

# **Materials Science and Engineering (BMEE209L)**

by

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# Content

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□ **Module: 3 Solidification, Diffusion, and Phase Transformation** covers the following:

- Solidification – Introduction
- Mechanism of Crystallization
- Driving Force for Solidification
- Solidification of Pure Metal
- Nucleation
- Homogeneous Nucleation
- Heterogeneous Nucleation
- Growth of a Pure Solid
  
- Diffusion – Introduction
- Diffusion Under Thermodynamic Driving Force
- Diffusion Mechanism
- Steady and Non-Steady State Diffusion
- Fick's First Law
- Fick's Second Law

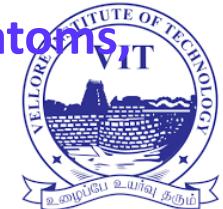


# Solidification – Introduction

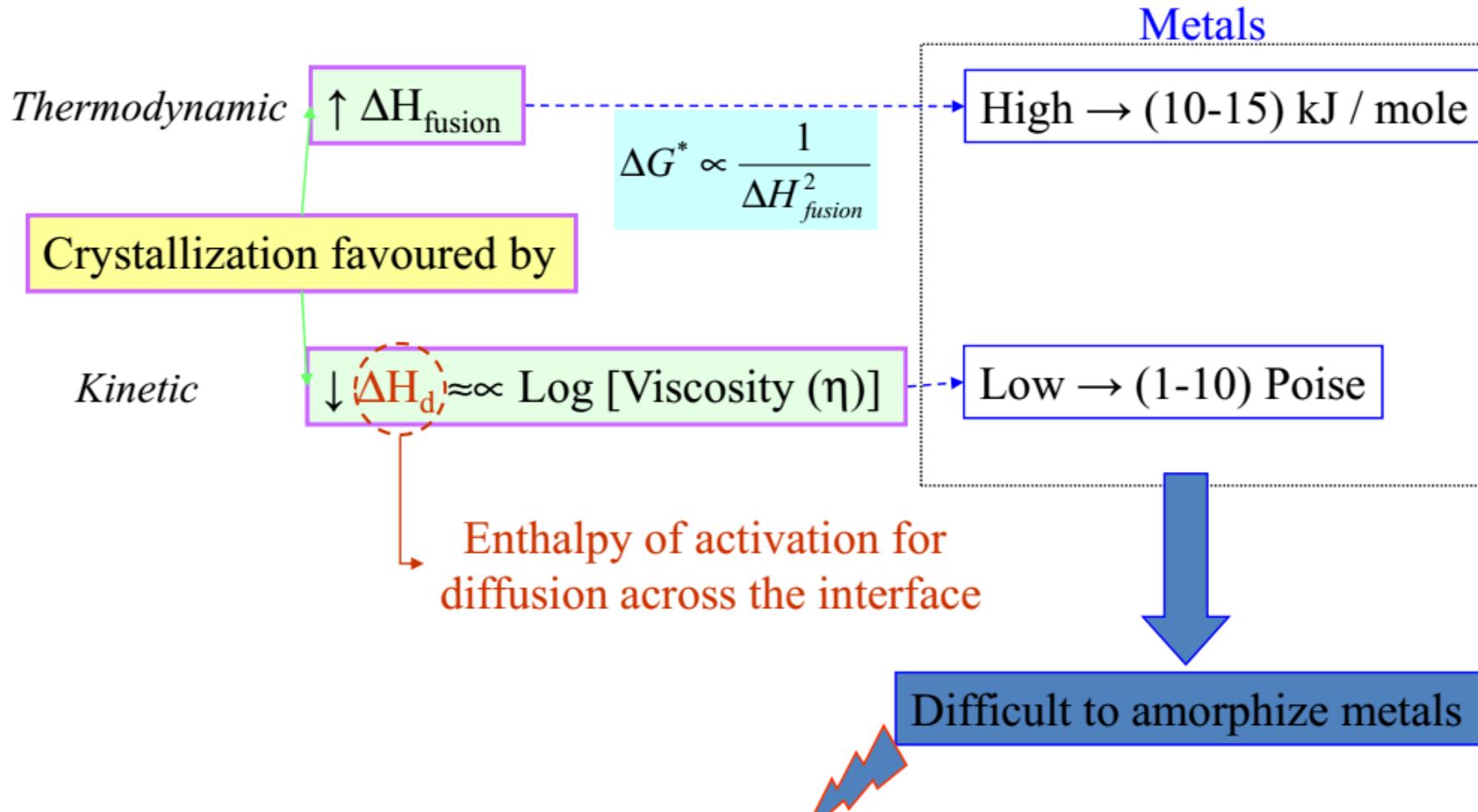
- Let us start understanding phase transformations using the example of the solidification of a pure metal.
- Three states of matter are distinguishable: gas, liquid, and solid.
- In the gaseous state the metal atoms occupy a great deal of space because of their rapid motion. The atoms move independently and are usually widely separated so that the attractive forces between atoms are negligible. The arrangement of atoms in a gas is one of complete disorder.
- At some lower temperature, the kinetic energy of the atoms has decreased so that the attractive forces become large enough to bring most of the atoms together in a liquid. And there is a continual interchange of atoms between the vapor and liquid across the liquid surface.
- The attractive forces between atoms in a liquid may be demonstrated by the application of pressure. A gas may be easily compressed into a smaller volume, but it takes a high pressure to compress a liquid. There is, however, still enough free space in the liquid to allow the atoms to move about irregularly.
- As the temperature is decreased, the motions are less vigorous and the attractive forces pull the atoms closer together until the liquid solidifies. Most materials contract upon solidification, indicating a closer packing of atoms in the solid state.
- The atoms in the solid are not stationary but are vibrating around fixed points, giving rise to the orderly arrangement of crystal structures.

# Mechanism of Crystallization

- Crystallization is the transition from the liquid to the solid state and occurs in two stages:
  - ✓ Nuclei formation
  - ✓ Crystal growth
- Although the atoms in the liquid state do not have any definite arrangement, it is possible that some atoms at any given instant are in positions exactly corresponding to the space lattice they assume when solidified.
- These chance aggregates or groups are not permanent but continually break up and reform at other points.
- The higher the temperature, the greater the kinetic energy of the atoms and the shorter the life of the group. When the temperature, of the liquid is decreased, the atom movement decreases, lengthening the life of the group, and more groups will be present at the same time.
- Atoms in a material have both kinetic and potential energy. Kinetic energy is related to the speed at which the atoms move and is strictly a function of temperature. The higher the temperature, the more active are the atoms and the greater is their kinetic energy. Potential energy, on the other hand, is related to the distance between atoms. The greater the average distance between atoms the greater is their potential energy.



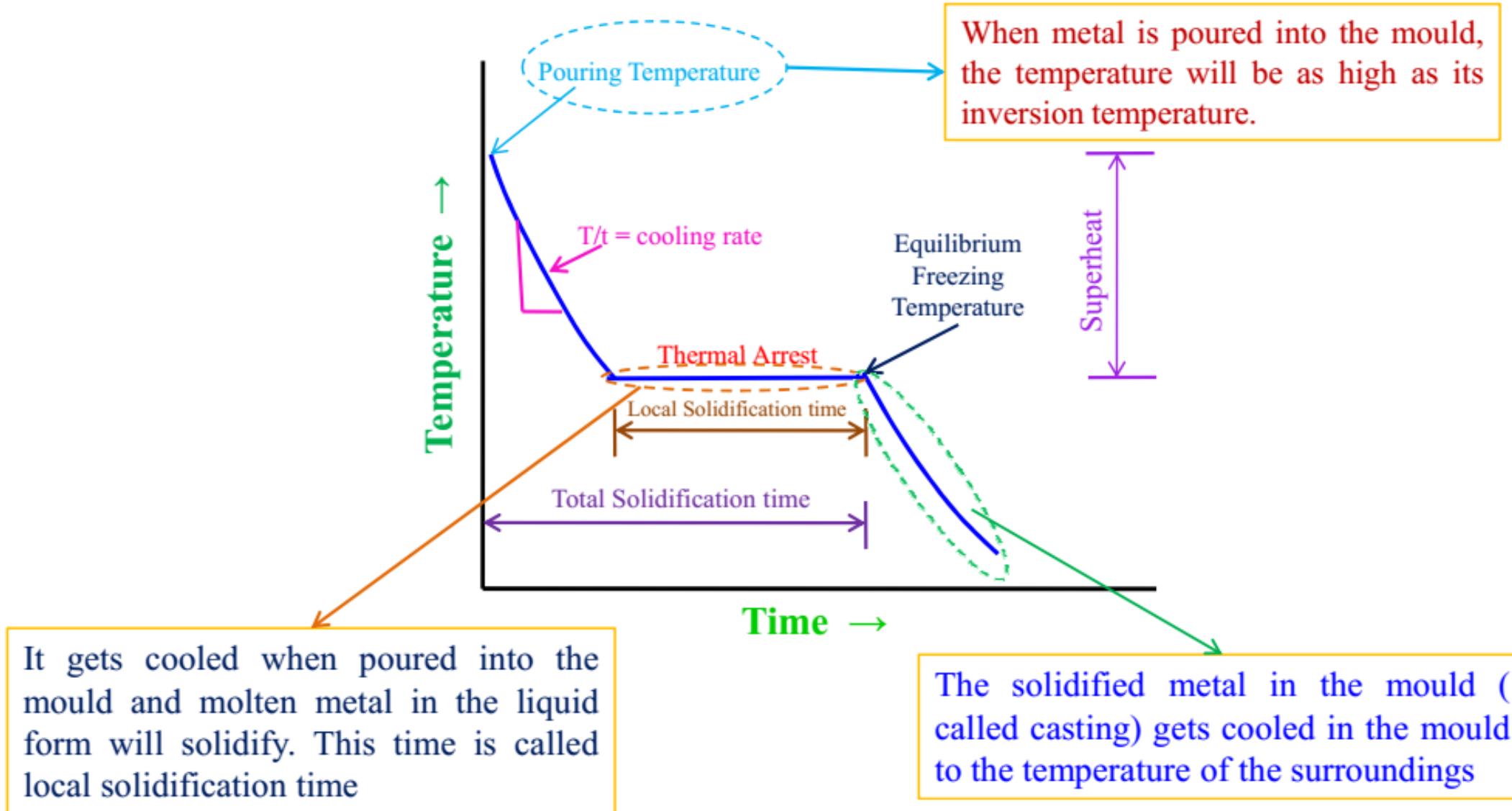
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Very fast cooling rates  $\sim 10^6$  K/s are used for the amorphization of alloys  
 $\rightarrow$  *splat cooling, melt-spinning.*



# Solidification (or) Freezing



# Driving Force for Solidification

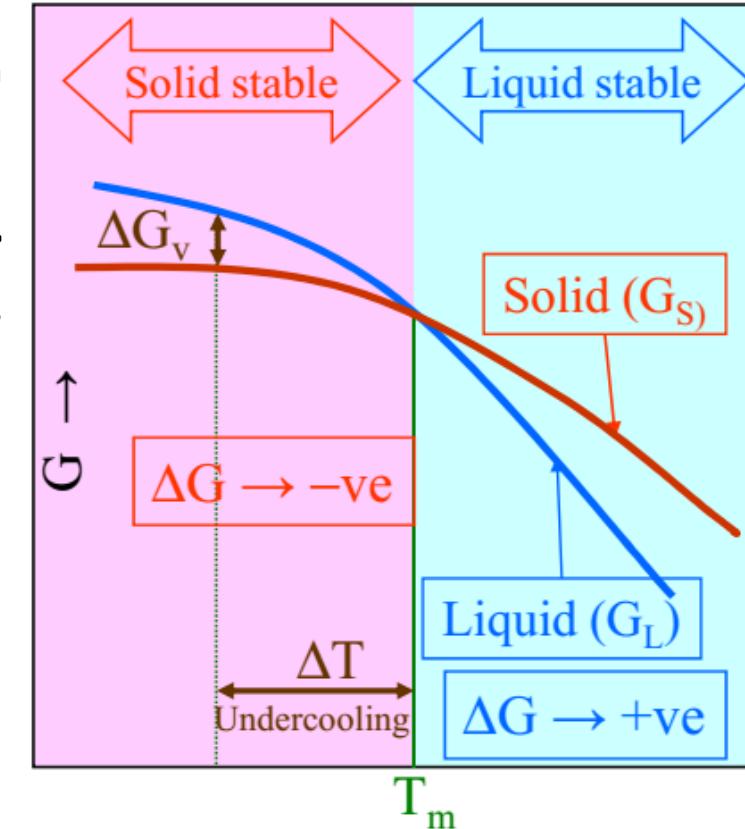
- In dealing with phase transformations, we are often concerned with the difference in free energy between two phases at temperatures away from the equilibrium temperature.
- For example if a liquid metal is under cooled by  $\Delta T$  below  $T_m$  before it solidifies, solidification will be accompanied by a decrease in free energy  $\Delta G$  (J/mol) as shown in figure.
- This free energy decreases provides the driving force for solidification. The magnitude of this change can be obtained as follows.
- The free energies of the liquid and solid at a temperature  $T$  are given by:

$$G^L = H^L - TS^L$$

$$G^S = H^S - TS^S$$

- Therefore, at a temperature  $T$ ,  $\Delta G = \Delta H - T\Delta S \rightarrow ①$

- Where,  $\Delta H = H^L - H^S$  and  $\Delta S = S^L - S^S$

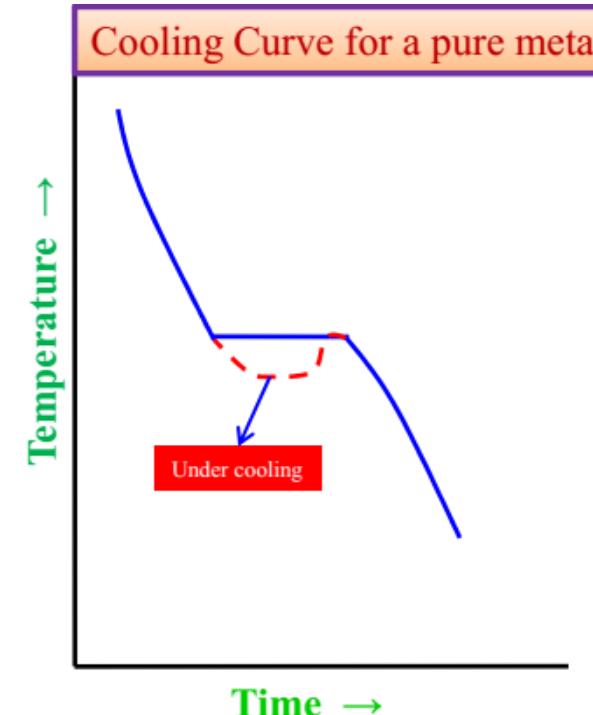


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- At the equilibrium melting temperature  $T_m$  the free energies of solid and liquid are equal, i.e.,  $\Delta G = 0$ .
- Consequently,  $\Delta G = \Delta H - T_m \Delta S = 0$
- And therefore at  $T_m$ , 
$$\Delta S = \frac{\Delta H}{T_m} = \frac{L}{T_m} \rightarrow ②$$
- This is known as the **entropy of fusion**. It is observed experimentally that the entropy of fusion is a constant  $\approx R$  (8.3 J/mol . K) for most metals (Richard's rule).
- For small under-coolings ( $\Delta T$ ) the difference in the specific heats of the liquid and solid ( $C_p^L - C_p^S$ ) can be ignored.
- Combining equations 1 and 2, thus gives, 
$$\Delta G \approx L - T \frac{L}{T_m}$$
- i.e., for small  $\Delta T$ , 
$$\Delta G \approx \frac{L \Delta T}{T_m}$$
      This is called **Turnbull's approximation**.

# Solidification of Pure Metal: Super-Cooling

- In a **pure metal** at its freezing point where both the liquid and solid states are at the same temperature. The kinetic energy of the atoms in the liquid and the solid must be the same, but there is a significant difference in potential energy.
- The atoms in the solid are much closer together, so that solidification occurs with a release of energy. This difference in potential energy between the liquid and solid states is known as the **latent heat of fusion**.
- However, energy is required to establish a surface between the liquid and solid. In pure materials at the freezing point insufficient energy is released by the heat of fusion to create a stable boundary, and some under cooling is always necessary to form stable nuclei.
- Subsequent release of the heat of fusion will raise the temperature to the freezing point. The amount of **undercooling** required may be reduced by the presence of solid impurities which reduce the amount of surface energy required.

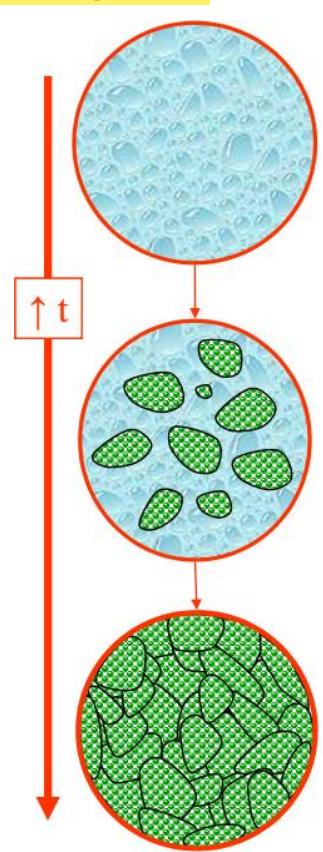
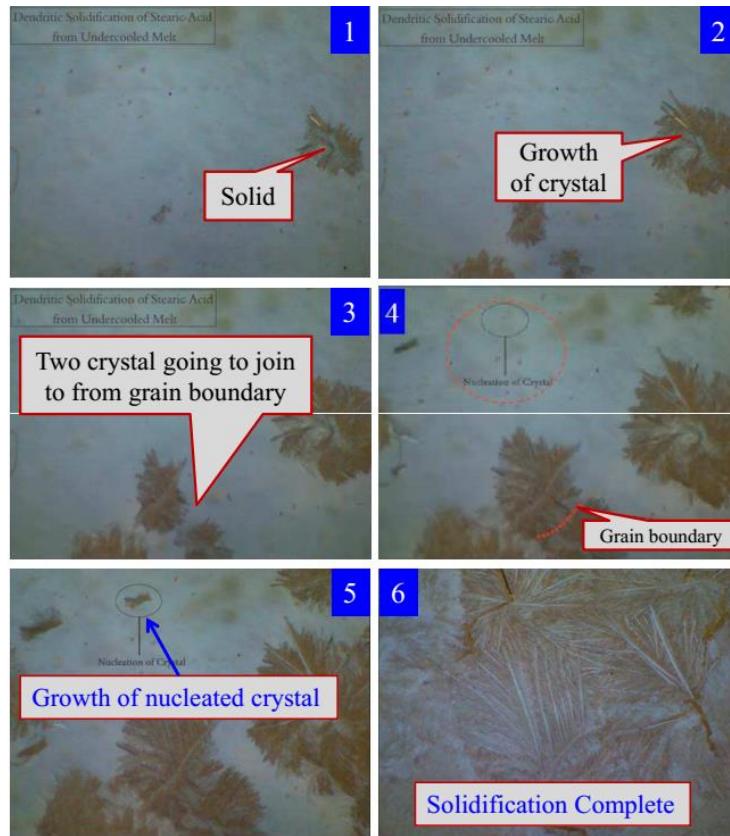


# Solidification of Pure Metal

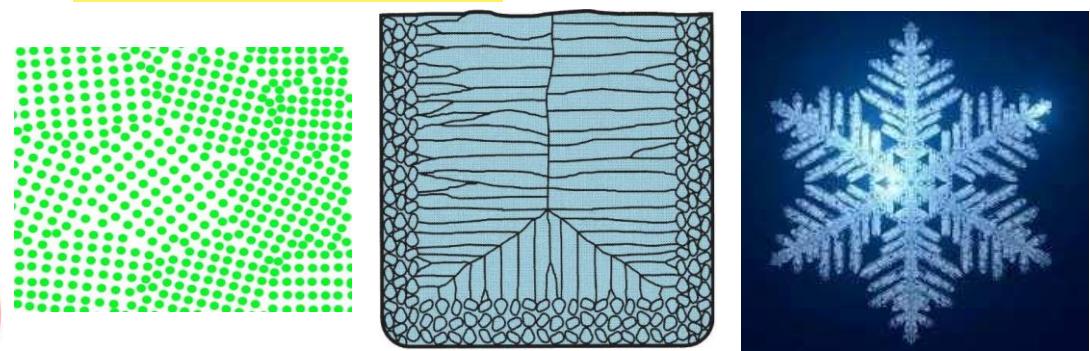
- When the temperature of the liquid metal has dropped sufficiently below its freezing point, stable aggregates or nuclei appear spontaneously at various points in the liquid. These nuclei, which have now solidified, act as centers for further crystallization.
- As cooling continues, more atoms tend to freeze, and they may attach themselves to already existing nuclei or form new nuclei of their own. Each nucleus grows by the attraction of atoms from the liquid into its space lattice.
- Crystal growth continues in three dimensions, the atoms attaching themselves in certain preferred directions, usually along the axes of the crystal this gives rise to a characteristic treelike structure which is called a dendrite.
- Since each nucleus is formed by chance, the crystal axes are pointed at random and the dendrites growing from them will grow in different directions in each crystal. Finally, as the amount of liquid decreases, the gaps between the arms of the dendrite will be filled and the growth of the dendrite will be mutually obstructed by that of its neighbors. This leads to a very irregular external shape.
- The crystals found in all commercial metals are commonly called grains because of this variation in external shape. The area along which crystals meet, known as the grain boundary, is a region of mismatch.

