

MSE-204 Thermodynamics for Materials Science

L8.1 MULTICOMPONENT PHASE DIAGRAMS

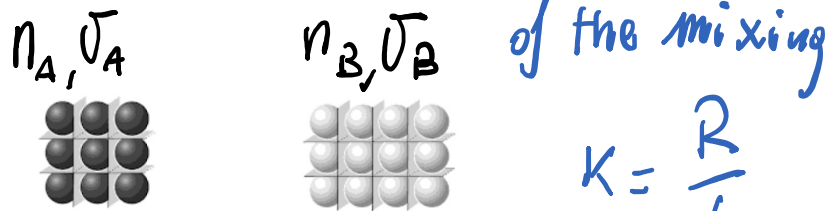
BINARY SOLUTIONS | THE MIXING PROCESS | IDEAL SOLUTIONS | LEVER RULE | BINARY PHASE DIAGRAMS

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PROPERTIES OF IDEAL SOLUTIONS of condensed phases $S = k \ln \Omega$ ^{$k = R/N_A$}

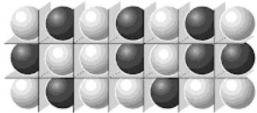
For an ideal solution, it is assumed that the original A and B and the mixed configurations have the same "crystal structure", and that the molecules (or atoms) are interchangeable between the lattice sites without causing any change on the molecular energy states or the total volume of the system.

a solution is called ideal if the energy of the solution is independent



$$k = \frac{R}{N_A}$$

$$V = V_A + V_B \quad n = n_A + n_B \quad x_A = \frac{n_A}{n} \quad x_B = \frac{n_B}{n} \quad x_A + x_B = 1$$



- Assumptions
- size of the atoms (A and B) is the same
 - crystal structure is the same
 - no change in energy upon mixing

$$\Delta_{mix} H = 0 \quad \Delta_{mix} U = 0 \quad \Delta_{mix} V = 0$$

$$\Delta_{mix} S = S_{mix} - S_{pure} =$$

$$\Omega = \frac{n!}{n_A! n_B!}$$

$$= k \ln \frac{n!}{n_A! n_B!} - k \ln 1 - k \ln 1$$

$$= k \ln (n_A + n_B)! - k \ln n_A! - k \ln n_B!$$

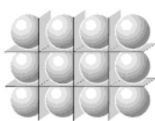
PROPERTIES OF IDEAL SOLUTIONS

For an ideal solution, it is assumed that the original A and B and the mixed configurations have the same "crystal structure", and that the molecules (or atoms) are interchangeable between the lattice sites without causing any change on the molecular energy states or the total volume of the system.

