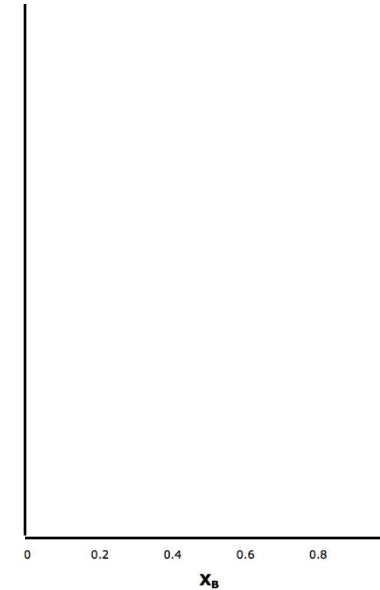
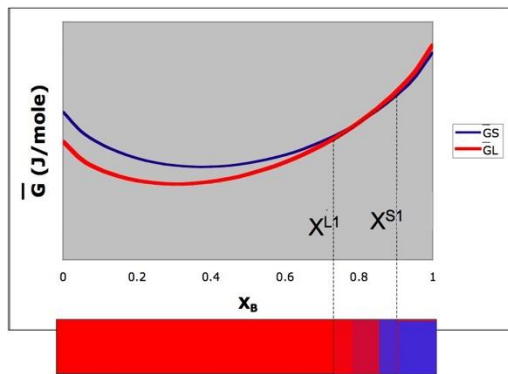
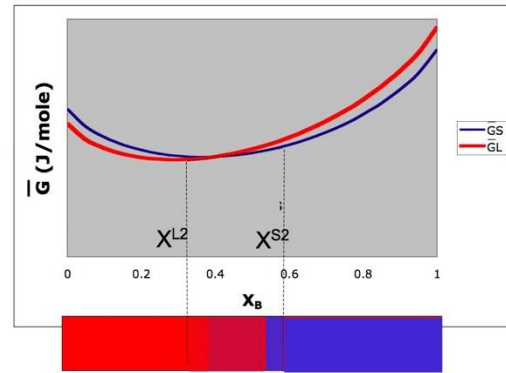
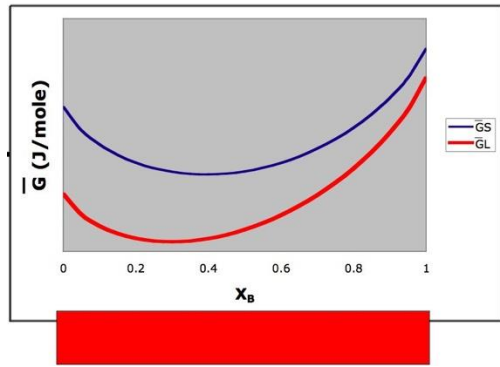
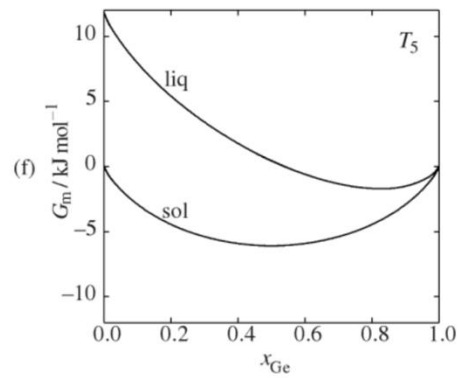
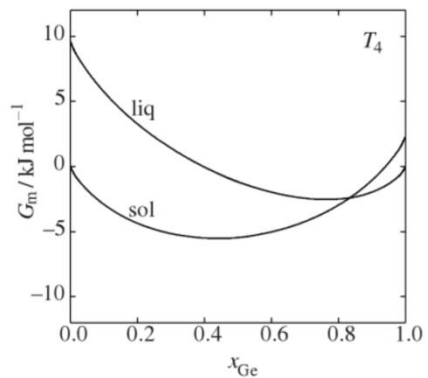
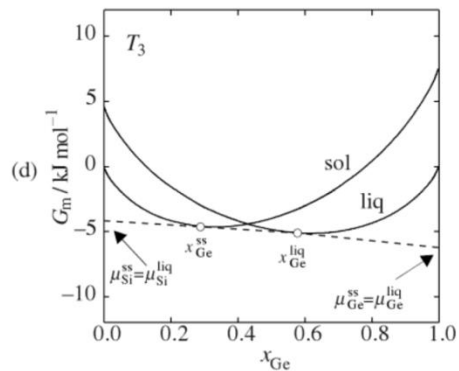
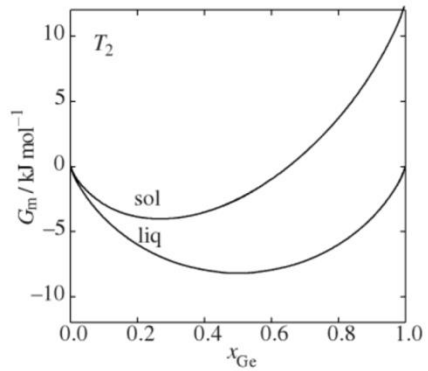
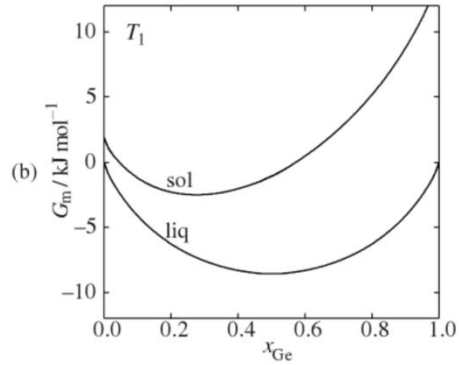
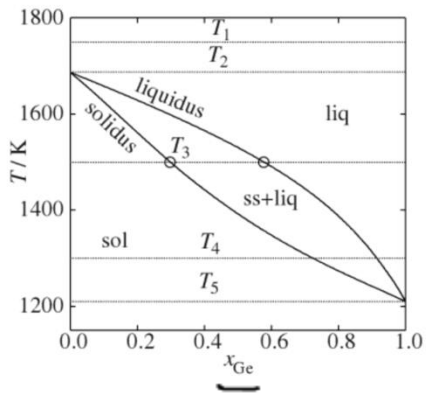


