Name:______________________________________

First three letters of last name

Chemistry 342

ANSWERS TO 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: $1\ \mathrm{J} = 1\ \mathrm{kg\ m^{-2}\ s^{-2}}$ $1\ \mathrm{atm} = 101325\ \mathrm{Pa}$

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

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

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

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

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

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

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

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

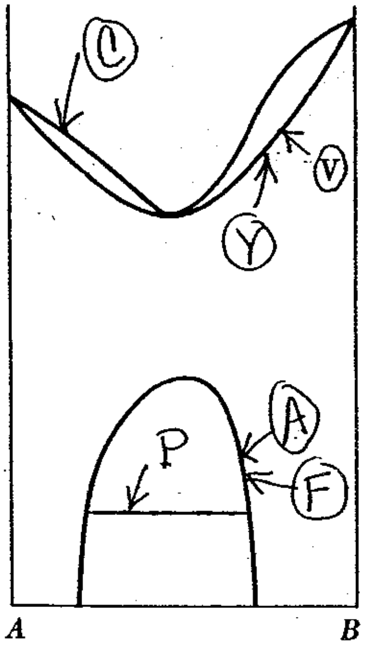
	score
1	
2	
3	
4	
5	
6	
7	
8	
9	
10	

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.

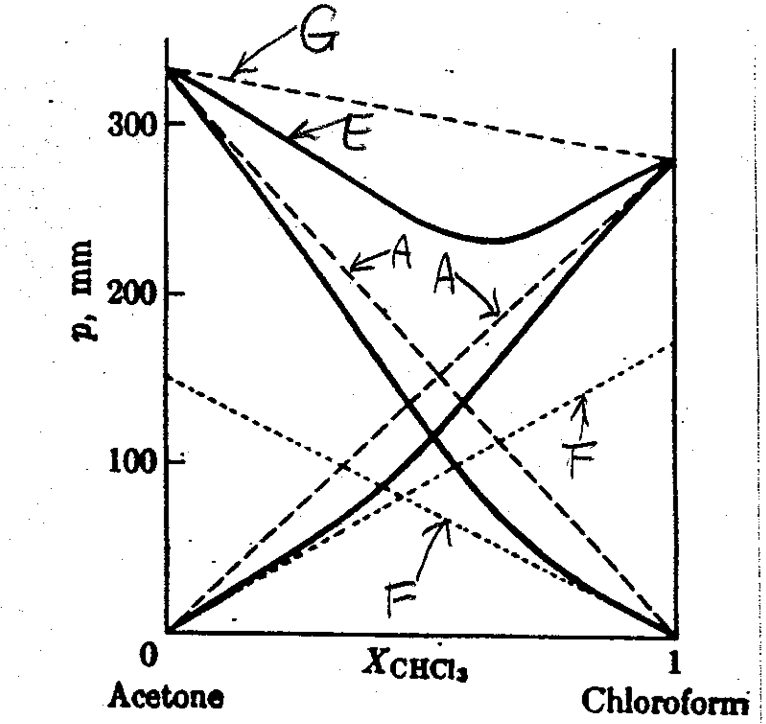
Equations:

(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) $dp/dT = \Delta_{vap}\boldsymbol{H}/\{T(V_{m,\text{gas}} - V_{m,\text{liquid}})\}$
(I) $\ln x_A = \Delta_{fus}\boldsymbol{H}/R\left[\dfrac{-1}{T} + \dfrac{1}{T^*}\right]$
(J) $(\partial\mu_{\text{gas}}/\partial T)_p = -\boldsymbol{S}_{m,gas}$
(K) $\mu^*_{\text{A,vap}} = \mu^\circ_T + RT\ln(p^*_A/1)$
(L) $\mu_{\text{A,liquid}}(T,p,x_A) = \mu_{\text{A,solid}}(T,p)$
(M) $\mu_A(T) = \mu_A{}^*{}_T + RT\ln x_A$
(N) $(\partial[\Delta_{\text{rxn}}\boldsymbol{G}^\circ/T]/\partial T)_p = -(\Delta_{\text{rxn}}\boldsymbol{H}^\circ/T^2)$
(O) $\ln\gamma_\pm = z_+z_-I^{1/2}(e^2/10\varepsilon k_B T)^{3/2}\{2\pi\rho N_{\text{Avog}}\}^{1/2}$
(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) $dp/dT = \Delta_{subl}\boldsymbol{H}/\{T(V_{m,\text{gas}} - V_{m,\text{crystal}})\}$
(S) F = 0
(T) F = 1   F′ = 0
(U) F = 2   F′ = 1
(V) $\mu(T) = \mu^\circ_T + RT\ln\dfrac{f}{1}$
(W) $\ln\dfrac{f}{p} = \displaystyle\int_0^p \frac{(Z-1)}{p}\,dp$
(X) $\boldsymbol{G}_{T,p} = \sum_i n_i\mu_i$
(Y) $(\partial\boldsymbol{G}/\partial T)_p = -\boldsymbol{S}$
(Z) $\Delta_{\text{rxn}}\boldsymbol{G} = (c\mu_C + e\mu_E) - (a\mu_A + b\mu_B)$
(Z') $\gamma_A(T) = \dfrac{p_A(T)}{x_A p_A^*(T)}$

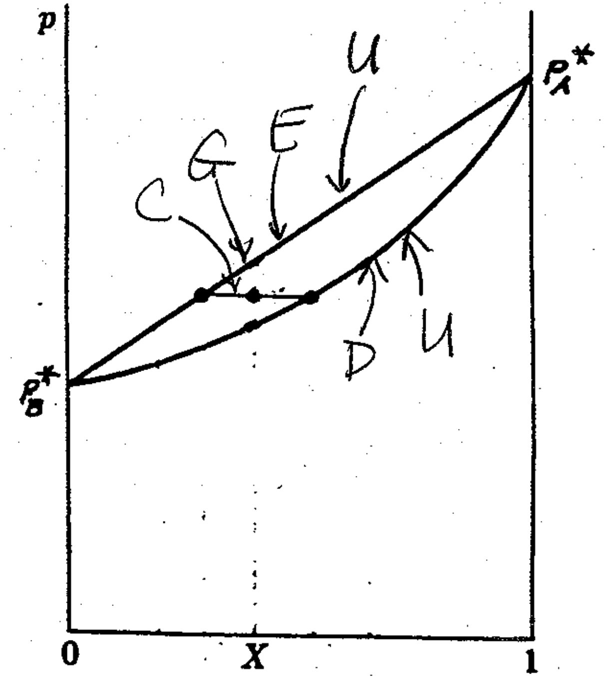
Your answer should look like the following example:



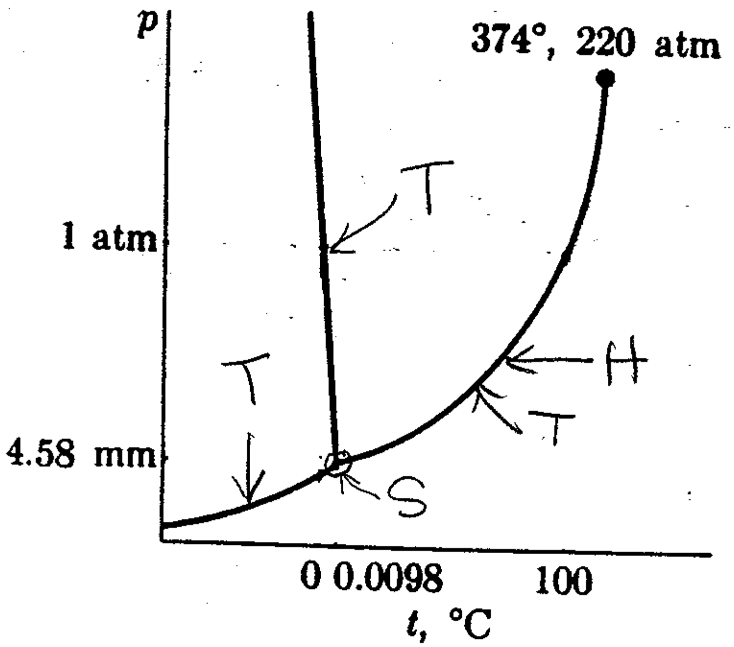
(a)


G
E
A
A
F
F
300
200
100
p, mm
0
X_{CHCl_3}
1
Acetone
Chloroform

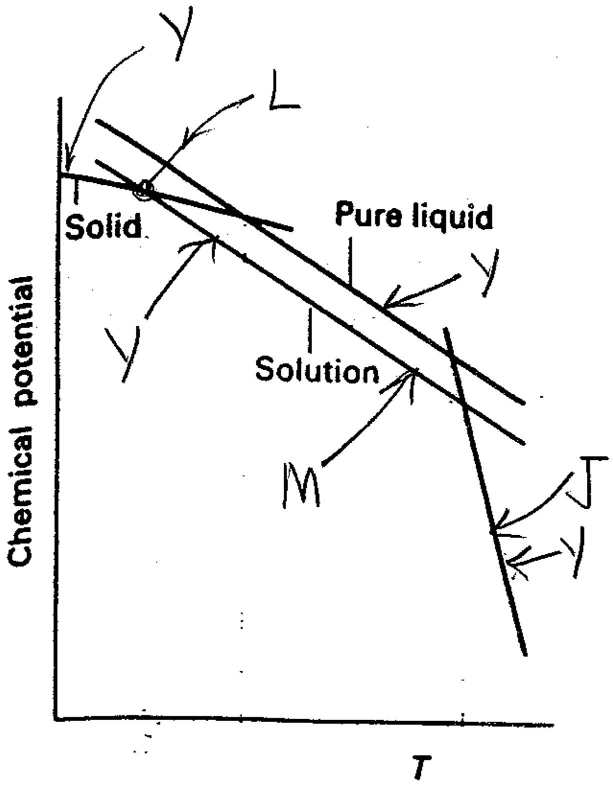
(b)


p
U
C
G
E
p_A^*
p_B^*
D
U
0
X
1

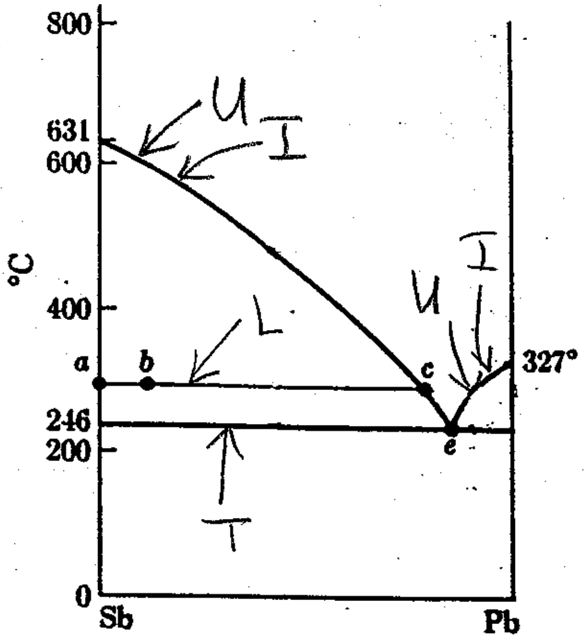
(c)


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

(d)

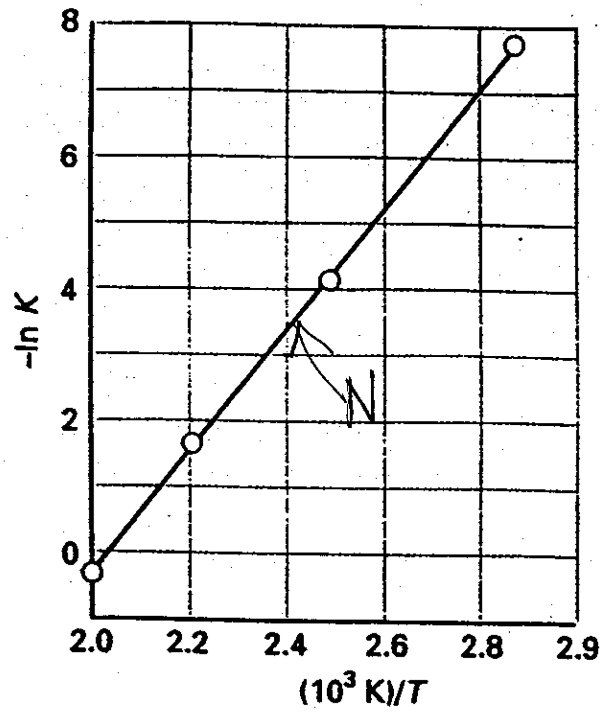

Y
L
Solid
Pure liquid
Y
Y
Solution
Chemical potential
M
J
Y
T

(e)



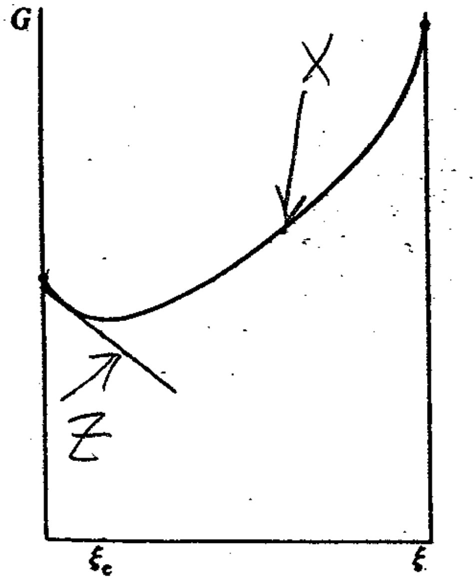
800
631
600
400
246
200
0
°C
a
b
c
e
327°
Sb
Pb
U
I
L
U
I
T

(f)



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

(g)



G
X
Z
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?

