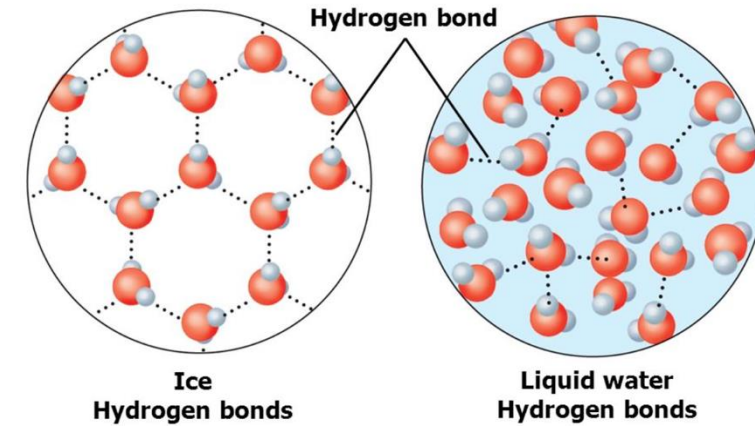
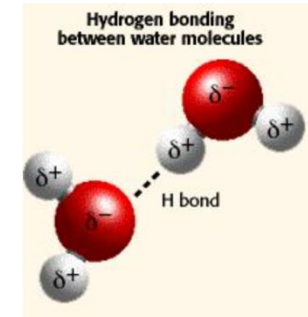
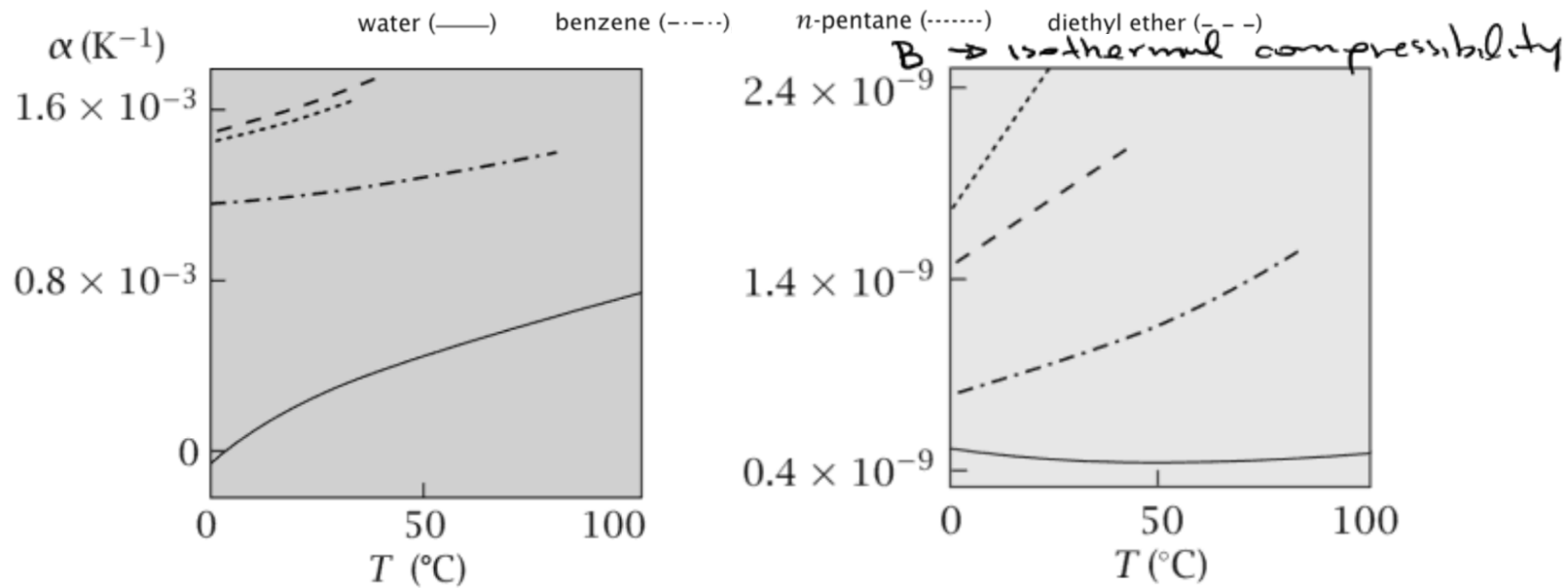