BINARY PHASE DIAGRAMS OF IDEAL SOLUTIONS

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.



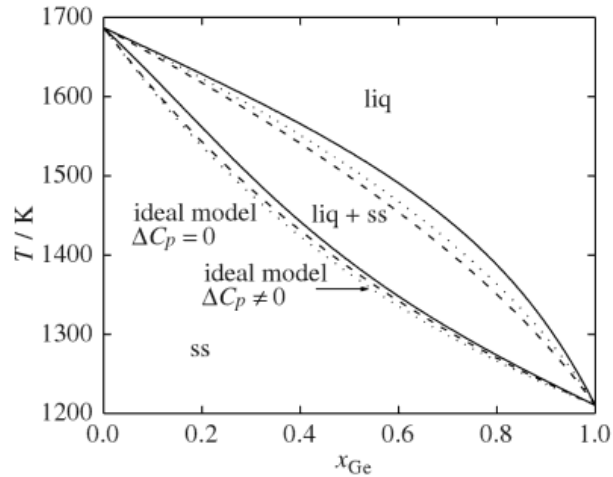
EXAMPLE: SI-GE BINARY PHASE DIAGRAM



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

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

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

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

MSE-204 Thermodynamics for Materials Science

L8.2 MULTICOMPONENT PHASE DIAGRAMS

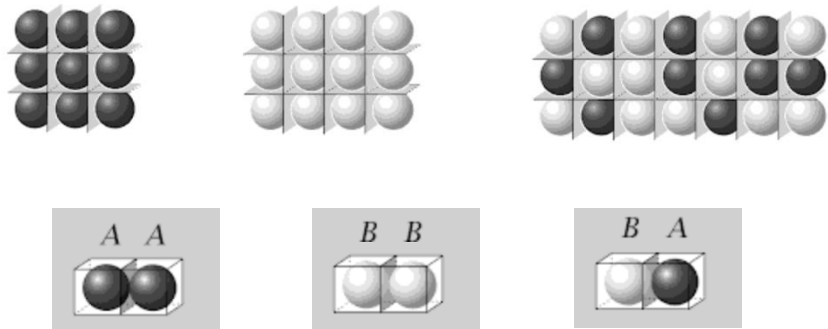
REGULAR SOLUTION MODEL | SPATIAL ARRANGEMENT OF ATOMS | MISCIBILITY GAP | INVARIANT POINTS |
INTERMEDIATE COMPOUNDS

Vaso Tileli | MXD 237

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.

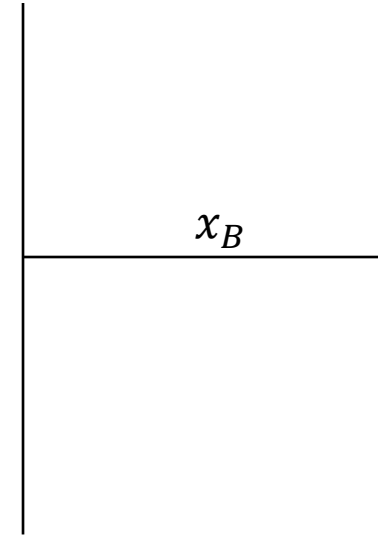
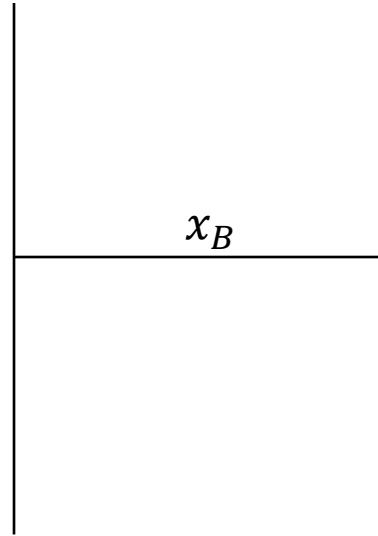
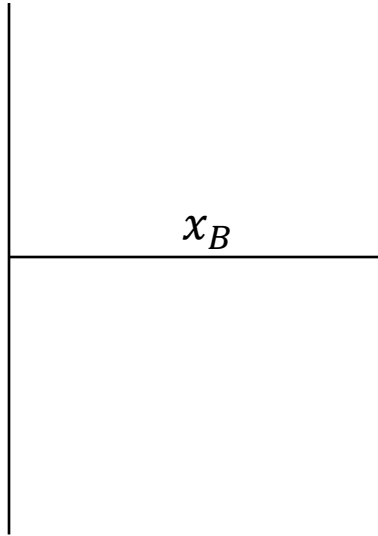


