Print in upper case the first three letters of your last name here: ☐☐☐

Your name: Jameson key

Chemistry 342

Third Exam

November 19, 1999

$1\ J = 1\ kg\ m^2\ s^{-2}$ $k_B = 1.38066\times10^{-23}\ J\ K^{-1}$ $R = N_{Avogadro}k_B$ 1.01325 bar = 1 atm

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

$p/p_0 = \exp[-(M/RT)gz]$ *barometric formula where* $g = 9.80665\ m\ s^{-2}$

van der Waals equation : $(p + a/V_m^2)(V_m - b) = RT$

monatomic gas molar heat capacity: $C_V = (3/2)R$

General relations for any equation of state:

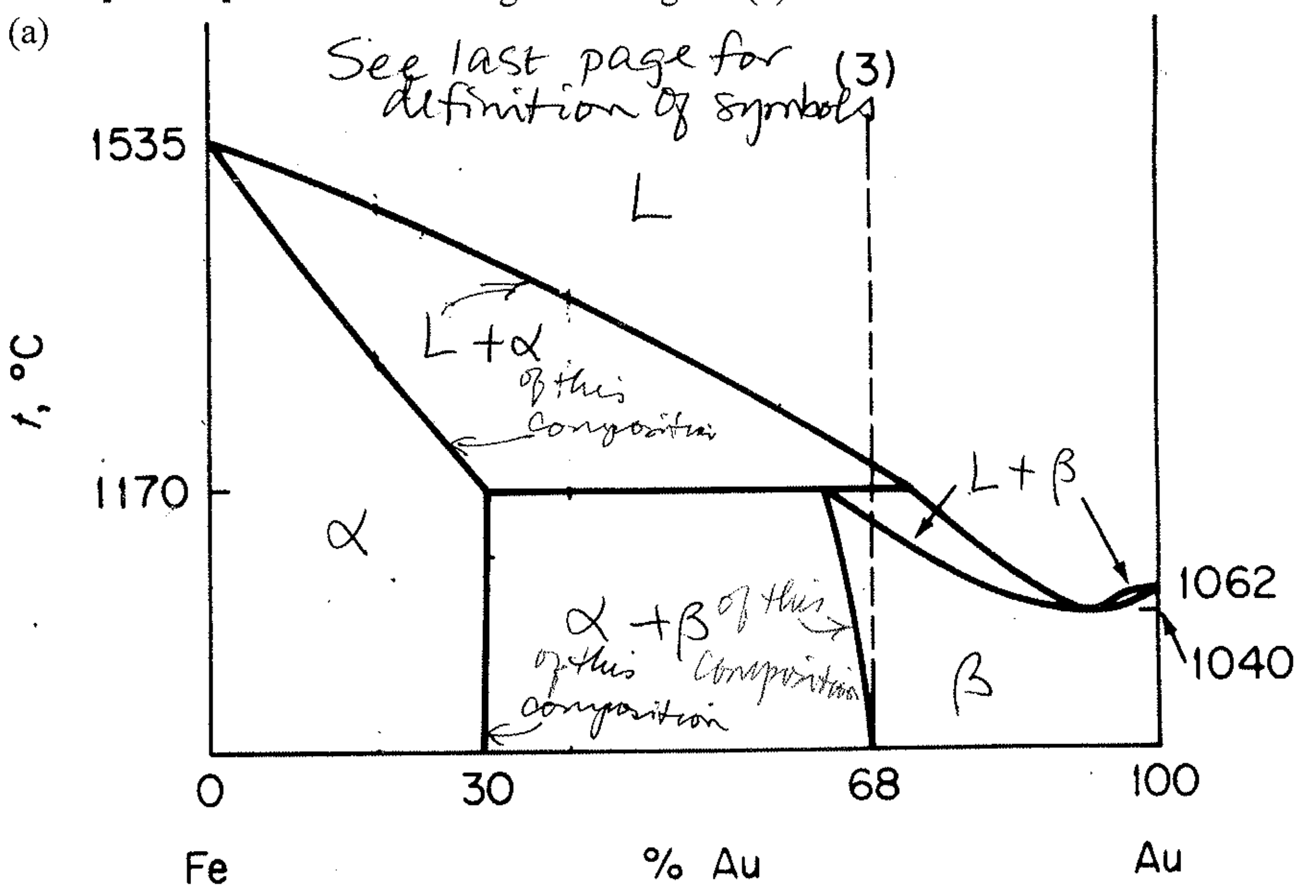
$(\partial U/\partial V)_T = T(\partial p/\partial T)_V - p$ $(\partial H/\partial p)_T = -T(\partial V/\partial T)_p + V$

