Name:____________________________________

First three letters of last name

Chemistry 342

Third Exam

April 22, 2005
2:00 PM in C6 Lecture Center

Write all work you want graded in the spaces provided. Both the logical solution to the problem and the answer to the question are required. What is required is an answer in terms of the original numerical data, including all numerical values and units of conversion factors. Use no intermediate calculated numbers, except where such numbers arise from answers to previous parts. The solution has to be worked out in the form of complete equations, with justification or basis for the use in the specific problem. Final numerical values must include the correct units.
In other words, the instructions are the same as for Exam 1.

POSSIBLY USEFUL INFO: $1\ \text{J} = 1\ \text{kg m}^{-2}\ \text{s}^{-2}$ $1\ \text{atm} = 101325\ \text{Pa}$

$(p + n^2a/V^2)(V - nb) = nRT$ $\Delta_{fus}\boldsymbol{H} = 6003\ \text{J mol}^{-1}$ for water

$R = 8.31441\ \text{J mol}^{-1}\ \text{K}^{-1} = 1.98718\ \text{cal mol}^{-1}\ \text{K}^{-1} = 0.082057\ \text{L atm mol}^{-1}\ \text{K}^{-1}$

$(\partial \boldsymbol{U}/\partial V)_T = T(\partial p/\partial T)_V - p$ $(\partial \boldsymbol{H}/\partial p)_T = -T(\partial V/\partial T)_p + V$ $\mu_{JT} \equiv (\partial T/\partial p)_{\boldsymbol{H}}$ $(\partial \boldsymbol{H}/\partial p)_T = -C_p\mu_{JT}$

$C_p - C_V = \{p + (\partial \boldsymbol{U}/\partial V)_T\}(\partial V/\partial T)_p$

special case : $[T_f/T_i]^{Cv/R}\} = [V_i/V_f]$ only for ideal gas undergoing reversible adiabatic process

$(\partial \boldsymbol{S}/\partial V)_T = (\partial p/\partial T)_V$

$(\partial \boldsymbol{S}/\partial p)_T = -(\partial V/\partial T)_p$

$C_p - C_V = \{p + (\partial \boldsymbol{U}/\partial V)_T\}(\partial V/\partial T)_p$

	score
1	
2	
3	
4	
5	
6	
7	
8	
9	
10	

1. In the following figures (a)-(h) attach these equation labels (A)-(Z') to each one of the appropriate straight or curved lines to which the equation applies. An equation may be used more than once, some equations may not be used at all, and some lines may not have applicable equations from the list.

Equations:

(A) $p_A/p^*_A = x_A$

(B) $y_A = p^*_A/p$

(C) $y_A - X_A = (n_{A(VAP)}/n_{(VAP)}) - (n_A/n)$

(D) $p = p^*_A p^*_B/\{p^*_A + (p^*_B - p^*_A)y_A)\}$

(E) $p = p_A + p_B$

(F) $p_B = K_H x_B$

(G) $p = p^*_A x_A + p^*_B(1 - x_A)$

(H) $dp/dT = \Delta_{vap}\boldsymbol{H}/\{T(V_{m,\mathrm{gas}} - V_{m,\mathrm{liquid}})\}$

(I) $\ln x_A = \Delta_{fus}\boldsymbol{H}/R\left[\frac{-1}{T} + \frac{1}{T^*}\right]$

(J) $(\partial\mu_{\mathrm{gas}}/\partial \mathrm{T})_p = -\boldsymbol{S}_{m,gas}$

(K) $\mu^*_{\mathrm{A,vap}} = \mu^{\circ}_T + RT\ln(p^*_A/1)$

(L) $\mu_{\mathrm{A,liquid}}(T,p,x_A) = \mu_{\mathrm{A,solid}}(T,p)$

(M) $\mu_A(T) = \mu_A{}^*{}_T + RT\ln x_A$

(N) $(\partial[\Delta_{\mathrm{rxn}}\boldsymbol{G}^{\circ}/T]/\partial T)_p = -(\Delta_{\mathrm{rxn}}\boldsymbol{H}^{\circ}/T^2)$

(O) $\ln\gamma_{\pm} = z_+z_-I^{1/2}(\mathrm{e}^2/10\varepsilon\mathrm{k_B}T)^{3/2}\{2\pi\rho\mathrm{N_{Avog}}\}^{1/2}$

(P) $g_B(T,p) = \mu_B{}^*(T,p) + RT\ln K_H/p_B{}^*$

(Q) $\ln K = 2\ln C_s + 2\ln\gamma_{\pm}$

(R) $dp/dT = \Delta_{subl}\boldsymbol{H}/\{T(V_{m,\mathrm{gas}} - V_{m,\mathrm{crystal}})\}$

(S) F = 0

(T) F = 1 F′ = 0

(U) F = 2 F′ = 1

(V) $\mu(T) = \mu^{\circ}_T + RT\ln\frac{f}{1}$

(W) $\ln\frac{f}{p} = \int_0^p \frac{(Z-1)}{p}\,dp$

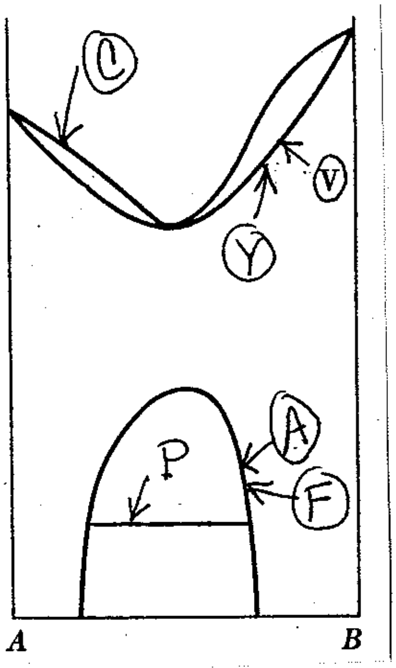
(X) $\boldsymbol{G}_{T,p} = \sum_i n_i\mu_i$