COMPOSITION DEPENDENCE OF VARIOUS THERMODYNAMIC FUNCTIONS OF A REGULAR SOLUTION

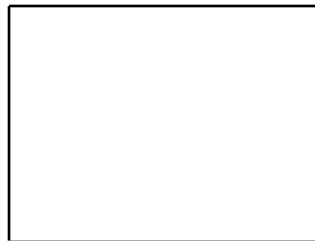
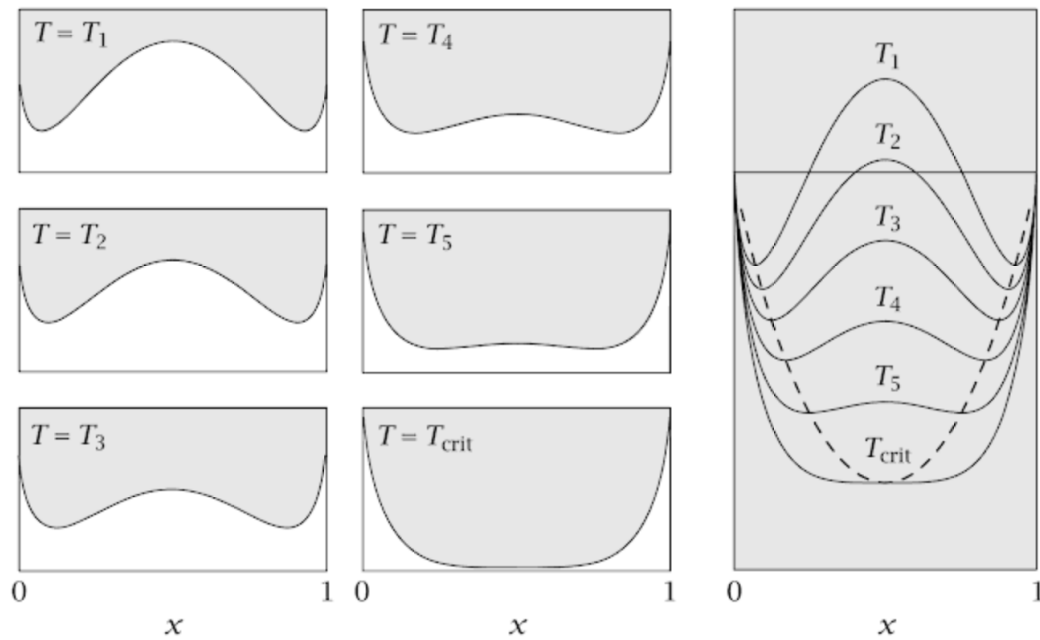
$$\Delta_{mix}\bar{U} = \Delta_{mix}\bar{H} = \Omega x_A x_B$$