# Contd...

- This mismatch leads to a non-crystalline (amorphous) structure at the grain boundary with the atoms irregularly spaced.
- Since the last liquid to solidify is generally along the grain boundaries, there tends to be higher concentration of impurity atoms in that area. The figure shows schematically the process of crystallization from nuclei to the final grains.

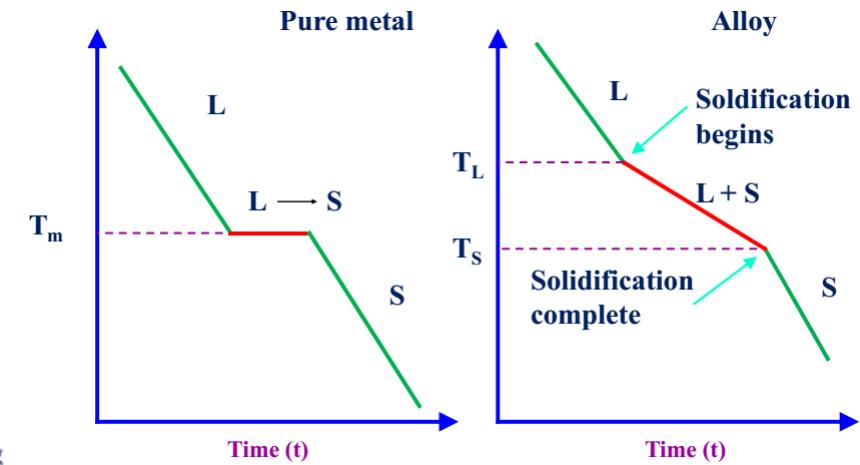
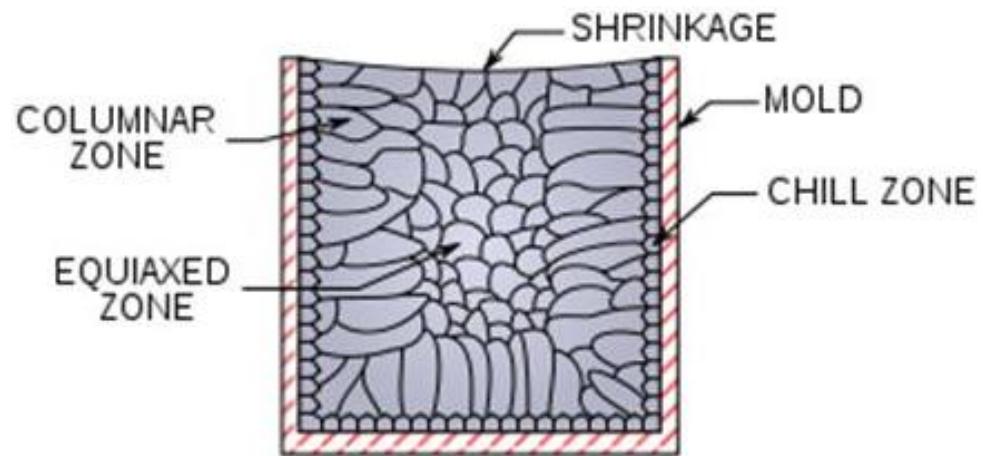
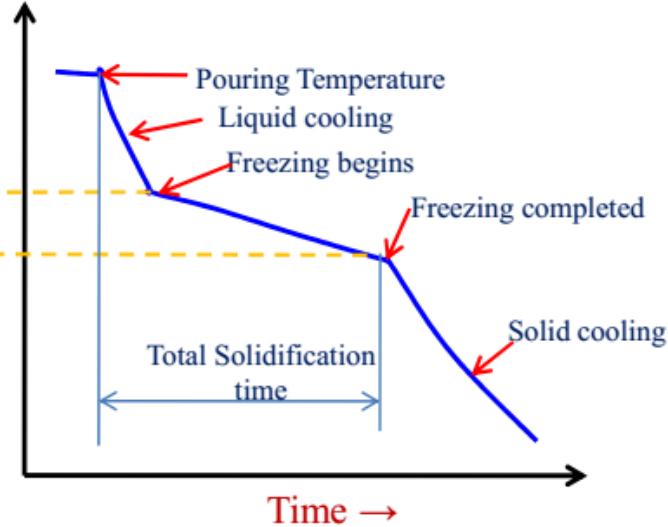
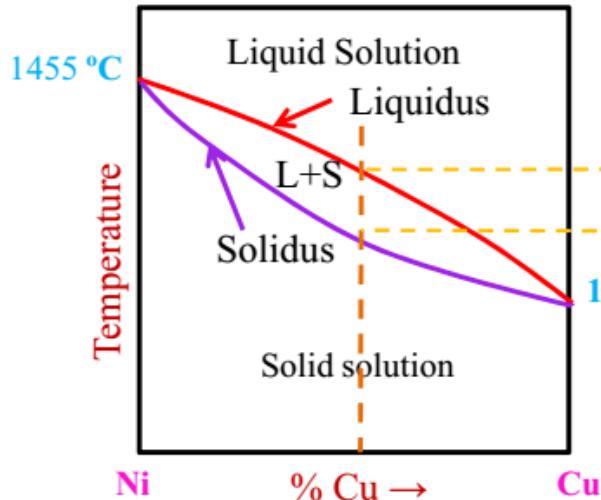


- Due to chilling action of mold wall, a thin skin of solid metal is formed at the wall surface immediately after pouring.
- Grain structure in a casting of a pure metal, showing randomly oriented grains of small size near the mold wall, and large columnar grains oriented toward the center of the casting.



# Solidification of Alloys

- Most alloys freeze over a temperature range.
- Phase diagram for a Cu-Ni alloy system and cooling curve for different alloy systems.
- Characteristic grain structure in an alloy casting, showing segregation of alloying components in center of casting.



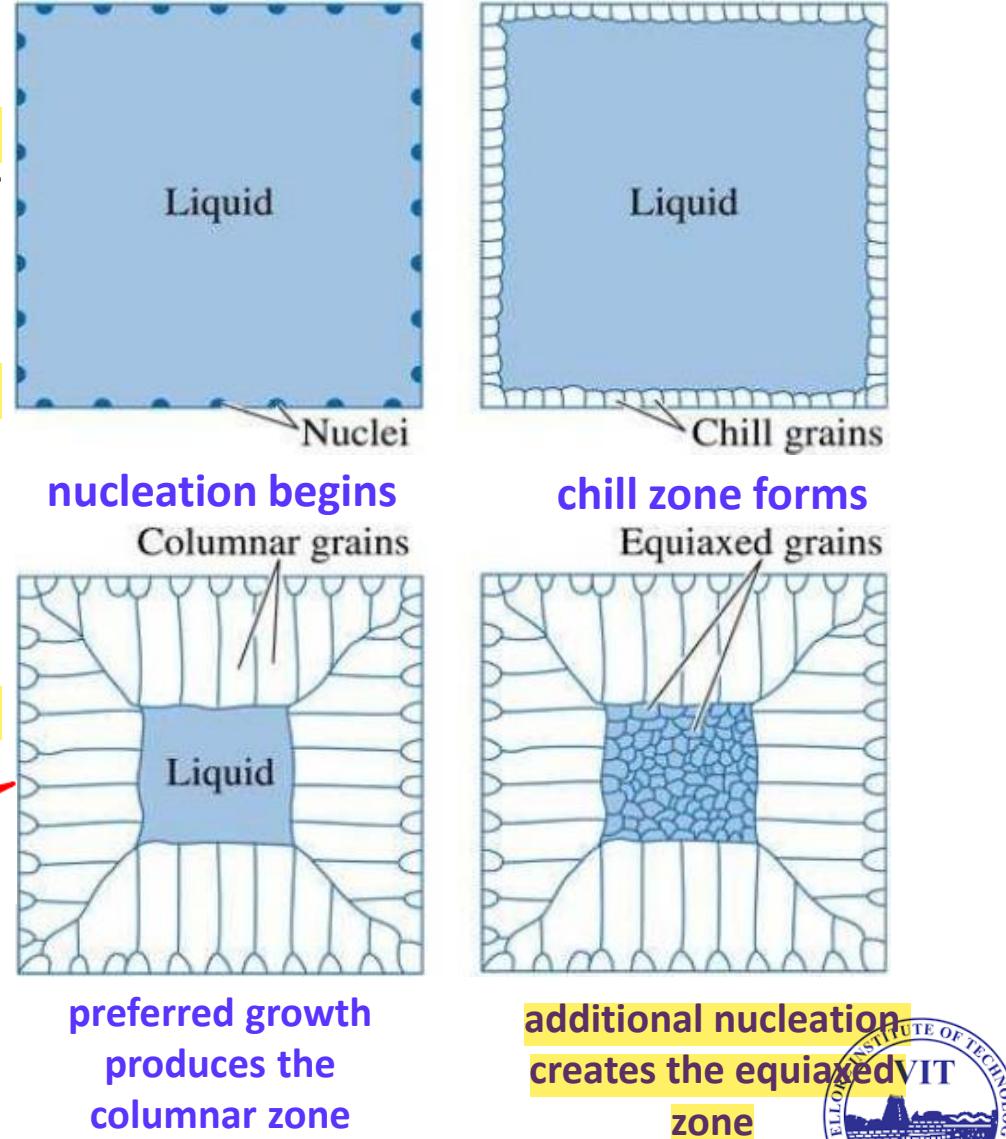
Comparison of cooling curves



# Cast Structure

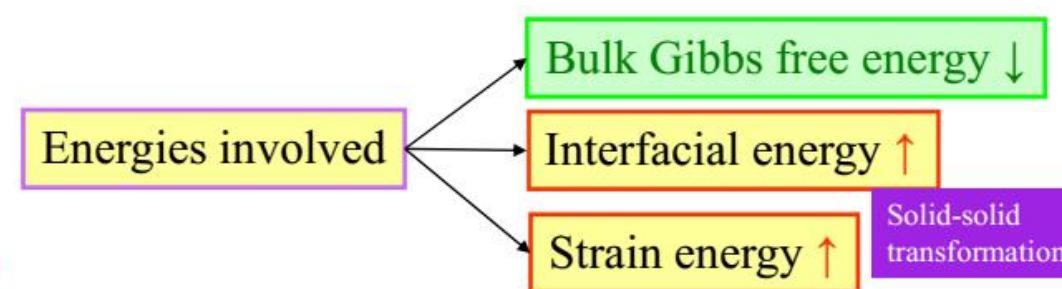
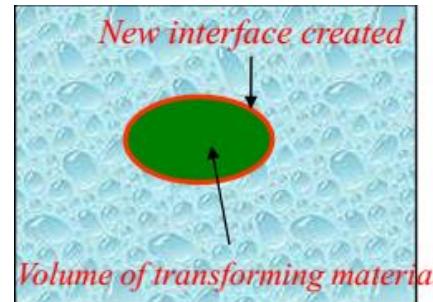
- ❑ **Chill Zone:** A region of small, randomly oriented grains that forms at the surface of a casting as a result of heterogeneous nucleation.
- ❑ **Columnar Zone:** A region of elongated grains having a preferred orientation that forms as a result of competitive growth during the solidification of a casting.
- ❑ **Equiaxed Zone:** A region of randomly oriented grains in the center of a casting produced as a result of widespread nucleation.

Figure: Development of the ingot structure of a casting during solidification:

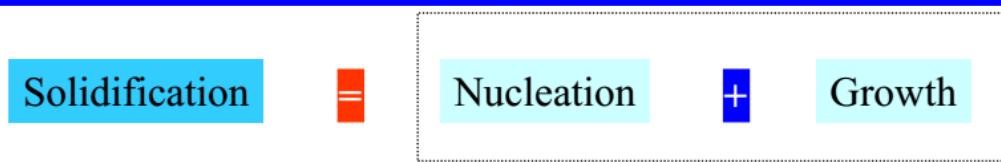


# Summary

- We have seen phase transformations using the example of the solidification of a pure metal.
- There is no change in composition involved as we are considering a pure metal. If we solidify an alloy this will involve long range diffusion.
- When a volume of material ( $V$ ) transforms three energies have to be considered:
  - ✓ reduction in  $G$  (assume we are working at constant  $T$  and  $P$ )
  - ✓ increase in  $\gamma$  (interface free-energy)
  - ✓ increase in strain energy
- In a liquid to solid phase transformation the strain energy term can be neglected as the liquid melt can flow to accommodate the volume change (assume we are working at constant  $T$  &  $P$ ).
- The process can start only below the melting point of the liquid (as only below the melting point the  $G_{\text{liquid}} < G_{\text{solid}}$ ), i.e., we need to Undercool the system. As we shall note, under suitable conditions (e.g. container-less solidification in zero gravity conditions), melts can be undercooled to a large extent without solidification taking place.



# Nucleation



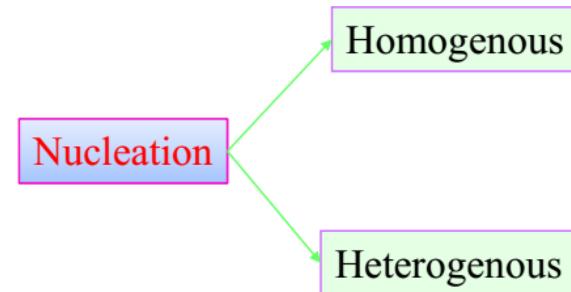
**Nucleation:** localized formation of a distinct thermodynamic phase.

Nucleation can occur in a **gas**, **liquid** or **solid** phase.

Some examples of phases that may form via nucleation include:

- ✓ In gas-creation of liquid droplets in saturated vapor
- ✓ In liquid-formation of gaseous bubbles crystals (e.g., ice formation from water) or glassy regions.
- ✓ In solid-Nucleation of crystalline, amorphous and even vacancy clusters in solid materials. Such solid state nucleation is important, for example, to the semiconductor industry.

Most nucleation processes are physical, rather than chemical.



- It occurs spontaneously and randomly, but it requires superheating or supercooling of the medium.

- **Liquid → solid**  
walls of container, inclusions

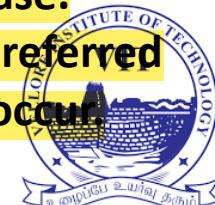
- **Solid → solid**  
inclusions, grain boundaries, dislocations, stacking faults

There are **two types** of nucleation: **homogeneous** and **heterogeneous**. This distinction between them made according to the site at which nucleating events occur.

For the **homogeneous type**, nuclei of the new phase form uniformly throughout the parent phase, whereas for the **heterogeneous type**, nuclei form preferentially at structural in-homogeneities such as container surfaces insoluble impurities grain boundaries, dislocations and so on.

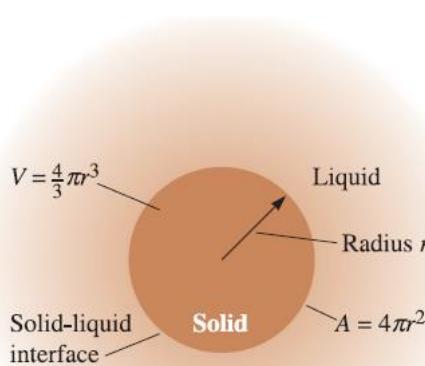
The probability of nucleation occurring at point in the parent phase is same throughout the parent phase.

In heterogeneous nucleation there are some preferred sites in the parent phase where nucleation can occur.



# Homogeneous Nucleation

- Let us consider L→S transformation taking place by homogenous nucleation. Let the system be undercooled to a fixed temperature  $\Delta T$ . Let us consider the formation of a spherical crystal of radius 'r' from the melt. We can neglect the strain energy contribution.
- Let the change in 'G' during the process be  $\Delta G$ . This is equal to the decrease in bulk free energy + the increase in surface free energy. This can be computed for a spherical nucleus as below.

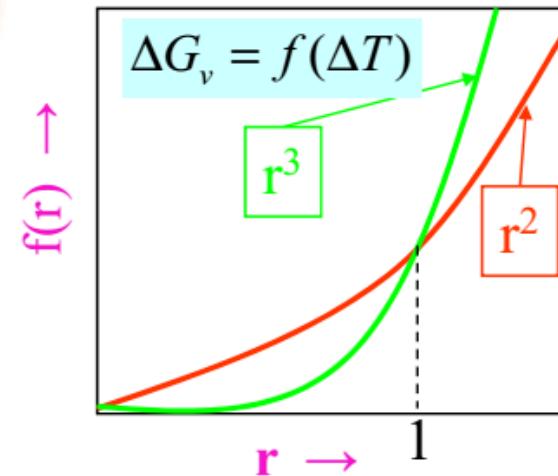


Free energy change on nucleation =

Reduction in bulk free energy + increase in surface energy + increase in strain energy

Neglected in L → S transformations

$$\Delta G = (\text{Volume}).(\Delta G) + (\text{Surface}).(\gamma)$$



$$\Delta G = \left( \frac{4}{3} \pi r^3 \right) (\Delta G_v) + (4\pi r^2) (\gamma)$$

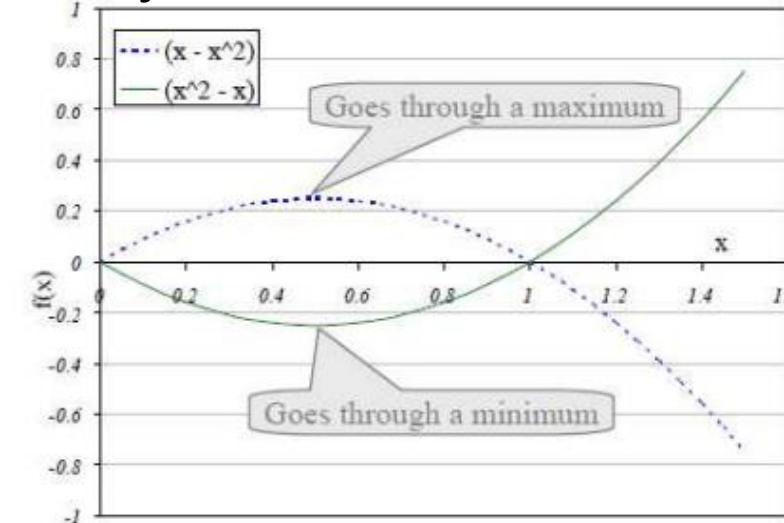
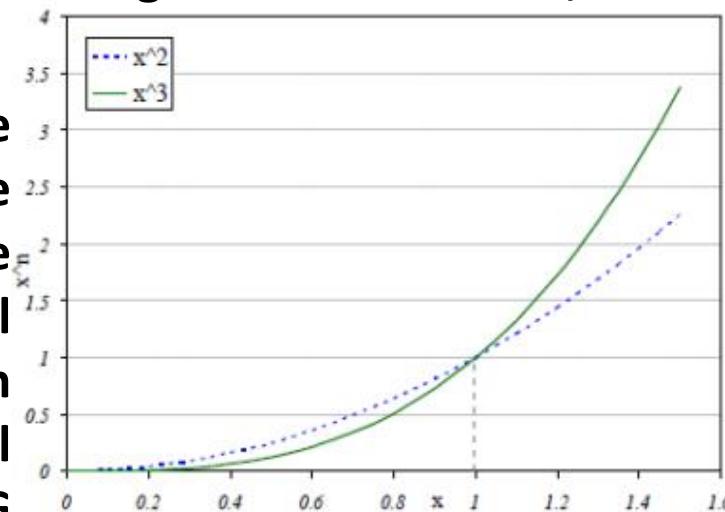
- Note that below a value of '1' the lower power of 'r' dominates; while above '1' the higher power of 'r' dominates.
- In the above equation these powers are weighed with other 'factors/parameters', but the essential logic remains.



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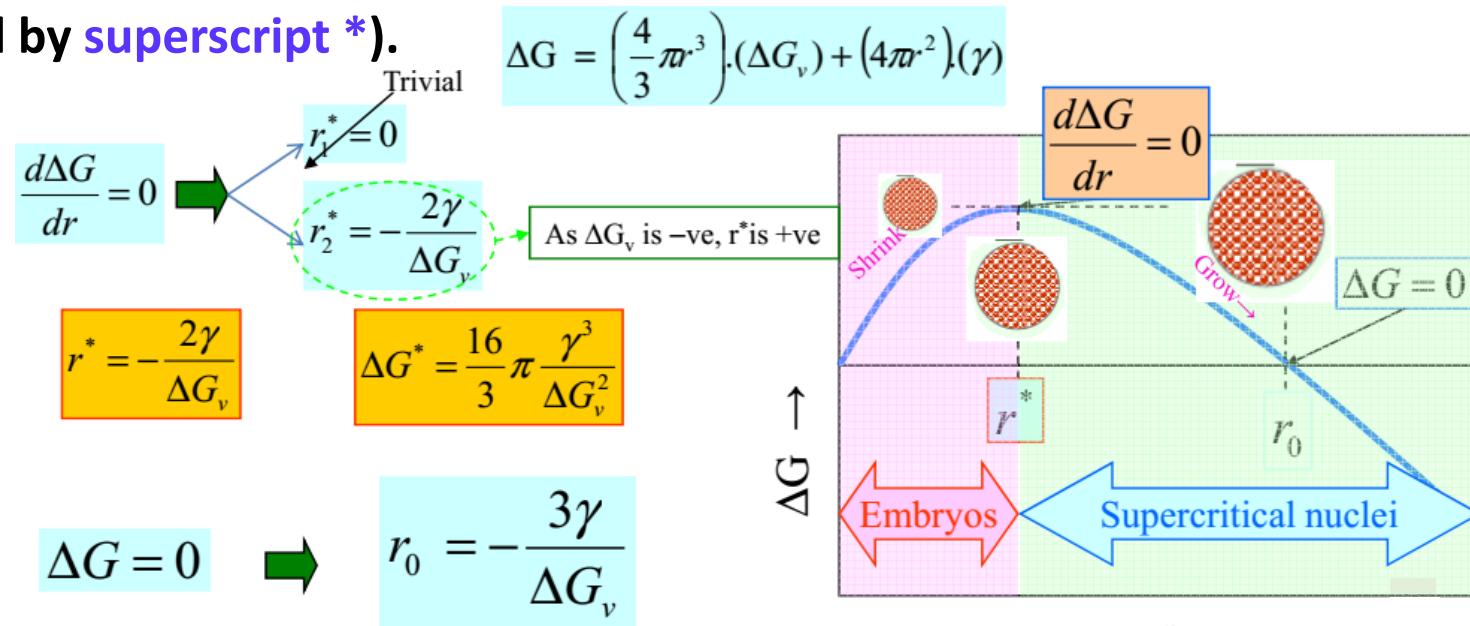
$$\Delta G = \left(\frac{4}{3}\pi r^3\right)(\Delta G_v) + (4\pi r^2)(\gamma)$$

- In the above equation, the  $r^3$  term is +ve and the  $r^2$  term is -ve. Such kinds of equations are often encountered in materials science, where one term is opposing the process and the other is supporting it. Example of such processes are crack growth (where surface energy opposes the process and the strain energy stored in the material supports crack growth).
- In the current case it is the higher power is supporting the phase transformation. Since the higher power dominates above '1', the function will go through a maximum as in figure below. This implies the  $\Delta G$  function will go through a maximum i.e., if the process just even starts it will lead to an increase in  $\Delta G$ .
- On the other hand the function with -ve contribution from the lower power (to  $\Delta G$ ) will go through a minimum and such a process will take place down-hill in G and stop.



