1) a) $\frac{T_m - T_m^b}{T_m^b} = 2\left(\frac{\gamma_{LW} - \gamma_{SW}}{H\rho\Delta_m h}\right)$ -5

$\rho = N/V$

$\Delta_m h = h_L - h_S \Rightarrow$ latent heat of melting per particle

$T_m(H) = T_i^b + 2\frac{(\gamma_{LW} - \gamma_{SW})}{\rho_s \Delta_{ms} H}$

we know $V = A_W H$

Using clapeyron allroach

$\Omega = U - TS - \mu N = -PA_W H + 2\gamma A_W$

with internal energy

$U = TS - PA_W H + 2\gamma A_W + \mu N$

$S =$ entropy, $P =$ Pressure, $\gamma =$ surface tension.

$P_L - P_S = 2\frac{(\gamma_{LW} - \gamma_{SW})}{H}$, $H =$ Pore size

$d\Omega = -SdT - PA_W dH + (2\gamma - PH)dA_W - \mu dN$

If we simplify $dA_W$ using $P_L - P_S = 2\frac{(\gamma_{LW} - \gamma_{SW})}{H}$

we have $(S_L - S_S)dT + \frac{2A_W(\gamma_{LW} - \gamma_{SW})}{H}dH + (N_L - N_S)d\mu = 0$

Now we integrate this from $H \to \infty$ as transition occurs at $T_m^b$

$\frac{dH}{H^2} = \frac{-dT}{2(\gamma_{LW} - \gamma_{SW})}\left[(\rho_L s_L - \rho_S s_S) + (\rho_L - \rho_S)\frac{d\mu}{dT}\right]$ using $\rho = N/V$ and $s = S/N$

$s =$ entropy per particle.

$\frac{d\mu}{dT} = \frac{\rho_L^b s_L^b - \rho_G^b - s_G^b}{\rho_L^b - \rho_G^b} \simeq -s_L^b$ $b =$ bulk liquid and gas phases

$$\text{so } \frac{dH}{H^2} = -\frac{(\rho_L - \rho_s)(s_L - s_L^b) + \rho_s(s_L - s_s)}{2(\gamma_{LW} - \gamma_{sw})}\, dT$$

for large b, $T_m - T_m^b$

$$\frac{dH}{H^2} = -\frac{\rho_s^b \Delta_m s^b}{2(\gamma_{LW} - \gamma_{sw})}\, dT$$

where $\Delta_m S^b = S_L^b - S_s^b$ = bulk entropy of melting for particle

Now we integrate

$$\int_H^\infty \frac{dH}{H^2} = -\frac{\rho_s^b \Delta_m S^b}{2(\gamma_{LW} - \gamma_{sw})} \int_{T_m}^{T_m^b} dT$$

$$\text{so } T_m(H) = T_T^b + \frac{2(\gamma_{LW} - \gamma_{sw})}{H \rho_s^b \Delta_m S^b}$$

$\gamma_{LW}$ = surface tension on liquid-wall surface

$\gamma_{sw}$ = surface tension on solid-wall surface

6) Thermodynamic Potential is the grand Potential

$$\Omega = U - TS - MN = -PA_w H + 2\gamma A_w$$

Internal energy

$$U = TS - PA_w H + 2\gamma A_w + MN$$

$S$ = entropy, $P$ = Pressure, $\gamma$ = surface tension

At equilibrium between solid and liquid phases i.e $\Omega_L = \Omega_S$

$$dU = -PdV + Tds + Md N$$

c) Kelvin equation $\Rightarrow \ln\left(\frac{P(r)}{P}\right) = \frac{2\gamma V_{molecule}}{K_B T r}$

Good +5

$$CCE = \frac{dP}{dT} = \frac{PL}{T^2 R}$$

when we integrate CCE

$$\int_1^2 dP = \int \frac{PL}{T^2 R} dT \quad \text{we have} \quad \ln\left(\frac{P_2}{P_1}\right) = \frac{L}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

we can substitute $\ln\left(\frac{P_2}{P_1}\right)$ to get r from the Kelvin equation

$$r = \frac{2\gamma T}{\rho L (T_1 - T_2)}$$ we replace the $V_{molecule}$ with density $\rho$

so $\rho L(T_1 - T_2) r = 2\gamma T$ , $T_1 - T_2 = \Delta T$

so $\rho L \Delta T_F = 2\gamma T$

so $\Delta T = \frac{2\gamma T}{\rho L r}$

This is the same as Gibbs Thomson equation.

