

CHEM 323
Fall 2008
In-Class 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.

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). If you change your mind on a question, cross out the incorrect answer and clearly indicate your final answer.

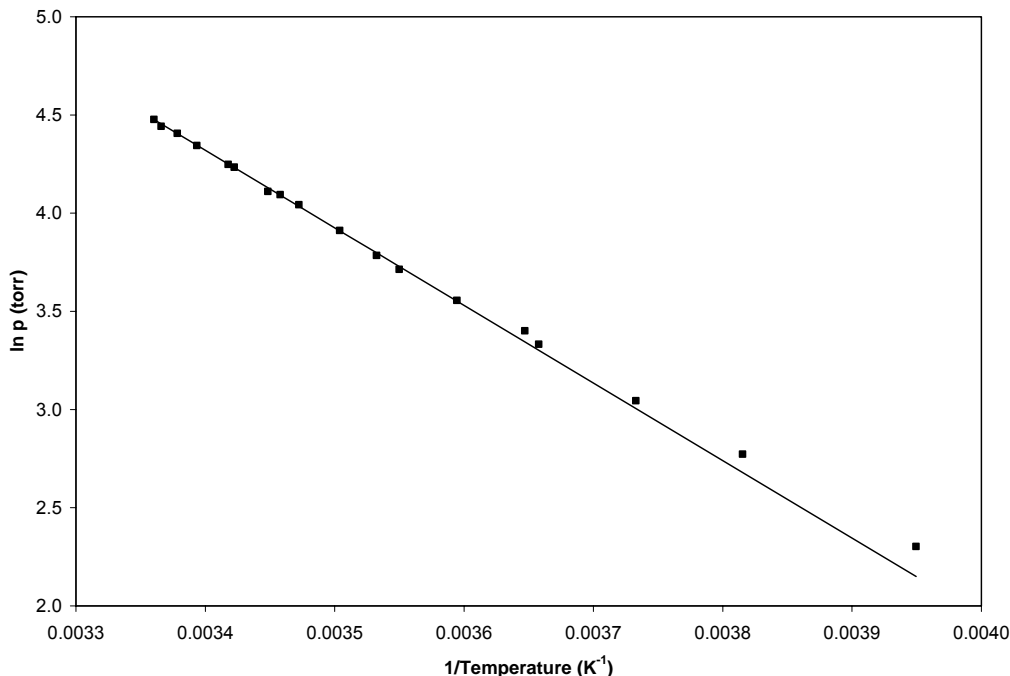
You may use the back of any page as additional workspace. Please indicate that you have done so.

There are **9** pages, **0** blank.

If you have any questions regarding the exam, please ask me. I will attempt to answer them, if I can, without giving away the answer.

Problem	Possible Points	Points Received
1	12	
2	8	
3	25	
4	18	
5	8	
6	8	
Free	21	21
Total	100	
	Bonus	
	Grand Total	

1. Shown below is a graph of the natural logarithm of the vapor pressure (in torr) as a function of the inverse of the absolute temperature ($297 \leq T \leq 255$ K) for the compound 3-hexyne, which is a liquid under the experimental conditions. A best fit line through the data at highest temperature (shown) has a slope of $-3950. \pm 34$ K and the intercept is 17.75 ± 0.12 .



a. (8 Points) What is $\Delta_{vap}H$ for 3-hexyne? Derive the necessary equation from an equation given on the equation sheet. Clearly state any necessary assumptions in the derivation.

Integration of the Clausius-Clapreyon equation, $\frac{d \ln p}{dT} = \frac{\Delta_{vap}H}{RT^2}$, assuming that $\Delta_{vap}H$ is independent of temperature, gives $\ln p = -\left(\frac{\Delta_{vap}H}{R}\right)\left(\frac{1}{T}\right) + C$, where C is the constant of integration. This is a straight line with a slope of $-\frac{\Delta_{vap}H}{R}$, which may be solved as follows for $\Delta_{vap}H$.

$$-\frac{\Delta_{vap}H}{R} = -3.95_0 \times 10^3 \text{ K}$$

$$\Delta_{vap}H = (3.95_0 \times 10^3 \text{ K})(8.31447 \text{ J} \cdot \text{K}^{-1} \cdot \text{mole}^{-1}) = +32.8 \text{ kJ} \cdot \text{mole}^{-1}$$

For 3-hexyne $\Delta_{vap}H$ is 32.8 kJ/mole.

b. (4 Points) Notice that in the graph that the best-fit line through the high-temperature data does not pass through the low-temperature data. Suggest reasons for this.

The most obvious explanation is that $\Delta_{\text{vap}}H$ is not constant over this temperature range. If $\Delta_{\text{vap}}H$ were not constant then we would have to integrate the actual expression to fit the data.