(Y) $(\partial\boldsymbol{G}/\partial T)_p = -\boldsymbol{S}$

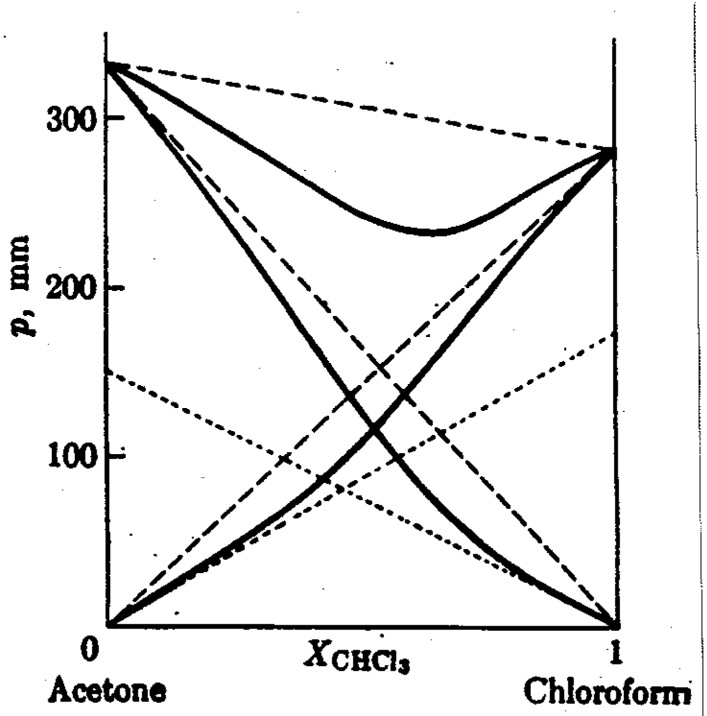
(Z) $\Delta_{\mathrm{rxn}}\boldsymbol{G} = (\mathrm{c}\mu_{\mathrm{C}} + \mathrm{e}\mu_{\mathrm{E}}) - (\mathrm{a}\mu_{\mathrm{A}} + \mathrm{b}\mu_{\mathrm{B}})$

(Z') $\gamma_{\mathrm{A}}(T) = \frac{p_{\mathrm{A}}(T)}{x_{\mathrm{A}}p_{\mathrm{A}}{}^*(T)}$

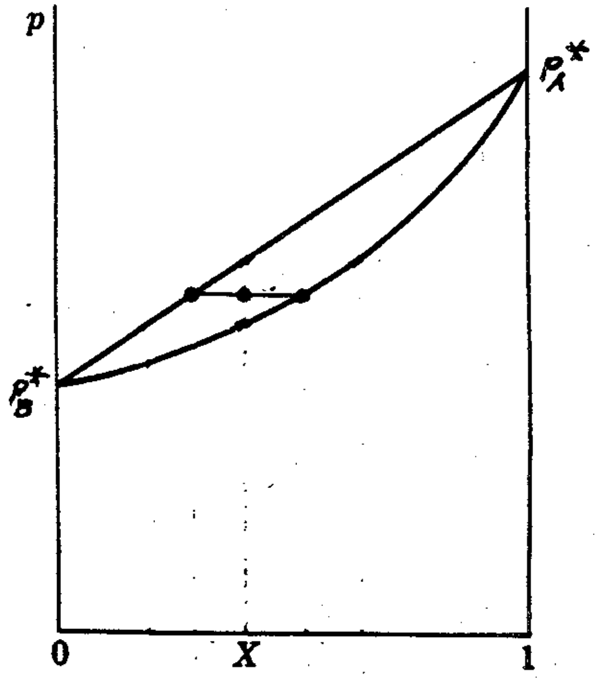
Your answer should look like the following example:



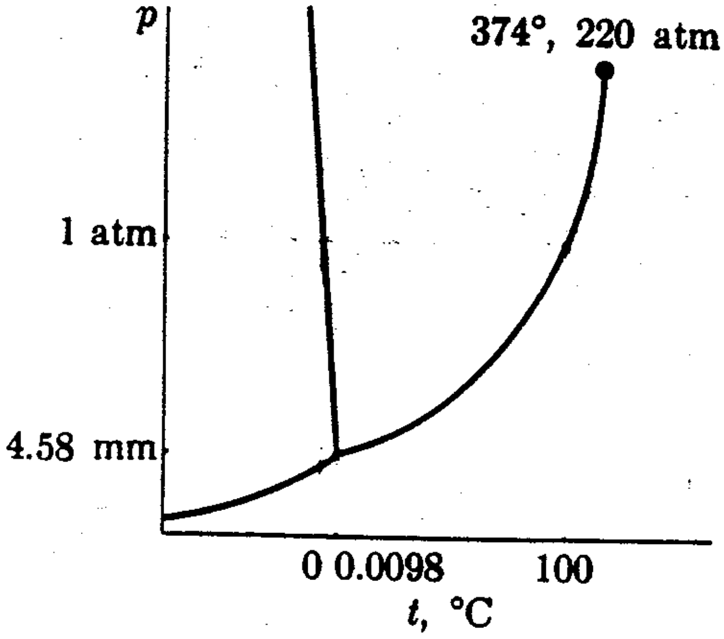
(a)