Stirling approximation
for large x

$$\ln x! = x \ln x - x$$

$$K \ln (n_A + n_B)! - K \ln n_A! - K \ln n_B!$$

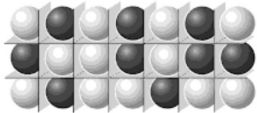


$$(n_A + n_B) \ln (n_A + n_B) - (n_A + n_B)$$

$$- n_A \ln n_A + n_A$$

$$- n_B \ln n_B + n_B$$

of moles



$$= -K (n_A \ln x_A + n_B \ln x_B)$$

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

$$\Delta_{mix} G = -RT (n_A \ln x_A + n_B \ln x_B)$$

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

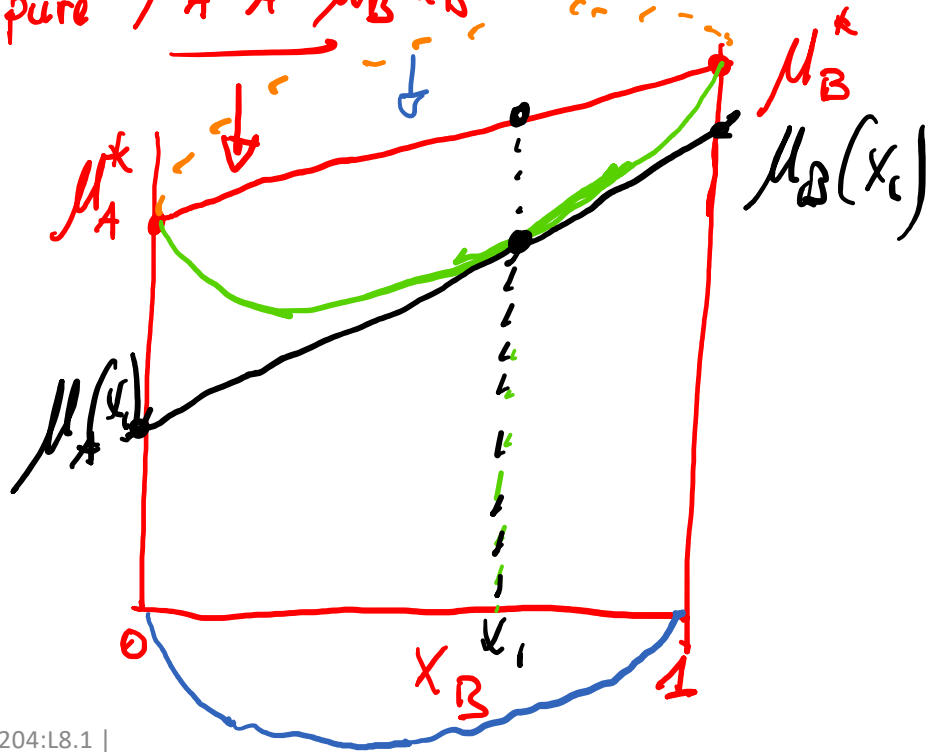
GRAPHICAL REPRESENTATION OF IDEAL SOLUTIONS

$$\Delta \bar{G}_{mix} = \bar{G}_{mix} - \bar{G}_{pure} \quad \rightarrow \quad \bar{G}_{mix} = \bar{G}_{pure} + \Delta \bar{G}_{mix}$$

H₂O + hexane
- - -

$$\bar{G}_{mix}(x_B) = \mu_A^*(1 - x_B) + \mu_B^*x_B + RT[(1 - x_B) \ln(1 - x_B) + x_B \ln x_B]$$

$$\bar{G}_{pure} = \mu_A^*x_A + \mu_B^*x_B$$



$$f(x_B) = \underbrace{\mu_A^*}_{\text{constant}}(1 - x_B) + \underbrace{\mu_B^*}_{\text{constant}}x_B$$

$$f(x_B) = \mu_A^* + x_B(\mu_B^* - \mu_A^*) = m + mx$$

DEPRESSION OF THE FREEZING POINT BETWEEN A SOLVENT AND A SOLUTE

It is known that the freezing point of a solution is lower than that of the pure solvent. Consider a solution in water of a crystalline, solid substance and suppose these two components do not form solid solution with each other. Let the substance (also called solute) be present as a pure solid and as a component of an ideal solution.

$$\mu_{\text{water}}^{\text{solid}} = \mu_{\text{H}_2\text{O}}^{\text{L}} = \mu_{\text{H}_2\text{O}}^{\text{O,L}} + RT \ln x$$

$$\ln x = \frac{\mu_{\text{H}_2\text{O}}^{\text{S}}}{RT} - \frac{\mu_{\text{H}_2\text{O}}^{\text{O,L}}}{RT}$$

$$\left(\frac{\partial \ln x}{\partial T} \right)_P = \frac{1}{R} \left(\frac{\partial \left(\frac{\mu_{\text{H}_2\text{O}}^{\text{S}}}{T} \right)}{\partial T} - \frac{\partial \left(\frac{\mu_{\text{H}_2\text{O}}^{\text{O,L}}}{T} \right)}{\partial T} \right)_P$$

