Info on final exam

Monday December 15th 10.15 - 13.15

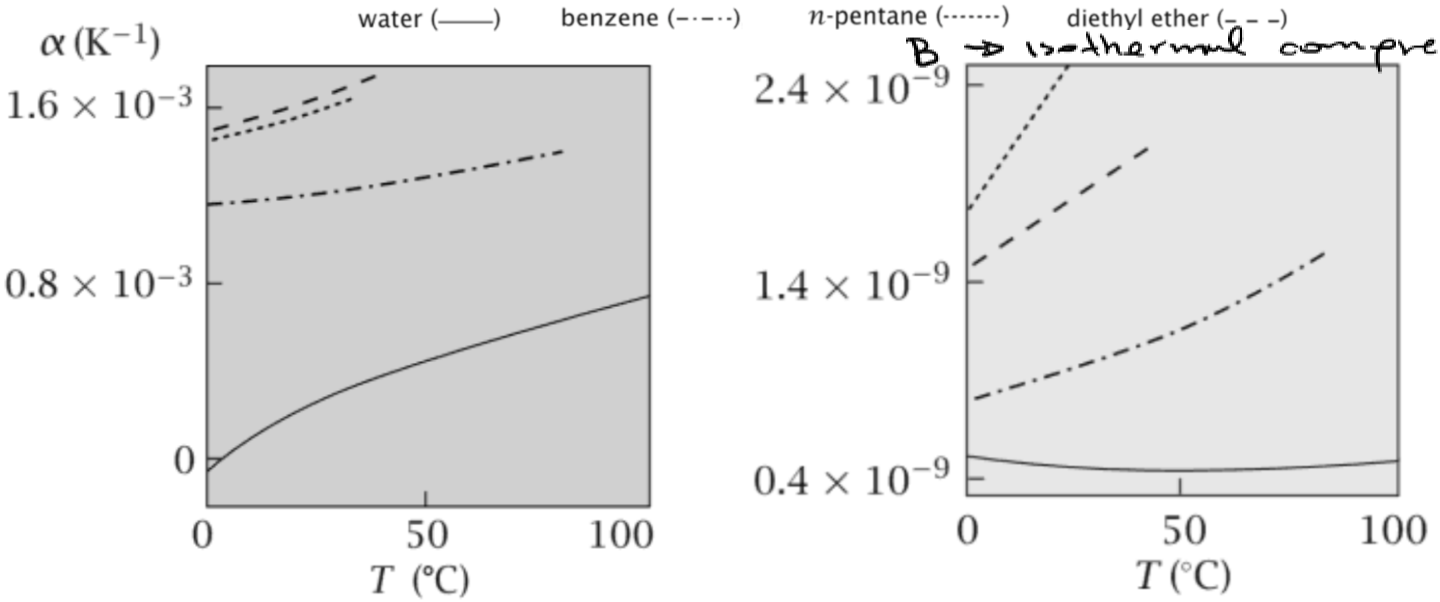
at room BC - 01

Open books, open notes || **NO** electronic devices

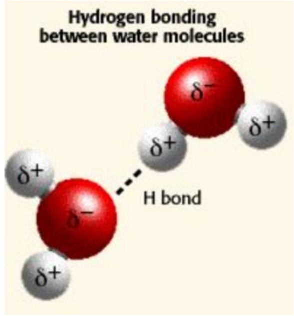
Ruler & calculator to bring

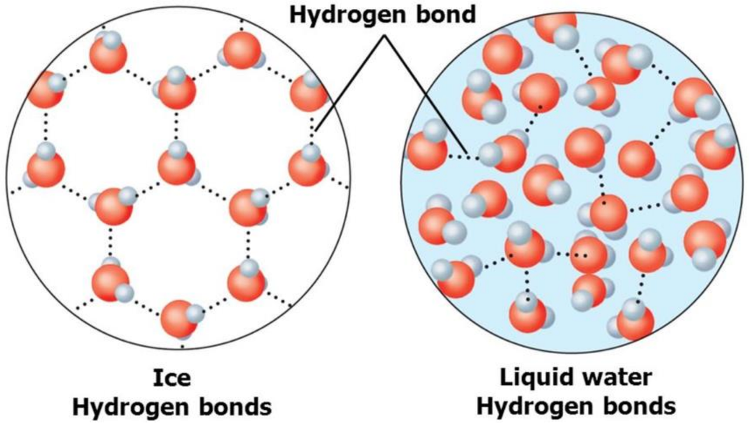
WATER DIFFERS FROM SIMPLE LIQUIDS: ENTROPY, VOLUME, & STRUCTURE

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.