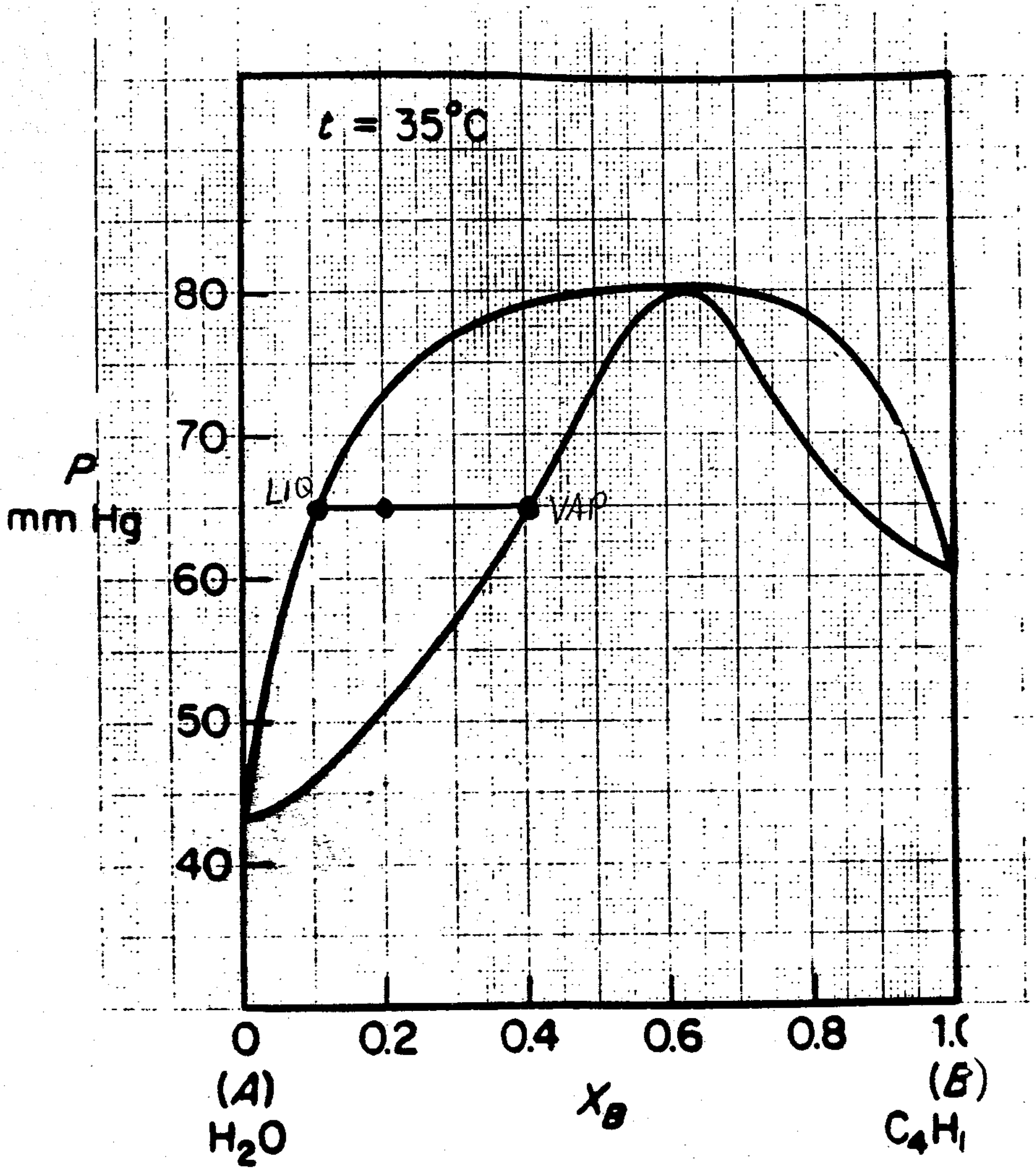
(i) Would the activity coefficient of B in a liquid solution of A+B be smaller or greater (which one?) than 1.0?

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

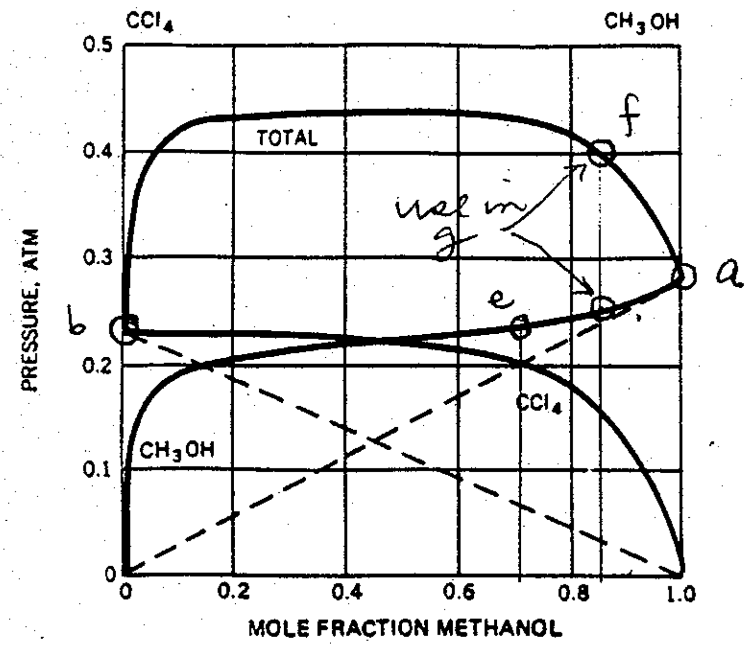
(a)	(b)	(c)	(d)	(e)
$y_B = 0.40$	$x_A = 0.90$	$n_{LIQ}/n_{VAP} = 2$	weaker	43 mm