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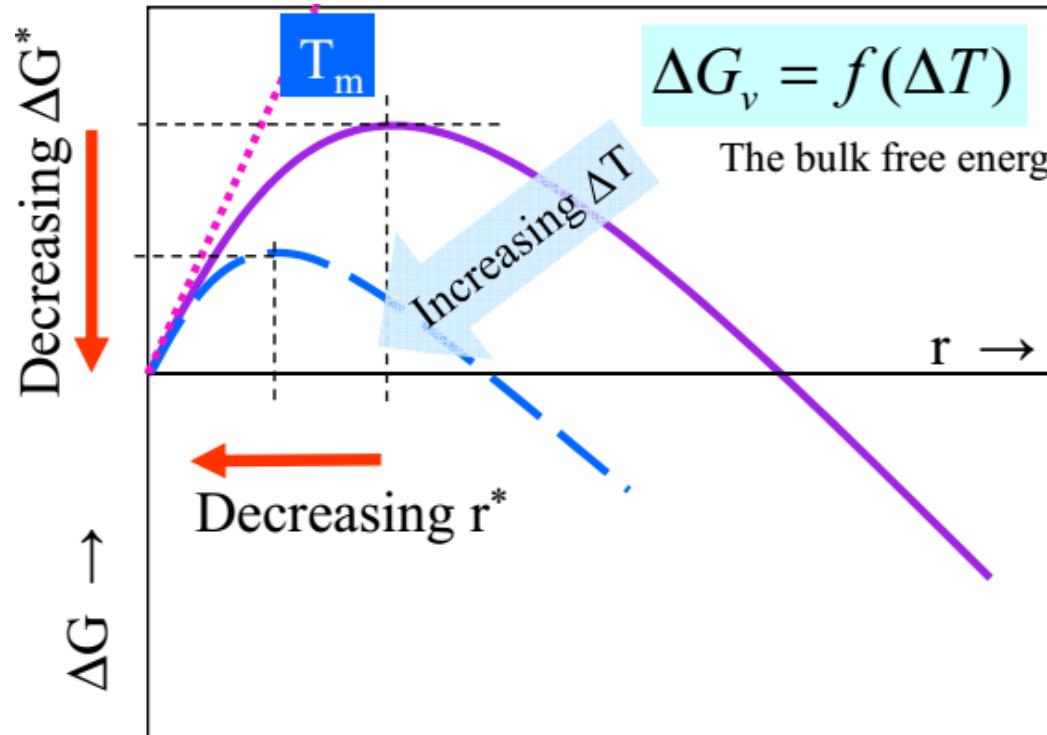
- As we have noted previously  $\Delta G$  vs  $r$  plot will go through a maximum (implying that as a small crystal forms 'G' will increase and hence it will tend to dissolve). The maximum of  $\Delta G$  vs  $r$  plot is obtained by, by setting  $d\Delta G/dr = 0$ . The maximum value of  $\Delta G$  corresponds to a value of 'r' called the critical radius (denoted by superscript \*).



- If by some 'accident' (technically a 'statistical random fluctuation') a crystal (of 'preferred' crystal structure) size  $> r^*$  (called supercritical nuclei) forms then it can grow down-hill in 'G'. Crystals smaller than  $r^*$  (called embryos) will tend to shrink to reduce 'G'. The critical value of  $\Delta G$  at  $r^*$  is called  $\Delta G^*$ . Reduction in G (below the liquid state) is obtained only after  $r_0$  is obtained (which can be obtained by setting  $\Delta G = 0$ ).

# Contd...

- What is the effect of undercooling ( $\Delta T$ ) on  $r^*$  and  $\Delta G^*$ ?
- We have noted that  $\Delta G_v$  is a function of undercooling ( $\Delta T$ ). At larger undercooling  $\Delta G_v$  increases and hence  $r^*$  and  $\Delta G^*$  decrease. This is evident from the equations for  $r^*$  and  $\Delta G^*$  as below.
- At  $T_m$ ,  $\Delta G_v$  is zero and  $r^*$  is infinity. → That the melting point is not the same as the freezing point. This energy (G) barrier to nucleation is called the 'nucleation barrier'.



$$r^* = -\frac{2\gamma}{\Delta G_v}$$

$$\Delta G^* = \frac{16}{3} \pi \frac{\gamma^3}{\Delta G_v^2}$$

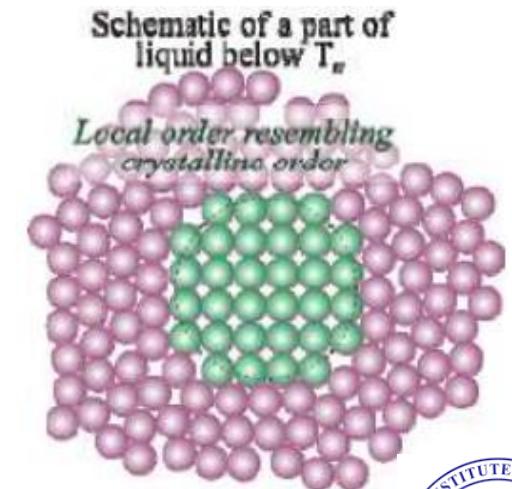
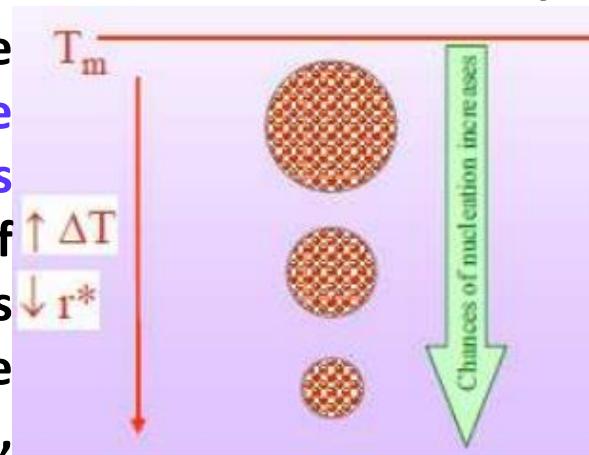
Using the Turnbull approximation (linearizing the G-T curve close to  $T_m$ ),  $\Delta G \approx \frac{L\Delta T}{T_m}$  we can get the value of  $\Delta G$  in terms of the enthalpy of solidification.

$$\Delta G^* = \frac{16}{3} \pi \gamma^3 \frac{T_m^2}{\Delta T^2 \Delta H^2}$$



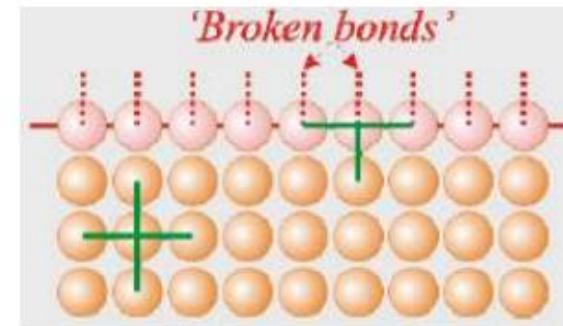
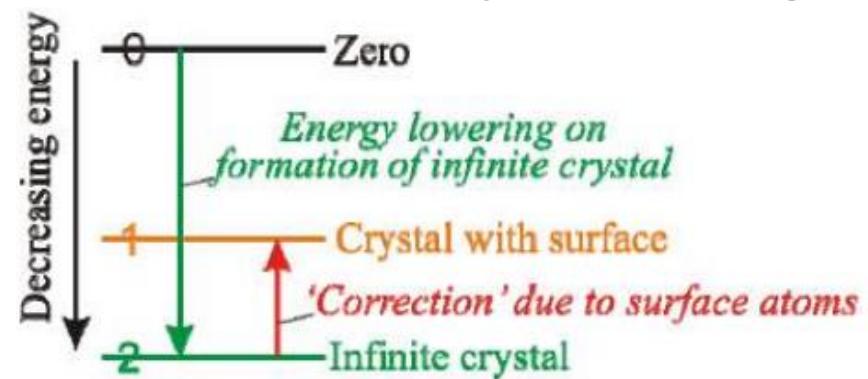
## How are Atoms Assembled to form a Nucleus of $r^*$ → “Statistical Random Fluctuation”

- To cause nucleation (or even to form an embryo) atoms of the liquid (which are randomly moving about) have to come together in an order, which resembles the crystalline order, at a given instant of time. Typically, this crystalline order is very different from the order (local order), which exists in the liquid.
- This ‘coming together’ is a random process, which is statistical in nature → i.e. the liquid is exploring ‘locally’ many different possible configurations and randomly (by chance), in some location in the liquid, this order may resemble the preferred crystalline order.
- Since this process is random (and statistical) in nature, the probability that a larger sized crystalline order is assembled is lower than that to assemble a smaller sized ‘crystal’.
- Hence, at **smaller under-cooling** (where the value of  $r^*$  is large) the chance of the formation of a supercritical nucleus is smaller and so is the probability of solidification (as at least one nucleus is needed → which can grow to cause solidification). At **larger under-cooling**, where  $r^*$  value is relatively smaller, the chance of solidification is higher.



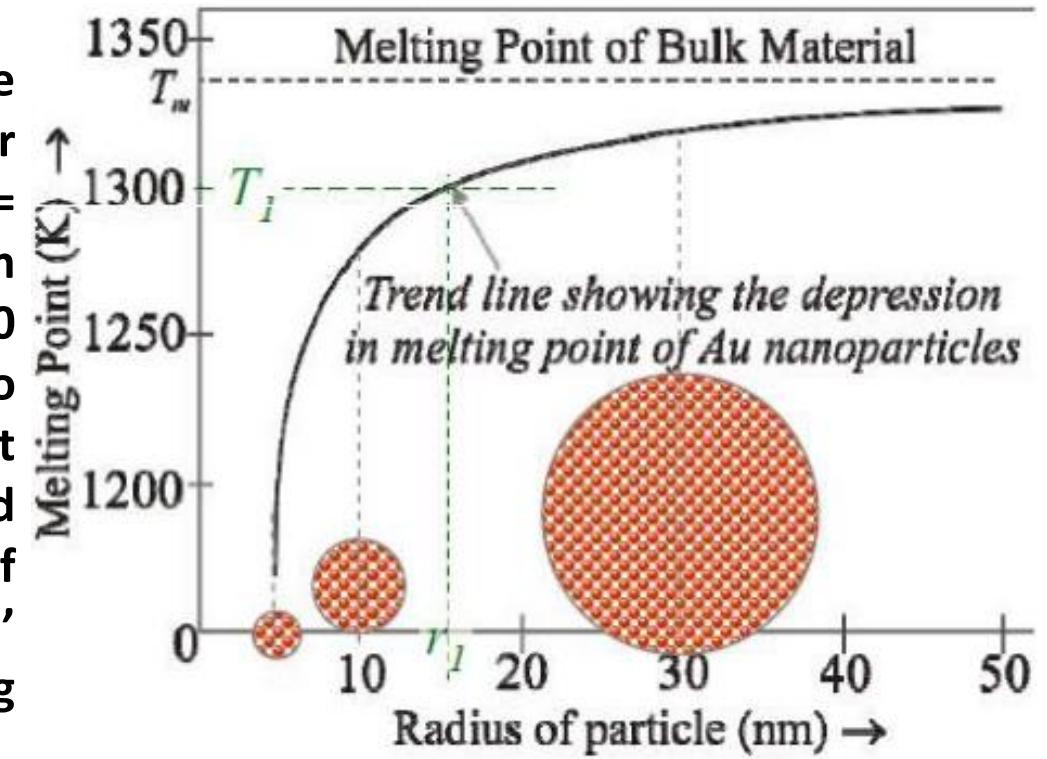
# What is Meant by the ‘Nucleation Barrier’ → An Alternate Perspective

- Here we try to understand: “What exactly is meant by the nucleation barrier?”.  
□ It is sometime difficult to understand as to the surface energy can make freezing of a small ‘embryo’ energetically ‘infeasible’ (as we have already noted that unless the crystallite size is  $> r_0$  the energy of the system is higher). Agreed that for the surface energy lowering is not as much as that for the bulk\*, but even the surface (with some ‘unsaturated bonds’) is expected to have a lower energy than the liquid state (where the crystal is energetically favored), i.e. the specific concern being: “can state-1 in figure below be above the zero level (now considered for the liquid state)?” → “Is the surface so bad that it even negates the effect of the bulk lowering?”  
□ We will approach this mystery from a different angle - by first asking the question: “what is meant by melting point?” & “what is meant by undercooling?”.



# Melting Point, Under-Cooling, and Freezing Point

- The plot below shows melting point of Au nanoparticles, plotted as a function of the particle radius. It is to be noted that the melting point of nanoparticles decreases below the ‘bulk melting point’ (a 5 nm particle melts more than 100 °C below  $T_m^{\text{Bulk}}$ ). This is due to surface effects (surface is expected to have a lower melting point than bulk ?\*) → actually, the current understanding is that the whole nanoparticle melts simultaneously (not surface layer by layer).
- Let us continue to use the example of Au. Suppose we are below  $T_m^{\text{Bulk}}$  ( $1337 \text{ K} = 1064 \text{ }^{\circ}\text{C}$ , i.e. system is under cooled w.r.t the bulk melting point) at  $T_1$  ( $=1300\text{K} \rightarrow \Delta T = 37 \text{ K}$ ) and suppose a small crystal of  $r_2 = 5 \text{ nm}$  forms in the liquid. Now the melting point of this crystal is  $\sim 1200 \text{ K}$  → this crystal will ‘melt-away’. Now we have to assemble a crystal of size of about 15 nm ( $= r_1$ ) for it ‘not to melt’. This needless to say is much less probable (and it is better to undercool even further so that the value of  $r^*$  decreases). Thus the mystery of ‘nucleation barrier’ vanishes and we can ‘think of’ melting point  $\equiv$  freezing point (for a given size of particle).
- $T_m$  is in heating for the bulk material and in cooling if we take into account the size dependence of melting point everything ‘sort-of’ falls into place.



# Homogenous Nucleation Rate

- The process of nucleation (of a crystal from a liquid melt, below  $T_m^{\text{Bulk}}$ ) we have described so far is a dynamic one. Various atomic configurations are being explored in the liquid state - some of which resemble the stable crystalline order. Some of these 'crystallites' are of a critical size  $r^*_{\Delta T}$  for a given undercooling ( $\Delta T$ ). These crystallites can grow to transform the melt to a solid → by becoming supercritical. Crystallites smaller than  $r^*$  (embryos) tend to 'dissolve'.
- As the whole process is dynamic, we need to describe the process in terms of 'rate' → **the nucleation rate** [ $dN/dt \equiv$  number of nucleation events/time].
- Also, true nucleation is the rate at which crystallites become supercritical. To find the **nucleation rate** we have to find the **number of critical sized crystallites ( $N^*$ )** and multiply it by the **frequency/rate** at which they become supercritical.
- If the **total number of particles** (which can act like potential nucleation sites – in homogenous nucleation for now) is  $N_t$ , then the number of critical sized particles given by an Arrhenius type function with a **activation barrier of  $\Delta G^*$** .

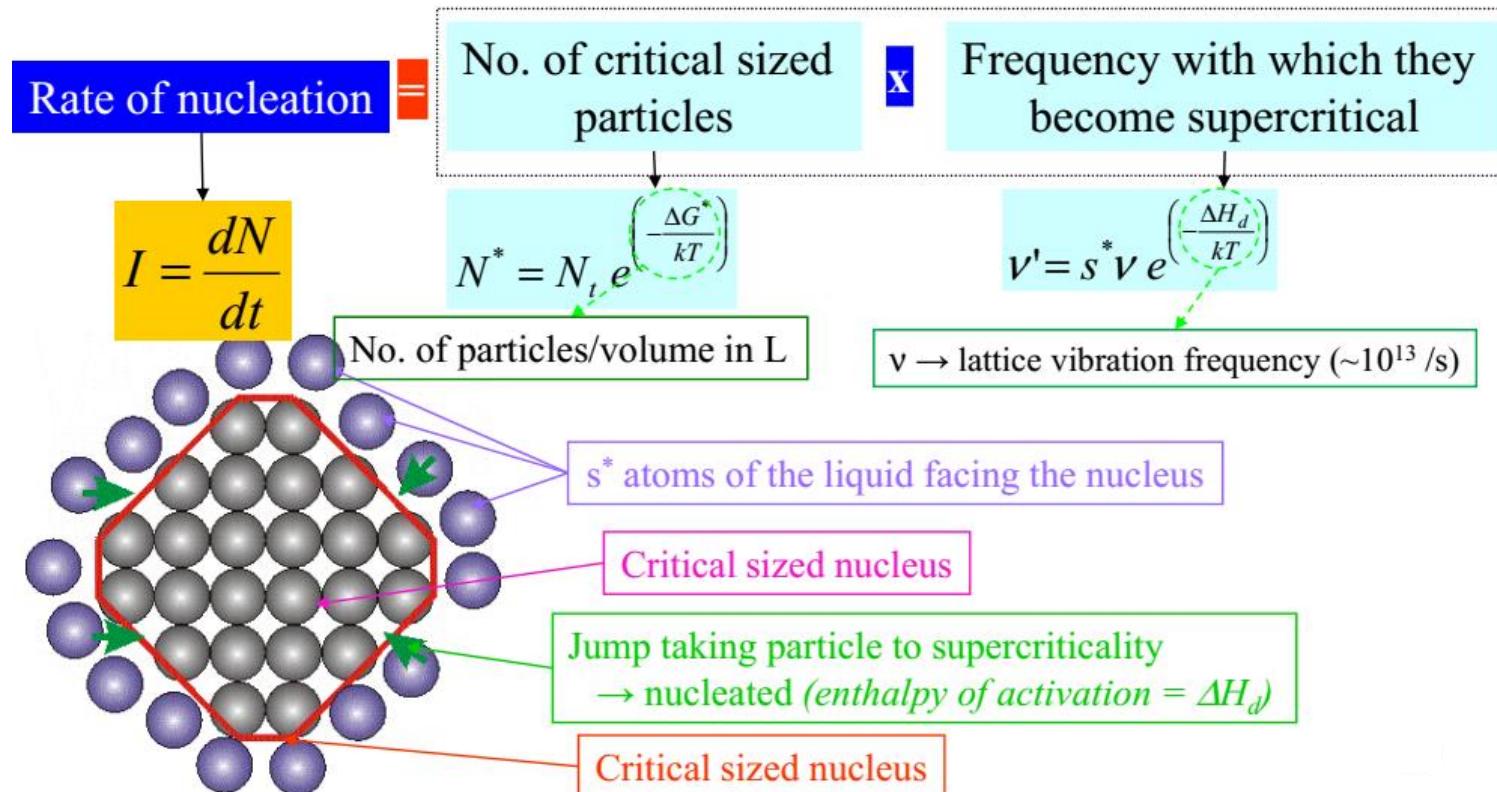
$$N^* = N_t e^{\left(-\frac{\Delta G^*}{kT}\right)}$$



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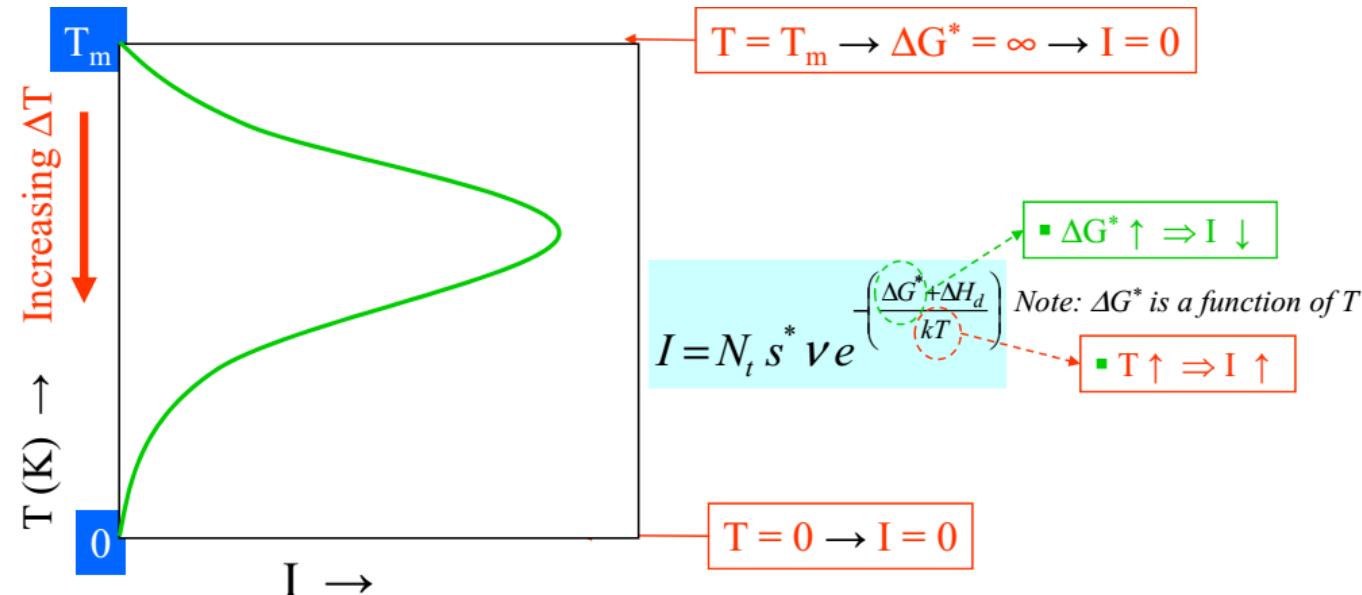
- The number of potential atoms, which can jump to make the critical nucleus supercritical are the atoms which are 'adjacent' to the liquid  $\rightarrow$  let this number be  $S^*$ .
- If the lattice vibration frequency is  $v$  and the activation barrier for an atom facing the nucleus (i.e. atom belonging to  $S^*$ ) to jump into the nucleus (to make it supercritical) is  $\Delta H_d$ , the frequency with which nuclei become supercritical due atomic jumps into the nucleus is given by:

$$v' = S^* v e^{\left(-\frac{\Delta H_d}{kT}\right)}$$



# Contd...

- The nucleation rate ( $I = dN/dt$ ) can be written as a product of the two terms as in the equation below.
- How does the plot of this function look with temperature?
- At  $T_m$ ,  $\Delta G^*$  is  $\infty \rightarrow I = 0$  (as expected if there is no undercooling there is no nucleation).
- At  $T = 0K$  again  $I = 0$ .
- This implies that the function should reach a maximum between  $T = T_m$  and  $T = 0$ .
- A schematic plot of  $I(T)$  (or  $I(\Delta T)$ ) is given in the figure below. An important point to note is that the nucleation rate is not a monotonic function of undercooling.



