Name:____

First three letters of last name

Chemistry 342

ANSWERS to Final Exam
May 3, 2005
1:00-3:00 PM in 308 BH

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 J = 1 kg m^{-2} s^{-2} 1 atm = 101325 Pa
$(p + n^2a/V^2)(V-nb) = nRT$
For water: $\Delta_{fus}\boldsymbol{H}$ = 6003 J mol^{-1} or 80 cal g^{-1}; heat capacities liquid, solid: 1 and 0.5 cal g^{-1} K^{-1}
R = 8.31441 J mol^{-1} K^{-1} =1.98718 cal mol^{-1} K^{-1} = 0.082057 L atm mol^{-1} K^{-1}
$(\partial \boldsymbol{U}/\partial V)_T = T(\partial p/\partial T)_V - p$ $(\partial \boldsymbol{H}/\partial p)_T = -T(\partial V/\partial T)_p + V$ $\mu_{JT} \equiv (\partial T/\partial p)_{\boldsymbol{H}}$ $(\partial \boldsymbol{H}/\partial p)_T = -C_p\mu_{JT}$
$C_p - C_V = \{p + (\partial \boldsymbol{U}/\partial V)_T\}(\partial V/\partial T)_p$
$[T_f/T_i]^{Cv/R} = [V_i/V_f]$ only for ideal gas undergoing reversible adiabatic process
$(\partial \boldsymbol{S}/\partial V)_T = (\partial p/\partial T)_V$
$(\partial \boldsymbol{S}/\partial p)_T = -(\partial V/\partial T)_p$
$C_p - C_V = \{p + (\partial \boldsymbol{U}/\partial V)_T\}(\partial V/\partial T)_p$
The limiting Debye-Hückel eqn: $\ln \gamma_\pm = -z_+z_-I^{1/2}(e^2/10\varepsilon k_B T)^{3/2}\{2\pi\rho N_{Avog}\}^{1/2}$
for water at 25°C as the solvent, $\ln \gamma_\pm = -z_+z_-I^{1/2}(1.17223)$
ionic strength $\equiv \frac{1}{2}\sum m_i z_i^2$

$$\ln \boldsymbol{a}_A = \Delta_{fus,A}\boldsymbol{H}/R\left[-\frac{1}{T} + \frac{1}{T^*}\right]$$

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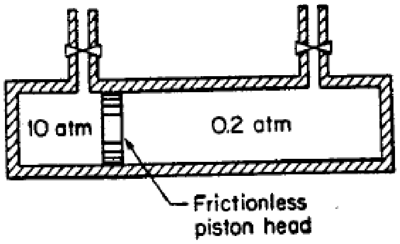
1. A cylinder which is closed at both ends has within it a frictionless piston head. Both the piston and the walls of the cylinder are of insulating materials so that no heat can pass through them. Initially the left side of the cylinder contains one mole of gas at 10 atm while the right side contains one mole of gas at 0.2 atm, as illustrated in the accompanying diagram.



Both sides are *initially* at the same temperature, 25°C, and the gas is ideal and monatomic. The catch holding the piston in place is released and the piston moves to its equilibrium position. **Calculate** the final temperature and pressure on each side and ΔU, ΔH, and ΔS for the overall process.

□ Outer walls are rigid, $\therefore$ $dV = 0$, $w = 0$

□ Insulated, $\therefore$ $q = 0$. Since piston is insulated $\therefore$ $q_{left}=0$, $q_{right}=0$. Also, frictionless, $\therefore$ $w_{left} = -w_{right}$

$\Delta U = q + w = 0 + 0$. $V_{\mathrm{i,left}}=(298R/10) = 2.445$ L, $V_{\mathrm{i,right}}=(298R/0.2) = 122.265$ L, $V_{\mathrm{total}} =124.71$ L

$dU = C_V dT + (\partial U/\partial V)_T dV$, □ ideal gas , $(\partial U/\partial V)_T =0$; $\therefore$ $\Delta U = \int C_V dT$

$\therefore \Delta U_{\mathrm{left}} + \Delta U_{\mathrm{right}} = C_V\,[T_{\mathrm{f,left}}-298]+ C_V\,[T_{\mathrm{f,right}}-298] =\Delta U_{\mathrm{tot}} = 0$; $\therefore$ $T_{\mathrm{f,left}}+ T_{\mathrm{f,right}}= 596$ (1)

Answer: $\Delta U_{\mathrm{tot}} =$ 0

At equilibrium, pressure is the same on both sides, call it p_f

$V_{f\,,\,\mathrm{total}} = 124.7\ \mathrm{L} = (RT_{f,left}/p_f) + (RT_{f,right}/p_f) = R[T_{\mathrm{f,left}}+ T_{\mathrm{f,right}}]/p_f = 0.082057(596)/p_f$. Solve for p_f .