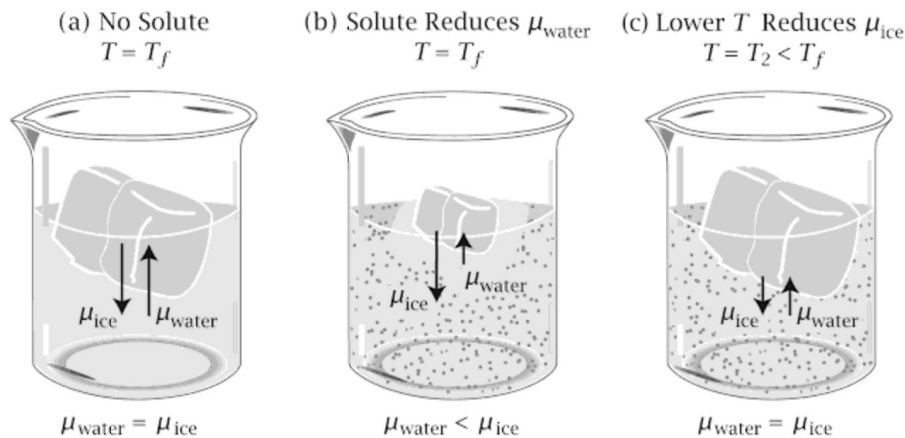
$$\left(\frac{\partial \ln x}{\partial T} \right)_P = \frac{1}{RT^2} \Delta h^{\text{S-L}}$$

Gibbs Helmholtz Eq

$$\frac{d \left(\frac{\mu}{T} \right)}{dT} = - \frac{h}{T^2}$$

DEPRESSION OF THE FREEZING POINT

The melting temperature of pure water is the point at which the escaping tendency of the water molecules from the liquid to the solid is the same as the escaping tendency from the solid to the liquid. Salt preferentially dissolves in the liquid, so, to a first approximation, salt is not an exchangeable component in this equilibrium. Salt reduces the escaping tendency of the water from the liquid to the solid, on balance, drawing water from the pure phase (ice) to the mixture (liquid+salt), and thus melting the ice.



$$d \ln x = \frac{\Delta h^+}{RT^2} dT$$

$$\int_{x=1} d \ln x = \int_{T_f} \frac{\Delta h}{RT^2} dT$$

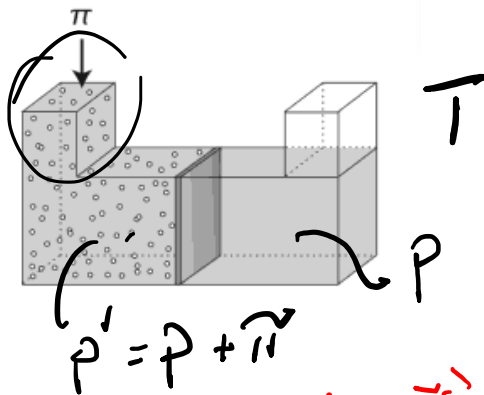
$$\ln \frac{x_f}{x_r} = \frac{\Delta h^+}{R} \left(\frac{1}{T_f} - \frac{1}{T} \right)$$

$$x_r = 1 \quad \ln x_f = \frac{\Delta h^+}{R} \left(\frac{1}{T_f} - \frac{1}{T} \right) \Rightarrow \ln \frac{1}{x_f} = \frac{\Delta h^+}{R} \left(\frac{1}{T} - \frac{1}{T_f} \right)$$

THE OSMOTIC PRESSURE OF AN IDEAL SOLUTION

In a solution, such as that of sugar and water, the solvent (water in this case) is the component whose mole fraction can be varied up to unity. Suppose that such a solution is separated from a quantity of the pure solvent (water in this case), at the same temperature by means of a membrane permeable only to the solvent molecules. Then, what is called the **osmotic pressure of the solution is the excess pressure which must be placed on it in order to prevent any diffusion of the solvent through the membrane.**

