3.020 Lecture 21

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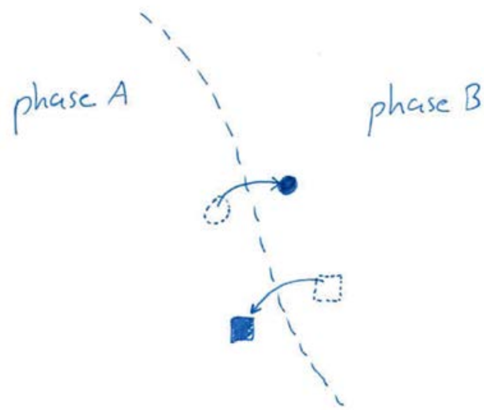
1 Phase coexistence and Common tangent construction

- Two components 1 & 2
- Two phases that can freely exchange matter, A & B
- Phase coexistence at equilibrium requires $dG = 0$



$$
\begin{aligned}
dG'|_{P,T} &= \sum_{i,k} \mu_k^i \quad dn_k^i \qquad k = 1, 2 \qquad -\textbf{components} \\
& \qquad\qquad\qquad\qquad i = A, B \qquad -\textbf{phases} \\
&= \mu_1^A dn_1^A + \mu_2^A dn_2^A + \mu_1^B dn_1^B + \mu_2^B dn_2^B \\
& \qquad\qquad \textbf{conservation of mass} \qquad dn_k^B = -dn_k^A \\
&= (\mu_1^A - \mu_1^B) dn_1^A + (\mu_2^A - \mu_2^B) dn_2^A
\end{aligned}
$$

$(\mu_i^A - \mu_i^B)$ are the coefficients
dn_i^A are the unconstrained, independent vars

$$dG'|_{P,T} = 0 \qquad \textbf{requires} \qquad \mu_1^A = \mu_1^B, \mu_2^A = \mu_2^B$$

Phases can freely exchange molecules/atoms A & B without changing overall free energy $\longrightarrow$ free energy is optimized.

- In general, each phase has its own solution model and partial molar properties of mixing

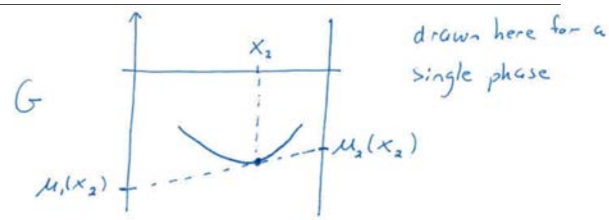
$$
\begin{aligned}
\mu_1^A &= \mu_1^\circ + \Delta\mu_{1,mix}^A \qquad & \mu_2^A &= \mu_2^\circ + \Delta\mu_{2,mix}^A \\
\mu_1^B &= \mu_1^\circ + \Delta\mu_{1,mix}^B \qquad & \mu_2^B &= \mu_2^\circ + \Delta\mu_{2,mix}^B
\end{aligned}
$$

- The reference states are fixed and μ_k° don't depend on the mixing process

$$\mu_1^A = \mu_1^B \qquad \Longrightarrow \qquad \Delta\mu_{1,mix}^A = \Delta\mu_{1,mix}^B$$
$$\mu_2^A = \mu_2^B \qquad \Longrightarrow \qquad \Delta\mu_{2,mix}^A = \Delta\mu_{2,mix}^B$$

