Solid State Chemistry-CHM-403 (P)

Lecture-1

Kinetics of Phase Transformations:

Phase transformations do not occur instantaneously.

Phase transformations (change of the microstructure) can be divided into three categories:

1. Diffusion Dependent: In this transformation, there is no change in phase composition or number of phases present (e.g. melting, solidification of pure metal, allotropic transformations, recrystallization, etc.). Diffusion-dependent phase transformations can be rather slow and the final structure often depend on the rate of cooling/heating.

2. Diffusion-dependent with changes in phase compositions and/or number of phases (e.g. eutectic or eutectoid transformations)

3. Diffusionless phase transformation - by cooperative small displacements of all atoms in structure

Phase transformations involve change in structure and (for multi-phase systems) composition ⇒ rearrangement and redistribution of atoms via diffusion is required.

The process of phase transformation involves:

(a) Nucleation (b) Growth

Nucleation of new phases: Formation of stable small particles (nuclei) of the new phase. Nuclei are often formed at grain boundaries and other defects sites. Nuclei grows into the surrounding matrix.

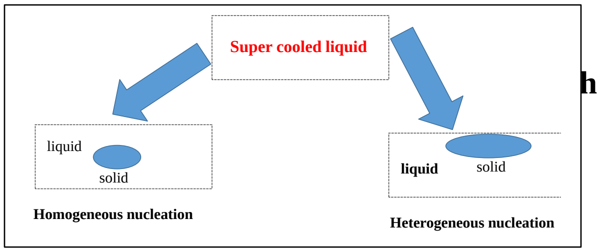
Growth of the new phase(s) at the expense of the original phase(s).

Nucleation

Nucleation can be

(i) Heterogeneous – the new phase appears on the walls of the container, at impurity particles, etc.

(ii) Homogeneous – solid nuclei spontaneously appear within the undercooled phase. Let's consider solidification of a liquid phase undercooled below the melting temperature as a simple example of a phase transformation.



hase transitions

It is convenient to analyze phase transformations occurring under conditions of constant temperature (T) and pressure (P) by using Gibbs free energy (G). G = H –TS, where H is the enthalpy and S is the entropy H = U + PV, where U is the internal energy.

Gibbs free energy (G = H –TS): Equilibrium is trade-off between minimization of enthalpy and maximization of entropy.

A change to a lower enthalpy state ($\Delta H < 0$) usually decreases the randomness ($\Delta S < 0$):

Homogeneous Nucleation:

This is the transition from undercooled liquid to a spherical solid in liquid and it is a spontaneous. (Gibb's free energy decreases). <u>It occurs spontaneously & randomly without preferential nucleation site.</u>

The formation of a solid nucleus leads to a Gibbs free energy change of

$$\Delta G = G2 - G1 = -\underbrace{Vs(GLV - GSV)}_{\textbf{Negative}} + \underbrace{A\,(SL)\gamma(SL)}_{\textbf{always Positive}}$$

Vs is the volume of solid sphere,

A (SL) is the solid/ liquid interfacial area.

γ(SL) is the solid/liquid interfacial energy

G_{LV} and G_{SV} are Gibbs free energies of liquid and solid respectively.

$$\Delta G = G2 - G1 = -Vs\Delta G + A\,(SL)\gamma(SL)$$

For a spherical nucleus with radius " r " = $Vs = \frac{4}{3}\,\pi r3$

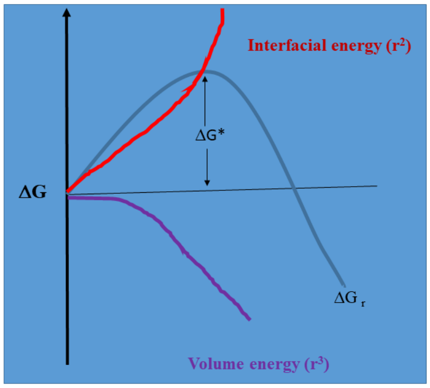
A (SL) is the solid/ liquid interfacial area = $4\pi r^2$

$$\Delta G = \frac{4}{3}\pi r3 + 4\pi r2\ \gamma(\mathrm{SL})$$

For nucleus with a radius r > r*, the Gibbs free energy will decrease if the nucleus grows. r* is the critical nucleus size.

At r= r*, $\frac{d}{dr}(\Delta G) = 0 = \frac{4}{3}\pi r3 + 4\pi r2\, \gamma(SL) \quad (from\ above)$

$r* = \frac{2\gamma}{\Delta G}$, Substituting r* value in the above equation gives $\Delta G * = 16\frac{\pi[\gamma(SL)]3}{}/3(\Delta G)2$



The difference between the Gibbs free energy of liquid and solid (also called "driving force" for the phase transformation) is proportional to the undercooling below the melting temperature, ΔT = Tm –T:

$\Delta G_v = \Delta H\, \Delta T / T_m$ where ΔH is the latent heat of melting or fusion

$$Therefore \quad r* = \left[\frac{2\gamma(SL)Tm}{\Delta Hm}\right] . \frac{I}{\Delta T}$$

$$\Delta G* = \left[16\pi[\gamma(SL)]3\frac{Tm}{}3(\Delta H)2\right] . \frac{I}{(\Delta T)2}$$

Both r* and G* decrease with increasing under cooling.