$p_f = 0.392$ atm. Since n and p_f are the same for both sides, $[V_{f,left}/V_{f,right}] = [T_{\mathrm{f,left}}/T_{\mathrm{f,right}}]$ (2)

Answer: p_f left side =, p_f right side = same, 0.392 atm

adiabatic ideal gas reversible: $dU=C_V dT +0 =0+dw =-RT/V dV$; $C_V=(3/2)R$ $\therefore$ $[T_f/T_i]^{3/2} = V_i/V_f$

Left: $[T_{\mathrm{f,left}}/298]^{3/2} = [2.445/V_{f,left}]$; Right: $[T_{\mathrm{f,right}}/298]^{3/2} = [122.265/V_{f,right}]$; Divide left eq by right,

$[T_{\mathrm{f,left}}/T_{\mathrm{f,right}}]^{3/2} = [2.445/122.265][V_{f,right}/V_{f,left}]$ (3) Using eq. (2) in eq (3) we get,

$[T_{\mathrm{f,left}}/T_{\mathrm{f,right}}]^{5/2} = [2.445/122.265]$; or $[T_{\mathrm{f,left}}/ T_{\mathrm{f,right}}] = [2.445/122.265]^{2/5} = 0.02091$

$T_{\mathrm{f,right}} /T_{\mathrm{f,left}} = 4.782$ (4); Substituting (1) into (4), $T_{\mathrm{f,right}} /(596-T_{\mathrm{f,right}}) = 4.782$; Solve for $T_{\mathrm{f,right}}$

$T_{\mathrm{f,right}} = 492.92$ K; $\therefore$ $T_{\mathrm{f,left}} = 103.08$ K

Answer: T_f = left side =, T_f right side = 103.08 K, 492.92 K

$dH = C_p dT + (\partial H/\partial p)_T\, dp$, □ ideal gas , $\therefore$ $(\partial H/\partial p)_T =0$,

and □ $\Delta T_{left} + \Delta T_{right} = 0$ from above, $\therefore \Delta H = 0$

Answer: $\Delta H_{\mathrm{tot}} =$ 0

$dS = (C_p/T)dT + (\partial S/\partial p)_T\, dp$; where $(\partial S/\partial p)_T = -\,(\partial V/\partial T)_p = -(R/p)$

$\Delta S = -{}^5/_2R\{\int dT/T_{left} + \int dT/T_{right}\} - R\{\int dp/p_{left} + \int dp/p_{right}\}$

$= -{}^5/_2R\{\ln(103.08/298) + \ln(492.92/298)\} -R\{\ln(0.392/10) + \ln(0.392/0.2)\} = -11.605 -21.3$

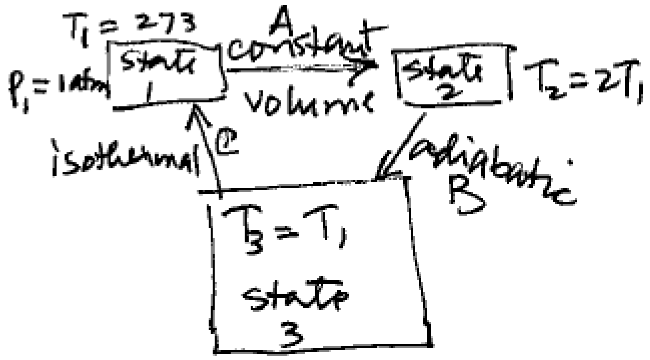
$= +9.69\ \mathrm{J\ K^{-1}}$

Answer: $\Delta S =$ 9.69 J $\mathrm{K^{-1}}$

2. One mole of an ideal gas of $C_V = 5.0$ cal mol^{-1} K^{-1} , initially at 0°C and 1 atm is put through the following reversible cycle: A: State 1 to state 2, heated at constant volume to twice the initial temperature. B: State 2 to state 3, expanded adiabatically until it is back to the initial temperature. C: State 3 to state 1, compressed isothermally back to state 1.

Find the p,T,V for each state. **Calculate** q, w, ΔU, and ΔH in cal for steps A and B, and for the cycle.