The only proper equilibrium is the equilibrium of chemical potential in the two regions.



$$\mu_w^m = \mu_w^{pure}$$

$$\pi = - \frac{RT \ln x}{V_{w,0}^*}$$

$$\mu_{H_2O}^{*,p}(p,T) = \mu^*(p',T) + RT \ln x$$

$$\mu^*(p) - \mu^*(p + \pi) = RT \ln x$$

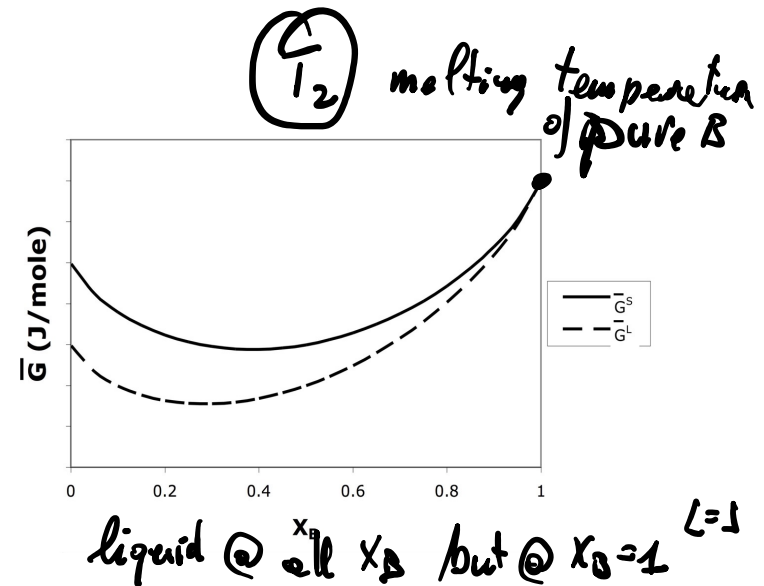
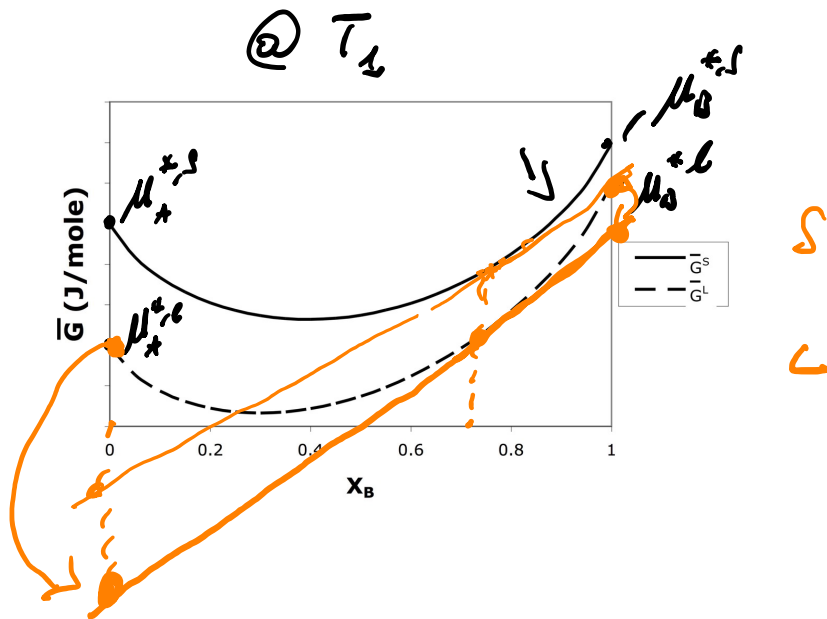
$$\int_p^{p+\pi} \left(\frac{\partial \mu^*}{\partial p} \right) dp = \int_p^{p+\pi} V_{H_2O}^* dp = V_{H_2O}^* (p + \pi - p) = V_{H_2O}^* \pi = RT \ln x$$

