Problem 1:

You are given a mixture of components 1 and 2 on your first day of work at A. Z. O. Trope Corporation. You know nothing initially, except that you need to separate these species, and you find a notebook that shows the values of their activity coefficients in a binary system of 1 and 2.

Part A:

Assuming a low temperature separation process, show the relationship between the vapor pressures of 1 and 2 and their activity coefficients at the azeotrope. Assume that you are given the vapor pressures of 1 and 2, P_1^{vap} and P_2^{vap}, at the temperature of the separation unit, T, and the activity coefficients can be assumed to be γ_1 and γ_2.

Solution:

$$Py_1 = P_1^{\text{vap}} x_1 \gamma_1 \qquad x_1 = y_1$$
$$Py_2 = P_2^{\text{vap}} x_2 \gamma_2 \qquad x_2 = y_2$$

At the azeotrope

P in both equations must be equal because it is the total system pressure, thus

$$P_1^{\text{vap}}\gamma_1 = P_2^{\text{vap}}\gamma_2$$

$$\frac{P_1^{\text{vap}}}{P_2^{\text{vap}}} = \frac{\gamma_2}{\gamma_1}$$

Part B:

You are given the vapor pressure of component 1 at a temperature T and the total pressure, P. Find an expression for the activity coefficient using P_1^{vap} and P for low values of P at the azeotrope.

Solution:

$$\gamma_1 = \frac{P}{P_1^{\text{vap}}}$$

Part C:

Given expressions for γ_1 and γ_2, find the mole fraction of component 2 at the azeotrope.

$$\ln(\gamma_1) = Bx_2^2 \quad \text{and} \quad \ln(\gamma_2) = Bx_1^2$$

Assuming that

$$\left|\ln \frac{P_1^{\text{vap}}}{P_2^{\text{vap}}}\right| < |B| \quad \text{and} \quad B < 2$$

<u>Solution:</u>

$$\frac{P_1^{\text{vap}}}{P_2^{\text{vap}}} = \frac{\exp\left[Bx_1^2\right]}{\exp\left[Bx_2^2\right]}$$

$$\frac{P_1^{\text{vap}}}{P_2^{\text{vap}}} = \exp\left[B\left(x_1^2 - x_2^2\right)\right]$$

$$\ln\left(\frac{P_1^{\text{vap}}}{P_2^{\text{vap}}}\right) = B\left(x_1^2 - x_2^2\right)$$

$$\frac{1}{B}\ln\left(\frac{P_1^{\text{vap}}}{P_2^{\text{vap}}}\right) = \left((1-x_2)^2 - x_2^2\right)$$

$$\frac{1}{B}\ln\left(\frac{P_1^{\text{vap}}}{P_2^{\text{vap}}}\right) = 1 - 2x_2$$

$$\frac{1}{2}\left(1 - \frac{1}{B}\ln\left(\frac{P_1^{\text{vap}}}{P_2^{\text{vap}}}\right)\right) = x_2$$

Part D:

Show the thermodynamic consistency of the equations for γ_1 and γ_2.

<u>Solution:</u>

Using the Gibbs-Duhem Equation...

$$\frac{x_1}{\gamma_1}\frac{\partial \gamma_1}{\partial x_1} + \frac{x_2}{\gamma_2}\frac{\partial \gamma_2}{\partial x_1} = 0$$

$$\frac{x_1}{\gamma_1}\frac{\partial\left(\exp\left[Bx_2^2\right]\right)}{\partial x_1} + \frac{x_2}{\gamma_2}\frac{\partial\left(\exp\left[Bx_1^2\right]\right)}{\partial x_1} = 0$$

$$\frac{x_1}{\exp\left[Bx_2^2\right]}\frac{\partial\left(\exp\left[Bx_2^2\right]\right)}{\partial x_1} + \frac{x_2}{\exp\left[Bx_1^2\right]}\frac{\partial\left(\exp\left[Bx_1^2\right]\right)}{\partial x_1} = 0$$