p, mm
300
200
100
0
X_{CHCl_3}
1
Acetone
Chloroform

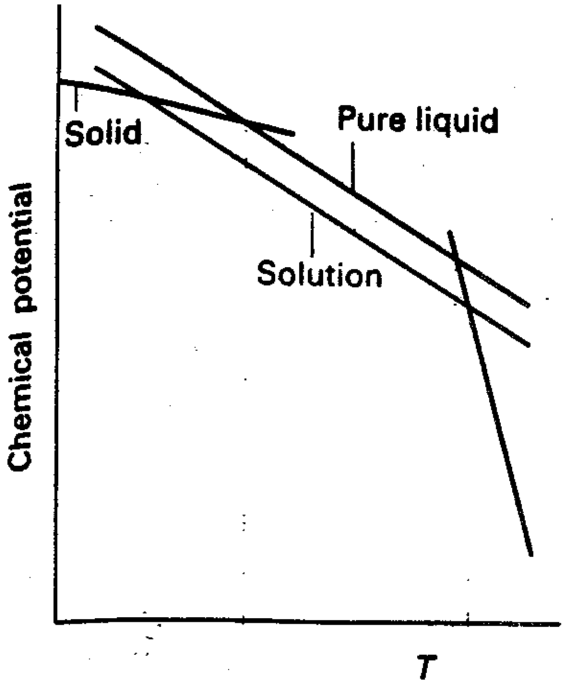
(b)


p
p_A^*
p_B^*
0
X
1

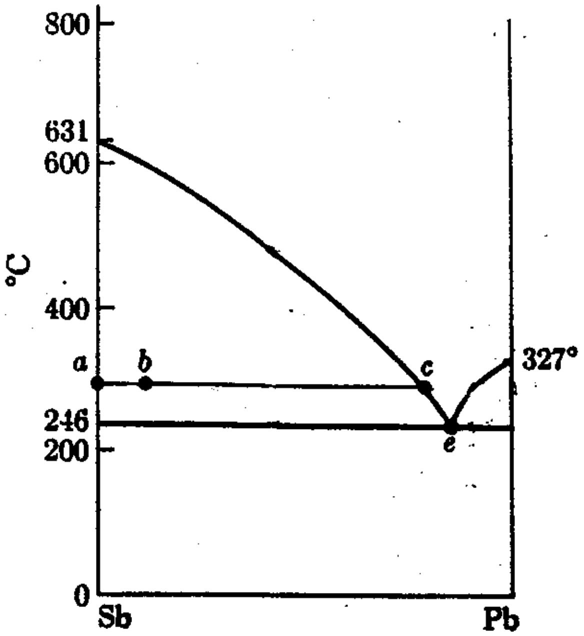
(c)


p
374°, 220 atm
1 atm
4.58 mm
0 0.0098
100
t, °C

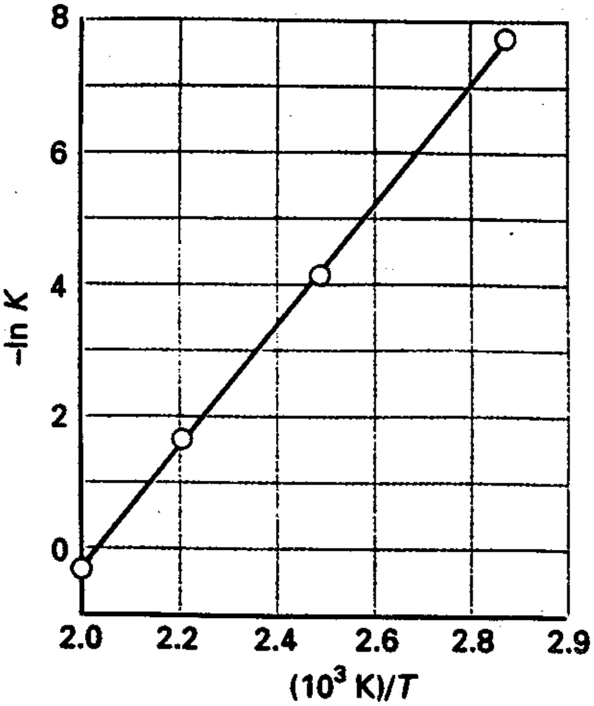
(d)


Solid
Pure liquid
Solution
Chemical potential
T

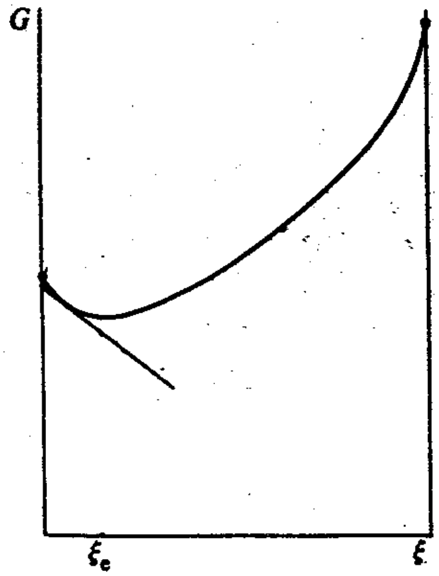
(e)