The second explanation, and the one more likely to be true, stems from the Clausius-Claperyon equation itself being a simplification of the Clausius equation, $\frac{dp}{dT} = \frac{\Delta_{\text{trs}}S}{\Delta_{\text{trs}}V}$,

and the assumption that we had to make to derive it. To derive the Clausius-Claperyon equation we assumed that $\Delta_{\text{vap}}V$ is almost entirely due to the volume of the gas formed upon vaporization and that the gas is ideal. The assumption that the gas dominates $\Delta_{\text{vap}}V$ is very good, but the ideality of the gas is not. The gas may be considered ideal at low pressure and at high temperature (relative to its boiling point). We don't know 3-hexyne's boiling point, but the fact that the low-temperature data begins to deviate from the best fit of the high-temperature data suggests that gas is not behaving ideally at low temperatures.

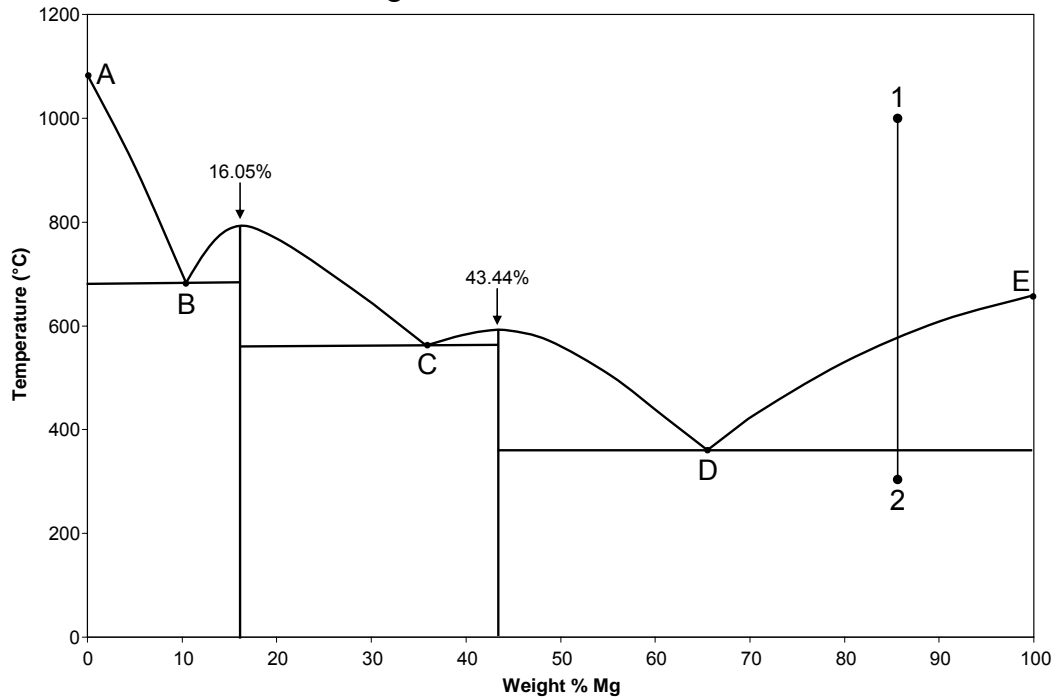
2a. (4 Points) Some compounds are completely miscible (e. g., ethanol and water) even though G^E for the mixture is positive at all compositions. Briefly explain how this can be the case.

Only the sign of $\Delta_{\text{mix}}G$ determines whether a solution will form, not G^E . Although G^E is one term in $\Delta_{\text{mix}}G$, it is not the only term. As long as the entropically-driven mixing term remains large enough to compensate for any intermolecular interactions and other entropy effects due to these interactions (the factors that contribute to G^E), then $\Delta_{\text{mix}}G$ will be negative and solution formation will occur.

b. (4 Points) A positive G^E may have either an enthalpic cause ($H^E \neq 0$) or an entropic cause ($S^E \neq 0$). What simple measurement would allow one to determine whether the cause of the positive G^E is enthalpic or entropic (or a combination of both)? Briefly explain.

From the definition of G , we may write $G^E = H^E - TS^E$. If we measure G^E as a function of temperature (at a constant composition and pressure) then a graph of G^E as a function of temperature will have an intercept of H^E and a slope of $-S^E$.

3. The solid-liquid phase diagram for the Cu-Mg system is shown below. The molar mass of Mg is 24.305 g/mole and that of Cu is 63.546 g/mole.



a. (5 Points) Which of the labeled points are eutectics? **D**

Which are monotectics? **B, C**

b. (8 Points) Determine the empirical formula of the compound corresponding to the vertical line at 43.44% Mg.