# Heterogeneous Nucleation

- We have already talked about the ‘nucleation barrier’ and the difficulty in the nucleation process.
- This is all the more so for fully solid state phase transformations, where the **strain energy term** is also involved (which opposes the transformation).
- The nucleation process is often made ‘easier’ by the presence of ‘defects’ in the system.
- In the solidification of a liquid this could be the mold walls.
- For solid state transformation **suitable nucleation sites** are: non-equilibrium defects such as **excess vacancies, dislocations, grain boundaries, stacking faults, inclusions and surfaces**.
- One way to visualize the **ease of heterogeneous nucleation** → heterogeneous nucleation at a defect will lead to destruction/modification of the defect (make it less “defective”). This will lead to some **free energy  $\Delta G_d$**  being released → thus reducing the activation barrier.

$$\Delta G_{\text{hetro, defect}} = (V)(\Delta G_v - \Delta G_s) + A\gamma - (\Delta G_d)$$

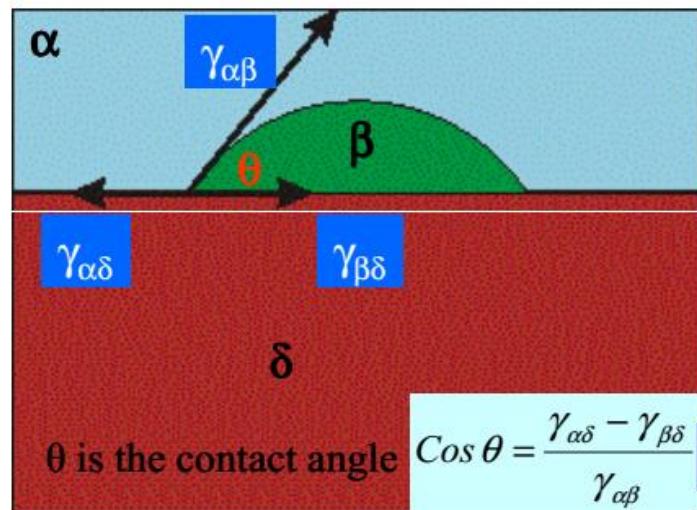
- **Increasing  $\Delta G_d$  (i.e. increasing  $\Delta G^*$ )**
  - Homogenous sites
  - Vacancies
  - Dislocations
  - Stacking Faults
  - Grain boundaries (triple junction), Interphase boundaries
  - Free surface



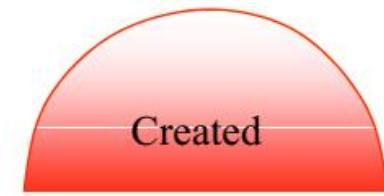
# Contd...

- Consider the nucleation of  $\beta$  from  $\alpha$  on a planar surface of inclusion  $\delta$ . The nucleus will have the shape of a lens (as in the figure below).
- Surface tension force balance equation can be written as in equation (1) below. The contact angle can be calculated from this equation (as in equation (3)).
- Keeping in view, the interface areas created and lost we can write the  $\Delta G$  equation as below (2).

The volume of liquid in a spherical tank of radius  $r$  is related to the depth  $h$  of the liquid, is given by:



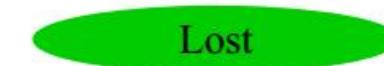
## Interfacial Energies



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



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



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

$$\text{Surface tension force balance} \longrightarrow \gamma_{\alpha\beta} \cos \theta + \gamma_{\beta\delta} = \gamma_{\alpha\delta} \rightarrow 1$$

$$\Delta G = (V_{\text{lens}}) \Delta G_v + (A_{\text{lens}}) \gamma_{\alpha\beta} + (A_{\text{circle}}) \gamma_{\beta\delta} - (A_{\text{circle}}) \gamma_{\alpha\delta} \rightarrow 2$$

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

$$A_{\text{lens}} = 2\pi r h$$

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

$$r_{\text{circle}} = r \sin\theta$$



# Contd...

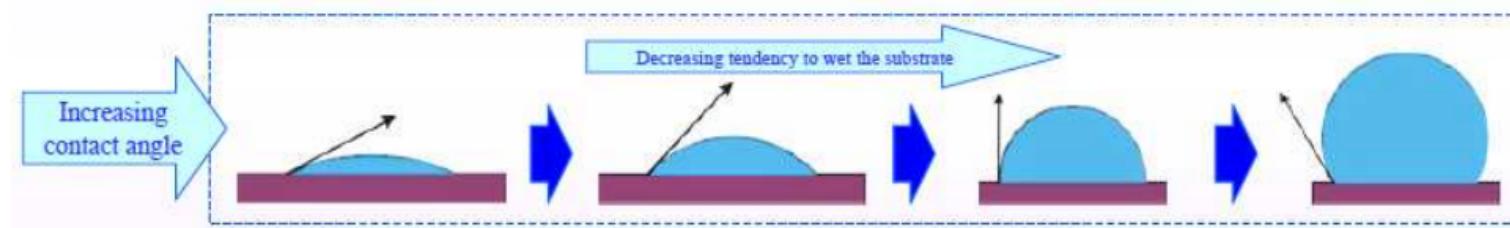
- Using the procedure as before (for the case of the homogenous nucleation) we can find  $r^*$  for heterogeneous nucleation. Using the surface tension balance equation we can write the formulae for  $r^*$  and  $\Delta G^*$  using a single interfacial energy  $\gamma_{\alpha\beta}$  (and contact angle  $\theta$ ).
- Further we can write down  $\Delta G^*_{\text{hetero}}$  in terms of  $\Delta G^*_{\text{homo}}$  and contact angle  $\theta$ .

$$\frac{d\Delta G}{dr} = 0 \rightarrow r_{\text{hetero}}^* = -\frac{2\gamma_{\alpha\beta}}{\Delta G_V} \quad \Delta G_{\text{hetero}}^* = \frac{4}{3}\pi \frac{\gamma_{\alpha\beta}^3}{\Delta G_V^2} (2 - 3\cos\theta + \cos^3\theta)$$

$$\Delta G_{\text{hetero}}^* = \frac{1}{4} G_{\text{homo}}^* (2 - 3\cos\theta + \cos^3\theta)$$

$$\frac{\Delta G_{\text{hetero}}^*}{G_{\text{homo}}^*} = \frac{1}{4} (2 - 3\cos\theta + \cos^3\theta)$$

Just a function of  $\theta \rightarrow$   
The contact angle



$$\frac{\Delta G_{\text{hetero}}^*}{G_{\text{homo}}^*} = \frac{1}{4} (2 - 3\cos\theta + \cos^3\theta) = f(\theta)$$

$$\theta = 0^\circ \rightarrow f(\theta) = 0$$

Complete wetting

$$\theta = 90^\circ \rightarrow f(\theta) = 1/2$$

Partial wetting

$$\theta = 180^\circ \rightarrow f(\theta) = 1$$

No wetting

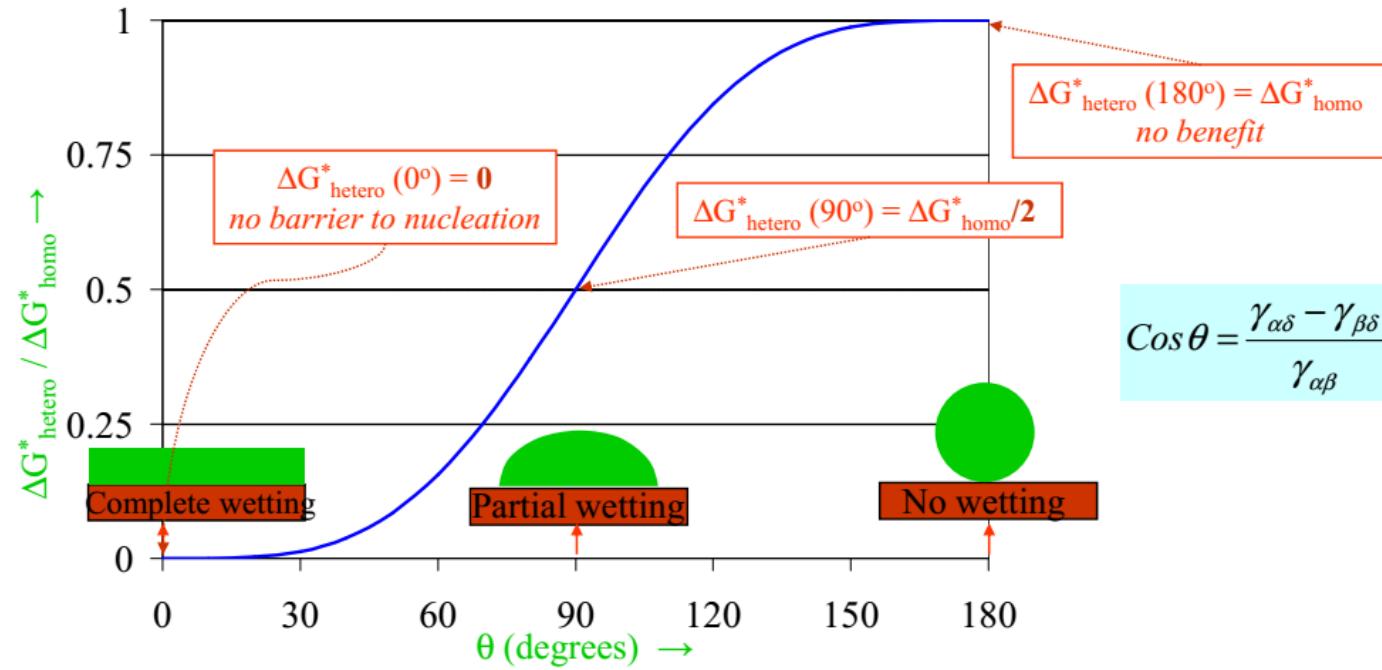
The plot of  $\Delta G_{\text{hetero}}^* / \Delta G_{\text{homo}}^*$  is shown in the next page

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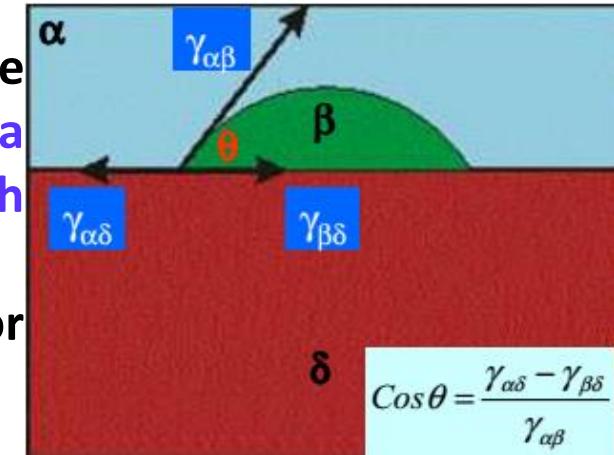
# Contd...

- Plot of  $\Delta G^*_{\text{hetero}} / \Delta G^*_{\text{homo}}$  is shown below. This brings out the benefit of heterogeneous nucleation vs homogenous nucleation.
- If the  $\beta$  phase nucleus (lens shaped) completely wets the substrate/inclusion ( $\delta$ -phase) (i.e.  $\theta = 0^\circ$ )  $\rightarrow$  then  $\Delta G^*_{\text{hetero}} = 0$   $\rightarrow$  there is no barrier to nucleation.
- On the other extreme if  $\beta$ -phase does not wet the substrate (i.e.  $\theta = 180^\circ$ )  $\rightarrow \Delta G^*_{\text{hetero}} = \Delta G^*_{\text{homo}} \rightarrow$  there is no benefit of the substrate. In reality the wetting angle  $\theta$  is somewhere between  $0^\circ - 180^\circ$ .
- Hence, we have to choose a heterogeneous nucleating agent with a minimum ' $\theta$ ' value.



# Choice of Heterogeneous Nucleating Agent

- Heterogeneous nucleation has many practical applications.
- During the solidification of a melt if only a few nuclei form and these nuclei grow, we will have a coarse grained material (which will have a lower strength as compared to a fine grained material due to Hall-Petch effect).
- Hence, nucleating agents are added to the melt (e.g. Ti for Al alloys, Zr for Mg alloys) for grain refinement.
- How to get a small value of  $\theta$ ? (so that 'easy' heterogeneous nucleation).
  - 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  $\rightarrow$  high  $\gamma_{\alpha\delta}$  or low  $\gamma_{\beta\delta}$ )
- How to get a low value of  $\gamma_{\beta\delta}$ ?
  - We can get a low value of  $\gamma_{\beta\delta}$ .
    - Crystal structure of  $\beta$  and  $\delta$  are similar.
    - lattice parameters are as close as possible.
  - Examples of such choices are:-
    - Seeding rain-bearing clouds  $\rightarrow$  AgI or NaCl  $\rightarrow$  nucleation of ice crystals.
    - Ni (FCC,  $a = 3.52 \text{ \AA}$ ) is used a heterogeneous nucleating agent in the production of artificial diamonds (FCC,  $a = 3.57 \text{ \AA}$ ) from graphite.

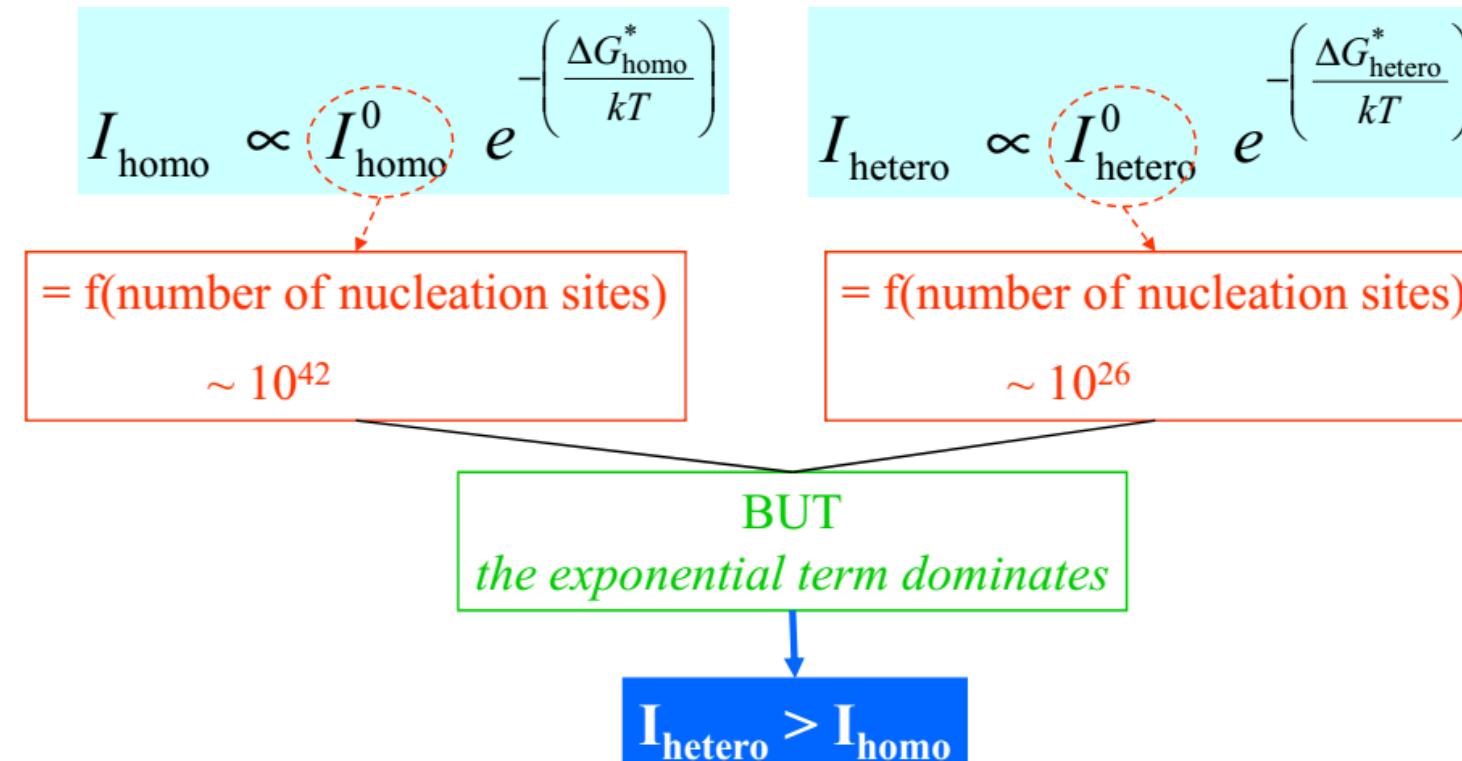


$$\cos \theta = \frac{\gamma_{\alpha\delta} - \gamma_{\beta\delta}}{\gamma_{\alpha\beta}}$$



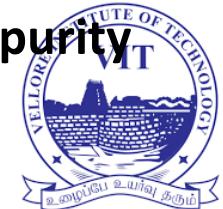
# Why Does Heterogeneous Nucleation Rate Dominate?

- To understand the above questions, let us write the nucleation rate for both cases as a pre-exponential term and an exponential term. The pre-exponential term is a function of the number of nucleation sites.
- However, the term that dominates is the exponential term and due to a lower  $\Delta G^*$  the heterogeneous nucleation rate is typically higher.



