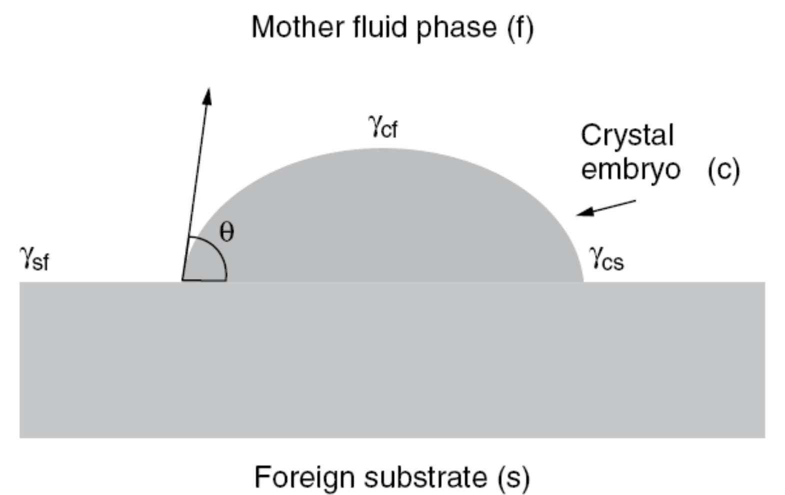
ΔΙΕΡΓΑΣΙΕΣ ΔΙΑΧΩΡΙΣΜΟΥ

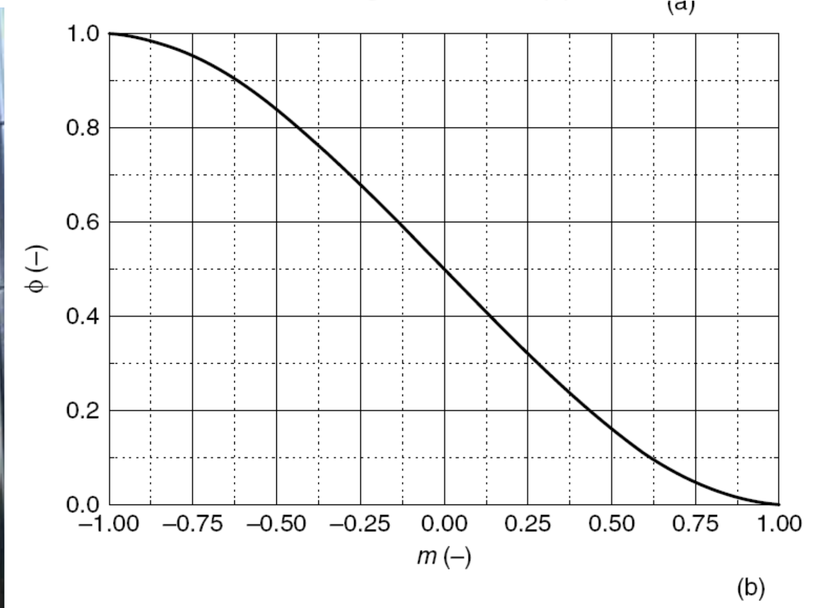
Μάθημα 8ο

Ακαδημαϊκό έτος 2017-2018

Ετερογενής πυρηνογένεση

- Η ομογενής 3D πυρηνογένεση μπορεί να γίνει απουσία εξωτερικών παραγόντων οι οποίοι επηρρεάζουν είτε την τιμή της κινητικής παραμέτρου A , είτε την διεπιφανειακή ενέργεια.
- Η παρουσία ξένων σωματιδίων ή άλλων ανωμαλιών στον αντιδραστήρα καταλύουν την 3D πυρηνογένεση. Αυτού του είδους η πυρηνογένεση είναι γνωστή ως 3D ετερογενής πυρηνογένεση.
- Ανάλογα με το σχήμα των εμβρύων που σχηματίζονται στο ξένο υπόστρωμα αναπτύσσονται σε 2 ή 3 διαστάσεις. Για παράδειγμα ένα φακοειδές έμβρυο αναπύσσεται σε 3 διαστάσεις ενώ ένα δισκοειδές σε 2.
- Η πυρηνογένεση σε ξένο υπόστρωμα μπορεί να είναι 2Δ ή 3Δ Αν το έμβρυο σχηματίζεται σε επίπεδη επιφάνεια (σχήμα σφαιρικού φακού) με γωνία διαβροχής ισορροπίας που ορίζεται μεταξύ 0 και π





$$\cos\theta = (\gamma_{sf} - \gamma_{cs})/\gamma_{cf} = m$$

$$\phi = (2+\cos\theta)(1-\cos\theta)^2/4$$

$$\Delta G'_{\text{crit}} = \phi \Delta G_{\text{crit}}$$

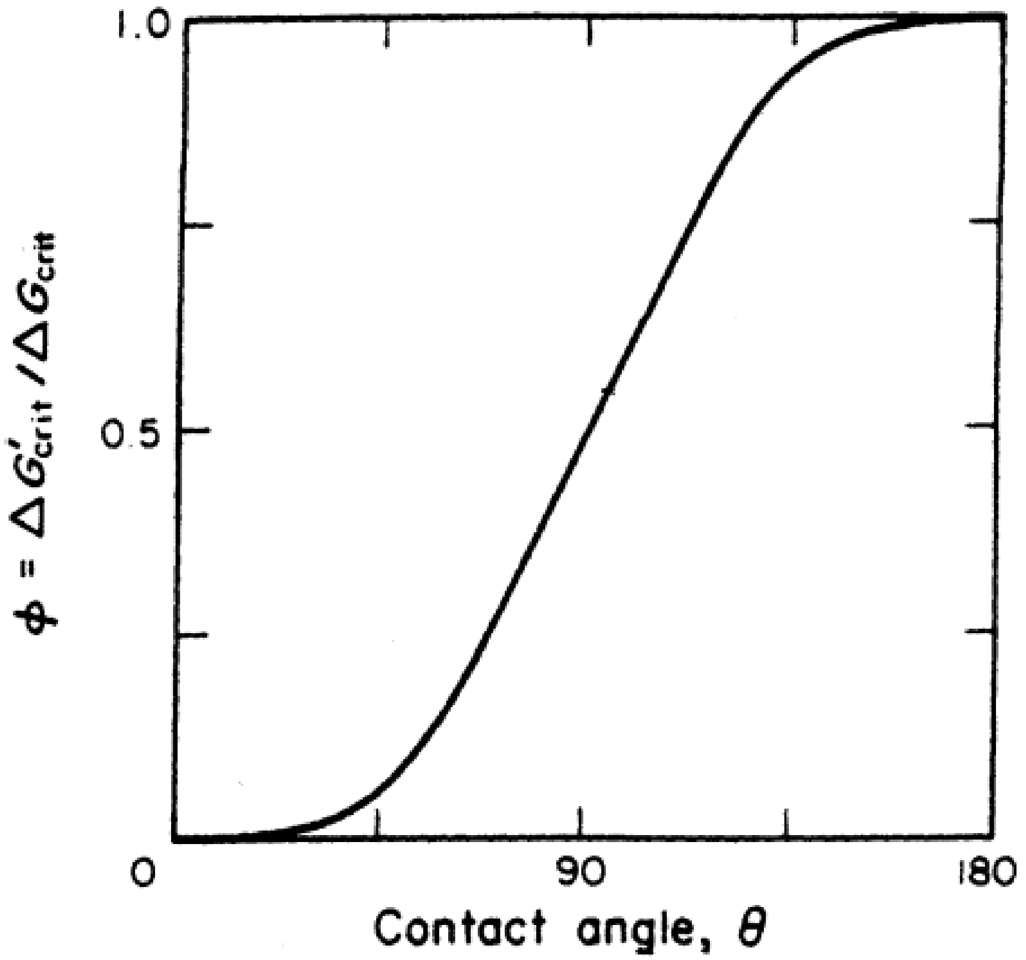


Figure 5.8. *Ratio of free energies of homogeneous and heterogeneous nucleation as a function of the contact angle*

Το φ παίρνει τιμές μεταξύ 0-1

Ανάλογα με την τιμή του $m = \cos\theta$, όπως φαίνεται στο προηγούμενο σχήμα (φ- m).

Για , $-1<m<1$ έχουμε ετερογενή πυρηνογένεση

Για $m=-1$ έχουμε ομογενή πυρηνογένεση

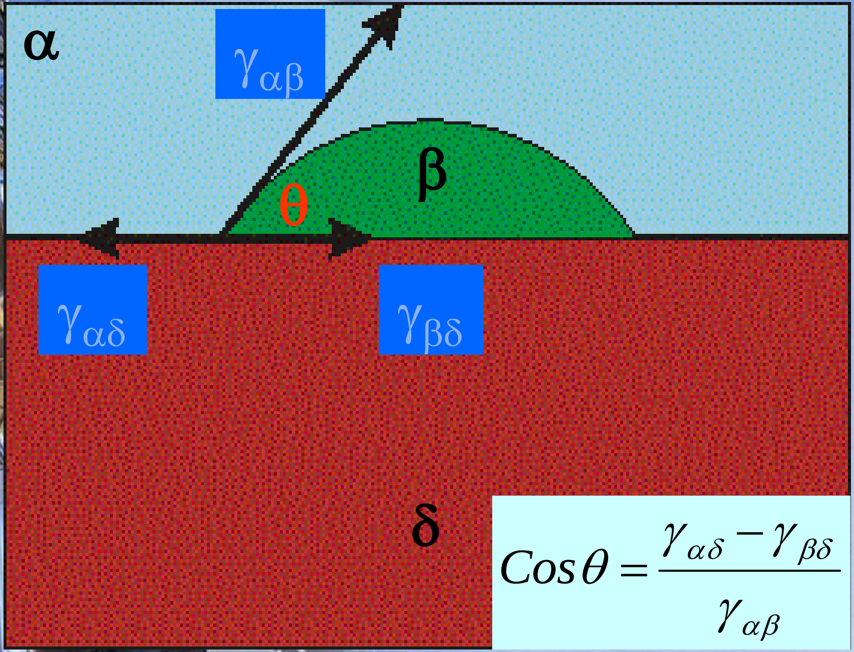
Για $\theta = 0$, $\varphi=0$

$\Theta=\pi/2$ $\varphi=1/2$ και για $\theta=\pi$ $\varphi= 1$.

Οι περιπτώσεις κατά τις οποίες $\theta = 0$ και $\theta = \pi$ αναφέρονται αντίστοιχα ως καταστάσεις πλήρους διαβροχής και πλήρους αδιαβροχοποίησης αντίστοιχα

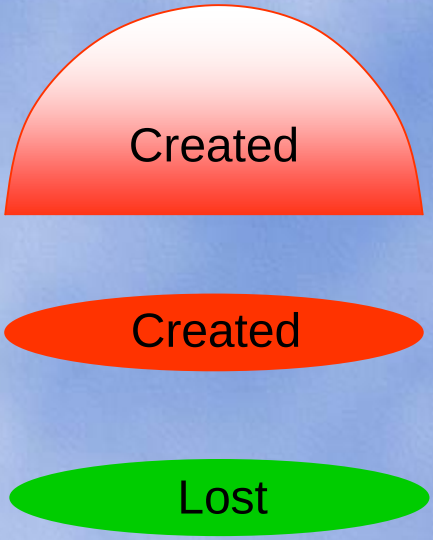
Heterogeneous nucleation

Consider the nucleation of β from α on a planar surface of inclusion δ



$$Cos\theta = \frac{\gamma_{\alpha\delta} - \gamma_{\beta\delta}}{\gamma_{\alpha\beta}}$$

Interfacial Energies



$A_{lens}\ \gamma_{\alpha\beta}$

$A_{circle}\ \gamma_{\beta\delta}$

$A_{circle}\ \gamma_{\alpha\delta}$

Surface tension force balance → $\gamma_{\alpha\beta} Cos\theta + \gamma_{\beta\delta} = \gamma_{\alpha\delta}$

$$\Delta G = (V_{lens})\Delta G_v + (A_{lens})\gamma_{\alpha\beta} + (A_{circle})\gamma_{\beta\delta} - (A_{circle})\gamma_{\alpha\delta}$$

$V_{lens} = \pi h^2(3r-h)/3$

$A_{lens} = 2\pi rh$

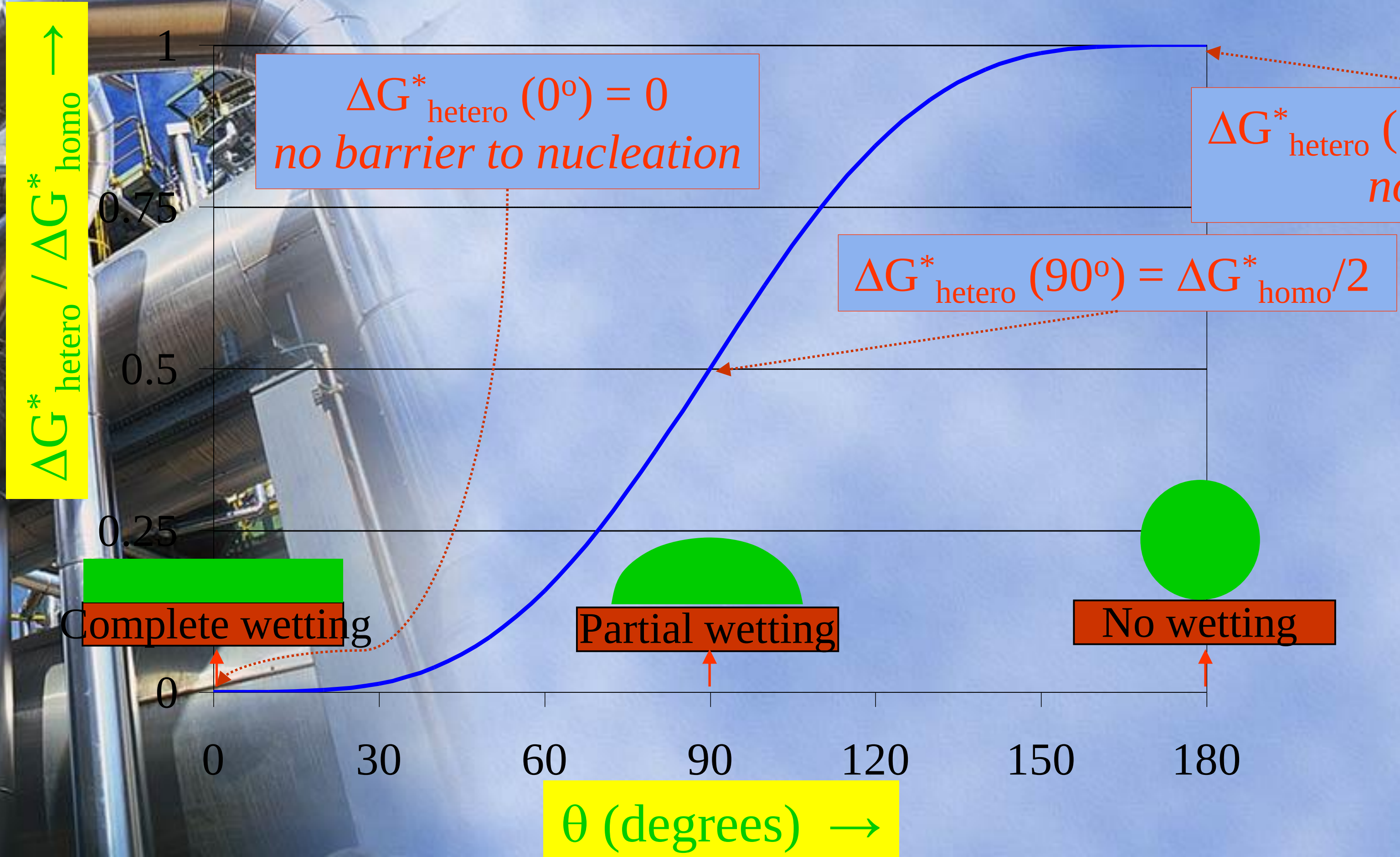
$h = (1-Cos\theta)r$

$r_{circle} = r\ Sin\theta$

$$\frac{d\Delta G}{dr} = 0 \Rightarrow r^{*}_{hetero} = -\frac{2\gamma_{\alpha\beta}}{\Delta G_v}$$

$$\Delta G^{*}_{hetero} = \frac{4}{3}\pi\frac{\gamma^{3}_{\alpha\beta}}{\Delta G^{2}_{v}}\left(2 - 3Cos\theta + Cos^{3}\theta\right)$$

$$\Delta G^{*}_{hetero} = \frac{1}{4}G^{*}_{homo}\left(2 - 3Cos\theta + Cos^{3}\theta\right)$$