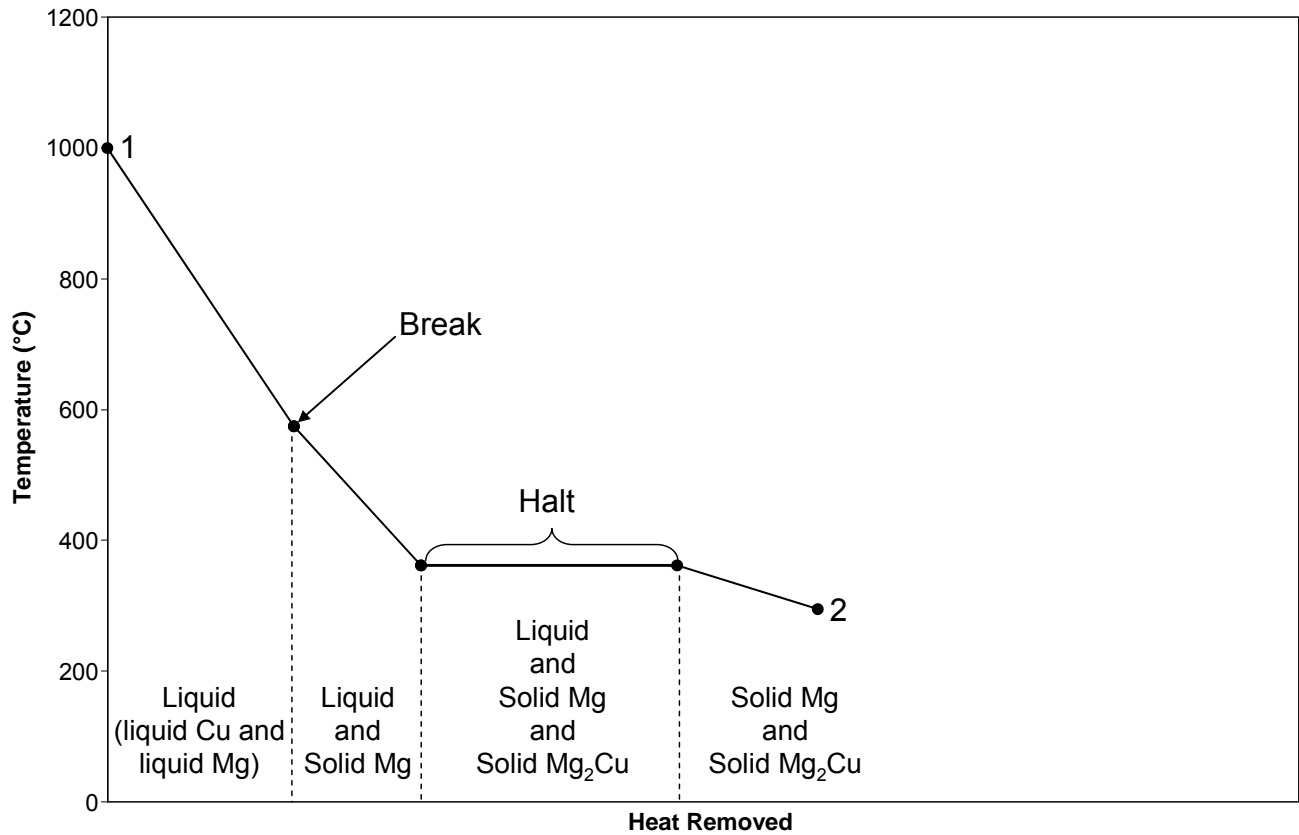
Assume 100.00 g of material total so that one has 43.44 g Mg and 56.56 g Cu.

$$43.44 \text{ g Mg} \left(\frac{1 \text{ mole Mg}}{24.305 \text{ g Mg}} \right) = 1.787_2 \text{ mole Mg}$$

$$56.56 \text{ g Cu} \left(\frac{1 \text{ mole Cu}}{63.546 \text{ g Cu}} \right) = 0.8900_6 \text{ mole Cu}$$

Now, find the smallest whole number ratio by dividing by the moles of Cu to give 2.008 mole Mg to 1 mole Cu. This is consistent with a compound with an empirical formula of Mg_2Cu .