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

In problem 1, the answers can be found by applying the following:
(a) The ends of a tie line provide the description of the two phases in equilibrium.
(b) number of degrees of freedom = #Components - #Phases + 2 (for T and p)

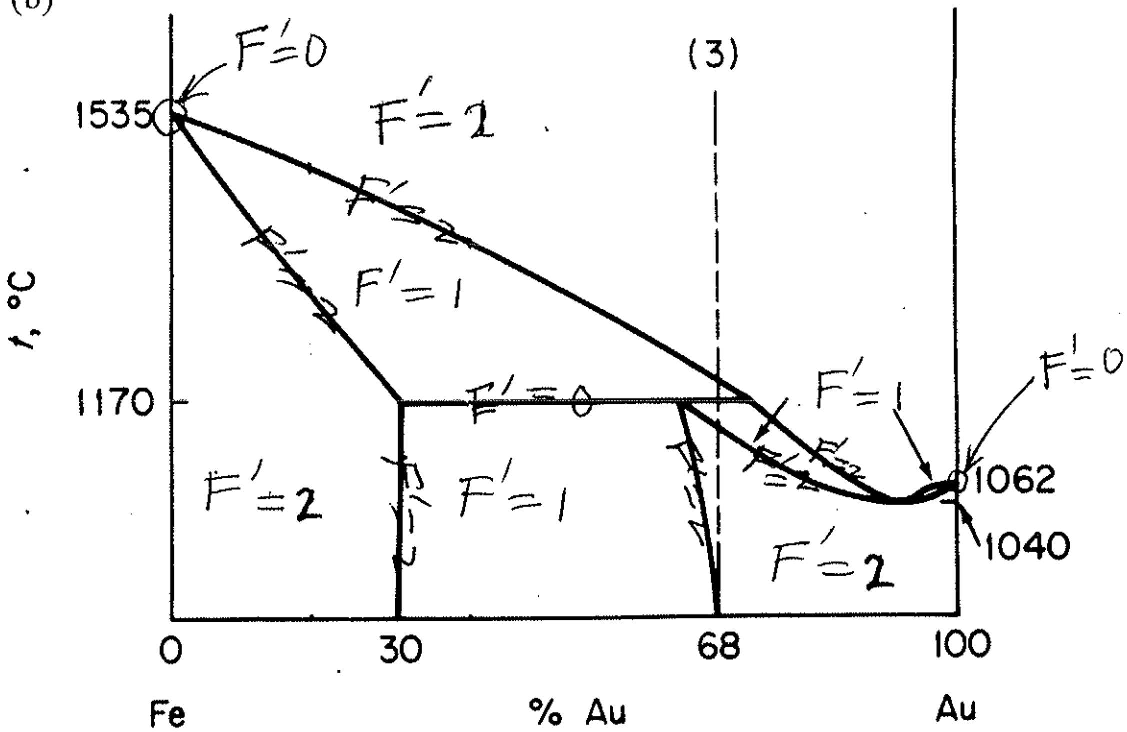
1. For the phase diagram shown below for the Fe Au system, **write the description of the phases present** in each region in diagram (a):

(a)

