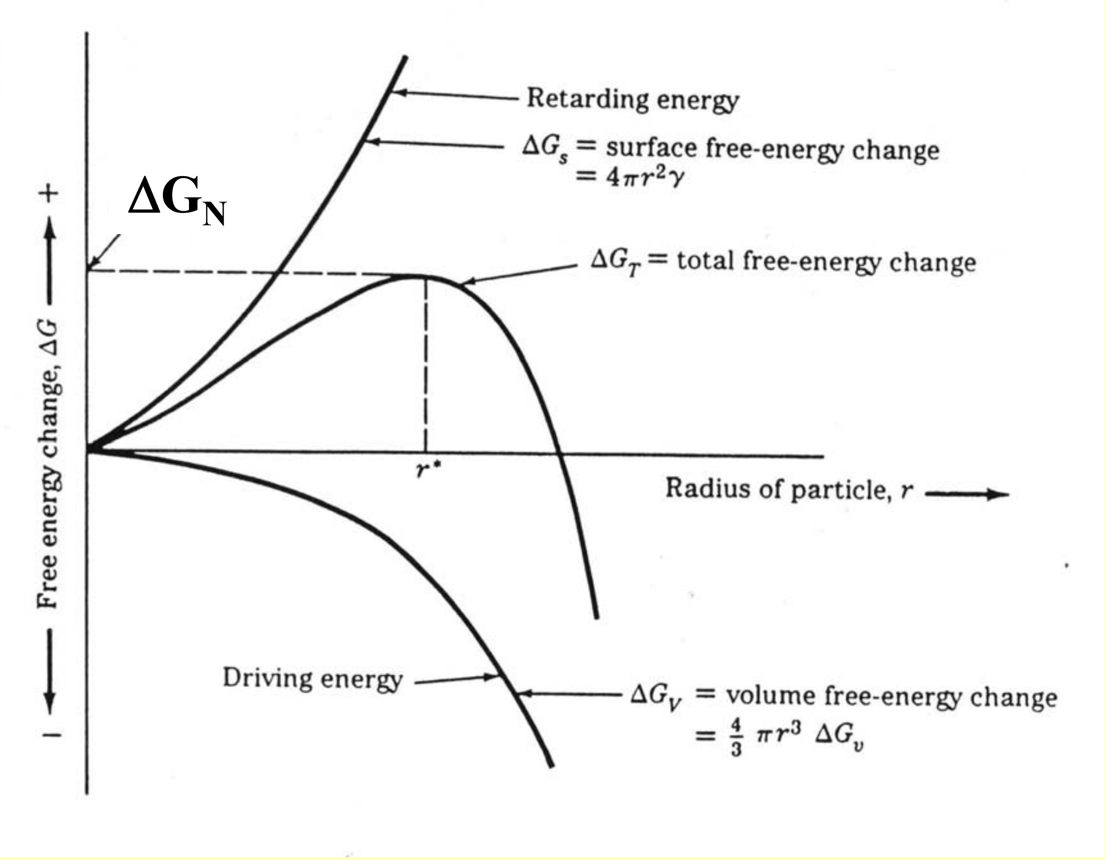
**S – supersaturation = the quotient of the actual concentration [M] and the concentration of the respective species at equilibrium with the flat crystal surface $[M_\propto]$, indicates how far away from equilibrium the system is:**

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

**$V_m$ – molar volume of the monomer composing the bulk crystal**

# Nucleation

**$\Delta G$**



**r: radius of spherical nuclei**

**r*: critical radius**

(r>r* seed grows by itself)

**$\Delta G_T$: total free energy change**

**$\Delta G_s$: surface free energy change**

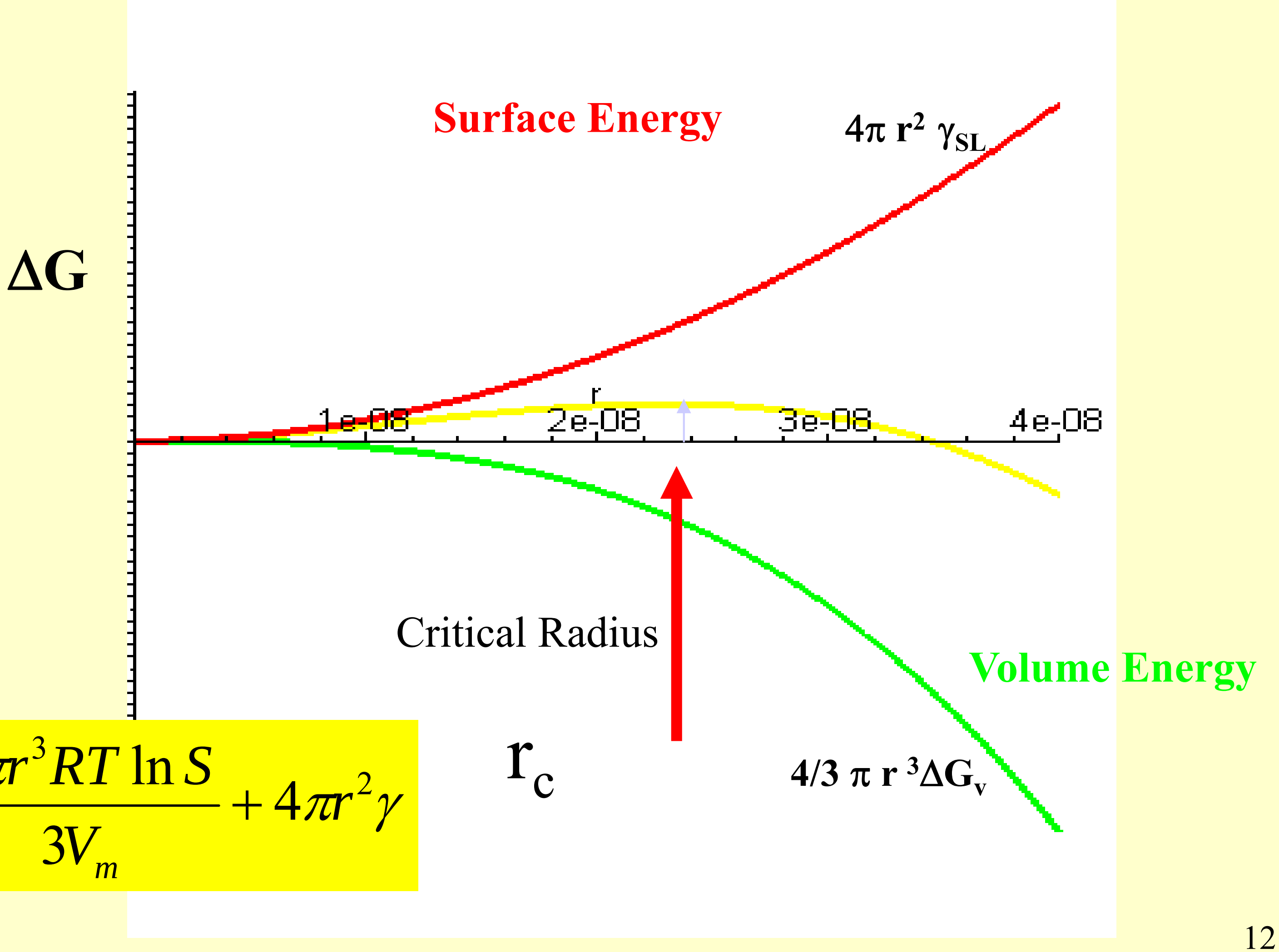
**$\Delta G_v$: volume free energy change**