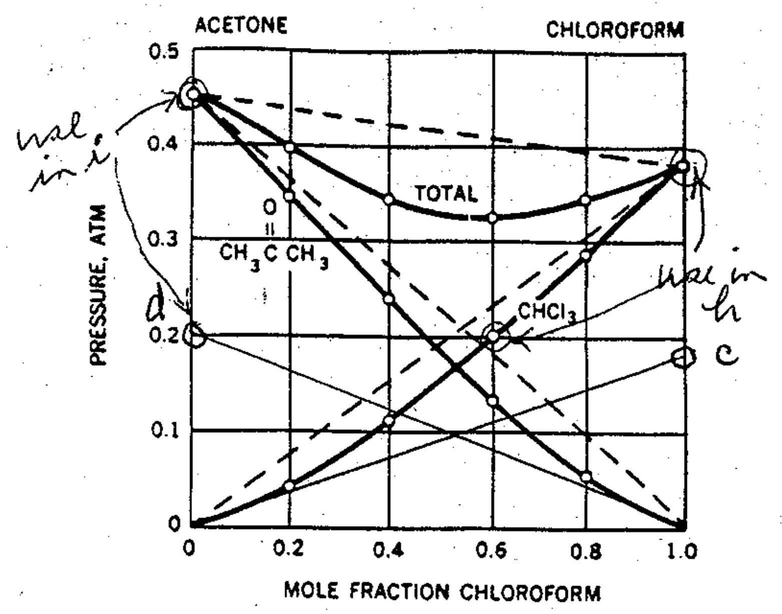
(f)	(g)	(h)	(i)	(j)
60 mm	$x_B = 0.6$	lower	greater	greater

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


t = 35°C
80
70
60
50
40
P
mm Hg
LIQ
VAP
0
0.2
0.4
0.6
0.8
1.(
(A)
H_2O
X_B
(B)
C_4H_1

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?	0.28 atm
(b) What is the vapor pressure of pure liquid CCl_4?	0.23 atm
(c) What is the Henry's law constant for $CHCl_3$ in acetone solution?	0.17 atm
(d) What is the Henry's law constant for acetone in $CHCl_3$ solution?	0.20 atm
(e) What is the partial vapor pressure of CH_3OH in a solution with $x_{CH3OH} = 0.70$?	0.23 atm
(f) What is the total vapor pressure of a solution of CH_3OH in CCl_4 with $x_{CCl4} = 0.15$?	0.40 atm
(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 $x_{CCl4} = 0.15$?	0.25/0.40=0.625
(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? $(\mu_i - \mu_i°) = RT \ln p_i/p_i^*$	8.3144(308)× ln(0.20/0.38) = -1643.7 J mol^{-1}
(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? Rational system $a_i = p_i/p_i^*$ in the limit $x_i \to 0$, $p_i = K_i x_i$ Henry's law $a_i = K_i x_i / p_i^*$ Thus, $\gamma_i = a_i/x_i = K_i/p_i^*$. *For acetone* $\gamma_{acet} = K_{acet}/p^*_{acet}$	$\gamma_{acet} = K_{acet}/p^*_{acet} = 0.20/0.45 = 0.444$

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 $\int V_m \, dp$ between 1 atm and 10^4 atm is = 161.450 L atm for liquid water at 50°C.

$d\boldsymbol{G} = -\boldsymbol{S}dT + Vdp$

$d\mu_{LIQ}(T,p) = Vdp$

$\mu_{LIQ}(T,p_2) - \mu_{LIQ}(T,1\text{ atm}) = \int V_m \, dp$

Definition of activity:

$\mu_{LIQ}(T,p_2) = \mu_{LIQ}{}^{o}{}_{T} + RT \ln \boldsymbol{a}_{LIQ}(T,p_2)$

$\mu_{LIQ}(T,p_2) - \mu_{LIQ}(T,1\text{ atm}) \quad = RT \ln \boldsymbol{a}_{LIQ}(T,p_2) / \boldsymbol{a}_{LIQ}(T,1\text{ atm})$

$\boldsymbol{a}_{LIQ}(T,1\text{ atm}) = 1$

Therefore, $\int V_m \, dp = RT \ln \boldsymbol{a}_{LIQ}(T,p_2)/1$

$161.450\text{ L atm} = RT \ln \boldsymbol{a}_{LIQ}(323\text{ K}, 10^4\text{ atm})$

$\ln \boldsymbol{a}_{LIQ}(323\text{ K}, 10^4\text{ atm}) = 161.450/(0.0820567 \times 323) = 6.09$

$\boldsymbol{a}_{LIQ}(323\text{ K}, 10^4\text{ atm}) = 439$

ASIDE: Incidentally, $\boldsymbol{a}_{LIQ}(T,p_2)$ is also $= f_{GAS}(T,p_2)/f_{GAS}(T,1\text{ atm})$ which reinforces the identification of activity with the chemical potential. This is how we do it for this system:

Liquid and vapor at equilibrium $\mu_{LIQ}(T,1\text{ atm}) = \mu_{VAP}(T,1\text{ atm}) \quad (2)$

$\mu_{LIQ}(T,p_2) = \mu_{VAP}(T,p_2) \quad (1)$

subtract equation (2) from eq(1)

$\mu_{LIQ}(T,p_2) - \mu_{LIQ}(T,1\text{ atm}) = \mu_{VAP}(T,p_2) - \mu_{VAP}(T,1\text{ atm})$