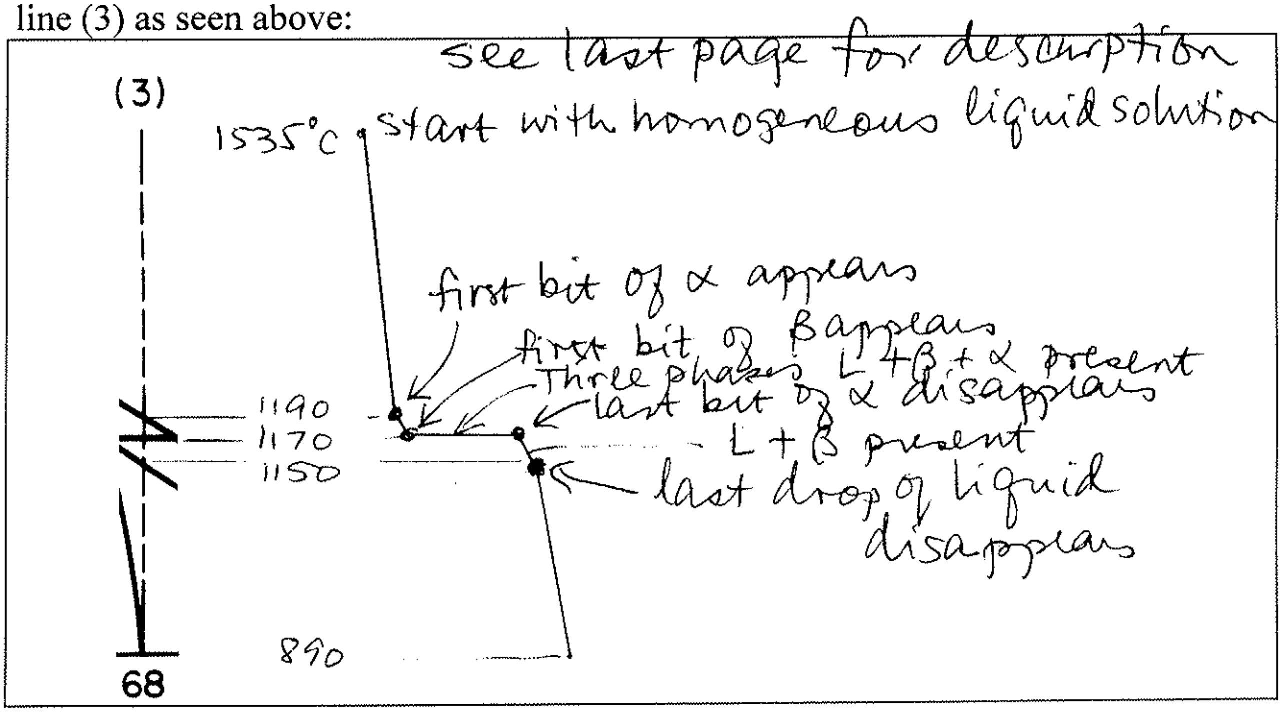


Write the number of degrees of freedom (in addition to pressure) in each region, line, intersection point in diagram (b): *Answer* use F′ = C - P + 1 = 3 - P {except at the 0% and 100% Au vertical lines, at which C=1}

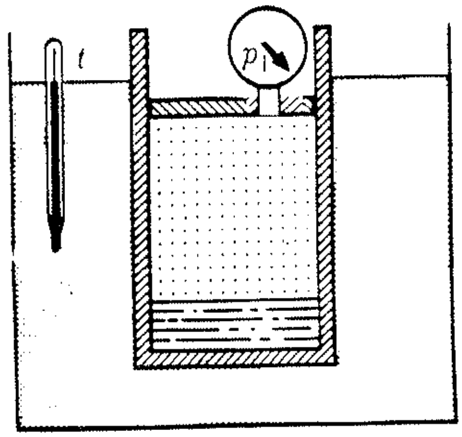
(b)



Draw a labeled cooling curve for a melt of composition 68% Au , along vertical line (3) as seen above:



2. 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.

	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
molefraction of B in the liquid phase	0.25
partial pressure of A in the vapor	0.02875 atm
molefraction 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:

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

$d\mu_{LIQ} = -S_{m,LIQ}\, dT + V_{m,LIQ}\, dp$

$d\mu_{VAP} = -S_{m,VAP}\, dT + V_{m,VAP}\, dp$

$-S_{m,LIQ}\, dT + V_{m,LIQ}\, dp = -S_{m,VAP}\, dT + V_{m,VAP}\, dp$

$(S_{m,VAP} - S_{m,LIQ})\, dT = (V_{m,VAP} - V_{m,LIQ})\, dp$

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

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

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

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 <u>if</u> $\Delta_{vap}H$ *is only weakly dependent on T,*
and <u>if</u> ideal gas behavior, $V_{m,gas} \approx RT/p$, then