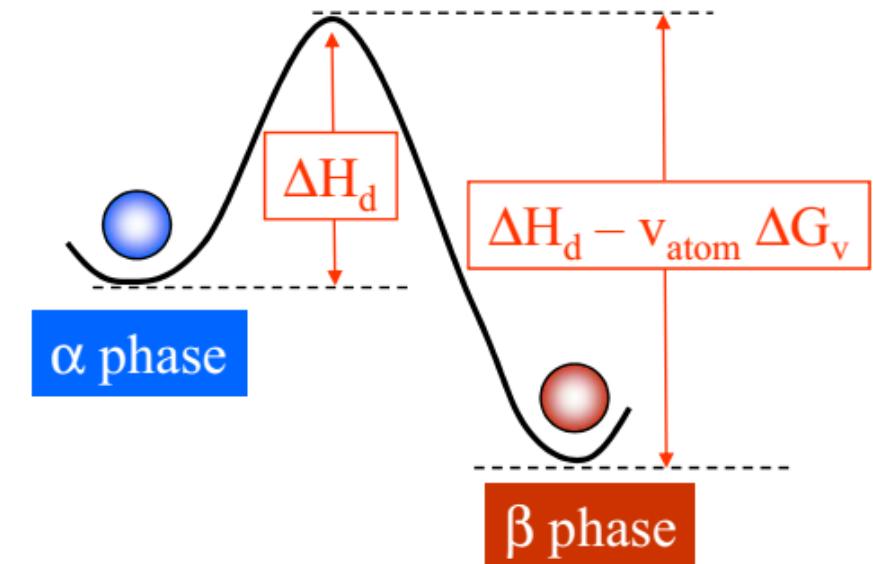
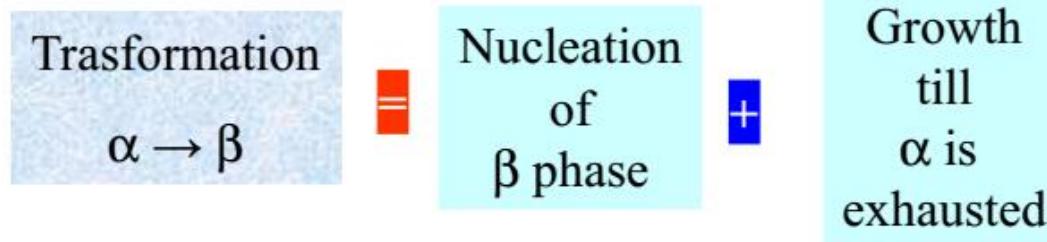
# Summary

- Compared to the heterogeneous nucleation (which starts at nucleation sites on surfaces) homogeneous nucleation occurs with much more difficulty in the interior of a uniform substance. The creation of a nucleus implies the formation of an interface at the boundaries of a new phase.
- Liquids cooled below the maximum heterogeneous nucleation temperature (melting temperature) but which are above the homogeneous nucleation temperature. (pure substance freezing temperature) are cooled super cooled.
- An example of super-cooling: pure water freezes at  $-42^{\circ}\text{C}$  rather than at its freezing temperature  $0^{\circ}\text{C}$ .
  
- **Nucleation:** The physical process by which a new phase is produced in a material.
- **Critical radius ( $r^*$ ):** The minimum size that must be formed by atoms clustering together in the liquid before the solid particle is stable and begins to grow.
- **Undercooling:** The temperature to which the liquid metal must cool below the equilibrium freezing temperature before nucleation occurs.
- **Homogeneous nucleation:** Formation of a critically sized solid from the liquid by the clustering together of a large number of atoms at a high undercooling (without an external interface).
- **Heterogeneous nucleation:** Formation of a critically sized solid from the liquid on an impurity surface.



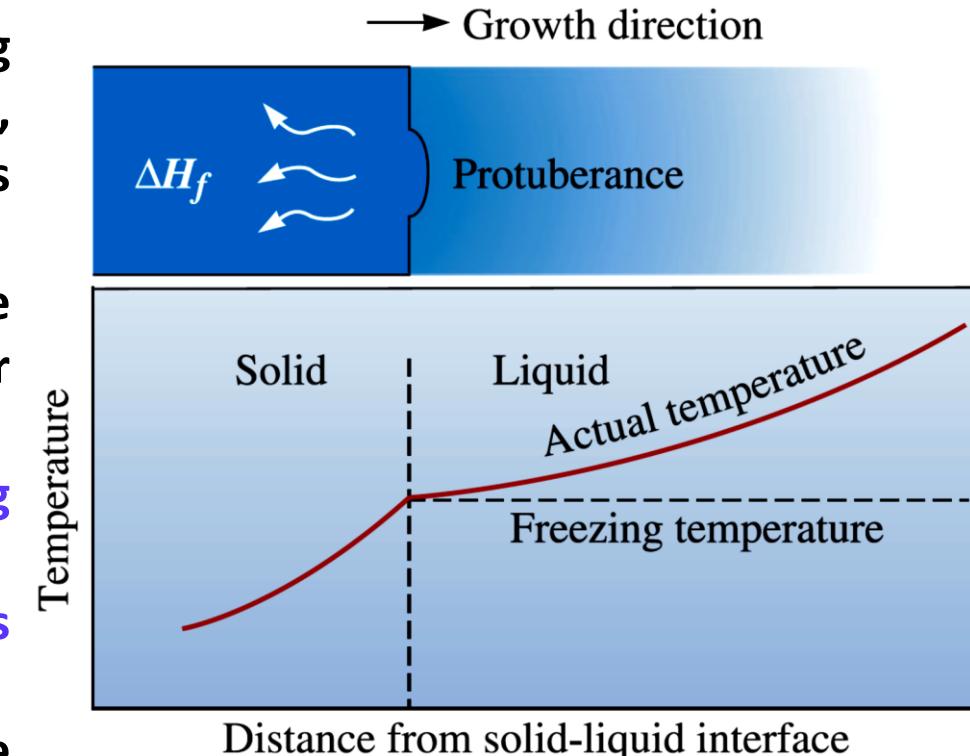
# Growth of a Pure Solid

- 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.
- There are basically **two different types of solid/liquid interface**: an atomically rough or diffuse interface associated with metallic systems, and an atomically flat or sharply defined interface often associated with nonmetals.
- Because of the differences in atomic structure these two types of interface migrate in quite different ways. **Rough interface** migrate by a continuous growth (planar) processes while **flat interface** migrate by lateral growth (dendritic/spiral growth and surface nucleation) process involving ledges.



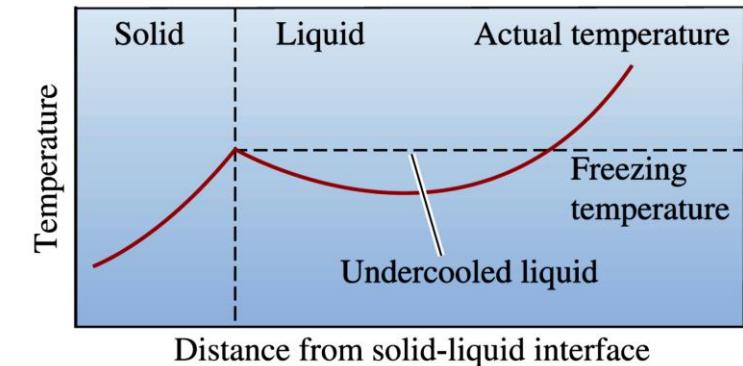
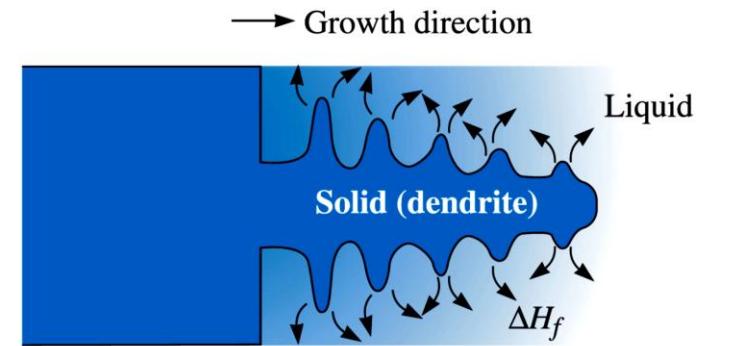
# Planar Growth

- When the temperature of the liquid is above the freezing temperature, a protuberance on the solid-liquid interface will not grow, leading to maintenance of a planar interface.
- Latent heat is removed from the interface through the solid.
- When a well-inoculated liquid (i.e., a liquid containing nucleating agents) cools under equilibrium conditions, there is no need for undercooling since heterogeneous nucleation can occur.
- Therefore, the temperature of the liquid ahead of the solidification front (i.e., solid-liquid interface) is greater than the freezing temperature.
- The temperature of the solid is at or below the freezing temperature.
- During solidification, the latent heat of fusion is removed by conduction from the solid-liquid interface.
- Any small protuberance that begins to grow on the interface is surrounded by liquid above the freezing temperature.



# Dendritic Growth

- If the liquid is undercooled (the temperature of the liquid is below the freezing temperature), a protuberance on the solid-liquid interface can grow rapidly as a dendrite.
- The latent heat of fusion is removed by raising the temperature of the liquid back to the freezing temperature.
- When the liquid is not inoculated and the nucleation is poor, the liquid has to be undercooled before the solid forms.
- Under these conditions, a small solid protuberance called a dendrite forms at the interface, is encouraged to grow since the liquid ahead of the solidification front is undercooled.
- The word dendrite comes from the Greek word dendron that means tree.
- Dendritic growth continues until the undercooled liquid warms to the freezing temperature due to the release of the latent heat.
- Any remaining liquid then solidifies by planar growth.



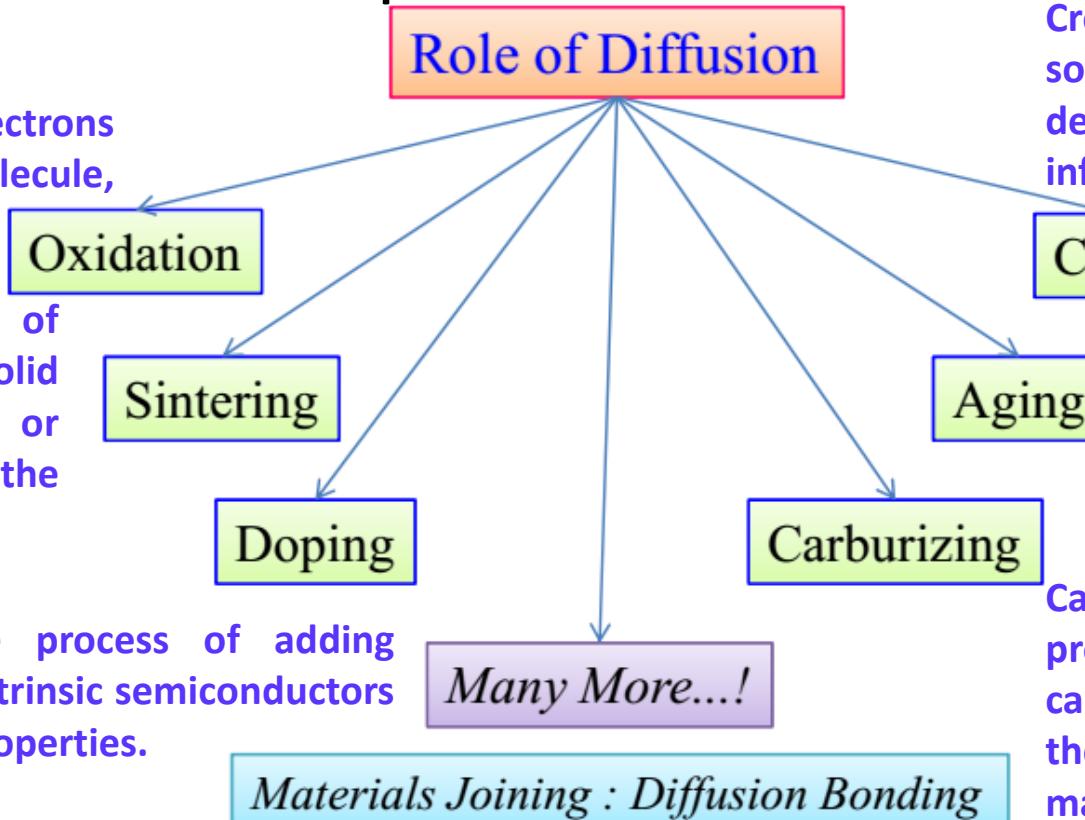
# Diffusion – Introduction

- Diffusion is defined as, random movement of atoms/molecules in solid, liquid and gas. For example dissolution of ink in water and smoke in air.
- It can also be defined as, Diffusion is a process of mass transport by atomic movement under the influence of thermal energy and a concentration gradient.
- To comprehend many materials related phenomenon one must understand diffusion.

Oxidation is the loss of electrons during a reaction by a molecule, atom or ion.

Sintering is the process of compacting and forming a solid mass of material by heat or pressure without melting it to the point of liquefaction.

Doping is the process of adding impurities to intrinsic semiconductors to alter their properties.



Creep is the tendency of a solid material to move slowly or deform permanently under the influence of mechanical stresses.

Age hardening, is a heat treatment technique used to increase the yield strength of malleable materials, including most structural alloys of Al, Mg, Ni, Ti, and some steels.

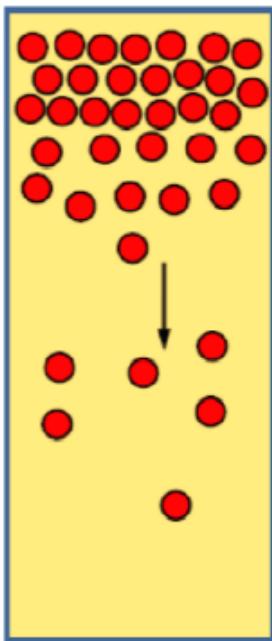
Carburization is a heat treatment process in which iron or steel absorbs carbon while the metal is heated in the presence of a carbon-bearing material, such as charcoal or CO.



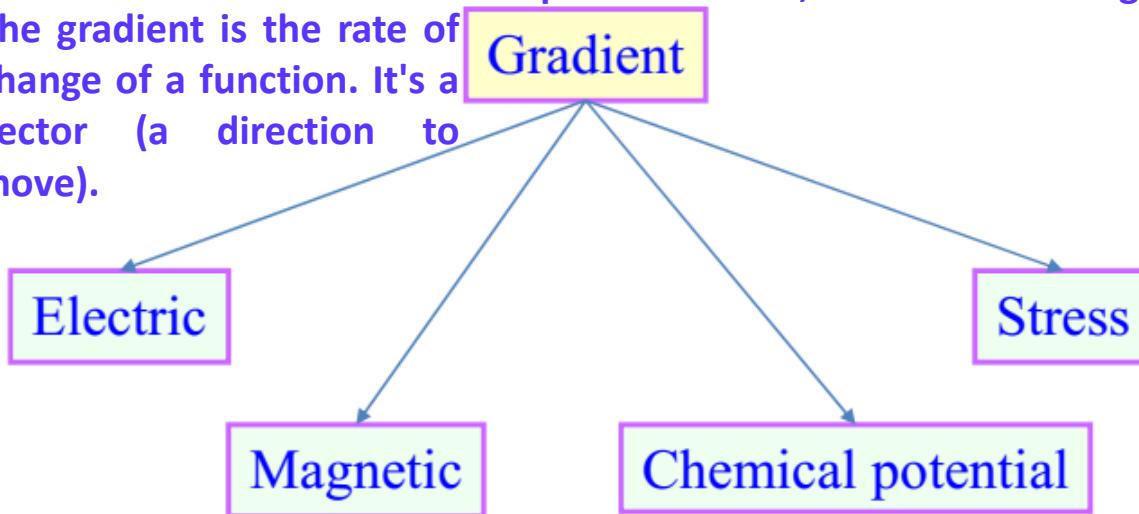
# Diffusion Phenomena

- Mass flow process by which species change their position relative to their neighbors.
- Driven by thermal energy and a gradient.
- Thermal energy → thermal vibrations → Atomic jumps
- Atoms move from higher to lower concentration region. If this movement is from one element to another e.g. Cu to Ni, then it is termed as Inter-diffusion. If the movement is within similar atoms as in pure metals, it is termed self-diffusion.

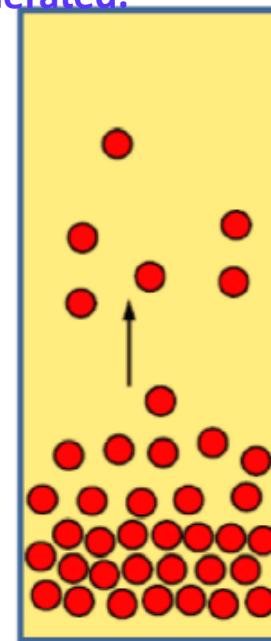
Thermal energy is the energy that comes from heat. This heat is generated by the movement of tiny particles within an object. The faster these particles move, the more heat is generated.



The gradient is the rate of change of a function. It's a vector (a direction to move).

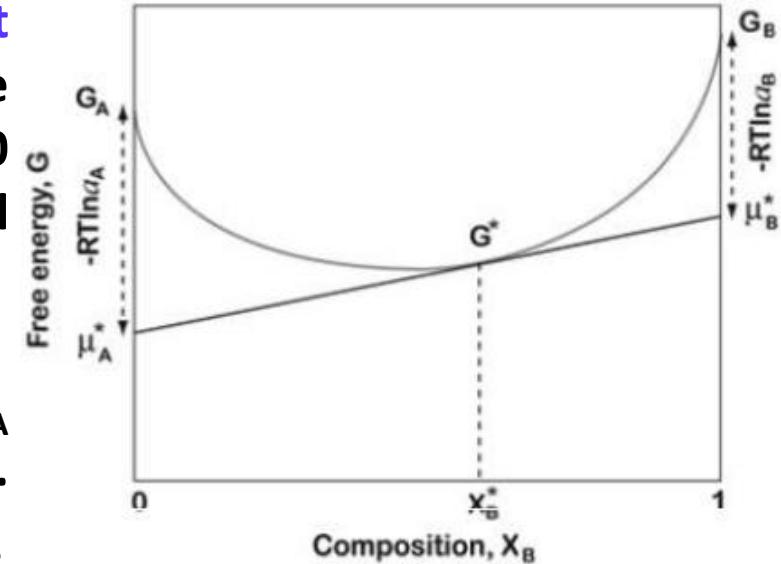


The chemical potential of a substance  $i$  is the partial molar derivative of the free energy  $G$ , the enthalpy  $H$ , the Helmholtz energy  $A$ , or the internal energy  $U$  of substance  $i$ .



# Diffusion Under Thermodynamic Driving Force

- As explained in the figure, the chemical potential of elements at any composition can be determined by taking a slope on the Gibb's free energy curve and then by extending it to  $X_B = 0$  (chemical potential of element A,  $\mu_A$ ) and  $X_B = 1$  (chemical potential of element B,  $\mu_B$ ).

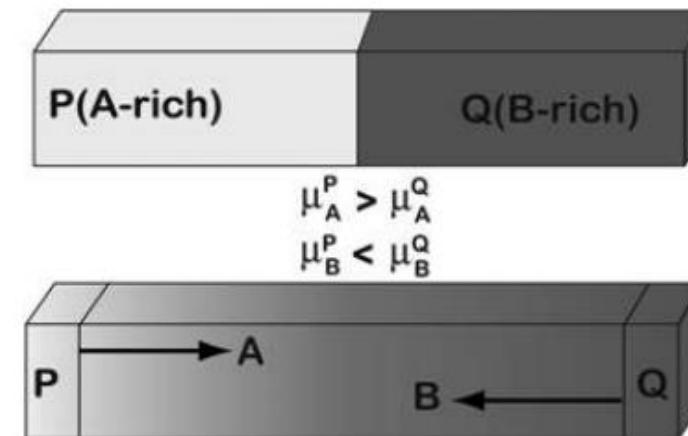
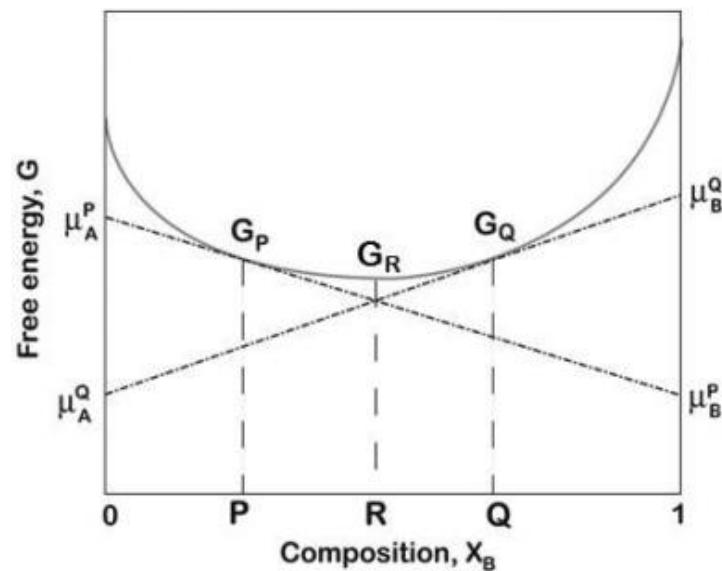


- From the chemical potentials, we can determine the activities,  $a_A$  and  $a_B$  from the knowledge of free energies of pure elements.
  - $- RT \ln a_A = G_A - \mu_A$
  - $- RT \ln a_B = G_B - \mu_B$
- So it must be clear that  $\mu_B$  decreases from  $G_B$  at  $X_B = 1$  to a infinitely small value close to  $X_B = 0$ .
- Following,  $a_B$  decreases from 1 at  $X_B = 1$  to 0 at  $X_B = 0$ . It may vary ideally, that is  $a_B = X_B$  or deviate positively/negatively, as explained previously.
- Similarly,  $\mu_A$  decreases from  $G_A$  at  $X_B = 0$  to a infinitely small value close to  $X_B = 1$ .  $a_B$  decreases from 1 at  $X_B = 0$  to 0 at  $X_B = 1$
- So,  $\mu_A$  and  $a_A$ , and  $\mu_B$  and  $a_B$  follow the same trend of increasing or decreasing with  $X_B$ .



# Contd...

- Now let us consider, two different AB alloys P (A-rich) and Q (B-rich).
- If these alloys are kept separately, these alloys will have free energy of  $G_P$  and  $G_Q$ , respectively.
- However, if we bond these two blocks, they will not be anymore in equilibrium condition.
  
- If the amount of material P and Q are taken such that overall mole fraction is R, then the equilibrium free energy will be  $G_R$ .
- So the system will try to move to its new equilibrium free energy.
- Now if we don't melt the alloy, it can only move to the equilibrium composition by solid state diffusion.