B → isothermal compressibility

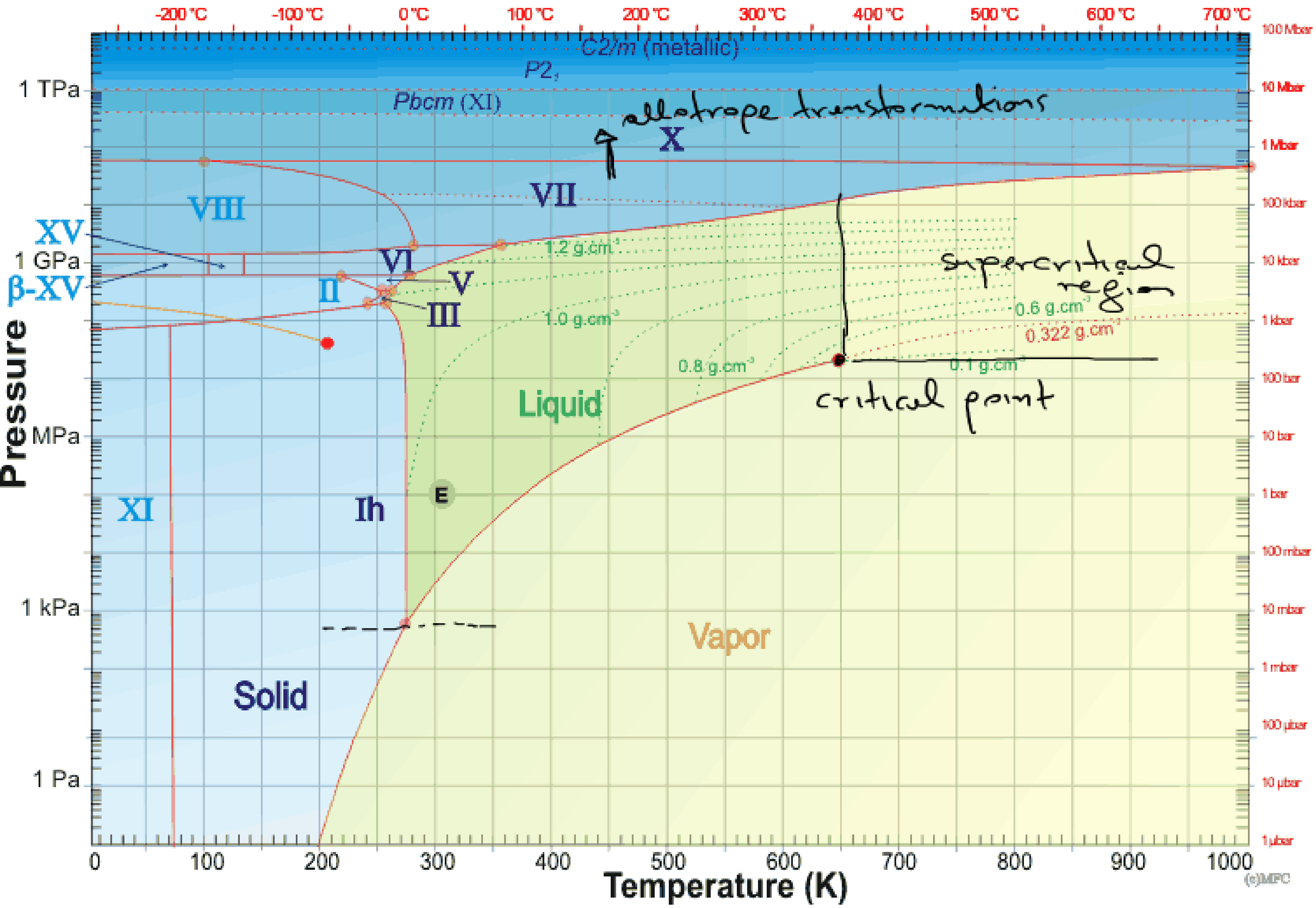




$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$$: thermal expansion coefficient

$C_{p\,water} = 4184\ J/kg\,K$

EXAMPLE OF SINGLE COMPONENT PHASE DIAGRAM: H_2O



allotrope transformations

supercritical region

critical point

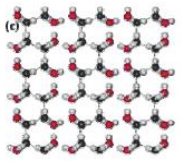
① negative slope between liquid & solid

$$\left[\frac{dp}{dT} = \frac{L}{T \cdot \Delta V}\right]_{fusion} \Rightarrow \boxed{V_\ell < V_s}$$

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

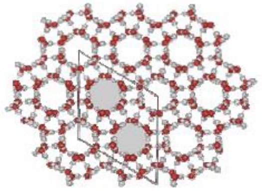
As one of your colleagues said, water expands when frozen

Ice Ih



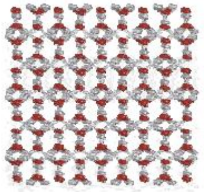
P6₃/mmc

Ice II



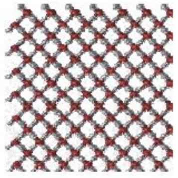
R(-3)

