

Key

Exam #1

Name James

Student ID \_\_\_\_\_

Exam Guidelines:

- Non-graphing calculator and pencil/pens are permitted.
- One 8.5 x 11" sheet of paper with only your own handwriting is allowed (one side only).
- No textbook or other resources.
- All other materials, books, and cell phones should be zipped in your backpack.
- Show all your work and provide complete explanations to receive credit.
- Time = 50 minutes

Extra Space for your work below:

Problem	Estimated Time	Score	Possible
1	15 min		22
2	15 min		20
3	15 min		18
XC	5 min		4

1. The vaporization curve of liquid naphthalene (the main component of mothballs) is described by the Antoine equation:  $\ln P^{\text{sat}} = A - \frac{B}{T}$ , where  $A = 9.84$  and  $B = 4218$ , where pressure is in bar and temperature in K.

- a. Calculate the boiling point of naphthalene at 1 bar (4 pts)

$$\ln(1) = 9.84 - \frac{4218}{T}$$

$$-9.84T = -4218$$

$$T = 429 \text{ K}$$

- b. The vapor pressure of naphthalene at room temperature (292 K) is  $5.9 \times 10^{-5}$  bar. Can you assume that the vapor is ideal? Why? (3 pts)

$P = 5.9 \times 10^{-5} \text{ bar}$  ← this is low pressure  $\approx 5.9 \times 10^{-5} \text{ atm}$   
 Gas is "more" ideal at low pressures and high Temp.  
 Assume ideal

- c. Write out an equation for the sublimation curve of the form  $\ln P = A + B/T$ , assuming:
- The enthalpy of sublimation of naphthalene is constant at 71.3 kJ/mol.
  - The volume of the solid is negligible and the vapor is ideal. (8 pts)

Clausius Clapeyron (assume valid for sublimation)

$$\ln \frac{P_2}{P_1} = \frac{-\Delta H_{\text{sub}}}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\ln \frac{P_2^{\text{sat}}}{P_1^{\text{sat}}} = \ln \left( \frac{5.9 \times 10^{-5}}{1} \right) = \frac{-71300 \text{ J}}{8.314 \text{ J/mol K}} \left( \frac{1}{T_2} - \frac{1}{292 \text{ K}} \right)$$

$$\ln \frac{P_2^{\text{sat}}}{P_1^{\text{sat}}} = -\frac{8580}{T} + 29.37 - 9.74$$

$$\ln P = 19.6 - \frac{8580}{T}$$

- d. Calculate the temperature of the triple point of naphthalene. (7 pts)

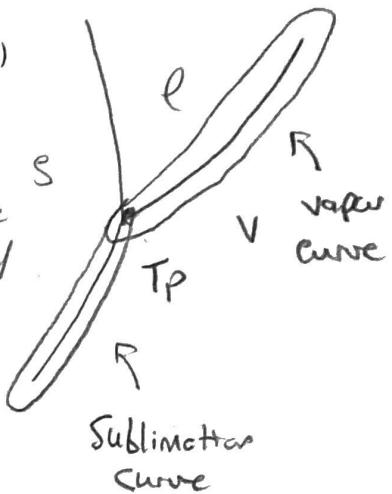
the triple point  $T$  is when

Sublimation curve = Vapor curve

their saturation pressures ( $\ln P$ ) will be the same  
the triple pt thus triple pt temp can be found

$$19.6 - \frac{8580}{T_p} = 9.84 - \frac{4218}{T_p}$$

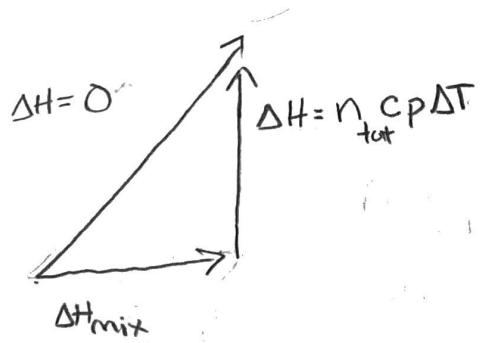
$$\text{solving, } T_p = 444 \text{ K}$$



2. 1.5 mol of water and 1 mol of acetone are mixed at 30 °C.