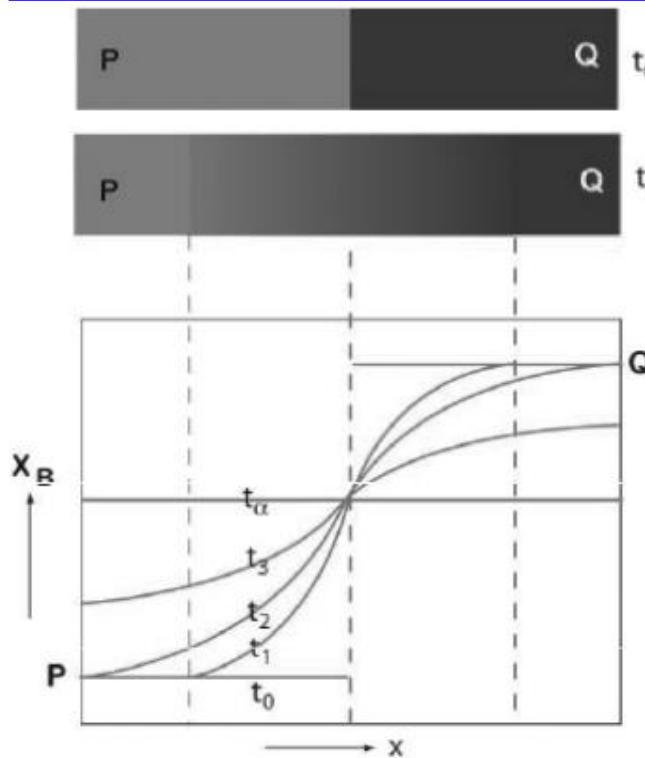


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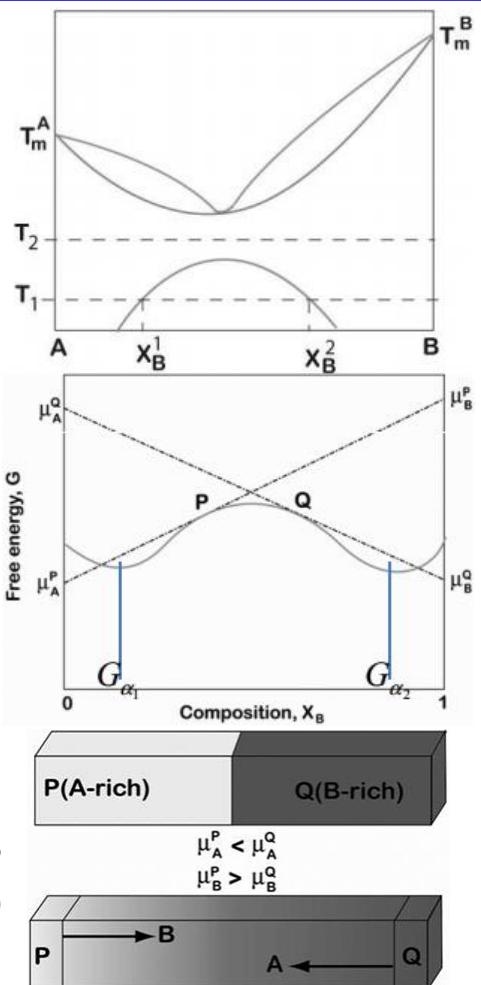
- If it is held at elevated temperature at which diffusion rate is reasonable, the system will reach to the equilibrium after certain time depending on the diffusion rate.
- It can be seen that at equilibrium alloy R, the chemical potential of A is  $\mu_A^R$ , which is lower than the chemical potential of the same element,  $\mu_A^P$ , in alloy P but higher than in alloy Q, that is  $\mu_A^Q$ .
- On the other hand,  $\mu_B^R$  is less than  $\mu_B^Q$  but higher than  $\mu_B^P$ .
- So to reach the equilibrium, the alloy P should decrease the chemical potential of A and increase the chemical potential of B. On the other hand, the alloy Q should increase the chemical potential of A and decrease the chemical potential of B.
  
- Since the chemical potential of A decreases from the A rich to the B rich alloy and the chemical potential of B decreases from B rich to A rich alloy, P should decrease the content of A and Q should decrease the content of B.
- In this condition it is possible only by the diffusion of element A out of P and diffusion of element B out of alloy Q, as shown in the figure in the previous slide.
- If we allow the system to go to equilibrium at temperature T, there will be no composition in the blocks P and Q at time zero that is  $t_0$ . Then with the increase in time in the order of  $t_3 > t_2 > t_1 > t_0$ , as shown in the figure (next slide), interaction zone increases. Following, after infinite time of annealing,  $t_\alpha$  it will reach to equilibrium composition.



# Contd...



- Note here that infinite time is rather notional. It means that long time enough to reach it to equilibrium.
- So this time will depend on the thickness of the blocks and the diffusion rate at the temperature of annealing.



- Now let us consider a system with miscibility gap.
- If we anneal two block with any compositions at temperature,  $T_2$ , the explanation of the diffusion process will be similar as explained before.
- However, if we couple two blocks with the composition of P and Q, which are inside the miscibility gap, different situation will happen.
- From the slopes taken at P and Q, we find,
 
$$\mu_A^P < \mu_A^Q \text{ and } \mu_B^P > \mu_B^Q$$
- That means, the chemical potential of A is less in A rich alloy, P compared to the A lean alloy, Q.
- Similarly, the chemical potential of B is higher in B lean alloy, P compared to the B rich alloy, Q.
- If we couple blocks of P and Q then the average free energy of the systems, let say, R depending on the relative amounts of P and Q.
- However, since the system always tries to decrease free energy, it will try to reach to the lowest free energy  $G_{\alpha 1}$  and  $G_{\alpha 2}$ .

# Contd...

- ❑ That means A rich alloy P should increase the content of A and the B rich alloy Q should increase the content of B.
- ❑ From the chemical potential point of view also it must be clear that B will diffuse out of the B lean alloy P towards Q and A will diffuse out of the B lean alloy Q towards P.
- ❑ The direction of elements is just opposite compared to the previous example explained.

- ❑ Since elements diffuse up the concentration gradient instead of down the concentration gradient, it is called **uphill diffusion**.
- ❑ In terms of chemical potential gradient:

$$J_A \alpha \frac{\mu_A^P - \mu_A^Q}{\Delta x} \Rightarrow J_A = -L_A \frac{d\mu_A}{dx} \quad \text{Since } A \text{ diffuse from } Q \text{ to } P \text{ and}$$

and B diffuse from P to Q

$$J_B \alpha \frac{\mu_B^Q - \mu_B^P}{\Delta x} \Rightarrow J_B = -L_B \frac{d\mu_B}{dx}$$

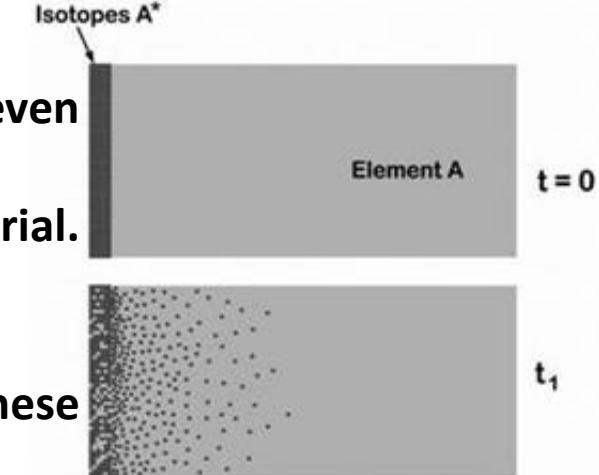
where, J = flux of solute atoms

- ❑ In terms of concentration gradient:
- $$J_A = D_A \frac{C_A^P - C_A^Q}{dx} \Rightarrow J_A = D_A \frac{dC_A}{dx}$$
- $$J_B = D_B \frac{C_B^Q - C_B^P}{dx} \Rightarrow J_B = D_B \frac{dC_B}{dx}$$



# Contd...

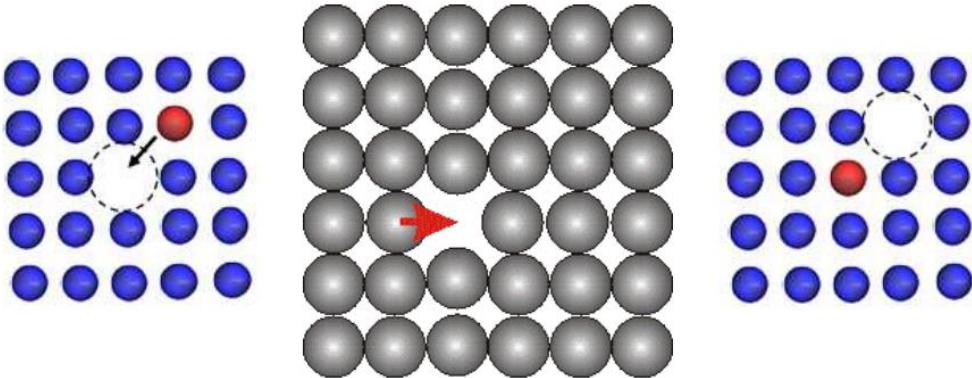
- In previous slides we have shown diffusion of elements because of **chemical potential driving forces**.
- However, diffusion occurs even without the presence of **thermo-dynamical driving force** or any other driving forces.
- For example, in pure material, where there are no forces present but atoms still tend to jump to another position.
- In a low melting point material, like in Sn or Pb, jump of atoms possible even at room temperature. However, jump of atoms in this case is completely random. Presence of driving forces rather make net flux of atoms to a particular direction.
- To test the possibility of diffusion without any driving forces tracer diffusion experiments are conducted. Radiotracer elements which has one or two neutron mass difference are deposited on a material of the same element and then annealed at elevated temperature.
- Concentration of these tracer elements can be measured at different depths even in low concentration because of radiation of different rays.
- As shown in a schematic figure, these tracer elements diffuse inside the material. Since both are pure elements there is no chemical potential difference.
- These tracer elements are used to trace the diffusion of elements.
- There will be very small gain (increase in entropy) because of spreading of these tracer elements.
- If we do not use the tracer elements we will not be able to detect the jump of atoms.



# Diffusion Mechanism

- Diffusion of atoms involves movement in steps from one lattice site to the another. An **empty adjacent site** and **breaking of bonds with the neighbor atoms** are the two necessary conditions for this.

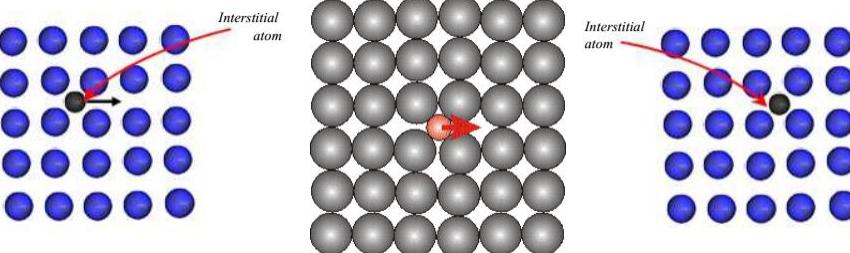
- **Vacancy mechanism**:- This mechanism involves movement of atoms (we are interested in substitutional atoms) from a regular lattice site to an adjacent vacancy. Since vacancy and atoms exchange position, the vacancy flux is in the opposite direction.



- **Interstitial mechanism**:- This mechanism Involves migration of atoms from one interstitial site to a neighboring empty interstitial site.

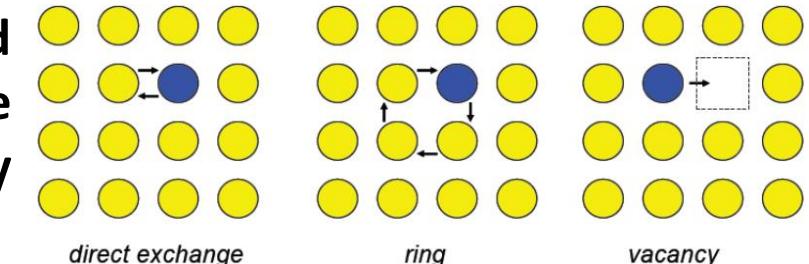
- Usually the solubility of interstitial atoms (e.g. carbon in steel) is small. This implies that most of the interstitial sites are vacant. Hence, if an interstitial species wants to jump, 'most likely' the neighboring site will be vacant and jump of the atomic species can take place.

- This mechanism is more prevalent for impurity such as **hydrogen, carbon, nitrogen, and oxygen** which are small enough to fit into an interstitial position.

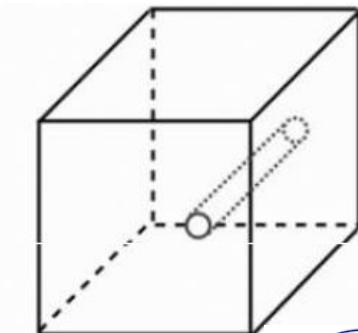
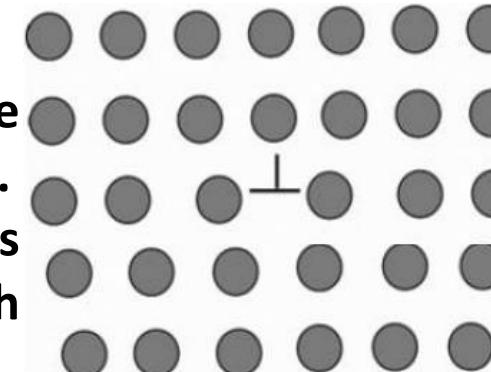


# Contd...

- **Atom interchange mechanism:** It is possible for movement to take place by a direct interchange between two adjacent atoms or by a four – atom ring interchange.
- However, these would probably occur only under special conditions, since the physical problem of squeezing between closely packed neighboring atoms would increase the barrier for diffusion.
- Note:- The rate of diffusion is much greater in a rapidly cooled alloy than in the same alloy slow cooled. The difference is due to the larger number of vacancies retained in the alloy by fast cooling.
- **Pipe diffusion:** When diffusion occurs via edge dislocation, it is called **pipe diffusion**.
- Since it feels like movement of atoms through a pipe.
- Note that both interstitial and substitutional diffusion can occur via dislocations.

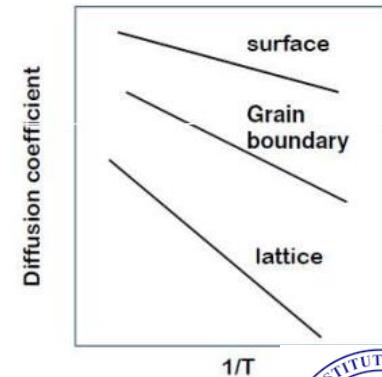
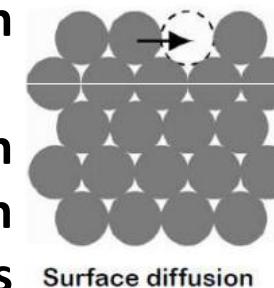
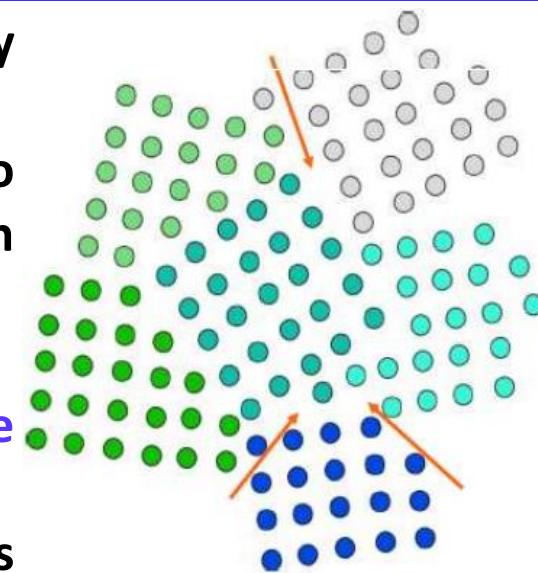


- Even impurities are attracted by the dislocations because of availability of more space and chance to release stress.
- This is also the reason (more open space) that it has lower activation barrier and diffusion rate through dislocation is higher than the diffusion through lattice.



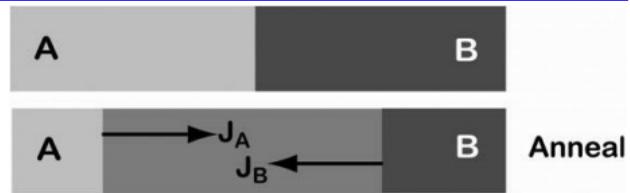
# Contd...

- **Grain boundary diffusion:** Diffusion occurs via grain boundaries even easily and it is called **grain boundary diffusion**.
- Since grain boundaries are relatively more open structure compared to atomic structure inside the grains, the barrier for diffusion through grain boundary is much less and the diffusion rate is higher.
- Rate of diffusion increases with the increase in misorientations.
- **Surface diffusion:** When diffusion occurs over a surface, it is called **surface diffusion**.
- Here activation energy for diffusion is the lowest since there are no atoms above the atom of interest, which exchanges position with the vacancy. So diffusion rate is the highest compared to other diffusion mechanisms.
- Note that both interstitial and substitutional diffusion can happen through, lattice, dislocations, grain boundaries and surface.
- Slope of the diffusion coefficient vs.  $1/T$  gives the activation barrier for diffusion. Activation barrier is the lowest and diffusion rate is the highest for the surface diffusion. Activation barrier is the highest and diffusion rate is the lowest for lattice diffusion.
- An **activation barrier** is a sort of energetic hurdle that a reaction must get over.



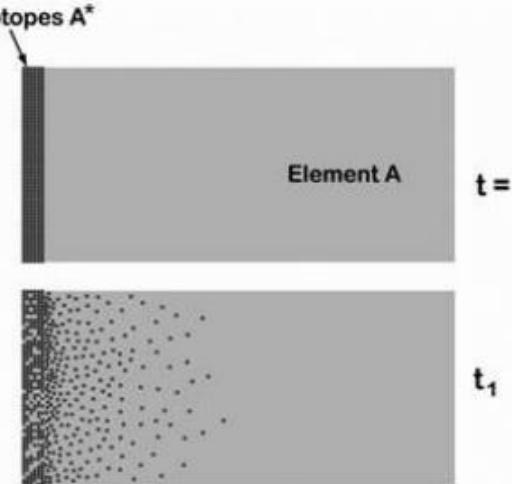
# Contd...

- **Diffusion couple:** When two blocks with different compositions are joined (coupled) together and annealed to allow diffusion between them, it is called **diffusion couple**.
- **Inter-diffusion (chemical diffusion):** Since elements in the diffusion couple inter-diffuse to each other, it is called **inter-diffusion**.
- The diffusion coefficient is in general called as inter-diffusion coefficient and if sometimes any new compound forms during the diffusion at the interface, occasionally, it is called **chemical diffusion coefficient**.
- Note that actually elements A and B diffuse. Diffusion of these elements are called **intrinsic diffusion of elements**.
- **Self diffusion:** When diffusion occurs without any presence of driving force, it is called **self diffusion**.
- Atoms vibrate at their positions and because of some violent jumps, it can cross the activation barrier to make the jump successful.
- Since there is no driving force to direct the jump of atoms to a particular direction, self diffusion is truly random in nature.
- This indicates that when a pure metal is kept at elevated temperature jump of atoms is always happening.
- In low melting point metals, like In or Sn, even at room temperature, atoms exchange their position.



# Contd...

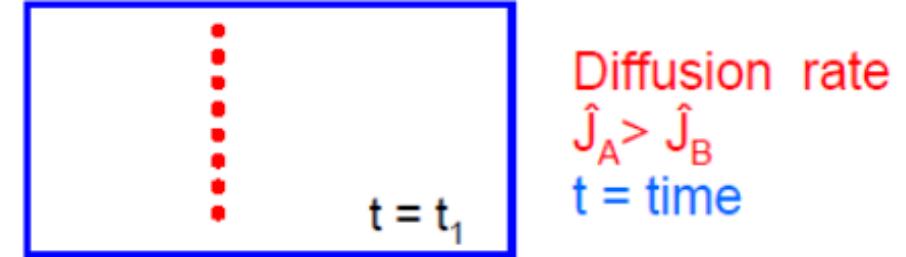
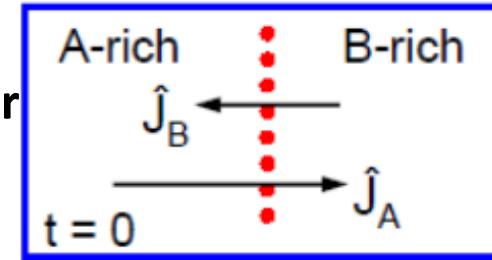
- However, since these are very small in size, we cannot follow a particular atom jump.
- We shall see that the jump can be many orders of magnitude in one second. This makes it even difficult to follow the jump of atoms.
- To obviate this problem, concept of **tracer diffusion** is introduced.
- **Tracer diffusion:** Radio isotopes are used in tracer method so that the movement of atoms can be traced and diffusion coefficient can be measured.
- It has only one or two neutron mass difference.
- Diffusion rate of these tracer atoms are called **tracer diffusion coefficient**.
- Note: Self diffusion coefficient ( $D_s$ ) is not necessarily equal to the tracer diffusion coefficient ( $D^*$ ). These two are related as:-
$$D^* = f D_s \quad f \text{ is the correlation factor } (f = 1 \text{ for interstitial diffusion})$$
- When tracer diffusion coefficient of element B in pure material A is measured, it is called **impurity diffusion coefficient**.