Ice VIII



I4₁/amd

Ice X

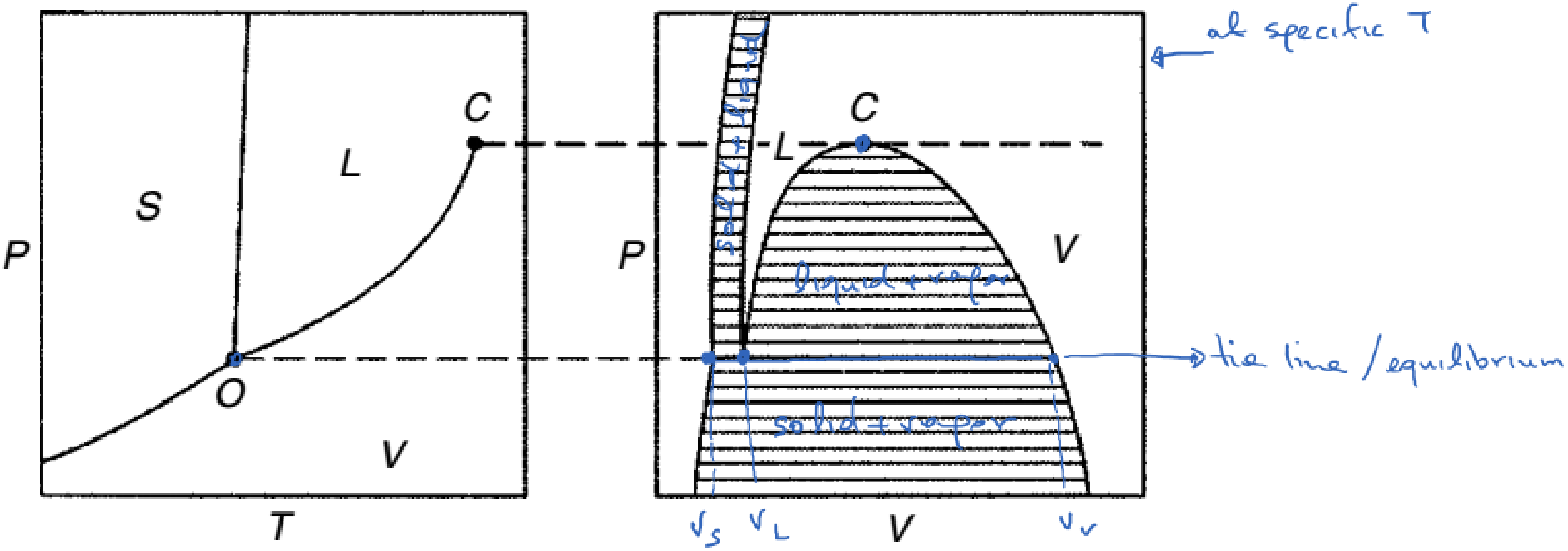


Pn3m

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.

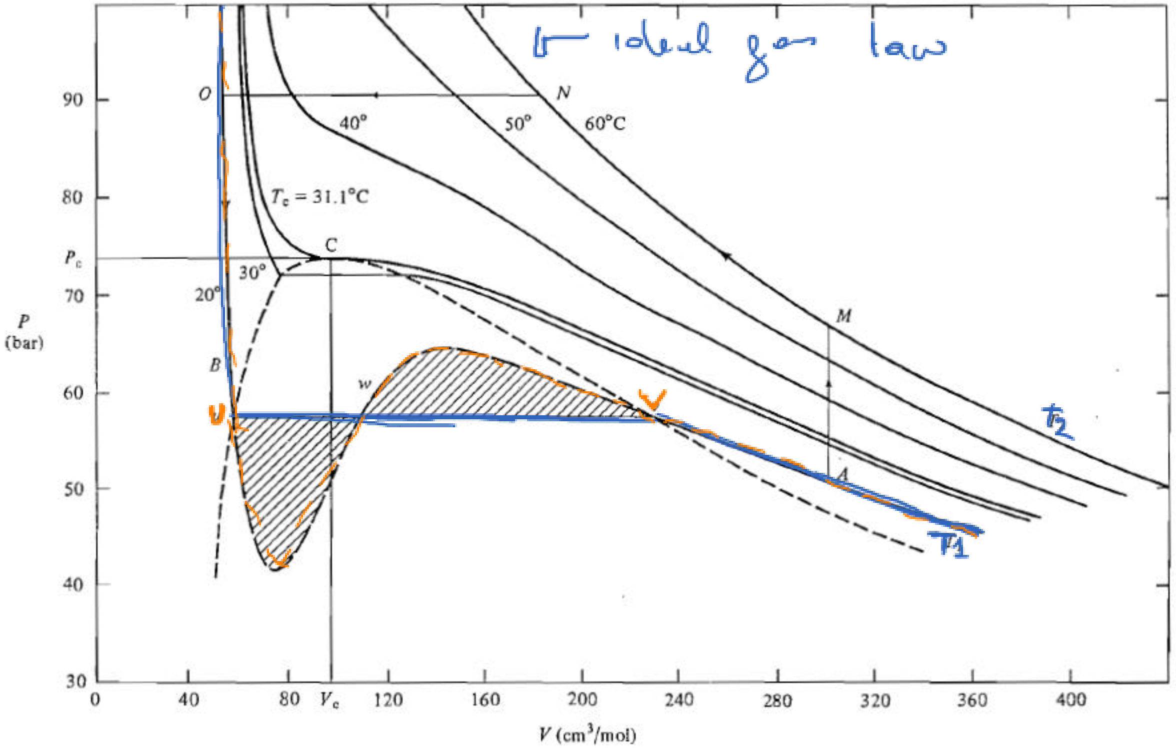
This will not be true of some property other than p or T is used in the description of the state of the two phases. Suppose the properties of the participating phases are described in terms of their pressure, P; and molar volume, v. While the conditions for equilibrium require the pressure to be the 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.



CRITICAL POINTS

Under certain conditions of temperature and pressure, the liquid and gas phases are indistinguishable.

Moreover, even under ordinary conditions where they are quite distinguishable, it is possible to pass from one to another by processes in which the substance remains perfectly homogeneous.