$$\Delta_{mix}\bar{S} = -R(x_A \ln x_A + x_B \ln x_B)$$

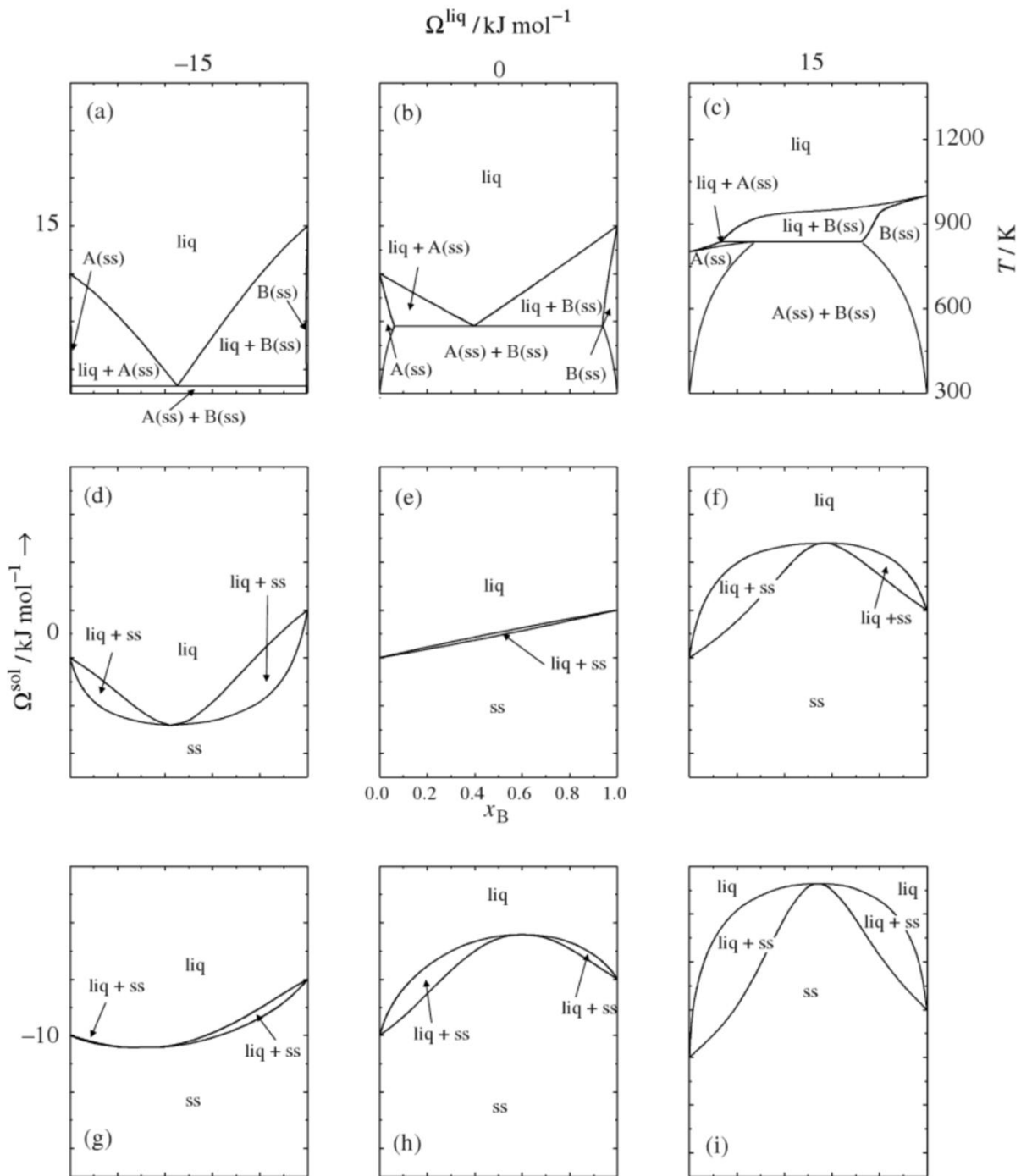
$$\Delta_{mix}\bar{G} = \Omega x_A x_B + RT(x_A \ln x_A + x_B \ln x_B)$$