A-B coexistence equilibrium condition

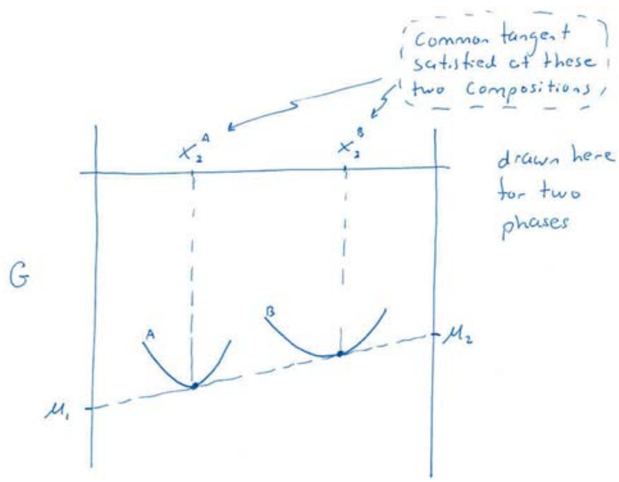
- graphical solution for PMPs



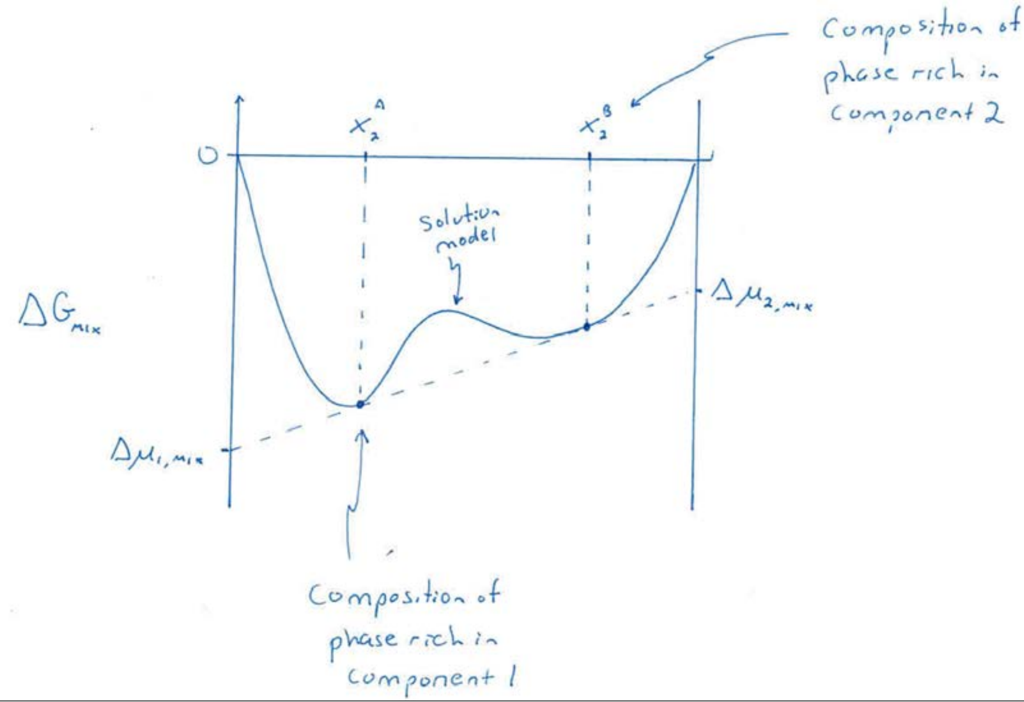
- common tangent condition for two-phase equilibrium

$$\mu_1^A = \mu_1^B, \mu_2^A = \mu_2^B$$

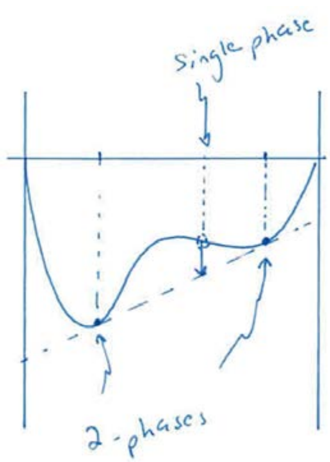
condition satisfied when phases A & B share a common tangent on free energy-composition diagram



- Examples of common tangent construction: Spinodal systems



- When common tangent is possible, free energy of the 2-phase system is lower overall than that of 1-phase system.



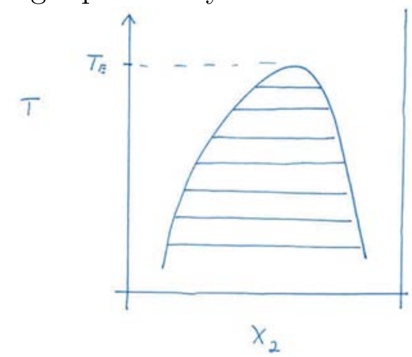
- Single phase

$$G = G^{\circ} + \Delta G_{mix}(X_2)$$

- Two phase

$$G = G^{\circ} + f^A \Delta G_{mix}(X_2^A) + f^B \Delta G_{mix}(X_2^B)$$

- Common tangents define the tie lines on a binary phase diagram e.g. spinodal system



- Mixing favored at high temp
  - fully miscible above T_E
- At low temp, system spontaneously unmixes
- Tie lines drawn in 2-phase region connect compositions that coexist at equilibrium

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- phase diagram emerges from free energy-composition diagrams