$$\frac{x_1}{\exp\left[Bx_2^2\right]}\frac{\partial\left(\exp\left[B\left(1-x_1\right)^2\right]\right)}{\partial x_1}+\frac{x_2}{\exp\left[Bx_1^2\right]}\frac{\partial\left(\exp\left[Bx_1^2\right]\right)}{\partial x_1}=0$$

$$\frac{x_1}{\exp\left[Bx_2^2\right]}\left(\exp\left[Bx_2^2\right]\right)\left(-2Bx_2\right)+\frac{x_2}{\exp\left[Bx_1^2\right]}\left(\exp\left[Bx_1^2\right]\right)\left(2Bx_1\right)=0$$

$$-2Bx_1x_2+2Bx_1x_2=0$$

These expressions for activity coefficient are thermodynamically consistent.

Part E:

Name two methods used to separate azeotropic mixtures.

<u>Solution:</u>

Answers will vary.

Problem 2:

a) Derive the following relationship:

$$\left(\frac{\partial\left(A/T\right)}{\partial T}\right)_V = -\frac{U}{T^2}$$

$$\frac{\partial}{\partial T}\left(\frac{A}{T}\right)_V = \frac{1}{T}\left(\frac{\partial A}{\partial T}\right)_V - \frac{A}{T^2}$$

$$\frac{\partial}{\partial T}\left(\frac{A}{T}\right)_V = \frac{1}{T}S - \frac{U - TS}{T^2}$$

$$\frac{\partial}{\partial T}\left(\frac{A}{T}\right)_V = \frac{S}{T} - \frac{U}{T^2} - \frac{S}{T}$$

$$\frac{\partial}{\partial T}\left(\frac{A}{T}\right)_V = -\frac{U}{T^2}$$

b) Find the Maxwell relationship below (show all work):

$$\left(\frac{\partial S}{\partial P}\right)_{T,N} =$$

$$\left(\frac{\partial S}{\partial P}\right)_{T,N}$$

$$\left(\frac{\partial S}{\partial P}\right)_{T,N} = \frac{\partial^2 G}{\partial P \partial T} = \frac{\partial}{\partial P}\left[\left(\frac{\partial G}{\partial T}\right)_{P,N}\right]_{T,N}$$

$$\left(\frac{\partial S}{\partial P}\right)_{T,N} = \frac{\partial^2 G}{\partial P \partial T} = \frac{\partial}{\partial P}\left[-S\right]_{T,N}$$

$$\frac{\partial^2 G}{\partial P \partial T} = \frac{\partial^2 G}{\partial T \partial P}$$

$$\frac{\partial^2 G}{\partial T \partial P} = \frac{\partial}{\partial T}\left[\left(\frac{\partial G}{\partial P}\right)_{T,N}\right]_{P,N}$$

$$\frac{\partial^2 G}{\partial T \partial P} = \frac{\partial}{\partial T}\left[V\right]_{P,N}$$

$$\boxed{\left(\frac{\partial S}{\partial P}\right)_{T,N} = -\left(\frac{\partial V}{\partial T}\right)_{P,N}}$$

Question 3

You and friend decide to go on vacation. You manage to rent a cabin high in the Rockies for some skiing. While staying there, you get hungry, and decide to cook dinner. Being a poor college student, you decide to cook some pasta.

Part A: You fill a pot with some water, and set it on the stove to boil. For some reason, this pot has a built in thermometer, which gets immersed in the water. What temperature, T_{rock}, will it read when the water boils? The following constants might be useful:

8

P_{atm}	Pressure at sea level
P_{rock}	Pressure at your cabin
T_{atm}	Boiling temperature of water at sea level
$C_{p,s}$	Heat capacity of solid water
$C_{p,l}$	Heat capacity of liquid water
$C_{p,v}$	Heat capacity of gaseous water
ΔH_{vap}	Heat of vaporization of water
ΔH_{fus}	Heat of fusion of water
β_s	Volume expansivity of ~~liquid~~ solid water
β_l	Volume expansivity of liquid water
β_v	Volume expansivity of gaseous water