Use the space below to draw your diagram(s):



reversible
$\therefore p_{op} = p_{gas}$
$\therefore dw = -p dV$
ideal : $(\partial \boldsymbol{U}/\partial V)_T = 0$
and $(\partial \boldsymbol{H}/\partial p)_T = 0$
adiabatic, reversible, ideal gas :
$d\boldsymbol{U} = dq + dw$ leads to
$nC_V dT = -p dV = -nRT/V dV$
$(C_V/R) dT/T = - dV/V$
integrates to $[T_f/T_i]^{Cv/R} = [V_i/V_f]$

State	p, atm	T, K	one mole V, L
1	$p_1 = 1$	$T_1 = 273$	$V_1 = nRT/p$ $= 0.08205\times273/1$ solve for V_1 ,V_1=22.4 L
2	$p_2 = nRT_2 /V_1$ $= 0.08205\times546/V_1$ solve for p_2	$T_2 = 2\times273$	V_1
3	$p_3 = nRT_3 /V_3$ $= 0.08205\times273/V_3$ solve for p_3	$T_3 = 273$	$[T_3/T_2]^{Cv/R} = [V_2/V_3]$ **for ideal gas undergoing reversible adiabatic process** $[1/2]^{2.5} = [V_1/V_3]$ solve for V_3 ,V_3=126.7 L
4=1	$p_1 = 1$	$T_1 = 273$	V_1

Show your equations and calculations in this space: (**but write your final answers in the tables on the next page**)

	A **constant V**	B **adiabatic**	C **isothermal**	overall
q	$\Delta \boldsymbol{U} = q + w$ $q = \Delta \boldsymbol{U} - w = \Delta \boldsymbol{U} - 0$ 1365 cal from $\Delta \boldsymbol{U}$ below	$q = 0$ adiabatic process	$q = -w$ (from $\Delta \boldsymbol{U} = 0$ below) -940 cal from $\boldsymbol{w}$ below	1365-940 = +425 cal
w	$dV = 0$ $w = -\int p_{op} dV = 0$	$w = \Delta \boldsymbol{U}$ -1365 cal from $\Delta \boldsymbol{U}$ below	$w = -\int p_{op} dV = \int -nRT/V dV$ $= -RT\ln(V_1/V_3)$ $= -1.987\times273\times2.5\ln(1/2)$ = +940 cal	-1365+940 = -425 cal

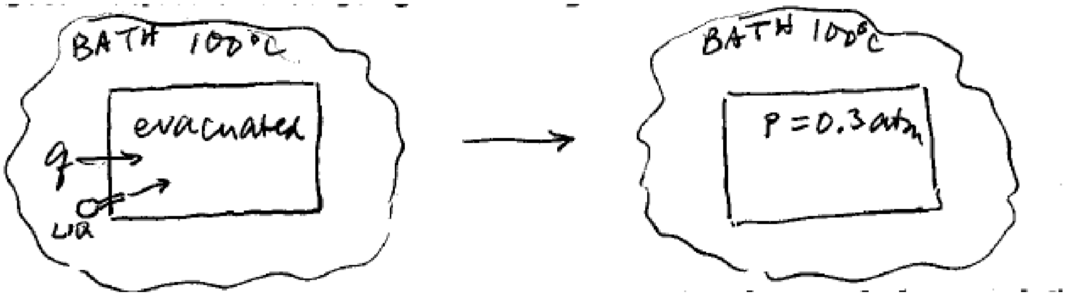
ΔU	$dU=C_VdT+(\partial U/\partial V)_TdV$ $\Delta U=\int C_VdT+0$ $=5[T_2-T_1]$ $=5\times273=+1365$ cal	$\Delta U=\int C_VdT+0$ $=5[T_3-T_2]$ $=5\times-273=-1365$ cal	isothermal process, $dU=C_VdT+0$ $dT=0$ $\Delta U=0$	**0 for any cycle**
ΔH	$dH=C_pdT+(\partial H/\partial p)_Tdp$ $(\partial H/\partial p)_T=0$ $\Delta H=\int C_pdT$ $=7[T_2-T_1]$ $=7\times273=+1911$ cal	$\Delta H=\int C_pdT+0$ $=7[T_2-T_1]$ $=7\times-273=-1911$ cal	$dH=C_pdT+0$ $dT=0$ $\Delta H=0$	**0 for any cycle**

Write your final numerical answers in the tables below:

Changes	q	w	ΔU	ΔH
step A	+1365 cal	0	+1365 cal	+1911 cal
step B	0	-1365 cal	-1365 cal	-1911 cal
step C	-940 cal	+940 cal	0	0
overall	+425 cal	-425 cal	0	0

3. One mole of liquid water is allowed to expand into an evacuated flask of volume such that the final pressure is 0.3 atm. The bulb containing the liquid and the flask are thermostated so that a constant temperature of 100°C is maintained. It is found that 11,000 cal of heat are absorbed when this process occurs. Calculate the values for w, q, ΔU, ΔH, ΔS, ΔG, ΔA. Neglect pV quantities for liquid water.