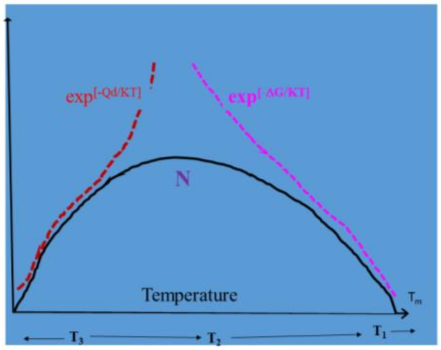
There is an energy barrier of ΔG^* for formation of a solid nucleus of critical size r*. The probability of energy fluctuation of size ΔG^* is given by the Arrhenius equation and the rate of homogeneous nucleation is

$$N = V_d \exp^{[-\Delta G/KT]} \text{ nuclei per } m^3 \text{ per sec}$$

Where V_d is frequency with which atoms from liquid attach to the solid nucleus. The rearrangement of atoms needed for joining the solid nucleus follow the same temperature dependence as the diffusion coefficient:

$$V_d \sim \exp^{[-Qd/KT]}$$

$$\text{Therefore } N = \exp^{[-Qd/KT]} \exp^{[-\Delta G/KT]}$$



From the above figure:

Case 1: $\Delta G* > Qd \Longrightarrow \exp^{(-\Delta G^*/KT)} << \exp^{(-Qd/KT)}$

$\Delta G * \textit{ is too high} - \textit{nucleation is suppressed}.$

Case 2: $\Delta G* < Qd \Longrightarrow \exp^{(-\Delta G^*/KT)} > \exp^{(-Qd/KT)}$

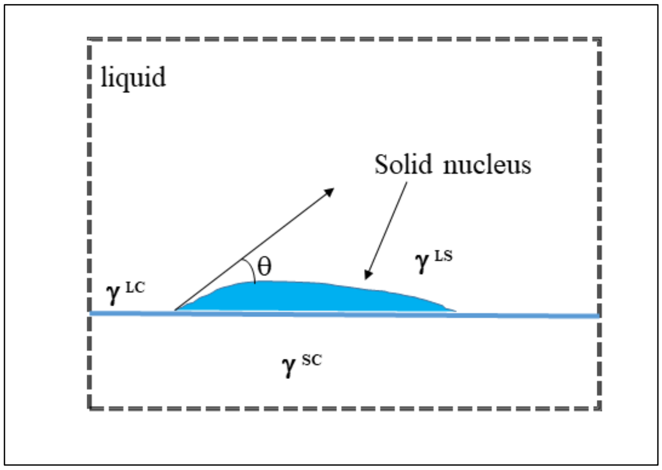
$\Delta G^* \sim 1/\Delta T2$ – decreases with T – sharp rise of homogeneous nucleation (diffusion is still active)

Case 3: $\exp^{(-Qd/KT)}$ is too small-low atomic mobility suppresses the nucleation rate.

Heterogeneous Nucleation

It occurs at preferential sites such as grain boundaries, dislocations or impurities. The new phase appears on the walls of the container, at impurity particles, grain boundaries, etc.

Let's consider a simple example of heterogeneous nucleation of a nucleus of the shape of a spherical cap on a wall of a container. Three surface energies: γ^{LC} –liquid container interface, γ^{LS} –liquid-solid interface, γ^{SC} –solid-container interface.



Balancing the interfacial tensions in the plane of the container wall gives

$\gamma^{LC} = \gamma^{SC} + \gamma^{LS}\cos(\theta)$ and the wetting angle θ is defined by $\cos(\theta) = (\gamma^{LC} - \gamma^{SC})/\gamma^{LS}$

The formation of the nucleus leads to a Gibbs free energy change of

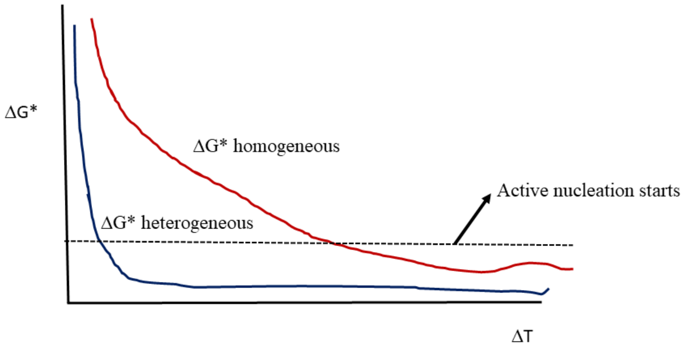
$\Delta G = -V_S\,\Delta G_v + A^{SL}\gamma^{SL} + A^{SC}\gamma^{SC} - A^{SC}\gamma^{LC}$

$$\Delta G\ (heter) = \left[\frac{4}{3}\pi r3\ \Delta Gv + 4\pi r2\ \gamma(\mathrm{SL})\right].S(\theta) = \Delta G\ (homo)\ S(\theta)$$