$dp/dT = \Delta_{vap}Hp/RT^2$

$\int dp/p \approx \Delta_{vap}H/R \int d(-1/T)$ 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}

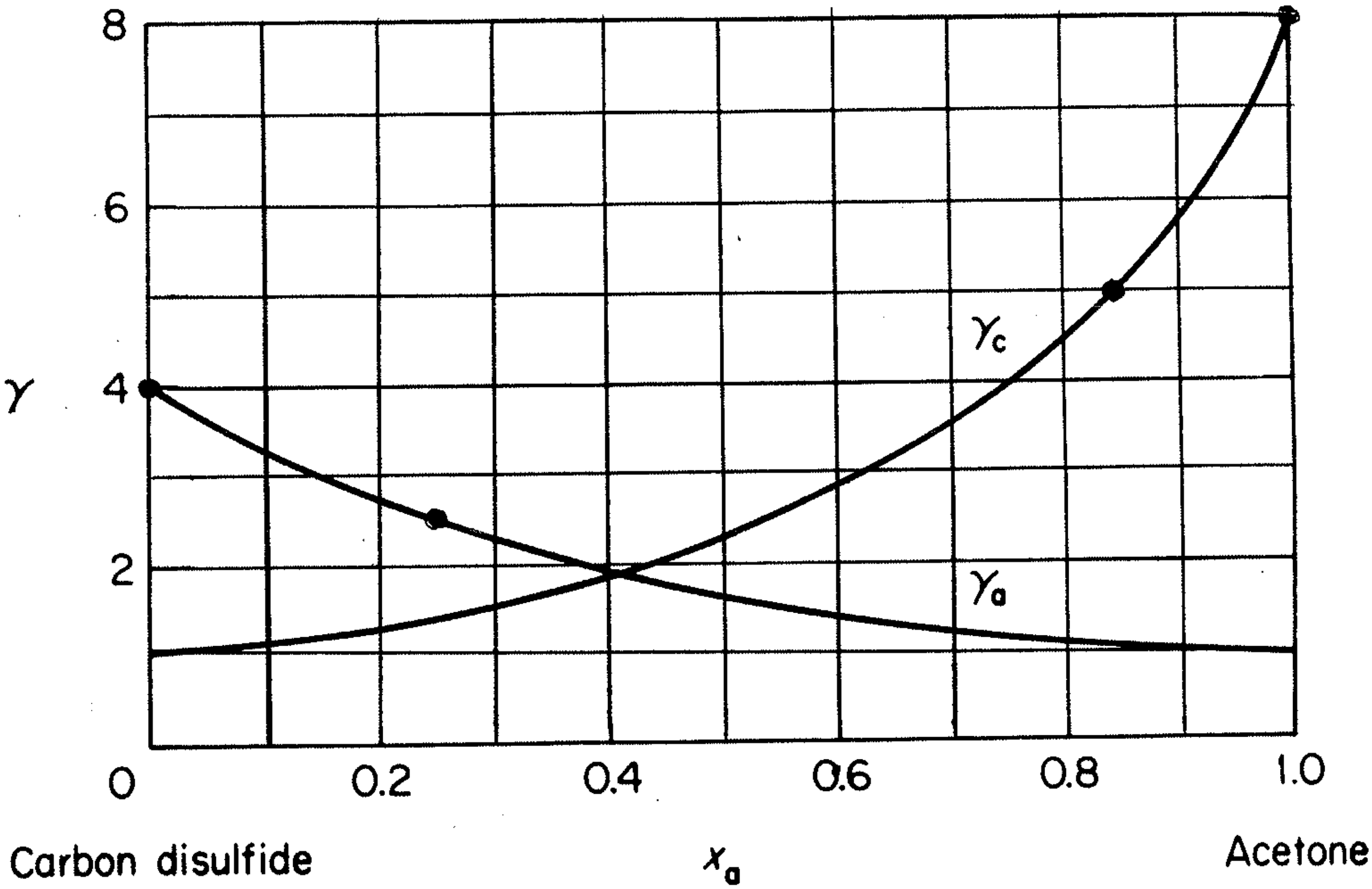
$n_{LIQ} = 0.223$ moles **Answer**

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**

3. The following figure shows the activity coefficients versus composition for carbon disulfide acetone solutions at 35°C in the rational system of activities. At 35°C the vapor pressures of liquid acetone and liquid carbon disulfide are respectively, 0.46 and 0.66 atm.