Pressure – Volume phase diagram for CO_2

The points u & v can be fixed:

$$\int_u^v v\,dp = 0$$

dashed line: saturation curve: dome curve that passes by u & v: the locus of this curve meets at the critical point, while its apex is the critical point:

defined mathematically by:

$$\left(\frac{\partial p}{\partial v}\right)_T = 0, \quad \left(\frac{\partial^2 p}{\partial v^2}\right)_T = 0, \quad \left(\frac{\partial^3 p}{\partial v^3}\right) > 0$$

$\Rightarrow$ conditions of metastability

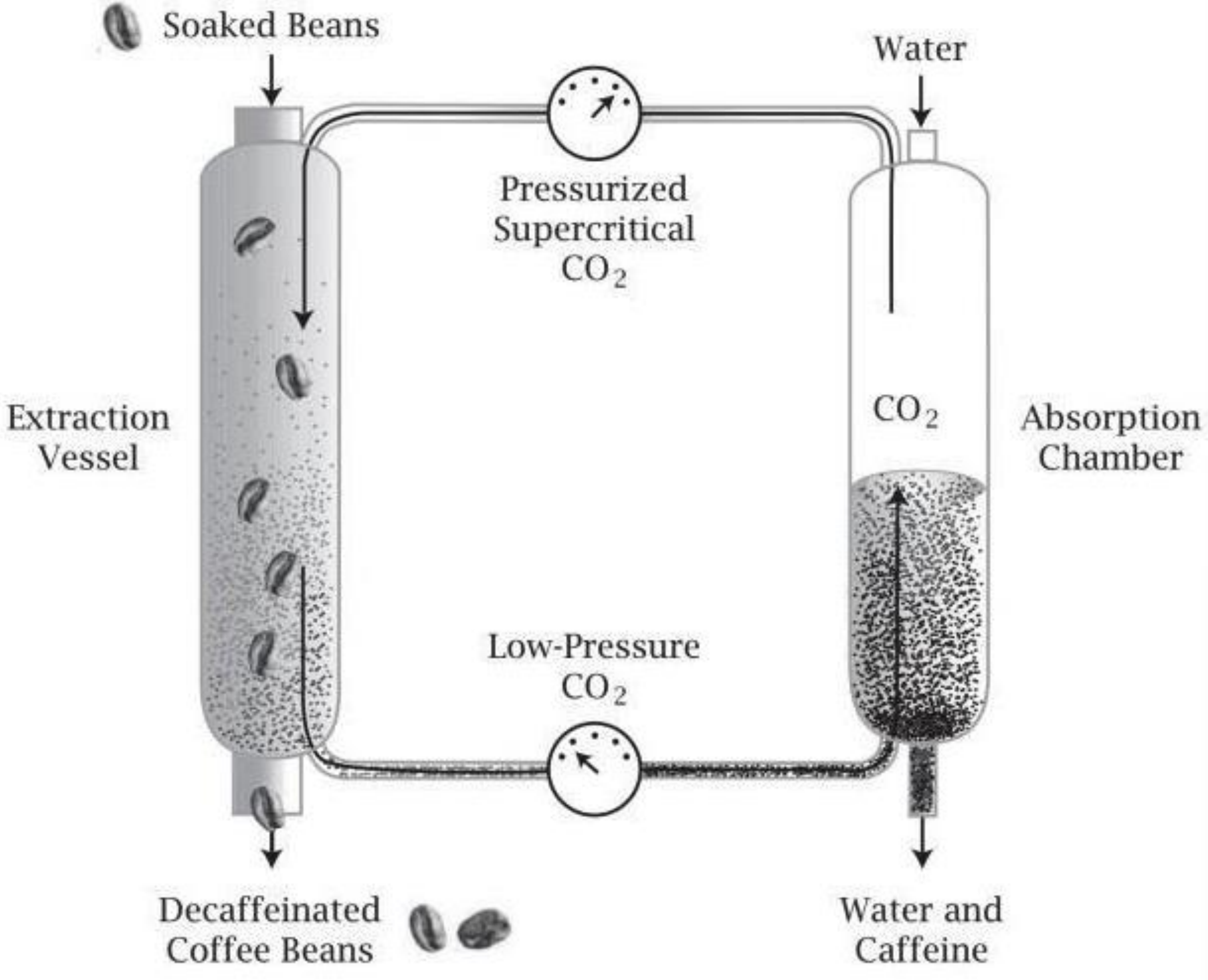
USE OF SUPERCRITICAL FLUIDS: DECAFFEINATION OF COFFEE BEANS

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

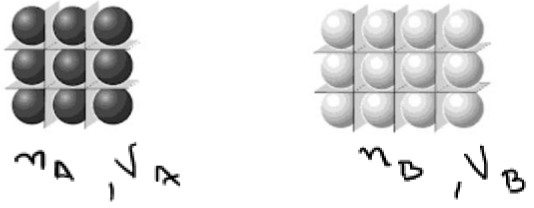
Vaso Tileli | MXD 237

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!!

$\Delta_{mix}U = 0$, $\Delta_{mix}H = 0$, $\Delta_{mix}V = 0$ ⇒ properties of ideal soln.