(Note: These constants only apply for part A. Disregard them and any connotations they imply for the rest of the problem)

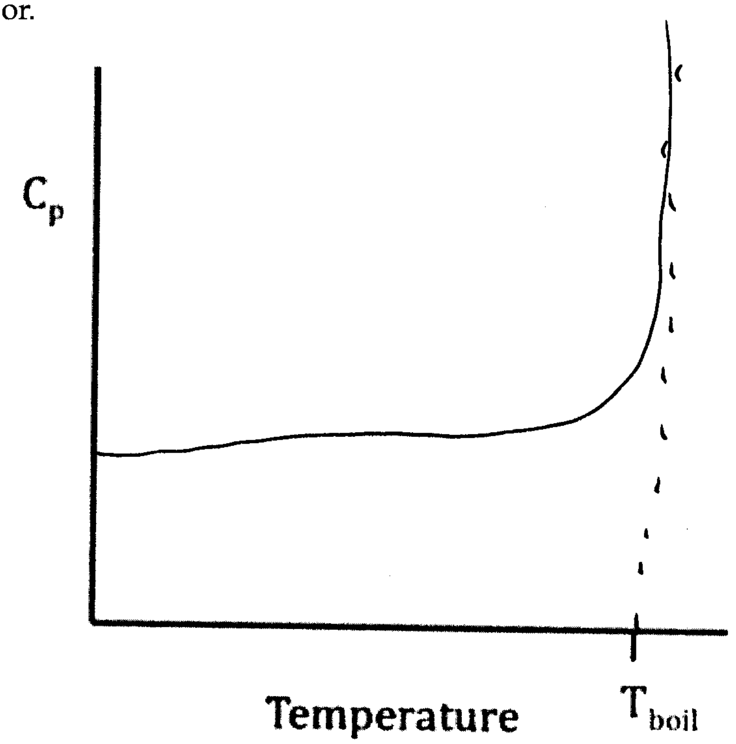
– Use Clausius – Clapeyron Equation

$$\ln\left(\frac{P_{atm}}{P_{rock}}\right) = \frac{\Delta H_{vap}}{R}\left(\frac{1}{T_{rock}} - \frac{1}{T_{atm}}\right)$$

$$\boxed{\left[\frac{R}{\Delta H_{vap}} \ln\left(\frac{P_{atm}}{P_{rock}}\right) + \frac{1}{T_{atm}}\right]^{-1} = T_{rock}}$$

Part B: After eating, you discover that a calorimeter was also attached to your pot (What a marvelous contraption this is). And what luck, it seems that the device kept a recording of the heat capacity of the water as it was being heated! Being the curious chemical engineer that you are, you decided to roughly sketch the plot of heat capacity of liquid water versus temperature around its boiling point. Please draw this curve below, and explain its behavior.

8



- at the boiling point $Cp \to \infty$

$$Cp = \left(\frac{dH}{dT}\right)_P$$

$$Cp\Big|_{T_{boil}} \approx \left(\frac{\Delta H_{vap}}{0}\right) \to \infty$$

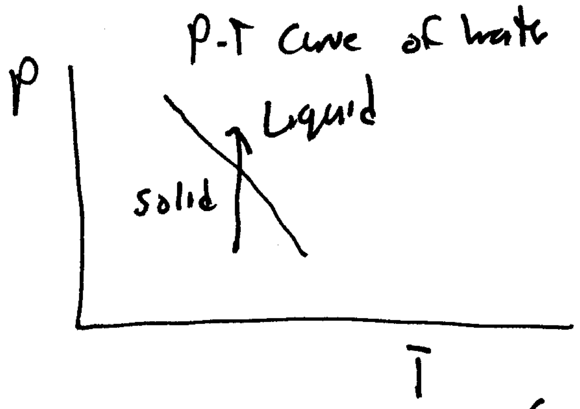
, dT at the boiling point is zero, as it is a phase change

Part C: Your friend decides to cook after you. However, there's a problem: the water lines have frozen. You could use the gas on the stove to melt ice, but gas is expensive, so you would rather not. Luckily, your friend has an idea. He's going to take a block of ice, and crush (compress) it into water between his hands! Will this actually work? Why or why not?

