

All questions are worth 10 points each. Answer all questions clearly, and show all work. Be sure to clearly number each answer and to draw lines to separate answers to different questions. If you use the back side of the paper, please clearly indicate the number of the question you are answering. Please also remember that I can only grade what I can read. Useful mathematical relations and values of constants not given in the questions are given on a separate page.

1. Classify the following statements as TRUE/FALSE:

(a)	The total volume of a solution made by mixing two miscible liquids is always the sum of the volumes of the two liquids.	<b>TRUE</b>	<b><u>FALSE</u></b>
(b)	Binary liquid systems that show positive deviation from Raoult's law will give rise to solutions that boil at temperatures lower than either of the pure liquids.	<b><u>TRUE</u></b>	<b>FALSE</b>
(c)	The triple-point on a one-component phase diagram has three degrees of freedom.	<b>TRUE</b>	<b><u>FALSE</u></b>
(d)	Enthalpy of sublimation is the sum of the enthalpies of fusion and vaporization.	<b><u>TRUE</u></b>	<b>FALSE</b>
(e)	A ternary phase diagram drawn on triangular graph paper corresponds to a fixed $T$ and $P$ .	<b><u>TRUE</u></b>	<b>FALSE</b>

2. Benzene and toluene form nearly ideal solutions. Calculate the vapor pressure of the solution at 300 K of a solution containing 0.600 mole fraction of toluene. [At 300 K,  $P^*_{\text{Toluene}} = 3.572$  kPa,  $P^*_{\text{Benzene}} = 9.657$  kPa]

$$P = 0.600 \times 3.572 \text{ kPa} + (1.000 - 0.600) \times 9.657 = 6.006 \text{ kPa}.$$

3. What is the composition of the vapor in equilibrium with the solution in Q. 2?

$$y_T = \frac{P_T}{P} = \frac{0.600 \times 3.576 \text{ kPa}}{6.006 \text{ kPa}} = 0.357.$$

$$y_B = 1 - y_T = 0.643.$$

4. The  $\Delta_{\text{vap}}H^\circ$  of Freon-12 ( $\text{CF}_2\text{Cl}_2$ ) at its normal boiling point of  $-29.2^\circ\text{C}$  is  $20.25\text{ kJ mol}^{-1}$ . Estimate the minimum pressure a can of hair spray with Freon-12 has to withstand at  $40^\circ\text{C}$ , the temperature of a can that has been standing in sunlight on a mild day. Assume that  $\Delta_{\text{vap}}H^\circ$  is constant over the temperature range considered.

The vapor pressure at the normal boiling point is equal to the atmospheric pressure.

Let  $P_1 = 1.000\text{ atm}$ , corresponding to  $T_1 = 243.95\text{ K}$ .  $T_2 = 313.15\text{ K}$ .

$$\ln\left(\frac{P_2}{P_1}\right) = \frac{25,200\text{ J mol}^{-1}}{8.3145\text{ J K}^{-1}\text{ mol}^{-1}}\left(\frac{1}{243.95} - \frac{1}{313.15}\right)\text{ K}^{-1}$$

$$P_2 = P_1 \times e^{2.2057} = 1.000\text{ atm} \times e^{2.2057} = 9.08\text{ atm}.$$

5. The boiling point of benzene is raised from its normal value of  $80.1$  to  $82.4^\circ\text{C}$  by the addition of  $13.76\text{ g}$  of biphenyl to  $100.00\text{ g}$  of benzene. Find the value of  $K_b$ , the boiling-point-elevation constant for benzene. [Molar masses: biphenyl:  $154.21\text{ g mol}^{-1}$ ; benzene:  $78.11\text{ g mol}^{-1}$ .]

Given:  $\Delta T_b = K_b m$ , where  $m$  is the molality.

$$\Delta T_b = 2.3\text{ K}. \quad K_b = \frac{\Delta T_b}{m}.$$

Molality = moles of solute per kilogram of solvent, by definition.

$$m = \left(\frac{13.76\text{ g}}{154.21\text{ g mol}^{-1}}\right) \times \frac{1}{0.1\text{ kg}} = 0.892\text{ mol kg}^{-1}.$$

$$\text{Therefore, } K_b = 2.3\text{ K}/(0.892\text{ mol kg}^{-1}) = 2.577\text{ K mol}^{-1}\text{ kg}$$

6. How many components are present in a system of  $\text{CaCO}_3(\text{s})$ ,  $\text{CaO}(\text{s})$  and  $\text{CO}_2(\text{g})$ , if we start with pure  $\text{CaCO}_3$  and heat it up?



Since we start with pure  $\text{CaCO}_3(\text{s})$ ,  $\text{CaO}(\text{s})$  and  $\text{CO}_2(\text{g})$  will always be formed in 1:1 ratio. Therefore,  $o = 1$ .

Therefore, number of components:  $c = n - e - o = 3 - 1 - 1 = 1$ .

7. A mixture of two almost completely immiscible liquids boils at a temperature lower than the boiling points of either of the two liquids. Why?