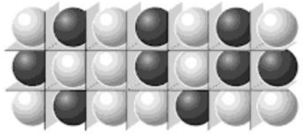


n_A, V_A n_B, V_B

$$\Delta_{mix}S = S_{mix} - S_{pure} = k_B \ln \frac{n!}{n_A!\,n_B!} - k_B\cancelto{0}{(\ln 1 + \ln 1)}$$

Stirling's theorem

$\ln x! = x\ln x - x$ & also $k_B = \frac{R}{N_A}$



$n = n_A + n_B$

$V = V_A + V_B$

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

$x_A + x_B = 1$

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

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

Divide by total n:

$$\Delta_{mix}\overline{G} = RT\left(x_A \ln x_A + x_B \ln x_B\right) = \overline{G}_{mix} - g_{pure}$$

$$g_{pure} = \mu_A^* x_A + \mu_B^* x_B$$

$$\Rightarrow \boxed{\overline{G}_{mix} = \underbrace{\mu_A^* x_A + \mu_B^* x_B}_{\text{pure}} + \underbrace{RT\left(x_A \ln x_A + x_B \ln x_B\right)}_{\text{change due to mixing}}}$$

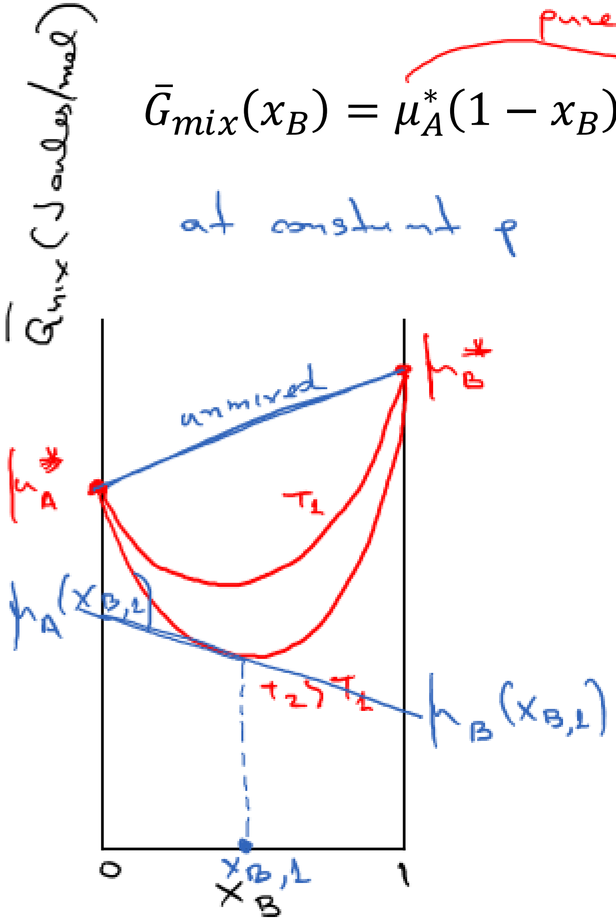
Assumptions:
- the size of atoms/molecules are equal
- the crystal structure is the same
- on average, the internal energy of the system does not change

GRAPHICAL REPRESENTATION OF IDEAL SOLUTIONS

$$\bar{G}_{mix}(x_B) = \overbrace{\mu_A^*(1-x_B)+\mu_B^* x_B}^{\text{pure state}} + \overbrace{RT[(1-x_B)\ln(1-x_B)+x_B\ln x_B]}^{\text{mixed state} \rightarrow \text{always negative}}$$

spontaneous

at constant p



A: heptane

B: hexene

$$\mu_B(T,p,x_{B,1}) = \mu_B^*(T,p) + RT\ln\gamma_B x_{B,1}$$

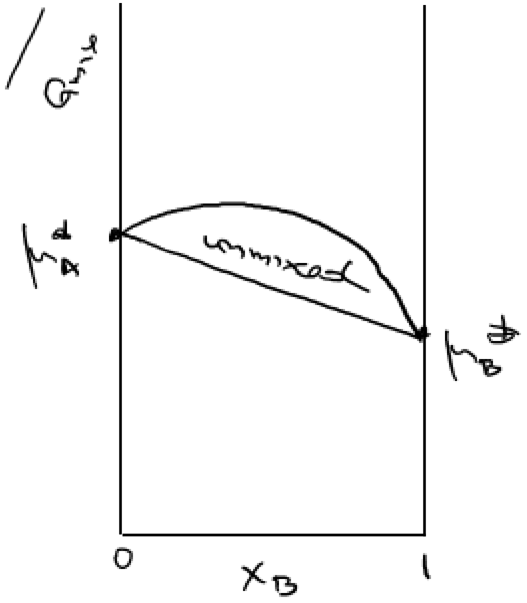
γ_B : activity coefficient = 1 for ideal soln.

