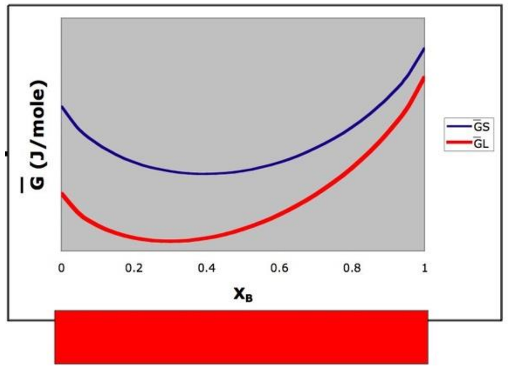
Binary Phase Diagrams of Ideal Solutions

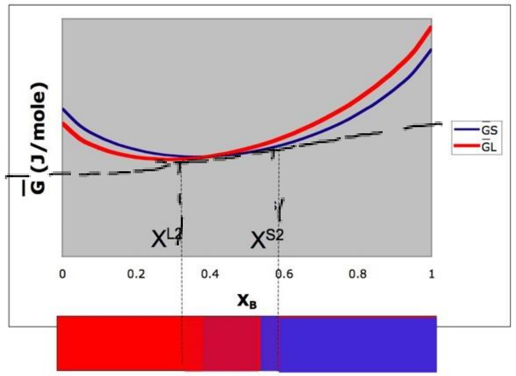
The phase equilibria as a function of composition for a fixed temperature (and fixed pressure) predicted by Free Energy vs composition diagrams can be used to create a binary phase diagram, which maps out stable phase in T vs composition space.