# Kirkendall Effect

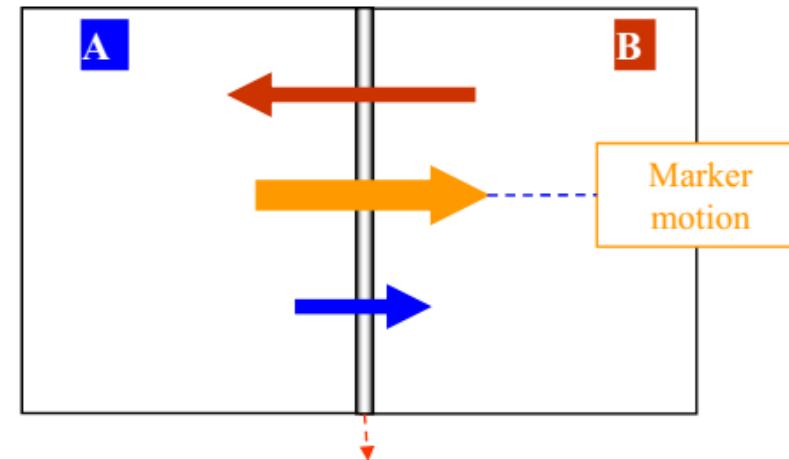
- If the diffusion rates of two metals A and B into each other are different, the boundary between them shifts and moves towards the faster diffusing metal. This is known as **kirkendall effect**.

- Named after the inventor **Ernest Kirkendall** (1914- 2005).



- It can be demonstrated experimentally by placing an inert marker at the interface.

- ✓ Materials A and B welded together with inert marker and given a diffusion anneal
  - ✓ Usually the lower melting component diffuses faster (say B)

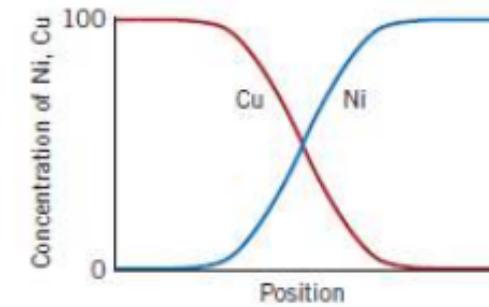
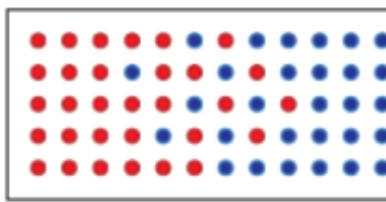
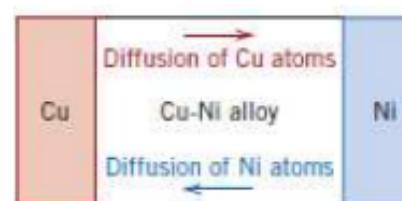
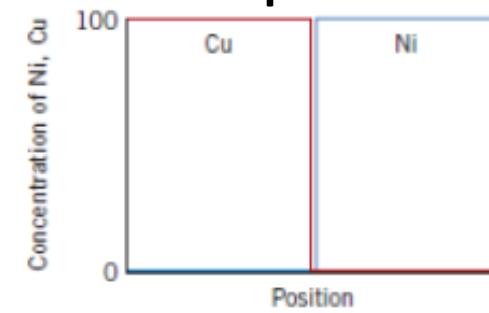
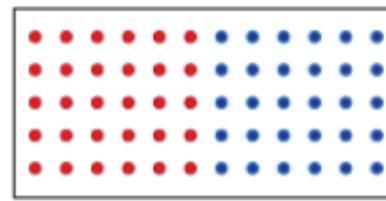
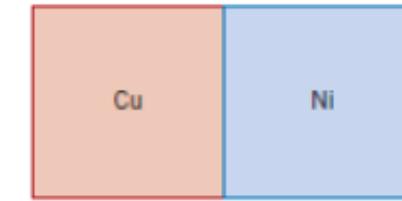


**Inert Marker** – thin rod of a high melting material which is basically insoluble in A & B



# Contd...

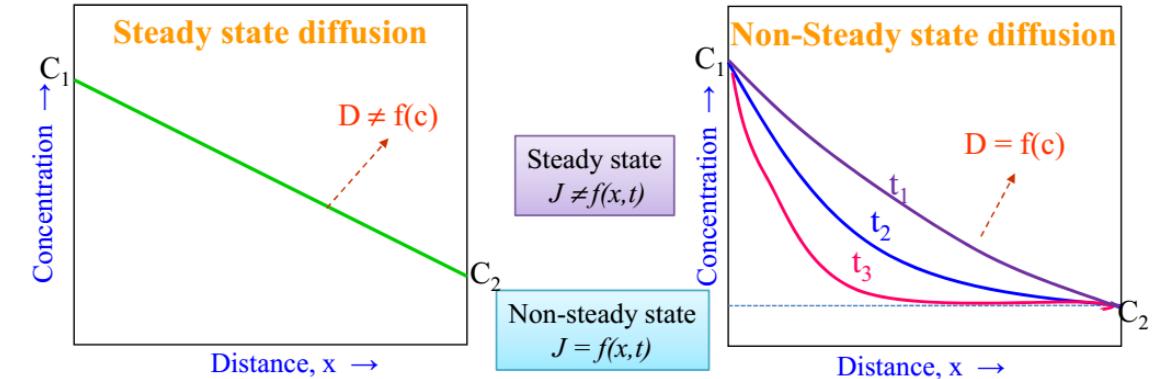
- Zn diffuses faster into Cu than Cu in Zn. A diffusion couple of Cu and Zn will lead to formation of a growing layer of Cu-Zn alloy (Brass).
- Same will happen in a Cu-Ni couple as copper diffuses faster in nickel than nickel in copper.
- Since this takes place by vacancy mechanism, pores will form in cu (of the Cu-Ni couple as the vacancy flux in the opposite direction (towards Cu) will condense to form pores.



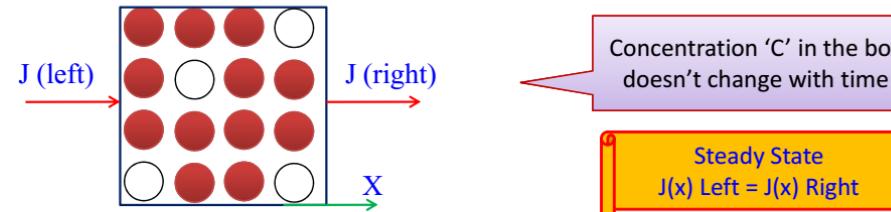
# Steady and Non-Steady State Diffusion

- Diffusional processes can be either steady-state or non-steady-state. These two types of diffusion processes are distinguished by use of a parameter called flux.
- It is defined as net number of atoms crossing a unit area perpendicular to a given direction per unit time. For steady-state diffusion, flux is constant with time, whereas for non-steady-state diffusion, flux varies with time.
- A schematic view of concentration gradient with distance for both steady-state and non-steady-state diffusion processes are shown:-

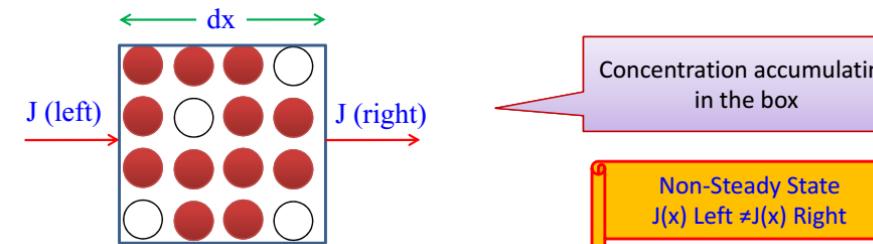
□ Flux ( $J$ ) (restricted definition) → Flow / area / time [Atoms /  $\text{m}^2 / \text{s}$ ]



Steady State : Concentration profile not changing with time.



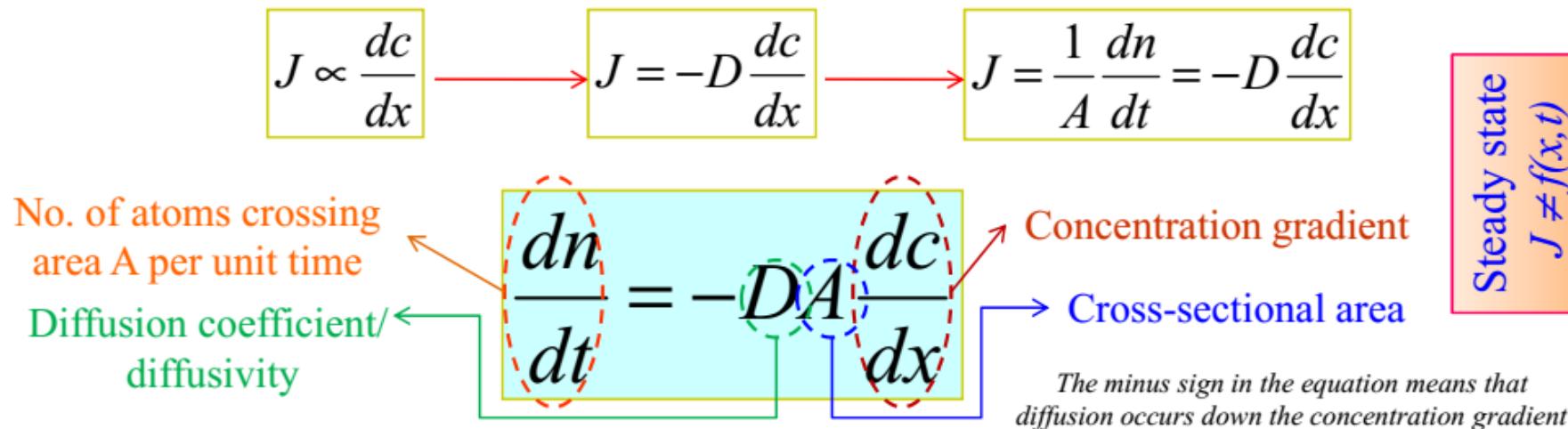
Non-Steady State : Concentration profile changes with time.



# Fick's First Law

- Steady-state diffusion is described by Fick's first law which states that flux,  $J$ , is proportional to the concentration gradient.
- The constant of proportionality is called diffusion coefficient (diffusivity),  $D$  ( $\text{cm}^2/\text{sec}$ ). Diffusivity is characteristic of the system and depends on the nature of the diffusing species, the matrix in which it is diffusing, and the temperature at which diffusion occurs.
- Thus under steady-state flow, the flux is independent of time and remains the same at any cross-sectional plane along the diffusion direction. for the one-dimensional case, Fick's first law is given by:

$$J \equiv \text{atoms / area / time} \propto \text{concentration gradient}$$

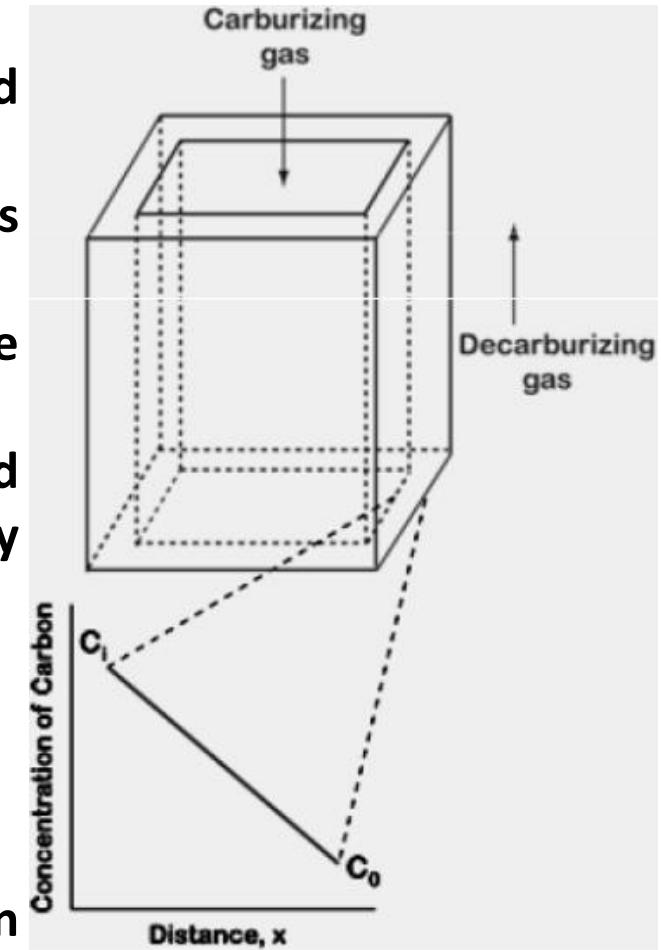


# Contd...

- In Fick's first law, minus sign comes from the fact that matter flows down the concentration gradient. It is not necessarily true in all the cases.
- Matter may also diffuse up the concentration gradient, which is called **uphill diffusion**.
- Fick's first law can directly be applied in the case of steady state, as shown in the example below.
- Steady state means that there will not be any change in the composition profile with time.
- If we pass carburizing gas through the pipe as shown in the figure and decarburizing gas outside the pipe, a steady composition profile may develop.
- Concentration gradient can be calculated following:

$$\frac{dc}{dx} = -\frac{C_i - C_0}{d} = -\frac{C_0 - C_i}{d}$$

- From this, one can calculate the flux from the known diffusion coefficients of carbon or the diffusion coefficient from the flux determined.



# Example – 1

- The steady-state diffusion is found in the purification of hydrogen gas. Compute the number of kilograms of hydrogen that pass per hour through a 6-mm-thick sheet of palladium having an area of  $0.25 \text{ m}^2$  at  $600^\circ\text{C}$ . Assume a diffusion coefficient of  $1.7 \times 10^{-8} \text{ m}^2/\text{s}$ , that the concentrations at the high and low-pressure sides of the plate are 2.0 and 0.4 kg of hydrogen per cubic meter of palladium, and that steady-state conditions have been attained.
- **Solution:** This Problem calls for the mass of hydrogen, per hour, that diffuses through a Pd sheet.
- Using Fick's first law:

$$M = JAt = -DAt \frac{\Delta c}{\Delta x}$$

$$= -(1.7 \times 10^{-8} \text{ m}^2 / \text{s})(0.25 \text{ m}^2)(3600 \text{ s} / \text{h}) \left[ \frac{0.4 - 2.0 \text{ kg/m}^3}{6 \times 10^{-3} \text{ m}} \right]$$

$$= 4.1 \times 10^{-3} \text{ kg/h}$$



# Example – 2

- A sheet of BCC iron 2 mm thick was exposed to a carburizing gas atmosphere on one side and a decarburizing atmosphere on the other side at 675 °C. After having reached steady state, the iron was quickly cooled to room temperature. The carbon concentrations at the two surfaces of the sheet were determined to be 0.015 and 0.0068 wt%. Compute the diffusion coefficient if the diffusion flux is  $7.36 \times 10^{-9} \text{ kg/m}^2\text{-s}$ .
- (Information : Density of carbon = 2.25 g/cm<sup>3</sup>, Density of iron = 7.87 g/cm<sup>3</sup>)
- Solution: This problem calls for computation of the diffusion coefficient for a steady-state diffusion situation. Let us first convert the carbon concentrations from weight percent to kilograms carbon per meter cubed using below equation.

For 0.015 wt% C

$$C'_c = \left[ \frac{C_c}{\frac{C_c}{\rho_c} + \frac{C_c}{\rho_{Fe}}} \times 10^3 \right]$$

$$C'_c = \left[ \frac{0.015}{\frac{0.015}{2.25} + \frac{99.985}{7.87}} \times 10^3 \right]$$

$$= 1.18 \text{ kgC/m}^3$$

Similarly, for 0.0068 wt% C

$$C''_c = \left[ \frac{0.0068}{\frac{0.0068}{2.25} + \frac{99.9932}{7.87}} \times 10^3 \right]$$

$$= 0.535 \text{ kgC/m}^3$$

$$D = -J \frac{X_A - X_B}{C_A - C_B}$$

$$= -(7.36 \times 10^{-9} \text{ Kg/m}^2\text{-s}) \left[ \frac{-2 \times 10^{-3} \text{ m}}{1.18 \text{ Kg/m}^3 - 0.535 \text{ Kg/m}^3} \right]$$

$$= 2.3 \times 10^{-11} \text{ m}^2/\text{s}$$



# Example – 3

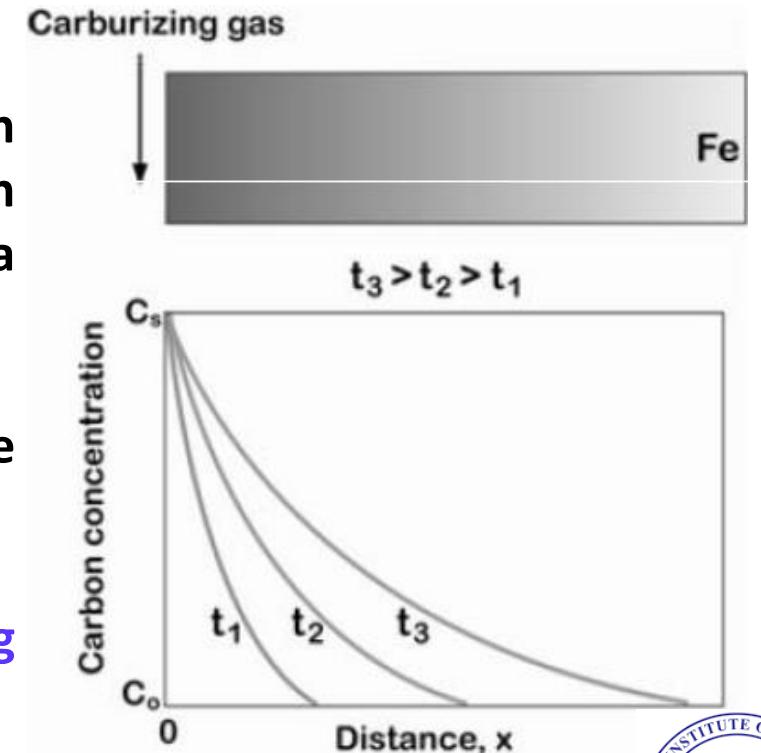
- A plate of Fe is exposed to a carburizing (C-rich) atmosphere on one side and a decarburizing (C-deficient) atmosphere on the other side at 700 °C (1300 °F). If a condition of steady state is achieved, calculate the diffusion flux of C through the plate, if the concentrations of C at positions of 5 and 10 mm ( $5 \times 10^{-3}$  and  $10^{-2}$  m) beneath the carburizing surface are 1.2 and 0.8 kg/m<sup>3</sup> respectively. Assume a diffusion coefficient of  $3 \times 10^{-11}$  m<sup>2</sup>/s at this temperature.
- **Solution:** Fick's first law, is used to determine the diffusion flux. Substitution of the values just given into this expression yields,

$$\begin{aligned} J &= -D \frac{C_A - C_B}{x_A - x_B} = -(3 \times 10^{-11} \text{ m}^2/\text{s}) \frac{(1.2 - 0.8) \text{ kg/m}^3}{(5 \times 10^{-3} - 10^{-2}) \text{ m}} \\ &= 2.4 \times 10^{-9} \text{ kg/m}^2 \cdot \text{s} \end{aligned}$$



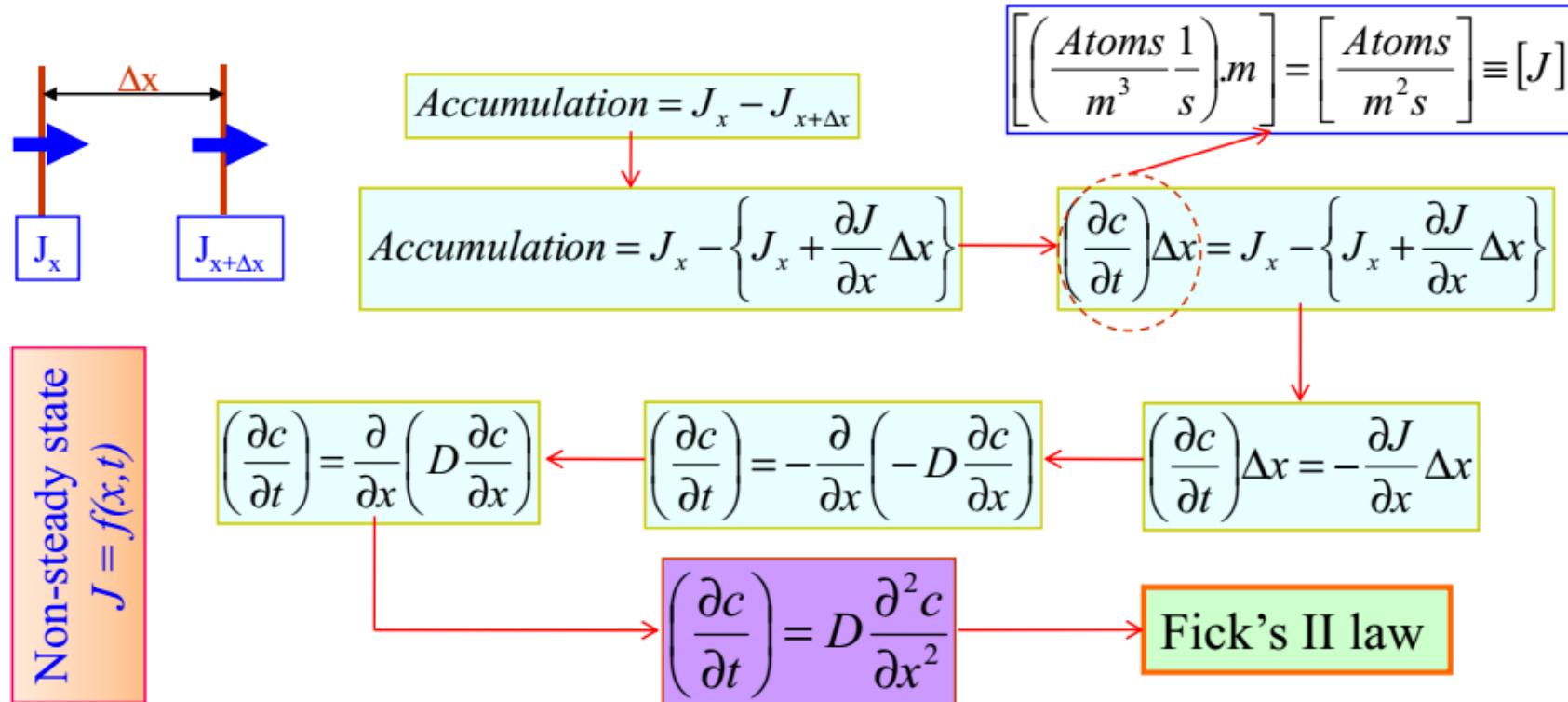
# Fick's Second Law

- However, just the Fick's first law may not be useful to relate the flux and the concentration profile, since, in most of the cases, systems develop **non steady state** concentration profile.
- It means that **concentration at a particular position changes with time**.
- For example, if we keep concentration of carbon on one of the Fe surfaces anneal, composition profile will change with time , as shown in the figure:
- We can't apply Fick's first law directly to evaluate the concentration profile that develops during diffusion in this case, since, as shown in the figure, composition changes with annealing time at a particular position.
- So we need to have a relation, which can relate time along with the concentration and the position.
- For that Fick's second law is derived. It is derived using **conservation of mass and Fick's first law**.