You may use this space to make any diagrams that may be helpful:



Use these boxes to write your equations and calculations, but place the numerical answers in the table on page 6.

w

no work is done in an **expansion into a vacuum ($p_{op}=0$)** : $w=0$

q

q = +11,000 cal (given) = q_{IRREV} **expansion into vacuum is always irreversible**

$\Delta \boldsymbol{U}$

$\Delta \boldsymbol{U} = q + w = = q_{\mathrm{IRREV}} + w_{\mathrm{IRREV}}$ = +11,000 cal + 0

$\Delta \boldsymbol{H}$

$\boldsymbol{H} \equiv \boldsymbol{U} + pV$; $\Delta \boldsymbol{H} = \Delta \boldsymbol{U} + p_f V_f - p_i V_i$ = 11,000 cal + nRT – *negligible pV for liquid*

nRT = 1 mol×1.987 cal $\mathrm{K^{-1}\ mol^{-1}}$×373 K = 741 cal

$\Delta \boldsymbol{H}$ = 11,000 cal +741 cal =11,740 cal

$\Delta \boldsymbol{S}$

Process was irreversible, so cannot use q = 11,000 directly to obtain ΔS. Instead, set up reversible steps:

(a) H_2O(liq, 100°C, 1 atm) → H_2O(gas, 100°C, 1 atm) $q_{rev} = q_p = \Delta \boldsymbol{H}$ =11,740 cal

to reversibly carry out the conversion from liquid to gas in a piston arrangement at 1 atm.

(b) H_2O(gas, 100°C, 1 atm) → H_2O(gas, 100°C, 0.3 atm) reversible expansion of the gas at contant temperature

$\Delta \boldsymbol{S}$(a) = q_{rev}/T = 11,740/373 = 31.5 cal $\mathrm{K^{-1}}$

Using $(\partial \boldsymbol{S}/\partial p)_T = -(\partial V/\partial T)_p$ For an ideal gas, pV/nRT, $V=nRT/p$, $-(\partial V/\partial T)_p = -nR/p$

$\Delta \boldsymbol{S}(b) = \int (C_p/T)dT + \int -(nR/p)dp = 0 - nR\ln(p_f/p_i)$

= -1 mol×1.987 cal $\mathrm{mol^{-1}\ K^{-1}}$×ln(0.3/1) = + 2.39 cal $\mathrm{K^{-1}}$

$\Delta \boldsymbol{S}$ = 31.5+ 2.39 cal $\mathrm{K^{-1}}$

= 33.89 cal $\mathrm{K^{-1}}$

$\Delta \boldsymbol{G}$

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

For the reversible steps set up above, we can calculate $\Delta \boldsymbol{G}$

$\Delta \boldsymbol{G}$(a) = 0 since this is an equilibrium at a constant T and p, between the two phases

$\Delta \boldsymbol{G}(b) = \int Vdp + \int -\boldsymbol{S}dT = \int Vdp = \int (nRT/p)dp = nRT\ln(p_f/p_i)$

= 1 mol×1.987 cal $\mathrm{mol^{-1}\ K^{-1}}$×ln(0.3/1) ×373 = - 893 cal

$\Delta \boldsymbol{G}$ = 0 - 893 cal

$\Delta \boldsymbol{A}$

$\boldsymbol{A} = \boldsymbol{U} - T\boldsymbol{S}$, at constant T : $\mathrm{d}\boldsymbol{A}_T = \mathrm{d}\boldsymbol{U} - T\mathrm{d}\boldsymbol{S}$

$\Delta \boldsymbol{A} = \Delta \boldsymbol{U} - T\Delta \boldsymbol{S}$ = 11,000 cal – 373 K×33.89 cal K^{-1} = -1640 cal

$\Delta \boldsymbol{A}$ = -1640 cal

Write the numerical answers and units in this table:

w	q	ΔU	ΔH	ΔS	ΔG	ΔA
0	11,000 cal	11,000 cal	11,740 cal	33.9 cal K^{-1}	-893 cal	-1640 cal

