

CHEM 323
Fall 2008
Take-Home Portion of Exam 2

Name: _____

Instructions

Write your answers in blue or black ink. Work done in pencil will be accepted, but you will not be able to appeal any apparent grading mistakes (except simple addition errors). Write neatly. If I can't read it, I can't grade it. Helpful hint: do your work on a separate sheet of paper and then copy your final answer to this booklet.

Show all work for full credit! For the word problems write your final answer in complete sentences. Indicate what you are doing at important steps (you do not need to tell me about every mathematical manipulation you do). Make all final graphs in Excel and please attach a copy of your completed worksheets at the end of this exam.

Before beginning this exam, download the file TakeHome2.xls from the class web page (under *Announcements*). Note that the data may not be presented to you in the form that you will ultimately need!

There are **11** pages, **1** blank.

You may use your book to look up any needed physical constants, equations, etc. However, you may not work with anyone else, and you may not ask any other faculty members to help you with the specific questions given here. You may ask any chemistry faculty member for help on the concepts involved, and you may ask me anything you want.

You may use the back of any page as additional workspace. Please indicate that you have done so.

Problem	Possible Points	Points Received
1	32	
2	27	
3	13	
4	18	
Worksheets	5	
Free	5	5
Total	100	
	Bonus	
	Grand Total	

1. The vapor pressures of CS₂ and methylal (dimethoxymethane, C₃H₈O₂) mixtures as a function of the CS₂ mole fraction at 35.17 °C are given in the first worksheet of TakeHome2.xls.

a. (18 Points) Fit the data to Raoult's Law and Henry's Law for each component. Prepare two graphs; one showing the fits for CS₂ and the other showing the fits for methylal. Both graphs must have the mole fraction of CS₂ as the x axis. Label each line as the Raoult's Law or the Henry's Law line. Tape these in the space provided below and on the next page. Fill in your results (along with the uncertainties at 95% confidence) in Table 1.