But,

$\mu_{VAP}(T,p_2) = \mu_{GAS}{}^{o}{}_{T} + RT \ln f(T,p_2) \quad (3)$

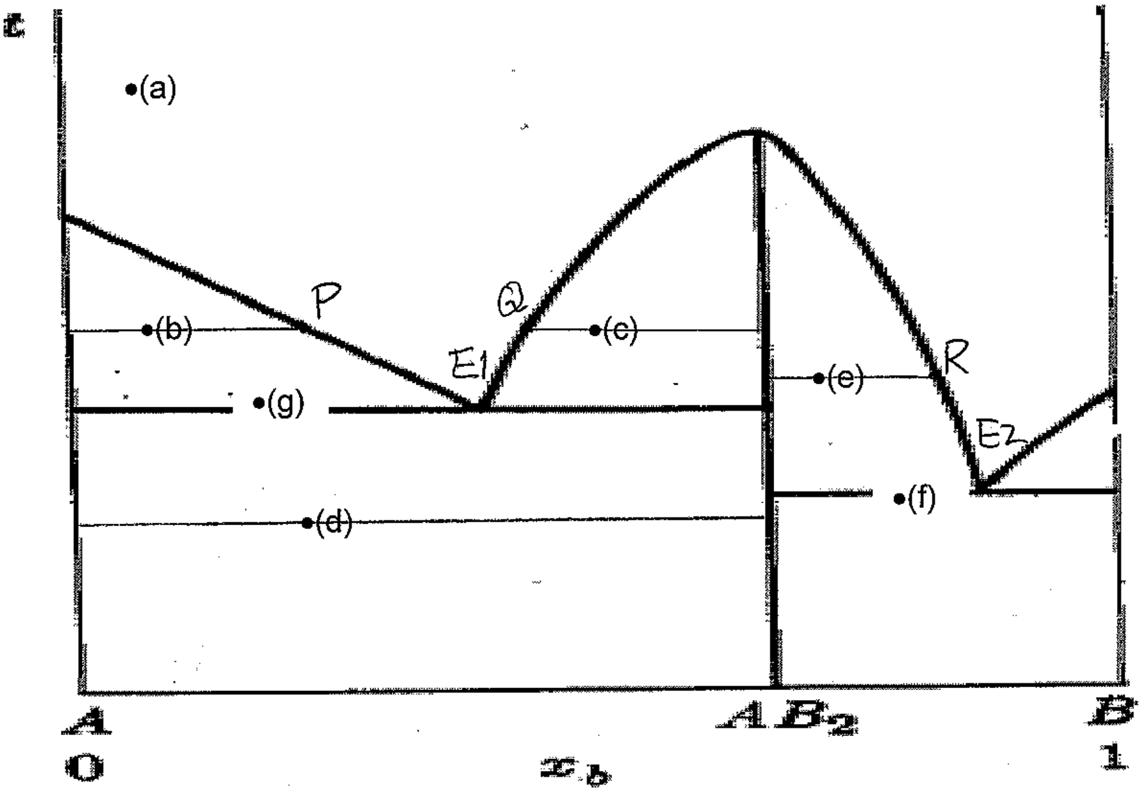
$\mu_{VAP}(T,1\text{ atm}) = \mu_{GAS}{}^{o}{}_{T} + RT \ln f(T,1\text{ atm}) \quad (4)$

Therefore, $\mu_{LIQ}(T,p_2) - \mu_{LIQ}(T,1\text{ atm}) \quad = RT \ln f_{GAS}(T,p_2)/f_{GAS}(T,1\text{ atm})$

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

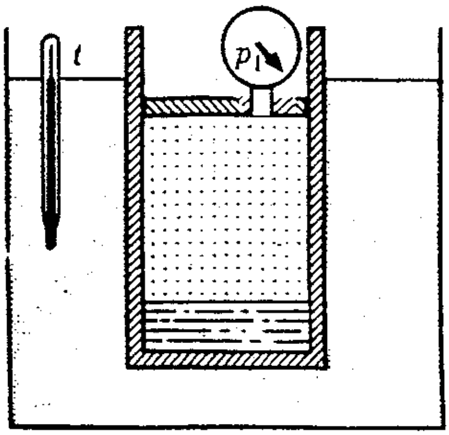
(1) the phases present
(2) the composition of each phase
(3) where possible, the relative amounts of each phase

Place your answers in the table below



state point	phases present	composition of each phase	relative amounts of each phase
(a)	1 phase: a liquid solution	same as overall composition given by point (a), $x_B=0.07$	all
(b)	2 phases: pure solid A and liquid solution	pure solid A, liquid of composition given by point P, $x_B=0.23$	$n_{\text{liq soln}} \bullet (x_P - x_{(b)}) = n_{\text{solid A}} \bullet (x_{(b)} - 0)$ $n_{\text{liq soln}}/n_{\text{solid A}} = (x_{(b)} - 0)/(x_P - x_{(b)}) = 1/2$, 33% LIQ
(c)	2 phases: pure solid AB_2 and liquid solution	pure solid AB_2, liquid of composition given by point Q, $x_B=0.44$	$n_{\text{liq soln}} \bullet (x_{(c)} - x_Q) = n_{\text{solid AB2}} \bullet (0.6667 - x_{(c)})$ $n_{\text{liq soln}}/n_{\text{solid AB2}} = (0.6667 - x_{(c)})/(x_{(c)} - x_Q)$ $= 7/3$, 70% LIQ
(d)	2 phases: pure solid A and pure solid AB_2	pure solid A, pure solid AB_2	$n_{\text{solid A}} \bullet (x_{(d)} - 0) = n_{\text{solid AB2}} \bullet (0.6667 - x_{(d)})$ $n_{\text{solid A}}/n_{\text{solid AB2}} = (0.6667 - x_{(d)})/(x_{(d)} - 0) = 2/1$ 66% solid A
(e)	2 phases: pure solid AB_2 and liquid solution	pure solid AB_2, liquid of composition given by point R, $x_B=0.83$	$n_{\text{liq soln}} \bullet (x_R - x_{(e)}) = n_{\text{solid AB2}} \bullet (x_{(e)} - 0.6667)$ $n_{\text{liq soln}}/n_{\text{solid AB2}} = (x_{(e)} - 0.6667)/(x_R - x_{(e)})$ $= 2/5$, 28% LIQ
(f)	if exactly on the line, 3 phases: pure solid AB_2, pure solid B, eutectic solution	pure solid AB_2, pure solid B, liquid of composition given by point E2, $x_B=0.87$	solid B is infinitesimal $n_{\text{eut soln}} \bullet (x_{E2} - x_{(f)}) = n_{\text{solid AB2}} \bullet (x_{(f)} - 0.6667)$ $n_{\text{eut soln}}/n_{\text{solid AB2}} = (x_{(f)} - 0.6667)/(x_{E2} - x_{(f)})$ $= 8/5$, 61% LIQ
(g)	3 phases: pure solid AB_2, pure solid A, eutectic solution	pure solid A, pure solid AB_2, liquid of composition given by point E1, $x_B=0.39$	solid AB_2 is infinitesimal, $n_{\text{eut soln}} \bullet (x_{E1} - x_{(g)}) = n_{\text{solid A}} \bullet (x_{(g)} - 0)$ $n_{\text{eut soln}}/n_{\text{solid A}} = (x_{(g)} - 0)/(x_{E1} - x_{(g)}) = 5/6$, 45%LIQ