800
631
600
400
°C
a
b
c
327°
246
200
e
0
Sb
Pb

(f)


8
6
4
2
0
−ln K
2.0
2.2
2.4
2.6
2.8
2.9
(10³ K)/T

(g)


G
ξe
ξ

2. From the graph on the next page determine the following and place your answers in the table below:

(a) The mole fraction of B in the vapor at 35°C and a pressure of 65 mm Hg for a system having over all 20 mole % B

(b) The mole fraction of A in the liquid at 35°C and a pressure of 65 mm Hg for a system having over all 20 mole % B

(c) The relative amounts of liquid and vapor for a system having over all 20 mole % B at 35°C and a pressure of 65 mm Hg

(d) Are the A-B intermolecular interactions stronger or weaker (which one?) than the A-A and B-B interactions?

(e) What is the vapor pressure of pure A at 35°C?

(f) What is the vapor pressure of pure B at 35°C?

(g) If an azeotrope is formed by this system, what is the approximate composition of the azeotropic mixture?

(h) If an azeotrope is formed by this system, would it boil at a higher or lower temperature (which one) than both A and B?

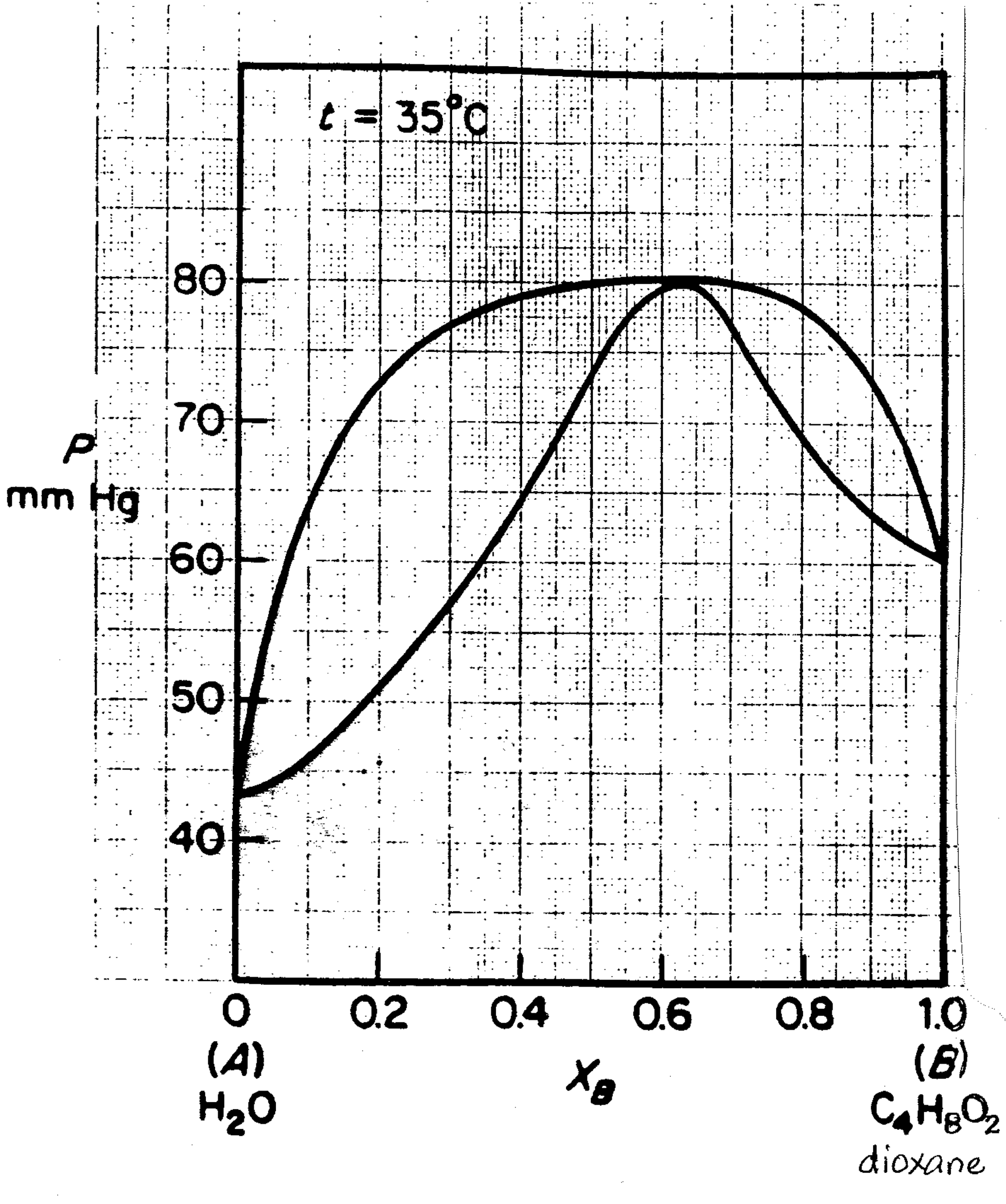
(i) Would the activity coefficient of B in a liquid solution of A+B be smaller or greater (which one?) than 1.0?