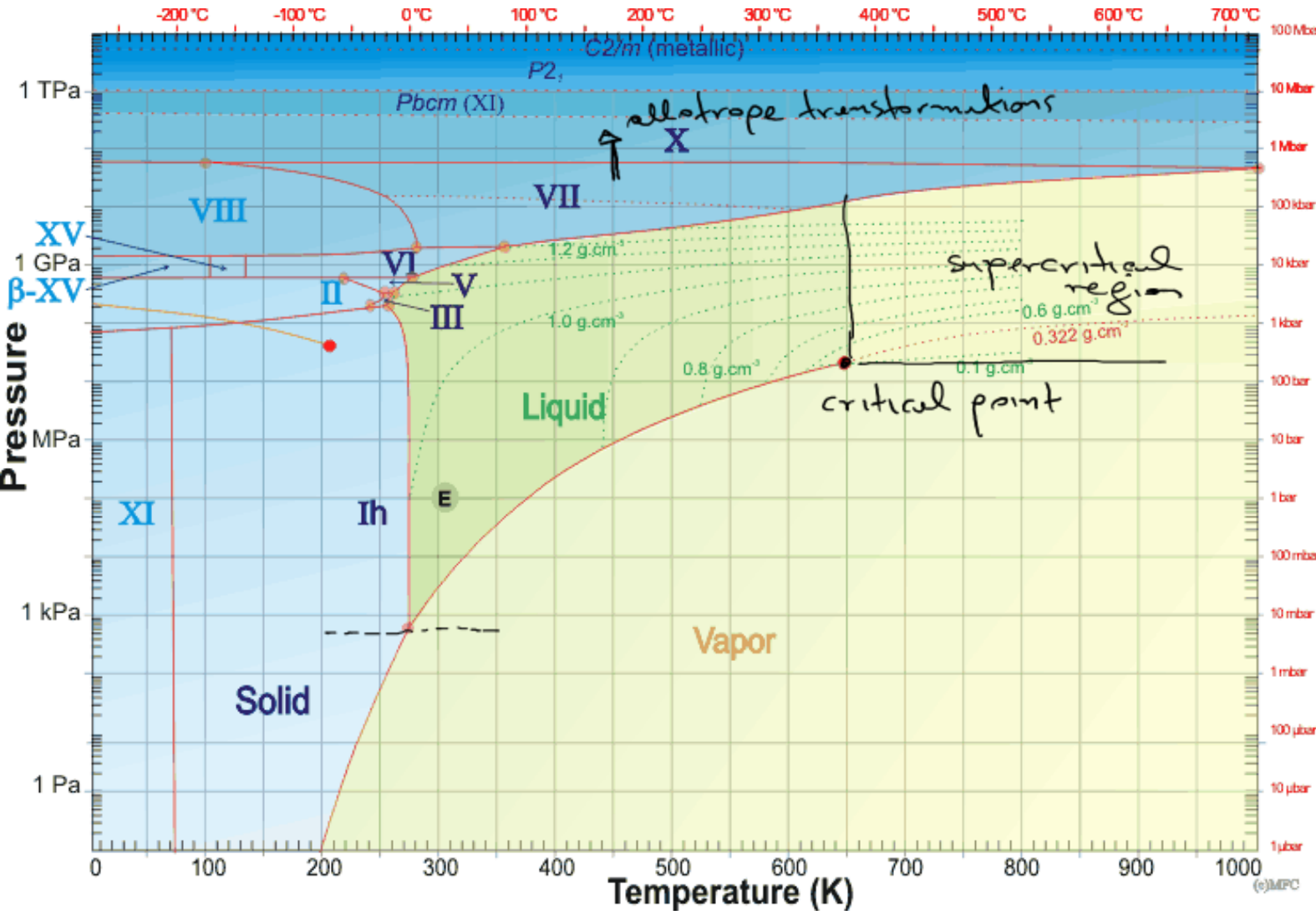
WATER DIFFERS FROM SIMPLE LIQUIDS: ENTROPY, VOLUME, & STRUCTURE

The thermal expansion coefficient and the isothermal compressibility are small for water, which is hydrogen bonded, than for simpler liquids like benzene which are not.



$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P : \text{thermal expansion coefficient}$$

EXAMPLE OF SINGLE COMPONENT PHASE DIAGRAM: H₂O

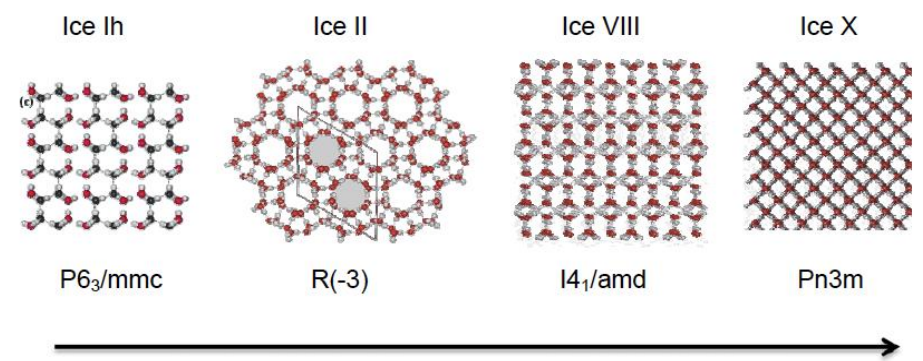


① negative slope between liquid & solid

$$\left[\frac{dp}{dT} = \frac{L}{T \cdot \Delta v} \right]_{\text{fusion}} \Rightarrow v_l < v_s$$

