

Don't get bogged down, and show your work! If you're stuck, try another problem. Remember to put units on everything!

True or False Section [2 points each; +2 for correct, 0 for no response, -1 for incorrect!]

i) At the eutectic point of a non-ideal binary solution, three phases coexist:

True

ii) Liquid-liquid coexistence in a binary liquid mixture cannot exist below the upper critical solution temperature.

False

iii) The fugacity coefficient of a pure ideal gas is always equal to the pressure.

False

iv) The stoichiometric coefficients ν_i are negative for reactants.

True

v) Equilibrium thermodynamics can be used to predict the rate of chemical reactions.

False

vi) If the reaction $A+B \rightleftharpoons C$ is exothermic, the equilibrium reaction coordinate increases with increasing temperature.

False

vii) For an ideal solution, the excess Gibbs free energy (G^E) is zero at all compositions.

True

viii) The entropy change of mixing is always negative for ideal solutions.

False

ix) If system pressure is low, activity coefficients can be assumed to be 1.0.

False

x) The fugacity coefficient for a component in a vapor mixtures does not depend on the temperature.

False

Problem 1:

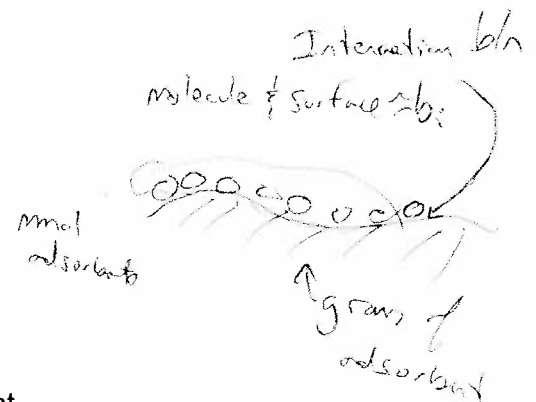
(a) The Langmuir model for the adsorption of gases onto solid substrates has the following form:

$$q_i = \frac{q_i^* p_i b_i}{1 + b_i p_i}$$

Explain the physical meaning of the model parameters b_i and q_i^* and how these parameters relate to processes on the molecular scale.

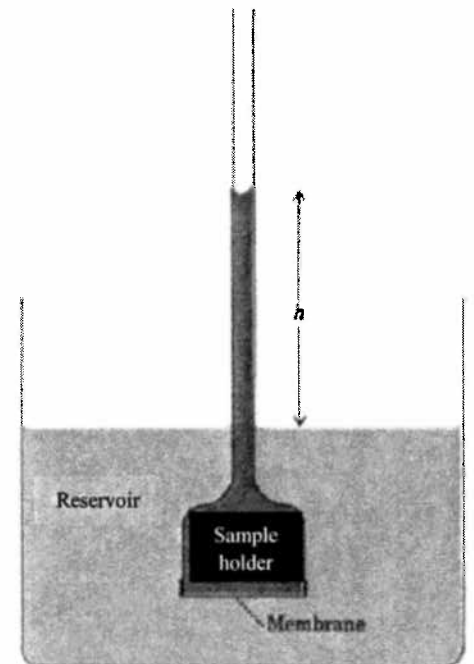
b_i : Langmuir affinity constant [bar^{-1}]

q_i^* : Saturation loading [$\frac{\text{mmol adsorbate}}{\text{g adsorbent}}$]



(b) In a chemical plant, polyethylene polymer is produced at different molecular weights for various industrial applications. By mistake, two bags (1 and 2) of polyethylene powder from different polymerization reactions have not been labeled properly. It is known that one of the batches of polymer has a much higher molecular weight than the other, but it is a mystery which bag contains which polymer.

In order to ship each bag of polymers to the correct customer, it is necessary to determine which bag contains the polymer with the highest molecular weight. In the production plant, you do not have the access to fancy research equipment to perform a full analysis of the polymers. In a corner of your lab, you find the following: a bottle of toluene (a good solvent for polyethylene), some beakers, an analytical balance that allows you make polymer solutions in toluene at known concentrations (g/L), and an old osmometer (see picture).



Your boss challenges you to identify the polymer with the highest molecular weight through a single measurement with the osmometer. Describe how you would do this.

