Lecture 7:

Solidification of pure metal: Phase rule, Concept of Free Energy, Entropy, Surface Energy (grain boundary) & under cooling, Nucleation & Growth, homogeneous & heterogeneous nucleation, directional solidification

1. Estimate the size of critical nucleus of tin when it is super cooled by 20°C. Assume nucleation to be homogeneous. The enthalpy change for solidification of tin is 0.42 GJ/m^3. The liquid / solid interfacial energy is 0.055 J/m^2. The melting point of tin is 232° C.
2. A metal under goes an allotropic transformation at room temperature at high pressure and at lower temperature at atmospheric pressure. Is the volume change associated with this transformation positive or negative?
3. Bismuth has a density of 9.8Mg/m^3 at room temperature. Its coefficient of linear expansion is 14.6x10^{-6} /° C. The density of liquid metal at melting point (271°C) is 10.07 Mg/m^3. Find our dT/dP and estimate its melting point at 100 atmosphere pressure. Latent heat = 10.9 kJ/mole (atomic weight = 209)
4. Derive an expression for critical nucleus size as a function of temperature and show with the help of a schematic graph its variation with temperature. Assuming that a stable nucleus should have at least 100 atoms which correspond to around 1nm radius mark the region of homogeneous nucleation.

Answer:

1. $\Delta f_v = -\Delta H_v\left(1-\frac{T}{T_m}\right) = -0.42\times\frac{20}{273+232} = -0.0166$ GJ/m^3 and Critical nucleus size = $r^* = -\frac{2\sigma}{\Delta f_v} = \frac{0.055}{0.0166\times 10^9}m = 3.3nm$

2. The effect of pressure on transformation temperature is given by: $\frac{dP}{dT} = \frac{\Delta H}{T\Delta V}$. In this case let the transformation be represented as

   $\alpha = \beta$ at 300°K & 10 atmosphere (say) (P1 & T1)

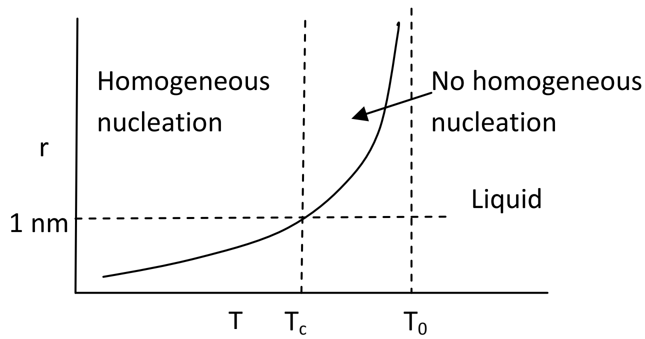
   $\alpha = \beta$ at 290°K & 1 atmosphere (say) (P2 & T2)

   $\Delta H > 0$ reaction is endothermic & $\frac{dP}{dT} = \frac{P_1-P_2}{T_1-T_2} < 0$

3. Let room temperature = 25°C, volume increase due to temperature change =$3\alpha\Delta T$ where α, is coefficient of linear expansion. Volume of 1gm mass at room temperature = $1/\rho_0$ & volume of solid Bi at melting point = $(1/\rho_0) + 3\alpha\Delta T$. Therefore density of solid Bi at melting point = $\frac{\rho_0}{1+3\rho_0\alpha\Delta T}$ = 9.7Mg/m^3. On melting density increases $\Delta V < 0$. $\Delta V = V_L - V_S = \frac{0.209}{1000}\times\left(\frac{9.7-10.07}{9.7\times 10.07}\right)$ = -7.9x10^{-7} m^3. $\frac{dP}{dT} = -\frac{10.9\times 1000}{(271+273)\times 7.9\times 10^{-7}} = -25.31\frac{MPa}{K}$ Note that 1bar = 100kPa and 100 bar = 10MPa. Therefore the change in melting point at 100 bar pressure = 2.53°C.

4. Critical radius = $r^* = -\frac{2\sigma}{\Delta f_v}$ Free energy change / unit volume for solidification = $\Delta f_v = \Delta H_v - T\Delta S_v$ where H & S are enthalpy & entropy terms. Suffix v denotes per unit volume. At melting

point (T_0) $\Delta f_v = 0$. Thus $\Delta S_v = \frac{\Delta H_v}{T_0}$ & $\Delta f_v = \Delta H_v \frac{T_0 - T}{T_0}$ Note that for solidification (it releases heat) ΔH_v is negative. Therefore $r^* = -\frac{2\sigma T_0}{\Delta H_v (T_0 - T)}$ It shows that r* approaches infinity as T approaches T0. As T approaches zero r* becomes exceedingly small since $\Delta H_v >> \sigma$. This is schematically shown as follows:



Homogeneous nucleation is possible below a specific temperature T_c