Demonstrate that you can plot the corresponding vapor pressure diagram *from the above given information* by **calculating the following**:

Definitions: $a_c = p_c / p_c^*$ $\gamma_c = a_c / a_{c,\text{ideal}} = a_c / x_c$ and $\lim_{x_c \to 0} p_c = x_c K_{Hc}$ for any solution.

Henry's Law constant for carbon disulfide

For $x_c \to 0$, $p_c = x_c K_{Hc}$ (solution obeys Henry's law in this limit)
$a_c = p_c / p_c^* = x_c K_{Hc} / p_c^*$ $\gamma_c = a_c / x_c = (x_c K_{Hc} / p_c^*) / x_c = K_{Hc} / p_c^*$
Read γ_c (at $x_c = 0$) = 8.0 and given $p_c^* = 0.66$; ∴ $K_{Hc} = 8.0 p_c^* = 5.28$ atm
Answer

Henry's law constant for acetone

for $x_a \rightarrow 0$, $p_a = x_a K_{H\,a}$ (solution obeys Henry's law in this limit)
$a_a = p_a / p_a^* = x_a K_{H\,a} / p_a^*$ $\gamma_a = a_a / x_a = (x_a K_{H\,a} / p_a^*) / x_a = K_{H\,a} / p_a^*$
Read γ_a (at $x_a = 0$) = 4.0 ; $\therefore$ $K_{H\,a} = 4.0\, p_a^* =$ 1.84 atm   Answer

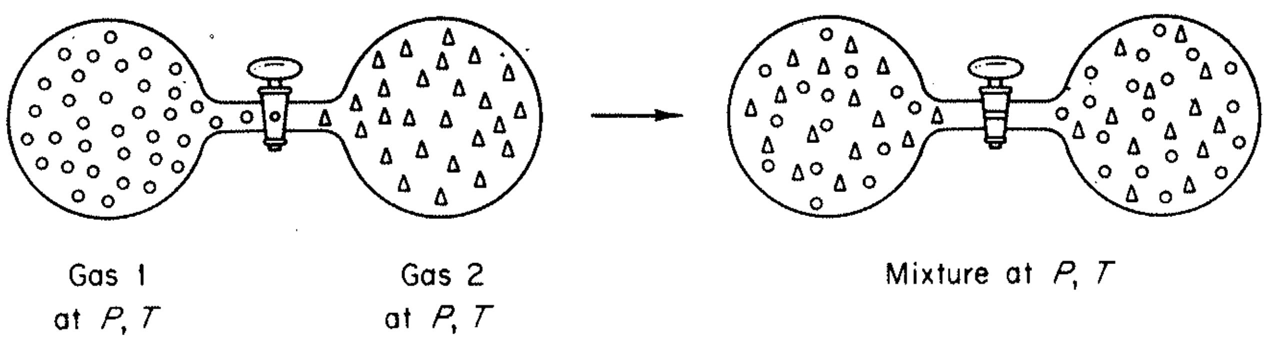
partial pressure contributed by carbon disulfide to the vapor pressure of a solution that has 15 mole percent carbon disulfide

Read γ_c(at $x_c = 0.15$) = 5.0 = a_c / x_c ; $\therefore a_c = 5.0(0.15) = 0.75 = p_c / p_c^*$;
$\therefore$ $p_c = 0.75(.66) = .495$ atm   Answer

partial pressure contributed by acetone to the vapor pressure of a solution that has 75 mole percent carbon disulfide

read γ_a(at $x_a = 0.25$) = 2.5 = a_a / x_a ; $\therefore a_a = 2.5(0.25) = 0.625 = p_a / p_a^*$;
$\therefore$ $p_a =$ 0.625(.46) = 0.2875 atm   Answer

4. Consider two ideal gases: n_1 moles of molecules of type 1 and n_2 moles of molecules of type 2. The initial and final conditions are shown below.