(j) Would the activity coefficient of A in a liquid solution of A+B be smaller or greater (which one?) than 1.0?

(a)	(b)	(c)	(d)	(e)

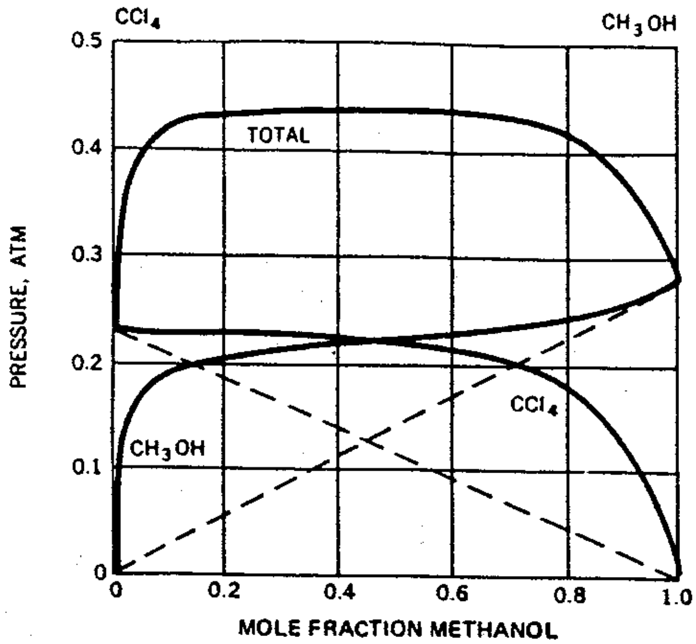
(f)	(g)	(h)	(i)	(j)

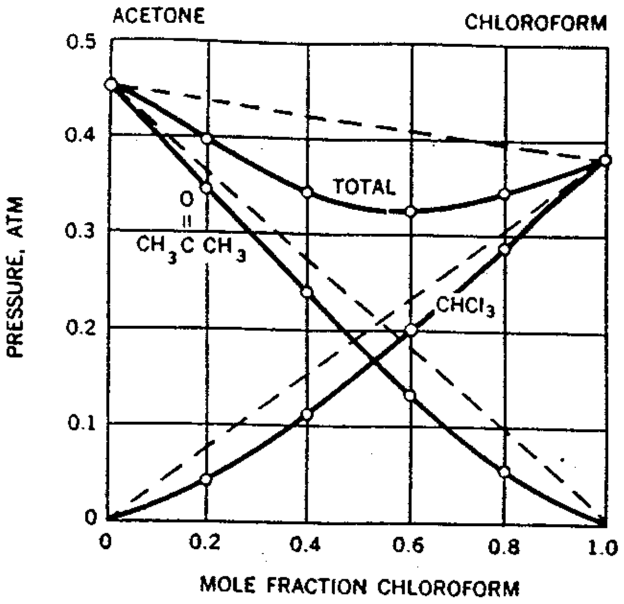
Show your calculations here, if calculations are required to answer above.



$t = 35°C$
P
mm Hg
80
70
60
50
40
0
0.2
0.4
0.6
0.8
1.0
(A)
H_2O
X_B
(B)
$C_4H_8O_2$
dioxane

3. Here are examples of two liquid solutions at 35°C:





From the graphical data above, provide the answers (to two significant digits and with units) to the following questions:

(a) What is the vapor pressure of pure liquid CH_3OH?

(b) What is the vapor pressure of pure liquid CCl_4?

(c) What is the Henry's law constant for $CHCl_3$ in acetone solution?

(d) What is the Henry's law constant for acetone in $CHCl_3$ solution?

(e) What is the partial vapor pressure of CH_3OH in a solution with $x_{CH3OH} = 0.70$?

(f) What is the total vapor pressure of a solution of CH_3OH in CCl_4 with $x_{CCl4} = 0.15$?

(g) What is the mole fraction of CH_3OH in the vapor in equilibrium with a liquid solution of CH_3OH in CCl_4 with $x_{CCl4} = 0.15$?

(h) What is $(\mu_i - \mu_i°)$ for $i = CHCl_3$ in a liquid solution of $x_{CHCl3} = 0.60$ in acetone at 35°C?