- a. Draw a schematic of the thermodynamic cycle (hypothetical path) you can use to calculate the final temperature of the mixture. You may assume that the mixing is adiabatic. (6 pts)

adiabatic mixing  $\Delta H = 0$



- b. The enthalpy of mixing acetone and water is shown in the graph. Estimate the following quantities. Show your work on the graph. (8 pts)

$$\Delta h_{\text{mix}} = -200 \text{ J/mol} \quad (\text{molar enthalpy of mixing})$$

$$\Delta H_{\text{mix}} = -500 \text{ J} \quad (\text{enthalpy of mixing}) \quad \Delta H_{\text{mix}} = n_{\text{tot}} \Delta h_{\text{mix}} = (2.5 \text{ mol})(-200 \text{ J/mol})$$

$$\overline{\Delta H}_{\text{mix,acetone}} = -880 \text{ J/mol} \quad (\text{partial molar enthalpy of mixing of acetone})$$

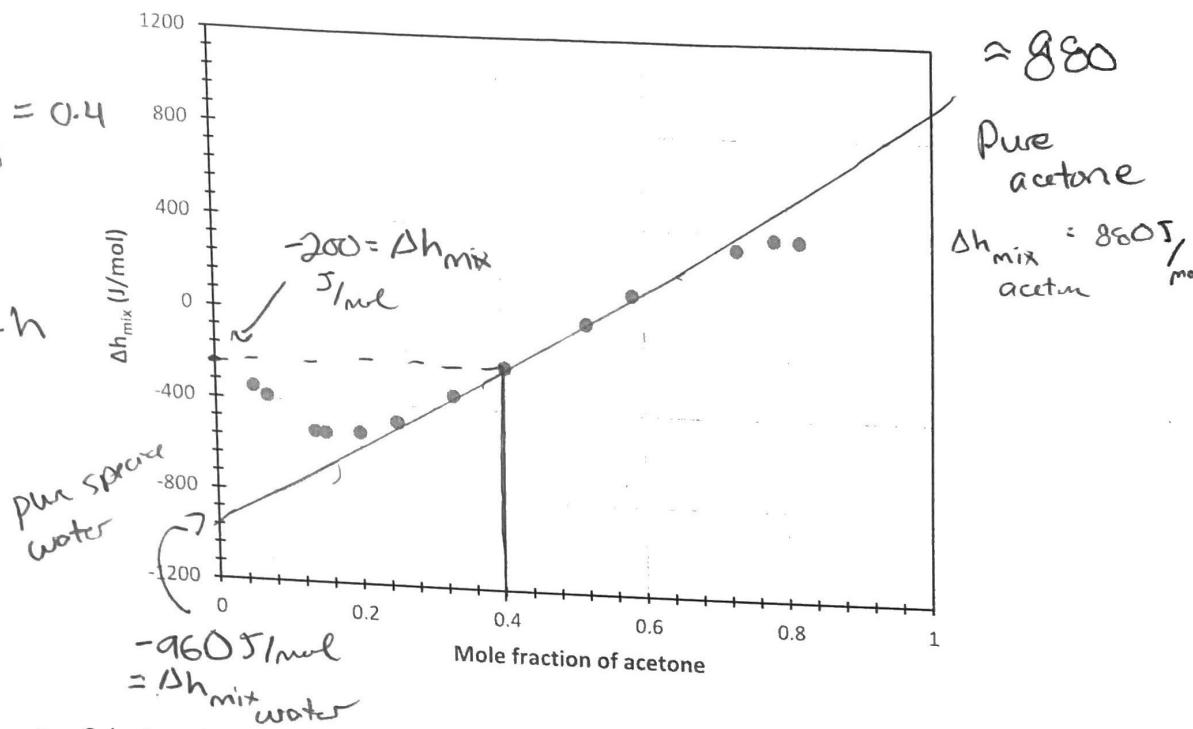
$$\overline{\Delta H}_{\text{mix,water}} = -1960 \text{ J/mol} \quad (\text{partial molar enthalpy of mixing of water})$$