Fundamentals: $dG = Vdp - SdT$; when $dT = 0$, $dG = Vdp$; for one mole of a pure substance, this becomes $d\mu = V_m dp$. Integrating between lower limit of 1 bar and upper limit of p, $\int d\mu = \int V_m dp = \int (RT/p) dp$ for an ideal gas, leads to

$$\mu(g, T, p) = \mu^{\ominus}(g, T, 1\text{ bar}) + RT \ln(p/1\text{ bar})$$

Write an equation that expresses the chemical potential of the gas in the left bulb at the initial conditions. From this **find** G_1 the Gibbs free energy for the gas in the left bulb at initial conditions.

$\mu_1(g, T, p) = \mu_1^{\ominus}(g, T, 1\text{ bar}) + RT\ln(p/1)$
$G_1 = n_1[\mu_1^{\ominus}(g, T, 1\text{ bar}) + RT\ln(p/1)]$

Write an equation that expresses the chemical potential of the gas in the right bulb at the initial conditions. From this **find** G_2 the Gibbs free energy for the gas in the right bulb at initial conditions.

$\mu_2(g, T, p) = \mu_2^{\ominus}(g, T, 1\text{ bar}) + RT\ln(p/1)$
$G_2 = n_2[\mu_2^{\ominus}(g, T, 1\text{ bar}) + RT\ln(p/1)]$

Hint: In a mixture of ideal gases, where p_i is the partial pressure of the ith species,
$(\partial\mu_i/\partial p)_T = \partial/\partial p(\partial G/\partial n_i)_{p,T} = \partial/\partial n_i(\partial G/\partial p)_T = (\partial V/\partial n_i)_{p,T} = RT/p_i$
or $d\mu_i = RT\, d(\ln p_i)$

Write an equation that expresses the chemical potential of the molecules of type 1 in the gas mixture at the final conditions.

$\mu_1(g, T, x_1, p) = \mu_1^{\ominus}(g, T, 1\text{ bar}) + RT\ln(p_1/1) = \mu_1^{\ominus}(g, T, 1\text{ bar}) + RT\ln(x_1 p/1)$
since $p_1 = x_1 p$ (Dalton) and $x_1 \equiv n_1/(n_1 + n_2)$ in the mixture

Write an equation that expresses the chemical potential of the molecules of type 2 in the gas mixture at the final conditions.

$\mu_2(g, T, x_2, p) = \mu_2^{\ominus}(g, T, 1\text{ bar}) + RT\ln(p_2/1) = \mu_2^{\ominus}(g, T, 1\text{ bar}) + RT\ln(x_2 p/1)$
where $p_2 = x_2 p$

Write an equation that expresses the Gibbs energy of the gas mixture at the final conditions.

$G_{\text{mixture}} = \{n_1\mu_1 + n_2\mu_2\}_{\text{in the mixture}}$
$= n_1[\mu_1^{\ominus}(g, T, 1\text{ bar}) + RT\ln(x_1 p/1)] + n_2[\mu_2^{\ominus}(g, T, 1\text{ bar}) + RT\ln(x_2 p/1)]$

Write an equation that expresses the ΔG for the process pictured above (in terms of molefractions x_1 and x_2).

$\Delta G = G_{\text{mixture}} - G_1 - G_2$
$= n_1 RT\ln(x_1 p/1) + n_2 RT\ln(x_2 p/1) - n_1 RT\ln(p/1) - n_2 RT\ln(p/1)$
$= n_1 RT\ln(x_1 p/p) + n_2 RT\ln(x_2 p/p) = n_1 RT\ln x_1 + n_2 RT\ln x_2$

5. In each of the following systems, it is desired that equilibrium be maintained between the two sides $\mathcal{A}$ and $\mathcal{B}$ by adjusting one variable (***bold***). **Calculate the value** that this variable has to be set to in each case, so as to maintain equilibrium.