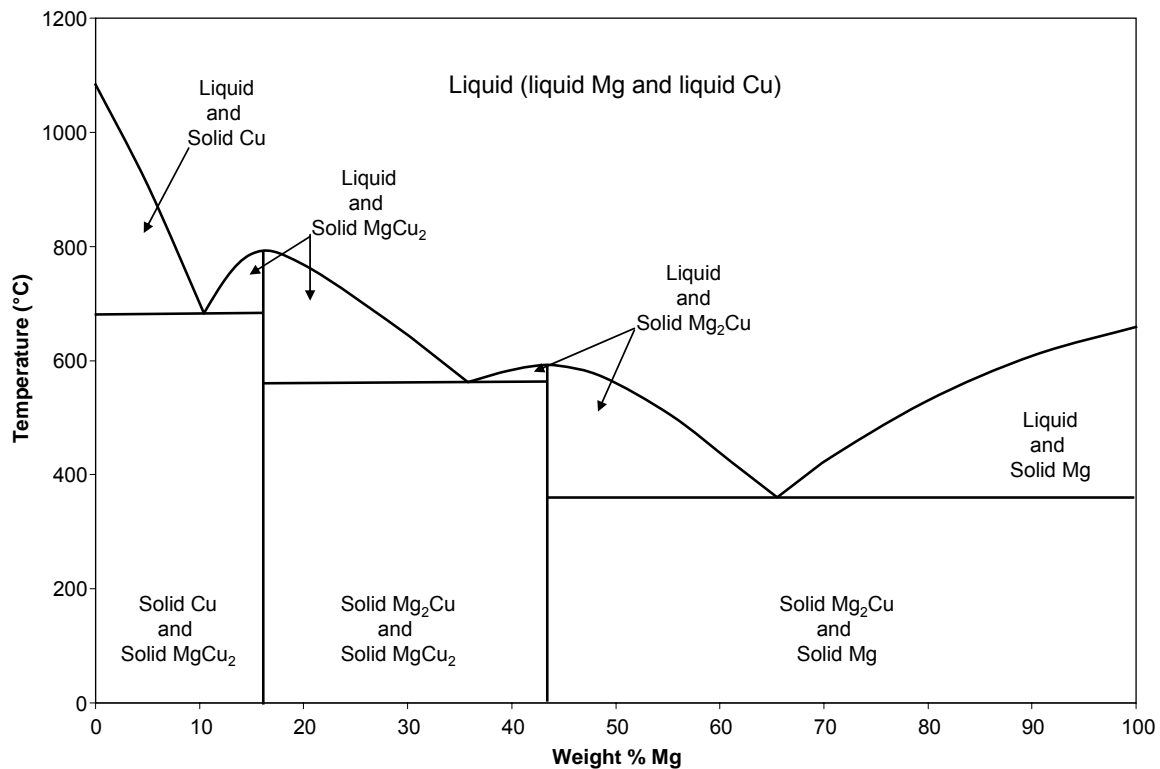
c. (8 Points) Draw the cooling curve for the isopleth from 1000 °C (point 1) to 300 °C. Clearly indicate breaks and halts and what phases, compounds, etc. are present at different parts of the cooling curve.



d. (4 Points) If you were to examine the physical structure of the mixture at point 2 on the isopleth, what would you see? Be as specific as you can.

What we would observe would depend on how fast the cooling occurred. With rapid cooling the solid may seem homogeneous on the macroscopic level, but at the microscopic level it would contain many small interspersed regions of solid Mg and Mg₂Cu. If the cooling was very slow then the solid would appear inhomogeneous on the macroscopic level with regions of pure solid Mg and pure solid Mg₂Cu clearly visible. There might be even be remnants of the flow patterns within the solid-liquid mixture as the solids were being mixed as the slushy mixture of liquid, solid Mg and solid Mg₂Cu solidified.

Post Exam Question. Fill in each region of the phase diagram for the Cu-Mg binary system with what phase(s) coexist in that region. Note that the vertical lines occur at weight percents Mg of 16.05 and 43.44.



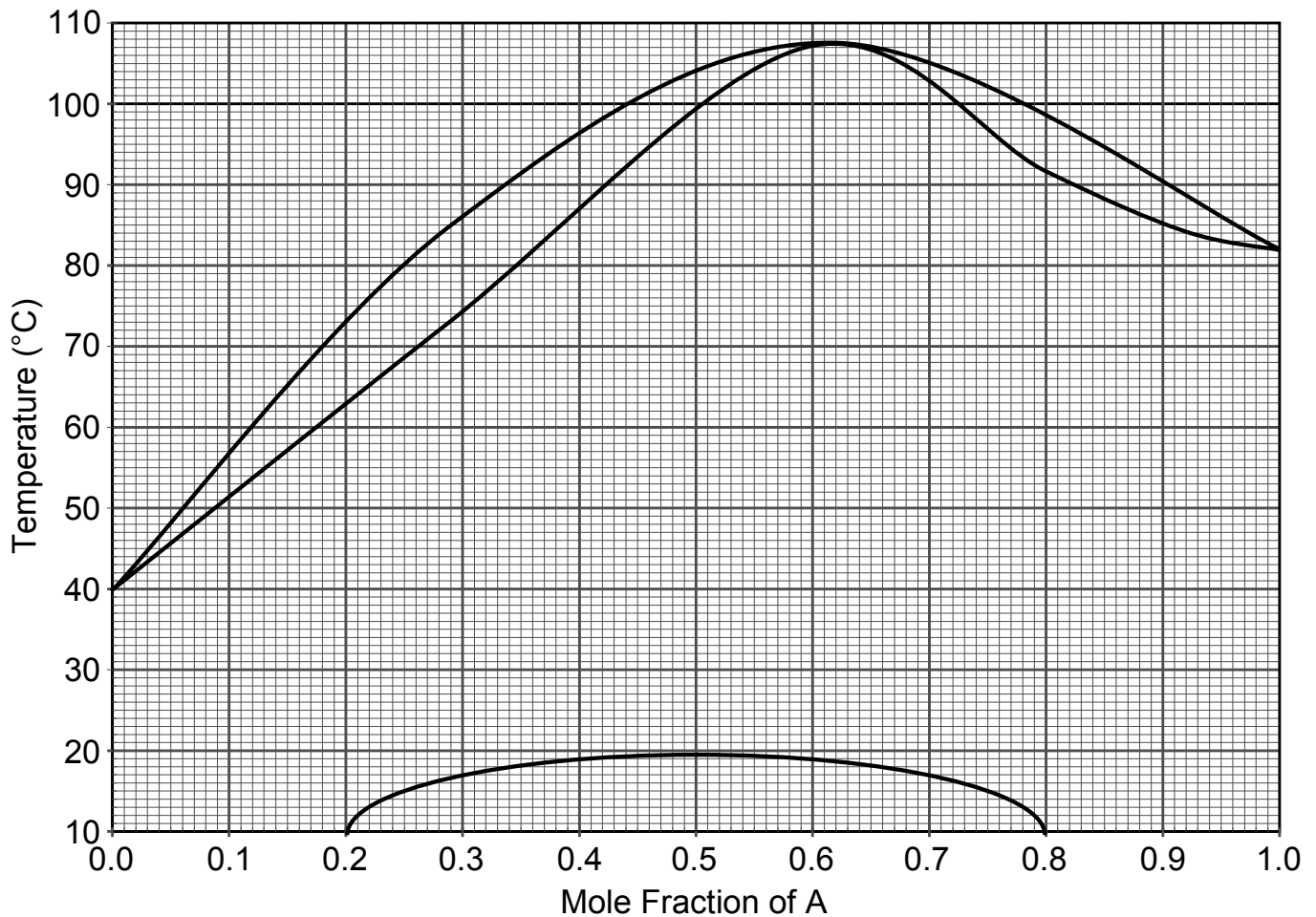
We've already determined the chemical formula of the compound formed with a weight % of Mg of 43.44. So, now we find the compound with a weight % of Mg of 16.05. Assume 100.00 g of material total so that one has 16.05 g Mg and 83.95 g Cu.