$$\overline{\Delta H}_{\text{mix,acetone}} = \text{graph at } x_a = 1 \text{ mol}$$

$$\overline{\Delta H}_{\text{mix}} = x_a^{\text{init}} \overline{\Delta H}_{\text{mix,acetone}} + x_a = 0$$

$$\chi_a \text{ acetone} = \frac{1}{1+1.5} = 0.4$$

$$\Delta h_{mix} = \bar{H} - \bar{h}$$



- c. Calculate the final temperature of the mixture. You may assume that the heat capacity of the mixture is  $94.8 \text{ J mol}^{-1} \text{ K}^{-1}$ . (6 pts)

$$n_{tot} \Delta h_{mix} + n_{tot} C_p (T_f - T_i) = 0$$

$$30^\circ\text{C} = 303 \text{ K}$$

$$n_{tot} (\Delta h_{mix} + C_p (T_f - T_i)) = 0$$

$$(2.5 \text{ mol}) \left( -200 \frac{\text{J}}{\text{mol K}} + \frac{94.8 \text{ J}}{\text{mol K}} (T_f - 303 \text{ K}) \right) = 0$$

$$T_f = 305 \text{ K}$$

3. The molar volume of mixtures of benzene and cyclohexane is equal to:

$$v = 89.2x_{BZ} + 108x_{CH} + 2.2x_{BZ}x_{CH} \text{ [cm}^3/\text{mol]}$$

- a. Show that the partial molar volume of cyclohexane is equal to  $\bar{V}_{CH} = 108 + 2.2x_{BZ}^2$  [cm<sup>3</sup>/mol] (8 pts)

$$\bar{V}_{CH} = 108 + 2.2x_{BZ} + 108x_{CH} + 2.2x_{BZ}x_{CH}$$

replace X with n

$$\underline{\bar{V}_{CH} = \frac{108 + 2n_{BZ} + 108n_{CH} + 2.2n_{BZ}n_{CH}}{(n_{BZ} + n_{CH})}}$$

memorize this derivation!

$$\bar{V}_{CH} = \left( \frac{\partial \bar{V}_{CH}}{\partial n_{CH}} \right)_{T, P, n_{BZ}} = \frac{108 + 2.2n_{BZ}}{(n_{BZ} + n_{CH})}$$

$$\bar{V}_{CH} = 108 + 2.2x_{BZ}(1+x_{CH}) \quad \text{factor out } 2.2 \left( \frac{n_{BZ}}{n_{BZ} + n_{CH}} \right)$$

$$\bar{V}_{CH} = 108 + 2.2x_{BZ}^2$$

- b. For a mixture of 4 mol benzene and 1 mol cyclohexane, calculate the: (6 pts)

- i. Total volume V

$$V = nV$$

$$x_{BZ} = \frac{4}{4+1} = 0.8$$

$$x_{CH} = \frac{1}{4+1} = 0.2$$

$$V = nv = (5) [89.2(0.8) + 108(0.2) + 2.2(0.8)(0.2)]$$

$$V = 466.56 \text{ cm}^3$$

- ii. Partial molar volume of cyclohexane  $\bar{V}_{CH}$  (you may use the result from above)

$$\bar{V}_{CH} = 108 + 2.2x_{BZ}^2$$

$$= 108 + 2.2(0.8)^2 = 109.4 \text{ cm}^3/\text{mol}$$

- iii. Molar volume of pure benzene  $v_{BZ}$

$$v_{BZ} = 89.2(1) + 108(0) + 2.2(1)(0)$$

$$\underline{v_{BZ} = 89.2 \text{ cm}^3/\text{mol}}$$

$$x_{BZ} = 1$$

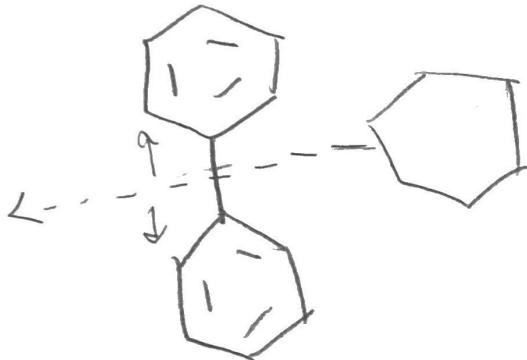
$$x_{CH} = 0$$

- c. Are the intermolecular interactions in the mixture between benzene and cyclohexane stronger or weaker than the intermolecular interactions in the pure species? Why? (4 pts)

weaker  
can also calculate  $\Delta V_{\text{mix}} = V - \{y_i v_i\}$   
if  $\Delta V_{\text{mix}} = +$ ,  
they are weaker