$\mathcal{A}$	$\mathcal{B}$	Equilibrium condition, answers
fresh water semi mem T = 298 K p = 0.0313 atm	sea water permeable brane 35000 ppm of dissolved salts (MW=58.5 g mol^{-1}) by weight T = 298 K ***p* = ?**	❀ $\mu_{H2O,\ solution}(298\text{ K}, p, x_{H2O})$ $= \mu^*_{H2O,\ liquid}(298\text{ K}, 0.0313\text{ atm})$ p = 14.58 atm
liquid D density 55 mol L^{-1} T = 298 K p = 200 atm	ideal vapor D + insoluble gas E, T = 298 K $p_D + p_E$ = 200 atm $\boldsymbol{p_D}$ **= ?**	given p^*_D = 0.60 atm ❀ $\mu_{D,\ LIQ}(298\text{ K}, 200\text{ atm})$ $= \mu_{D,VAP}(298\text{ K}, p_D)$ ❀ $\mu^*_{D,\ LIQ}(298\text{ K}, p^*_D)$ $= \mu_{VAP}(298\text{ K}, p^*_D)$ in the absence of gas E p_D = 0.696 atm
water with dissolved CO_2 (0.1 mole %) T = 278 K	CO_2 gas T = 278 K $\boldsymbol{p_{CO2}}$ **= ?**	$K_H = 1.25\times10^6$ atm at 278 K ❀ $\mu_{CO2\ in\ solution}(278\text{ K}, x_{CO2} = 0.001, p_{CO2})$ $= \mu_{CO2\ GAS}(278\text{ K}, p_{CO2})$ p_{CO2} = 1250 atm
liquid water density 55.55 mol L^{-1} T = same	water vapor p = 0.20 bar ***T* = ?**	$\Delta_{vap}\boldsymbol{H}$ = 40.7 kJ mol^{-1} at 373 K ❀ $\mu_{H2O,\ LIQ}(T, p = 0.20\text{ bar})$ $= \mu_{H2O,\ VAP}(T, p = 0.20\text{ bar})$ ❀ $\mu_{H2O,\ LIQ}(373\text{ K}, p = 1\text{ atm})$ $= \mu_{H2O,\ VAP}(373\text{ K}, p = 1\text{ atm})$ T = 332 K

Write the derivations here, leading from the completed equilibrium statement(❀) to the working equation used for the calculating the answers.

❀ $\mu_{H2O,\ solution}(T,p,x_A) = \mu^*_{H2O,\ liquid}(T,\ 0.0313\ \text{atm})$ (1)

If the solution is ideal, then

$\mu_{H2O,solution} = \mu^*_{H2O,liquid} + RT\ln x_{H2O}$ (ideal solution)

specifically, 35000 grams of salt per 10^6 grams water means

$x_{salts} = (35000/58.5)/\{35000/58.5 + 10^6/18\} = 0.01065$, $x_{H2O} = 0.98935$

$\mu_{H2O,solution}(T,p,x_A) = \mu^*_{H2O,liquid}(T,p) + RT\ln x_{H2O}$ (2)

Eq. (2) substituted into (1) gives:

$\mu^*_{H2O,liquid}(T,\ p) + RT\ln x_A = \mu^*_{H2O,liquid}(T,\ 0.0313\ \text{atm})$

rearrange to:

$\mu^*_{H2O,liquid}(T,p) - \mu^*_{H2O,liquid}(T,\ 0.0313\ \text{atm}) = -RT\ln x_{H2O}$

Since $(\partial\mu/\partial p)_T = V_m$, the left hand side is

$$\int_{0.0313}^{p} V_m\,dp = V_m(p - 0.0313) = V_m(p - 0.0313)$$

$\therefore\ V_m(p - 0.0313) = -RT\ln x_{H2O}$ This is the working eqn.

or approximately $V_m(p - 0.0313) = RT\,x_{salts}$

$V_{m,\ H2O} = (18/1000)$ and $\ln x_{H2O} = \ln 0.98935 = -0.010707$ solve for p