FREE ENERGY DIAGRAMS OF MULTI-PHASE BINARY IDEAL SOLUTIONS

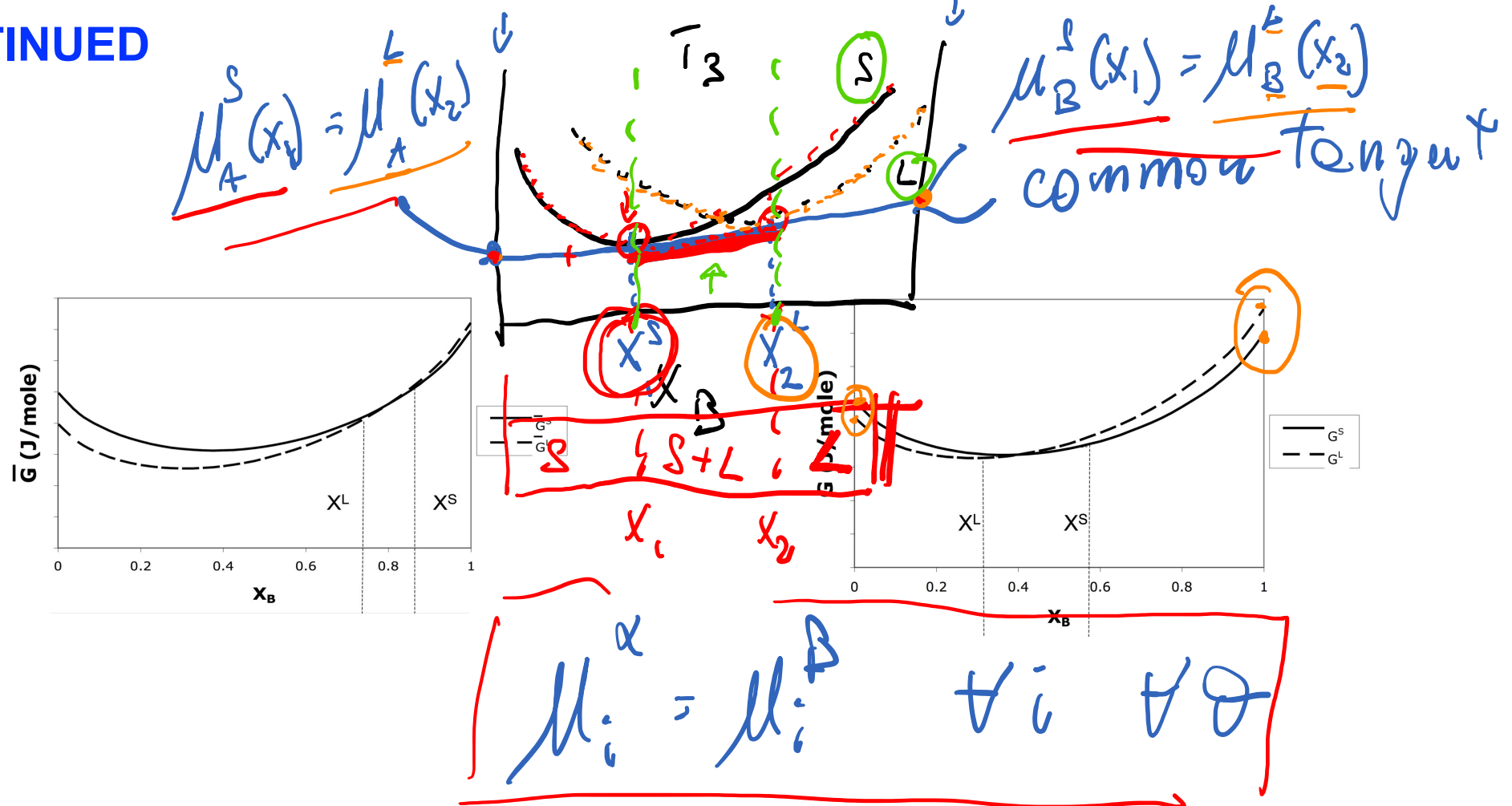
Let's see what effect will have the variation of the temperature at the molar Gibbs free energy when the pressure is kept constant in a two-component, two phase system.