# Contd...

- Most interesting cases of diffusion are **non-steady-state** processes since the concentration at a given position changes with time, and thus the flux changes with time.
- This is the case when the diffusion flux depends on time, which means that a type of atoms accumulates in a region or depleted from a region (which may cause them to accumulate in another region). Fick's second law characterizes these processes, which is expressed as:



# Solution to Fick's Second Law

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- Solution of the Fick's second law depends on initial and boundary conditions.
  - Further, D, in some cases, may be considered constant. That means D does not change with concentration or position.
  - However, this condition meets only in very limited cases.
- 
- In most of the practical examples, D is a function of concentration. In this case, solution to the Fick's second law is complicated.
  - So in the beginning, we shall solve the Fick's second law for constant D.
  - Solutions are mainly for two different types of conditions, small and large time values.
- 
- When diffusion annealing time is small, solution is expressed with integrals or error functions. For long annealing time, it is expressed in terms of trigonometrical series.
  - Note that the long or short annealing time is rather relative. By saying long annealing time, we mean that the complete sample is affected by the diffusion process and may lead to homogenization.
  - By saying short annealing time, we mean that experiments are conducted such that whole material is not affected by the diffusion process.

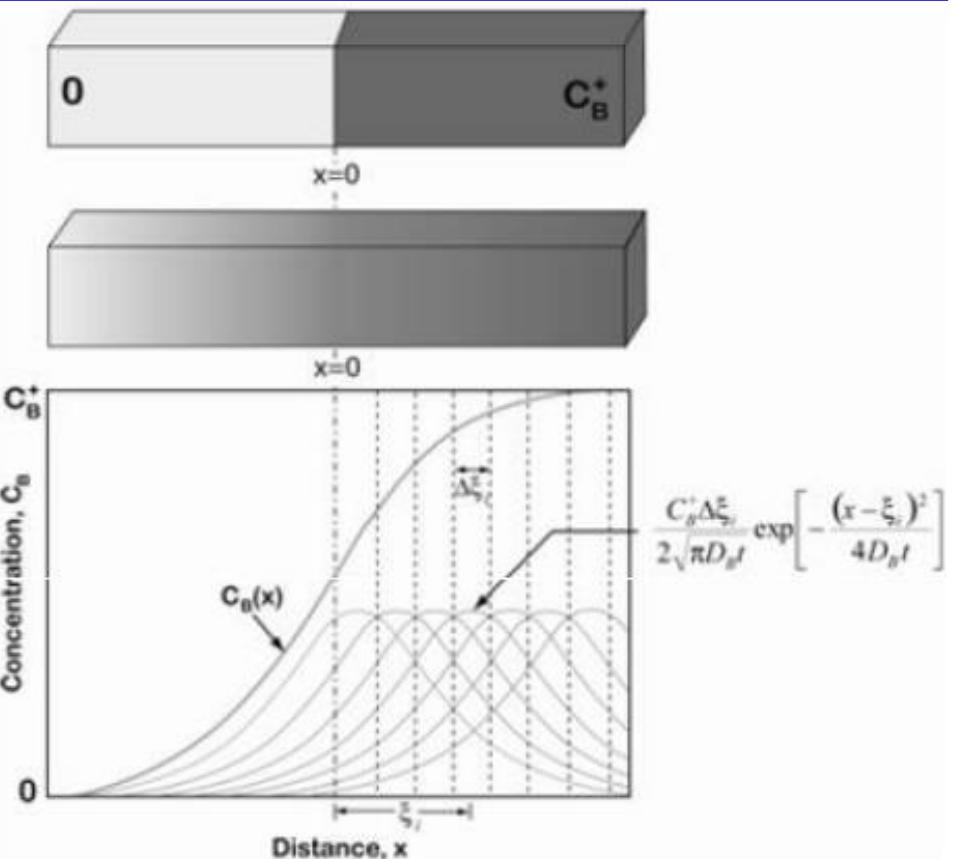


# Solution in semi infinite diffusion couples (error function analysis)

- Let us consider now the semi infinite diffusion couple of two blocks with concentration of,

$$C_B = 0 \quad \text{and} \quad C_B = C_B^+$$

- It means that, in a A-B binary system, it is bonding between two blocks made of pure A and an alloy of AB.
- Here, because of the difference in the composition, diffusion will be driven by the chemical potential gradient.
- However, the solution can be used only in the case where the concentration and the chemical potential difference of the end members is not much.
- That means diffusion coefficients do not vary significantly with the composition.
- Semi infinite** means that, we anneal for a certain annealing time such that the end of the initial materials are not affected by the diffusion of elements.



# Contd...

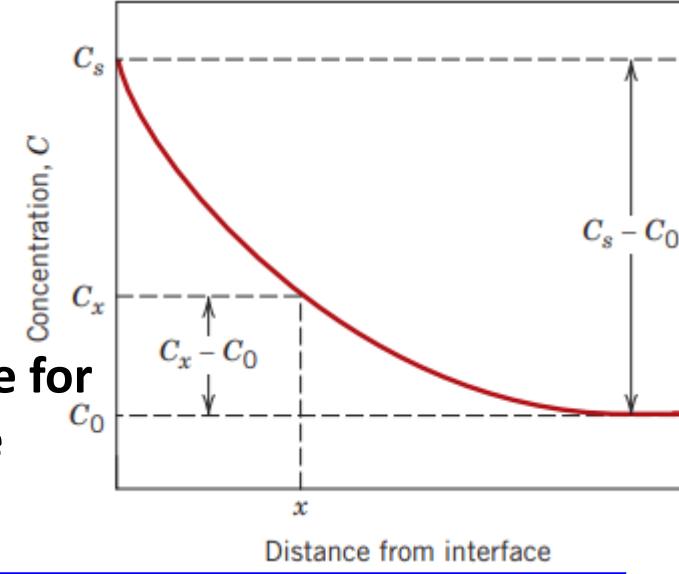
- One practically important solution is for a semi-infinite solid in which the surface concentration is held constant.
  - Frequently, the source of the diffusing species is a gas phase, the partial pressure of which is maintained at a constant value.
  - Furthermore, the following assumptions are made:
    - Before diffusion, any of the diffusing solute atoms in the solid are uniformly distributed with concentration of  $C_0$ .
    - The value of  $x$  at the surface is zero and increases with distance into the solid.
    - The time is taken to be zero the instant before the diffusion process begins.
- These conditions are simply stated as follows:
- Initial condition
- For  $t = 0, C = C_0$  at  $0 \leq x \leq \infty$
- Boundary conditions
- For  $t > 0, C = C_s$  (the constant surface concentration) at  $x = 0$   
For  $t > 0, C = C_0$  at  $x = \infty$
- Application of these conditions
- $$\frac{C_x - C_0}{C_s - C_0} = 1 - \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$
- where  $C_x$  represents the concentration at depth  $x$  after time  $t$ . The expression  $\operatorname{erf}(x/2\sqrt{Dt})$  is the Gaussian error function, values of which are given in mathematical tables for various  $x/2\sqrt{Dt}$  values; a partial listing is given in Table .  
where  $x/2\sqrt{Dt}$  has been replaced by the variable  $z$ .



# Contd...

$z$	$\text{erf}(z)$								
0	0	0.5	0.5204999	1	0.8427007	1.5	0.9661051	2	0.9953223
0.01	0.0112834	0.51	0.5292436	1.01	0.8468104	1.51	0.9672767	2.01	0.9955248
0.02	0.0225646	0.52	0.5378986	1.02	0.850838	1.52	0.9684135	2.02	0.9957195
0.03	0.0338412	0.53	0.5464641	1.03	0.8547842	1.53	0.9695162	2.03	0.9959063
0.04	0.0451111	0.54	0.5549392	1.04	0.8586499	1.54	0.9705857	2.04	0.9960858
0.05	0.056372	0.55	0.5633234	1.05	0.8624361	1.55	0.9716227	2.05	0.9962581
0.06	0.0676216	0.56	0.5716158	1.06	0.8661435	1.56	0.9726281	2.06	0.9964235
0.07	0.0788577	0.57	0.5798158	1.07	0.8697733	1.57	0.9736026	2.07	0.9965822
0.08	0.0900781	0.58	0.5879229	1.08	0.8733261	1.58	0.974547	2.08	0.9967344
0.09	0.1012806	0.59	0.5959365	1.09	0.8768031	1.59	0.975462	2.09	0.9968805
0.1	0.1124629	0.6	0.6038561	1.1	0.880205	1.6	0.9763484	2.1	0.9970205
0.11	0.1236229	0.61	0.6116812	1.11	0.883533	1.61	0.9772068	2.11	0.9971548
0.12	0.1347584	0.62	0.6194115	1.12	0.8867879	1.62	0.9780381	2.12	0.9972836
0.13	0.1458671	0.63	0.6270464	1.13	0.8899706	1.63	0.9788428	2.13	0.997407
0.14	0.156947	0.64	0.6345858	1.14	0.8930823	1.64	0.9796218	2.14	0.9975253
0.15	0.167996	0.65	0.6420293	1.15	0.8961238	1.65	0.9803756	2.15	0.9976386
0.16	0.1790118	0.66	0.6493767	1.16	0.8990962	1.66	0.9811049	2.16	0.9977472
0.17	0.1899925	0.67	0.6566277	1.17	0.9020004	1.67	0.9818104	2.17	0.9978511
0.18	0.2009358	0.68	0.6637822	1.18	0.9048374	1.68	0.9824928	2.18	0.9979506
0.19	0.2118399	0.69	0.6708401	1.19	0.9076083	1.69	0.9831526	2.19	0.9980459
0.2	0.2227026	0.7	0.6778012	1.2	0.910314	1.7	0.9837905	2.2	0.9981372
0.21	0.2335219	0.71	0.6846653	1.21	0.9129555	1.71	0.984407	2.21	0.9982244
0.22	0.2442959	0.72	0.6914328	1.22	0.9155339	1.72	0.9850028	2.22	0.9983079
0.23	0.2550226	0.73	0.6981037	1.23	0.9180501	1.73	0.9855785	2.23	0.9983878
0.24	0.2657001	0.74	0.7046778	1.24	0.9205052	1.74	0.9861346	2.24	0.9984642
0.25	0.2763264	0.75	0.7111554	1.25	0.9229001	1.75	0.9866717	2.25	0.9985373
0.26	0.2868897	0.76	0.7175365	1.26	0.9252359	1.76	0.9871903	2.26	0.9986071
0.27	0.2974182	0.77	0.7238214	1.27	0.9275136	1.77	0.9876909	2.27	0.9986739
0.28	0.3078801	0.78	0.7300102	1.28	0.9297342	1.78	0.9881742	2.28	0.9987377
0.29	0.3182835	0.79	0.7361032	1.29	0.9318986	1.79	0.9886405	2.29	0.9987986
0.3	0.3286268	0.8	0.7421008	1.3	0.9340079	1.8	0.9890905	2.3	0.9988568
0.31	0.3389082	0.81	0.7480031	1.31	0.9360631	1.81	0.9895245	2.31	0.9989124
0.32	0.349126	0.82	0.7538106	1.32	0.9380651	1.82	0.9899432	2.32	0.9989655
0.33	0.3592787	0.83	0.7595236	1.33	0.940015	1.83	0.9903468	2.33	0.9990162
0.34	0.3693645	0.84	0.7651426	1.34	0.9419137	1.84	0.9907359	2.34	0.9990646
0.35	0.3793821	0.85	0.7706679	1.35	0.9437622	1.85	0.991111	2.35	0.9991107
0.36	0.3893297	0.86	0.7761001	1.36	0.9455614	1.86	0.9914725	2.36	0.9991548
0.37	0.399206	0.87	0.7814397	1.37	0.9473124	1.87	0.9918207	2.37	0.9991968
0.38	0.4090095	0.88	0.7866872	1.38	0.949016	1.88	0.9921562	2.38	0.9992369
0.39	0.4187387	0.89	0.7918431	1.39	0.9506733	1.89	0.9924793	2.39	0.9992751
0.4	0.4283924	0.9	0.7969081	1.4	0.9522851	1.9	0.9927904	2.4	0.9993115
0.41	0.4379691	0.91	0.8018827	1.41	0.9538524	1.91	0.9930899	2.41	0.9993462
0.42	0.4474676	0.92	0.8067676	1.42	0.9553762	1.92	0.9933782	2.42	0.9993793
0.43	0.4568867	0.93	0.8115635	1.43	0.9568572	1.93	0.9936556	2.43	0.9994108
0.44	0.4662251	0.94	0.8162709	1.44	0.9582966	1.94	0.9939226	2.44	0.9994408
0.45	0.4754817	0.95	0.8208907	1.45	0.959695	1.95	0.9941793	2.45	0.9994694
0.46	0.4846554	0.96	0.8254236	1.46	0.9610535	1.96	0.9944263	2.46	0.9994966
0.47	0.4937451	0.97	0.8298702	1.47	0.9623729	1.97	0.9946637	2.47	0.9995226
0.48	0.5027497	0.98	0.8342314	1.48	0.9636541	1.98	0.994892	2.48	0.9995472
0.49	0.5116683	0.99	0.838508	1.49	0.9648979	1.99	0.9951114	2.49	0.9995707

Concentration profile for  
non steady-state  
diffusion



- Suppose that it is desired to achieve some specific concentration of solute,  $C_1$ , in an alloy; the left-hand side of the previous Equation now becomes,

$$\frac{C_1 - C_0}{C_s - C_0} = \text{constant}$$

- This being the case, the right-hand side of the previous Equation is also a constant, and subsequently,

$$\frac{x}{2\sqrt{Dt}} = \text{constant}$$

$$\frac{x^2}{Dt} = \text{constant}$$

- Some diffusion computations are facilitated on the basis of this relationship.



# Example – 4

- An FCC iron–carbon alloy initially containing 0.55 wt.% C is exposed to an oxygen-rich and virtually carbon-free atmosphere at 1325 K (1052 °C). Under these circumstances the carbon diffuses from the alloy and reacts at the surface with the oxygen in the atmosphere; i.e., the carbon concentration at the surface position is maintained essentially at 0 wt.% C. (This process of carbon depletion is termed decarburization.) At what position will the carbon concentration be 0.25 wt% after a 10 h treatment? The value of D at 1325 K is  $4.3 \times 10^{-11} \text{ m}^2/\text{s}$ .
- **Answer:** This problem asks that we determine the position at which the carbon concentration is 0.25 wt% after a 10 h heat treatment at 1325 K when  $C_o = 0.55 \text{ wt\% C}$ .

$$\frac{C_x - C_o}{C_s - C_o} = \frac{0.25 - 0.55}{0 - 0.55} = 0.5455 = 1 - \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

$$\operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right) = 0.4545$$

- Using tabulation of error function values and linear interpretation,

$$\frac{Z - 0.40}{0.45 - 0.40} = \frac{0.4545 - 0.4284}{0.4755 - 0.4284} \quad Z = 0.4277$$

$$\left(\frac{x}{2\sqrt{Dt}}\right) = 0.4277$$

$$x = 2(0.4277)\sqrt{Dt} = (0.8554)\sqrt{(3.6 \times 10^4 \text{ s})(4.3 \times 10^{-11} \text{ m}^2/\text{s})} \\ = 1.06 \times 10^{-3} \text{ m} = 1.06 \text{ mm}$$

Z	Erf (Z)
0.40	0.4284
Z	0.4545
0.45	0.4755



# Example – 5

- Iron–carbon alloy that initially has a uniform carbon concentration of 0.25 wt.% and is to be treated at 950 °C (1750 °F). If the concentration of carbon at the surface is suddenly brought to and maintained at 1.20 wt.%, how long will it take to achieve a carbon content of 0.80 wt.% at a position 0.5 mm below the surface? The diffusion coefficient for carbon in iron at this temperature is  $1.6 \times 10^{-11} \text{ m}^2/\text{s}$ ; assume that the steel piece is semi-infinite.
- **Answer:** This is a non steady-state diffusion problem in which the surface composition is held constant. Values for all the parameters in this expression except time t are specified in the problem as follows:

$$C_0 = 0.25 \text{ wt\% C}$$

$$C_s = 1.20 \text{ wt\% C}$$

$$C_x = 0.80 \text{ wt\% C}$$

$$x = 0.50 \text{ mm} = 5 \times 10^{-4} \text{ m}$$

$$D = 1.6 \times 10^{-11} \text{ m}^2/\text{s}$$

$z$	$\text{erf}(z)$
0.35	0.3794
$z$	0.4210
0.40	0.4284

$$\frac{z - 0.35}{0.40 - 0.35} = \frac{0.4210 - 0.3794}{0.4284 - 0.3794}$$

Thus,

or

$$\frac{C_x - C_0}{C_s - C_0} = \frac{0.80 - 0.25}{1.20 - 0.25} = 1 - \text{erf}\left[\frac{(5 \times 10^{-4} \text{ m})}{2\sqrt{(1.6 \times 10^{-11} \text{ m}^2/\text{s})(t)}}\right]$$

$$z = 0.392$$

Therefore,

$$0.4210 = \text{erf}\left(\frac{62.5 \text{ s}^{1/2}}{\sqrt{t}}\right)$$

$$\frac{62.5 \text{ s}^{1/2}}{\sqrt{t}} = 0.392$$

and solving for  $t$ , we find

$$t = \left(\frac{62.5 \text{ s}^{1/2}}{0.392}\right)^2 = 25,400 \text{ s} = 7.1 \text{ h}$$

- Now, determine the value of  $z$  for which the error function is 0.4210. An interpolation is necessary as,



# Example – 6

- Nitrogen from a gaseous phase is to be diffused into pure iron at 675 °C in non steady state. If the surface concentration is maintained at 0.2 wt.% N, what will be the concentration 2 mm from the surface after 25 h? The diffusion coefficient for nitrogen in iron at 675 °C is  $1.9 \times 10^{-11} \text{ m}^2/\text{s}$ .
- **Answer:-** This problem asks us to compute the nitrogen concentration  $C_x$  at the 2 mm position after a 25 h diffusion time, when diffusion is non steady-state.

$$\frac{C_x - C_o}{C_s - C_o} = \frac{C_x - 0}{0.2 - 0} = 1 - \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

$$= 1 - \operatorname{erf}\left(\frac{2 \times 10^{-3} \text{ m}}{2\sqrt{(1.9 \times 10^{-11} \text{ m}^2/\text{s})(25\text{h})(3600\text{s/h})}}\right) = 1 - \operatorname{erf}(0.765)$$

- Using tabulation of error function values and linear interpretation,

$$\frac{0.765 - 0.750}{0.800 - 0.750} = \frac{y - 0.7112}{0.7421 - 0.7112} \quad y = \operatorname{erf}(0.765) = 0.7205$$

$$\frac{C_x - 0}{0.2 - 0} = 1.0 - 0.7205$$

$$C_x = 0.056 \text{ wt\% N}$$

Z	Erf (Z)
0.750	0.7112
0.765	y
0.800	0.7421



# Example – 7

- The diffusion coefficients for copper in aluminum at 500 °C and 600 °C are  $4.8 \times 10^{-14}$  and  $5.3 \times 10^{-13} \text{ m}^2/\text{s}$  respectively. Determine the approximate time at 500 °C that will produce the same diffusion result (in terms of concentration of Cu at some specific point in Al) as a 10-h heat treatment at 600 °C.
- **Answer:** This is a diffusion problem in which at both 500 °C and 600 °C the composition remains the same at some position, say  $x_0$  and therefore,

$$\frac{x_0^2}{D_{500}t_{500}} = \frac{x_0^2}{D_{600}t_{600}}$$

$$D_{500}t_{500} = D_{600}t_{600}$$

$$t_{500} = \frac{D_{600}t_{600}}{D_{500}} = \frac{(5.3 \times 10^{-13} \text{ m}^2/\text{s})(10 \text{ h})}{4.8 \times 10^{-14} \text{ m}^2/\text{s}} = 110.4 \text{ h}$$