ΔG^{*}_{hetero} (0°) = 0
no barrier to nucleation

ΔG^{*}_{hetero} (180°) = ΔG^{*}_{homo}
no benefit

ΔG^{*}_{hetero} (90°) = $\Delta G^{*}_{homo}/2$

$$Cos\theta = \frac{\gamma_{\alpha\delta} - \gamma_{\beta\delta}}{\gamma_{\alpha\beta}}$$

$$I_{\text{homo}} \propto I^{0}_{\text{homo}}\, e^{-\left(\frac{\Delta G^{*}_{\text{homo}}}{kT}\right)}$$

$$I_{\text{hetero}} \propto I^{0}_{\text{hetero}}\, e^{-\left(\frac{\Delta G^{*}_{\text{hetero}}}{kT}\right)}$$

= f(number of nucleation sites)

~ 10^{42}

= f(number of nucleation sites)

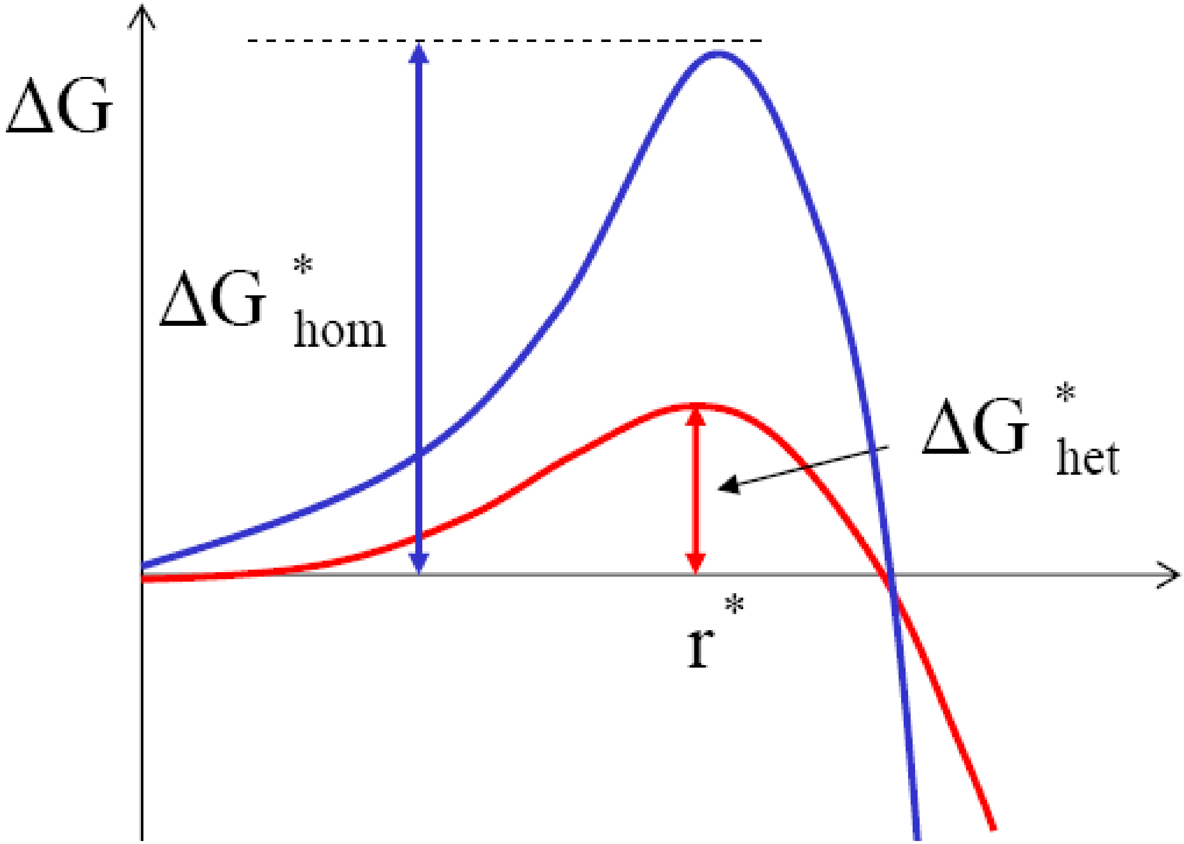
~ 10^{26}

BUT

the exponential term dominates

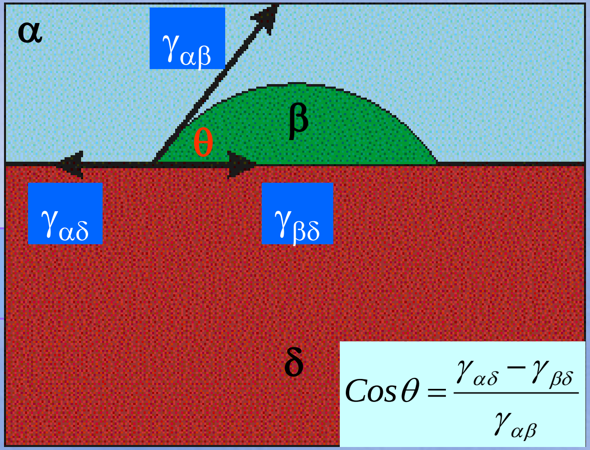
$I_{\text{hetero}} > I_{\text{homo}}$

$$r^{*} = \frac{2\gamma^{SL}}{\Delta G_{v}} \qquad \Delta G^{*}_{het} = S(\theta)\Delta G^{*}_{hom}$$



heterogeneous nucleation starts at a lower undercooling

Choice of heterogeneous nucleating agent



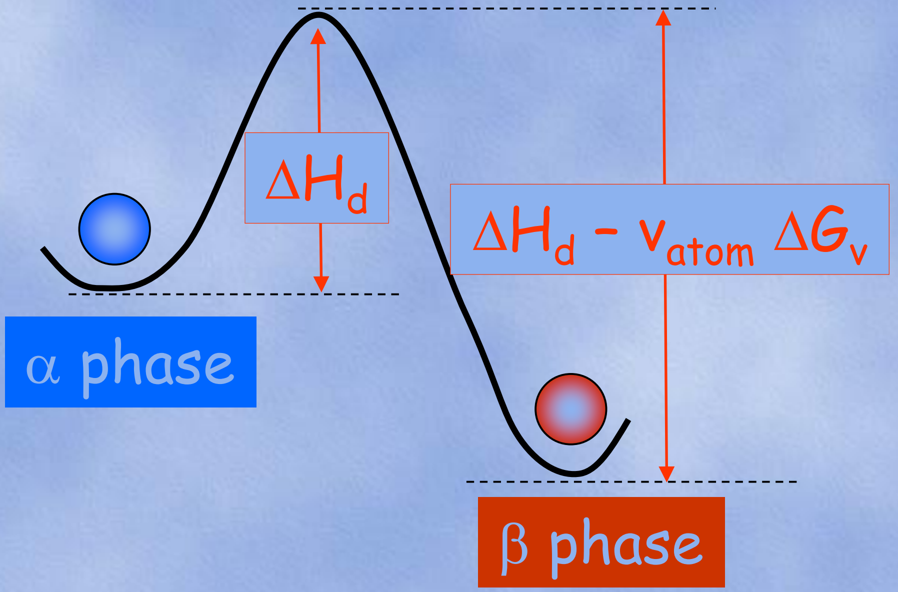
$$Cos\,\theta = \frac{\gamma_{\alpha\delta} - \gamma_{\beta\delta}}{\gamma_{\alpha\beta}}$$

- Small value of θ
- Choosing a nucleating agent with a low value of $\gamma_{\beta\delta}$ (low energy $\beta\delta$ interface)
- (Actually the value of $(\gamma_{\alpha\delta} - \gamma_{\beta\delta})$ will determine the effectiveness of the heterogeneous nucleating agent → high $\gamma_{\alpha\delta}$ or low $\gamma_{\beta\delta}$)
- low value of $\gamma_{\beta\delta}$ →
  Crystal structure of β and δ are similar and lattice parameters are as close as possible
- Seeding rain-bearing clouds → AgI or NaCl → nucleation of ice crystals
- Ni (FCC, a = 3.52 Å) is used a heterogeneous nucleating agent in the production of artificial diamonds (FCC, a = 3.57 Å) from graphite

Trasformation $\alpha \rightarrow \beta$ = Nucleation of β phase + Growth till α is exhausted

Growth

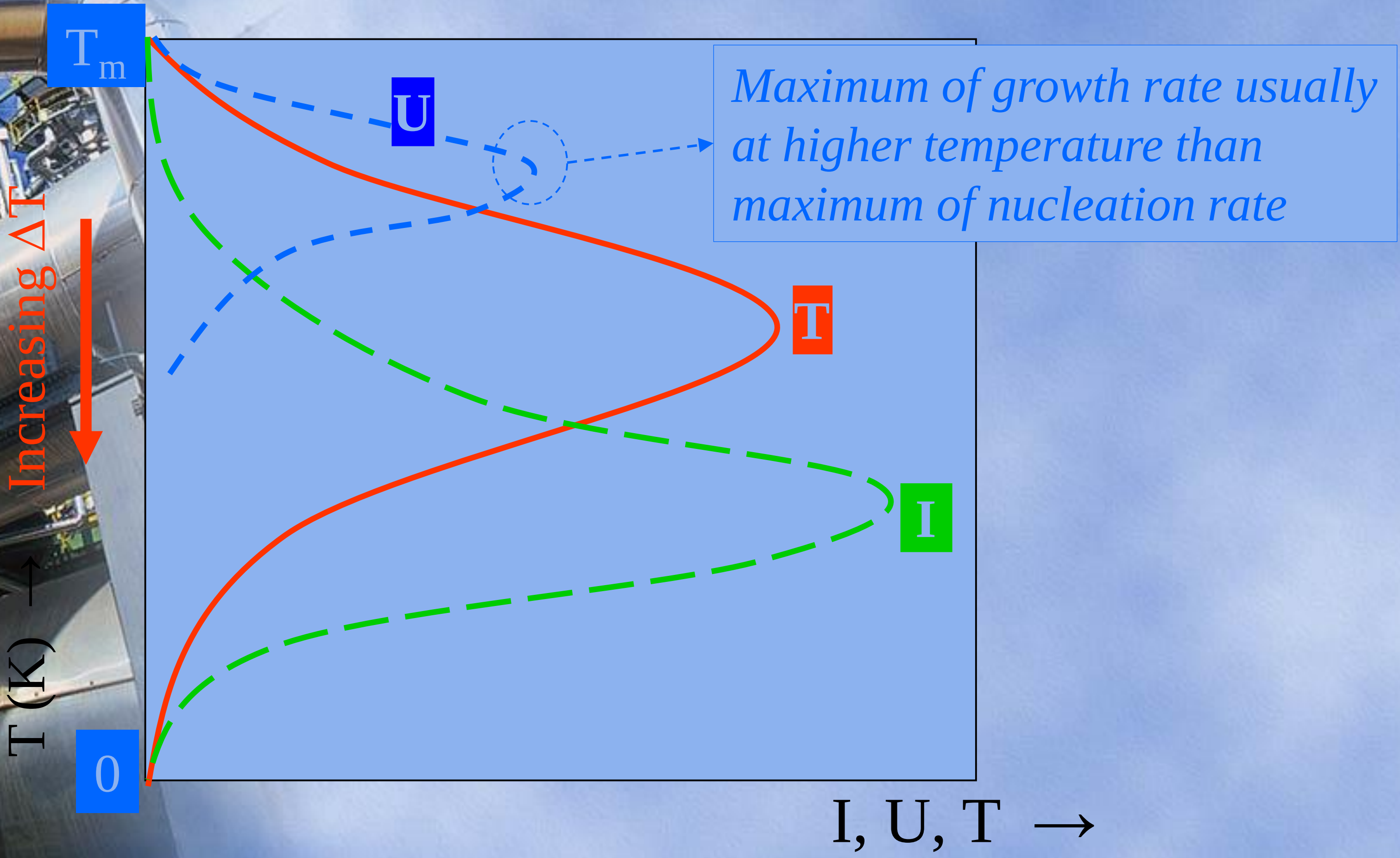
- At transformation temperature the probability of jump of atom from $\alpha \rightarrow \beta$ (across the interface) is same as the reverse jump
- Growth proceeds below the transformation temperature, wherein the activation barrier for the reverse jump is higher