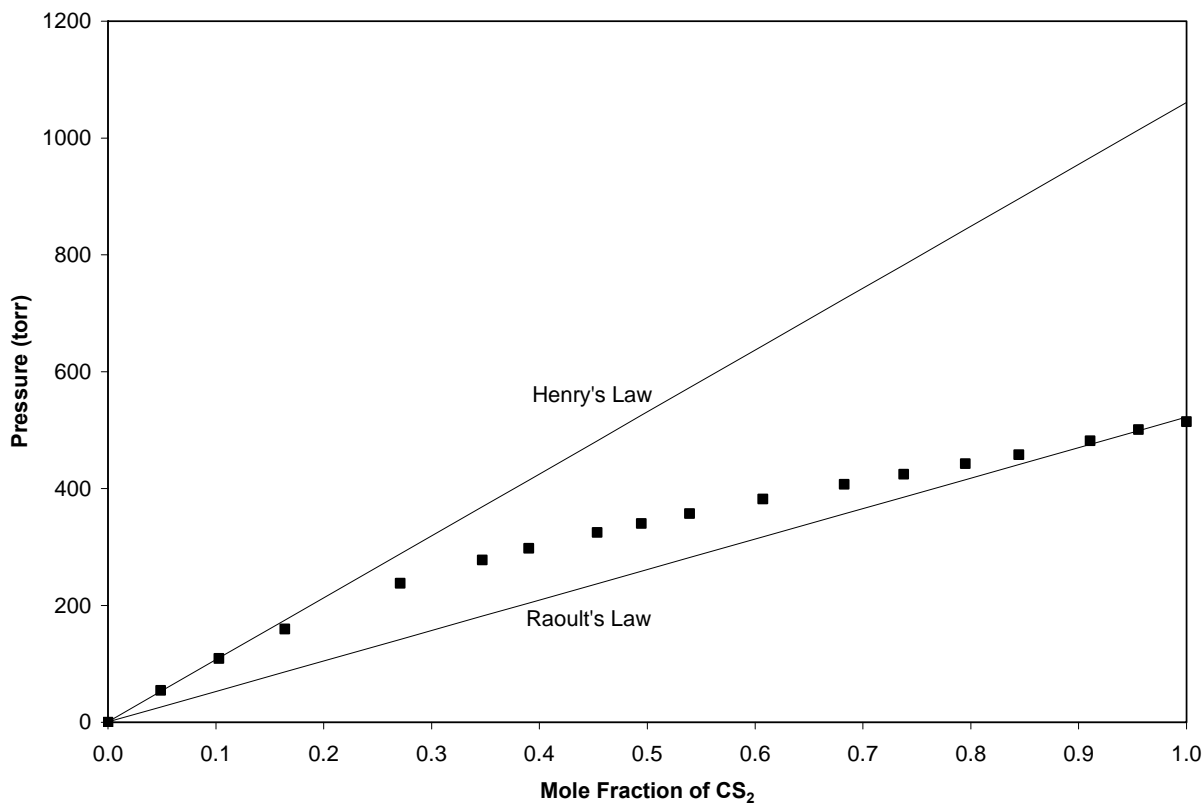


Figure 1. Best fit lines showing Henry's Law and Raoult's Law behavior for CS₂ in the CS₂-methylal system. Values for the vapor pressure of CS₂ and its Henry's Law constant in methylal are given in Table 1.