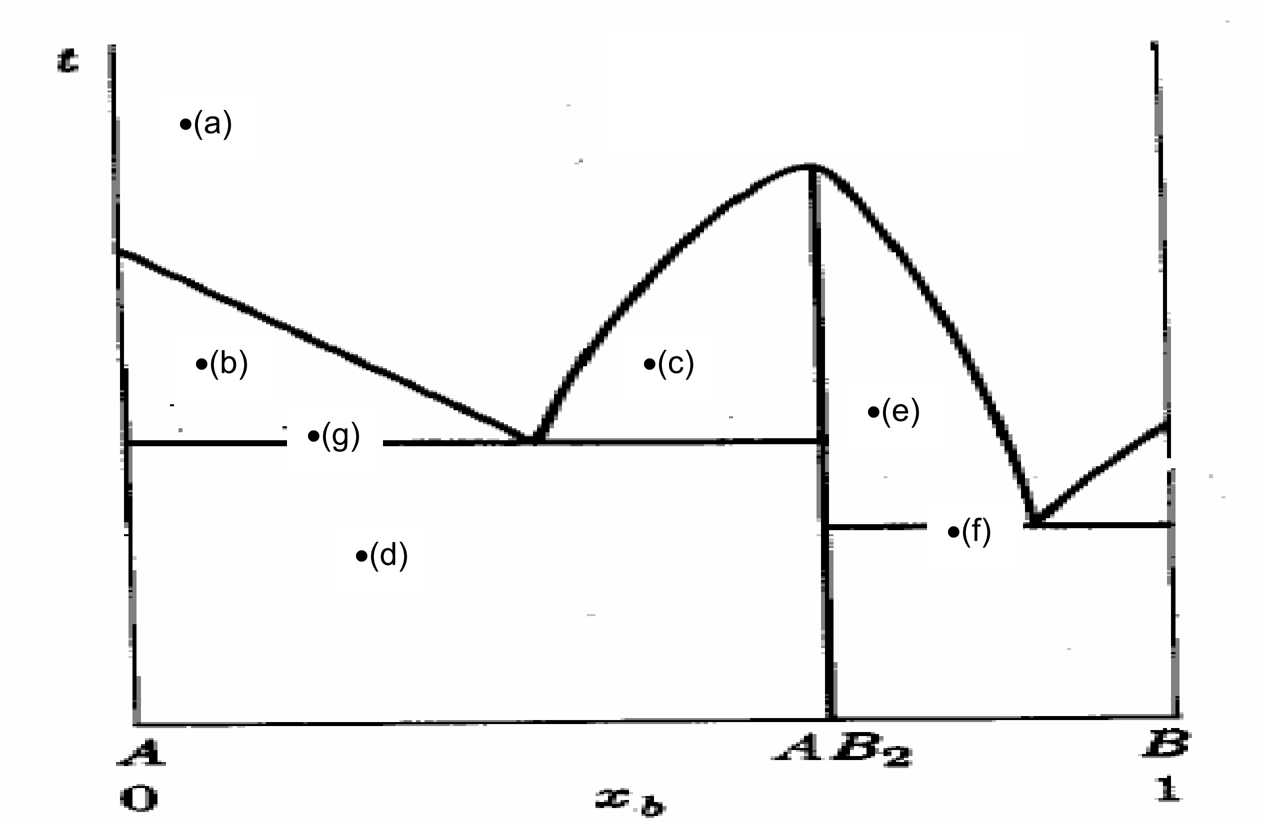
(i) What is the activity coefficient for acetone in a liquid solution which is nearly zero mole fraction of acetone in $CHCl_3$ at 35°C?

4. The activity of pure liquid water at 1 atm is 1, according to the definition of the standard state as a pure liquid at 1 atm. Calculate the activity of pure liquid water at 50°C and 10^4 atm, given that the integral $\int V_m \, \mathrm{d}p$ between 1 atm and 10^4 atm is = 161.450 L atm for liquid water at 50°C.

5. For the state points labeled (a) through (k) describe the system as explicitly as you can in terms of

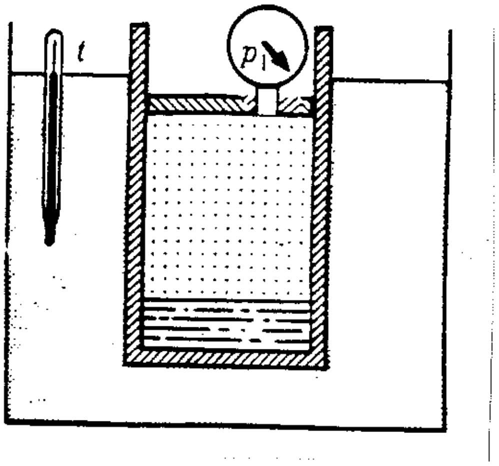
(1) the phases present
(2) the composition of each phase
(3) where possible, the relative amounts of each phase

Place your answers in the table below



state point	phases present	composition of each phase	relative amounts of each phase
(a)			
(b)			
(c)			
(d)			
(e)			
(f)			
(g)			

6. A mixture of 0.3 moles of liquid A and 0.2 moles of liquid B are placed in the container shown and the ideal solution is allowed to come to thermal and mechanical equilibrium. The bath temperature is maintained at 21.5°C. The pressure gauge reads 0.060 atm.



At their normal boiling points 110.6°C and 80.1°C respectively, the enthalpies of vaporization of A and B are respectively, 34.4 and 30.8 kJ mol^{-1} and the densities of liquid A and B at this temperature are respectively 9.407 and 11.247 mol L^{-1}. Describe the system at equilibrium by filling in the following table with numbers (not formulas) and their corresponding units. (Do all the derivations and calculations in the space provided below the table.)

	numerical values and units
vapor pressure of pure liquid A at 21.5°C	
vapor pressure of pure liquid B at 21.5 °C	
mole fraction of B in the liquid phase	
partial pressure of A in the vapor	
mole fraction of A in the vapor phase	
number of moles of liquid	
number of moles of vapor	
number of moles of A in the liquid phase	
number of moles of B in the vapor phase	