**$\Delta G_N$: 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:**

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

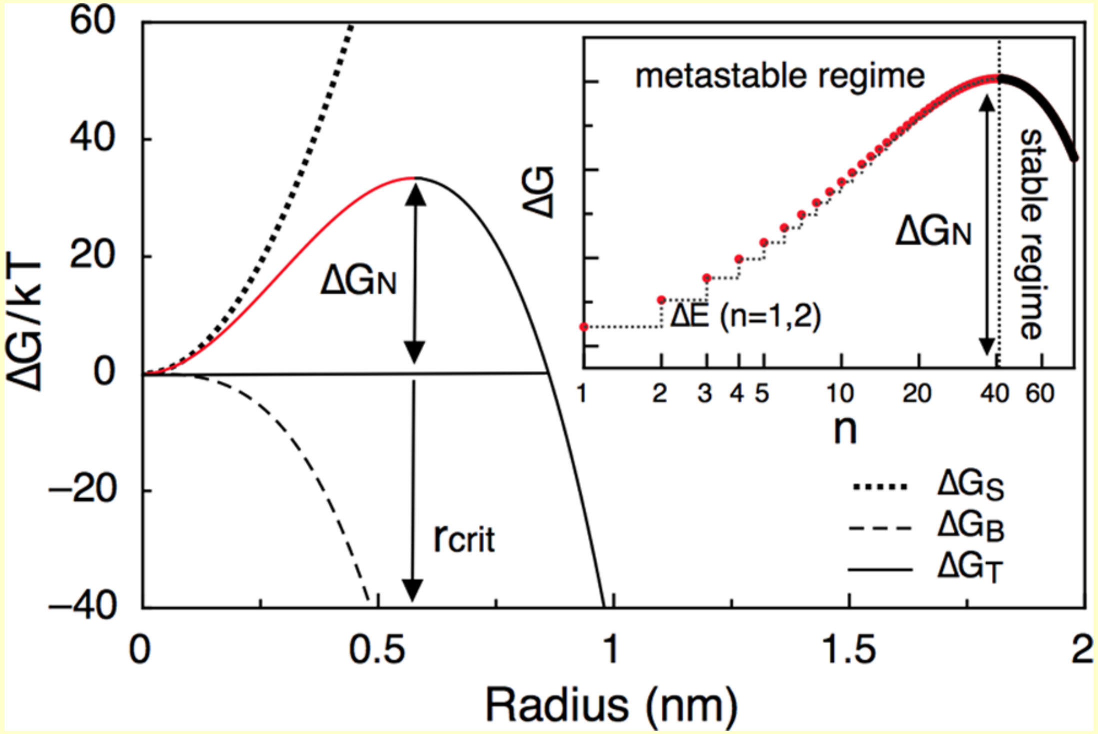
**S = supersaturation**

**At larger supersaturation, the critical radius of nuclei is smaller**

# Nucleation - Critical Free Energy $\Delta G_N$

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

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



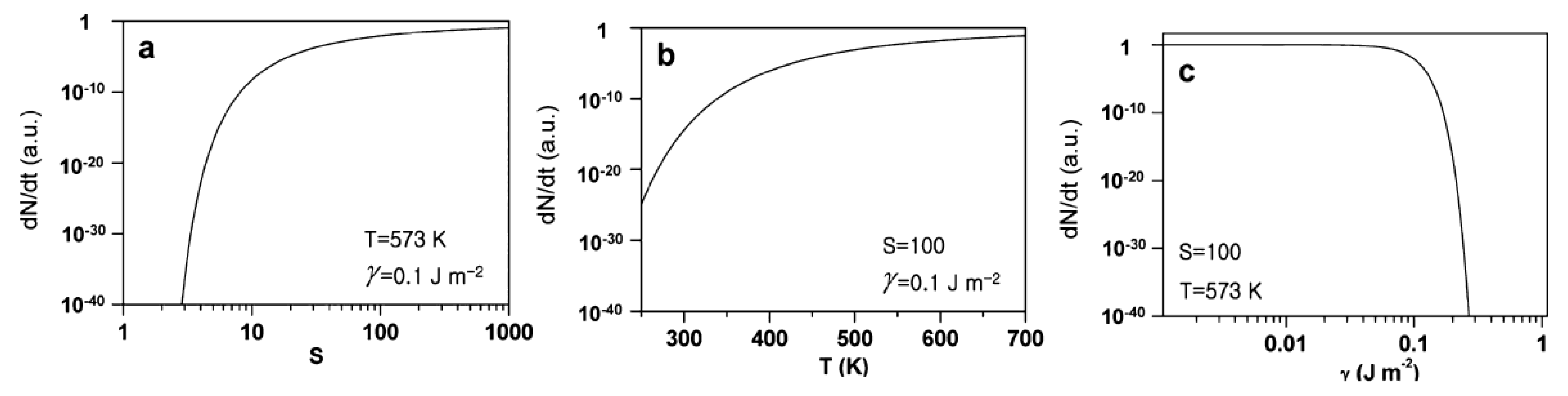
# Rate of Nucleation

**$\Delta G_N$ – 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



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

$V_m = 3.29 \times 10^{-5}\ \mathrm{m}^3\ \mathrm{mol}^{-1}$ (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**