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	0.03834 atm
vapor pressure of pure liquid B at 21.5 °C	0.1245 atm
mole fraction of B in the liquid phase	0.25
partial pressure of A in the vapor	0.02875 atm
mole fraction of A in the vapor phase	0.479
number of moles of liquid	0.223 moles
number of moles of vapor	0.277 moles
number of moles of A in the liquid phase	0.167 moles
number of moles of B in the vapor phase	0.144 moles

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

$d\mu_{LIQ} = d\mu_{VAP}$

$d\mu_{LIQ} = -\boldsymbol{S}_{m,LIQ}\,dT + V_{m,LIQ}\,dp$

$d\mu_{VAP} = -\boldsymbol{S}_{m,VAP}\,dT + V_{m,VAP}\,dp$

$-\boldsymbol{S}_{m,LIQ}\,dT + V_{m,LIQ}\,dp = -\boldsymbol{S}_{m,VAP}\,dT + V_{m,VAP}\,dp$

$(\boldsymbol{S}_{m,VAP} - \boldsymbol{S}_{m,LIQ})dT = (V_{m,VAP} - V_{m,LIQ})dp$

$\therefore dp/dT = (\boldsymbol{S}_{m,VAP} - \boldsymbol{S}_{m,LIQ}) / (V_{m,VAP} - V_{m,LIQ})$ the ***Clapeyron equation***

$(\boldsymbol{S}_{m,gas} - \boldsymbol{S}_{m,liquid}) = \Delta_{vap}\boldsymbol{H}/T$

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

On this curve are sets of (p,T) values at which liquid coexists with gas.

Since $V_{m,gas} >> V_{m,liquid}$ If desired, can actually take $V_{m,liquid}$ into account since these are given.

and if $\Delta_{vap}\boldsymbol{H}$ *is only weakly dependent on T,*

and if ideal gas behavior, $V_{m,gas} \approx RT/p$, then

$dp/dT = \Delta_{vap}\boldsymbol{H}p/RT^2$

$\int dp/p \approx \Delta_{vap}H/R \int d(-1/T)$ integrate from the normal boiling point to any other (p,T)

$$\ln (p/1\ \text{atm}) \approx \Delta_{vap}H/R \left[-\frac{1}{T} + \frac{1}{T_b} \right]$$

By definition of normal boiling point: at the normal boiling point $T = 110.6+273$, liquid A has an equilibrium vapor pressure equal to 1 atm. At some other temperature $T = 21.5+273.1$, the vapor pressure of pure liquid A is given by the Clapeyron eqn:

$$\ln (p/1\ \text{atm}) \approx (34.4\times10^3/8.3144) \left[-\frac{1}{294.6} + \frac{1}{383.7} \right] \quad \text{solve for } p$$

$p = p^*_A(T = 294.6) = 0.03834$ atm Answer

Do the same for B, the vapor pressure of pure liquid B is given by:

$$\ln (p/1\ \text{atm}) \approx (30.8\times10^3/8.3144) \left[-\frac{1}{294.6} + \frac{1}{353.2} \right] \quad \text{solve for } p$$

$p = p^*_B(T = 294.6) = 0.1245$ atm Answer

Given that an ideal solution is formed by A and B, the partial vapor pressures are given by Raoult's law

$p_A/p^*_A = x_A \qquad p_B/p^*_B = x_B$ *Raoult's law*

$p = p_A + p_B = x_A\, p^*_A + x_B\, p^*_B$ *summing up the partial pressures*

$0.060\ \text{atm} = x_A(0.0383) + x_B(0.1245) = (1-x_B)(0.0383) + x_B(0.1245)$ *solve for* x_B

$x_B = 0.25 \quad \therefore x_A = 0.75$ Answer

$p_A = x_A\, p^*_A = 0.75(0.03834\ \text{atm}) = 0.02875$ atm Answer

molefraction of A in the vapor is $y_A = p_A/p = 0.02875/0.060 = 0.479$ Answer

Conservation of moles of each component gives the *lever rule*:

$n_{LIQ}\,(x_A - X_A) = n_{VAP}\,(X_A - y_A)$

Given: total moles = 0.2+0.3 and molar composition: $X_A = 0.3/(0.2+0.3) = 0.60$ and $x_A = 0.75$ $y_A = 0.479$ from above calculations. Therefore,

$n_{LIQ}(0.75 - 0.60) = n_{VAP}(0.60 - 0.479) = (0.50 - n_{LIQ})(0.60 - 0.479)$ *solve for* n_{LIQ}

$n_{LIQ} = 0.223$ moles Answer

By difference, $n_{VAP} = 0.277$ moles Answer

moles of A in the liquid = $x_A\, n_{LIQ} = 0.75(0.223) = 0.167$ moles Answer

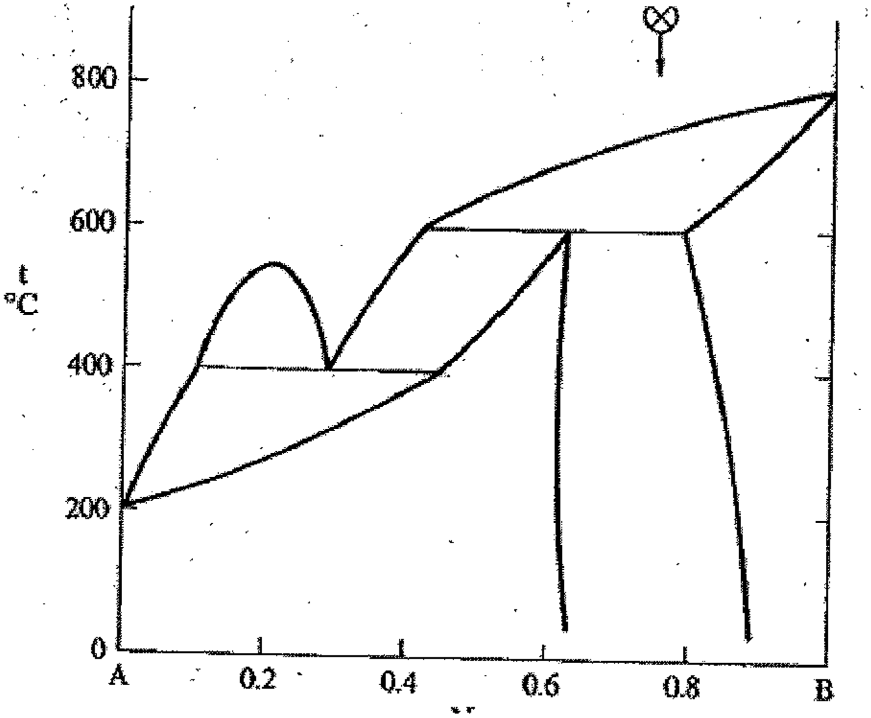
moles of B in the vapor = $y_B\, n_{VAP} = (1 - 0.479)(0.277) = 0.144$ moles Answer