p = constant

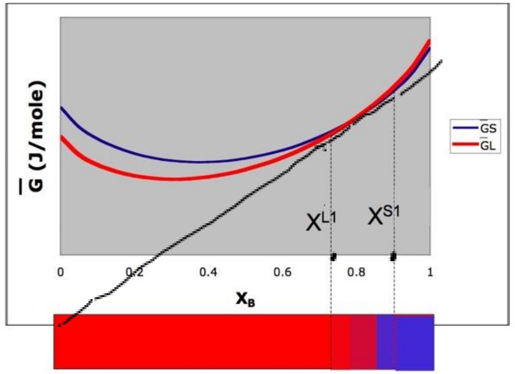
T_1



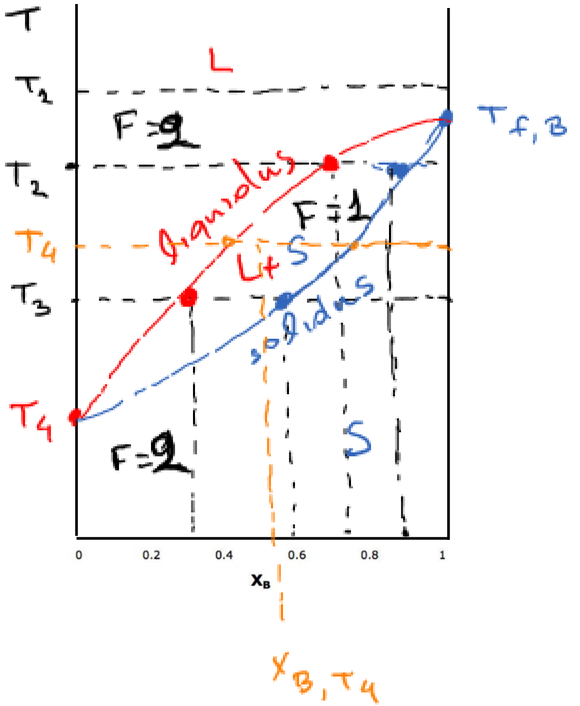
T_3



T_2



$T_1 > T_2 > T_3$

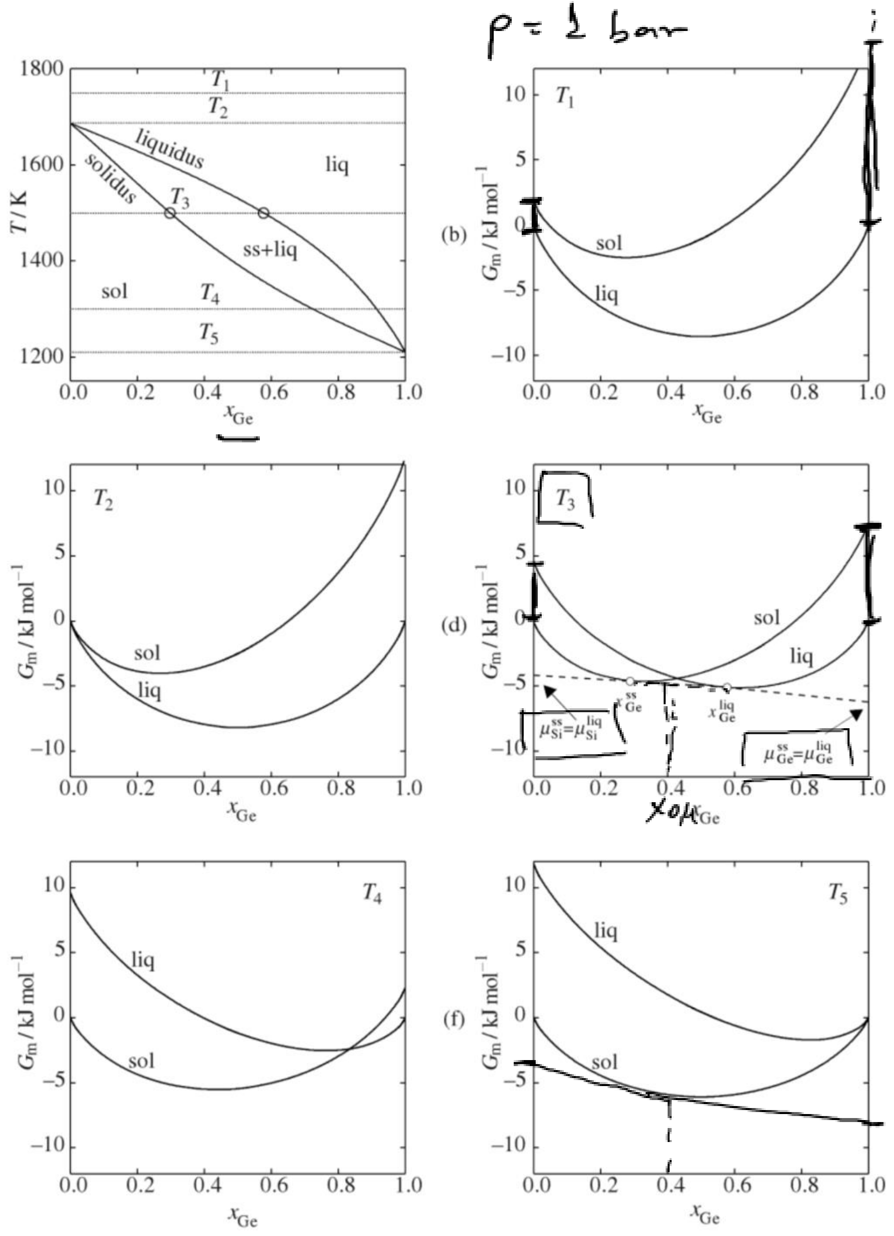


* Apply lever rule

\- Apply the Gibbs phase rule

$$F = n + \overset{T,p}{2} - \varphi \quad || \Rightarrow F = n + 1 - \varphi$$

Example: Si-Ge Binary Phase Diagram



$$\bar{G}_{mix}(x_{Ge})^{liq} = \mu^{o,liq}_{Si}(1-x_{Ge}) + \mu^{o,liq}_{Ge}x_{Ge} + RT[(1-x_{Ge})\ln(1-x_{Ge}) + x_{Ge}\ln x_{Ge}]$$

$$\bar{G}_{mix}(x_{Ge})^{sol} = \mu^{o,sol}_{Si}(1-x_{Ge}) + \mu^{o,sol}_{Ge}x_{Ge} + \underbrace{RT[(1-x_{Ge})\ln(1-x_{Ge}) + x_{Ge}\ln x_{Ge}]}_{\text{curvature}}$$