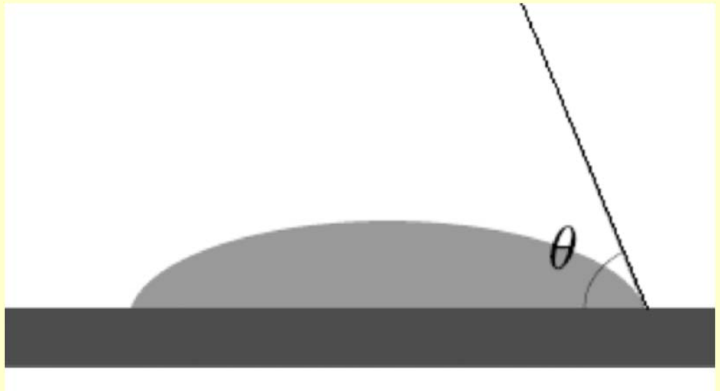
**Solidification can start on a wall**

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

**Adding impurities on purpose = inoculation**

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

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

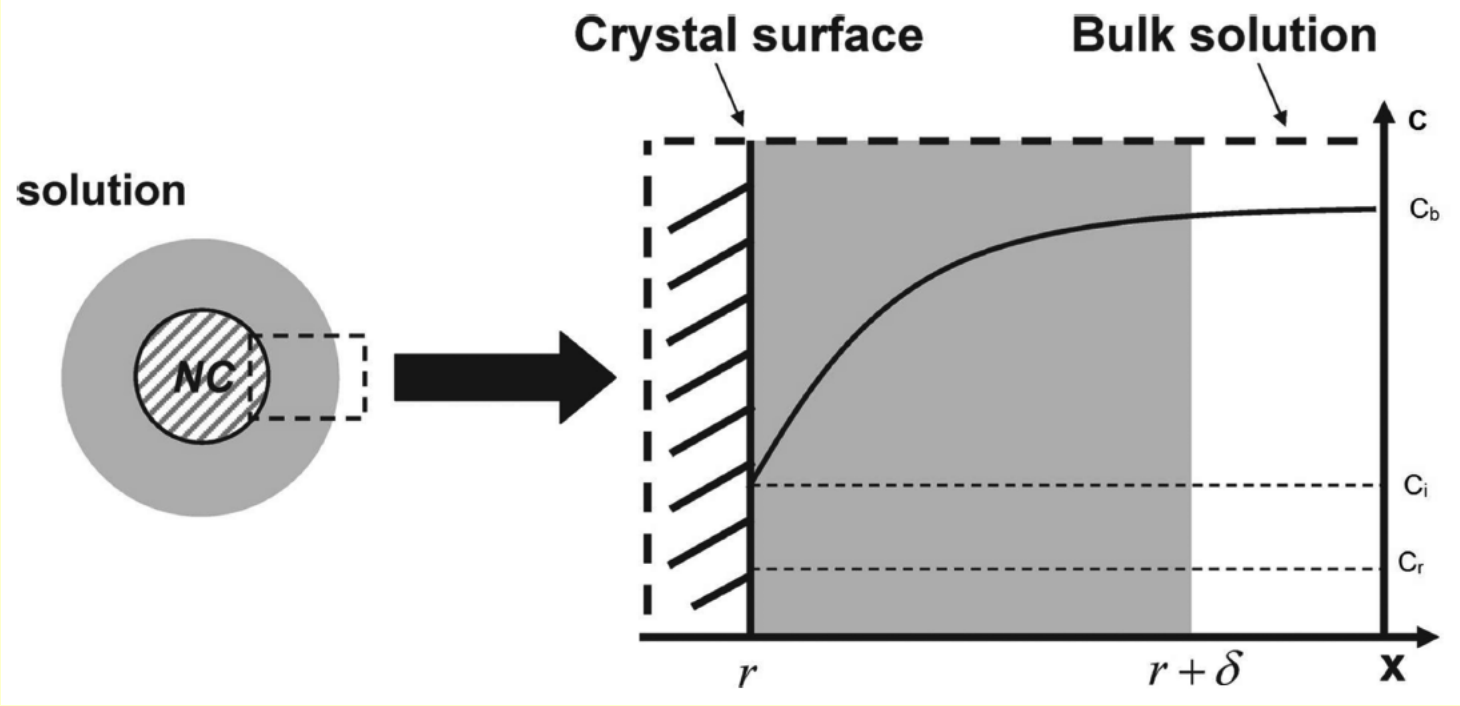


# Growth

**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

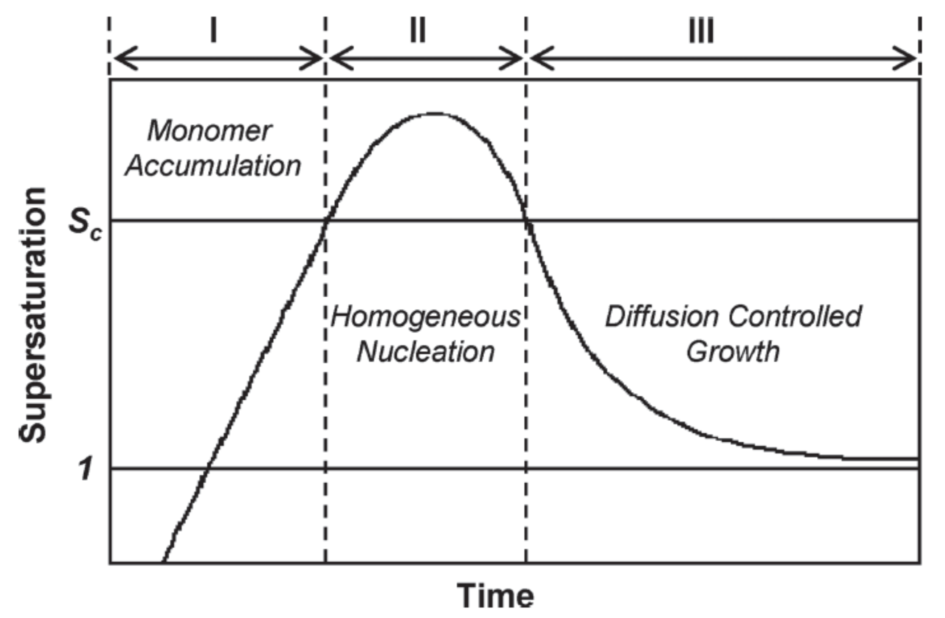
**Growth by diffusion**
**the growth rate of spherical particles (dr/dt)**