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. $f_B(\text{liquid solution}) = f_B(\text{solid})$
F. $\mu_B(\text{solid}) = \mu^\circ{}_B(\text{gas}) + RT\ln f_B(\text{liquid solution})$
G. $\boldsymbol{G}_{\text{final}} = n_A[\mu^\circ{}_A + RT\ln f_A(\text{liquid solution})] + n_B[\mu^\circ{}_B + RT\ln f_B(\text{liquid solution})]$
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. $\mu_A(\text{liquid solution}) = \mu^\circ{}_A(\text{gas}) + RT\ln f_A(\text{liquid solution})$
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. $\ln X_A = -\pi V_B(\text{liquid})/RT$ INCORRECT
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. $\ln a_B = p_B/p^*{}_B$ INCORRECT
V. $a_B = p_B/p^*{}_B$
W. $a_A = -\pi V_B(\text{liquid})/RT$ INCORRECT
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	D,E,F,J,M,S
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	A,B,C,K,Q
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	I,Y
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	G
5	sufficient solid B is placed into a liquid A in a container	most solid B dissolves, a small amount remains in solid phase	E,J,K

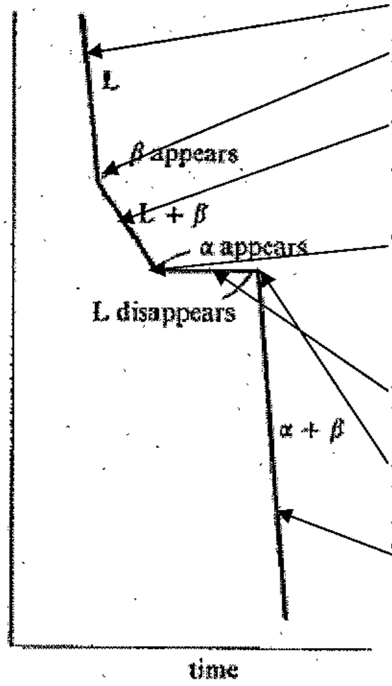
8. Draw a cooling curve for a solution starting at the state point ⊗ . The abscissa is in mole fraction of B.



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



Cooling of liquid solution containing A and B of constant composition ⊗

First hint of solid solution β appears, still mostly liquid solution of composition ⊗

Two phases: solid solution β and liquid solution both cooling, with composition of liquid solution changing according to line and composition of solid solution β changing according to line

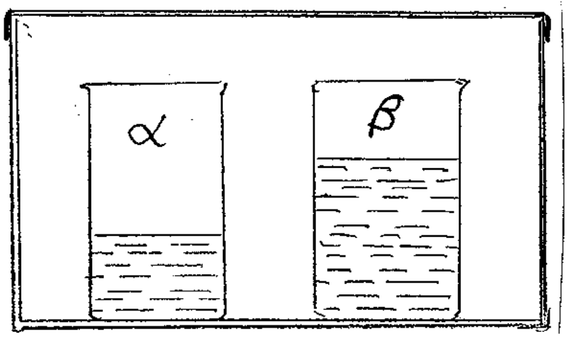
Three phases: First hint of solid solution α appears, still mostly solid solution β and liquid solution.

Liquid solution is diminishing while solid solution α growing, still mostly solid solution β.

Last vestige of liquid solution disappears, leaving only solid solution α and solid solution β

Two phases solid solution α and solid solution β continue to cool

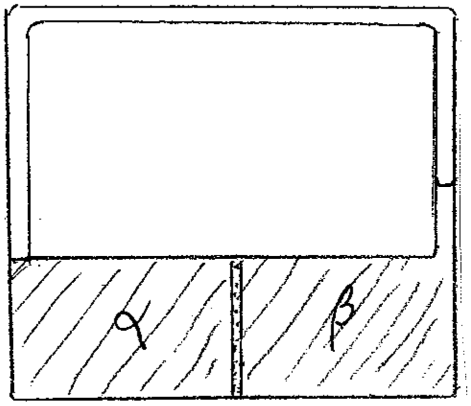
9. (a) Two containers containing solutions of a non-volatile solute in solvent A are placed in a closed container as shown below. Originally, the solution in container α was prepared from 0.1 mole of solute and 1000 g solvent A, and the solution in container β was prepared from 0.05 mole of solute and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



Since both liquid solutions are in equilibrium with the same vapor, both liquid solutions should have the same activity (concentration) when equilibrium is achieved. The total solute is 0.15 moles and the total solvent is 3000 g. Therefore the final equilibrium concentration in each beaker has to be molality = (0.15/3)= 0.05 molal. In each container, the solute is non-volatile and cannot equilibrate, so have to remain in the beakers; the solvent can move into the vapor phase and then into the beakers. Container α has 0.1 mol of solute, therefore has to end up with 2000 g solvent, while container β has 0.05 mol of solute, therefore has to end up with 1000 g solvent.

container	amount of solute	amount of solvent
α	0.1 mol	2000 g
β	0.05 mol	1000 g

(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.