$$16.05 \text{ g Mg} \left(\frac{1 \text{ mole Mg}}{24.305 \text{ g Mg}} \right) = 0.6603_5 \text{ mole Mg}$$

$$83.95 \text{ g Cu} \left(\frac{1 \text{ mole Cu}}{63.546 \text{ g Cu}} \right) = 1.321_0 \text{ mole Cu}$$

Now, find the smallest whole number ratio by dividing by the moles of Mg to give 2.001 mole Cu to 1 mole Mg. This is consistent with a compound with an empirical formula of MgCu_2 .

4. The liquid-vapor phase diagram for the binary system consisting of compounds A and B at 1 bar of pressure is shown below as a function of the mole fraction of A.



a. (6 Points) Describe how the temperature in the column and the composition of the distillate changes when a solution with a mole fraction of A equal to 0.90 is heated to boiling and is then fractionally distilled on a column of 10000 theoretical plates. Be specific!

The temperature of the liquid would rise until boiling starts at 85 °C. Pure compound A would distill from the column while the remaining liquid is depleted in A. As the mole fraction of A in the remaining liquid falls, the boiling point rises until the solution reaches the azeotropic composition ($\chi_A = 0.62$) when the temperature will be 108 °C. Pure compound A will continue to distill off as the temperature rises, but only until the azeotrope is reached. When the azeotrope distills the composition and the temperature will remain unchanged until all of the liquid (A and B together at $\chi_A = 0.62$) has distilled.

b. (8 Points) A mixture that has a mole fraction of A equal to 0.60 is prepared at 30.0 °C and cooled to 12.0 °C. Determine the composition of the two phases that form and find the ratio of the amount of the phase present in the greatest amount to the one that is present in the smallest amount.

Two phases are formed. Phase α has $\chi_A = 0.21$ while phase β has $\chi_A = 0.79$. The length of the tie line for phase α is 0.39 (0.60 – 0.21) and the length of the tie line for phase β is 0.19 (0.79 – 0.60). Then by the lever rule ($n_\alpha l_\alpha = n_\beta l_\beta$) we can write the following, since β will be in excess.

$$\frac{n_\beta}{n_\alpha} = \frac{l_\alpha}{l_\beta} = \frac{0.39}{0.19} = 2.1$$

Under these conditions there will be 2.1 times as much of a phase with $\chi_A = 0.79$ than the phase with $\chi_A = 0.21$.