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

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

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

# La Mer Mechanism

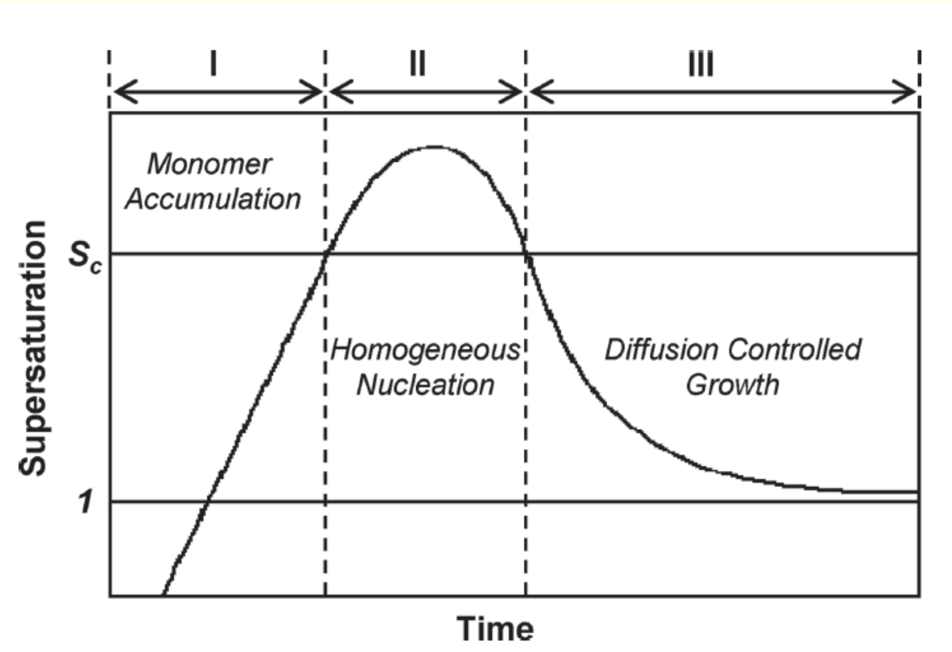


**3 Separate stages:**

- 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

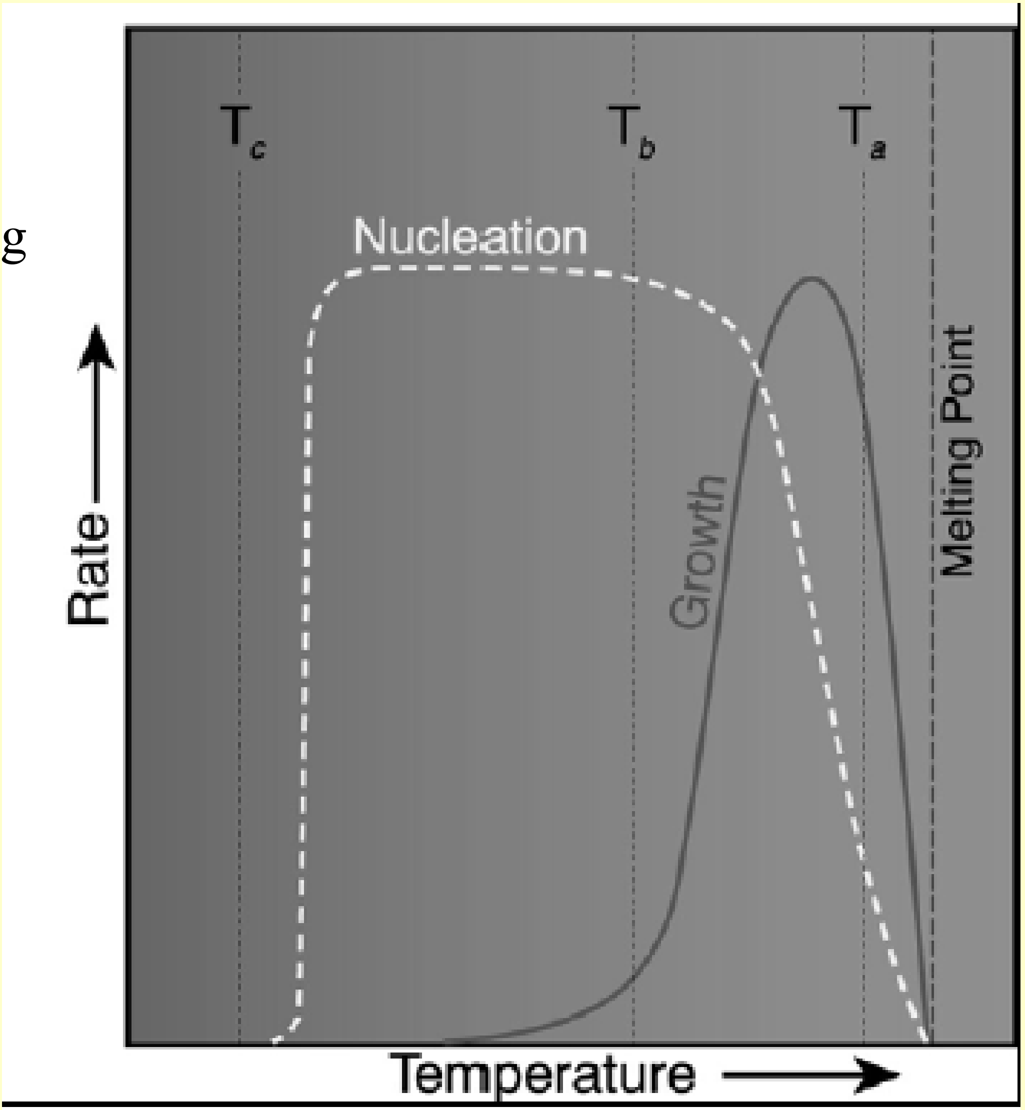
# Nucleation vs. Crystal Growth

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

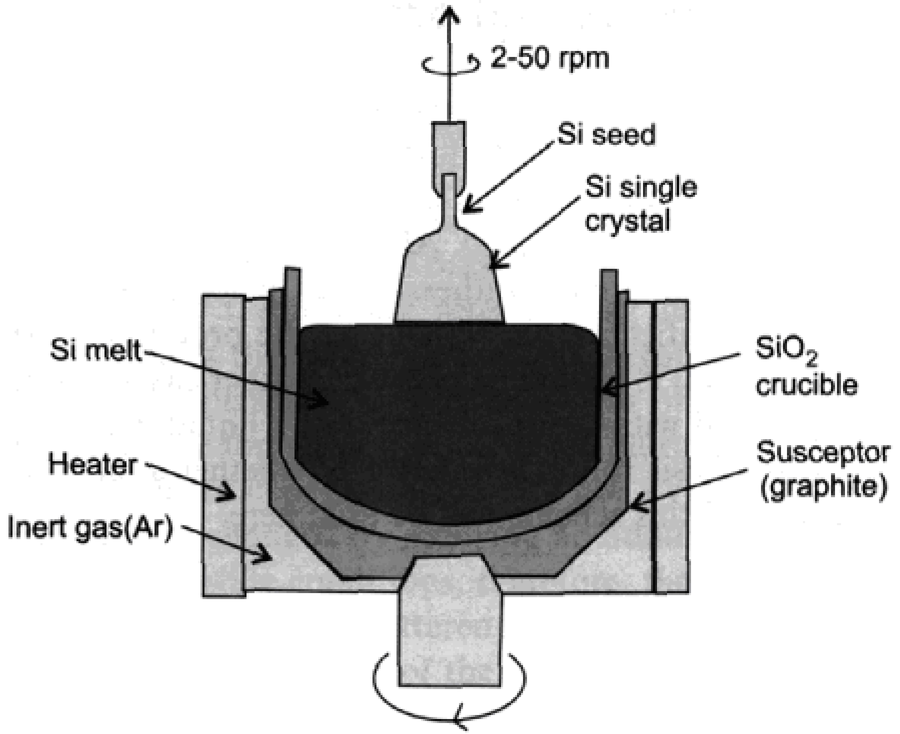
**CZOCHRALSKI or KYROPOULOS METHOD**

Jan Czochralski
(1885 – 1953)