$B_7/B_7$  are nonpolar and will have higher intermolecular interactions with each other than the cyclohexane, which will overall weaken the  $B_7/B_7$  bond.  
 $\Delta V_{\text{mix}}$  is expected to increase as a result

- d. Extra credit: Draw the structures of benzene and cyclohexane and show how benzene molecules interact with each other and how cyclohexane changes this interaction. (+4 pts)



Exam #1

Name \_\_\_\_\_

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**Exam Guidelines:**

- Open notes, open book, open internet
- NO COLLABORATION!
- Show all your work and provide complete explanations to receive credit.
- Upload on gradescope

Problem	Estimated Time	Score	Possible
1	15 min		12
2	20 min		18
3	10 min		10
Total			40

Extra Space for your work below:

Useful thermodynamic data:

Sublimation point of dry ice at 1 atm: -78 °C

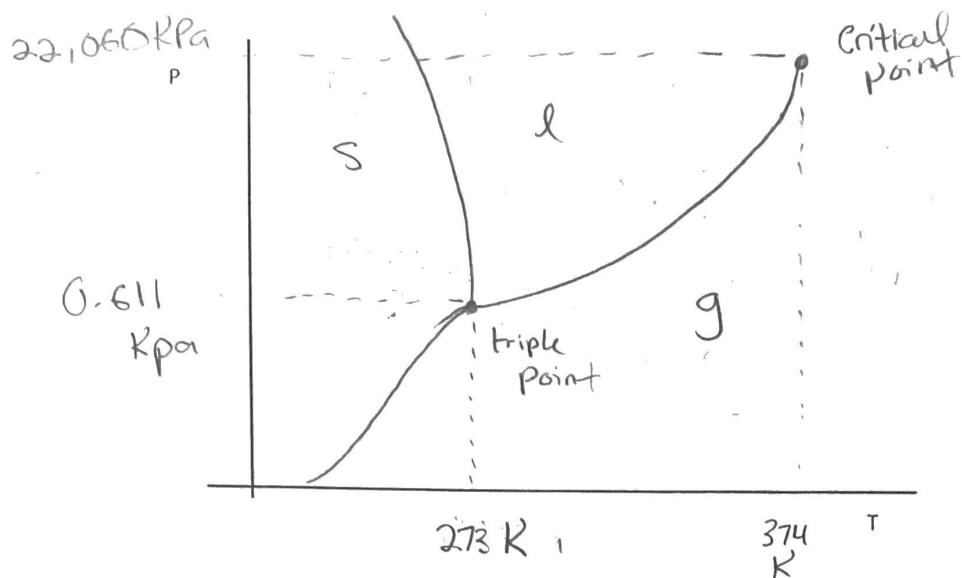
Melting point of acetone: -94 °C

Enthalpy of sublimation of CO<sub>2</sub>:  $\Delta\hat{h}_{\text{sub}} = 571 \text{ J/g}$

Density of acetone: 784 kg/m<sup>3</sup>.

Heat capacity of acetone:  $\hat{c}_{p,\text{ace}} = 2.17 \text{ J g}^{-1} \text{ K}^{-1}$

1. Draw a P-T phase diagram for water. Label the critical and triple points, along with their coordinates. (4 pts)



- a. Why is the slope of the solid-liquid equilibrium line negative? (4 pts)

the density of water as a solid < density as liquid  
therefore as pressure increases the T melting decreases

- b. Calculate the specific (i.e. per kg) Gibbs free energy of liquid water and water vapor at 200 °C and 400 kPa. Which phase is more stable? (4 pts)