1. Speed of moving of curves

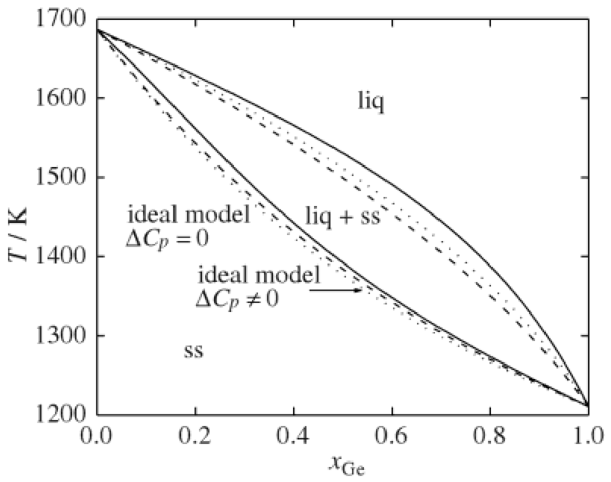
$$\left(\frac{\partial \mu}{\partial T}\right)_p = -S$$

2. under ΔS, they cross once. ⇒ curvature has the same characteristics

3. Tilt of curves at the axes

$$\Delta\mu_i^{o} = \Delta_{mix}\bar{H}_i - T\,\Delta_{mix}\bar{S}_i = \Delta_{mix}h_i - T\,\Delta_{mix}s_i$$

Width of solidus and Liquidus Lines



Solidus Line: $$x_A^s \exp\left[-\frac{\Delta_{fus}h_A}{R}\left(\frac{1}{T}-\frac{1}{T_{f,A}}\right)\right] + x_B^s \exp\left[-\frac{\Delta_{fus}h_B}{R}\left(\frac{1}{T}-\frac{1}{T_{f,B}}\right)\right] = 1$$

Liquidus Line: $$x_A^l \exp\left[-\frac{\Delta_{fus}h_A}{R}\left(\frac{1}{T}-\frac{1}{T_{f,A}}\right)\right] + x_B^l \exp\left[-\frac{\Delta_{fus}h_B}{R}\left(\frac{1}{T}-\frac{1}{T_{f,B}}\right)\right] = 1$$

We assume $\Delta c_{p,i} = 0$ $\quad c_{p,i}^l = c_{p,i}^s$

The width of the two-phase domain: $x_B^l - x_B^s = \frac{\Delta_{fus}s}{4R}\frac{\Delta T_f}{T_o}$ where $T_o = \frac{1}{2}(T_{f,A} + T_{f,B})$

$\varepsilon_{Si-Si} \simeq 2.5\,eV$, $\varepsilon_{Ge-Ge} \simeq 1.5\,eV$

$\Rightarrow \varepsilon_{Si-Ge} \simeq 2\,eV$

$x_{Ge}^l - x_{Ge}^s = 0.28$ analytical expre.

0.32 → experimentally

$$\Delta\mu_i^{(s\to l)} = \Delta_{mix}h_i + \int_{T_{f,i}}^{T} c_{p,i}\,dT - T\left(\Delta_{mix}s_i + \int_{T_{f,i}}^{T}\frac{c_{p,i}}{T}\,dT\right)$$

⇒ The heat capacity has a minimum effect on the phase diagram

But what determines what happens is the energetics (entropy)

MSE-204 Thermodynamics for Materials Science

L8.2 Multicomponent Phase Diagrams

Regular Solution Model | Spatial Arrangement of Atoms | Miscibility Gap | Invariant Points | Intermediate Compounds

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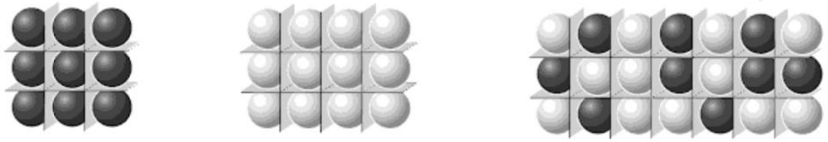
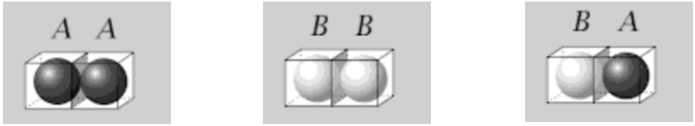
Spatial Arrangement under the Regular Solution Model

Under the **quasi-chemical model** it is assumed that the heat of mixing, $\Delta_{mix}H$, is only due to bond energies between adjacent atoms and that the volumes of pure A and pure B are equal to the final volume of the mixture.