**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**

# Growth of Single Crystals

**CZOCHRALSKI or KYROPOULOS METHOD**



Diam 300 mm
Length 2 m
Weight 265 kg

# Growth of Single Crystals

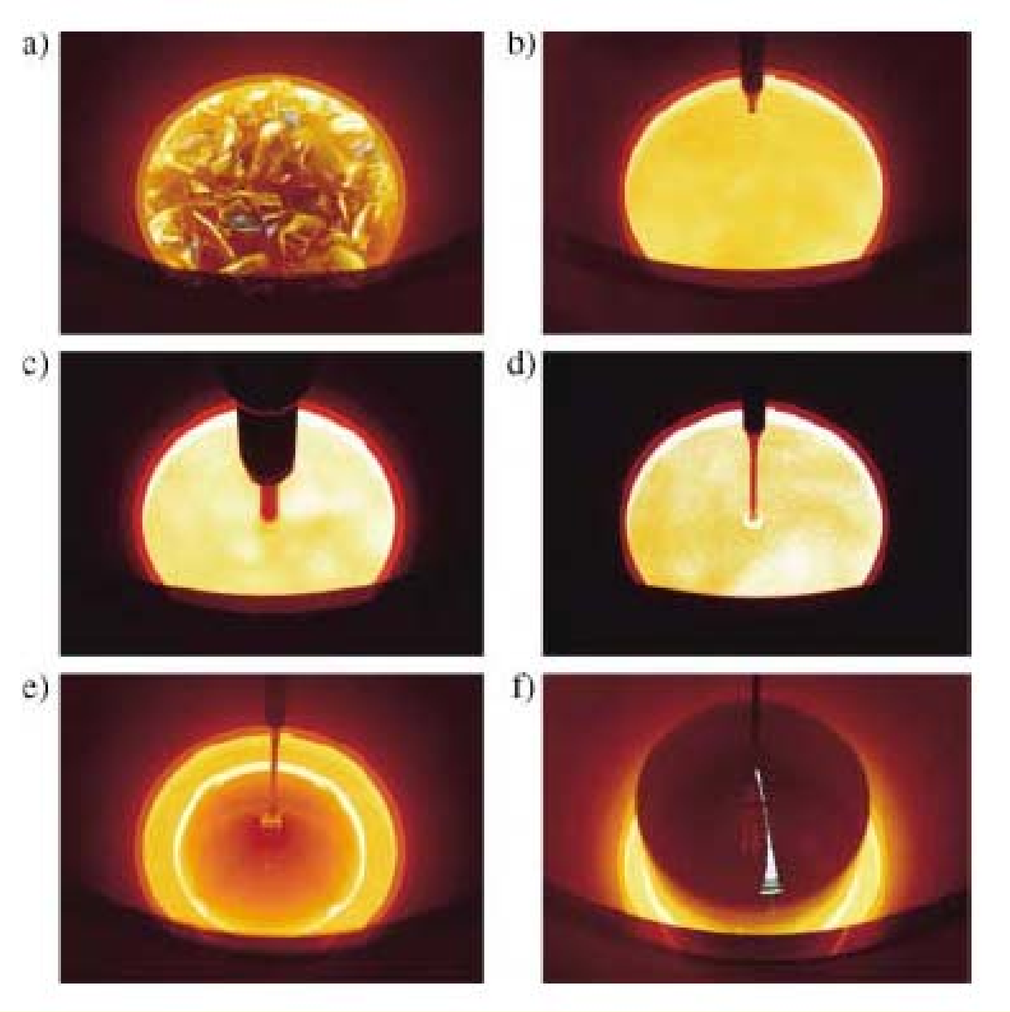
**Growing bimetallic crystals like GaAs**

**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”)**

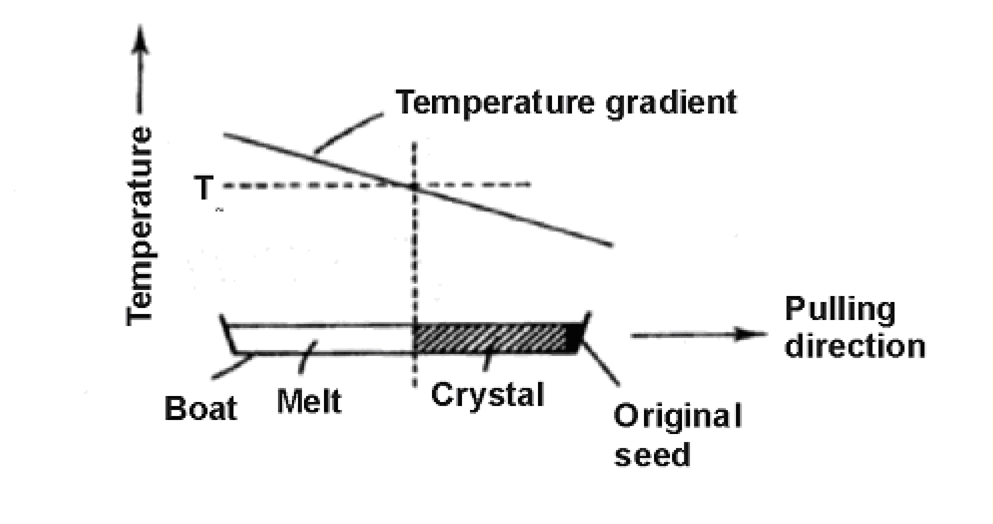
**e) Adjustment of the shoulder of the desired single crystal diameter (“shoulder”; four positions which portray the fourfold drawing axis [100] are visible at the hot, light marginal zone of the single crystal)**

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

# Growth of Single Crystals

## STOCKBARGER AND BRIDGMAN METHODS

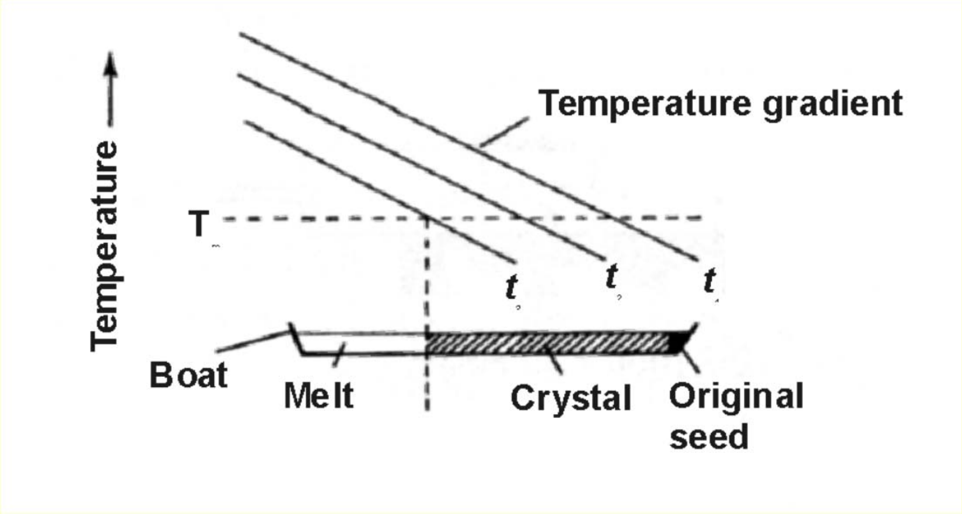
**Stockbarger method is based on a crystal growing from the melt, involves the relative displacement of melt and a temperature gradient furnace, fixed gradient and a moving melt/crystal**