$$\Rightarrow \mu_B(T,p,x_{B,1}) = \mu_B^*(T,p) + RT\ln x_{B,1}$$

if $p = 1$ (atm/bar) $\Rightarrow \mu_B^*(T,p) = \mu_B^o(T)$

$$\Rightarrow \mu_B(T,x_{B,1}) = \mu_B^o(T) + RT\ln x_{B,1}$$

This case is NOT described by the ideal solution model



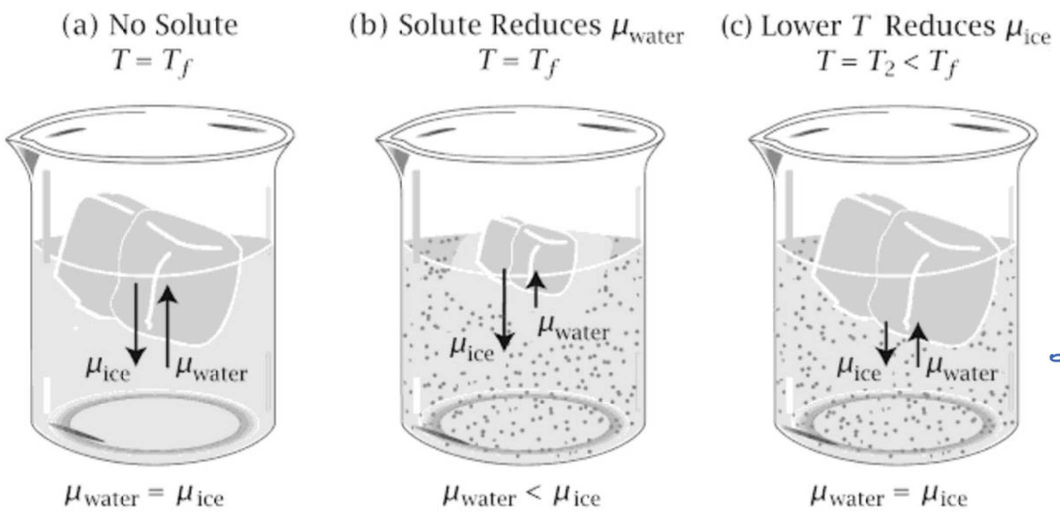
A: water

B: hexane

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.

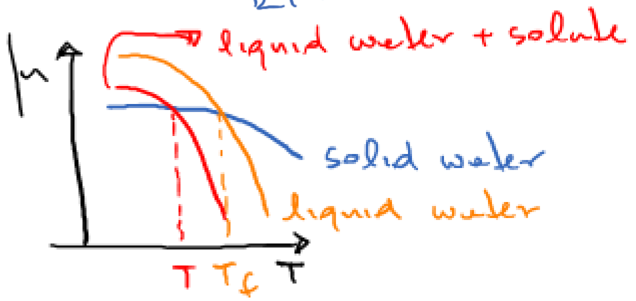
when we are at the freezing point: $\mu_{\text{solid water in solution}} = \mu_{\text{liquid water in solution}} = \mu^*_{\text{pure solid water}}$



$$\mu^*_{\text{solid water}} = \mu^*_{\text{pure liquid water}} + RT \ln x_{\text{water in the solution}}$$

$$\ln x_{\text{water}} = \frac{\mu^*_{\text{solid water}}}{RT} - \frac{\mu^*_{\text{pure liquid water}}}{RT}$$

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

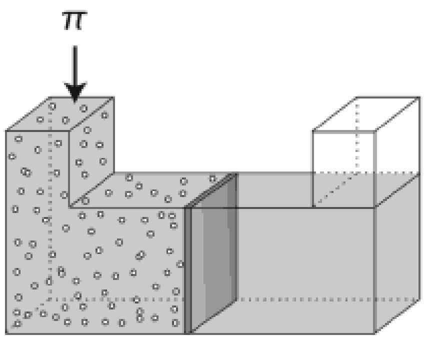


https://www.sciencesource.com/preview.asp?item=2418703&itemw=4&itemf=0002

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.



$$\mu_{\text{pure water}} = \mu_{\text{water in the solution}}$$

$$\Rightarrow \mu^*_{\text{pure water}}(p) = \mu^*_{\text{water in solution}}(p+\pi) + RT\ln x_{\text{water in solution}}$$

$$\Rightarrow RT\ln x_{\text{water in solution}} = \overbrace{\mu^*_{\text{pure water}}(p)}^{\text{initial}} - \overbrace{\mu^*_{\text{water in solution}}(p+\pi)}^{\text{final state}}$$

$$= -\Delta\mu_{\text{water in solution}}(p, p+\pi)$$

$$= -\int_p^{p+\pi}\left(\frac{\partial\mu}{\partial p}\right)_T dp$$

$$\Rightarrow RT\ln x_{\text{water in solution}} = -\int_p^{p+\pi} v_{\text{water}}\,dp = -v_{\text{water}}(p+\pi-\cancel{p})$$

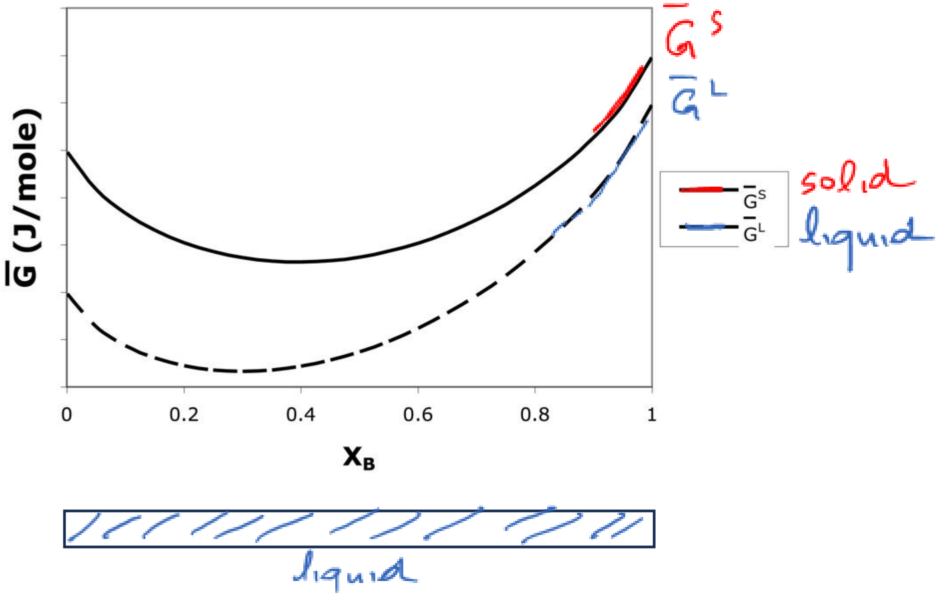
$$\Rightarrow \pi = -\frac{RT\ln x_{\text{water in solution}}}{v_{\text{water}}}$$