Transformation rate = f(Nucleation rate, Growthrate)

$$\boxed{T} = \frac{dX_{\beta}}{dt} = f(\boxed{I}, \boxed{U})$$

$$X_{\beta} = 1 - e^{-\left(\frac{\pi I U^{3} t^{4}}{3}\right)}$$

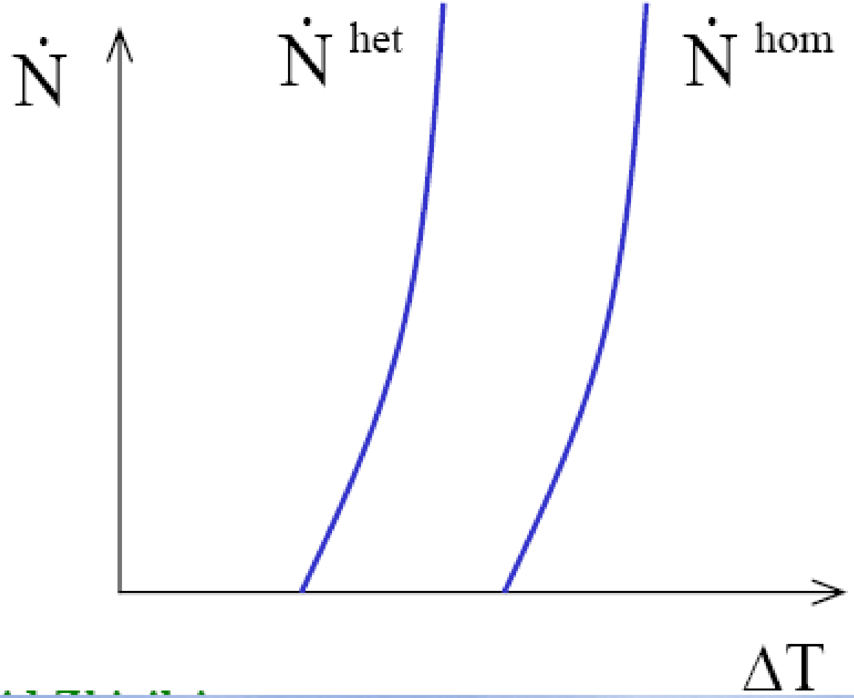


Maximum of growth rate usually at higher temperature than maximum of nucleation rate

$$\dot{N}^{hom} \sim \exp\left(-\frac{\Delta G^{*}_{hom}}{kT}\right)$$

$$\dot{N}^{het} \sim \exp\left(-\frac{\Delta G^{*}_{het}}{kT}\right)$$

$$\dot{N}^{het} >> \dot{N}^{hom}$$



Microphysics of Cold Clouds

If a cloud extends above the *freezing level* (0°C level) it is called a *cold cloud*.

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Even though the temperature may be below 0°C, water droplets can still exist in clouds, in which case they are referred to as *supercooled droplets*.

Microphysics of Cold Clouds

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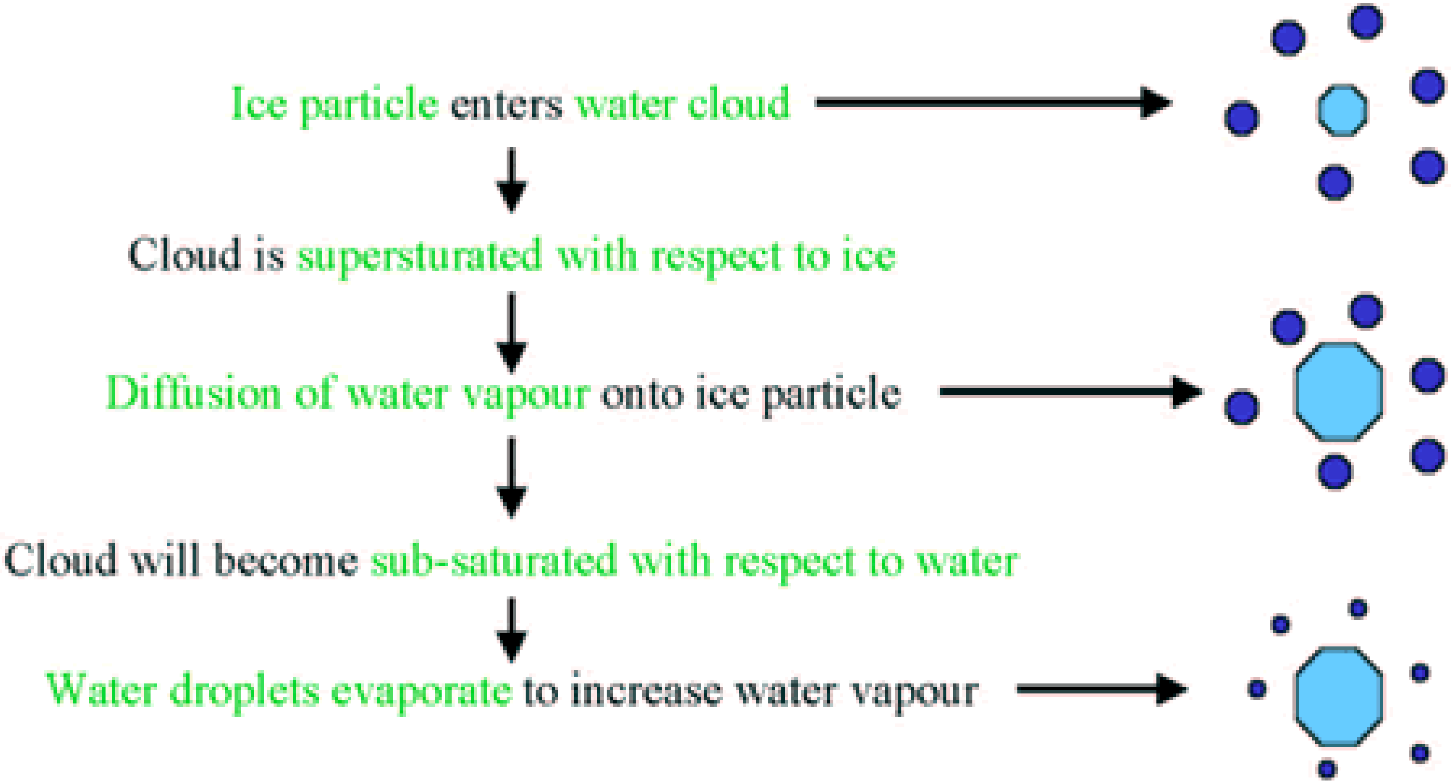
Even though the temperature may be below 0°C, water droplets can still exist in clouds, in which case they are referred to as *supercooled droplets*.

Cold clouds may also contain ice particles. If a cold cloud contains both ice particles and supercooled droplets it is said to be a *mixed cloud*.

In this section we are concerned with the origins and concentrations of ice particles in clouds, the ways ice particles grow, and the formation of precipitation in cold clouds.

Bergeron process



Ice particle enters water cloud →

↓

Cloud is supersturated with respect to ice

↓

Diffusion of water vapour onto ice particle →

↓

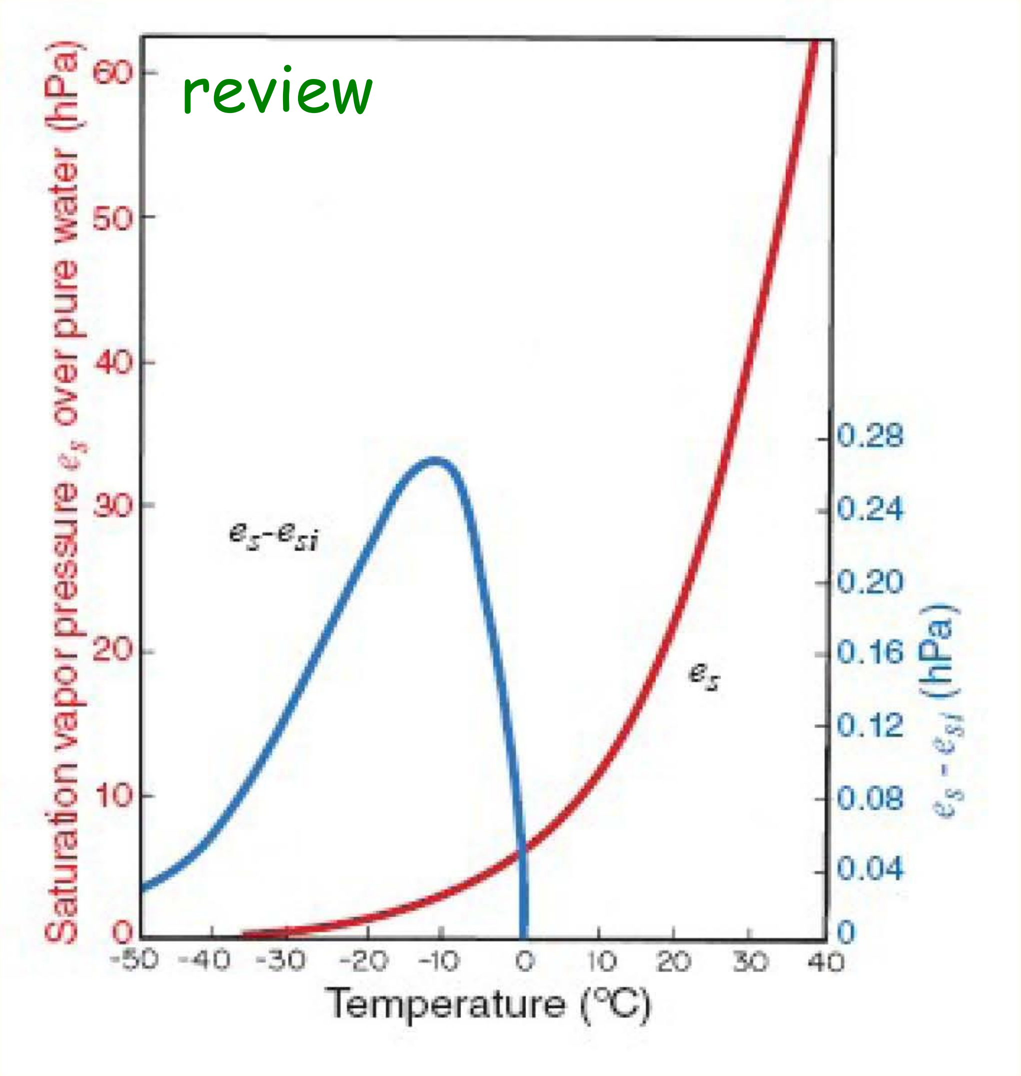
Cloud will become sub-saturated with respect to water

↓

Water droplets evaporate to increase water vapour →

Ice particles grow at the expense of water droplets

Bergeron-Findeisen Process



Saturation vapour pressure over water (Red) and the difference between the saturation pressures over water and over ice (Blue).

Ice Clouds: Nucleation and Growth

- Nucleation
  - Homogeneous, heterogeneous, ice nuclei
  - Habits (shapes)

Sources: Steve Platnick

Ice Clouds: Nucleation and Growth

- Nucleation

  - Homogeneous, heterogeneous, ice nuclei
  - Habits (shapes)

- Ice crystal growth

  - Growth from vapor (diffusion)
  - Bergeron process (growth at expense of water droplets)
  - Ice multiplication process
  - Collision/coalescence (riming, aggregation)

- Size distributions

  - Microphysical measurements, temperature dependencies

Ice Clouds – Nucleation

- Some nucleation pathways
  - Homogeneous freezing of solution droplets (w/out assistance of aerosol particles)

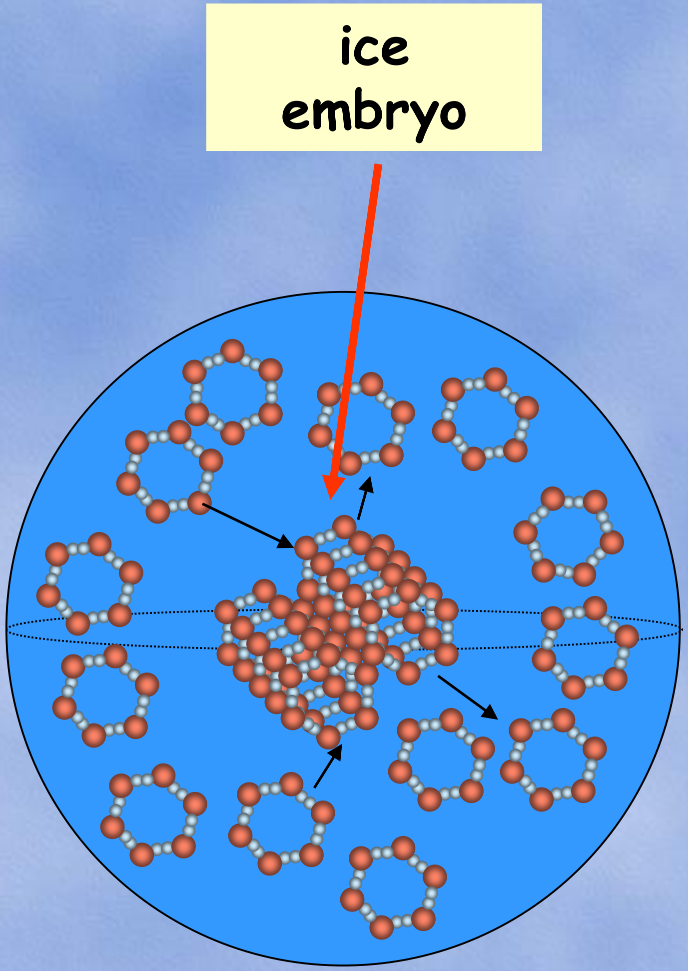
    requires very cold temperatures (~ -40 C and below)

  - Heterogeneous freezing (via aerosol particles that may or may not contain/be imbedded in water). Ice nuclei not well understood.
    - Contact freezing (ice nuclei contact with solution droplet)
    - Deposition on ice nuclei

reference: P. Demott, p. 102, "Cirrus", Oxford Univ Press, 2002; Rogers and Yau, "A short course in cloud physics".

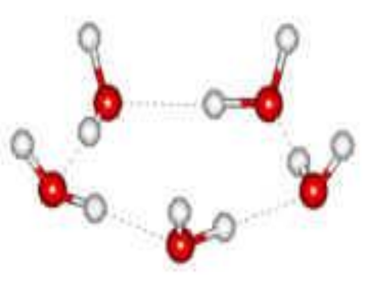
Homogeneous Freezing - conceptual schematic

- Water molecules arrange themselves into a lattice.
- Embryo grows by chance aggregation .
- Ice nucleus cluster number/concentrations are in constant flux
  - in equilibrium, molecular clusters in Boltzmann distribution
- Chance aggregation number/concentrations increases with decreasing temperature.