We introduce the interaction parameter, which is defined as *Ω*. It quantifies the energy change due to mixing. Ω has a simple atomistic interpretation: it compares the energy of the bond between dissimilar atoms with the arithmetic mean of the bonds between like atoms.

A-A B-B AB , BA





ε_{AA} ε_{BB} ε_{AB}

$$\varepsilon = \varepsilon_{AB} - \frac{1}{2}(\varepsilon_{AA} + \varepsilon_{BB})$$

Assumptions: - p is constant
- $\Delta_{mix}\bar{V} = 0$, crystal structure is the same
- A & B are randomly distributed across the mixed state
← no excess of entropy

internal energy

$$\bar{U}_{mix} = P_{AA}\varepsilon_{AA} + P_{BB}\varepsilon_{BB} + P_{AB}\cdot\varepsilon_{AB}$$

$$\Delta_{mix}\bar{U} = \bar{U}_{mix} - U_{pure} = P_{AB}\cdot\varepsilon$$

$$P_{AB} = \frac{1}{2}z\cdot N_A(2x_Ax_B) = zN_A x_Ax_B$$

$$\Delta_{mix}\bar{U} = zN_A\cdot\varepsilon\cdot x_Ax_B$$

I define $\Omega = zN_A\cdot\varepsilon$

$$\Rightarrow \Delta_{mix}\bar{U} = \Omega x_Ax_B$$

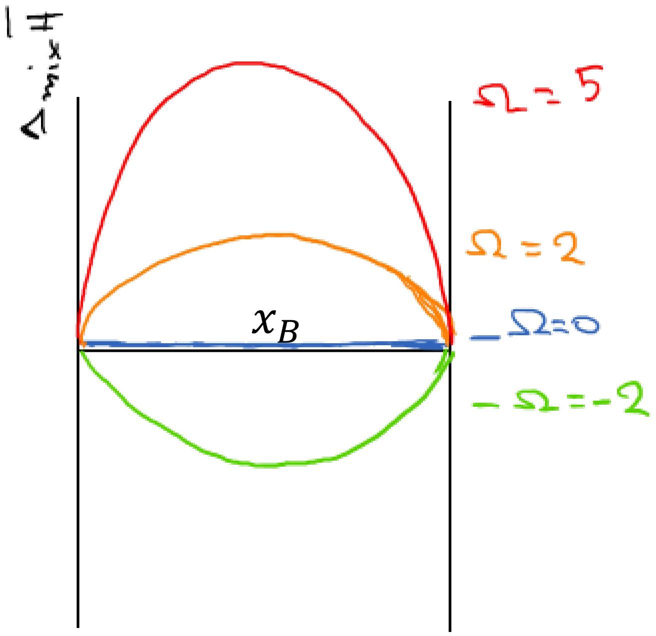
$$\Delta_{mix}\bar{H} = \Delta_{mix}\bar{U} + \cancel{\Delta(pV)}^{\,0} = \Omega x_Ax_B$$

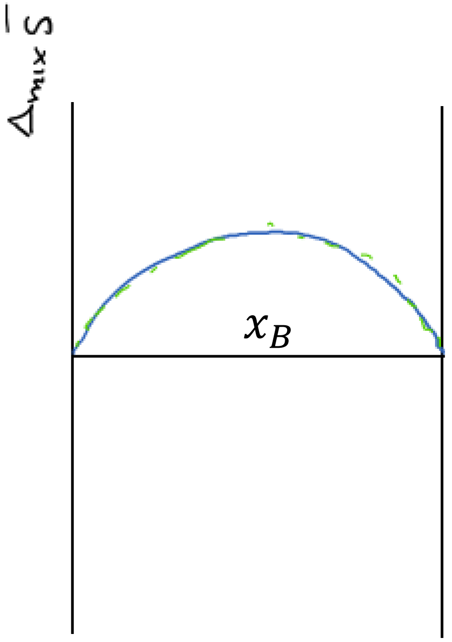
$$\Delta_{mix}\bar{G} = \underbrace{\Omega x_Ax_B}_{\text{excess Gibbs free energy}} + \underbrace{RT(x_A\ln x_A + x_B\ln x_B)}_{IS}$$