PHASE DIAGRAM OF A REGULAR SOLUTION: MISCIBILITY GAP FOR $\Omega > 0$ AS A FUNCTION OF TEMPERATURE

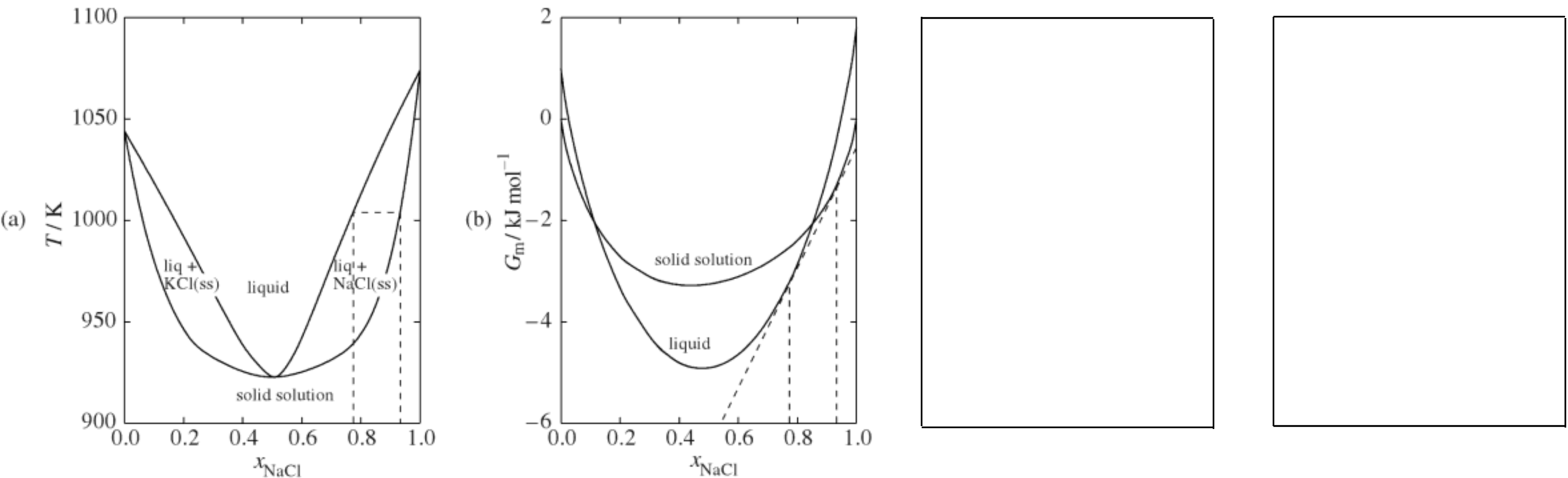


PHASE DIAGRAM OF A BINARY SYSTEM CONSISTING OF SOLID AND LIQUID SOLUTION PHASES FOR SELECTED COMBINATIONS OF Ω



