

Binary Phase Equilibria & Phase Diagrams p 22

Vapor-Liquid Eq.

$$\mu_A(g) = \mu_A(l)$$

$$\mu_A(l) = g_A(l) + RT \ln(\delta_A x_A)$$

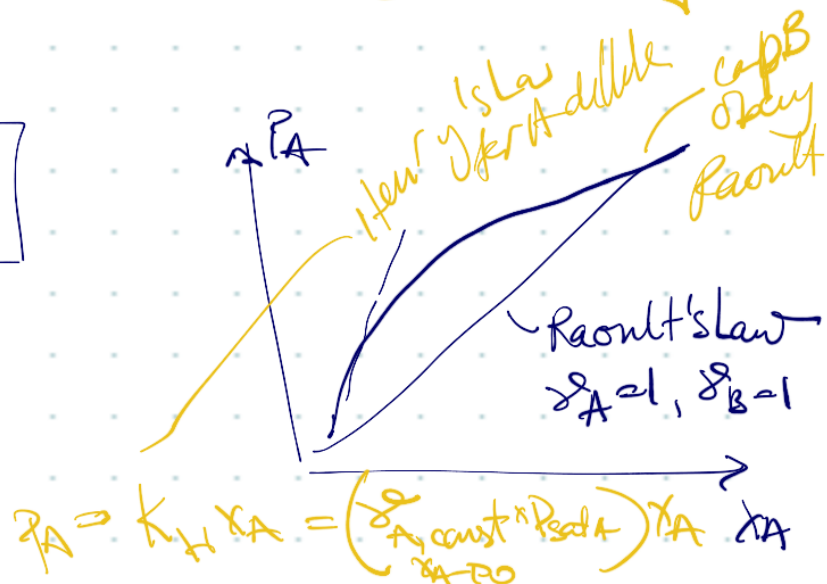
$$\mu_A(g) = g_A^\circ(g) + RT \ln p_A$$

same temp

$$\Rightarrow \frac{p_A}{\delta_A x_A} = \exp \left[\frac{-[g_A^\circ(g) - g_A(l)]}{RT} \right]$$

$$x_A = 1, \delta_A = 1 \Rightarrow p_A = p_A^{\text{sat}}(T) = \exp \left[\frac{-\Delta G^\circ(g,l)}{RT} \right]$$

$$p_A = \delta_A x_A p_A^{\text{sat}}$$



Liquid-Liquid Equilibrium

$$\frac{x_A^{\text{II}}}{x_A^{\text{I}}} = \frac{\gamma_A^{\text{I}}}{\gamma_A^{\text{II}}} = \text{"distribution coefficient of A"}$$

Method of Ideal Binary Condensed Phases

$$g_A(L) + RT \ln x_{AL} = g_A(S) + RT \ln x_{AS}$$

$$g_B(L) + RT \ln x_{BL} = g_B(S) + RT \ln x_{BS}$$

$$x_{AL} + x_{BL} = 1$$

$$x_{AS} + x_{BS} = 1$$

$$x_{BL} = \frac{1 - e^{\alpha}}{e^{\beta} - e^{\alpha}}$$

THE LIQUIDUS LINE

$$x_{BS} = e^{\beta} \left(\frac{1 - e^{\alpha}}{e^{\beta} - e^{\alpha}} \right)$$

THE SOLIDUS LINE

$$\alpha = \frac{g_A(L) - g_A(S)}{RT} \quad \beta = \frac{g_B(L) - g_B(S)}{RT}$$

$$\Delta g_{L-S} \approx \left(1 - \frac{T}{T_M} \right) \Delta h_{L-S}$$

$$\Rightarrow \alpha = \left(1 - \frac{T}{T_{MA}} \right) \frac{\Delta h_{LSA}}{RT}$$

$$\beta = \left(1 - \frac{T}{T_{MB}} \right) \frac{\Delta h_{LSB}}{RT}$$

Phase Separation

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⊕ deviation from ideality:

↓

A-B interaction

weaker
<

A-A interactions
B-B

↓
separation of two distinct phases "partially miscible"

$$h^{ex} = \sum x_A x_B$$

$\Omega < 0 \Rightarrow$ A-B more stable than ideal solution
↓

no phase separation
 $\Omega > 0 \Rightarrow$ A-B less stable than ideal solution

↓

excess enthalpy > entropy of mixing
overcomes

↓

phase separation

$$g_A + RT \ln \gamma_{AI} x_{AI} = g_A + RT \ln \gamma_{AII} x_{AII}$$

$$g_B + RT \ln \gamma_{BI} x_{BI} = g_B + RT \ln \gamma_{BII} x_{BII}$$

$$RT \ln \gamma_A = -2x_B^2 \quad RT \ln \gamma_B = -2x_A^2$$

$$\Rightarrow \left(\frac{-2}{RT} \right) (x_{BI}^2 - x_{BII}^2) = \ln \left(\frac{1-x_{AII}}{1-x_{AI}} \right)$$

same for $(1-x_{BI})$ and $(1-x_{BII}) \rightarrow$ symmetric functions by $x_B = 0.5$

$$\Rightarrow \Gamma = \frac{-2}{RT} = \frac{\ln \left(\frac{1-x_B}{x_B} \right)}{1-2x_B}$$



$\Gamma < 2 \Rightarrow$ no solutions \Rightarrow no phase separation

$\Gamma \geq 2 \Rightarrow$ phases I or II form \Rightarrow

$$\Gamma = \frac{2}{2R} \quad \frac{T}{T^*} = \frac{2(1-2x_B)}{\ln \left(\frac{1-x_B}{x_B} \right)}$$

critical solution temperature

Binary Phase Diagram

• Free energy curve:

$$g(T) = g_{\text{comp}}(T) + h^{\text{ex}} - T \Delta S^{\text{mix}}$$

$$\begin{cases} g_{\text{comp}} = X_A g_A + X_B g_B \\ \Delta S^{\text{mix}} = -R(X_A \ln X_A + X_B \ln X_B) \\ h^{\text{ex}} = \Omega X_A X_B \end{cases}$$

• Common tangent rule: $dg = \mu_A dx_A + \mu_B dx_B$

$$\left(\frac{dg}{dx_B}\right)_I = \mu_{BI} - \mu_{AI} \quad \left(\frac{dg}{dx_B}\right)_{II} = \mu_{BII} - \mu_{AII}$$

Phase Equilibrium condition: $\mu_{AI} = \mu_{AII} \quad \mu_{BI} = \mu_{BII}$

$$\boxed{\left(\frac{dg}{dx_B}\right)_I = \left(\frac{dg}{dx_B}\right)_{II}} \quad \text{COMMON TANGENT RULE}$$

existing phases (I & II)
are points on the
free energy curve $g(T)$
that have a common tangent

Melting / Solidification of a Ideal 2 Component System

$$g(L) = x_A g_A(L) + x_B g_B(L) + RT(x_A \ln x_A + x_B \ln x_B)$$

$$g(S) = x_A g_A(S) + x_B g_B(S) + RT(x_A \ln x_A + x_B \ln x_B)$$

$$g_A(L) = g_A(S) + \left(1 - \frac{T}{T_{m,A}}\right) \Delta h_{m,A}$$

$$g_B(L) = g_B(S) + \left(1 - \frac{T}{T_{m,B}}\right) \Delta h_{m,B}$$

$g_A(S)$ and $g_B(S) \rightarrow$ arbitrary \rightarrow they affect the free energy curves, but not the composition @ the common tangency points.

for convenience: $g_A(S) = 0$ $g_B(S) = 0$

eg: $T_{m,A} = 1406 \text{ K}$

$\Delta h_A = 15.5 \text{ kJ/mol}$

$$\Rightarrow g_A(1500 \text{ K}) = 0 - \left(1 - \frac{1500}{1406}\right) 15.5$$