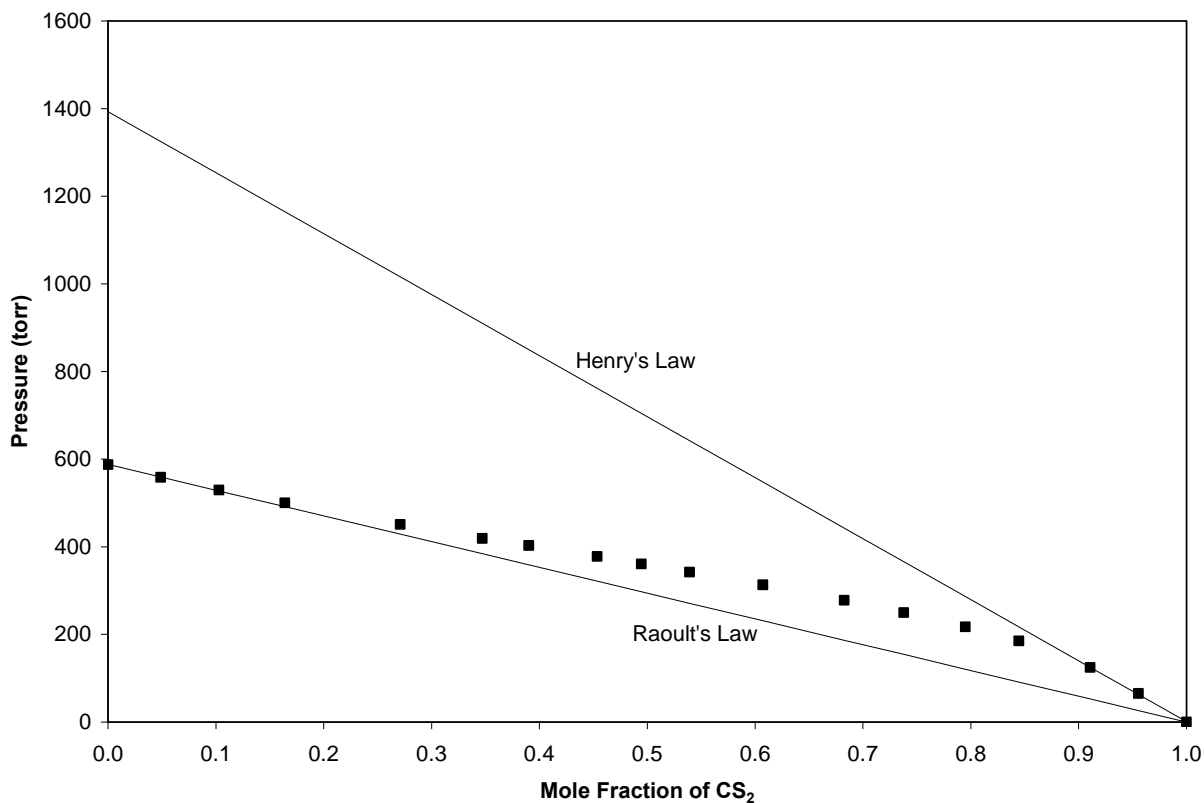


Figure 2. Best fit lines showing Henry's Law and Raoult's Law behavior for methylal in the CS₂-methylal system. Values for the vapor pressure of methylal and its Henry's Law constant in CS₂ are given in Table 1.

	CS ₂	Methylal
Henry's Law Constant (torr)	(1.06 ± 0.03) x10³	(1.39 ± 0.04) x10³
Vapor Pressure (torr)	522. ± 9	588. ± 2

Table 1. Henry's Law constants and vapor pressures for CS₂ and methylal determined from mixtures of the two.

b. (10 Points) Calculate the activity of each component in this system at each measured point on a Raoult's law basis. Determine the excess Gibbs energy, G^E , at each measured point. Prepare a graph of G^E (in kJ/mole) as a function mole fraction of CS_2 and tape it in the space below.

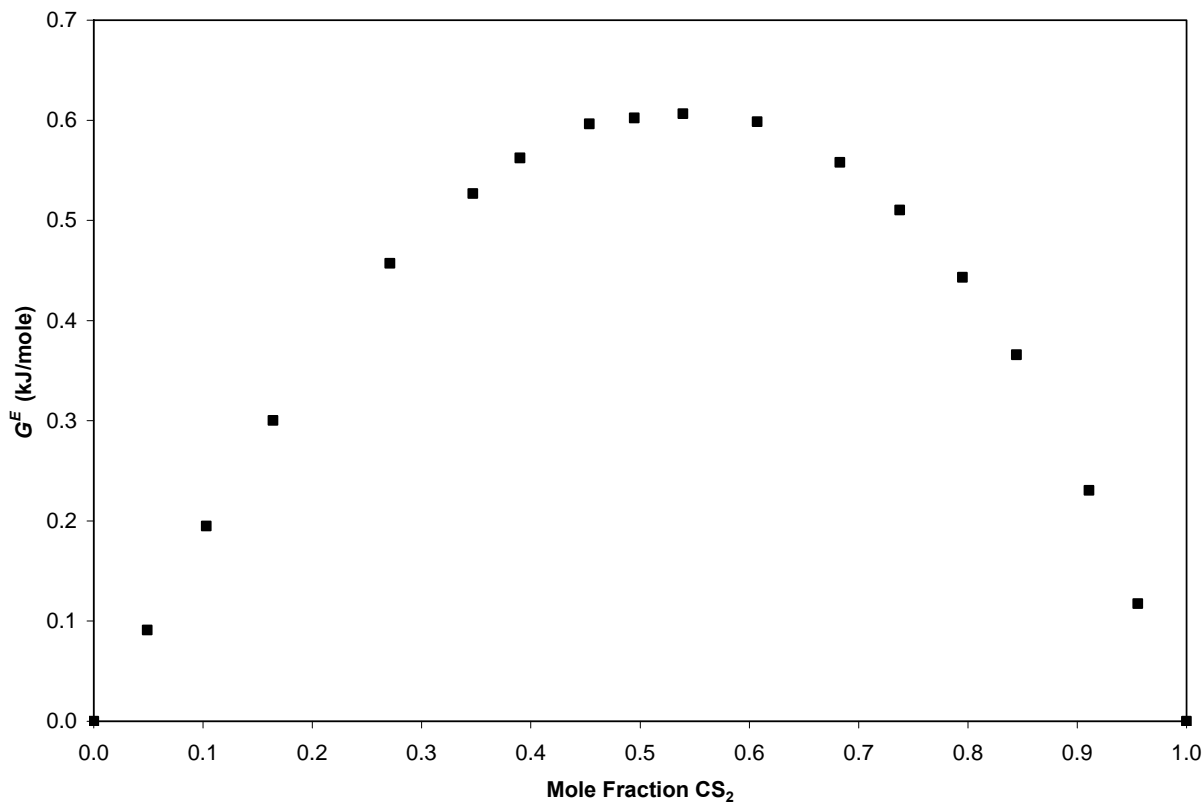
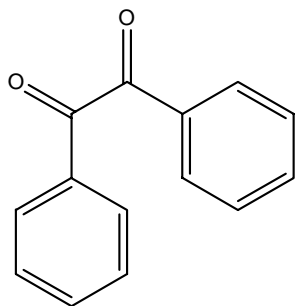


