

$$\frac{T_m - T_m^b}{T_m^b} = \frac{2(\gamma_{lw} - \gamma_{sw})}{H \rho \Delta m h} \quad (1) a$$

T_m^b = bulk melting temperature

γ_{lw} and γ_{sw} = liquid and solid wall

$\rho = M/V$ is the density

$\Delta m h = h_L - h_S$ is the latent heat of melting per particle.

$$T_m(H) = T_m^b + \frac{2(\gamma_{lw} - \gamma_{sw})}{\rho \Delta m h}$$

Given the $V = A_w H$

making use of Clapeyron approach.

$$\Omega = dU - TS - p dV = -p A_w H + 2\gamma A_w$$

with internal energy

$$dU = TS - p A_w H + 2\gamma A_w + p dV$$

Where S is the entropy, p is the pressure and γ is the surface tension. The thermodynamic potentials of the two phases are equation $\Omega_L = \Omega_S$

$$p_L - p_S = \frac{2(\gamma_{lw} - \gamma_{sw})}{H}$$

$$d\Omega = -S dT - p A_w dH + (2\gamma - p H) dA_w - n d\mu$$

$$\frac{dH}{H^2} = - \frac{dT}{2(\gamma_{lw} - \gamma_{sw})} \left[(p_L s_L - p_S s_S) + (p_L - p_S) \frac{d\mu}{dT} \right]$$

$$\frac{d\mu}{dT} = \frac{p_L^L s_L^L - p_G^L s_G^L}{p_L^L - p_G^L} = -s_L^L$$

$$\frac{dH}{H^2} = - \frac{(p_L - p_S)(s_L - s_L^L) + p_S(s_L - s_S) dT}{2(\gamma_{lw} - \gamma_{sw})}$$

a)

For sufficiently large confining distances (and corresponding small shift in the melting $T_m - T_m^b$, one can approximate

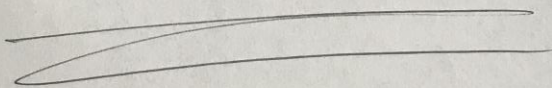
$$\frac{dH}{H^2} = - \frac{P_s^b \Delta m_s^b}{2(\gamma_{lw} - \gamma_{sw})} dT$$

$$\Delta m_s^b = s_L^b - s_s^b$$

The final step to recover the C&T equation is to integrate this equation along thermodynamic path connecting the confined system for finite H and corresponding T_m and and unconfinned one $H \rightarrow \infty$ and bulk melting temperature T_m^b

$$\int_H^\infty \frac{dH}{H^2} = \frac{-P_s^b \Delta m_s^b}{2(\gamma_{lw} - \gamma_{sw})} \int_{T_m}^{T_m^b} dT$$

$$T_m(H) = T_m^b + \frac{2(\gamma_{lw} - \gamma_{sw})}{HP_s^b \Delta m_s^b}$$



(13) from Confined Clapeyron⁽¹⁵⁾ approach

$$\Omega = U - TS - pV = -PA_{WH} + 2\gamma A_W$$

With inter energies

$$U = TS - PA_{WH} + 2\gamma A_W + \mu N$$

Where S = entropy

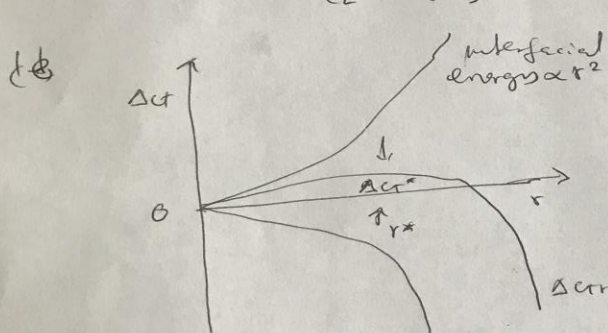
p = pressure

γ = surface tension

-10

Coexistence between the liquid and solid phase
thermodynamic potentials of the 2 phase are equal

$$\Omega_L = \Omega_S.$$



for given undercooling ΔT

$$r^* = \frac{2\gamma_{SL}}{\Delta G_v} = \left(\frac{2\gamma_{SL} T_m}{L_v} \right) \frac{1}{\Delta T}$$

For given undercooling ΔT , r^* correspond to a maximum excess free energy
 $r < r^* \rightarrow$ cluster or embryo
 $r > r^* \rightarrow$ nuclei