During COVID, open internet  
look up  $\hat{h}^l$ ,  $\hat{h}^v$ ,  $\hat{s}^l$  and  $\hat{s}^v$  in steam tables at 200°C and 400kPa

$$\hat{g}^l = \hat{h}^l - T \hat{s}^l$$

more stable = smaller  $\hat{g}$

$$\hat{g}^v = \hat{h}^v - T \hat{s}^v$$

2. Mixtures of acetone and dry ice (solid CO<sub>2</sub>) are often used to cool down reactions in a lab setting. An insulated thermos beaker of acetone is filled with 100 mL acetone at 20 °C. You slowly add a piece of dry ice (2 g, at -78 °C) into the acetone. You can assume that the acetone quantity remains constant.

a. What is the temperature of the acetone after all the CO<sub>2</sub> has sublimed away? (8 pts)

$$\Delta H_1 + \Delta H_2 = 0$$

$$100 \text{ mL acetone} \frac{0.784 \text{ g}}{\text{mL}} = 78.4 \text{ g acetone}$$

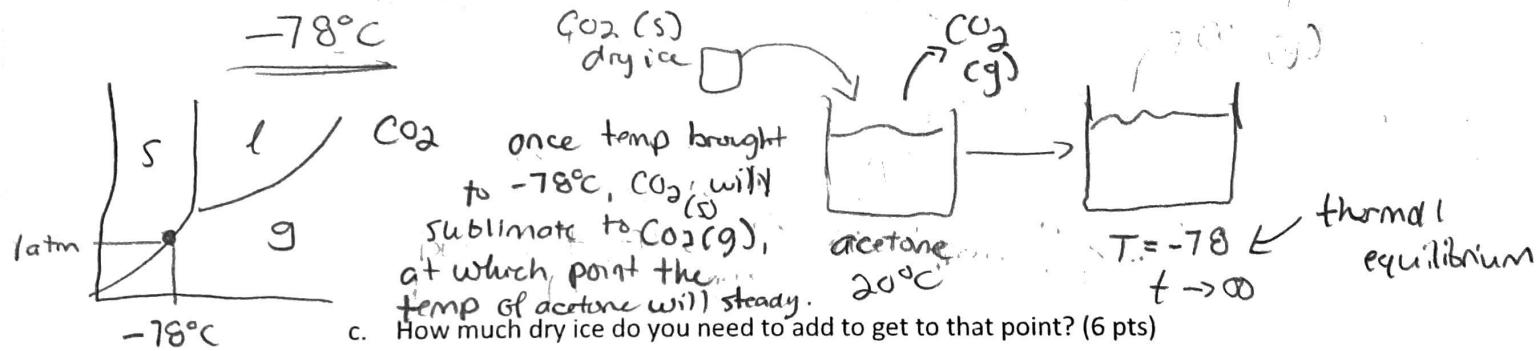
$$C_p = 2.175 \frac{\text{J}}{\text{gK}}$$

$$m_{\text{ace}} C_p \Delta T + m_{\text{CO}_2} \hat{\Delta h}_{\text{sub}} = 0$$

$$(78.4 \text{ g}) \left( \frac{2.175}{\text{gK}} \right) (T_f - 293 \text{ K}) + 2 \text{ g} \left( \frac{571 \text{ J}}{\text{g}} \right) = 0$$

$$T_f = 286 \text{ K} \approx 13^\circ\text{C}$$

- b. You keep adding dry ice until the temperature stabilizes and there is an infinitesimally small piece of dry ice. What temperature will the system be at? Why? (4 pts)



- c. How much dry ice do you need to add to get to that point? (6 pts)

$$m_{\text{ace}} C_p \Delta T + m_{\text{CO}_2} \hat{\Delta h}_{\text{sub}} = 0$$

$$m_{\text{CO}_2} = - \frac{m_{\text{ace}} C_p \Delta T}{\hat{\Delta h}_{\text{sub}}} = - \frac{(78.4) \left( \frac{2.175}{\text{gK}} \right) (-78 - 20)}{571 \text{ J/g}}$$

$$m_{\text{CO}_2} = 29.2 \text{ g CO}_2$$

3. The enthalpy of mixing of components A and B is given by the formula  $\Delta h_{\text{mix}} = C(x_A^2)$ , where C is a constant and  $x_A$  is the mole fraction of component A.