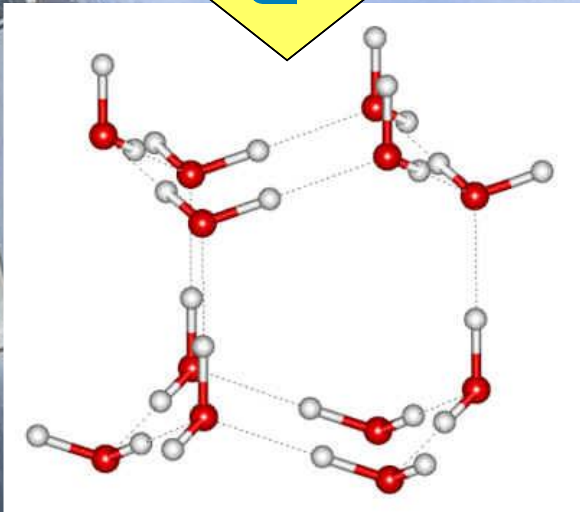
Ice Molecules Arranged in Lattice

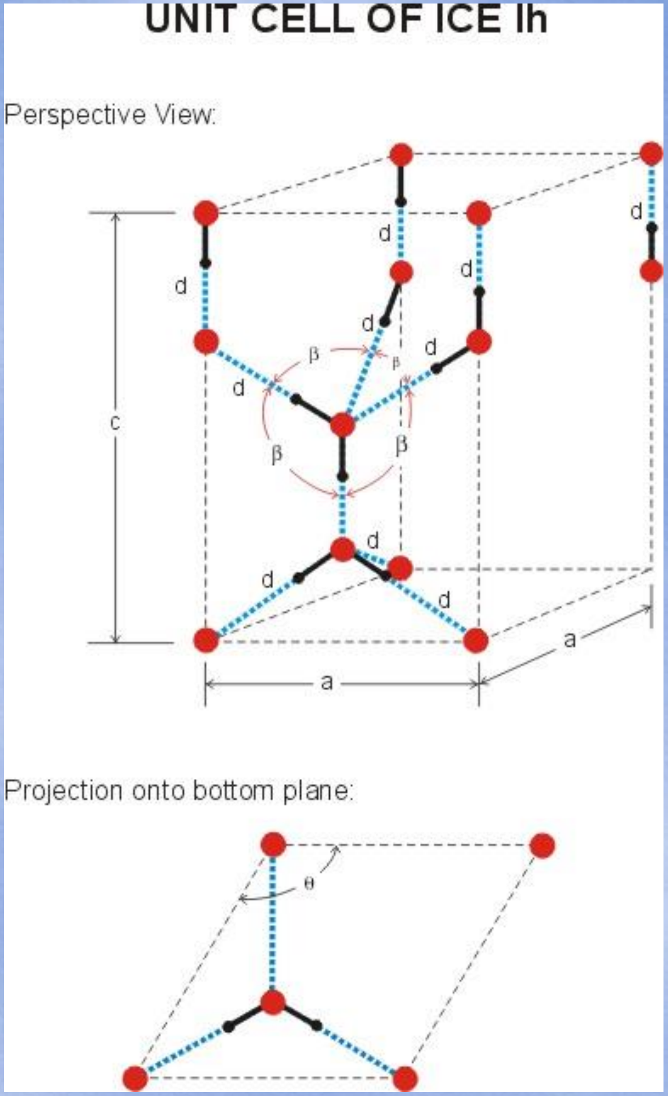
Liquid water



Freezing

Ice





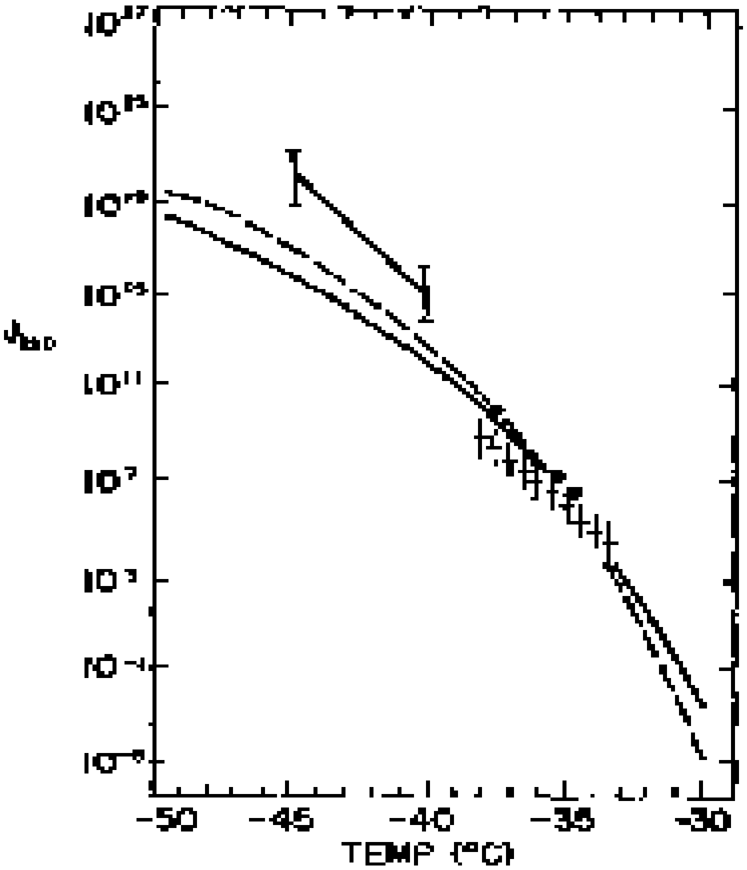


Figure 8.3: Homogeneous freezing nucleation rate of pure water J_{Ls0} ($cm^{-3}s^{-1}$) verses temperature. Various estimates shown include experimental data from DeMott and Rogers (1990) (crosses) and Hagen et al. (1981) (bars), field data from Sassen and Dodd (1988) (solid circles), and theoretical approximations from DeMott and Rogers (1990) (solid line) and Heymsfield and Sabin (1989) (dashed). [From DeMott et al., 1994.]

Ice Clouds – Heterogeneous Nucleation

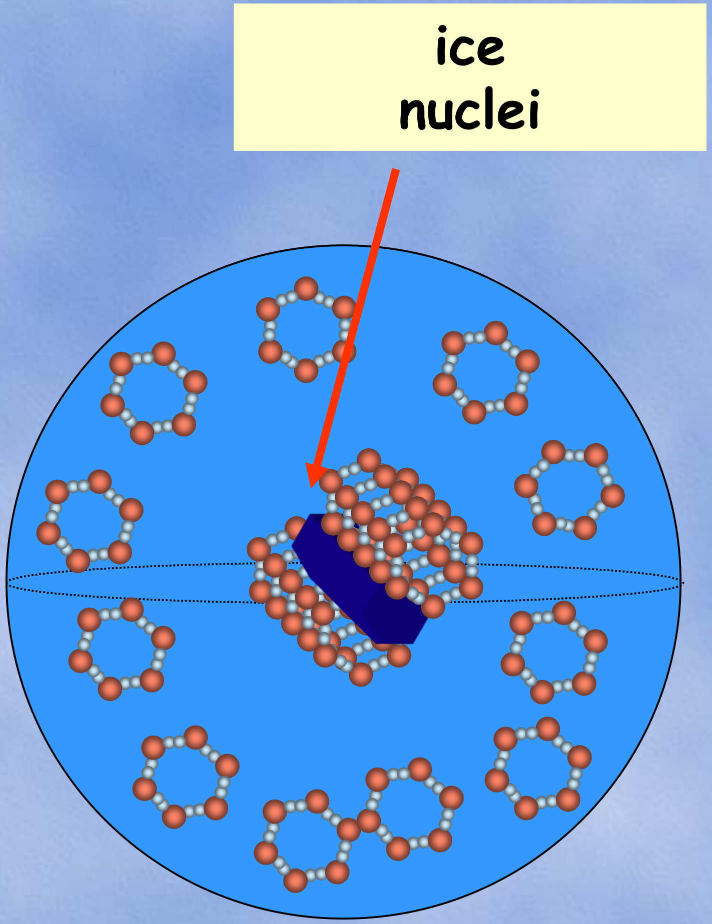
- Overview

  - **Vapor deposition** directly to aerosol particle (insoluble or perhaps dry soluble particles).
  - **Contact freezing:** particle collides with water droplet
  - **Condensation freezing:** from mixed aerosol particle (soluble component of particle initiates condensation, insoluble component causes freezing instantly)
  - **Immersion freezing**: same as above but insoluble particle causes freezing at a later time, e.g., at a colder temperature (but at temperatures greater than for homogeneous freezing)
  - Theoretical basis less certain than for homogeneous freezing.

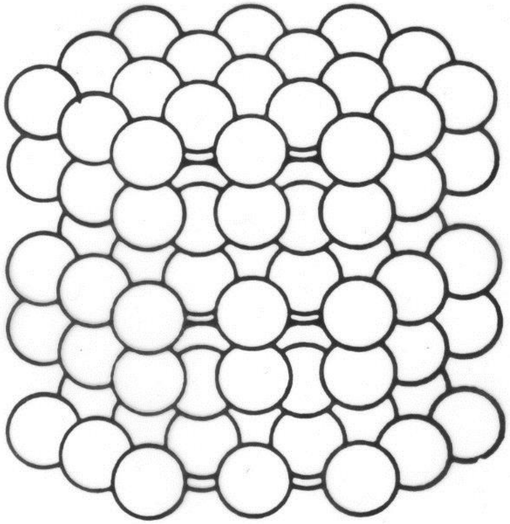
- Ice nuclei
  - minerals (clay), organic material (bacteria), soot, pure substances (AgI)
  - Deposition requires high supersaturation w.r.t. ice (e.g., 20% for AgI at -60 C, *Detwiler & Vonnegut,* 1981).

Heterogeneous Freezing - conceptual schematic

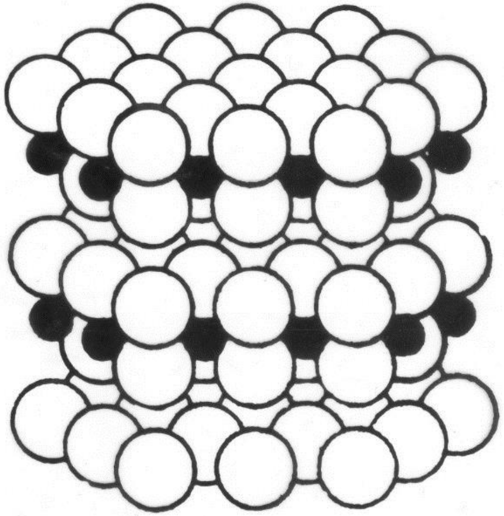
- Freezing is aided by foreign substances, ice nuclei
- Ice nuclei provide a surface for liquid water to form ice structure
- Ice embryo starts at a larger size
- Freezing occurs at warmer temperatures than for homogeneous freezing



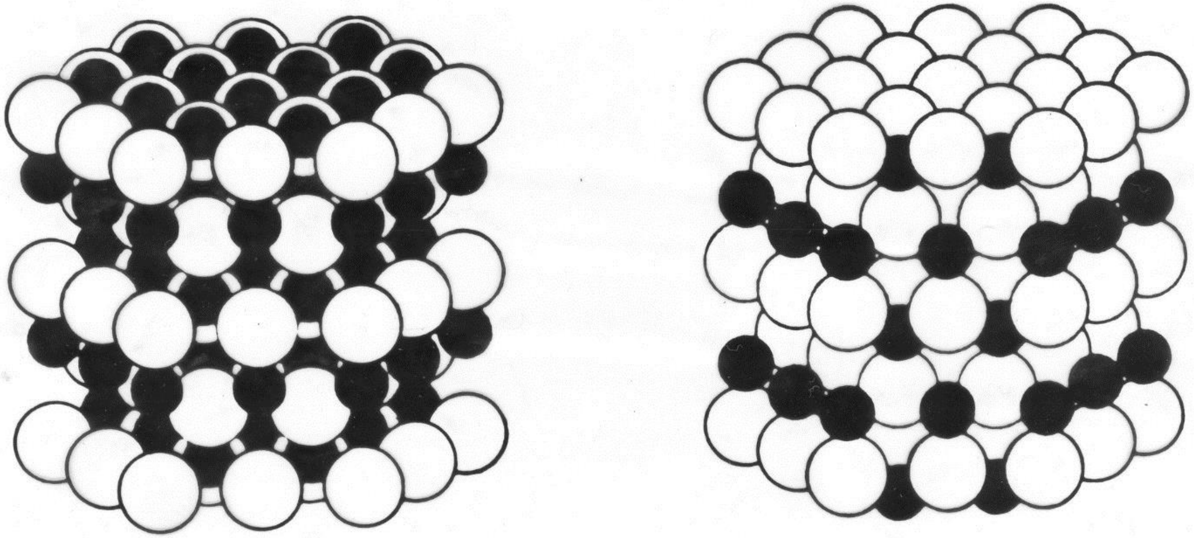
- Vonnegut (1947): Material should have crystal properties similar to ice.
  - AgI (Silver iodide)
  - PbI_2 (Lead iodide)
- Experiment: Introduce AgI and PbI_2 into super-cooled clouds.
  - PbI_2 worked well, AgI not so well.
  - Soluble salt fouled up AgI, cleaner sample better.
  - Making AgI smoke did better yet!
- Fukuta (1958): Found 78 inorganic materials effective at temperatures > -20° C.



Ice



Lead iodide



Silver iodide

AgI

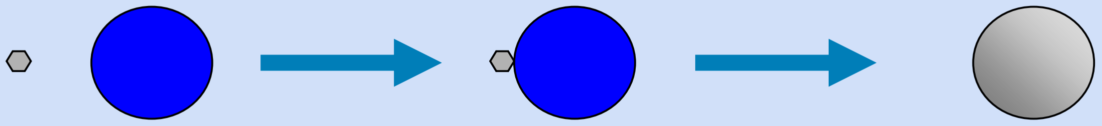
- AgI widely used in cloud seeding
  - Studied extensively
- Reynolds (1951): AgI less effective after surface changes caused by photo-decomposition in sunlight.
- Corrin, et al. (1967): Pure AgI less efficient than AgI containing hygroscopic impurities.
- Edwards and Evans (1960, 1968):
  - AgI works better as freezing nuclei than deposition nuclei.

Observations

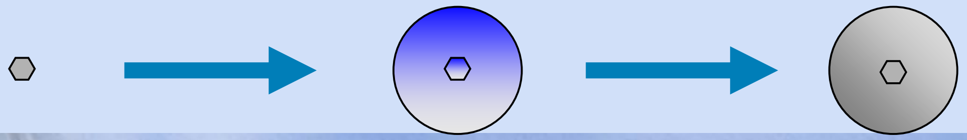
- Organic nuclei can be ice nuclei.
  - Large number found that work at temps near 0° C.
- Kaolinite - most common atmospheric ice nuclei
  - mineral
  - found in many soil types
- Remark: Ice crystals that have been evaporated (sublimated) can grow into another crystal at higher temperatures than original.
  - Trained nuclei
  - Present with evaporation of cirrus clouds.