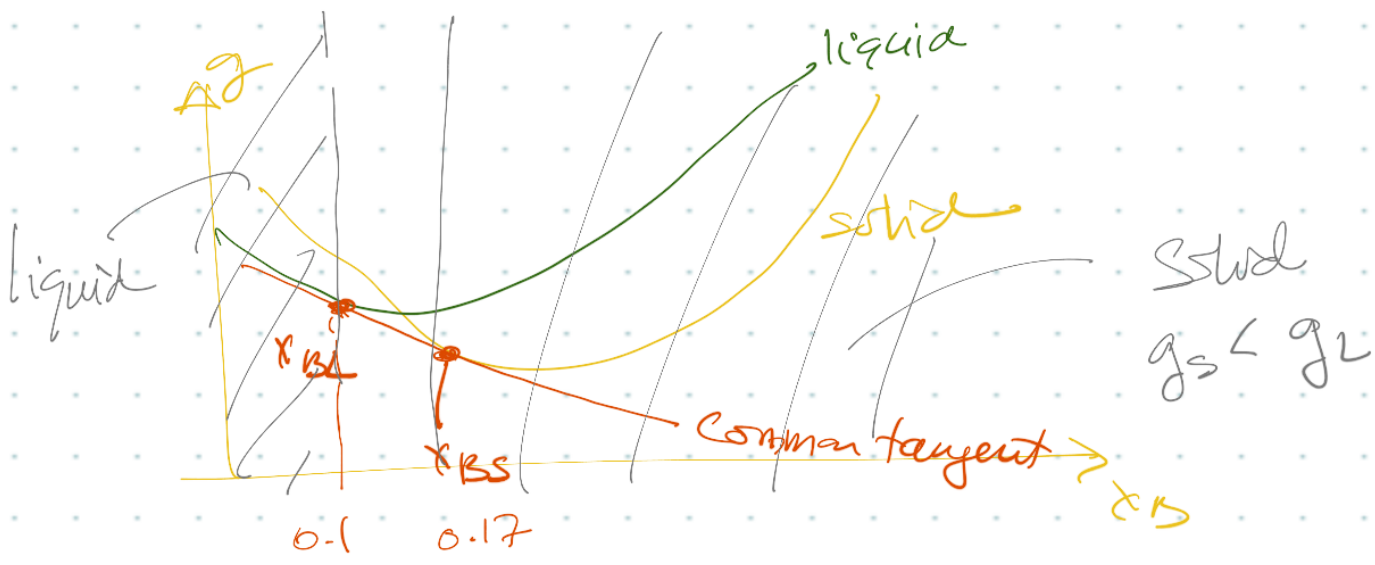
$$\approx g_A = -1.04 \text{ kJ/mol}$$

$T_{m,B} = 230$

$\Delta h_B = 23 \text{ kJ/mol}$

\rightarrow

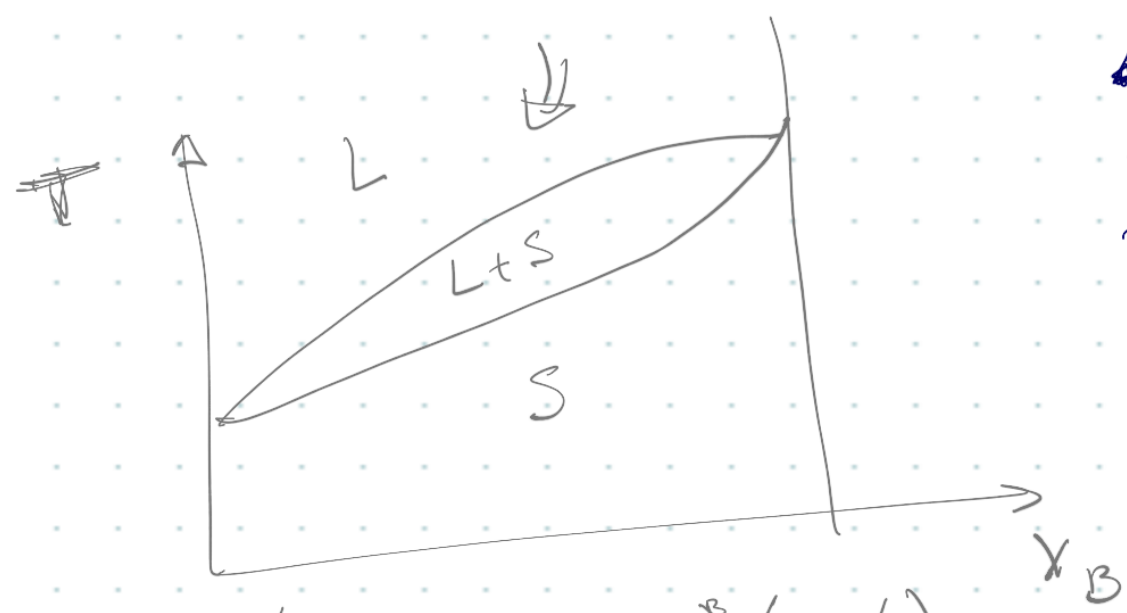
$$g_B(1500 \text{ K}) = 2.80 \text{ kJ/mol}$$