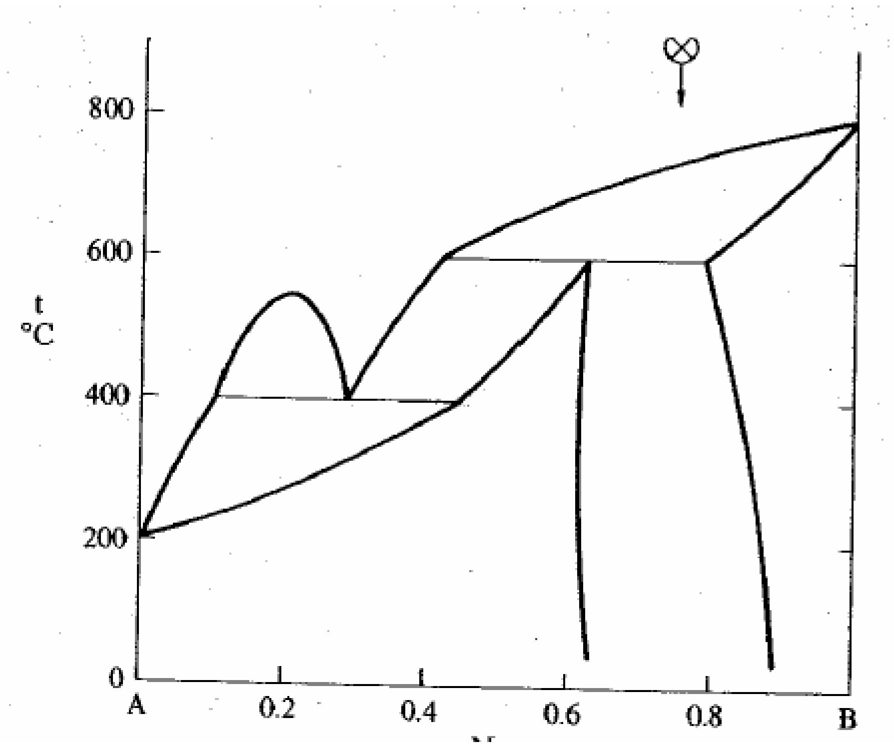
Provide the basis for your numerical answers by doing the derivations and calculations in this space and on the next page:

7. When equilibrium is reached in the following systems, which of the following conditions apply? Choose as many as apply and place only the letters in the Ans. column in the table below.

A. $\mu_B(\text{liquid}) = \mu^\circ{}_B(\text{gas}) + RT\ln p_B{}^*$
B. $\mu_B(\text{liquid solution}) = \mu^\circ{}_B(\text{gas}) + RT\ln p_B(\text{liquid solution})$
C. $\ln (1/x_B) = V_{mB}\, p_h/RT$
D. $x_B = \exp\{-\Delta_{fus}\boldsymbol{H}_B[(1/T_f) - (1/T_f{}^*)]\}$
E. $\boldsymbol{f}_B(\text{liquid solution}) = \boldsymbol{f}_B(\text{solid})$
F. $\mu_B(\text{solid}) = \mu^\circ{}_B(\text{gas}) + RT\ln \boldsymbol{f}_B(\text{liquid solution})$
G. $\boldsymbol{G}_{\text{final}} = n_A[\mu^\circ{}_A + RT\ln \boldsymbol{f}_A(\text{liquid solution})] + n_B[\mu^\circ{}_B + RT\ln \boldsymbol{f}_B(\text{liquid solution})]$
H. $p_B = X_B\, p_B{}^*$
I. $p_B = K_{H,B}\, X_B$
J. $\mu_B(\text{solid}) = \mu_B(\text{liquid solution})$
K. $\mu_A(\text{liquid solution}) = \mu^\circ{}_A(\text{gas}) + RT\ln \boldsymbol{f}_A(\text{liquid solution})$
L. $\mu_A(\text{solid}) = \mu_A(\text{liquid solution})$
M. $x_A = \exp\{-\Delta_{fus}\boldsymbol{H}_B[(1/T_f) - (1/T_f{}^*)]\}$
N. $y_A = x_A p^*{}_A / [x_A(p^*{}_A - p^*{}_B) + p^*{}_B]$
O. $p_2/p_1 = \exp\{-[\Delta_{vap}\boldsymbol{H}/R][(1/T_2) - (1/T_1)]\}$
P. $\ln a_B = \ln[p/1\text{ atm}] + [\Delta_{vap}\boldsymbol{H}_B/R][(1/T_b) - (1/T^*{}_b)]$
Q. $(\partial\mu_B(\text{liquid solution})/\partial p_h)_T = (\partial\mu^\circ{}_B(\text{liquid solution})/\partial p_h)_T + RT(\partial\ln \boldsymbol{a}_B/\partial p_h)_T = V_{m,B}(\text{liquid})$
R. $\ln X_A = -\pi V_B(\text{liquid})/RT$
S. $\ln a_B = -\Delta_{fus}\boldsymbol{H}_B[(1/T_f) - (1/T_f{}^*)]$
T. $\ln a_B = \Delta_{vap}\boldsymbol{H}_B[(1/T_b) - (1/T_b{}^*)]$
U. $\ln a_B = p_B/p^*{}_B$
V. $a_B = p_B/p^*{}_B$
W. $a_A = -\pi V_B(\text{liquid})/RT$
X. $d\mu_A = d\mu_B$
Y. $a_B = p_B/K_{H,B}$
Z. $(m_\pm{}^s) = (m_+)^p(m_-)^q$