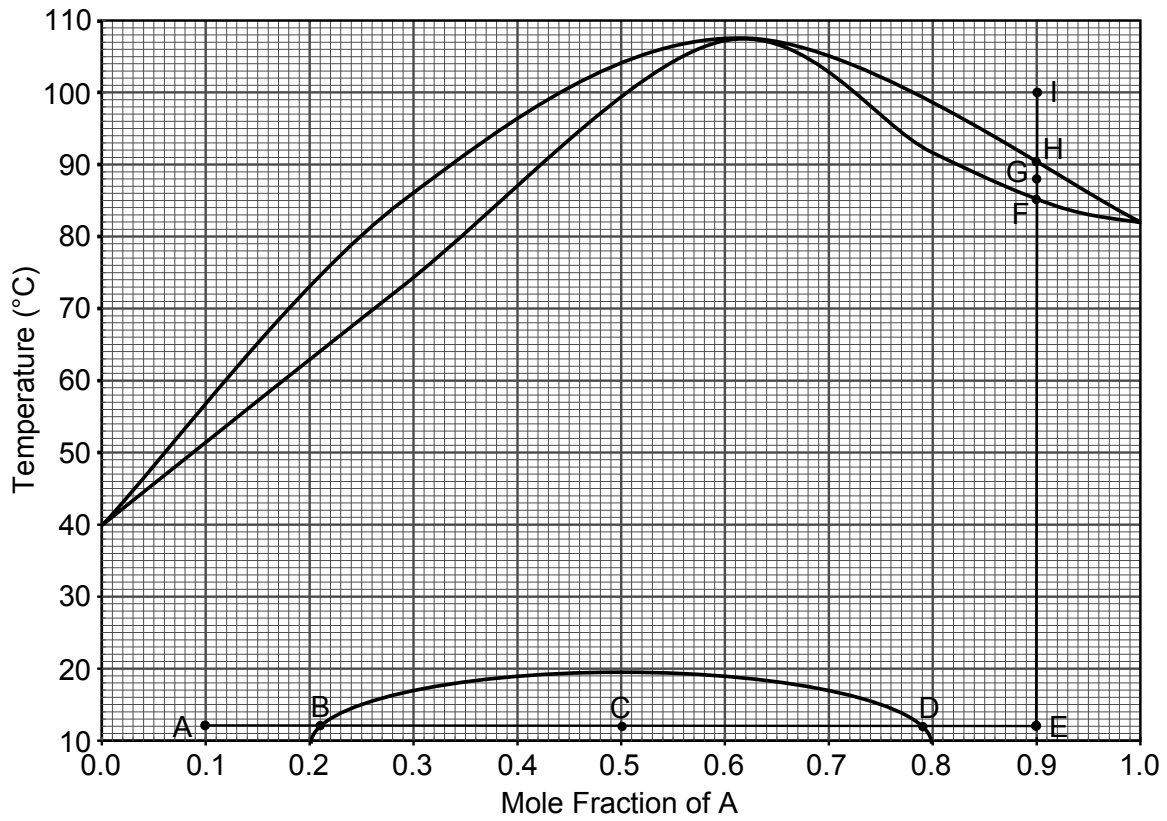
c. (4 Points) Qualitatively describe how the temperature-composition phase diagram for this system at 50 bar differ would from the one shown.

From the Clausius-Claperyon equation, $\frac{d \ln p}{dT} = \frac{\Delta_{vap}H}{RT^2}$, we know that, when the pressure increases, the temperature at which boiling occurs will increase because $\Delta_{vap}H$ is always positive (because we've defined it for the conversion of the liquid to the gas). Therefore, the lines defining the liquid-vapor transition will shift to higher temperature at 50 bar relative to 1 bar. While the azeotrope's composition and boiling temperature may change with pressure, we have insufficient information to determine how, or even whether, this would occur.

For the liquid-liquid equilibrium, we would need to use the Clausius equation, $\frac{dp}{dT} = \frac{\Delta_{trs}S}{\Delta_{trs}V}$. Since we do not know either $\Delta_{trs}S$ or $\Delta_{trs}V$ for this phase equilibrium, we cannot predict how it will change with pressure. The two likely possibilities are that 1) the upper consolute temperature will decrease, or stay the same, with increasing pressure (the region where two liquid phases coexist will shrink) or 2) the upper consolute temperature will increase with increasing pressure (the two-liquid-phase region will grow). In the second case, it is possible that the region where two liquid phases are in equilibrium will overlap the liquid-vapor region to give a complex phase diagram, like that shown in class.

Post-Exam Question. A solution that has a mole fraction of A equal to 0.10 is titrated with pure liquid A until the mole fraction of A in the solution is 0.90 (points A through E). The solution is then heated to 100 °C (points E through I). Fill in the table on the answer sheet with the number of phases existing at each point, the composition of each phase and the ratio of the amount of the two phases present. If only one phase exists, please write its composition under the heading "Composition of A-

Rich Phase” and enter “—” under the heading “Ratio of the Amount of the A-rich Phase to the A-poor Phase”.