Heterogeneous Freezing - conceptual schematic

- Contact
  - Water droplet freezes instantaneously upon contact with ice nuclei

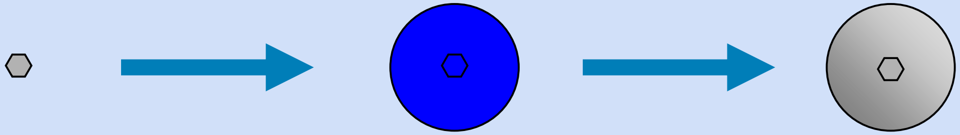


- Condensation followed by instantaneous freezing
  - Nuclei acts as CCN, then insoluble component freezes droplet

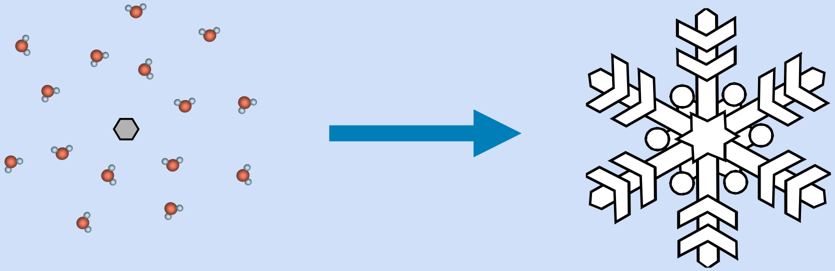


Heterogeneous Freezing - conceptual schematic

- Immersion
  - Ice nuclei causes freezing sometime after becoming embedded within droplet



- Deposition
  - Ice forms directly from vapor phase



(a) *Growth from the vapour phase.*

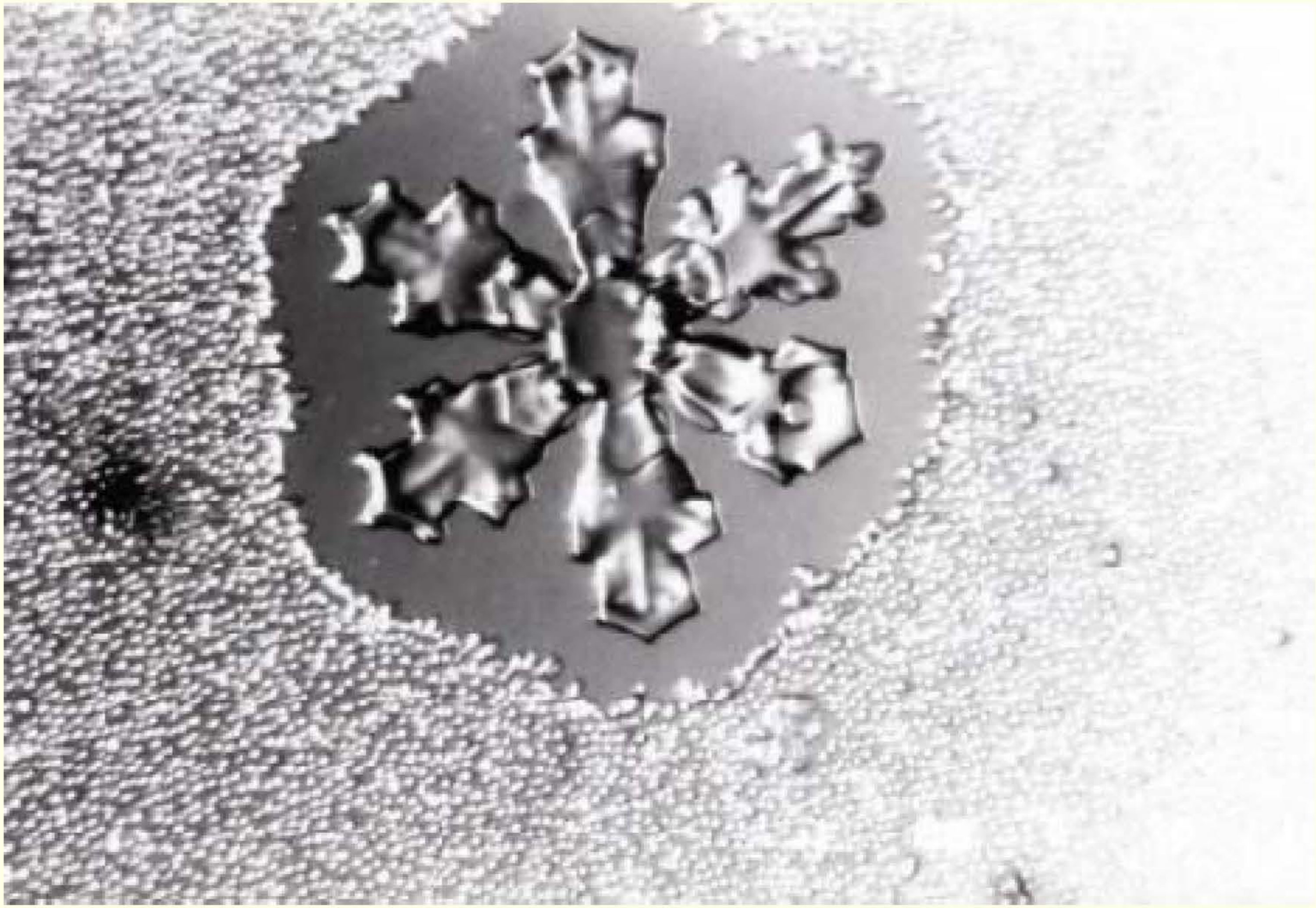
In a mixed cloud dominated by supercooled droplets, the air is close to saturated with respect to liquid water and is therefore *supersaturated with respect to ice*.

For example, air saturated with respect to liquid water at -10°C is supersaturated with respect to ice by 10%.

This value is much higher than the supersaturation of cloudy air with respect to liquid water, which rarely exceed 1%.

Consequently, in mixed clouds dominated by supercooled water droplets, in which the cloudy air is close to water saturation, *ice particles will grow from the vapour phase much more rapidly than droplets*.

In fact, if a growing ice particle lowers the vapour pressure in its vicinity below water saturation, adjacent droplets will evaporate (Figure below).



Laboratory demonstration of the growth of an ice crystal at the expense of surrounding supercooled water drops.

New nuclei, during heterogeneous nucleation may be formed from embryos which are enclosed in cavities of the substrate

These embryos would not have been stable on flat surfaces

The maximum diameter of a cylindrical cavity which could hold a stable embryo is (Turnbull, 1950):

$$d_{\max} = \frac{4\gamma_{\mathrm{cl}} \cos\theta}{\Delta G_v}$$

Embryos may function as seeds for a new phase provided that:

$$d_{\max} \geq 2r_{\mathrm{c}}$$

The Metastable Zone Width

- In homogeneous systems the nuclei of the new phase are formed as soon as the system is supersaturated.
- This state may be stable (metastableς) and the system may stay at this state for practically infinite time periods
- The new phase may be nucleated past a time period (induction time) depending onT, P, the presence of impurities and from mechanical disturbances
- Nucleation is facilitated through the introduction of seed crystals and from high supersaturation values.
- There is a supersaturation limit in which the new hase forms spontaneously and instantaneously.
- This supersaturation value is **the upper limit of the metastable equilibrium** and defines ***the width of the metastable zone (MZW)***

Secondary Nucleation

- Nucleation is easier in the presence of crystallites
- KBr (Gyulai, 1948)
- Sucrose (Powers 1963)
- Generation of crystals because of fluid mechanical shear

Sung, Estrin and Youngquist (1973)

Fluid mechanical shear in crystallizers induced by stirrers

Strickland-Constable (1968)

Development of new nuclei from the powder accompanying seed crystals

Breakages

Collisions

Contact nucleation

Clontz and McCabe (1971)

- $MgSO_4 \cdot 7H_2O$
- The fast growing crystal faces contained fewer nuclei in comparison with the faster growing faces
- Correlation between crystal growth and secondary nucleation
- Broken crystals (produced from energy input and collisions) are in semi-glass state. Grow slower
- Distribution of crystal growth rates
- New nuclei may be formed because of internal stresses in the crystals

Seed crystals

- The best method to induce crystallization (particle size and shape control)
- Seeds are not necessarily crystals of the crystallizing substance
- AgI-ice
- Crystal compatibility or similarity not unique criteria

Pseudomonas syringae, **ice**

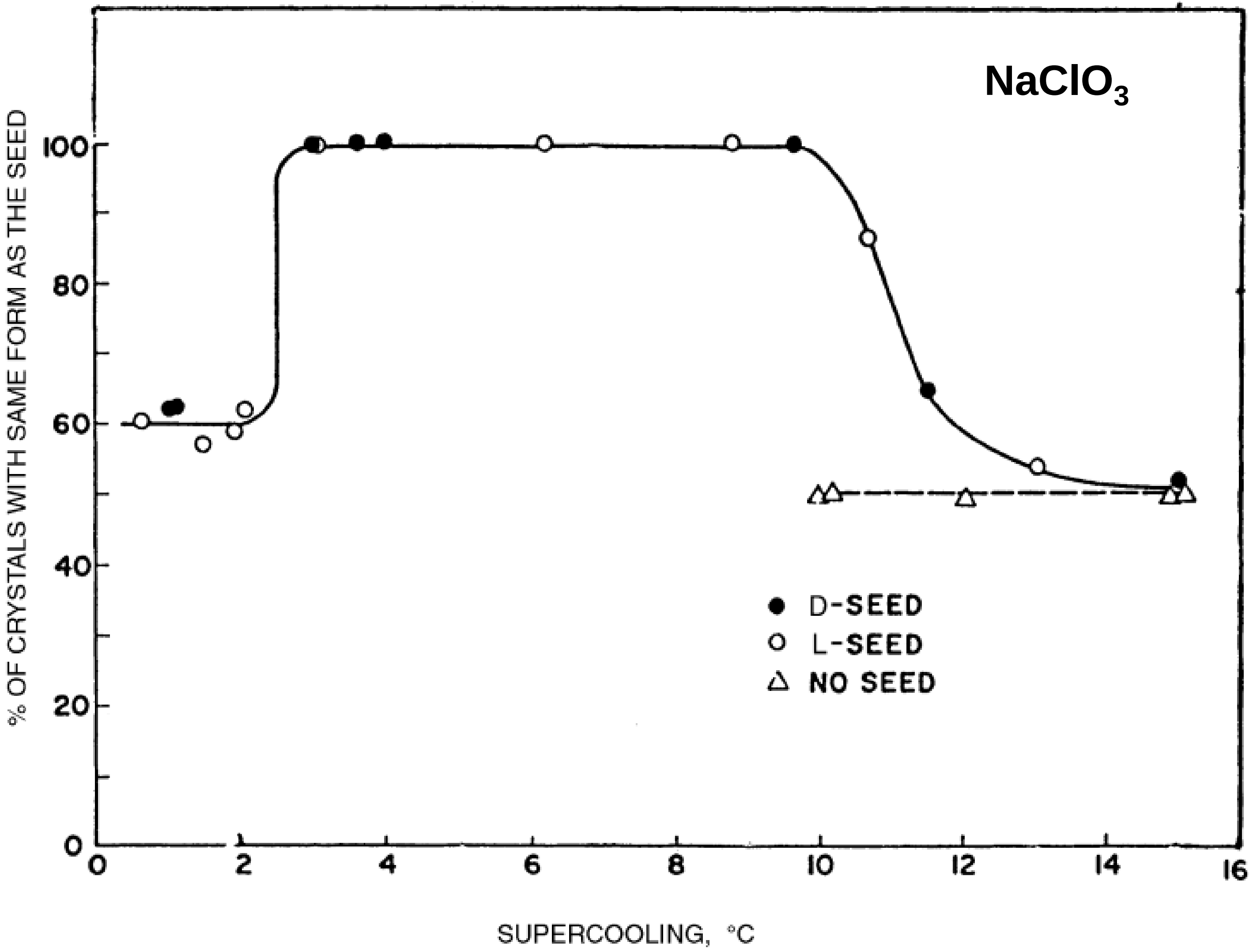


Figure 5.9. *Seeded nucleation of sodium chlorate enantiomorphs in non-agitated solution. (After Denk and Botsaris, 1972)*

Introduction of seeds by chance

- Xylitol (1895 liquid)
- 1941..solid mp 61°C 1943 another solid mp 93 °C..
- Benzophenone and sugars mellibiose, levulose, and turanose were liquids now, they aare produced as solids.
- Monocrystals of piezocrystals of anhydrous ethylenediamine tartrate were found following years of production as liquids
- Ampicillin (anhydrous or trihydrate):After several years was found as monohydrate as well

Δευτερογενής Πυρηνογένεση (Secondary nucleation)

Definition : Formation of new crystals in the presence of crystals of the same type («parent") in stirred supersaturated solutions

- ❖ Secondary nucleation depends on the properties of the mother crystals but also from the operational parameters of the crystallizer
- ❖ Takes place at low supersaturation values (at conditions in which , primary nucleation is impossible)

- ❖ In continuous industrial crystallizers, nucleation is for the most part secondary

Secondary nucleation

(continued)

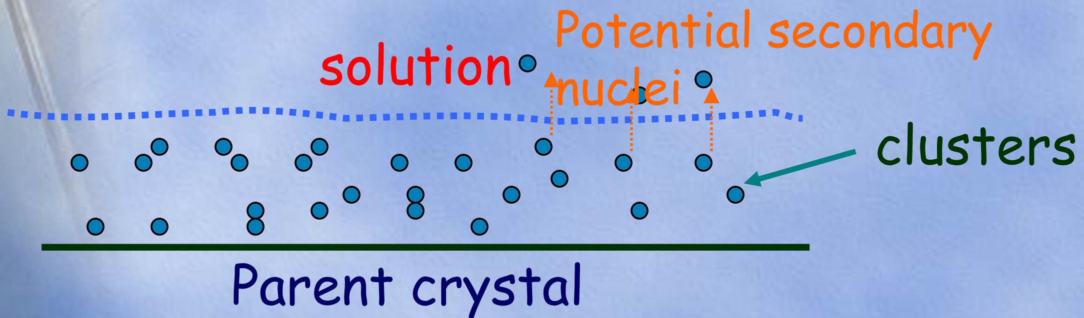
Mechanisms of secondary nucleation :

- **initial breeding** : release into the solution of small particles of crystalline dust

- **contact nucleation** :

crystal-wall
The shocks crystal-stirrer produce new fragments (nuclei)
crystal-crystal

- **"true" secondary nucleation** : the layer adjacent to the parent crystal surface acts as a stock of nuclei liable to be released