One measurement: Cannot compare solutions of polymer 1 & 2 w/ pure solvent

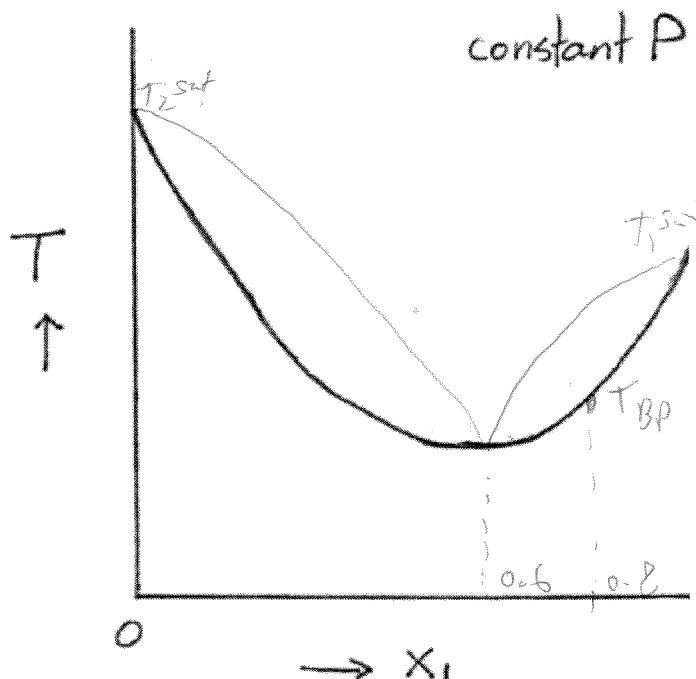
⇒ Directly compare solutions at same concentration [g/L] w/ each other: solution ① in sample holder, solution ② in reservoir.

IF $M_1 > M_2$, then $\pi_1 < \pi_2$ & h becomes \ominus

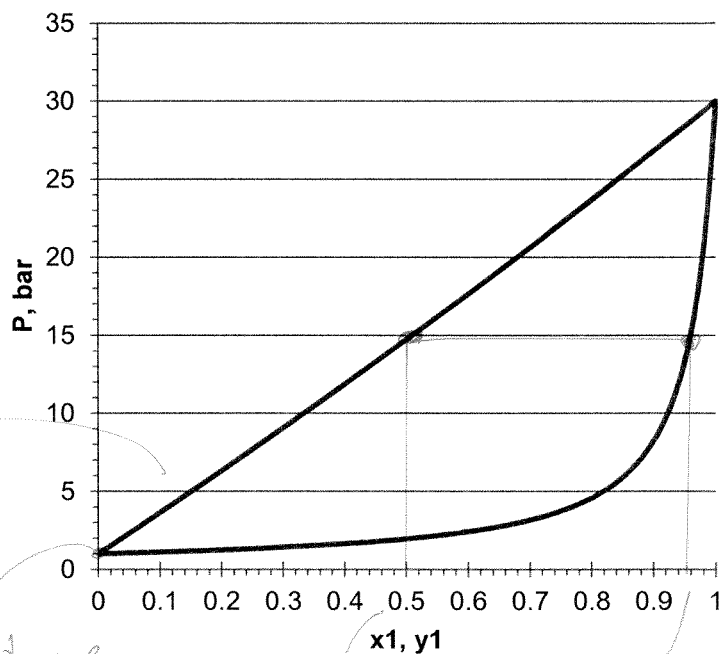
IF $M_1 < M_2$, then $\pi_1 > \pi_2$ & h becomes \oplus

(c) The figure to the right represents an incomplete VLE phase diagram for a binary mixture (species 1 & 2). You know the system exhibits an azeotrope at 40 mol% of species 2.

Please complete the diagram. Describe the key features of your graph to get full credit. Highlight the bubble point temperature at a composition of 80 mol% of species 1.



Problem 2: The phase diagram shown below is for a binary mixture of substances 1 and 2, at a constant temperature of 298 K. Use the information in the phase diagram to estimate the fugacity coefficient of component 2 in the mixture ($\tilde{\phi}_2$) at 15 bar. State your assumptions where appropriate.



$$y_1 P \tilde{\phi}_1 = x_1 \gamma_1 P_1^{sat}$$

$$y_2 P \tilde{\phi}_2 = x_2 \gamma_2 P_2^{sat}$$

Totally linear
liquid line \equiv Ideal Sol'n.

$$\therefore y_2 P \tilde{\phi}_2 = x_2 P_2^{sat}$$

$$\therefore \tilde{\phi}_2 = \frac{(0.5)(1 \text{ Bar})}{(0.975)(15 \text{ Bar})} = 0.034$$

Problem 3: The presence of dissolved salt affects both the boiling and freezing of water. First, we look at the effect of salt at high temperatures.

If steam at 300°C is in equilibrium with pure water, the saturation pressure is 8593 kPa. Additional thermodynamic data for steam at 300°C and various pressures up to the saturation pressure are presented below.