Point	Number of Phases Present	Composition of A-poor Phase	Composition of A-Rich Phase	Ratio of the Amount of the A-rich Phase to the A-poor Phase
A	1		0.100	-----
B	2	0.210	0.790	0
C	2	0.210	0.790	1.00
D	2	0.210	0.790	∞
E	1		0.900	-----
F	2	0.900	0.964	0
G	2	0.850	0.930	1.7
H	2	0.815	0.900	∞
I	1		0.900	-----

5. (8 Points) For uranium hexafluoride (MW = 352.02 g/mole) the vapor pressure for the solid (p_{solid}) and the liquid (p_{liquid}) are given by the following equations (pressure in units of Pa and temperature in K). Calculate the temperature and pressure at the triple point.

$$\ln p_{solid} = 29.411 - \frac{5893.5 \text{ K}}{T} \qquad \ln p_{liquid} = 22.254 - \frac{3479.9 \text{ K}}{T}$$

At the triple point all three phases of UF₆ coexist. Therefore, they all have the same temperature and vapor pressure. It is easiest to let $p_{solid} = p_{liquid}$ and solve for T and then substitute this value for the triple point temperature back into one of the given equations to solve for $p_{solid} = p_{liquid} = p_{triple}$. Since, $p_{solid} = p_{liquid}$ we may write

$$29.411 - \frac{5893.5 \text{ K}}{T} = 22.254 - \frac{3479.9 \text{ K}}{T}$$

$$29.411T - 5893.5 \text{ K} = 22.254T - 3479.9 \text{ K}$$

$$7.157T = 2413.6 \text{ K}$$

$$T = 337.2_3 \text{ K}$$

Substituting this back into the equation for p_{solid} gives

$$\ln p_{solid} = 29.411 - \frac{5893.5 \text{ K}}{337.2_3 \text{ K}} = 11.93_4$$

$$p_{solid} = e^{11.93_4} = 1.5 \times 10^5 \text{ Pa}$$

Thus, the triple point temperature is 337.2 K and the triple point pressure is 1.5×10^5 Pa for UF₆.

6. (8 Points) For the conversion of aragonite to calcite at 25.0 °C, $\Delta G^0 = -1.046$ kJ/mole. The density of aragonite is $2.93 \text{ g}\cdot\text{cm}^{-3}$ and that of calcite is $2.71 \text{ g}\cdot\text{cm}^{-3}$ at 25.0 °C. Assuming that the densities are independent of pressure, what pressure would be required to have the two forms of CaCO₃ (FW 100.09 g/mole) co-exist at 25.0 °C?

The equation $\left(\frac{\partial G}{\partial p}\right)_T = V$ implies that $\left(\frac{\partial \Delta G}{\partial p}\right)_T = \Delta V$ for a reaction (in this case the reaction CaCO_3 (s, aragonite) \rightarrow CaCO_3 (s, calcite)). Integrating this expression and assuming that ΔV is independent of pressure, which we can say since the densities are independent of temperature, gives $\Delta G(p_2) - \Delta G(p_1) = (\Delta V)(p_2 - p_1)$.

First, find ΔV . The definition of density, ρ , is $\rho = \frac{m}{V}$. Solving for V gives $V = \frac{m}{\rho}$. For the molar volume, V_M , the mass is 100.09 g and the molar volumes are

$$\text{calcite: } V_M(\text{calcite}) = \frac{m}{\rho} = \frac{100.09 \text{ g}}{2.71 \text{ g} \cdot \text{cm}^{-3}} = 36.9_3 \text{ cm}^3$$

$$\text{aragonite: } V_M(\text{aragonite}) = \frac{m}{\rho} = \frac{100.09 \text{ g}}{2.93 \text{ g} \cdot \text{cm}^{-3}} = 34.1_6 \text{ cm}^3$$

$$\text{So, } \Delta V_M = V_M(\text{aragonite}) - V_M(\text{calcite}) = (36.9_3 - 34.1_6) \text{ cm}^3 = +2.7_7 \text{ cm}^3.$$

Now we may solve for p_2 the pressure at which the two forms of CaCO_3 coexist (note that $\Delta G(p_2) = 0$ and that $1 \text{ J/m}^3 = 1 \text{ Pa}$).

$$\Delta G(p_2) - \Delta G(p_1) = (\Delta V_M)(p_2 - p_1)$$

$$p_2 = \frac{\Delta G(p_2) - \Delta G(p_1)}{\Delta V_M} + p_1 = \frac{0 + 1.046 \times 10^3 \text{ J} \cdot \text{mole}^{-1}}{(+2.7_7 \text{ cm}^3 \cdot \text{mole}^{-1}) \left(\frac{1 \text{ m}}{100 \text{ cm}} \right)^3} + 1.000 \times 10^5 \text{ Pa}$$

$$p_2 = \frac{1.046 \times 10^3 \text{ J} \cdot \text{mole}^{-1}}{(+2.7_7 \times 10^{-6} \text{ m}^3 \cdot \text{mole}^{-1})} + 1.000 \times 10^5 \text{ Pa} = 3.7_7 \times 10^8 \text{ Pa} + 1.000 \times 10^5 \text{ Pa} = 3.8 \times 10^8 \text{ Pa}$$

$$p_2 = 3.8 \times 10^8 \text{ Pa} \left(\frac{1 \text{ bar}}{1 \times 10^5 \text{ Pa}} \right) = 3.8 \times 10^3 \text{ bar}$$

The two forms of CaCO_3 would coexist at a pressure of 3.8×10^3 bar and a temperature of 25.0 °C. Note the extremely high pressure required to bring these relatively incompressible materials into equilibrium, as we expect from the general rule that, for "normal" pressures the equilibrium between incompressible materials is independent of pressure.