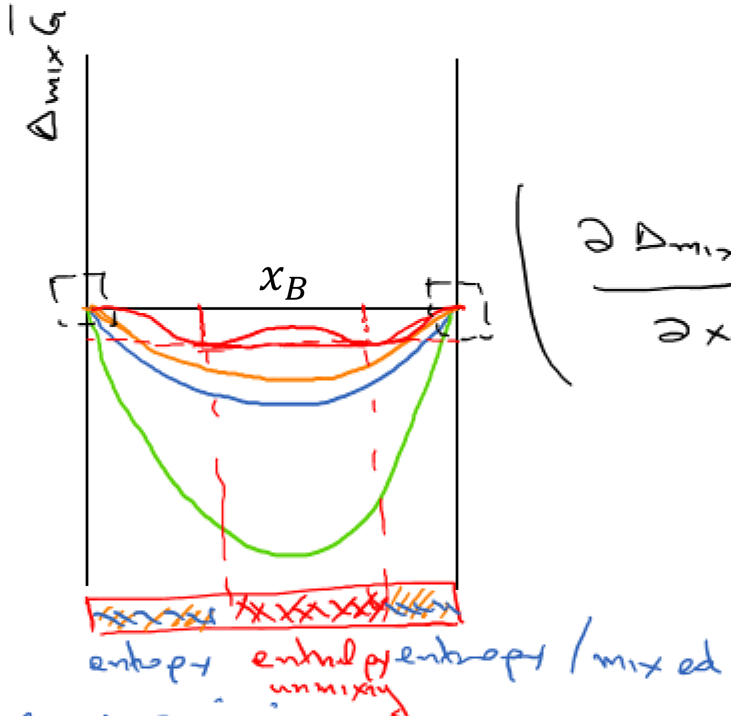
Composition Dependence of Various Thermodynamic Functions of a Regular Solution

at some T, p is constant

$$\Delta_{mix}\bar{U} = \Delta_{mix}\bar{H} = \Omega x_A x_B \qquad \Delta_{mix}\bar{S} = -\mathrm{R}(x_A \ln x_A + x_B \ln x_B) \qquad \Delta_{mix}\bar{G} = \Omega x_A x_B + \mathrm{RT}(x_A \ln x_A + x_B \ln x_B)$$







$$\left(\frac{\partial \Delta_{mix}\bar{G}}{\partial x_B}\right)_{\substack{x_B \to 0 \\ x_B \to 1}} \simeq \text{negative}$$

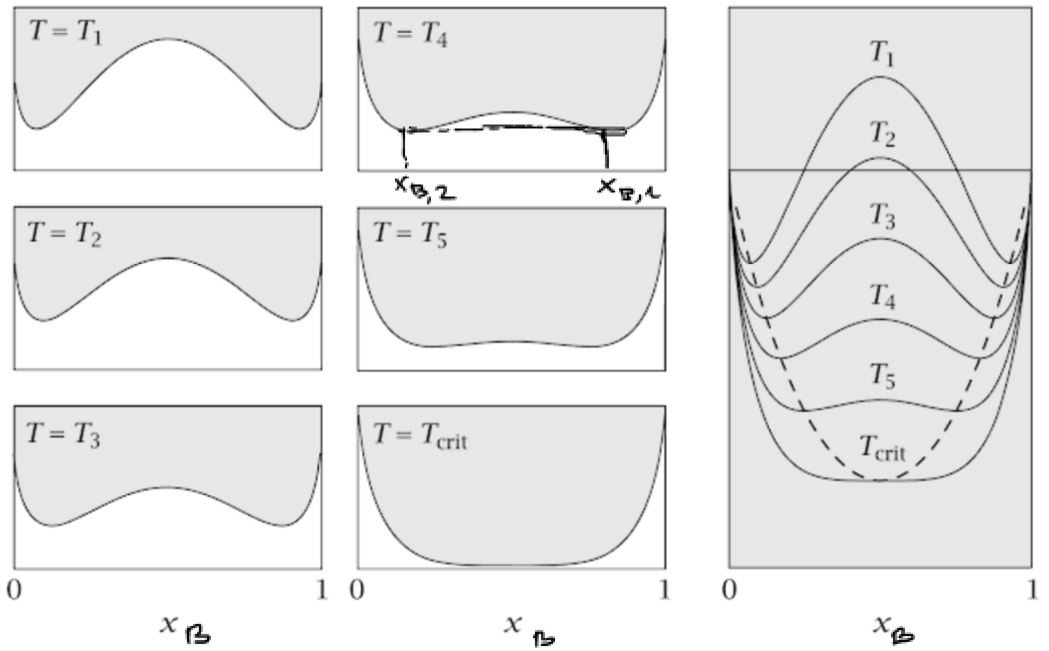
when $\Omega = 0$ ⇒ ideal solution (IS) ⇒ spontaneous mixing