two-phase region

graphical solution

analytical solution



same problem treated in two different ways.

$$x_{BL} = \frac{1 - e^{\alpha}}{e^{\beta} - e^{\alpha}}$$

$$x_{BS} = e^{\beta} \left(\frac{1 - e^{\alpha}}{e^{\beta} - e^{\alpha}} \right)$$

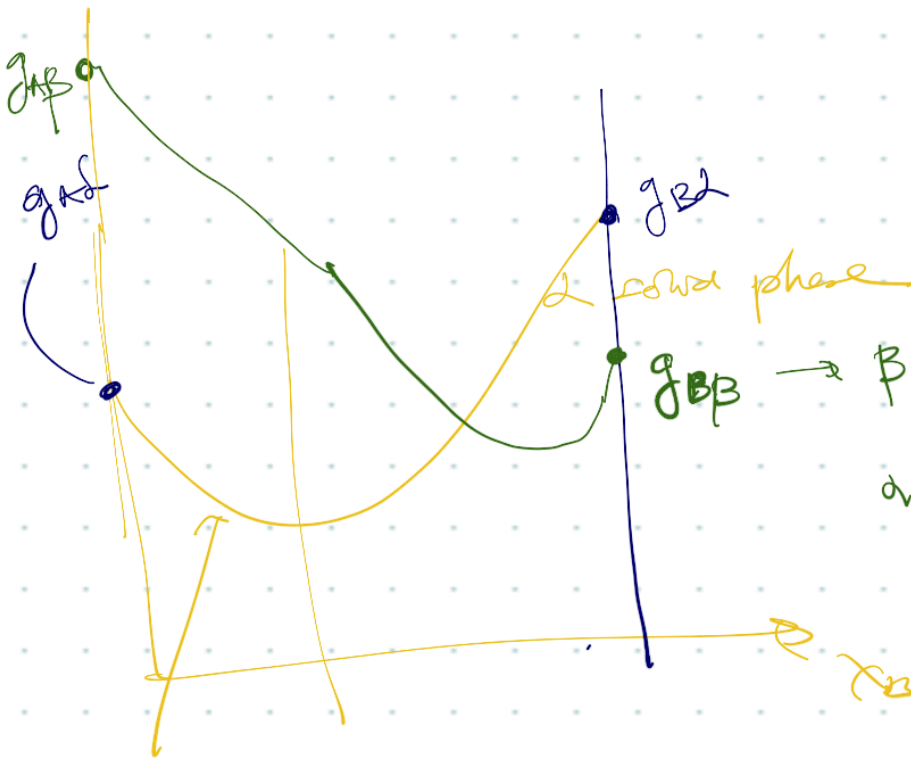
$$\alpha = \frac{g_A(L) - g_A(S)}{RT}$$

$$\beta = \frac{g_B(L) - g_B(S)}{RT}$$

Eutectic Phase Diagram

Liquid $g_L(x_B)$ curve \uparrow w/ temp more than

Solid $g_S(x_B)$ curves because liquids have higher entropy



$$\left(\frac{\partial g}{\partial T}\right)_P = -S$$

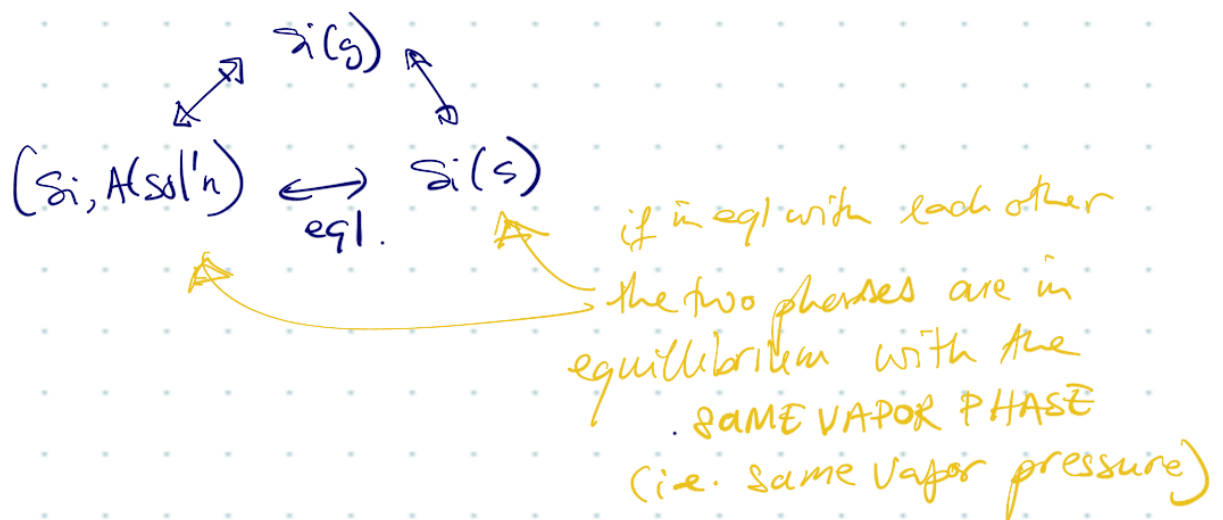
α solid phase
 $g_{S2}^0 \rightarrow \beta$ crystal structure more stable for B than α crystal structure

stabilization of dilute solution by entropy of mixing,
 then increases due to h^* \rightarrow crystal structure defects
 shape depends on nonideality: $\boxed{g^{ex}}$

Example Problem

Au-Si "degenerate eutectic phase diagram"

- 1) calculate γ_{AuL} , γ_{SiL} along the two liquidus curves
- 2) Is this a "regular solution?"