FREE ENERGY DIAGRAMS OF MULTI-PHASE BINARY IDEAL SOLUTIONS

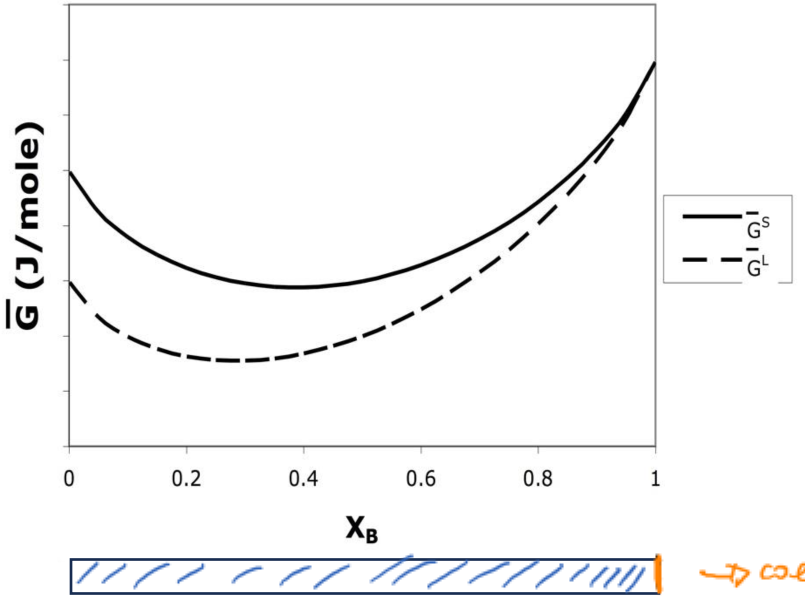
Let's see what effect will have the variation of the temperature at the molar Gibbs free energy when the pressure is kept constant in a two-component, two phase system.