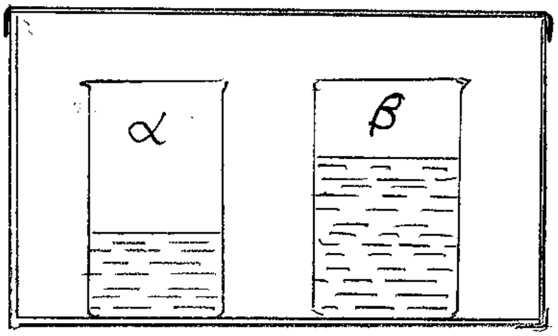
	system	process	Ans
1	pure solid B and liquid solution of B with a non-volatile solute are present in a container	B melting or B freezing out	
2	compartment 1 has pure liquid B, compart ment 2 has a liquid solution of A in B, they are separated by a molecular sieve permeable to B only	osmosis	
3	a small quantity of dry ice is introduced into a bottle containing liquid water and the bottle is sealed off.	CO_2 goes into solution	
4	n_A moles of liquid A and n_B moles of liquid B are in two bulbs at temperature T separated by a partition	partition is removed	
5	sufficient solid B is placed into a liquid A in a container	most solid B dissolves, a small amount remains in solid phase	

8. Draw a cooling curve for a solution starting at the state point ⊗ . The abscissa is in mole fraction of B.



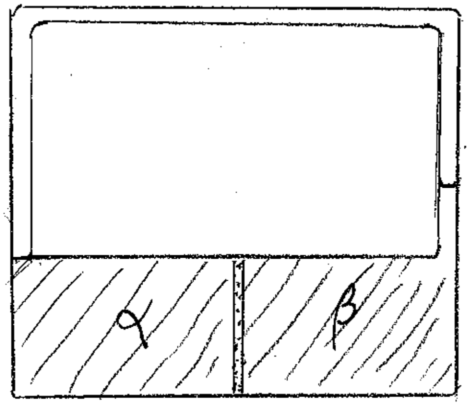
Describe what would be observed through the clear wall in the apparatus in which heat is systematically withdrawn from the system at a constant rate,
(1) along each line on the cooling curve
(2) at each point where the cooling curve exhibits a change in slope dT/dt

9. (a) Two containers containing solutions of a non-volatile solute in solvent A are placed in a closed container as shown below. Originally, the solution in container α was prepared from 0.1 mole of solute and 1000 g solvent A, and the solution in container β was prepared from 0.05 mole of solute and 2000 g solvent A. When equilibrium was finally reached, what are the amounts of solute and solvent in each container?



container	amount of solute	amount of solvent
α		
β		

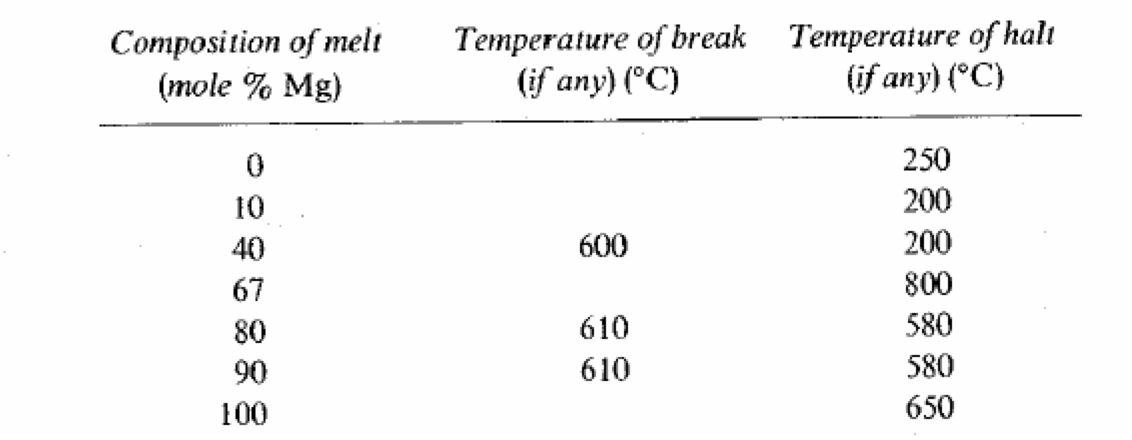
(b) Two solutions of a non-volatile solute in solvent A are in sections separated by a semi-permeable membrane in a closed container as shown below, where the U-shaped "dead space" has a negligible volume. Originally, the solution in side α was prepared from 0.1 mole of solute and 1000 g solvent A, and the solution in side β was prepared from 0.05 mole of solute and 2000 g solvent A. The heights h_α and h_β (measured as shown) are originally 0.0 and 12 cm respectively. After equilibrium was finally reached, what are the heights h_α and h_β ? The cross-sectional area of the uprights is a cm^2. The density of the solvent is d g mL^{-1}. Define symbols for any additional information you need to have and write your answer in the table terms of these quantities.



side	height, cm
α	$h_\alpha =$
β	$h_\beta =$

(c) One kg of ice is formed in a container sitting outdoors in winter, at an ambient temperature of -15 °C. Calculate the number of moles of a salt ($CaCl_2$) that will have to be added to the ice in the container in order to cause all but an infinitesimal amount of ice to melt. Assume that $\gamma_\pm = 1.0$

10. The following information is obtained on cooling curve data on the system Sn-Mg. Sketch the simplest melting point diagram consistent with these data. Label the phase regions and give the compositions of any compounds formed.



Composition of melt (*mole %* Mg)	*Temperature of break* (*if any*) (°C)	*Temperature of halt* (*if any*) (°C)
0		250
10		200
40	600	200
67		800
80	610	580
90	610	580
100		650