The volume of liquid water is SMALLER than that of solid water

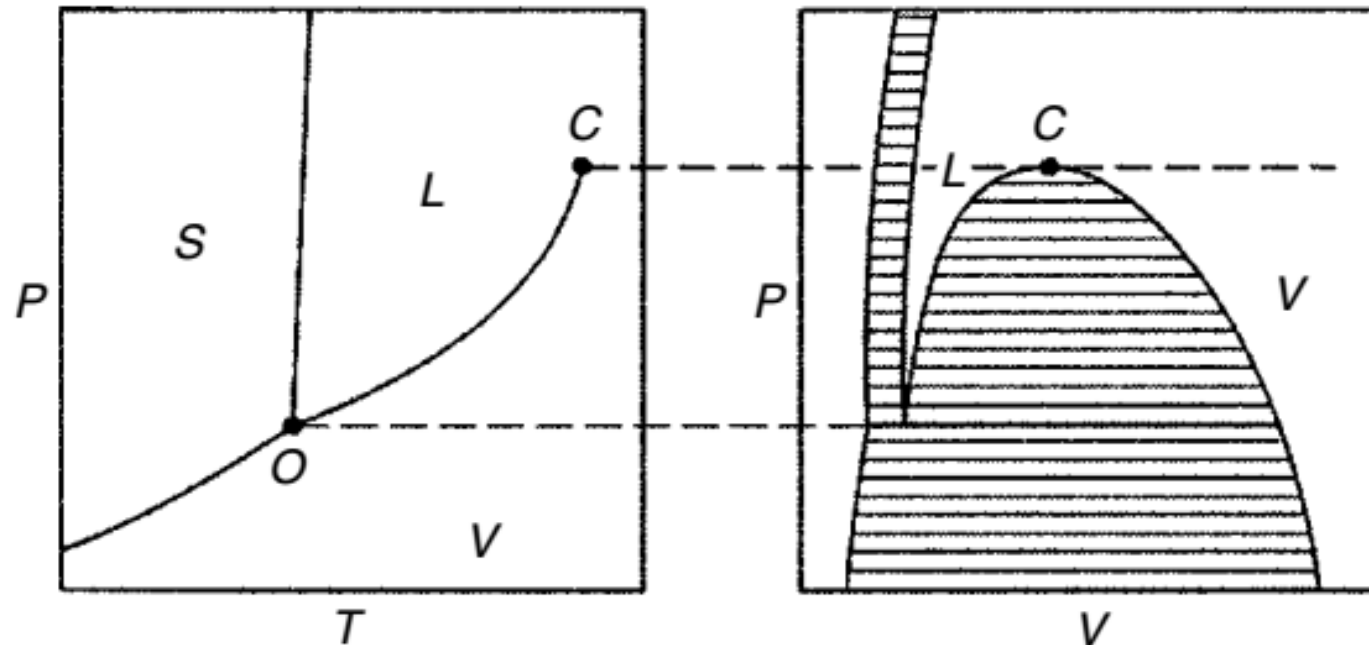
As one of your colleagues said, water expands when frozen



ALTERNATIVE REPRESENTATIONS OF SINGLE COMPONENT PHASE DIAGRAMS

The two phase coexistence in a p, T diagram is a line (i.e., a region of zero width) because the pressure and temperature of the alpha phase in the two phase system is required to be the same as that of the beta phase. The corresponding states of the two equilibrated phases are represented by the same point in the p, T space. Thus the phase boundaries for the alpha phase, and that for the beta phase, coincide.

This will not be true of some property other than p or T is used in the description of the state of the two phases. Suppose the properties of the participating phases are described in terms of their pressure, P ; and molar volume, v . While the conditions for equilibrium require the pressure to be the same in both phases, the molar volumes will not, in general, be the same. The resulting plot of the phase relationships is very different in appearance from the simple p, T .