$$\mu_i^*(T, P)$$

$$\bar{G}_{mix} = \mu_A^* x_A + \mu_B^* x_B + RT[(1 - x_B) \ln(1 - x_B) + x_B \ln x_B]$$

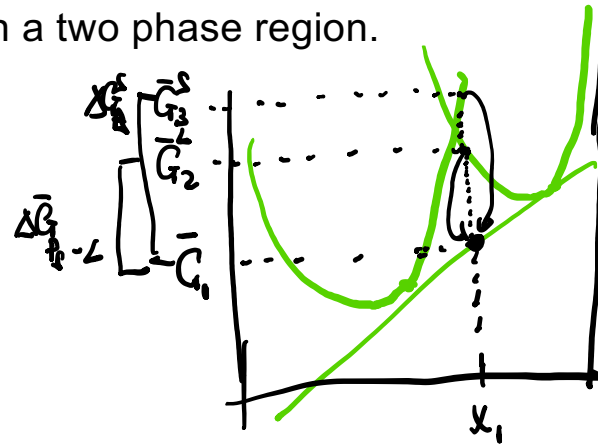
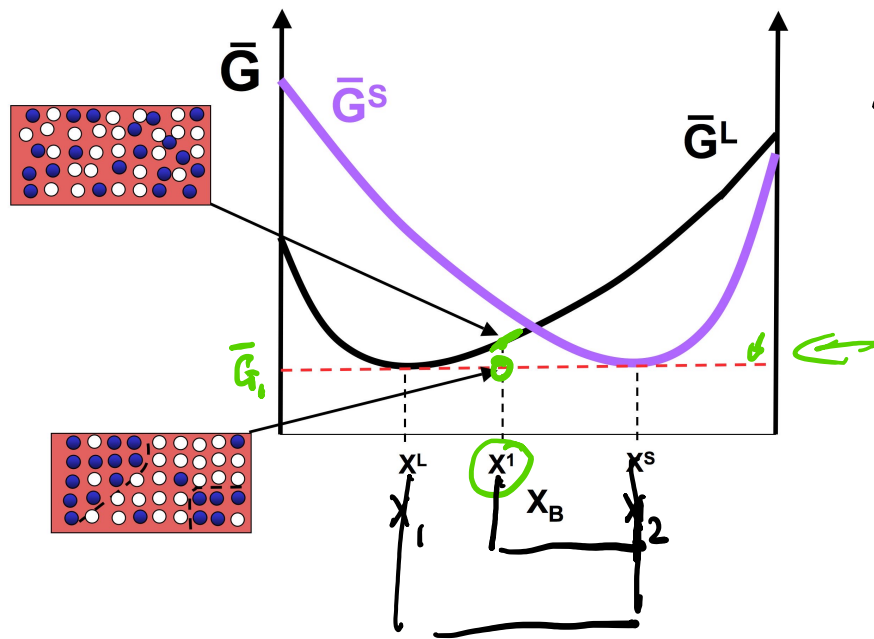


FREE ENERGY DIAGRAMS OF MULTI-PHASE BINARY IDEAL SOLUTIONS | CONTINUED



COMMON TANGENT AND THE LEVER RULE

The lever rule determines the amount x of a phase in a two phase region.