Figure 3. The excess Gibbs energy, G^E , in the CS_2 -methylal system as a function of the mole fraction of CS_2 .

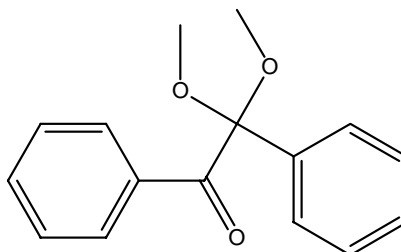
c. (4 Points) What does Fig. 3 suggest about the nature of the intermolecular interactions present in this system?

Since G^E is positive for all compositions, it suggests, assuming a regular solution ($H^E \neq 0$ and $S^E = 0$), that repulsive interactions between the particles are more important than attractive interactions. However, if entropic effects are important (as when the solute disrupts a hydrogen bonding network in the solvent) then S^E will play a role in mixing.

2. The temperatures at which breaks and halts occur in the cooling curves of the benzil-2, 2-dimethoxy-1, 2-diphenylethanone (BDK) system are given in the second worksheet of TakeHome2.xls as a function of the mass fraction of benzil. Note that you will first need to convert the given mass fractions to mole fractions and the given temperatures to the absolute temperature scale.



Benzil



2,2-Dimethoxy-1, 2-diphenylethanone (BDK)

a. (10 Points) Fit each half of the liquidous curve to the Schroder-van Laar equation to determine $\Delta_{fus}H$ for each component in the mixture. A useful form of this equation relates the temperature at which the two phases are in equilibrium, T , to the melting temperature one component, T^* , the mole fraction of this component, and its enthalpy of fusion, $\Delta_{fus}H$. This form of the equation is

$$T = \left(\frac{1}{T^*} - \frac{R \ln \chi}{\Delta_{fus}H} \right)^{-1}$$

It is important to note that one needs two separate equations to describe

the liquidous line (one above the eutectic and one below the eutectic) and that you use the mole fraction of the component that is present in excess. You may either use LoggerPro (include your 95% confidence limits), or the Solver function in Excel to perform these fits. Write your values of $\Delta_{fus}H$ in Table 2.

b. (4 Points) For benzil $\Delta_{fus}H$ is $92.7 \text{ J}\cdot\text{g}^{-1}$. Convert this to kJ/mole and compare it to the $\Delta_{fus}H$ that you found for benzil in part a.

Converting to kJ/mole gives $\Delta_{fus}H$ for benzil as 19.5 kJ/mole.

$$\left(\frac{92.7 \text{ J}}{1 \text{ g}} \right) \left(\frac{210.23 \text{ g}}{1 \text{ mole}} \right) = 19.5 \text{ kJ/mole}$$

The value of $\Delta_{fus}H$ calculated here is within approximately 6% (% error = -6.15%) of the accepted value. The two values are in reasonable agreement.

c. (3 Points) Determine the eutectic temperature from a best fit line through the solidous points. Write its value (and its uncertainty) in Table 2.