4. 100 g of ice at 0°C and 90 g of a metal at -2°C are dropped into an insulated beaker containing 150 g of water at 100°C. **Calculate** ΔS for the system for the process that then occurs. Data for water are given on the first page of the exam. The heat capacity of the metal is 2.0 cal $\mathrm{g}^{-1}\,\mathrm{K}^{-1}$

It is first necessary to set up a heat balance in order to determine the final temperature. Inspection of the data suggests that all of the ice will melt, so the overall process can be written as a sum of the following steps:

(a) 100 g(ice, 0°C, 1 atm) → 100 g(liqw, 0°C, 1 atm)
(b) 100 g(liqw, 0°C, 1 atm) → 100 g(liqw, t°C, 1 atm)
(c) 150 g(liqw, 100°C, 1 atm) → 150 g(liqw, t°C, 1 atm)
(d) 90 g(metal, -2°C, 1 atm) → 90 g(metal, t°C, 1 atm)

Since the beaker is insulated, $q = 0$. $\therefore q = q(\mathrm{a}) + q(\mathrm{b}) + q(\mathrm{c}) + q(\mathrm{d}) = 0$

$$100\ \mathrm{g}\times 80\ \mathrm{cal\ g^{-1}} + 100\ \mathrm{g}\times 1\ \mathrm{cal\ g^{-1}\ K^{-1}}\times(\mathrm{t}-0) + 150\ \mathrm{g}\times 1\ \mathrm{cal\ g^{-1}\ K^{-1}}(\mathrm{t}-100)$$
$$+\ 90\ \mathrm{g}\times 1\ \mathrm{cal\ g^{-1}\ K^{-1}}\times(\mathrm{t} - -2) = 0$$

Solve for t: $8000 + 100\mathrm{t} - 15000 + 150\mathrm{t} + 90\mathrm{t} + 180 = 0$;
$340\mathrm{t} = 15000-8000-180$; t = 20.0°C or T = 293 K

The entropy change: $\Delta \boldsymbol{S} = \Delta \boldsymbol{S}(\mathrm{a}) + \Delta \boldsymbol{S}(\mathrm{b}) + \Delta \boldsymbol{S}(\mathrm{c}) + \Delta \boldsymbol{S}(\mathrm{d})$

$\Delta \boldsymbol{S}(\mathrm{a}) = q_{rev}/T = 8000/273 = 29.3\ \mathrm{cal\ K^{-1}}$

$\Delta \boldsymbol{S}(\mathrm{b}) = \int (C_p/T)\mathrm{d}T + \int (\partial \boldsymbol{S}/\partial p)_T\,\mathrm{d}p = 100\ \mathrm{g}\times 1\ \mathrm{cal\ g^{-1}\ K^{-1}}\times \ln(293/273) = 7.07\ \mathrm{cal\ K^{-1}}$; □dp = 0

$\Delta \boldsymbol{S}(\mathrm{c}) = \int (C_p/T)\mathrm{d}T + \int (\partial \boldsymbol{S}/\partial p)_T\,\mathrm{d}p = 150\ \mathrm{g}\times 1\ \mathrm{cal\ g^{-1}\ K^{-1}}\times \ln(293/373) = -36.2\ \mathrm{cal\ K^{-1}}$

$\Delta \boldsymbol{S}(\mathrm{d}) = \int (C_p/T)\mathrm{d}T + \int (\partial \boldsymbol{S}/\partial p)_T\,\mathrm{d}p = 90\ \mathrm{g}\times 2\ \mathrm{cal\ g^{-1}\ K^{-1}}\times \ln(293/271) = 14.05\ \mathrm{cal\ K^{-1}}$

$\therefore \Delta \boldsymbol{S} = 29.3 + 7.07 - 36.2 + 14.05 = 14.22\ \mathrm{cal\ K^{-1}}$

Answer	14.22 cal K^{-1}

5. On ideal solutions:

(a) Liquids A and B form an ideal solution. At 50°C, the total vapor pressure of a solution consisting of one mole of A and 2 moles of B is 250 mm Hg; on addition of one more mole of A to the solution, the vapor pressure increases to 300 mm Hg. **Calculate the vapor pressures** of pure A and of pure B.