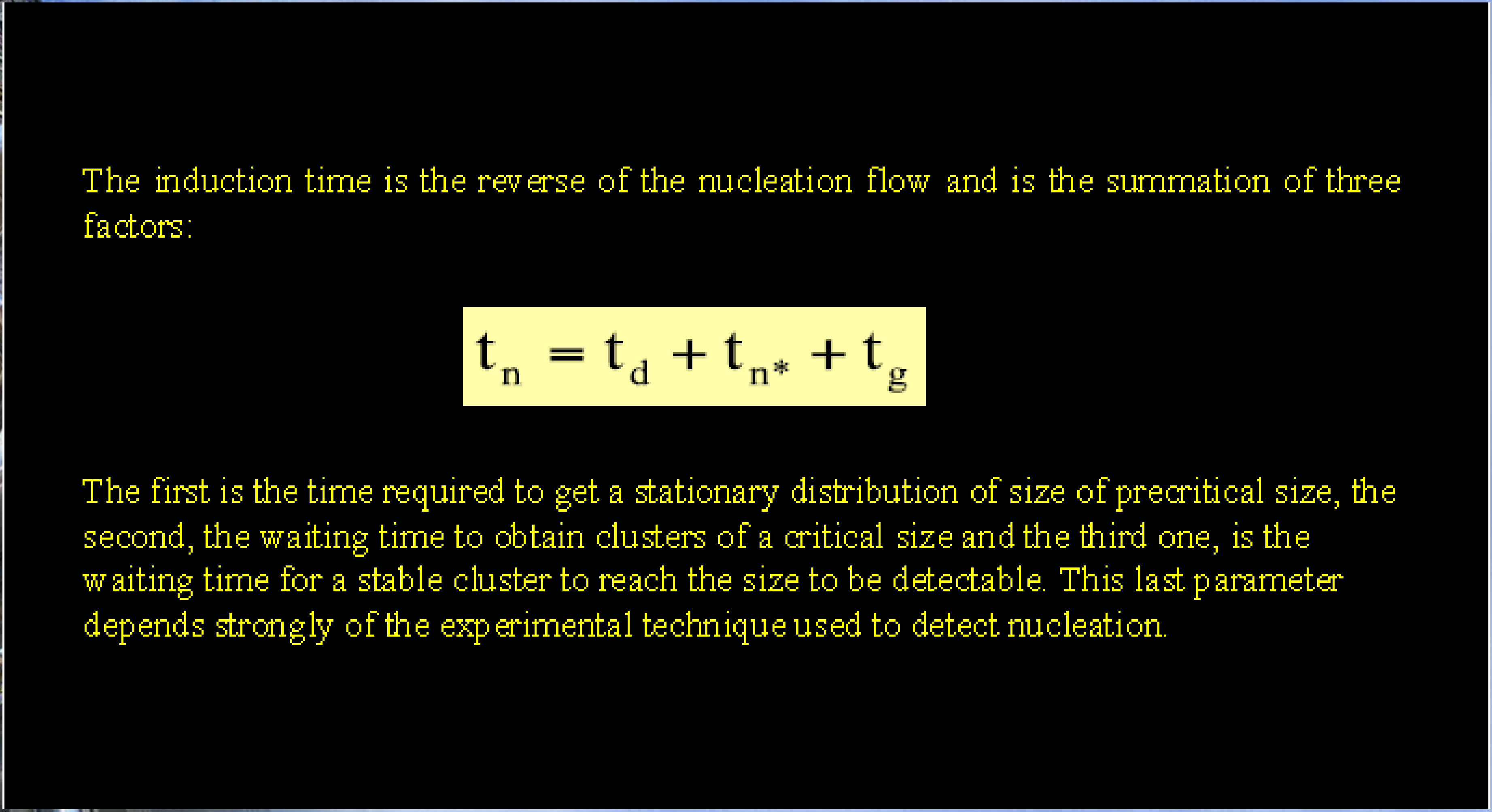
Rate of secondary nucleation :

❖ The nuclei production rate depends on :
- the input power of the stirring device
- the concentration in solid of the suspension
- the supersaturation

❖ Only empirical laws : $B_{II} = k\, s^{b}\, S^{j}\, w^{d}$

❖ B_{II} : number of nuclei produced per unit volume and time
s : supersaturation level, w : stirrer rotation rate ; S, surface area of the parent crystals, with b = 0.5 - 2.5 ; j = 1 ; d = 0 - 8 (2 - 4)

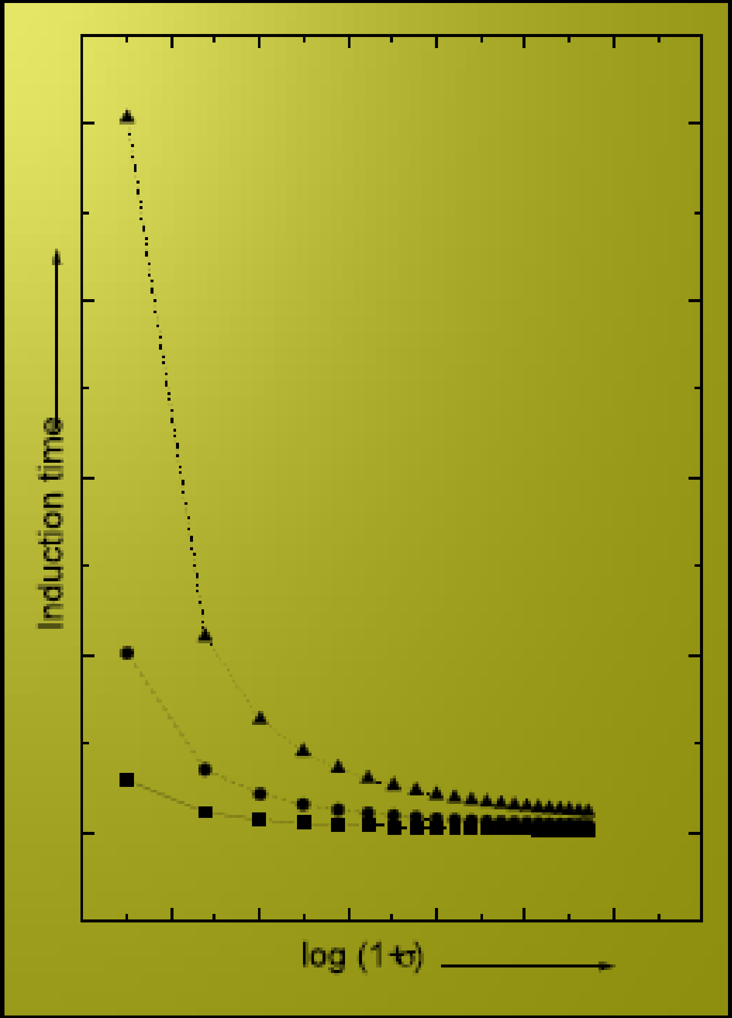
Η περίοδος εκκόλαψης (ή χρόνος επαγωγής- induction time)



The induction time is the reverse of the nucleation flow and is the summation of three factors:

$$t_n = t_d + t_{n*} + t_g$$

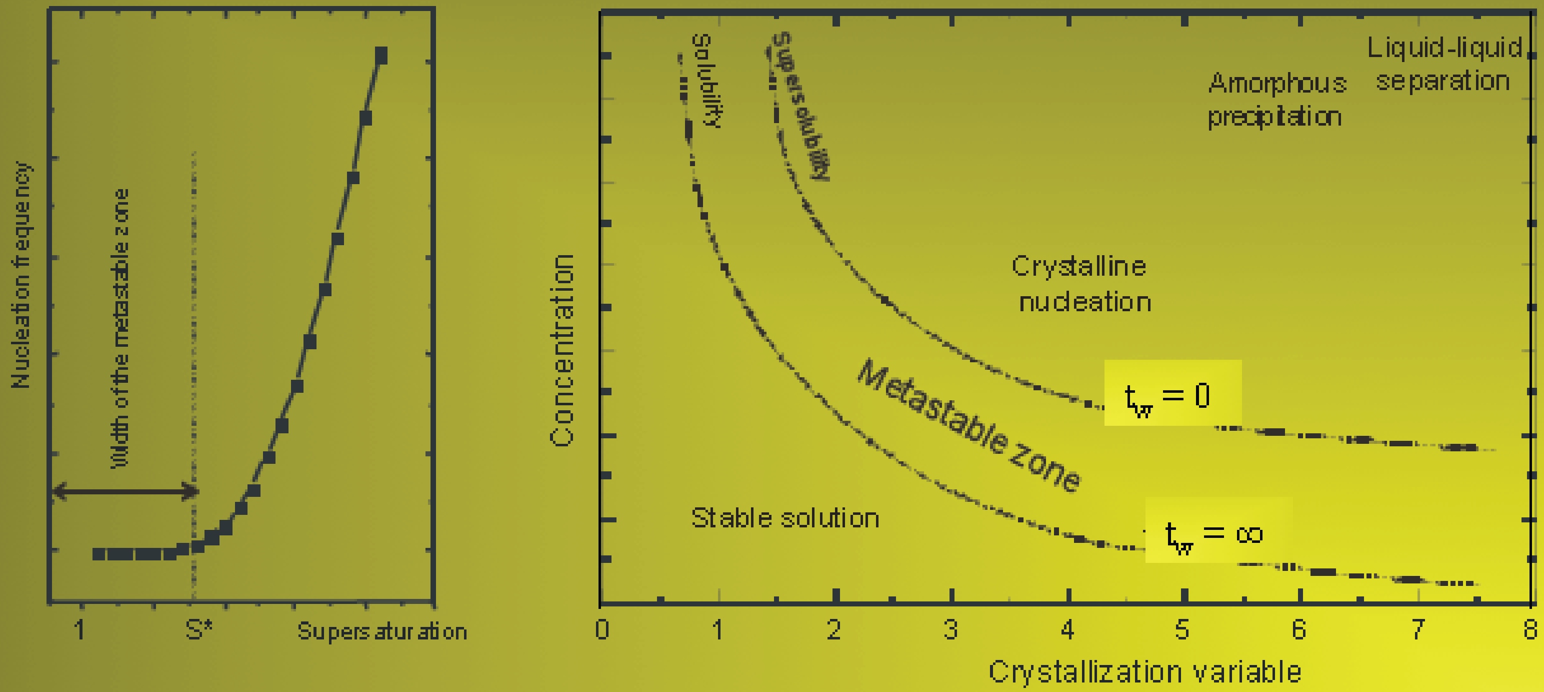
The first is the time required to get a stationary distribution of size of precritical size, the second, the waiting time to obtain clusters of a critical size and the third one, is the waiting time for a stable cluster to reach the size to be detectable. This last parameter depends strongly of the experimental technique used to detect nucleation.



$$t_N = \frac{\kappa^{te}}{J_N} = \kappa_1 \exp\left(\frac{\kappa_2}{T^3 \ln(1+\sigma)^2}\right)$$

$t = 1/J$

Nucleation is a probablistic phenomenon



Metastable Zone Width

- Nucleation is in fact rather heterogeneous than homogeneous

$$J = k_{\mathrm{n}} \Delta c_{\mathrm{max}}^{n}$$

Δc_{max} maximum possible supersaturation or metastable zone width (MZW)

$$J = q\dot{\theta}$$

$$\text{where } \dot{\theta} = -\mathrm{d}\theta/\mathrm{d}t$$

q mass of the crystalline substance deposited per unit mass of the solvent upon cooling of the solution by 1°C

$$q = \varepsilon \frac{\mathrm{d}c^*}{\mathrm{d}\theta}$$

$$\varepsilon = R/[1 - c(R - 1)]^2$$

R the ratio of MW of the hydrate to the anhydrous substance

C concentration expressed as mole of anhydrous dissolved compound per unit mass of solvent

$$\Delta c_{\max} = \left(\frac{\mathrm{d}c^*}{\mathrm{d}\theta}\right)\Delta\theta_{\max}$$

$$\varepsilon\left(\frac{\mathrm{d}c^*}{\mathrm{d}\theta}\right)\dot{\theta} = k_{\mathrm{n}}\left[\left(\frac{\mathrm{d}c^*}{\mathrm{d}\theta}\right)\Delta\theta_{\max}\right]^n$$

Or taking logs

$$\log\dot{\theta} = (n - 1)\log\left(\frac{\mathrm{d}c^*}{\mathrm{d}\theta}\right) - \log\varepsilon + \log k_{\mathrm{n}} + n\log\Delta\theta_{\max} \quad \text{(I)}$$

The nuclei are not detected as soon as they reach critical size, but when they reach a detectable size (e.g. 10μ) both nucleation and crystal growth have taken place

The slope of the previous linear relationship is not n but

(3g+4+n)/4 Nyvlt (1983)

$$\frac{dm}{dt} = K_G A (c - c^*)^g$$

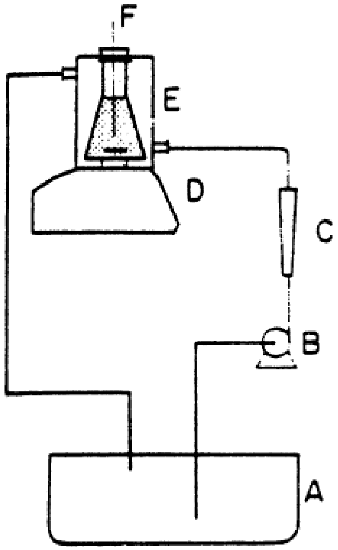
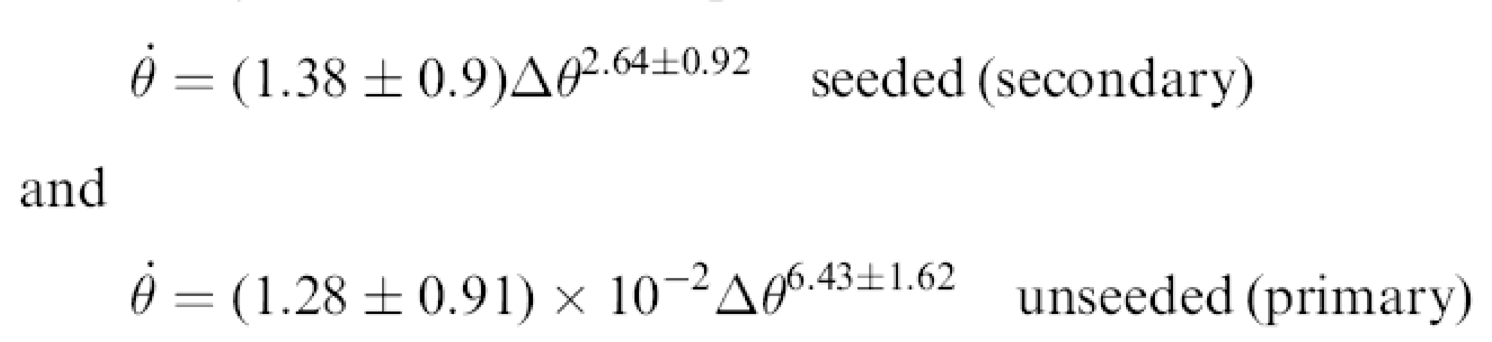