- a. Derive a formula for the partial molar enthalpy of mixing of components A and B, expressed as a function of  $x_A$  and/or  $x_B$ . (6 pts)

$$\Delta h_{\text{mix}} = C(x_A^2)$$

$$n_{\text{tot}} = n_A + n_B$$

$$x_A = \frac{n_A}{n_A + n_B}$$

$$\Delta H_{\text{mix}} = n_{\text{tot}} \Delta h_{\text{mix}} = (n_A + n_B) C x_A^2 = C(n_A + n_B) \frac{n_A^2}{(n_A + n_B)^2} = C \frac{n_A^2}{n_A + n_B}$$

$$\Delta \bar{H}_{\text{mix},A} = \left( \frac{\partial \Delta H_{\text{mix}}}{\partial n_A} \right)_{T, P, n_B} = C \frac{(n_A + n_B) 2n_A - n_A^2}{(n_A + n_B)^2} = C \left[ \frac{2n_A(n_A + n_B)}{(n_A + n_B)^2} - \frac{n_A^2}{(n_A + n_B)^2} \right]$$

$$\Delta \bar{H}_{\text{mix}, A} = C \left( \frac{2n_A}{n_A + n_B} - \frac{n_A^2}{(n_A + n_B)^2} \right) = 2C x_A \left( 1 - \frac{x_A^2}{2} \right)$$

- b. Is the formula given thermodynamically consistent? (4 pts)

yes if I rewrite as

$$\Delta \bar{H}_{\text{mix}, A} = 2Cx_A - Cx_A^2$$

$\Delta \bar{H}_{\text{mix}, A} = Cx_A$    
 Answer in terms of  $x_A$

this is  $\Delta h_{\text{mix}}$

Cx\_A

Name \_\_\_\_\_

**Exam #1****Exam Guidelines:**

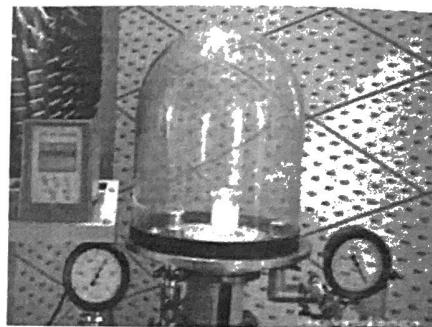
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- Time = 50 minutes

Problem	Estimated Time	Score	Possible
1	10 min		20
2	10 min		20
3	30 min		60
<b>Total</b>			<b>100</b>

Extra Space for your work below:

1. Answer each of the following questions. Your score will be based on how well you demonstrate your understanding of thermodynamics in your explanations.

- A. In class, we saw a video of water placed in a vacuum. What caused the water to rapidly boil when vacuum was achieved, as shown in the picture? To receive full credit, you must use "Gibbs energy" in your answer.



Under atm pressure, water molecules not enough energy

under vacuum, water molecules have more energy to boil

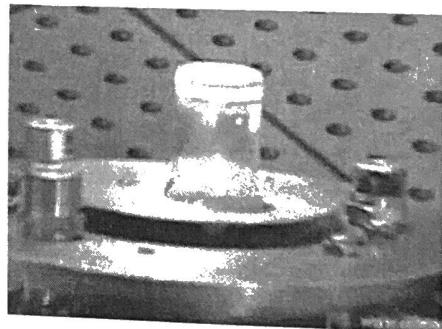
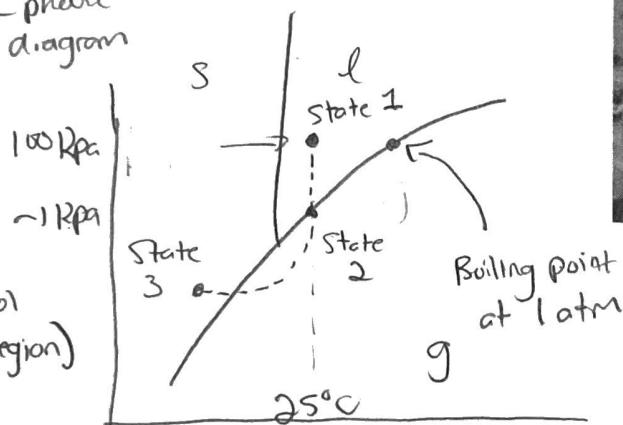
in the absence of air pressure, thus  $g \rightarrow g'$ .  
as pressure decreases and  $T$