$p = p_A + p_B$; Raoult's law holds: $p = x_A p^*_A + (1-x_A)p^*_B$

Two solutions, vapor pressures in mm Hg:

$250 = (1/3)p^*_A + (2/3)p^*_B$

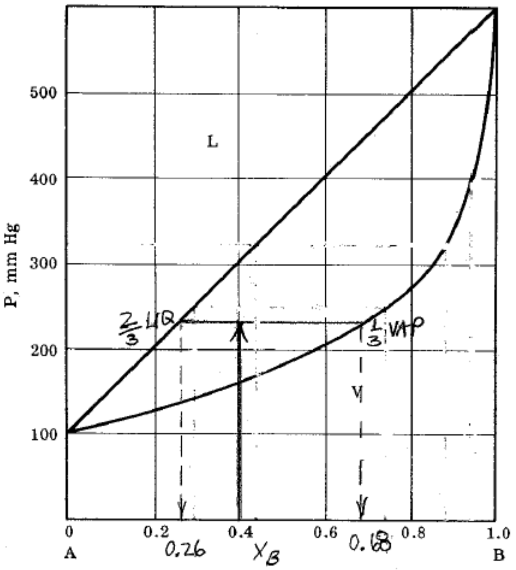
$300 = (1/2)p^*_A + (1/2)p^*_B$

Solve the simultaneous equations for p^*_A and p^*_B

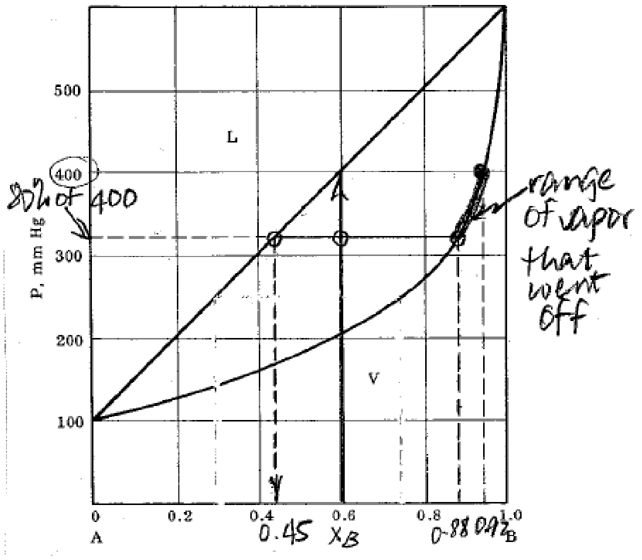
Answers, mm Hg	A: 450	B: 150

(b) Liquids A and B form an ideal solution. At 80°C, the pressure-composition diagram of a solution consisting of A and B is shown below:

first experiment:



second experiment:



In one experiment, a liquid solution containing 60 mole % of A is placed in a previously evacuated container of such size that at 80°C, one-third of the liquid vaporizes. **Calculate the compositions** of the final liquid and vapor phases.

Since 1/3 of the liquid vaporizes, look for a tie line which will, by conservation of number of moles of A and B(the lever rule), predict $\boldsymbol{n_{LIQ}:n_{VAP} = 2/3:1/3}$ (see graph). The ends of this tie line provide the liquid and vapor compositions. We read liquid composition is $x_B = 0.26$ and vapor composition is $y_B = 0.68$. That is, $x_A = 0.74$ and $y_A = 0.32$

Answers, mole % A	liquid: 74%	vapor: 32%

In a second experiment, 2 moles of a liquid solution of $x_A = 0.4$ is evaporated in an open container at a constant temperature of 80°C until the total vapor pressure falls to 80% of its initial value. **What is the final liquid composition**, and roughly **how many moles of liquid remain** after the evaporation to this point?

Initial vapor pressure would have been 400 mm Hg (read off the graph), 80% of this is 320 mm Hg which corresponds to $x_B = 0.45$ (read off the graph). Thus, $x_A = 0.55$. Initial vapor composition corresp. to 400 mm Hg is $y_B = 0.94$, while final vapor composition corrresp. to 320 mm Hg is $y_B = 0.88$, giving an average value of about $y_B = 0.92$ or $y_A = 0.08$. Apply the **conservation of number of moles of A**:

total moles A = $2.0 \bullet X_{A,overall} = n_{LIQ} \bullet x_A + n_{VAPOR} \bullet y_A$; where $n_{LIQ} + n_{VAPOR} = 2.0$

$2.0 \bullet 0.40 = n_{LIQ} \bullet 0.55 + (2.0 - n_{LIQ}) \bullet 0.08$ Solve for n_{LIQ}