$$n X_B = n^L X_B^L + n^S X_B^S$$

$$X_B = \frac{n^L}{n} X_B^L + \frac{n^S}{n} X_B^S$$

$$\frac{n^L}{n} = f^L \quad \frac{n^S}{n} = f^S \quad f^L + f^S = 1$$

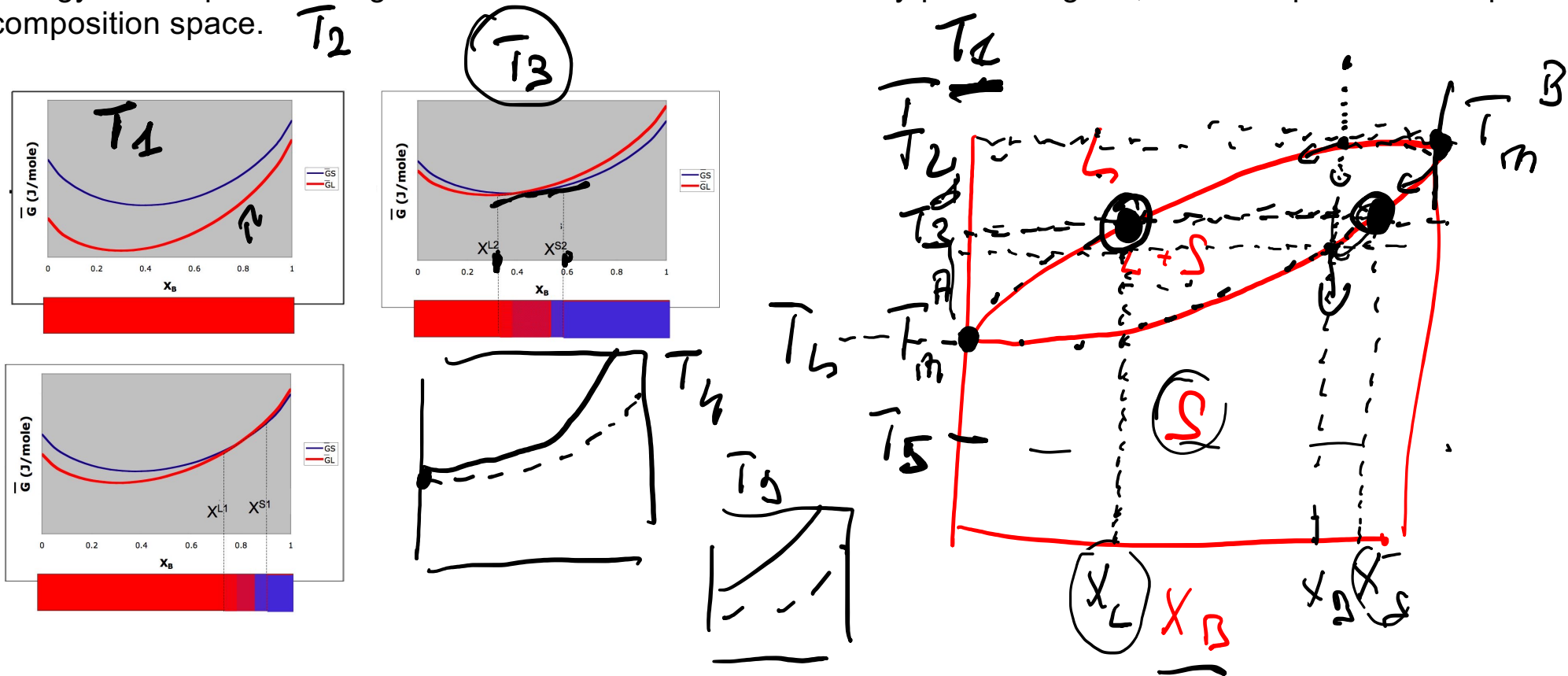
$$X_B = f^L X_B^L + (1 - f^L) X_B^S$$

$$f^L = \frac{X_B^S - X_B}{X_B^S - X_B^L} \quad f^S = \frac{X_B - X_B^L}{X_B^S - X_B^L}$$

BINARY PHASE DIAGRAMS

IDEAL SOLUTION MODEL

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