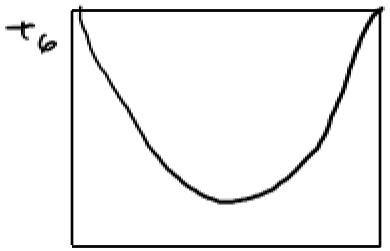
when $\Omega < 0$ ⇒ favors mixing (A-B)

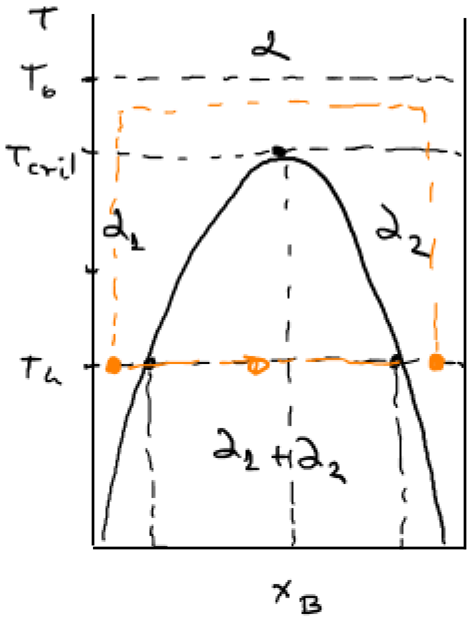
when $\Omega > 0$ ⇒ favors unmixing (A-A, B-B)

Phase Diagram of a Regular Solution: Miscibility Gap for $\Omega > 0$ as a Function of Temperature