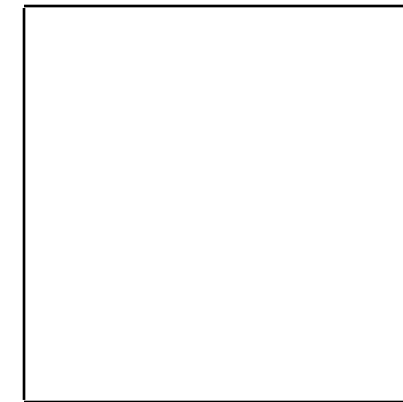
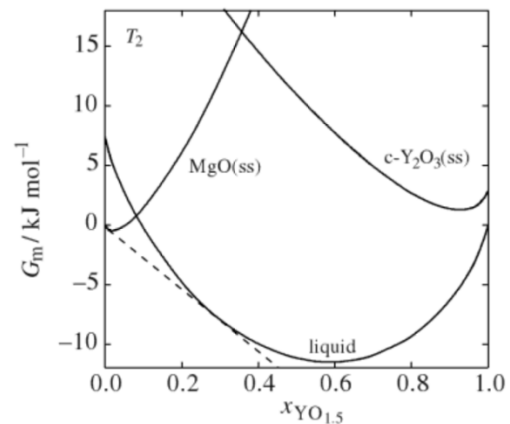
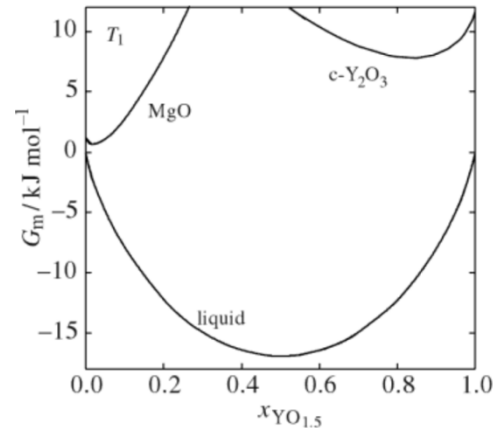
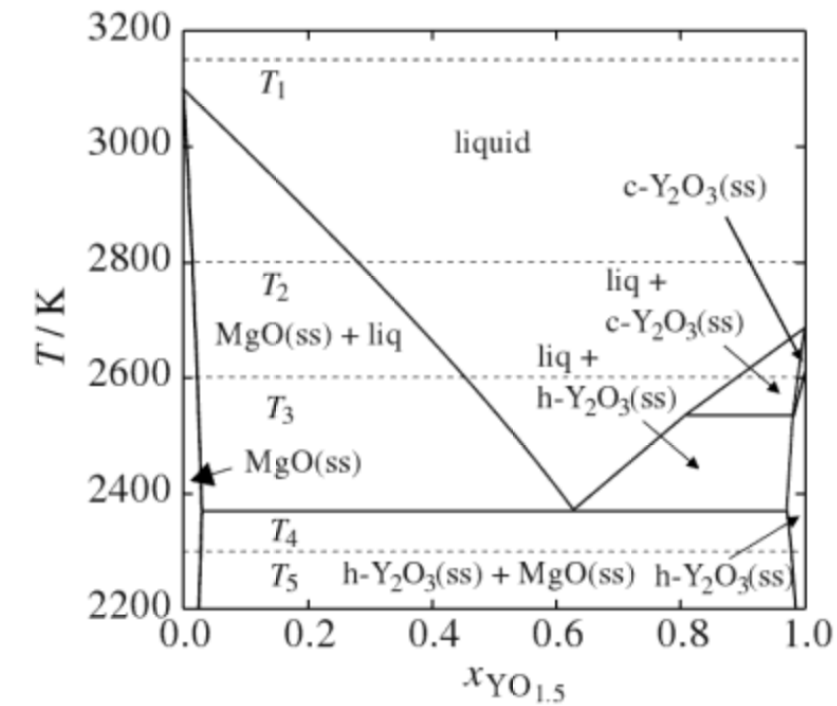
CONGRUENT PHASE DIAGRAMS