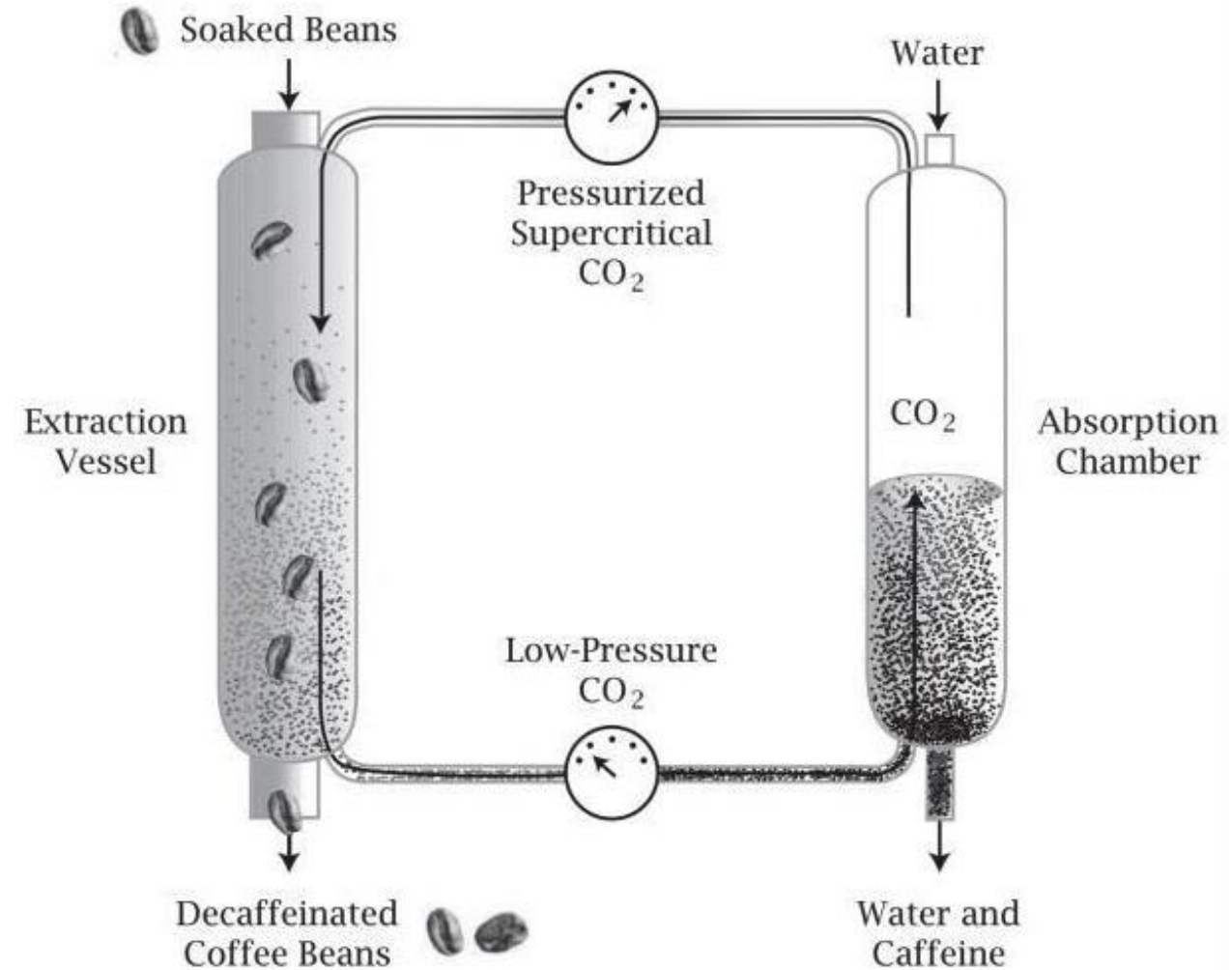
USE OF SUPERCRITICAL FLUIDS: DECAFFEINATION OF COFFEE BEANS

To remove caffeine from coffee, coffee is mixed with CO_2 at a temperature and pressure above the critical point of the CO_2 .

The supercritical CO_2 dissolves the caffeine (small black dots), decaffeinating the coffee beans.

The fluid mixture of CO_2 with caffeine then flows into a chamber where the pressure is lowered below the critical point so caffeine partitions into water.

The carrier CO_2 is recaptured and the caffeine is dumped into the aqueous phase.



MSE-204 Thermodynamics for Materials Science

L8.1 MULTICOMPONENT PHASE DIAGRAMS

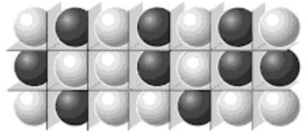
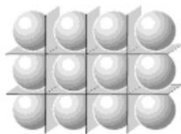
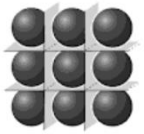
BINARY SOLUTIONS | THE MIXING PROCESS | IDEAL SOLUTIONS | LEVER RULE | BINARY PHASE DIAGRAMS

Vaso Tileli | MXD 237

PROPERTIES OF IDEAL SOLUTIONS (IS) OF CONDENSED PHASES

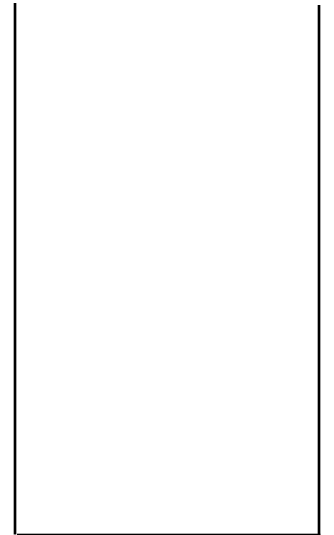
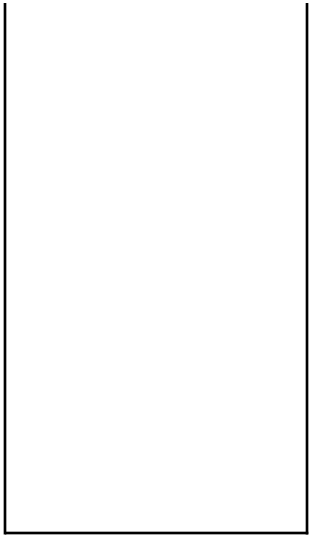
For an ideal solution, it is assumed that the original A and B and the mixed configurations have the same “crystal structure”, and that the molecules (or atoms) are interchangeable between the lattice sites without causing any change on the molecular energy states or the total volume of the system.