P [kPa]	H [kJ/kg]	S [kJ/kg·K]
10	3076.7	9.283
100	3074.5	8.217
1000	3051.6	7.125
8593	2749.6	5.706

[H and S for saturated vapor]

(a) Starting from the formal definition of fugacity, $d\hat{G} = RTd(\ln f)$, use these data to show that the fugacity coefficient of saturated steam at 300°C is equal to 0.78.

$d\hat{G} = RTd(\ln f)$, Integrate from reference point (\hat{G}^{ref}, f^{ref}) to (\hat{G}, f) :

$$\frac{\hat{G} - \hat{G}^{ref}}{RT} = \ln\left(\frac{f}{f^{ref}}\right)$$

Need a reference point! At low P, $f = P \Rightarrow$ use 10 kPa data
 @ $f^{ref} = 10 \text{ kPa}$, $\hat{G}^{ref} = \hat{H}^{ref} - T\hat{S}^{ref} = -40.3 \text{ kJ/mol}$
 @ Sat'n: $\hat{G} = \hat{H} - T\hat{S} = -9.3 \text{ kJ/mol} \Rightarrow$ Solve for f . $f = 6705 \text{ kPa}$
 $\phi_{steam} = f/P = 6705/8593 = 0.78$

(b) If the behavior of the saturated steam is accurately described by the virial equation of state, what is the virial coefficient at 300°C? What does the calculated value tell you about molecular interactions in saturated steam?

$$\phi^{sat} = \exp\left[\frac{BP^{sat}}{RT}\right] \Rightarrow B = \frac{RT \ln \phi}{P^{sat}} = \frac{8.314 \cdot 573.15 \cdot \ln(0.78)}{8593} = -0.1372 \text{ J/mol/kPa}$$

$$= -137.2 \text{ cm}^3/\text{mol}$$

⊖ B value: Attractive Interactions.

Now salt is dissolved in water at a concentration of 2 mol%. The mixture is heated to 300°C, where it is kept in equilibrium with steam that does not contain any salt.

(c) Calculate the fugacity of liquid water in the salt/water mixture at 300°C.

$$\hat{f}_{water}^L = x_w \gamma_w \hat{f}_w^L \quad (x_w = 0.98, \therefore \gamma_w \approx 1) \quad \hat{f}_w^L = \hat{f}_w^v \text{ for pure water in eqbm.}$$

$$\hat{f}_w^v = 6705 \text{ kPa (From (a))}$$

$$\hat{f}_w^L = (0.98)(6705 \text{ kPa}) = 6571 \text{ kPa}$$

(d) Estimate the pressure of the steam in equilibrium with the salt/water mixture at 300°C.

$$\tilde{f}_w^L = \tilde{f}_w^V = f_w^V = \phi_w^V \cdot P \rightarrow P = 2424.5 \text{ kPa}$$

$\hookrightarrow 0.78$ (reduction from pure water - makes sense)

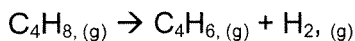
(e) Finally, the salt solution is cooled down at atmospheric pressure until ice forms. For pure water, the enthalpy of melting is 334 kJ/kg at 1 atm. At which temperature will the salt solution freeze?

$$\ln(x_w \gamma_w) = \frac{-\Delta \hat{H}_w^{fus}}{RT_{m,w}} \left(\frac{T_{m,w}}{T} - 1 \right)$$

≈ 1 (arrow pointing to $x_w \gamma_w$)

Solve for T: $T = 271.1 \text{ K}$

Problem 4: Butadiene is prepared by the gas-phase catalytic dehydrogenation of 1-butene:



(a) Calculate the standard Gibbs free energy of reaction and reaction enthalpy.

	$\Delta \hat{H}_F^{298} [\text{kJ/mol}]$	$\Delta \hat{G}_F^{298} [\text{kJ/mol}]$	ν_i	
Butadiene (2)	109.240	149.730	1	$\Delta \hat{H}_{rxn}^{298} = 109.780 \text{ kJ/mol}$
Hydrogen (3)	0	0	1	$\Delta \hat{G}_{rxn}^{298} = 79.49 \text{ kJ/mol}$
1-Butene (1)	-54.0	70.240	-1	

(b) Calculate the equilibrium constant at 298K. What does the answer tell you about the reaction?

$$K_{298} = \exp \left[\frac{-\Delta \hat{G}_{rxn}^{298}}{RT} \right] = 1.16 \times 10^{-14} \leftarrow \text{Rxn essentially does not occur @ 298K.}$$