$n_{LIQ} = 1.36$

Answers, liquid:	$x_A = 0.55$	moles= 1.36

(c) Two moles of a 50 mole % solution of propyl alcohol in ethyl alcohol is distilled until the normal boiling point of the solution rises to 90°C. The condensate is allowed to accumulate in a cooled receiver and, after being mixed to insure uniformity, its vapor pressure is found to be 1,066 mm Hg when measured at 90°C. The vapor pressures of pure ethyl and propyl alcohols are 1,190 and 574 mm Hg, respectively. Assuming that the solutions and vapors are ideal, **calculate** (1) the mole fraction of ethyl alcohol in the 90°C-boiling liquid in the distilling flask, (2) the mole fraction of ethyl alcohol in the distillate, and (c) the number of moles of ethyl alcohol that were distilled.

At the normal boiling point,

$p_{eth} + p_{prop} =$ **760 mm Hg**

The liquid solution in the flask: 760 mm Hg = $x_{eth} \bullet 1190 + x_{prop} \bullet 574 = x_{eth} \bullet 1190 + (1 - x_{eth}) \bullet 574$

Solve for x_{eth} ; $x_{eth} = 0.30$ This is the x_{eth} in the flask.

The distillate: 1,066 mm Hg = $x_{eth} \bullet 1190 + x_{prop} \bullet 574 = x_{eth} \bullet 1190 + (1 - x_{eth}) \bullet 574$

Solve for x_{eth} ; $x_{eth} = 0.80$ This is the x_{eth} in the distillate.

Conservation of number of moles of ethyl alcohol:

total moles eth = $2.0 \bullet X_{A,eth} = n_{flask} \bullet x_{eth,flask} + n_{distillate} \bullet x_{eth,distillate}$; where $n_{flask} + n_{distillate} = 2.00$

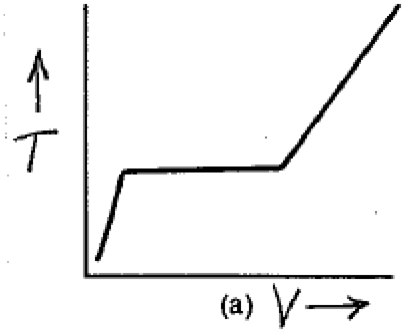
$0.50 \bullet 2.0 = (2.0 - n_{distillate}) \bullet x_{eth,flask} + n_{distillate} \bullet x_{eth,distillate} = (2.0 - n_{distillate}) \bullet 0.30 + n_{distillate} \bullet 0.80$

Solve for $n_{distillate}$. $n_{distillate} = 0.80$.

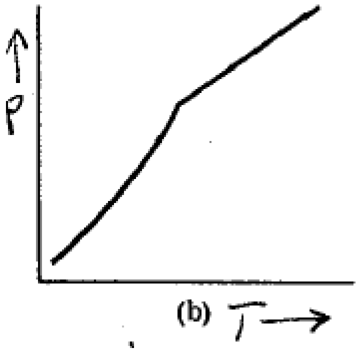
n_{eth} distilled = $n_{distillate} \bullet 0.80 = 0.64$ moles

Answers:	x_{eth} in flask = 0.30	x_{eth} in distillate =0.80	n_{eth} distilled = 0.64

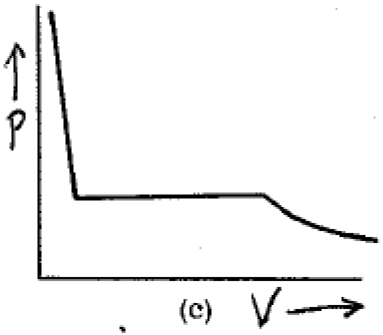
6. It takes a three dimensional plot of *p* versus *V* versus *T* to show the complete behavior of a substance. If one of these three variables is kept constant, a plot of the other two is possible. One thus has isotherms (*p* versus *V* or *V* versus *p*, with *T* constant), *isobars* (*T* versus *V* or *V* versus *T*, with *p* constant) or *isochors* (*p* versus *T* or *T* versus *p*, with *V* constant). The three diagrams (a), (b), (c) shown below give an isotherm, an isochor, and an isobar for water. State which diagram is which (i.e., **label each diagram** with the proper term: iso_____) and also **write the proper labels** (*p*,*V*, *T*) **for the ordinate and abscissa of each diagram.**



isobar



isochor



isotherm

Write the explanation for your choices here:

The most obvious clues are the plateaus, which must correspond to phase change.