A solution is called ideal if the free energy of the solution is independent of the enthalpy of the mixed state!!



GRAPHICAL REPRESENTATION OF IDEAL SOLUTIONS

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



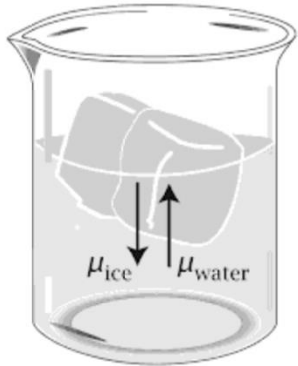
DEPRESSION OF THE FREEZING POINT

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.

when we are at the freezing point:

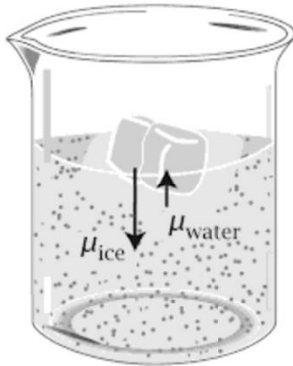
$$f_{\text{solid water in solution}} = f_{\text{liquid water in solution}} = f_{\text{pure solid water}}$$

(a) No Solute
 $T = T_f$



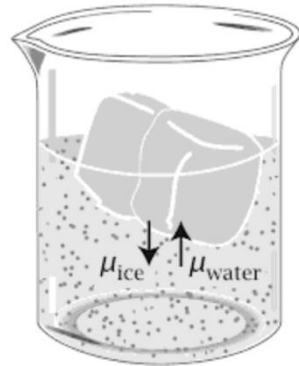
$$\mu_{\text{water}} = \mu_{\text{ice}}$$

(b) Solute Reduces μ_{water}
 $T = T_f$



$$\mu_{\text{water}} < \mu_{\text{ice}}$$

(c) Lower T Reduces μ_{ice}
 $T = T_2 < T_f$



$$\mu_{\text{water}} = \mu_{\text{ice}}$$

$$f_{\text{solid water}} = f_{\text{pure liquid water}} + RT \ln x_{\text{water in the solution}}$$

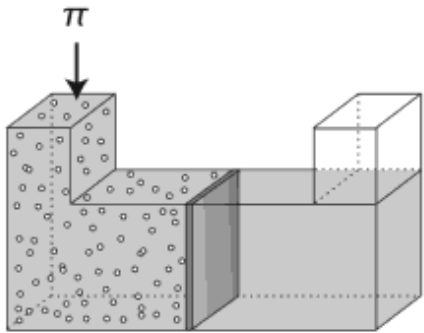
$$\ln x_{\text{water}} = \frac{f_{\text{solid water}}}{RT} - \frac{f_{\text{pure liquid water}}}{RT}$$

$$d \ln x_{\text{water}} = \frac{\Delta h_{\text{fusion}}}{RT^2} dT \Rightarrow \ln \left(\frac{1}{x_{\text{water}}} \right) = \frac{\Delta h_{\text{fusion}}}{R} \left(\frac{1}{T} - \frac{1}{T_f} \right)$$

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.