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, a congruent phase transition corresponds to a complete transformation from one phase to another with no change in composition.



EUTECTIC PHASE DIAGRAMS

Most of materials are highly miscible in the liquid state, but have very limited mutual miscibility in the solid state. Thus much of the phase diagram at low temperatures is dominated by a 2-phase field of two different solid structures- one that is highly enriched in component A (the α phase) and one that is highly enriched in component B (the β phase). These binary systems, with unlimited liquid state miscibility and low or negligible solid state miscibility, are referred to as eutectic systems.



OTHER TYPES OF INVARIANT POINTS

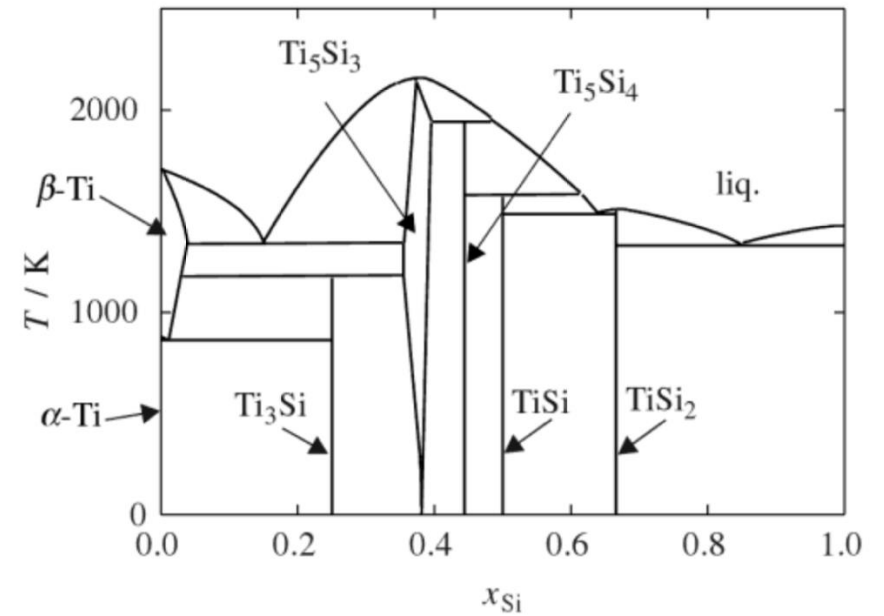
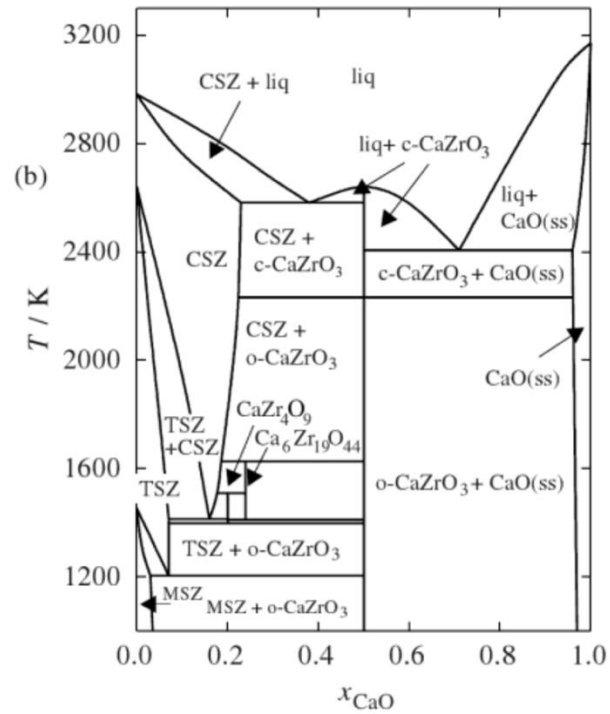
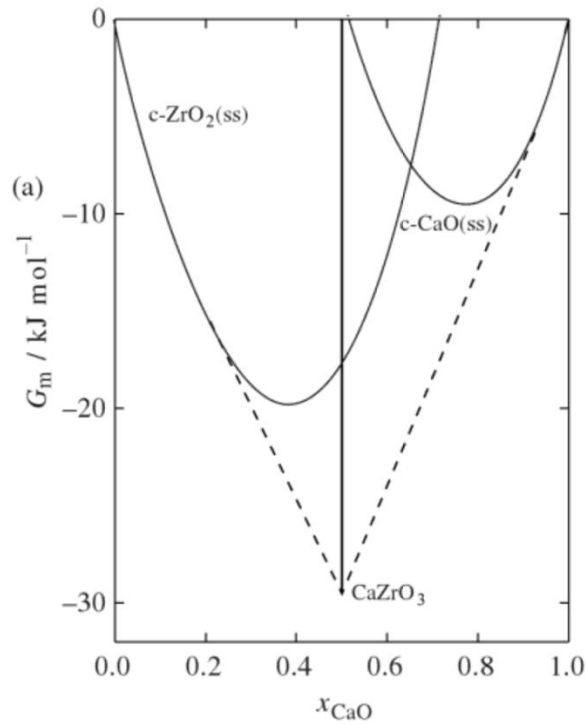
Other transformations that occur in binary systems at a fixed composition and temperature (for constant pressure) are given titles as well:

- Eutectic: $L \rightleftharpoons (\alpha + \beta)$ (upper region is liquid)
- Peritectic: $(\alpha + L) \rightleftharpoons \beta$ (upper two-phase region is solid + liquid)