As this should be the same temperature in every cooling curve for this system, a simple best-fit line was found that passed through the data.

d. (5 Points) Determine the eutectic composition from your best fit lines in parts *b* and *d*. No uncertainty needed. Show your work below.

Solve the Schroder-van Laar equation for χ .

$$\ln \chi = \frac{\Delta_{fus} H}{R} \left(\frac{1}{T^*} - \frac{1}{T} \right)$$

When $T = T_{eutectic}$, $\chi = \chi_{eutectic}$. So, we only need to substitute in the appropriate values and solve for χ .

For benzil,

$$\ln \chi = \frac{2.06_{74} \times 10^4 \text{ J} \cdot \text{mole}^{-1}}{8.31447 \text{ J} \cdot \text{K}^{-1} \cdot \text{mole}^{-1}} \left(\frac{1}{369.3 \text{ K}} - \frac{1}{320.4 \text{ K}} \right)$$

$$\ln \chi = 2.48_6 \times 10^3 (0.002707_8 - 0.003121_0) = 2.48_6 \times 10^3 (-0.000413_2) = -1.02_7$$

$$\chi = 0.35_7$$

For BDK,

$$\ln \chi = \frac{2.20_{38} \times 10^4 \text{ J} \cdot \text{mole}^{-1}}{8.31447 \text{ J} \cdot \text{K}^{-1} \cdot \text{mole}^{-1}} \left(\frac{1}{339.6 \text{ K}} - \frac{1}{320.4 \text{ K}} \right)$$

$$\ln \chi = 2.65_0 \times 10^3 (0.002944_6 - 0.003121_0) = 2.65_0 \times 10^3 (-0.000176_4) = -0.467_4$$

$$\chi = 0.626_5$$

Remember that this mole fraction is in BDK, not benzil. So, we need to subtract this from 1.000 to get the mole fraction in benzil. This yields a eutectic composition of 0.373₄.

Averaging the two values of the eutectic composition gives a final value of 0.37 as the eutectic composition in terms of the mole fraction of benzil in the mixture.

	Benzil	BDK
Melting Point (K)	369.3 ± 0.3	339.6 ± 0.3
$\Delta_{fus}H$ (kJ/mole)	20.7 ± 0.4	22.0 ± 0.9
Eutectic Temperature (K)		320.4 ± 0.3
Eutectic Composition (mole fraction of benzil)		0.37

Table 2. Summary of the results for the benzil-BDK system.

Note that the fits to the Schroder-van Laar equation were performed in LoggerPro and that the melting point of each pure substance was an adjustable parameter in the fit.

e. (5 Points) Prepare a solid-liquid phase diagram for this system (with the mole fraction of benzil on the x axis) which includes best fit lines through the liquidous and solidous points. Tape it in the space below.