Below T_m , ΔG_v is positive, so formation of small volume of solid has negative contribution, if γ_{SL} is isotropic

$$\Delta G_r = -\frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma_{SL}$$

c) Kelvin equation $\Rightarrow \ln\left(\frac{p_{cr}}{p}\right) = \frac{2\gamma V_{molecule}}{k_B T r}$

$$CCB = \frac{dp}{dT} = \frac{pL}{T^2 R}$$

Integrating CCB

$$\int_1^2 dp = \int \frac{pL}{T^2 R} dT \text{ gives } \ln\left(\frac{p_2}{p_1}\right) = \frac{L}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Substituting $\ln\left(\frac{p_2}{p_1}\right)$ gives r from the Kelvin equation

$$\gamma = \frac{2\sigma T}{pL(T_1 - T_2)}$$

Good +5

$$pL(T_1 - T_2)r = 2\sigma T$$

$$pL\Delta T = 2\sigma T \quad T_1 - T_2 = \Delta T$$

$$\Delta T = \frac{2\sigma T}{pLr} \text{ Same as Clausius-Clapeyron equation}$$

Oswald-Fendlich equation $(OFE) = x_a = x_a^0 \exp\left[-\frac{2V_m \gamma}{R_g T R_{FE}}\right]$

x_a = mole fraction

V = molar volume

R_{FE} = radius

γ = interfacial tension

R_g = universal gas constant

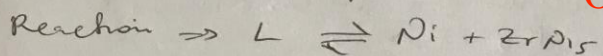
T = Temperature.

d) -20

e) -20

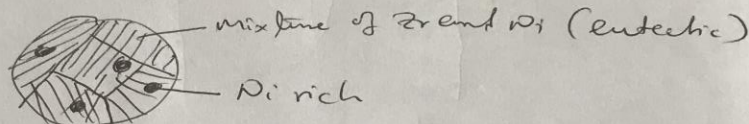
2 (b) This eutectic region with 3 phases in equilibrium.
 This is an invariant point with liquid, Ni and ZrNi₅
 Triple point is Eutectic point

OK

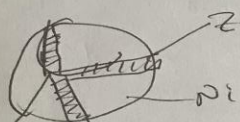


$F = C - P + 1$ (at constant pressure of 1 atm)

$F = 2 - 3 + 1 = 0$



(c)



phase fraction of Ni

$$\frac{15 - 5}{15 - 0} = \frac{10}{15} = 0.67$$

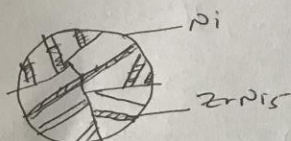
-5

phase fraction of Zr = 0.33

Composition of Ni = 100% Ni or 0% Zr

Composition of ZrNi₅ = 85% Ni or 15% Zr

(d)



Fast Cooling

fraction of Ni = 0.67

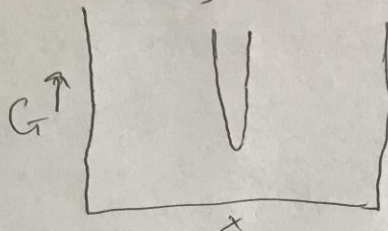
fraction of Zr = 0.33

Composition of Ni = 100% Ni

Composition of ZrNi₅ = 85% Ni

(e)

- d) ~~An~~ is for
 An intermetallic is formed when two metals bond chemically to form a compound with composition and crystalline structure. The Gibbs energy shows that intermetallics are usually narrow



Intermetallics phases

$ZrNi_5$	$\Rightarrow$ 15% Zr	at room temperature to 1170°C
Zr_2Ni_7	$\Rightarrow$ 22% Zr	✓ ✓ ✓ ✓ 1438°C
$ZrNi_5$	$\Rightarrow$ 25% Zr	✓ - ✓ ✓ 920°C
Zr_8Ni_{21}	$\Rightarrow$ 28% Zr	- - ✓ ✓ 1180°C
Zr_7Ni_{10}	$\Rightarrow$ 41% Zr	✓ - - - 1163°C
Zr_9Ni_{11}	$\Rightarrow$ 45% Zr	- - - - 975°C - 1157°C

- e) Ni-20%Cu is a complete solid solution, therefore it is an isomorphous system.

lever rule is used to determine phase fractions and compositions. The matrix phase is solid solution α (Cu_{0.8}Ni_{0.2}) which is made up of Cu and Ni at lower temperature below solidus. There are solid solution α and liquid solution between solidus and liquidus. We have full solubility above the liquidus.

Mixture of Cu and Ni is the spherical domain.

Solid α composition $\Rightarrow$ 84% Ni

Liquid composition $\Rightarrow$ 76% Ni

e) -20