- 3) Is the data consistent with the zeroth law of thermodynamics?



$$(1) \quad g_{Au,S} = g_{Au,L} + RT \ln(\gamma_{Au,L} x_{Au,L})$$

$$\Rightarrow \exp\left[\frac{g_{Au,S} - g_{Au,L}}{RT}\right] = \gamma x$$

$$\Rightarrow \gamma_{Au,L} = \frac{e^{-d}}{x_{Au,L}}$$

$$d = \frac{g_{Au,S} - g_{Au,L}}{RT} = \left(1 - \frac{T}{T_{M,Au}}\right) \frac{\Delta h_{m,Au}}{RT}$$

$$\Delta h_{m,Au} = 1540 \text{ kJ/mol}$$

$$T_{M,Au} = 1336 \text{ K} \Rightarrow \text{calculate } \gamma_{Au}(x_{Au})$$

$$(2) \quad \text{regular solution: } h^{ex} = \Omega x_A x_B \quad \delta^{ex} = 0 \Rightarrow$$

$$\boxed{RT \ln \gamma_A = \Omega x_B^2} \Rightarrow \frac{RT \ln \gamma_A}{(1-x_A)^2} = \text{CONSTANT}$$

↓
check if this is true

$\gamma < 1 \Rightarrow$ attractive interactions in the liquid phase

(3)

Vapor \rightleftharpoons liquid \rightleftharpoons solid
solution

$$P_{Au} = \gamma_{AuL} X_{AuL} P_{sat, Au(L)} \approx P_{sat, Au(S)}$$

\Downarrow

$$\gamma_{Au, L} X_{AuL} = \frac{P_{sat, Au(S)}}{P_{sat, Au(L)}}$$

\Downarrow
Vap. pressures of
liquid need to be
extrapolated below
m.p.