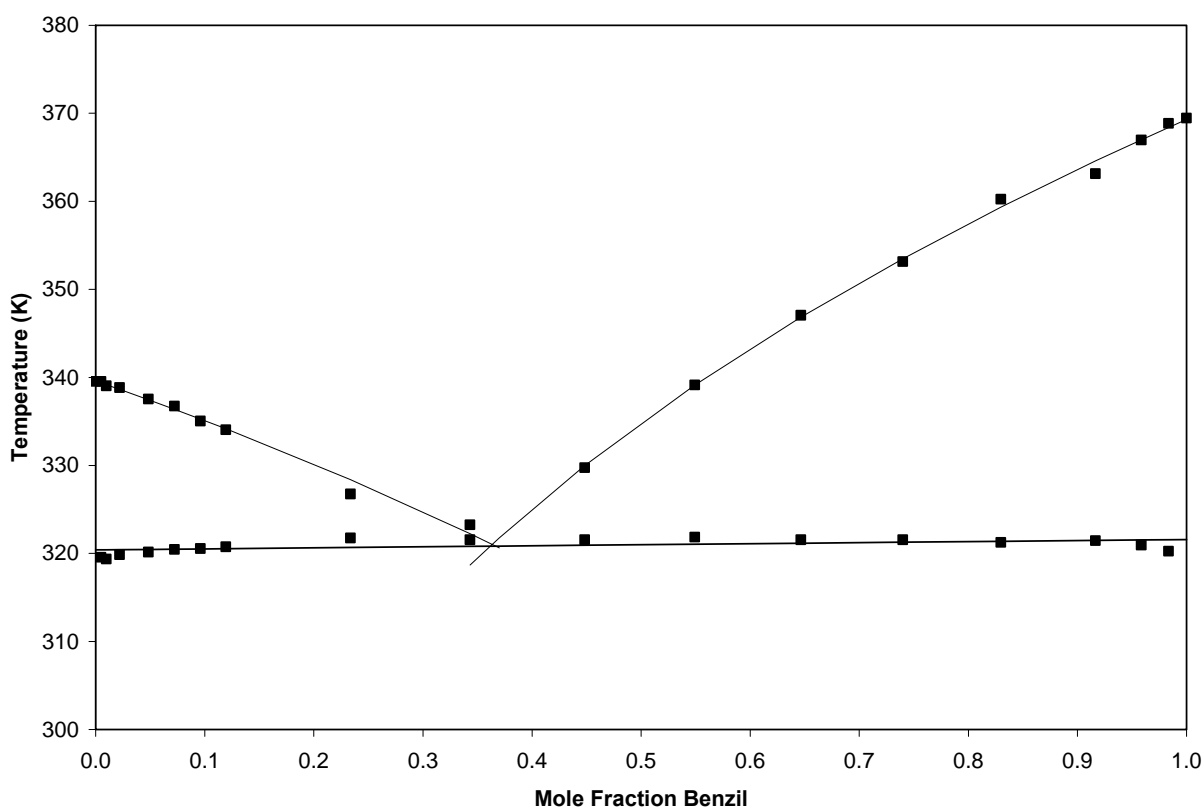


Figure 4. Solid-liquid phase diagram for the benzil-BDK system. The lines through the points are best fits of the data, as described in the text.

Note that the fits of the liquidous curves have been extended slightly to show clearly their intersection at the eutectic point.

3a. (5 Points) Data for the methanol-CCl₄ system are given in the third worksheet of TakeHome2.xls. Use them to construct a temperature-composition diagram with the mole fraction of methanol as the x axis (like Fig. 6.6 or Fig. 6.7 in the text).