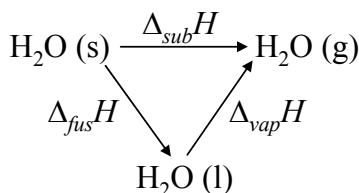
Post-Exam Question. The enthalpies of vaporization and of fusion for water are $2490.0 \text{ J}\cdot\text{g}^{-1}$ and $333.5 \text{ J}\cdot\text{g}^{-1}$, respectively, at $0.0 \text{ }^\circ\text{C}$. The vapor pressure of water at $0.0 \text{ }^\circ\text{C}$ is $611. \text{ Pa}$. Calculate the sublimation vapor pressure of ice at $-15.0 \text{ }^\circ\text{C}$, assuming that the enthalpy changes are independent of temperature.

First rewrite the Clausius-Claperyon equation substituting $\Delta_{sub}H$ for $\Delta_{vap}H$ to give

$$\frac{d \ln p}{dT} = \frac{\Delta_{sub}H}{RT^2}. \text{ Integrating this expression (note that it is a definite integral), assuming}$$

$$\text{that } \Delta_{vap}H \text{ is independent of temperature, gives } \ln\left(\frac{p_2}{p_1}\right) = \frac{\Delta_{sub}H}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right).$$

To use this expression we need to find $\Delta_{sub}H$, which we aren't given, but we can find it from $\Delta_{fus}H$ and $\Delta_{vap}H$ at $0.0 \text{ }^\circ\text{C}$ using the following cycle (assuming the enthalpies do not change with temperature) because enthalpy is a state function.



From this we can write $\Delta_{sub}H = \Delta_{fus}H + \Delta_{vap}H$, and calculate $\Delta_{sub}H$ at $-15.0 \text{ }^\circ\text{C}$ to be $2823.5 \text{ J}\cdot\text{g}^{-1}$.

Substituting in the other given information gives the following.

$$\ln\left(\frac{p_2}{611. \text{ Pa}}\right) = \frac{\left(2823.5 \frac{\text{J}}{\text{g}}\right)\left(18.011 \frac{\text{g}}{\text{mole}}\right)}{8.31447 \text{ J}\cdot\text{K}^{-1}\cdot\text{mole}^{-1}}\left(\frac{1}{273.15 \text{ K}} - \frac{1}{258.15 \text{ K}}\right)$$

$$\ln\left(\frac{p_2}{611. \text{ Pa}}\right) = (6116.3_3)(0.003660_9 - 0.003873_7)$$

$$\ln\left(\frac{p_2}{611. \text{ Pa}}\right) = (6116.3_3)(-0.000212_8) = -1.30_1$$

$$\frac{p_2}{611. \text{ Pa}} = e^{-1.30_1} = 0.27_2$$

$$p_2 = 1.7 \times 10^2 \text{ Pa}$$

The sublimation vapor pressure of ice at $-15.0 \text{ }^\circ\text{C}$ is $1.7 \times 10^2 \text{ Pa}$.

Post-Exam Question. If 68.4 g of sucrose is dissolved in 1000. g of water, what is the vapor pressure above the solution at 20.0 °C and what is the freezing point of the solution? You are given that the vapor pressure of pure water at 20.0 °C is 2.3149 kPa.

If we assume that water is an ideal solvent, we can use Raoult's Law to calculate the vapor pressure above the solution because sucrose is not volatile. First, find the mole fraction of water.

$$68.4 \text{ g sucrose} \left(\frac{1 \text{ mole}}{342.30 \text{ g}} \right) = 0.199_8 \text{ mole sucrose}$$

$$1000. \text{ g H}_2\text{O} \left(\frac{1 \text{ mole}}{18.011 \text{ g}} \right) = 55.52_1 \text{ mole H}_2\text{O}$$

$$\chi_{\text{H}_2\text{O}} = \frac{55.52_1}{55.52_1 + 0.199_8} = \frac{55.52_1}{55.72_0} = 0.9964_1$$

The vapor pressure is thus $p_{\text{H}_2\text{O}} = \chi_{\text{H}_2\text{O}} p_{\text{H}_2\text{O}}^* = (0.9964_1)(2.3149 \text{ kPa}) = 2.307 \text{ kPa}$.

For the freezing point use $\Delta T = K_f b$, **where** $K_f = 1.86 \text{ K} \cdot \text{kg} \cdot \text{mol}^{-1}$ **for water.**

$$\Delta T = K_f b = (1.86 \text{ K} \cdot \text{kg} \cdot \text{mol}^{-1}) \left(\frac{0.199_8 \text{ mole}}{1.000 \text{ kg}} \right) = 0.372 \text{ K}$$

The temperature at which this solution freezes will be 0.372 °C lower than that of pure water, or -0.372 °C.