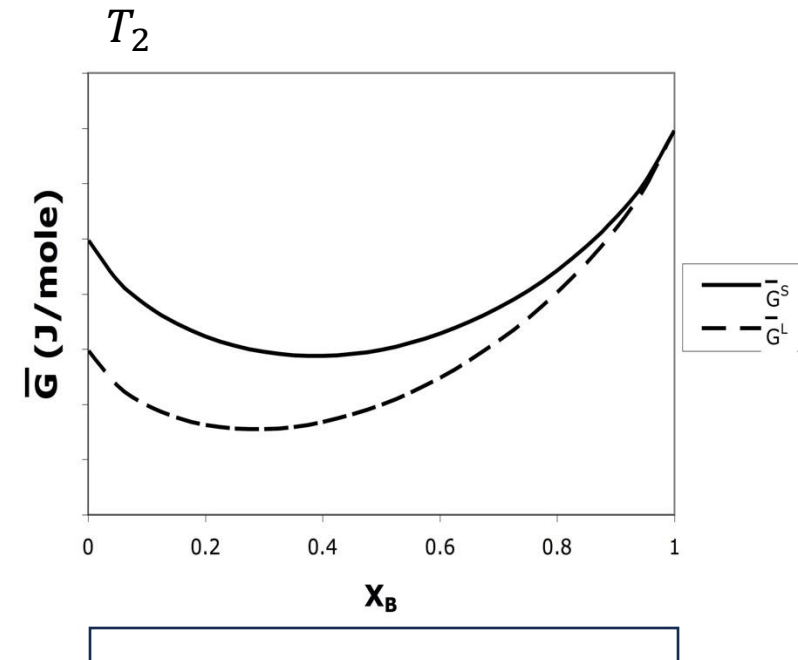
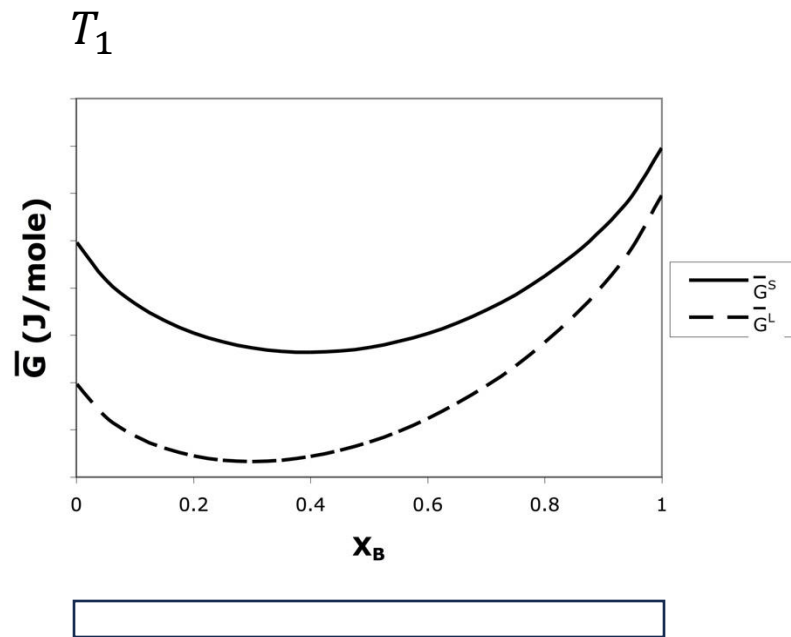


$$\begin{aligned}
 & \mu_{\text{pure water}} = \mu_{\text{water in solution}} \\
 \Rightarrow & \mu_{\text{pure water}}(p) = \mu_{\text{water in solution}}(p+\pi) + RT \ln x_{\text{water in solution}} \\
 \Rightarrow & RT \ln x_{\text{water in solution}} = \underbrace{\mu_{\text{pure water}}(p)}_{\text{initial}} - \underbrace{\mu_{\text{water in solution}}(p+\pi)}_{\text{final state}} \\
 & = -\Delta \mu_{\text{water in solution}}(p, p+\pi) \\
 & = -\int_p^{p+\pi} \left(\frac{\partial \mu}{\partial p} \right)_T dp \\
 \Rightarrow & RT \ln x_{\text{water in solution}} = -\int_p^{p+\pi} v_{\text{water}} dp = -v_{\text{water}}(p+\pi - p) \\
 \Rightarrow & \pi = -\frac{RT \ln x_{\text{water in solution}}}{v_{\text{water}}}
 \end{aligned}$$

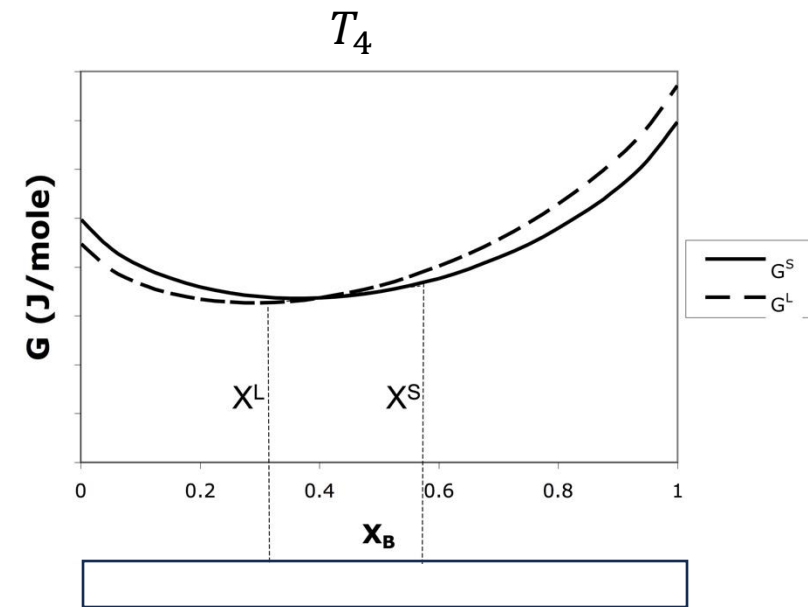
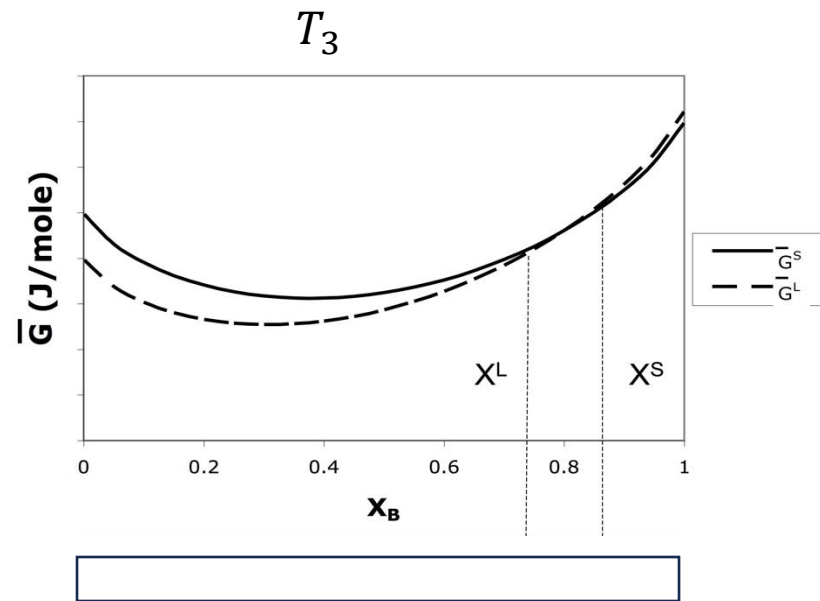
FREE ENERGY DIAGRAMS OF MULTI-PHASE BINARY IDEAL SOLUTIONS