Since the liquids are practically immiscible, the mole fractions of each liquid in one layer is almost 1, and almost 0 in the other. Therefore, the total vapor pressure exerted by the two liquids will be the sum of their vapor pressures:

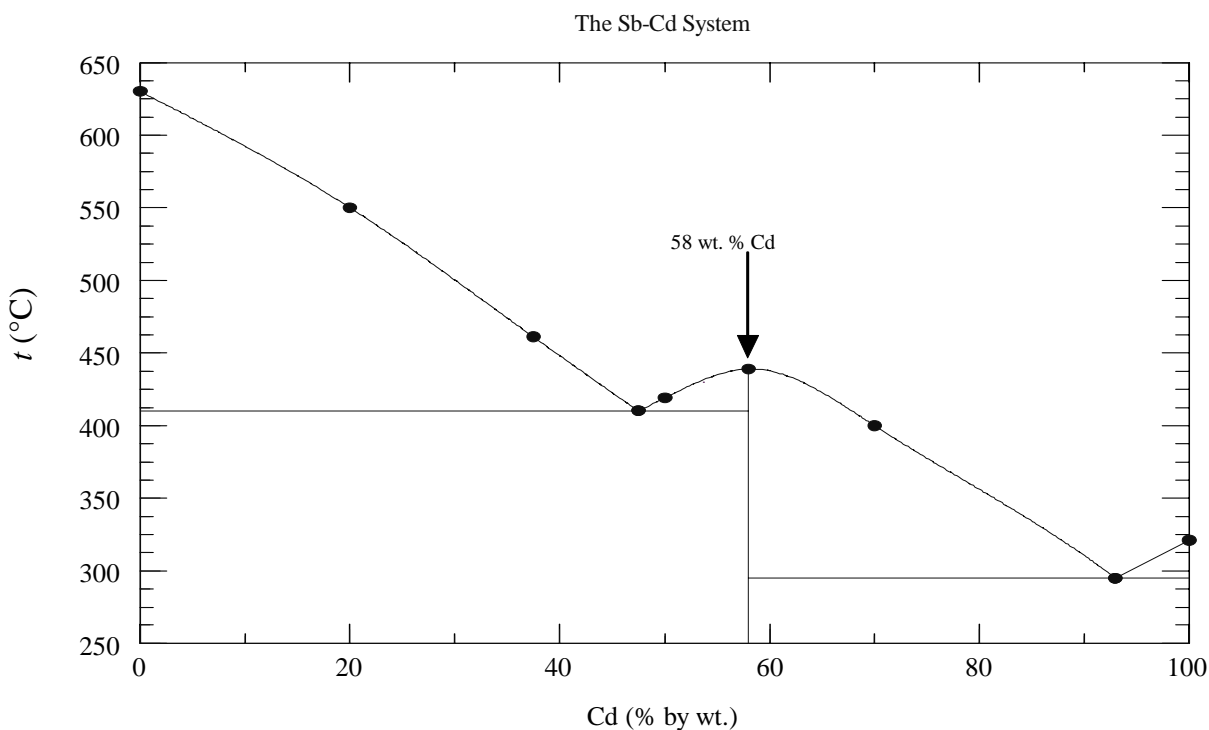
$$P = P_A^* + P_B^*.$$

Since the sum is greater than either of the pure vapor pressures, the liquid will boil at a temperature lower than either of the boiling points of the pure liquids.

8. Water and aniline are partially miscible in each other at low temperatures, but become increasingly more miscible as temperature increases, and have an upper critical solution point of ( $x_{\text{Aniline}} = 0.450$  and  $T_{\text{uc}} = 440 \text{ K}$ ). Sketch a qualitatively correct phase diagram for this system based on this information. Be sure to clearly indicate the quantities represented on each axis, and also the number of phases in each region.

See Fig. 6.12, p. 241

9. The phase diagram of the Cadmium-Antimony system is given below. Label all the areas of this diagram. If necessary, find the formula of any compounds formed in order to complete the labeling. [Atomic weights: Sb = 121.757 g mol<sup>-1</sup>, Cd = 112.411 g mol<sup>-1</sup>.]



See solution to HW 8, Q. 3.

10. The ternary phase diagram for *n*-heptane, methylcyclohexane, and aniline is given on the next page. The axes are labeled in wt % of the various components.

- Draw tie-lines connecting the compositions in equilibrium with each other (two tie-lines cannot intersect).
- Which of the two liquids (if any) are completely miscible with each other in all proportions?

*n*-heptane and methylcyclohexane.

- If a solution is prepared by mixing together 25 g of *n*-heptane, 35 g of aniline and 40.0 g of methylcyclohexane, how many phases will be present?