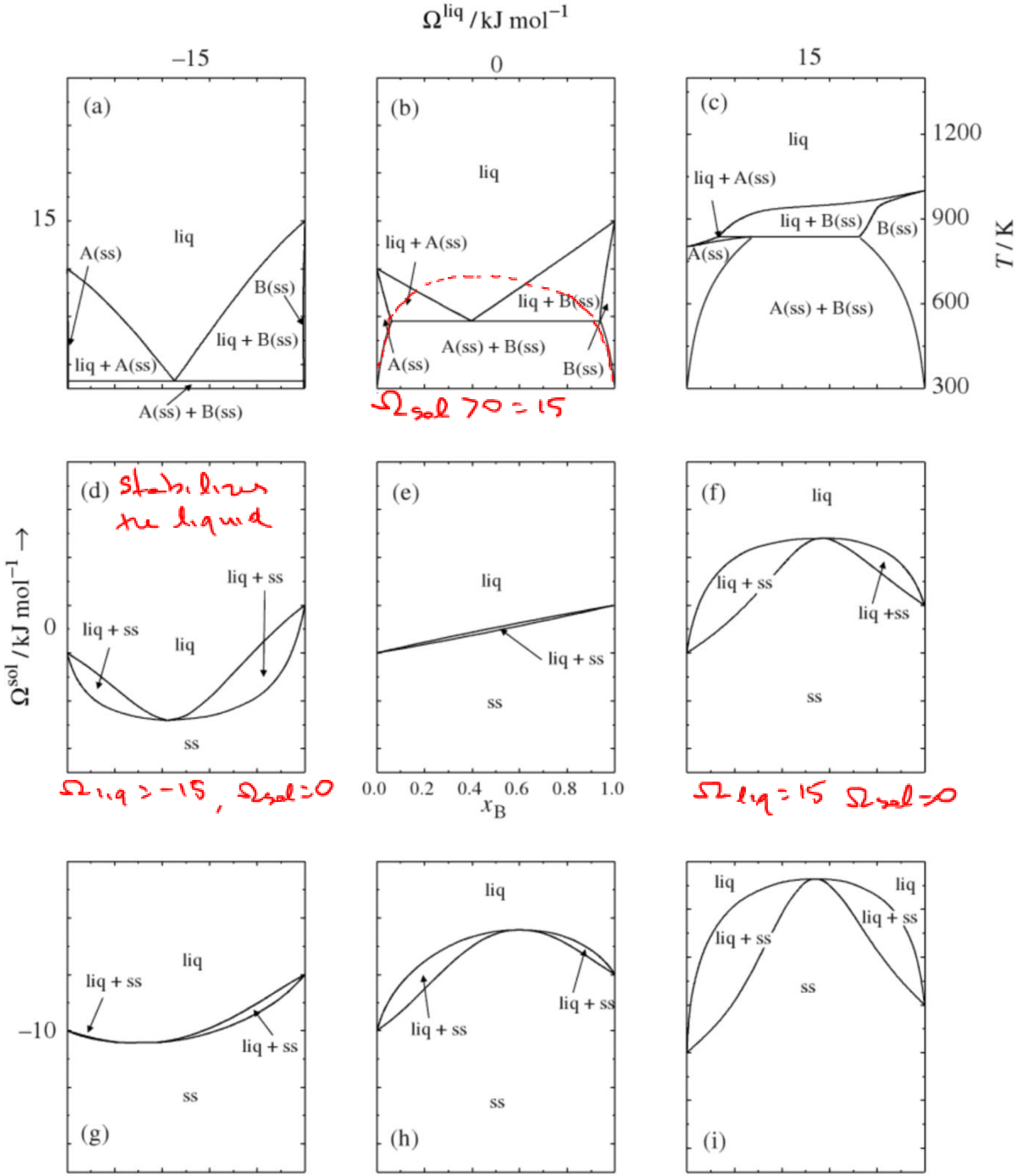
Ω is positive







$\Rightarrow$ miscibility gap



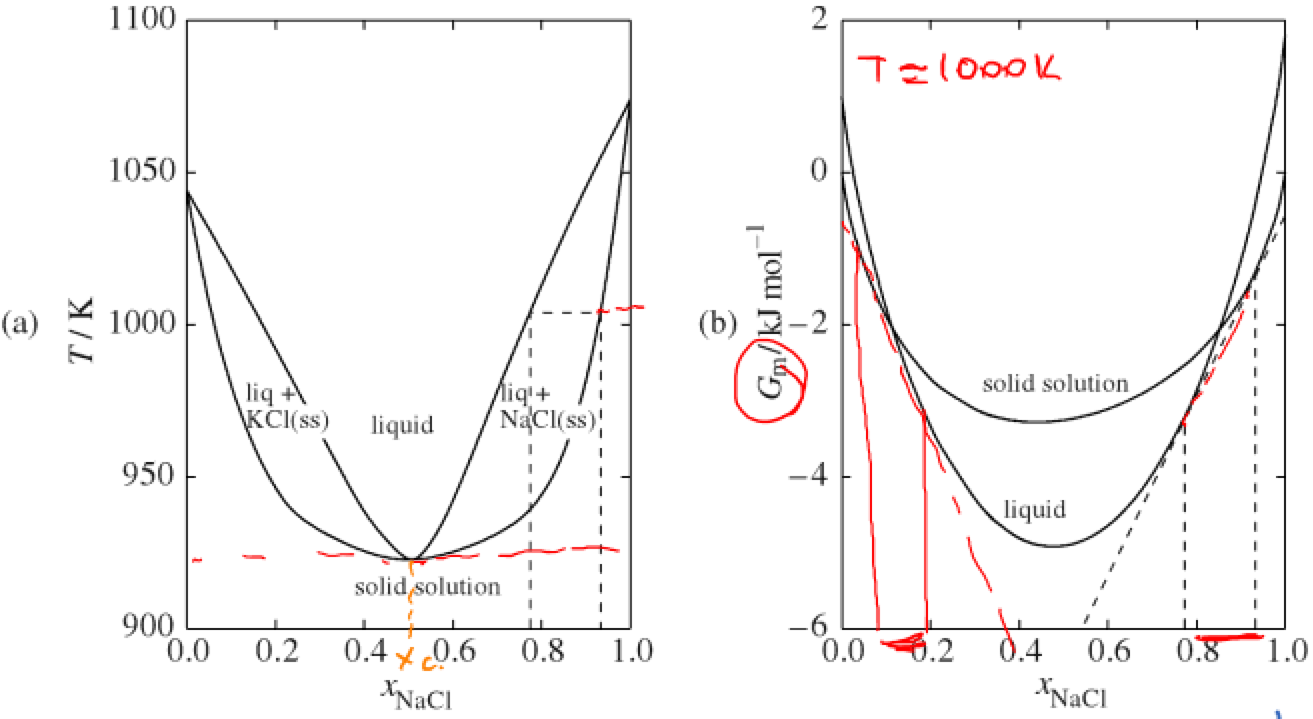
PHASE DIAGRAM OF A BINARY SYSTEM CONSISTING OF SOLID AND LIQUID SOLUTION PHASES FOR SELECTED COMBINATIONS OF Ω