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.

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

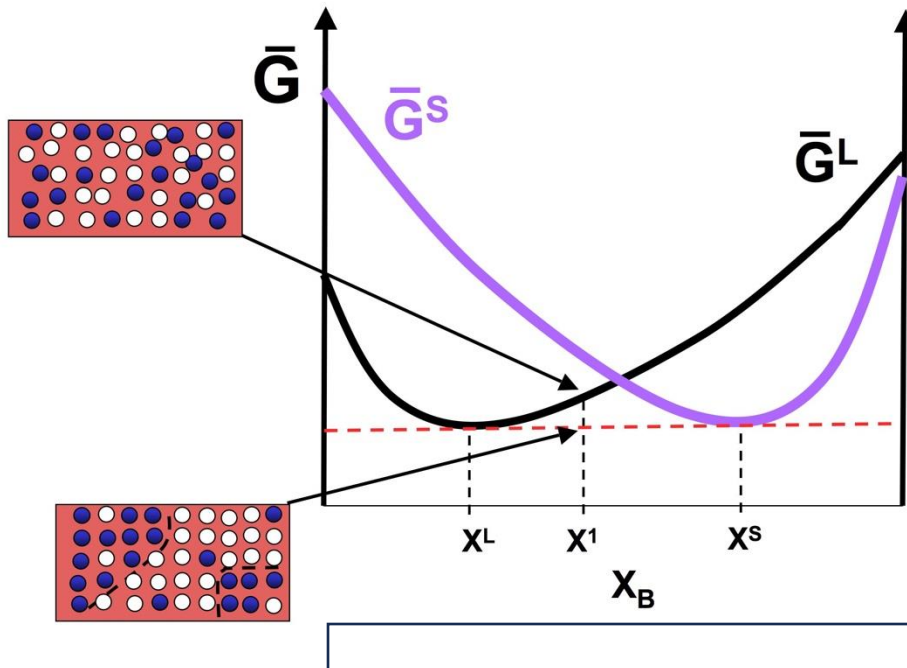


FREE ENERGY DIAGRAMS OF MULTI-PHASE BINARY IDEAL SOLUTIONS | CONTINUED



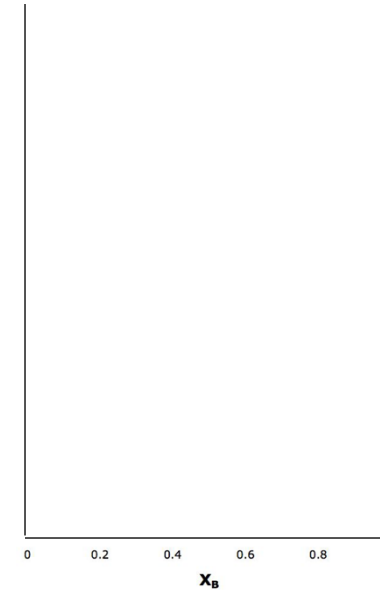
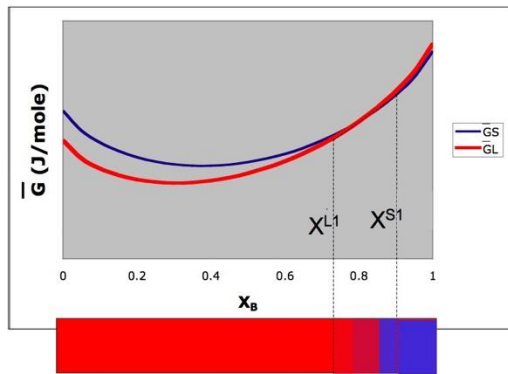
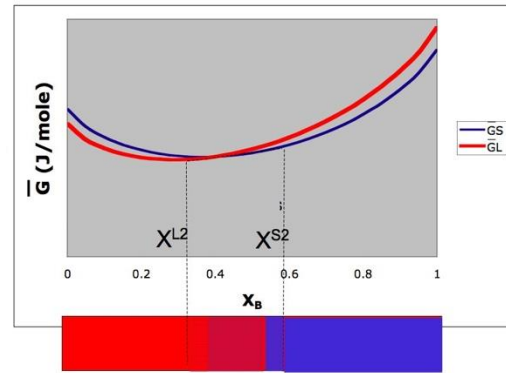
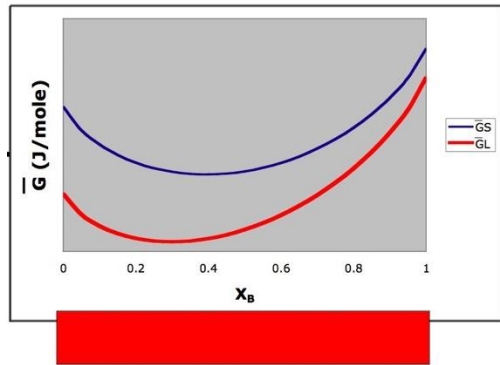
COMMON TANGENT AND THE LEVER RULE