Oswald-Freundlich Equation (OFE) $= x_a = x_a^{\circ} \exp\left[\frac{2V_a \gamma}{R_a T R_{seg}}\right]$

$X_a$ = mole fraction

$V$ = molar volume

$R_{seg}$ = radius

$\gamma$ = interfacial tension

$R_a$ = universal gas constant

$T$ = Temperature

d) $P_{acc}(A_1, B_2 \rightarrow A_2, B_1) = \min\left\{1, \frac{P_A(U_2, N_2) P_B(U_1, N_1)}{P_A(U_1, N_1) P_B(U_2, N_2)}\right\}$ -10

The RHS second term is the density of states ratio in the grand canonical ensemble

e) For heterogenous +10

$\Delta G = \Delta G_{homogenous} \times f(\theta) \Rightarrow$ Shape factor $= \frac{2 - 3\cos\theta + \cos^3\theta}{4}$

$\Delta G_n = \Delta G_V + \Delta G_S$

For a sphere of radius $r$, $A = 4\pi r^2$ So $dA = 8\pi r\,dr$

$V = 4/3\pi r^3$, So $dV = 4\pi r^2 dr$

$\Delta G_r = -\Delta G_V V + \gamma A = -\Delta G_V (4/3\pi r^3) + \gamma(4\pi r^2)$

$\frac{dG_r}{dr} = -\Delta G_V (4\pi r^2) + \gamma(8\pi r) = 0$

$r^* = \frac{4\gamma}{\Delta G_V} = \frac{4\gamma T_m}{L_V \Delta T}$

$\Delta G_r = -4/3\pi r^3 \Delta G_V + 4\pi r^2 \gamma_{sl}$

$r^* = \frac{2\gamma}{\Delta G_V} = \left(\frac{2\gamma T_m}{L_V}\right) 1/\Delta T$

for heterogenous we add the $f(\theta)$

So $\Delta G_{het} = 2\gamma r^* \times f(\theta)$

$f(\theta) = \frac{2 - 3\cos\theta + \cos^3\theta}{4}$

2) a) This Ni-20% Cu is a complete Solid Solution and Liquid Solution Phase diagram so it is a fully isomorphous system +5

The composition and phase fractions can be determined using the Lever rule

The matrix phase is a full solid solution $\alpha$ (Cu Ni) consisting of Cu and Ni at temperatures below the Solidus. Between the solidus and liquidus, there is the Solid Solution $\alpha$ and Liquid Solution. Above the liquidus, we have the Liquid Solution with full solubility.

The spherical domain is a mixture of Cu and Ni

using lever rule

$\alpha$ composition => 84 at % Ni

Liquid composition => 76 at % Ni

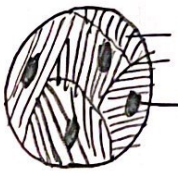
b) This is the eutectic region with 3 phases in equilibrium. It is an invariant point with Liquid, Ni and $ZrNi_5$ are in equilibrium

Triple point is the eutectic point

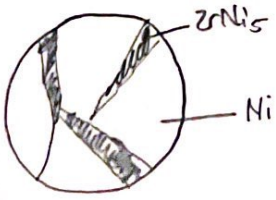
Reaction => $L \rightleftharpoons Ni + ZrNi_5$ OK

$F = C - P + 1$ (at constant pressure of 1 atm)

$F = 2 - 3 + 1 = 0$




c)




Slow Cool

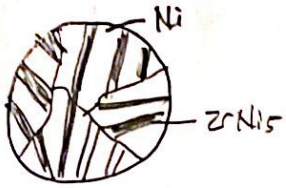
Phase fraction of Ni = $\frac{15-5}{15-0} = \frac{10}{15} = 0.67$ -5

Phase fraction of Zr = 0.33

Composition of Ni = 100% Ni or 0% Zr

Composition of $ZrNi_5$ = 85% Ni or 15% Zr

c) cont'd.




fast cool

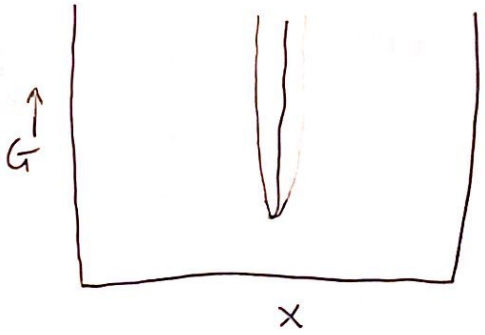
fraction of Ni = 0.67

" " Zr = 0.33

Combination of Ni = 100% Ni

" " ZrNi5 = 85% Ni

d) An intermetic forms when two metals bond chemically to form a compound with a specific composition and crystalline structure. The Gibbs energy curve for intermetallics is usually narrow




-2

Intermetallic phases

$ZrNi_5$ => 15 at% Zr at r.t to 1170°C

$Zr_2Ni_7$ => 22 at% Zr at r.t to 1438°C

$ZrNi_5$ => 25 at% Zr at r.t to 920°C

$Zr_8Ni_{21}$ => 28 at% Zr at r.t to 1180°C

$Zr_7Ni_{10}$ => 41 at% Zr at room temperature to 1163°C

$Zr_9Ni_{11}$ => 45 at% Zr at 975°C to 1157°C

e)

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