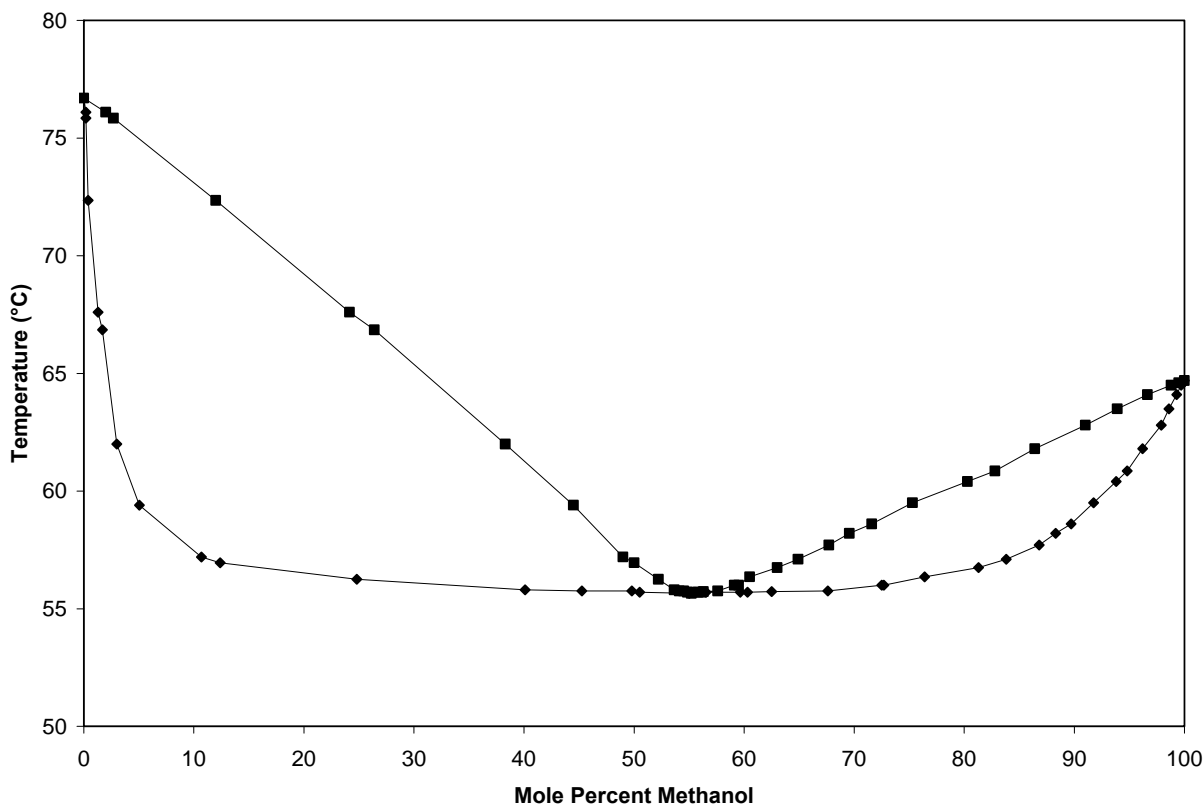
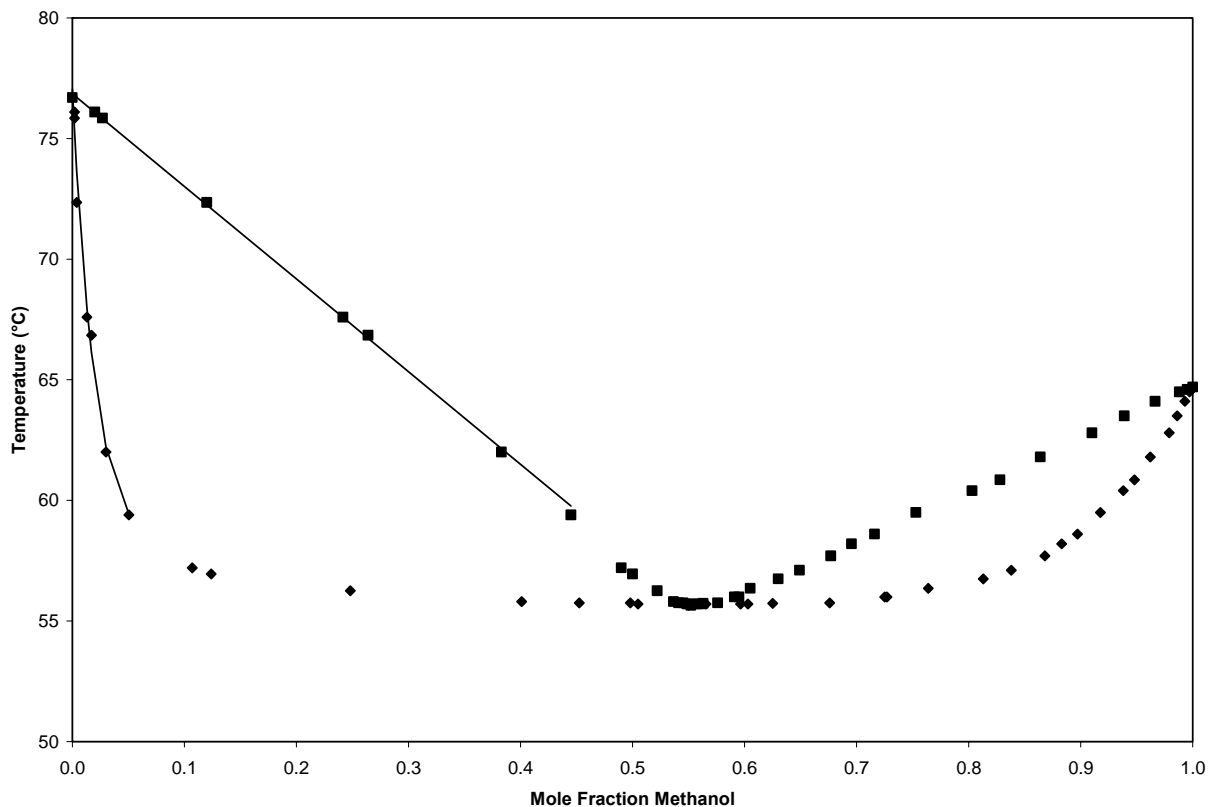