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

$T_1 > T_{f,B} > T_{f,A}$



$T_2 = T_{f,B} > T_{f,A}$ $T_2 < T_1$

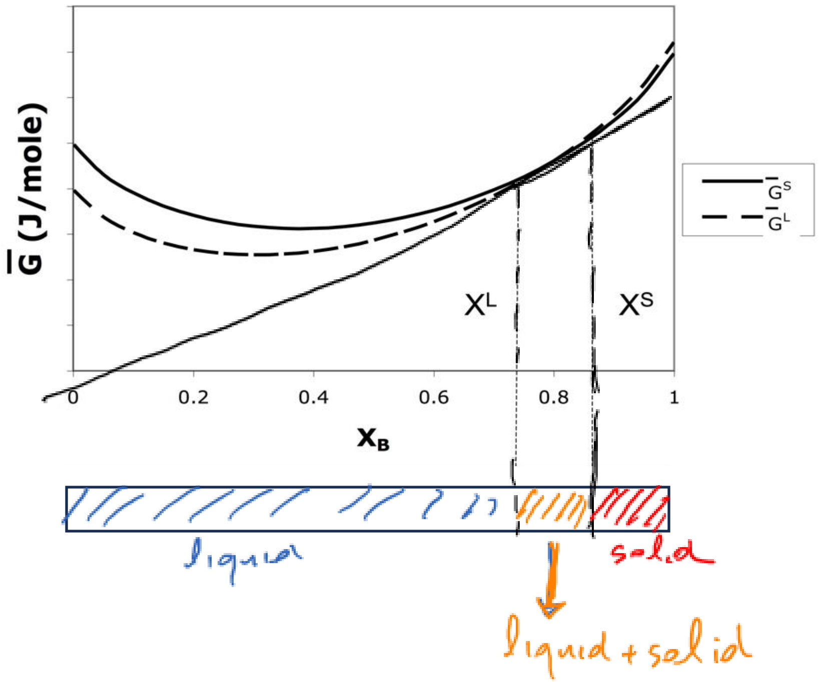


→ coexistence of liquid + solid

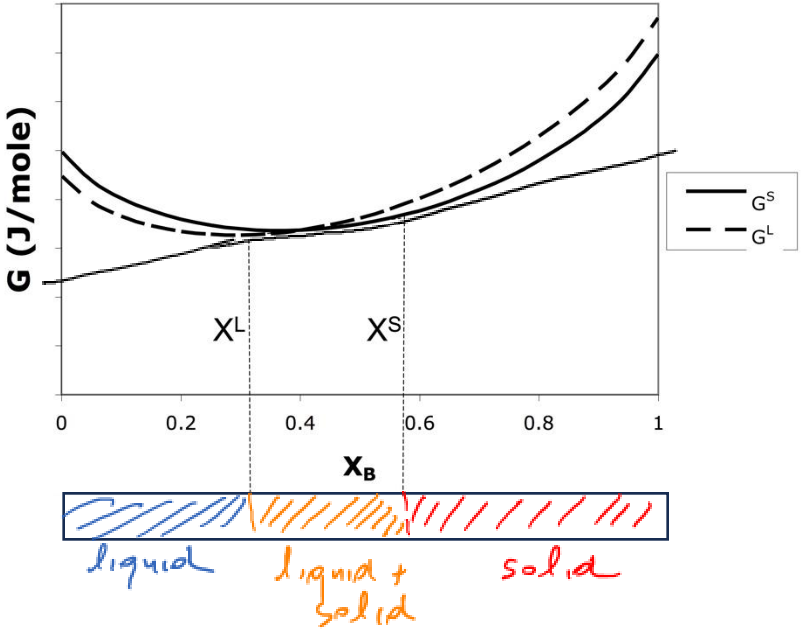
FREE ENERGY DIAGRAMS OF MULTI-PHASE BINARY IDEAL SOLUTIONS | CONTINUED

$T_4 < T_3$

$T_{f,B} > T_3 > T_{f,A}$

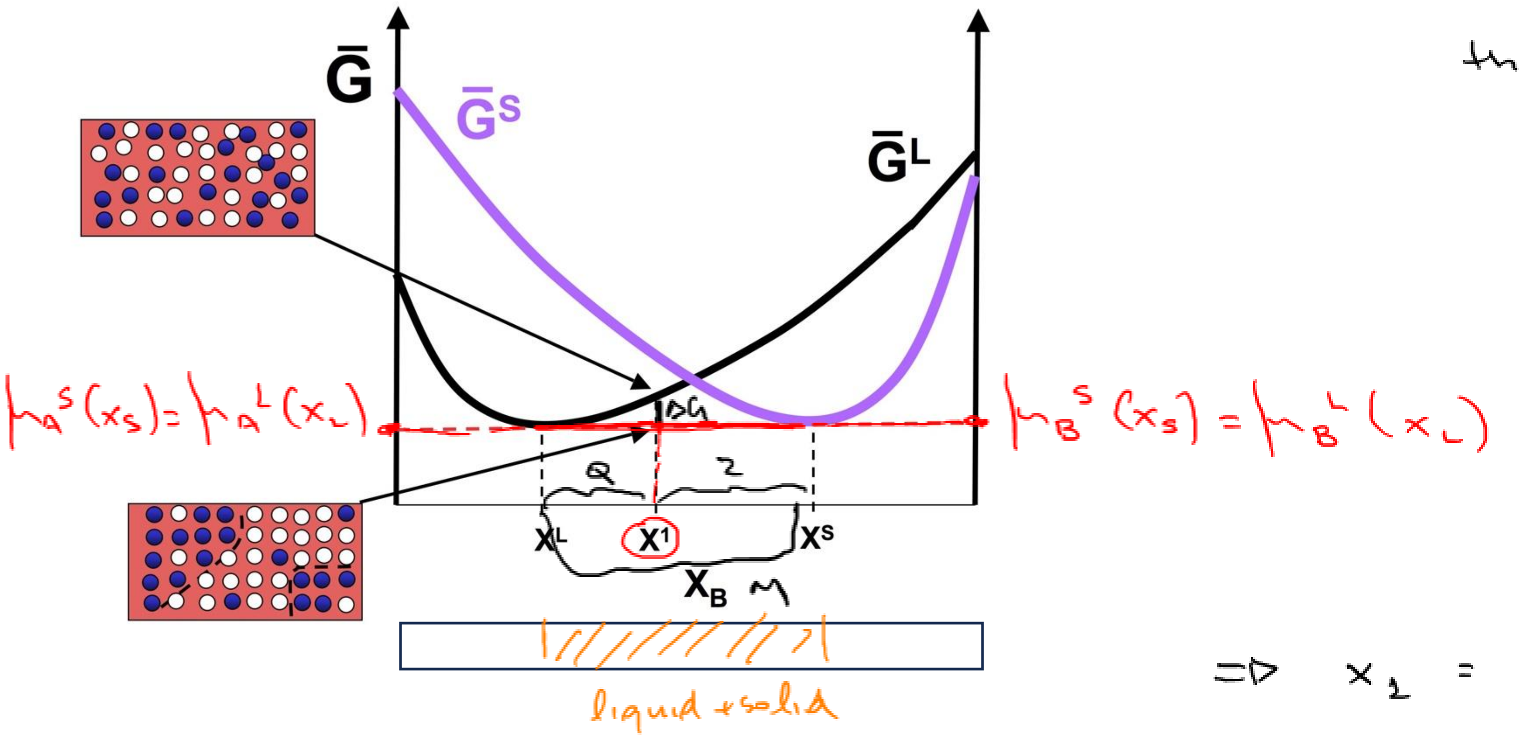


$T_{f,B} > T_4 > T_{f,A}$



COMMON TANGENT AND THE LEVER RULE

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



$\mu_A^S(x_S) = \mu_A^L(x_L)$

$\mu_B^S(x_S) = \mu_B^L(x_L)$

For the fraction of each phase that coexist:

$$n x_1 = n^L x_B^L + n^S x_B^S$$

$\frac{n^L}{n}$: f^L : fraction of all of the moles of the components that are present in the liquid phase

$$f^L + f^S = 1$$

$$\Rightarrow x_1 = f^L x_B^L + (1 - f^L) x_B^S$$

$$\Rightarrow f^L = \frac{x_B^S - x_1}{x_B^S - x_B^L} = \frac{z}{M} \quad \& \quad f^S = \frac{Q}{M}$$