- Eutectoid: $\alpha \rightleftharpoons (\beta + \gamma)$ (upper region is solid)
- Peritectoid: $(\alpha + \beta) \rightleftharpoons \gamma$ (upper two-phase region is solid + solid)

Name of reaction	Equation	Phase diagram characteristic
Eutectic	$L \begin{array}{c} \xrightarrow{\text{Cooling}} \\ \xleftarrow{\text{Heating}} \end{array} \alpha + \beta$	
Peritectic	$\alpha + L \begin{array}{c} \xrightarrow{\text{Cooling}} \\ \xleftarrow{\text{Heating}} \end{array} \beta$	
Eutectoid	$\alpha \begin{array}{c} \xrightarrow{\text{Cooling}} \\ \xleftarrow{\text{Heating}} \end{array} \beta + \gamma$	
Peritectoid	$\alpha + \beta \begin{array}{c} \xrightarrow{\text{Cooling}} \\ \xleftarrow{\text{Heating}} \end{array} \gamma$	

INTERMEDIATE COMPOUNDS IN PHASE DIAGRAMS

Stable compounds can form between the two extremes of pure component A and pure component B in binary systems. These are referred to as intermediate compounds.



When the intermediate compound melts to a liquid of the same composition as the solid, it is termed a congruently melting compound. Congruently melting intermediates subdivide the binary system into smaller binary systems with all the characteristics of typical binary systems.