9

Assume your friend works out a lot, and is strong, **really** strong, so strong that he can generate lots of pressure with his hands. Also assume that any ice he crushes is compressed isothermally due him wearing insulating gloves.

Yes, it will work



- isothermal compression (moving vertically on a P-T curve) will transition from Solid to Liquid, as the solid-liquid eq curve has a negative slope

$$\left(\frac{dP}{dT}\right)_{S-L} = \frac{\Delta S}{\Delta V}, \quad \Delta S = S^L - S^S > 0$$

$$\Delta V = V^L - V^S < 0$$

$$\therefore \left(\frac{dP}{dT}\right)_{S-L} < 0$$

Your friend manages to get some water somehow. He puts it on the stove, and turns on the heat. However, he throws a little bit of olive oil into the water first (So the pasta doesn't stick he claims). The mole fraction of oil in the pot is very low, so low that it falls within the Henry's Law regime. Here, instead of the typical equilibrium condition, the partial pressure of oil in solution is given as:

$$P_{\text{oil, l}} = H x_{\text{oil}}$$

Where, $P_{\text{oil,l}}$ is the partial pressure of oil in the liquid, x_{oil} is the mole fraction of oil in the liquid, and H is called a Henry's law coefficient. Water still follows the usual equilibrium criteria.

Use the following constants:

x_{oil}	Mole fraction of oil in the liquid
H	Henry's law constant of oil in water
P^{sat}	Saturation vapor pressure of water

Part D: Find the mole fractions of oil and water in the first bubble of vapor that will form that is in equilibrium with this solution, and the pressure at which this occurs (Your answers should only include x_{oil}, H, and P^{sat}). Assume the liquid and vapor behave ideally save for the use of Henry's law for the oil in the liquid state

12

What is the molecular basis for oil's partial pressure being dependent on a Henry's law constant, and not its pure vapor pressure, when the oil is very dilute?

4

$$y_{oil} P = x_{oil} H$$

$$y_w P = x_w P^{sat}$$

$$\sum y_i P = P = x_{oil} H + x_w P^{sat}$$

$$\boxed{P = x_{oil}(H - P^{sat}) + P^{sat}}$$

$$y_{oil} = \frac{x_{oil} H}{P}$$

$$\boxed{y_{oil} = \frac{x_{oil} H}{x_{oil}(H - P^{sat}) + P^{sat}}}$$

$$y_w = \frac{x_w P^{sat}}{P} = \frac{(1 - x_{oil}) P^{sat}}{P}$$

$$\boxed{y_w = \frac{(1 - x_{oil}) P^{sat}}{x_{oil}(H - P^{sat}) + P^{sat}}}$$

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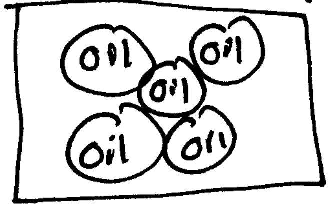
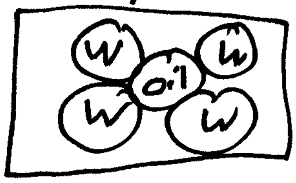
-cause of Henry's Law:

Solvent boxes:

Raoult's Law/ Pure Component



Henry's Law



- In the case of pure oil, oil is always surrounded by other molecules. For Henry's Law however, it is always surrounded by water molecules
- What governs the volatility of oil is in part determined by its molecular interactions with neighboring molecules. In Henry's Law, this is water molecules, not other oil molecules. Therefor, P^{sat}_{oil} would be a poor descriptor of oil's volatility if it was dilute. Instead, we use a Henry's Law constant, H