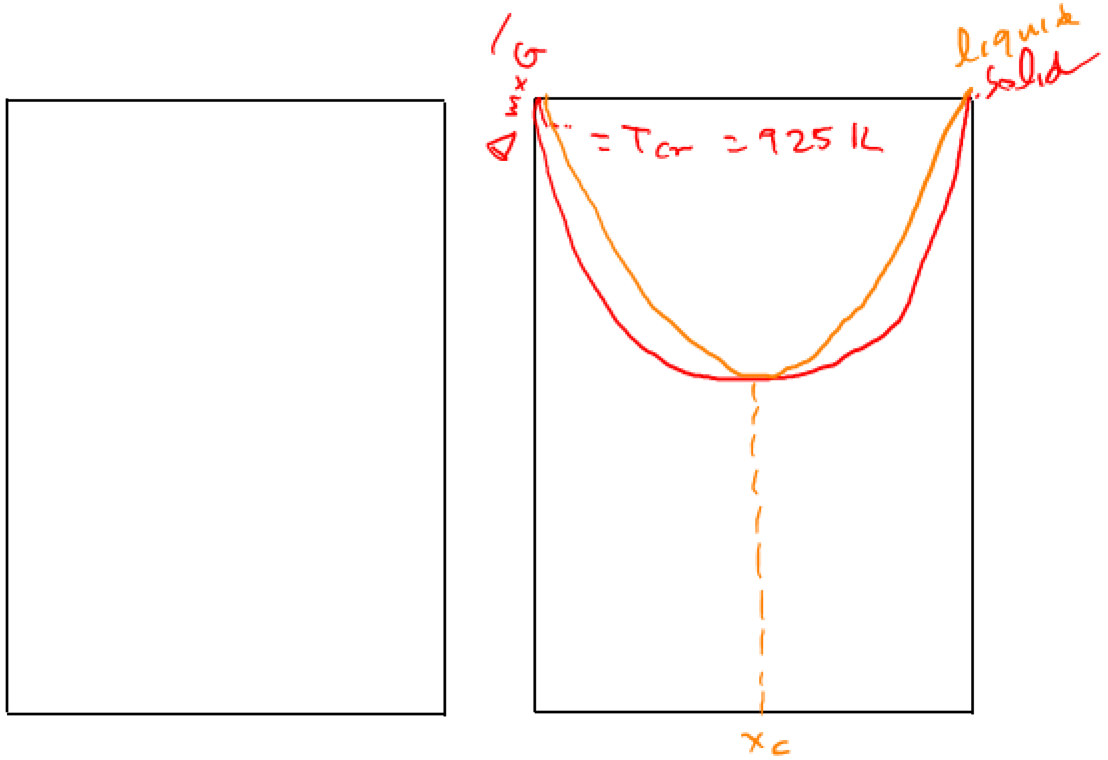
$$\Delta_{mix}\bar{G} = \Delta_{mix}\bar{H} - T\,\Delta_{mix}\bar{S}$$

Congruent phase diagrams

KCl – NaCl

This particular system is characterized by negative deviation from the ideal behavior in the liquid state and positive deviation from ideality in the solid state. Remember that a negative Gibbs free energy of mixing corresponds to a stabilization of the solution, which manifests as a deeper curvature of the G-x curve compared to the ideal solution. Correspondingly, a positive deviation from ideal behavior destabilizes the solution and the G-x curve becomes shallower. Thus, <u>a congruent phase transition corresponds to a complete transformation from one phase to another with no change in composition</u>.





At x_c: $F = n + 1 - \varphi$

$F = 1 + 1 - 2 = 0$

The congruent point is an invariant point