# 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**



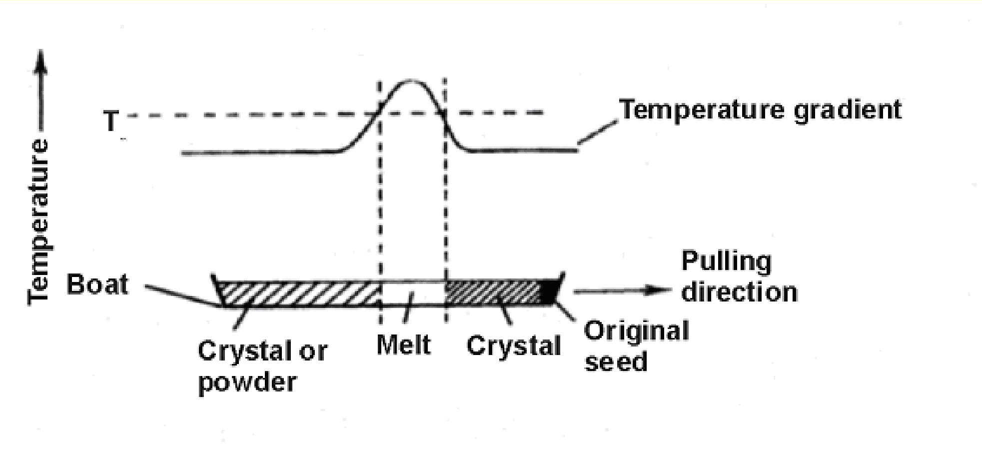
Both methods are founded on the controlled solidification of a stoichiometric melt of the material to be crystallized
Enables oriented solidification
Melt passes through a temperature gradient
Crystallization occurs at the cooler end
Both methods benefit from seed crystals and controlled atmospheres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

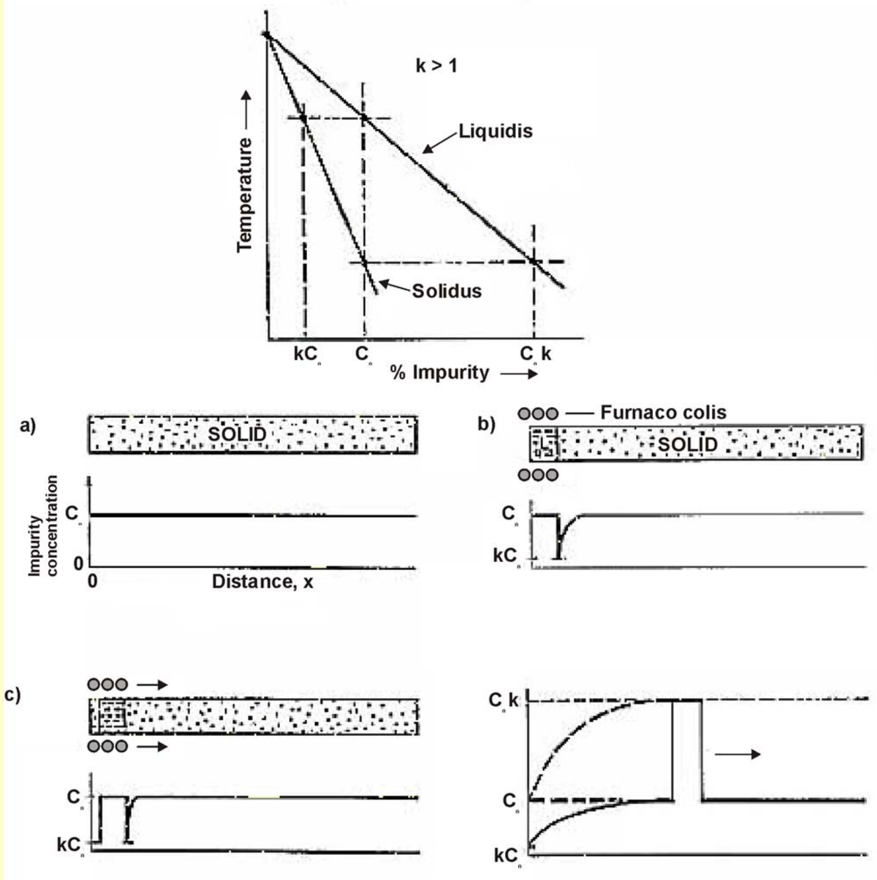
**Thermal profile furnace, RF, arc, electron beam heating**
**Material contained in a boat (must be inert to the melt)**
**Only a small region of the charge is melted at any one time**
**Initially part of the melt is in contact with the seed**
**Boat containing sample pulled at a controlled velocity 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 !!)

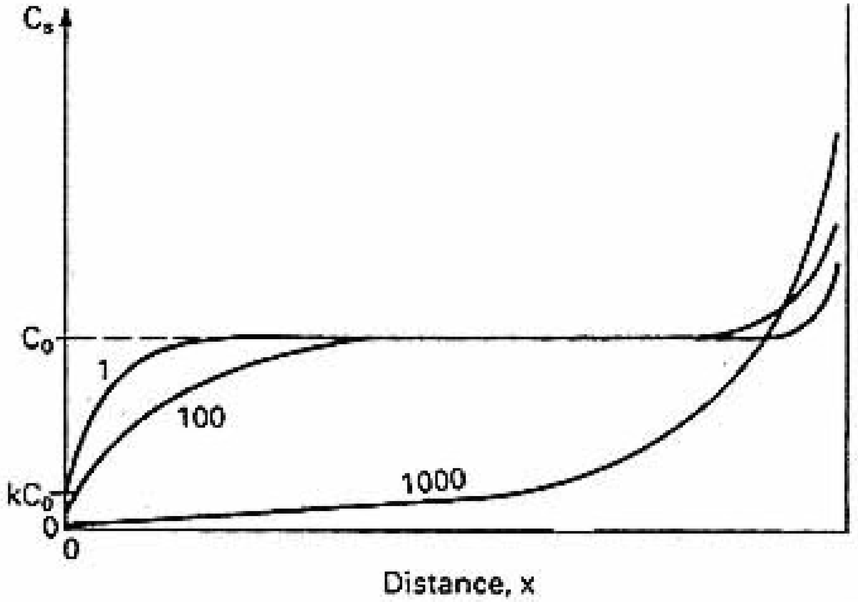
- segregation coefficient k:

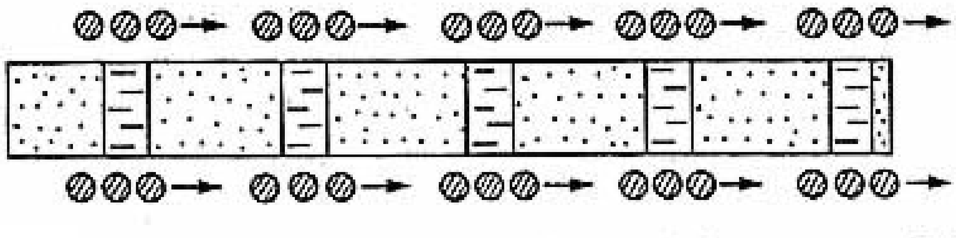
$$k = c_{solid}/c_{liquid}$$

(c: concentration of an impurity)

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

# Zone Melting



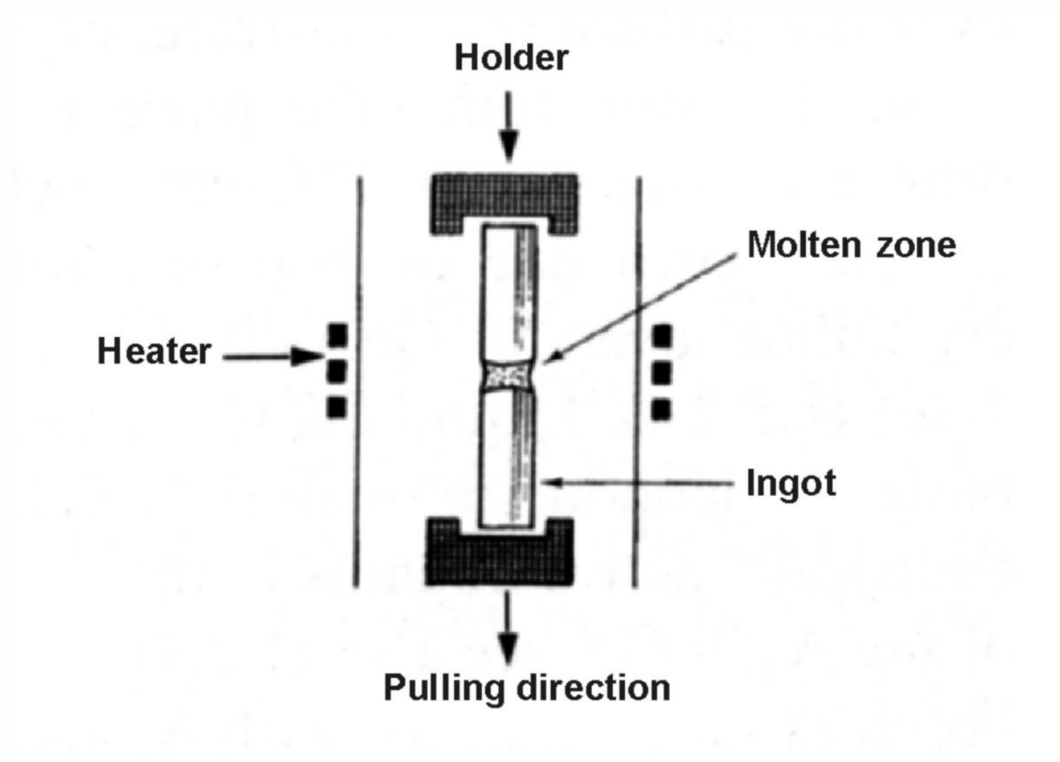


A multi-heater arrangement gives much faster zone refining

# 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**

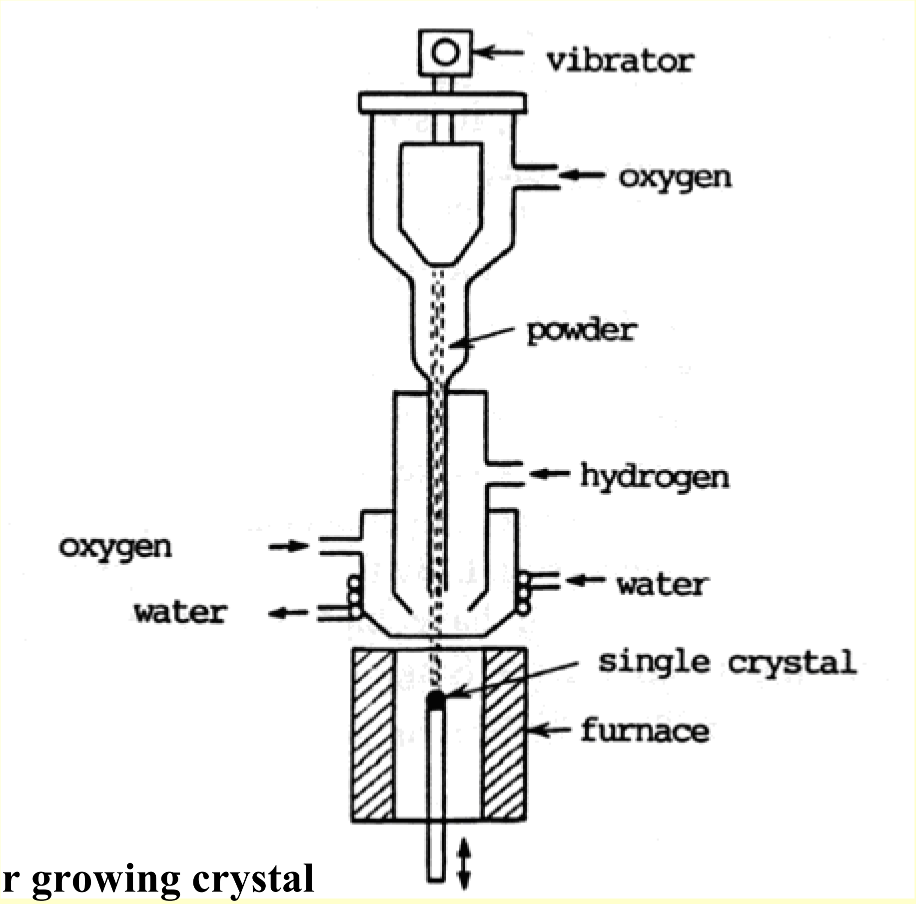
# Verneuil Fusion Flame Method

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**

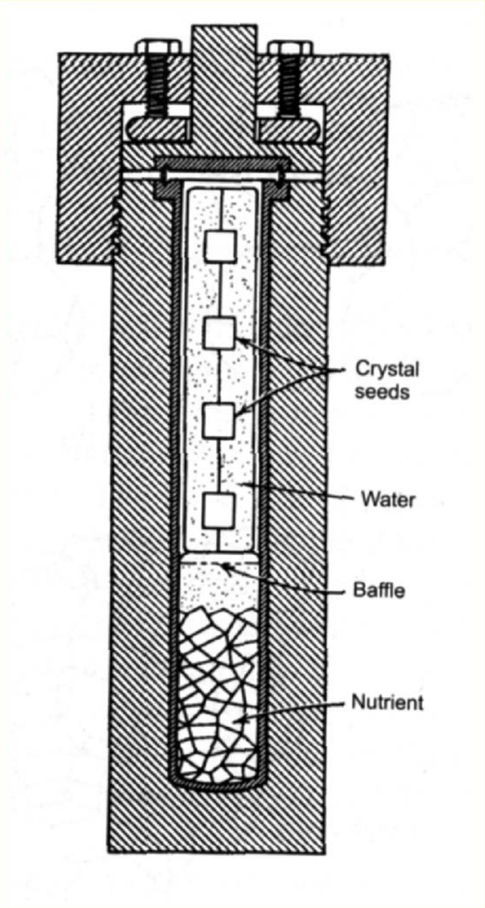
a frequency converter - converts the infrared light at 1053 nm into the ultraviolet at 351 nm

# 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: $\alpha$-$AlPO_4$ (Berlinite) important for its high piezoelectric coefficient (larger than $\alpha$-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: $\alpha$-$Al_2O_3$**
**Sapphire: $Cr_2^{6+}/Al_2O_3$**
**Emerald: $Cr^{3+}/Be_3Al_2Si_6O_{18}$**
**Berlinite: $\alpha$-$AlPO_4$**
**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 °C

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 $\alpha$-$AlPO_4$**