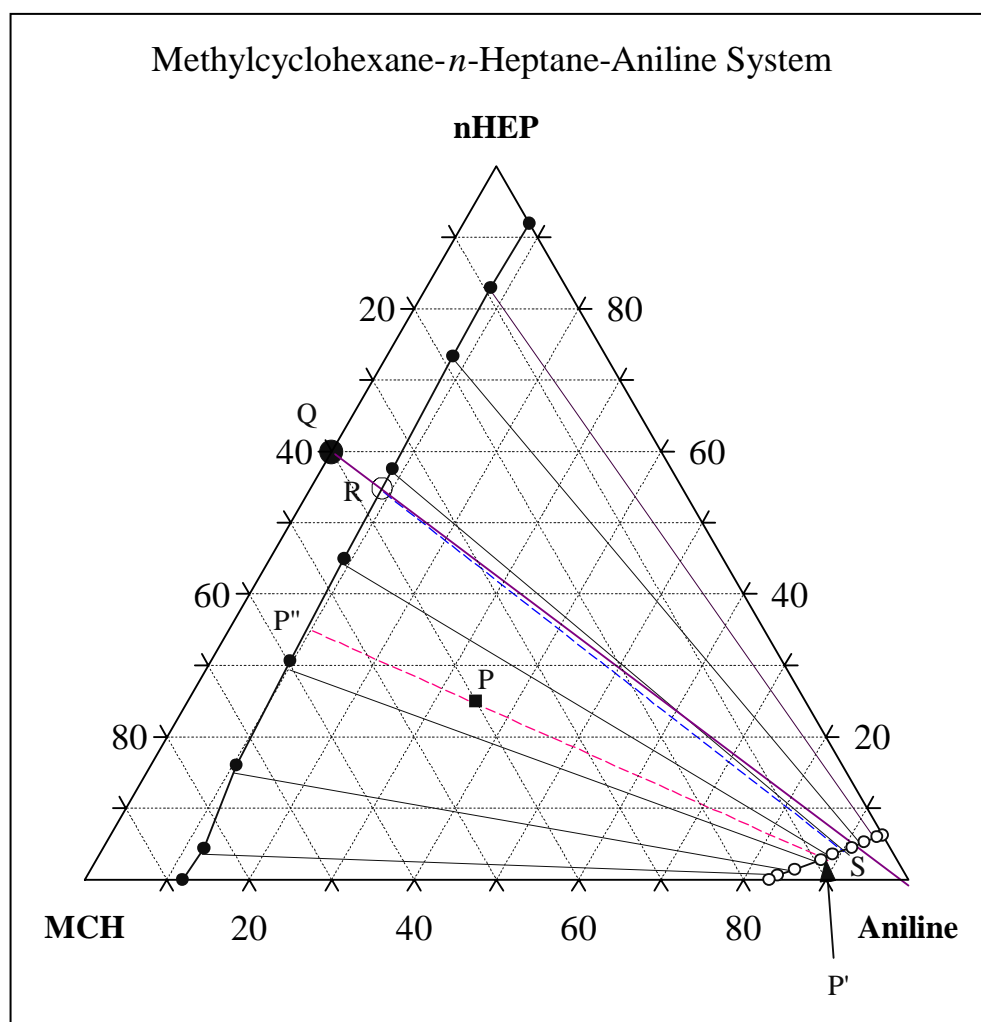
Two phases. See point *P* on the graph.

- A 40% by weight solution of methylcyclohexane in *n*-heptane is prepared. How many phases are present?

One phase. Point *Q* on the graph.

(e) If aniline is added to the solution in part (d) above, at what composition will a new phase appear?

When the composition reaches the point R, a new phase will appear. The composition, in terms of wt %, at this point is approximately (37 % MCH, 54 % n-heptane, 9 % aniline).



**11. BONUS QUESTION:**

Let us take another look at the phase diagram in Q. 9. Sketch cooling curves that would result when solutions with the following compositions are cooled from some temperature higher than 650 °C:

(a) 0 wt% Cd, (b) 20 wt% Cd, (c) 48 wt% Cd (the first Eutectic), (d) 50 wt% Cd, (e) 58 wt% Cd

See the left-hand side of Fig. 6.17 to see how to draw cooling curves.

**Constants, conversion factors, and Useful Mathematical Relations:**

Gas constant  $R = 0.083145 \text{ L bar K}^{-1} \text{ mol}^{-1} = 8.3145 \text{ J K}^{-1} \text{ mol}^{-1}$ .

$$1 \text{ bar} = 10^5 \text{ Pa}$$

$$1 \text{ L} = 1 \text{ dm}^3 = 10^3 \text{ cm}^3 = 10^{-3} \text{ m}^3$$

- For a binary liquid system comprised of components  $A$  and  $B$ ,

Raoult's Law:  $P_A = x_A P_A^*$ ,

Dalton's Law:  $P_A = y_A P$ ,

Bubble Point Line:  $P = x_A P_A^* + (1 - x_A) P_B^*$ ,

Dew Point Line:  $P = P_A^* P_B^* / [P_A^* + (P_B^* - P_A^*) y_A]$ ,

- The Clausius-Clapeyron equation:

$$\ln \frac{p_2}{p_1} = \frac{\Delta_{vap} H_m^\circ}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right).$$

- Boiling point elevation:

$$\Delta T_b = K_b m,$$

where  $m$  is the molality.

- The number of components in a system:  $c = n - e - o$ , where  $n$  = number of chemical species,  $e$  = number of equilibria between them, and  $o$  = number of other relationships between them.