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

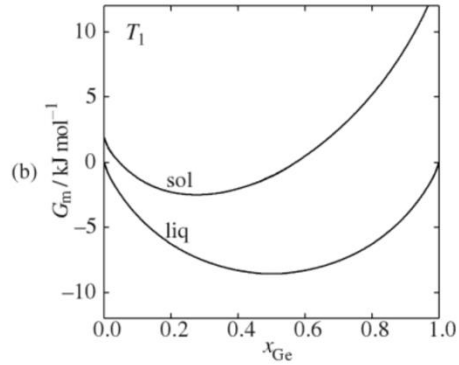
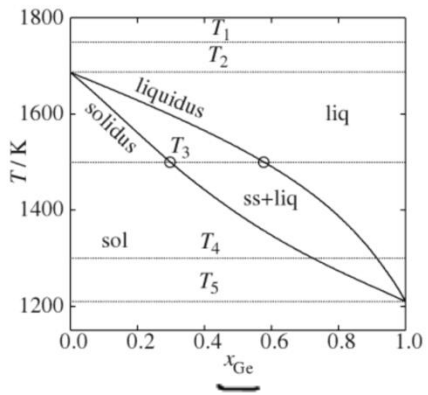


BINARY PHASE DIAGRAMS OF IDEAL SOLUTIONS

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.

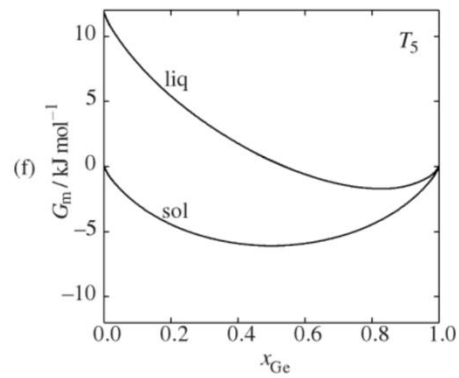
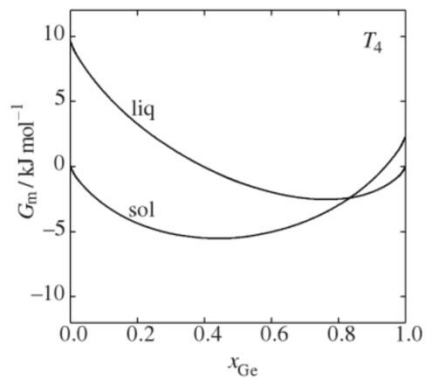
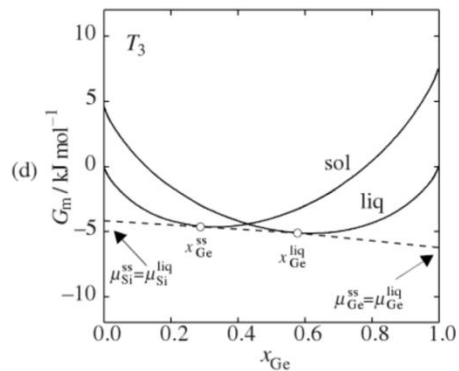
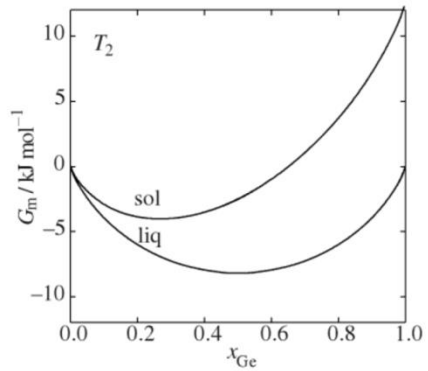


EXAMPLE: SI-GE BINARY PHASE DIAGRAM



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

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



WIDTH OF SOLIDUS AND LIQUIDUS LINES