**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 $^oC$, Mineralizer 10M $HI/I_2$**
**Metal seed at hot end 500 $^oC$.**
**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 $^oC$**

**Diamonds**

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

## HYDROTHERMAL SYNTHESIS

**Carbon films on SiC fibers**

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

**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

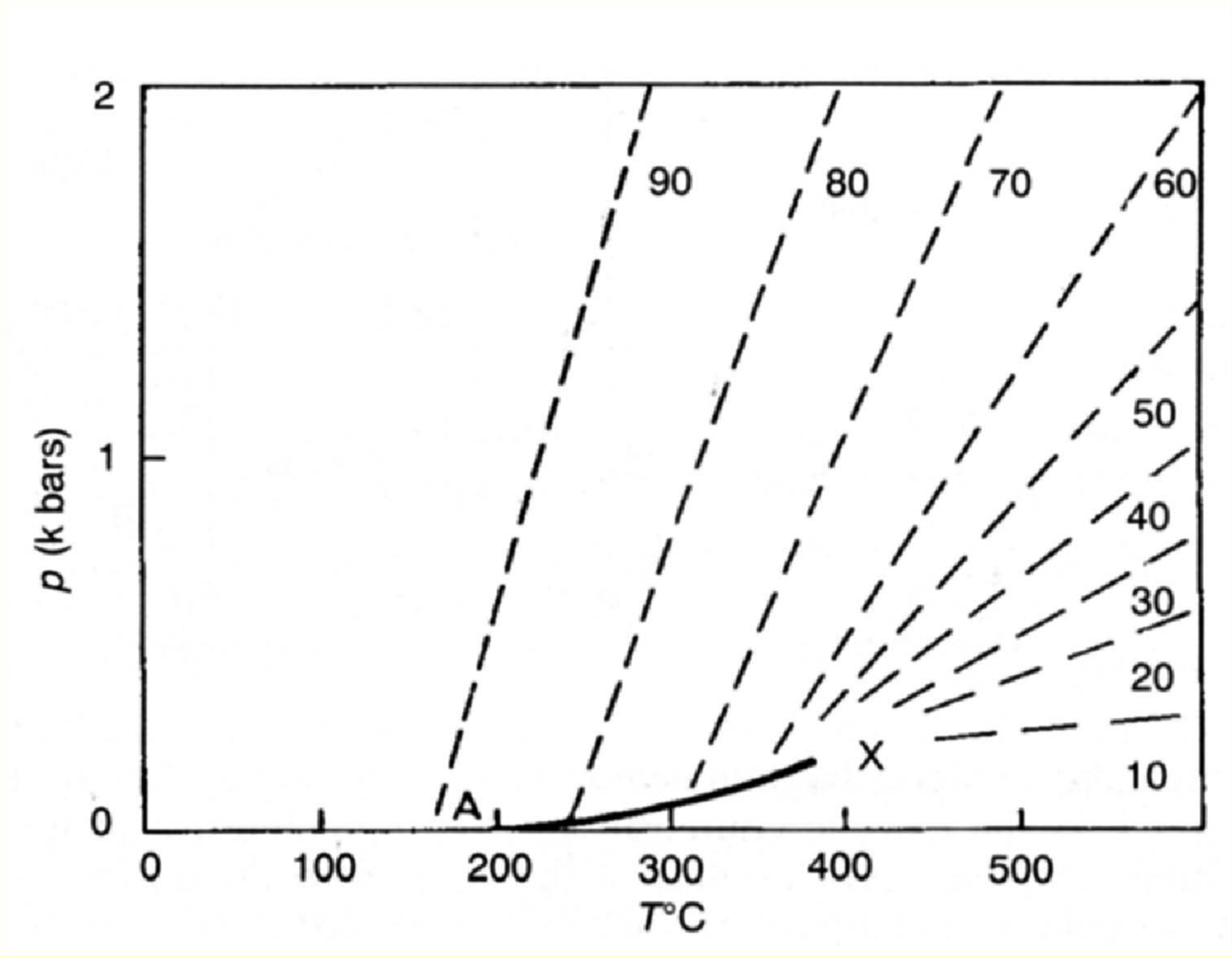
Density of liquid water decreases with T
Density of water vapor increases with T

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**

**$AgI + KI \rightleftharpoons K^+ + [AgI_2]^-$**

**© 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)**

**$CuCl + HCl \rightleftharpoons H^+ + [CuCl_2]^- \rightleftharpoons CuCl$**

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

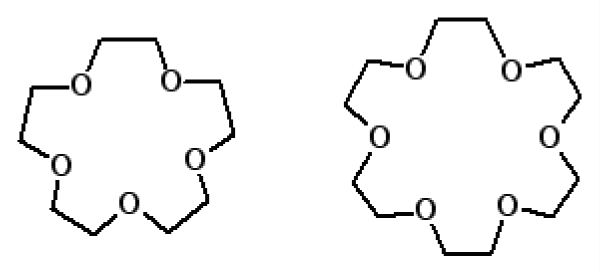
**PbO + hot KOH solution, slow cooling provides PbO as 2 mm yellow needles and 1 mm red blocks**

## 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**
**$Cr_2O_3$, $Fe_2O_3$**