see answer on last page

side	height, cm
α	h_α =
β	h_β =

(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 $\gamma_\pm = 1.0$

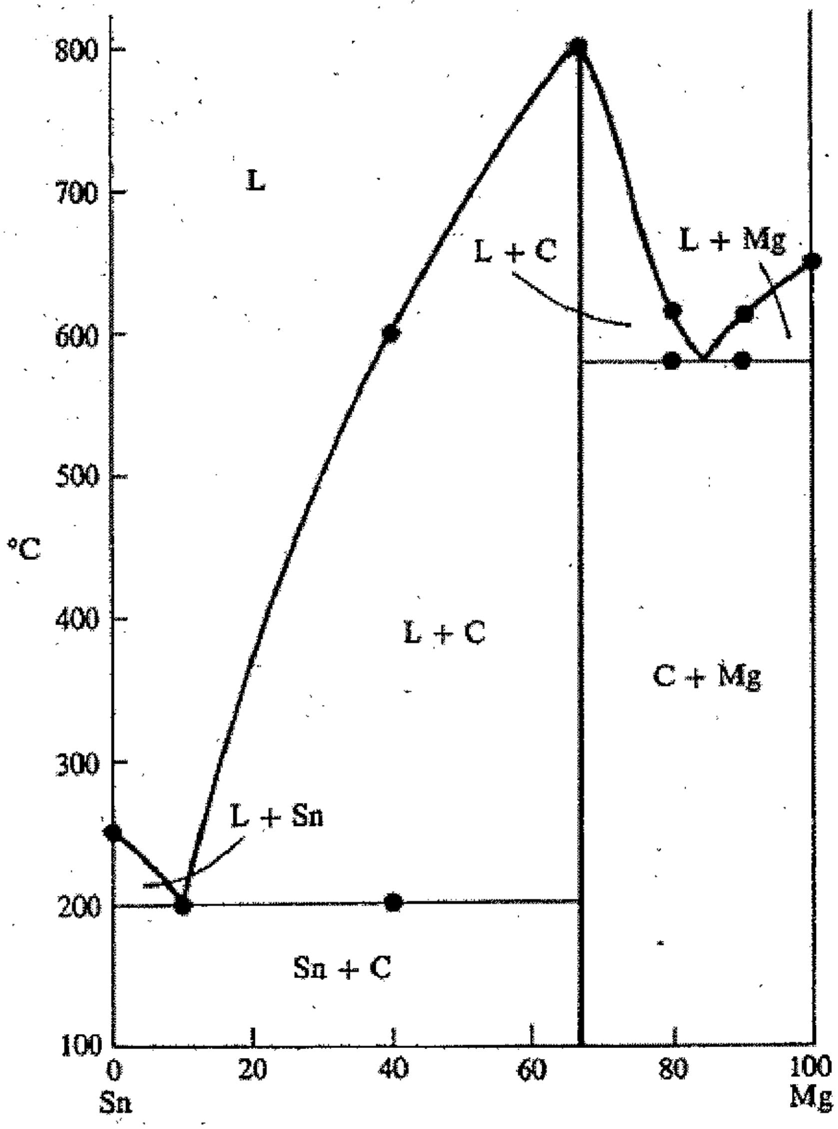
The freezing point depression is given by

$$a_{solute} = \frac{\Delta_{fusion,solvent}H}{R} \times \left[\frac{1}{T_f} - \frac{1}{T_f*}\right] = \frac{6003 Jmol^{-1}}{8.3144} \times \left[\frac{1}{258.16} - \frac{1}{273.16}\right]$$

We have used the molar $\Delta_{fus}H$ = 6003 J mol^{-1} for water, T_f* = 273.16K, and given T_f = 258.16K. We use the activity based on the practical definition using molality, and remember that $CaCl_2$ is a strong electrolyte. $a_\pm = \gamma_\pm m_\pm$ where, $(m_\pm)^s = (p^p q^q)m^s$. Here, p=1, q=2, s=3, and given $\gamma_\pm$ =1, $a_{solute} = a_\pm$ = $(1^1 2^2)m^3$. Therefore we can solve for m, the moles of $CaCl_2$ that needed to be added to 1kg of ice.

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



The presence of a congruent melting point at 67% indicates a compound of this composition, corresponding to formula Mg_2Sn.

9(b). The two sides do not have the same concentration. Therefore the solvent will move from the side that has the lower concentration of solute (0.025 m) on β side to the α side (0.1 m) that has higher concentration of solute, as in problem 9(a), approximately 1000 g of solvent has to move from the β side to the α side in order to have the same chemical potential on both sides of the membrane. Let us consider two stages: First, equalize the concentration on both sides, that is have 1000 g of solvent move from side β to α. Since h_α started at zero, all the extra 1000 g solvent will go to into h_α.

After first step, x_α and x_β are equal and

$$x_\beta = 1 - \frac{0.05}{0.05 + \frac{1000}{MW}} \quad \text{and} \quad h_\alpha = \frac{1000}{da}$$

Second, there is a further correction, because after this much solvent has moved, the α side will be under a greater hydrostatic pressure than the β side. To compensate for this, some of the solvent has to move back so as to have a somewhat greater solvent concentration on the β side.

Aside: Hydrostatic pressure $p_h = hdg$ where h is the height, *d* is the density and g is the acceleration of gravity. Pascal is kg m^{-1} s^{-2}, 1 atm = 101325 Pa. Where h is in cm, d in g cm^{-3}, g= 980.665 cm s^{-2}, we find

$$p_h = hdg\ \text{g cm}^{-2}\ \text{s}^{-2} \times (\text{kg}/1000\ \text{g}) \times (\text{m}/100\ \text{cm})^{-2}\ \text{Pa} \times (1\ \text{atm}/\ 101325\ \text{Pa})$$

Thus, we need to multiply h_α in cm by the factor (10/101325) to get hydrostatic pressure p_h in atm: $p_{h,\alpha} = h_\alpha \times (10/101325)$

So that both sides will have the same value of $\mu_{solvent}$, the following must be true:

$$\overline{V}_{B,liq} h_\alpha \frac{10}{101325} + RT\ln x_\alpha = \overline{V}_{B,liq} h_\beta \frac{10}{101325} + RT\ln x_\beta$$

where $\overline{V}_{B,liq} = MW_{solvent}/d$ and x_α and x_β are the respective mole fractions of solvent on each side. At the final stage,

$$\overline{V}_{B,liq}(h_\alpha - h_\beta) \times \frac{10}{101325} = RT\ln\frac{x_\beta}{x_\alpha}$$

Let us rewrite the ln as follows : $\ln\frac{x_\beta}{x_\alpha} = \ln\left[1 + \frac{(x_\beta - x_\alpha)}{x_\alpha}\right] \approx \frac{(x_\beta - x_\alpha)}{x_\alpha}$

$$\frac{MW_{solvent}}{d}(h_\alpha - h_\beta) \times \frac{10}{101325} = \frac{(x_\beta - x_\alpha)}{x_\alpha}.$$

Let *G* grams of solvent have moved back to β side to accomplish this. That would mean that

$$x_\beta = 1 - \frac{0.05}{0.05 + \frac{1000+G}{MW}};\ x_\alpha = 1 - \frac{0.1}{0.1 + \frac{2000-G}{MW}};\ \frac{(x_\beta - x_\alpha)}{x_\alpha} = \frac{MW \times 0.15G}{(2000-G)(0.05MW + 1000 + G)}$$

and $h_\alpha = \frac{1000-G}{da}$. Taking h_β=0 since it is the β side that lost solvent, we can solve for *G* in

$$\frac{MW_{solvent}}{d}\frac{(1000-G)}{da} \times \frac{10}{101325} = \frac{MW \times 0.15G}{(2000-G)(0.05MW + 1000 + G)}$$

Once we have *G* everything (h_α, x_α, x_β) I is known. To solve the problem we needed the molecular weight of the solvent *MW*, in addition to the given density *d* and cross-sectional area *a*.