(c) On an industrial scale, the reaction is performed at 900K and 1 bar. The Gibbs free energy of reaction under these circumstances is 10.62 kJ/mol. If the feed to the reactor is pure 1-butene, find the equilibrium conversion, which is defined as the fraction of reactant that has reacted.

$$K_{900} = \exp\left[\frac{-106200}{8.314 \cdot 900K}\right] = 0.242 = \frac{y_2 y_3}{y_1} \cdot P \quad \checkmark 1 \text{ Bar}$$

$$n_{1,eq} = 1 - \xi$$

$$n_{2,eq} = \xi$$

$$n_{3,eq} = \xi$$

$$K = \left(\frac{\xi}{(1-\xi)}\right)^2 \cdot \left(\frac{1+\xi}{1-\xi}\right) = \frac{\xi^2}{1-\xi^2}$$

$$\Rightarrow \xi = 0.441 = \text{Conversion}$$

(d) To improve the conversion and suppress side reactions, steam is mixed with the 1-butene before it is fed to the reactor. The water acts as inert diluent and does not participate in the dehydrogenation reaction. If 9 moles of water are added to the reactor per mole of 1-butene, calculate the new conversion. The reactor temperature and pressure remain 900K and 1 bar.

K_{900} remains the same (0.242)

New Composition:

$$n_{1,eq} = 1 - \xi$$

$$n_{2,eq} = \xi$$

$$n_{3,eq} = \xi$$

$$n_{H_2O} = 9 \text{ mol}$$

$$K = \left(\frac{\xi}{(10+\xi)}\right)^2 \cdot \left(\frac{10+\xi}{1-\xi}\right) = \frac{\xi^2}{10-9\xi-\xi} = 0.242$$

$$\xi = 0.77 = \text{Conversion}$$

Problem 5: In an experiment designed to develop relationships for the solubility of methane (1) in methanol (2), a vessel containing a vapor-liquid mixture of the two species comes to equilibrium at 0.0°C and 20 bar. The liquid is sampled and found to contain 0.2 mole % methane.

(a) Simplify the following expressions from the virial equation of state assuming the vapor phase can be considered an ideal solution (i.e. the Lewis-Randall Rule applies):

$$\ln \hat{\phi}_1 = \frac{P}{RT} [B_{11} + y_2^2 (2B_{12} - B_{11} - B_{22})]$$

$$\ln \hat{\phi}_2 = \frac{P}{RT} [B_{22} + y_1^2 (2B_{12} - B_{11} - B_{22})]$$

$$B_{11} = -53.9 \text{ cm}^3/\text{mol}, B_{12} = -166 \text{ cm}^3/\text{mol}, B_{22} = -4068 \text{ cm}^3/\text{mol}$$

For an IS: $\hat{\phi}_i = \phi_i$, which means $1=2$, ~~hence~~ $B_{12} = B_{11} = B_{22}$

$$\ln \hat{\phi}_1 = \frac{PB_{11}}{RT} \rightarrow \hat{\phi}_1 = 0.954$$

$$\ln \hat{\phi}_2 = \frac{PB_{22}}{RT} \rightarrow \hat{\phi}_2 = 0.03$$

(b) Using the results from Part a, estimate the composition of the vapor phase. Do not neglect ϕ_i^{sat} or the Poynting correction factors.

At the given conditions P_2^{sat} at 0.0°C = 0.0401 bar, $V_2^l = 40 \text{ cm}^3/\text{mol}$; also, $R = 83.14 \text{ cm}^3 \cdot \text{bar}/(\text{mol} \cdot \text{K})$.

$$y_1 P \hat{\phi}_1 = x_1 \gamma_1 \phi_1^{\text{sat}} p_1^{\text{sat}} \exp \left[\frac{V_1 (P - p_1^{\text{sat}})}{RT} \right] \quad \text{Too many unknowns!}$$

$$y_2 P \hat{\phi}_2 = x_2 \gamma_2 \phi_2^{\text{sat}} p_2^{\text{sat}} \exp \left[\frac{V_2 (P - p_2^{\text{sat}})}{RT} \right]$$

$$\phi_2^{\text{sat}} = \frac{P_2^{\text{sat}} B_{22}}{RT} = 0.992$$

$$y_2 = \frac{(0.992)(1)(0.992)(0.0401 \text{ bar})}{(20 \text{ bar})(0.03)} \exp \left[\frac{40 \text{ cm}^3 (\text{bar} - 0.0401 \text{ bar})}{(83.14)(273 \text{ K})} \right]$$

$$y_2 = 0.068$$

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$$y_1 = 0.932$$

Good luck on the final - know