$(p - 0.0313) = 0.082057\times298\times0.010707/\ (18/1000) = 14.545$ atm

$p = 14.577$ atm *Answer*

❀ $\mu_{D,\ LIQ}(T,\ 200\ \text{atm}) = \mu_{D,\ VAP}(T,p_D)$] Subtract

❀ $\mu_{D,\ LIQ}(T,\ p^*_D) = \mu_{D,\ VAP}(T,p^*_D)$ in the absence of gas E]

$\mu_{D,\ LIQ}(T,\ 200\ \text{atm}) - \mu_{D,\ LIQ}(T,\ p^*_D) = \mu_{D,\ VAP}(T,p_D) - \mu_{D,\ VAP}(T,p^*_D)$

This equation is the integrated form of $\int d\mu_{LIQ} = \int d\mu_{VAP}$

Since $dG = Vdp - SdT$, $(\partial\mu/\partial p)_T = V_m$ so that $\int d\mu_{LIQ} = \int d\mu_{VAP}$ becomes

$\int V_{m\,LIQ}\,dp = \int V_{m\,VAP}\,dp$

LHS integrated from $p^*_D = 0.6$ atm to $p_{tot} = p_D + p_E = 200$ atm

RHS integrated from $p^*_D = 0.6$ atm to p_D

LHS = $V_{m\,LIQ}(p_{tot} - p^*_D)$

<u>If</u> the vapor behaves ideally, then

RHS = $\int V_{m\,VAP}\,dp = \int RTdp/p = RT\ln(p_D/p^*_D)$

$V_{m\,LIQ}(p_{tot} - p^*_D) = RT\ln(p_D/p^*_D)$ this is the working equation

$V_{m\,LIQ}(200 - 0.6) = RT\ln(p_D/0.6)$

$(1/55)(200-0.6) = (0.082057)(298)\ln(p_D/0.6)$

Solve for p_D, $p_D = 0.696$ atm *Answer*

❀ $\mu_{CO2\ in\ solution}(T{=}278,\ x_{CO2} = 0.001,\ p_{CO2}) = \mu_{CO2\ GAS}(T{=}278,\ p_{CO2})$
very dilute solutions obey Henry's law, which relates the concentration in solution to the partial pressure in the gas : $p_{CO2} = x_{CO2} K_H$

$p_{CO2} = (0.001)(1.25\times10^6) = 1250$ atm — *Answer*

❀ $\mu_{H2O,LIQ}(T = 373,\ p=1\ \text{atm}) = \mu_{H2O,VAP}(T= 373,\ p=1\ \text{atm})$ equilibrium pt

❀ $d\mu_{H2O,LIQ} = d\mu_{H2O,VAP}$, as in problem 2, this leads to Clapeyron eq.

$$\ln(p/1\ \text{atm}) \approx \Delta_{vap}H/R \left[-\frac{1}{T} + \frac{1}{T_b}\right]$$ use $p = 0.20$ bar, given

$$\ln(0.20\text{x}0.987/1\ \text{atm}) \approx (40.7\times10^3/8.3144)\left[-\frac{1}{T} + \frac{1}{373}\right]$$ solve for T

$T = 332$ K — *Answer*

1. Description of phases for part (a) and the cooling curve:
L = liquid solution of Fe and Au
α phase = a solid solution of Fe and Au, containing 30% Au or less, maximum Au is 30% at all temperatures when it exists
β phase = a solid solution of Fe and Au, containing ≈ 68% Au or more, minimum amount of Au in this phase is 65% at 1170°C, up to 68% at 890°C

Cooling curve for composition (3)
Starting at 1535°C, the temperature drops with time according to the heat capacity of the liquid solution of composition (3).
A break occurs in the cooling profile at about 1190°C when α phase first forms.
With continued cooling, liquid and α phase change in composition along their respective lines, α phase increasing in amount.
At 1170°C the solution is now also in equilibrium with β phase, and there is a halt in the cooling curve (no change in temperature over a period of time) while α and β phases (30% Au and 65% Au respectively) crystallize out. The phase reaction is that of a *peritectic system* or L + α →β. Phase α is used up first in the phase reaction, however, so L and β phase remain at the end of the halt in the cooling curve.
With further cooling, L and β phase compositions shift along their respective curves, with β phase increasing in proportion, and at about 1150°C only β phase remains. Further cooling of the β phase occurs down to 890°C.