Figure 5.10. *Apparatus for measuring metastable limits in agitated solutions: A, cooling water-bath; B, pump; C, flow meter; D, magnetic stirrer; E, Perspex water jacket; F, thermometer*

Heating ca.. 4-5 ° above mp and cooling at constant rate. Record temperature at which first crystals appear

The difference from mp is the maximum possible supercoiling for a given cooling rate

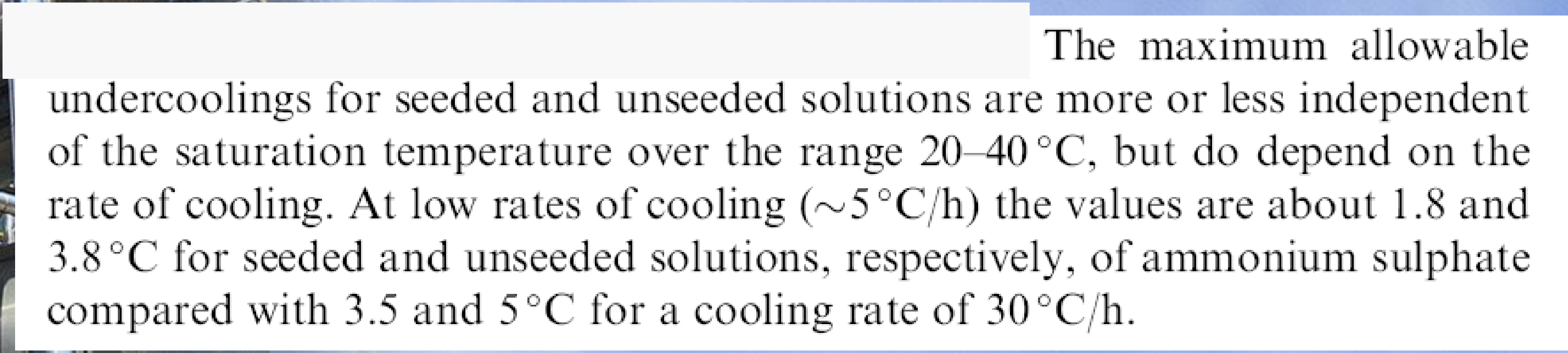
Cooling rate and maximum allowable supercooling



$$\dot{\theta} = (1.38 \pm 0.9)\Delta\theta^{2.64\pm0.92} \qquad \text{seeded (secondary)}$$

and

$$\dot{\theta} = (1.28 \pm 0.91) \times 10^{-2}\Delta\theta^{6.43\pm1.62} \qquad \text{unseeded (primary)}$$



The maximum allowable undercoolings for seeded and unseeded solutions are more or less independent of the saturation temperature over the range 20–40 °C, but do depend on the rate of cooling. At low rates of cooling (~5 °C/h) the values are about 1.8 and 3.8 °C for seeded and unseeded solutions, respectively, of ammonium sulphate compared with 3.5 and 5 °C for a cooling rate of 30 °C/h.

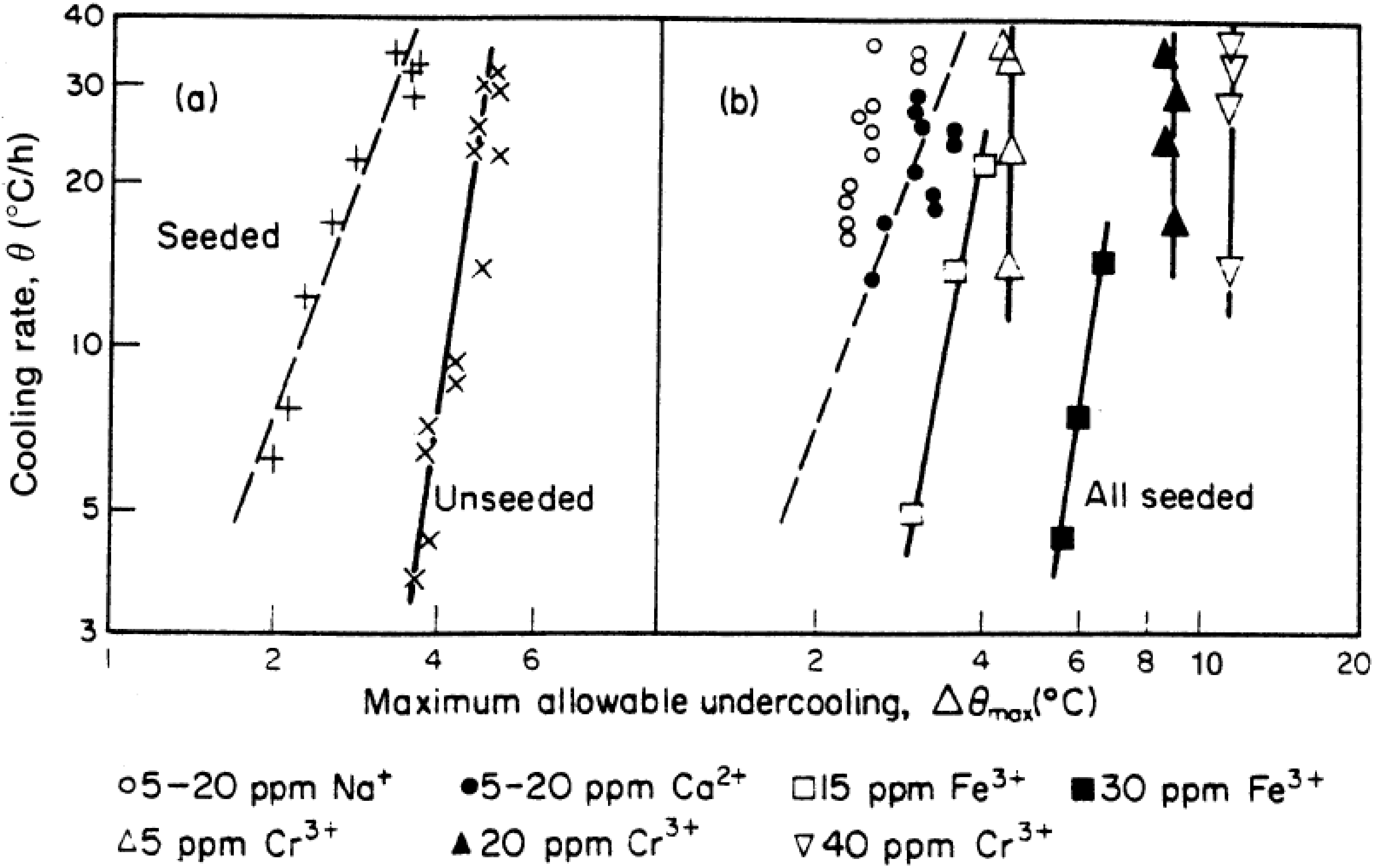


Figure 5.11. *Nucleation characteristics of ammonium sulphate aqueous solution:* (*a*) *pure solutions, seeded and unseeded;* (*b*) *effect of impurities in seeded solutions. The broken line represents data from* (*a*). (*After Mullin, Chakraborty and Mehta, 1970*)

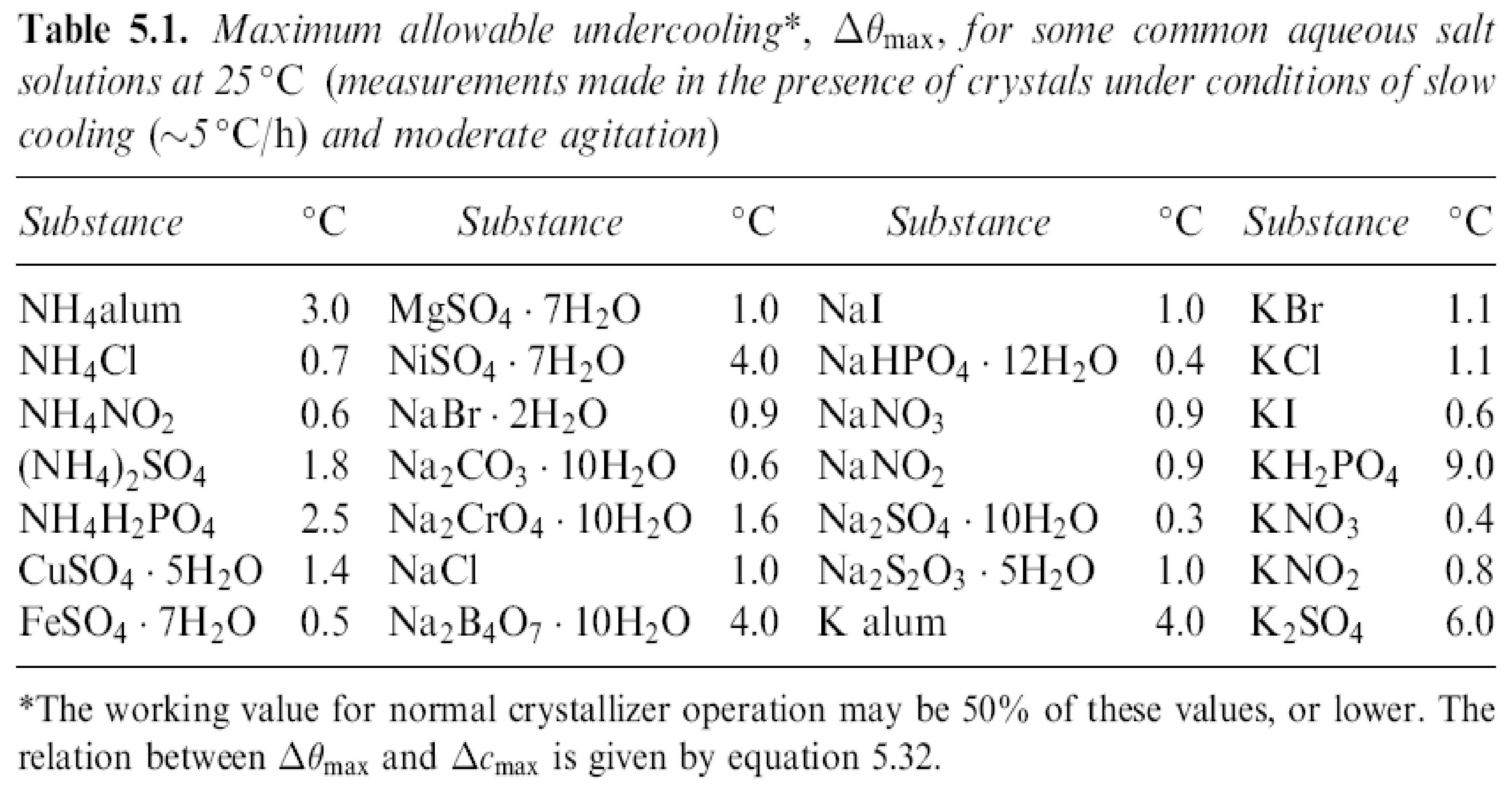


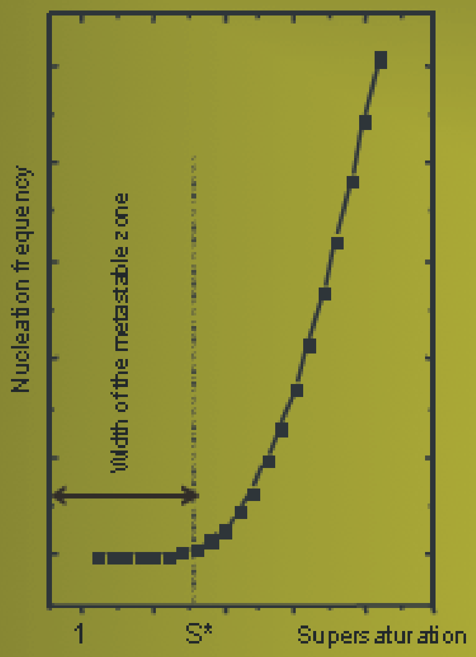
Table 5.1. *Maximum allowable undercooling*, $\Delta\theta_{max}$, for some common aqueous salt solutions at 25 °C (measurements made in the presence of crystals under conditions of slow cooling (~5 °C/h) and moderate agitation)*

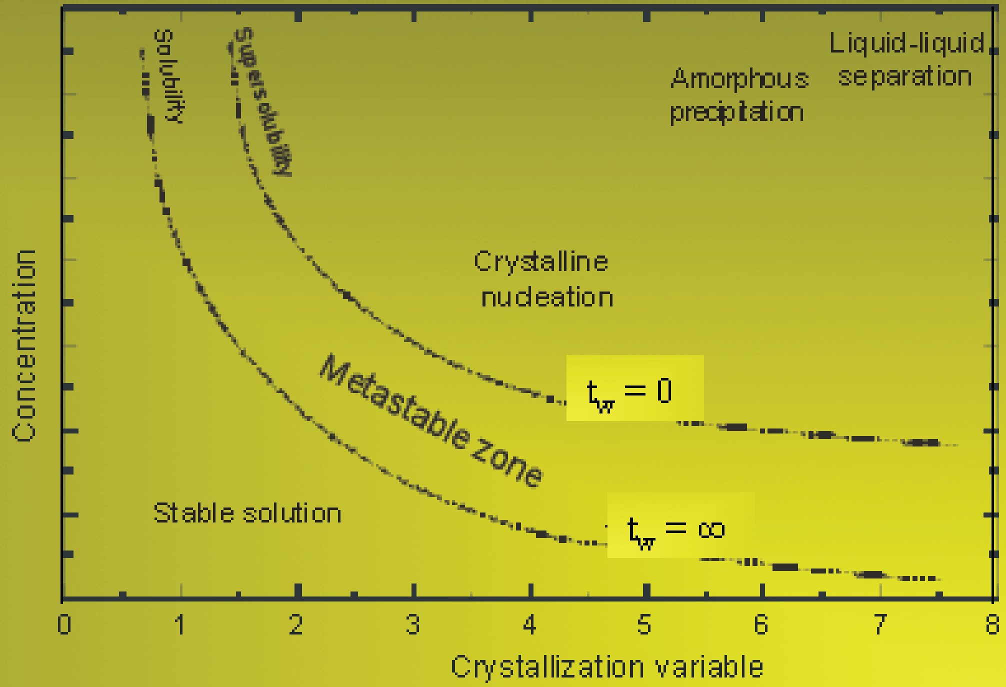
Substance	°C	*Substance*	°C	*Substance*	°C	*Substance*	°C
NH_4alum	3.0	$MgSO_4 \cdot 7H_2O$	1.0	NaI	1.0	KBr	1.1
NH_4Cl	0.7	$NiSO_4 \cdot 7H_2O$	4.0	$NaHPO_4 \cdot 12H_2O$	0.4	KCl	1.1
NH_4NO_2	0.6	$NaBr \cdot 2H_2O$	0.9	$NaNO_3$	0.9	KI	0.6
$(NH_4)_2SO_4$	1.8	$Na_2CO_3 \cdot 10H_2O$	0.6	$NaNO_2$	0.9	KH_2PO_4	9.0
$NH_4H_2PO_4$	2.5	$Na_2CrO_4 \cdot 10H_2O$	1.6	$Na_2SO_4 \cdot 10H_2O$	0.3	KNO_3	0.4
$CuSO_4 \cdot 5H_2O$	1.4	NaCl	1.0	$Na_2S_2O_3 \cdot 5H_2O$	1.0	KNO_2	0.8
$FeSO_4 \cdot 7H_2O$	0.5	$Na_2B_4O_7 \cdot 10H_2O$	4.0	K alum	4.0	K_2SO_4	6.0

*The working value for normal crystallizer operation may be 50% of these values, or lower. The relation between $\Delta\theta_{max}$ and Δc_{max} is given by equation 5.32.