Figure 5. Liquid-vapor phase diagram for the methanol-CCl₄ system. *Note that lines passing through the data were added as aids to the eye.*

b. (8 Points) Determine the composition of the liquid and vapor at 65.0 °C when the initial solution had a mole percent of methanol equal to 15.00%. Describe your method and tape any Excel graphs, Logger Pro output, etc. that you used in your calculation to the next page and label each with a proper figure caption. The more precise the answer (with proper justification), the more points you will receive.

The data in the region of 65.0 °C were fit to empirical functions in the mole fraction of methanol. The liquidous line was fit to the equation $T = Ae^{-Bx} + C$, where $A = 19. \pm 1$ K, $B = 50. \pm 8$, and $C = 58. \pm 1$ K. The vapor line was fit to the equation $T = A\chi + B$ with $A = -38.4 \pm 0.3$ and $B = 76.86 \pm 0.07$ K. These fits are shown in the figure on the next page.

Substituting in $T = 65.0$ °C into each equation and solving for χ gives $\chi_{vapor} = 0.309$ and $\chi_{liquid} = 0.02$.



4. The data in the table below represent the compositions of solutions (as mole fractions) which are in equilibrium in the water-benzonitrile-ethanol system at 25.0 °C. In the table water = A, benzonitrile = B and ethanol = C. The first three columns of the table give the composition of one of the two solutions (labeled 1), while the last three give the composition of the other solution (labeled 2). The last row is the calculated plait point.

χ_A (1)	χ_B (1)	χ_C (1)	χ_A (2)	χ_B (2)	χ_C (2)
0.944	0.0001	0.055	0.057	0.856	0.087
0.885	0.003	0.112	0.081	0.764	0.155
0.853	0.007	0.140	0.124	0.642	0.234
0.842	0.010	0.148	0.141	0.621	0.238
0.801	0.017	0.182	0.225	0.502	0.273
0.764	0.024	0.212	0.328	0.377	0.295
0.708	0.051	0.241	0.446	0.244	0.310
0.600	0.115	0.285	0.600	0.115	0.285

a. (10 Points) Draw the phase diagram for this system, using the blank graph on p. 11. Label the region where one phase is present ($P = 1$) and the region where two phases are present ($P = 2$).

b. (3 Points) Based on your graph, is the stated composition of the plait point reasonable?

The tie lines should converge to the plait point because at the plait point the tie line has a length of zero. From the behavior of the tie lines in the three-component phase diagram it appears that they are converging to a point near the calculated plait point. Therefore, it is likely that the calculated plait point is correct.

c. (5 Points) How would the mixture with the composition $\chi_A = 0.400$, $\chi_B = 0.200$ and $\chi_C = 0.400$ actually exist? Would it be one phase, or two? If it exists as two phases, give their compositions.

A mixture with this composition is in the one phase region.