If pressure remains constant, the boiling point Temp decreases (state 2)  
See figure below

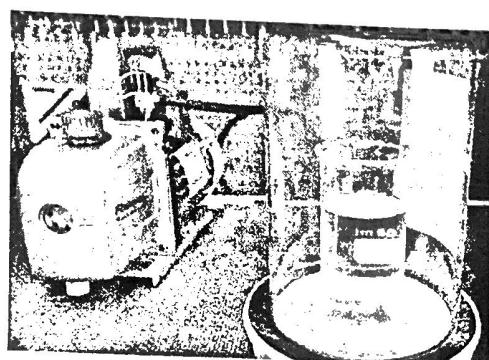
- B. At the end of the process, there was ice formed in the beaker, as shown in the picture. Using thermodynamics, explain why the ice formed.

Consider the phase diagram

It then freezes  
because the water  
loses thermal energy  
from itself after evaporating  
(endothermic) so it will cool  
down to state 3 (solid region)



- C. A student in the class found a video on YouTube that we watched which showed water boiling but did not show ice form. Why? Use your understanding of thermodynamics in your explanation.



- D. Do we add sulfuric acid to water or water to sulfuric acid when mixing? Explain.

Sulfuric acid to water. Extremely exothermic and better to add acid to large volume of water to dilute initially rather than have large concentration initially of Sulfuric acid

- E. In studio 3, you did an experiment where you mixed ethanol and water. Is it better to add ethanol to water or water to ethanol? Explain.

water to ethanol. Water has higher density so will mix more completely

2. Consider a binary mixture of 2 moles species 1 and 3 moles species 2 at 20 °C. The volume is given by the following equation

$$y_1 = \frac{2}{2+3} = 0.4$$

$$y_2 = \frac{3}{2+3} = 0.6$$

$$v = 75y_1 + 50y_2 - 7.5y_1y_2 \left[ \frac{\text{cm}^3}{\text{mol}} \right]$$

- A. Determine numerical values for the following:

i.  $v = \frac{nV}{\text{tot}} = 5(75(0.4) + 50(0.6) - 7.5(0.4)(0.6))$

$V = 291 \text{ cm}^3$        $v = 58.2 \frac{\text{cm}^3}{\text{mol}}$

ii.  $v_1 = 75(0.4)$        $v_2 = 50(0.6)$

$v_1 = 75 \frac{\text{cm}^3}{\text{mol}}$        $v_2 = 50$

iii.  $\Delta v_{\text{mix}} = v - \sum y_i v_i$        $\Delta v_{\text{mix}} = 58.2 \frac{\text{cm}^3}{\text{mol}} - ((75)(0.4) + (50)(0.6))$

$$\Delta v_{\text{mix}} = v - (y_1 v_1 + y_2 v_2)$$

$\Delta v_{\text{mix}} = -1.8 \frac{\text{cm}^3}{\text{mol}}$

- B. Select which of the following is correct and explain your reasoning

$\Delta v_{\text{mix}} = - \rightarrow \bar{v}_i < v_i$

$\Delta v_{\text{mix}} = 0 \rightarrow \bar{v}_i = v_i$

$\Delta v_{\text{mix}} = + \rightarrow \bar{v}_i > v_i$

for a  $\Delta v_{\text{mix}} = \text{negative}$ , the partial molar volume is less than pure species molar volume

$$\bar{v}_i = \frac{v_i}{n_1 + n_2} = 75 - 7.5y_2^2 = 75 - 7.5(0.6)^2$$

$$\bar{v}_i = 72.3 \frac{\text{cm}^3}{\text{mol}}$$

$$v_i = \frac{v}{n_1 + n_2} \bar{v}_i > v_i \quad \bar{v}_i > v_i \quad v_i = 75 \frac{\text{cm}^3}{\text{mol}}$$

proven through meth