$t = 1/J$

Nucleation is a probablistic phenomenon





Metastable Zone Width

- Nucleation is in fact rather heterogeneous than homogeneous

$$J = k_\mathrm{n} \Delta c_\mathrm{max}^n$$

Δc_{max} maximum possible supersaturation or metastable zone width (MZW)

$$J = q\dot{\theta}$$

$$\text{where } \dot{\theta} = -\mathrm{d}\theta/\mathrm{d}t$$

q mass of the crystalline substance deposited per unit mass of the solvent upon cooling of the solution by 1°C

The MZW depends on the presence of foreign ions or contaminants present in the supersaturated solutions

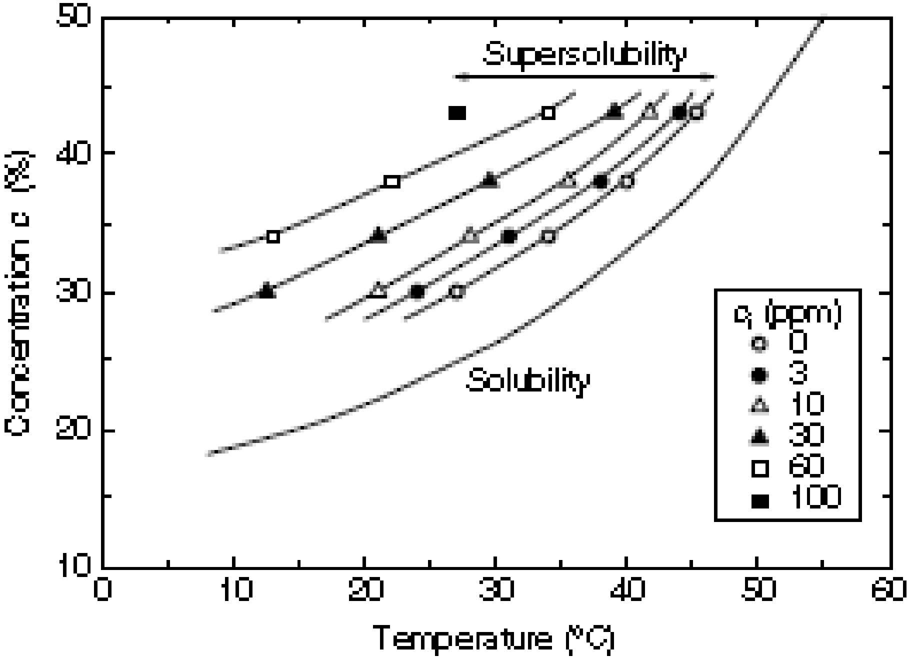
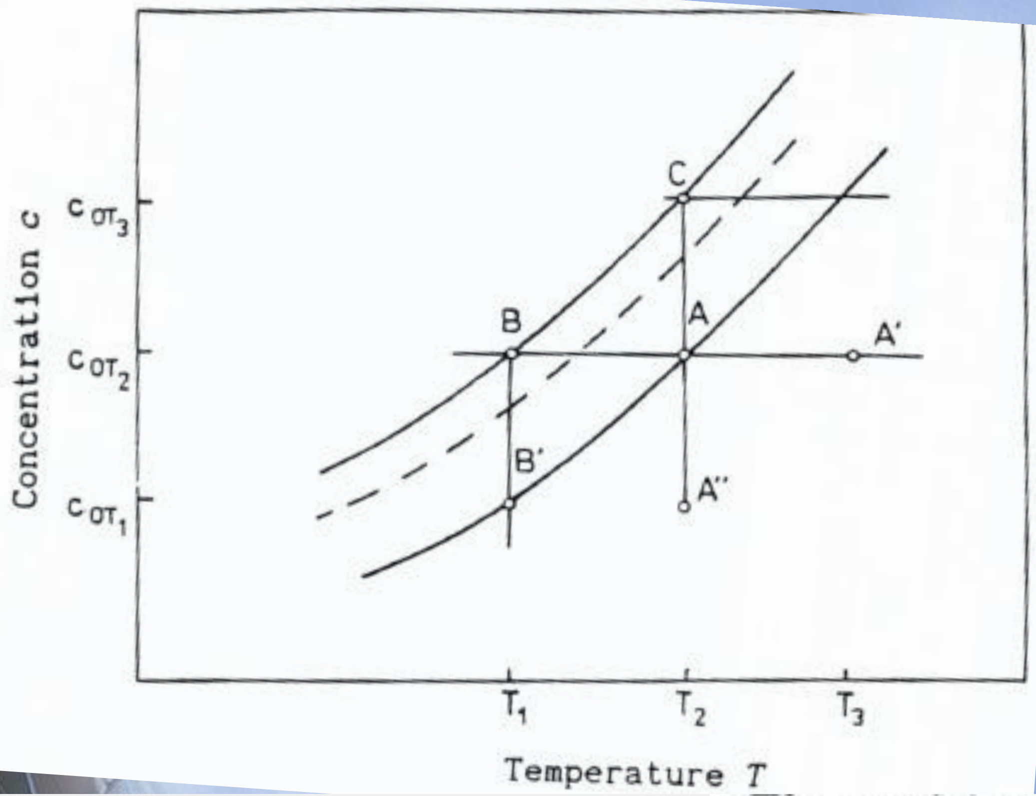


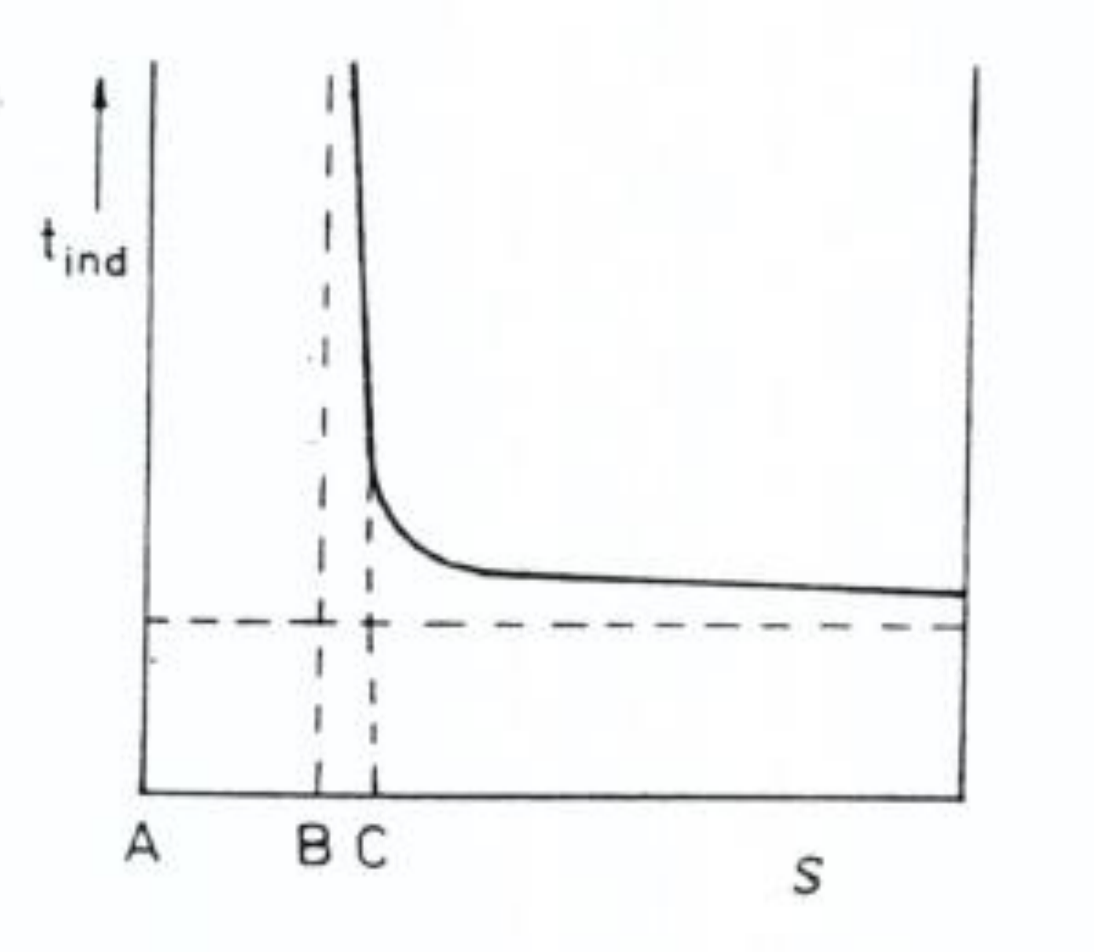
Figure 2.25 Effect of Cr(III) ions on the metastable zone (supersolubility) of KDP solution. No effect of Cr(III) ions was found on solubility. Reproduced from O. Shimomura and M. Suzuki. J. Cryst. Growth 98, 850. Copyright (1989), with permission from Elsevier

Threshold inhibitors



The position of the boundary of the metastability state (point B) is expressed by the maximum supercooling $\Delta T_{max} = (T_2 - T_1)$ corresponding to the maximum concentration difference $\Delta c_{max} = (c_{oT_2} - c_{oT_1})$. These maximum values of supercooling and concentration difference are related by

$$\Delta c_{max} \simeq \Delta T_{max}(\mathrm{d}c_o/\mathrm{d}T).$$



$$0 < t_{ind} < \infty \quad \text{metastable}$$

$$t_{ind} = 0 \quad \text{unstable}$$

Dependence of induction time on supersaturation

Estimation of MSZW

- Metastable zone characteristic feature of supersaturated substances
- Expressed as Δc_{max} or $\Delta \tau_{max}$
- Width of MSZ for a substance depends on a number of factors (physical purity of solution, presence of foreign substances dissolved in the solution etc.) and assumes different values depending on the method of measurements.

Quantitative classification of inorganic compounds with respect to the stability of their supersaturated solutions (i.e. measure of the MSZW) done by Matusevich [1968, Moscow, Industrial Crystallization]:

Valency of anions and of the anions of the crystallizing salts, number of water molecules in the crystalline salt, temperature coefficient of solubility, solubility, type of unit cell

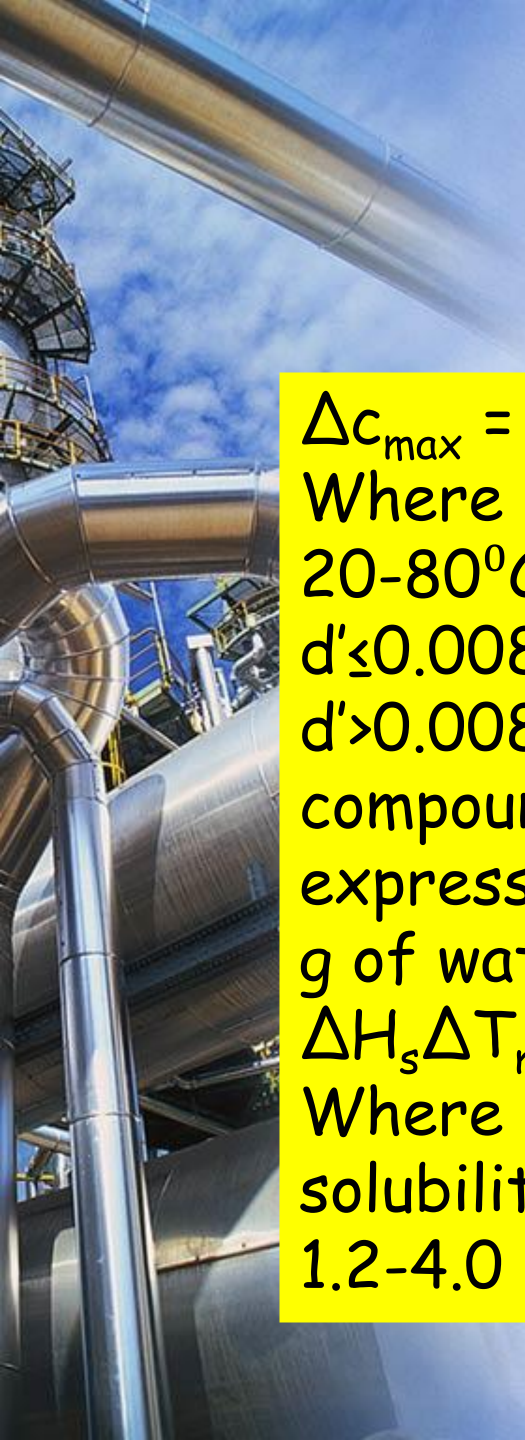
In general: MSZW increases with increasing temperature coefficient of solubility and with decreasing solubility

Based on experimental data MSZW has been related with physic-chemical properties of the systems:

$$\sigma_{\max} = \sigma(T)d'$$

$$d' = c_0 \frac{d(\ln c_0)}{dT}$$

Where $\sigma(T\alpha)$ a constant depending on temperature with values ranging between 2-7 for aqueous solutions



Experimental results:

$\Delta c_{max} = bMc_0$
Where in the temperature range between $20\text{-}80^0C$, $b=0.181\times10^{-3}\exp(0.006T)$ for $d' \leq 0.008$ and $b=0.855\times10^{-3}\exp(-0.0163T)$ for $d' > 0.008$, M the molecular weight of the compound and the concentration is expressed in g of the anhydrous salt per 100 g of water.

$\Delta H_s \Delta T_{max} \approx$ constant
Where ΔH_s is the molar enthalpy of solubility and the constant varies between 1.2-4.0 kJ mol^{-1}