Where $S(\theta) = \frac{(2+Cos\theta)(1-Cos\theta)2}{4} \leq 1$

At r= r*, $\frac{d}{dr}(\Delta G) = 0 = (\pi r^2 \Delta Gv + 8\pi r\gamma SL)S(\theta) = 0$

$$r* = \frac{2\gamma}{\Delta G}$$



$$\text{Therefore } \Delta G^*_{\text{heterogeneous}} = S(\theta)\, \Delta G^*_{\text{homogeneous}}$$

$$\text{If } \theta = 10^\circ,\ \text{then } S(\theta) = (2 + \cos\theta)(1-\cos\theta)^2/4 = 10^{-4}$$

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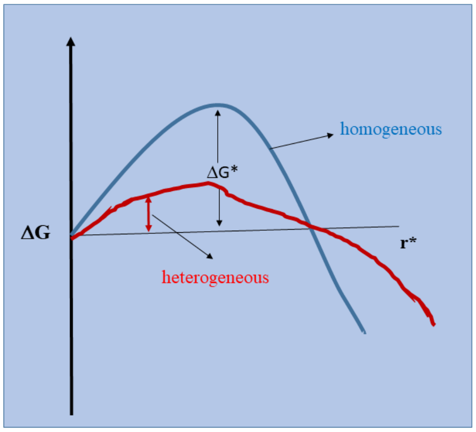
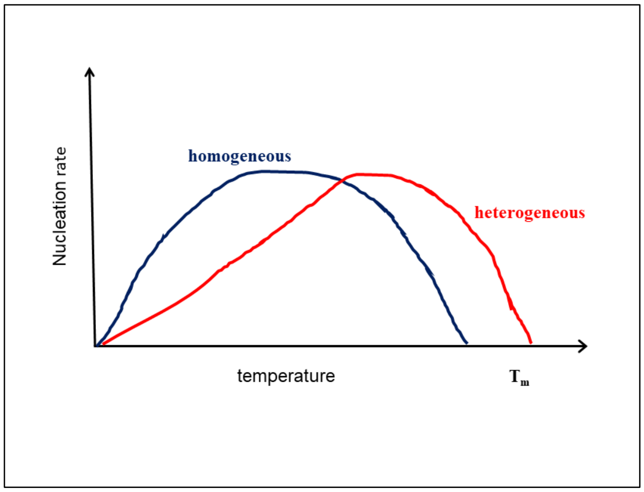


Heterogeneous nucleation starts at a lower undercooling.



Growth

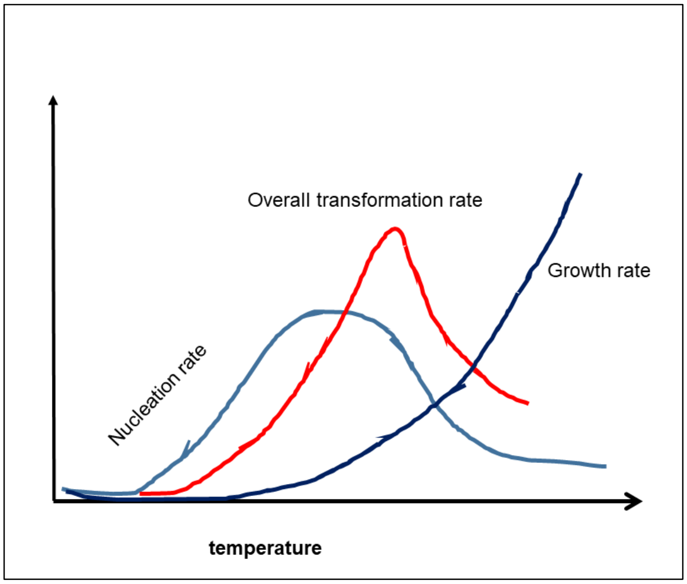
Once a stable nucleus of the new phase exceeding the critical size r* is formed, it starts to grow. Atomically rough interfaces migrate by continuous growth, whereas atomically flat interfaces migrate by ledge formation and lateral growth.

In multi-component systems, non-congruent phase transformations can involve long-range solute diffusion necessary for achieving the equilibrium phase composition. The atomic rearrangements necessary for growth of a one component phase or growth in a congruent phase transformation, as well as the long-range diffusion of components in multi-component systems, involve thermally-activated elementary processes and can be described by Arrhenius equation:

Growth rate: C exp $^{(-QA/KT)}$

Rate of phase transformations

Total rate of a phase transformation induced by cooling is a product of the nucleation rate and growth rate (diffusion controlled -slows down with T decrease).



At high T (close to Tm): low nucleation and high growth rates. It leads to formation of microstructure with large grains.

At low T (strong undercooling): high nucleation and low growth rates. It leads to formation of fine structure with small grains.

AVRAMI MODEL FOR GROWTH

1. Nucleation occurs randomly and homogeneously
2. Growth rate does not depend on the extent of transformation
3. Growth occurs at the same rate in all directions