(c) is the easiest to recognize, and is clearly an isotherm involving the region of condensation seen as a plateau in the plot where y=*p*, x=*V*. At a fixed temperature, starting at large V and low p, the gas decreases its volume as pressure is increased, then the liquid starts to form and is in equilibrium with the gas, with no change in pressure until all the gas is turned into liquid, then the volume hardly changes even as the pressure is greatly increased since the liquid is not very compressible.

(b) must be a plot of y=*p*, x=*T*, hence is an isochor. The first portion is a curve which shows an increase in liquid vapor pressure with increasing *T* until the break in the curve (a temperature is reached at which all the liquid has been converted to vapor) and the subsequent linear portion is simply Charles' law for the all-gas system.

(a) by elimination, must be an isobar with y=*T* and x=*V.* At a given fixed pressure, the flat region corresponds to the volume increasing at a fixed temperature (the boiling temperature at the given pressure) while liquid is being converted to vapor.

7. (a) Suppose that a piece of metal with a volume of 0.1 liter at 1 atm is compressed adiabatically by a shock wave of 10^5 atm to a volume of 0.090 liter. **Calculate** the $\Delta \boldsymbol{U}$ and $\Delta \boldsymbol{H}$ of metal in kJ. (Assume the compression occurs at a constant pressure of 10^5 atm.)

initial (0.1 L, 1 atm) $\rightarrow$ final (0.090 L, 10^5 atm)
$p_{op} = 10^5$ atm

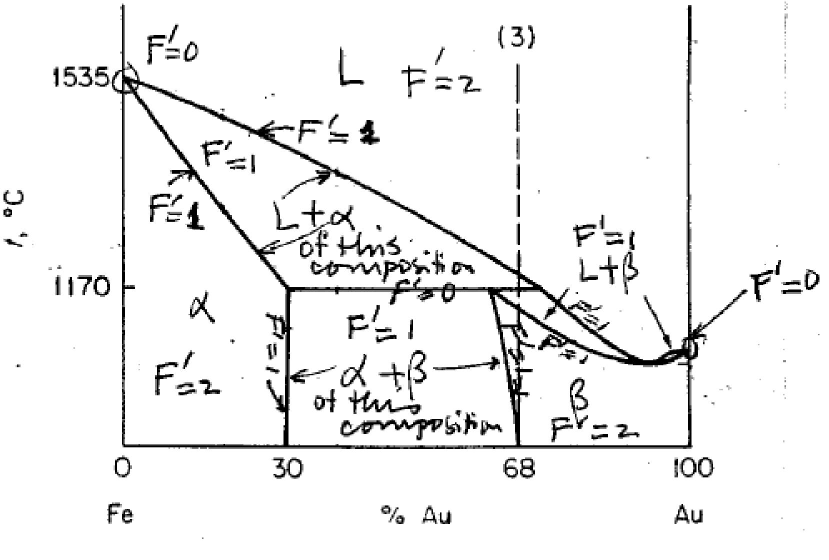
$\Delta \boldsymbol{U} = q + W$ $q = 0$ (adiabatic)
$dW = -p_{op}dV$ p_{op} = constant = 10^5 atm
$W = -10^5 \text{ atm} \int_{0.10}^{0.090} dV = 10^3 \text{ L atm}$
$= 10^3 \text{ L atm} \times (8.3144/0.082057) = 101.3\times10^3 \text{ J}$

Numerical Answer: $\Delta \boldsymbol{U}$ = 101.3 kJ

$\Delta \boldsymbol{H} = \Delta \boldsymbol{U} + (p_f V_f - p_i V_i)$
$(p_f V_f - p_i V_i) = [10^5(0.090) - 1(0.1)]\ 8.3144/0.082057 = 9.119\times10^5 \text{ J}$
$\Delta \boldsymbol{H} = 101.3 + 911.9 = 1013.2 \text{ kJ}$

Numerical Answer: $\Delta \boldsymbol{H}$ = 1013.2 kJ

(b) For the phase diagram below for the Fe Au system, write the **description of the phases present** in each region in the diagram. You may use symbols but define them completely below the diagram. And **write the number of degrees of freedom** (in addition to pressure) in each region, line, intersection point in the diagram.



where L = homogeneous liquid solution of Fe and Au
α = a solid solution of Fe and Au containing 30% Au or less
β= a solid solution of Fe and Au containing 65% Au or more, minimum amount of Au in this phase is 65% at 1170°C, up to 68% at 890°C.

8. For each of the following processes, **state which** of the quantities ΔT, $\Delta \boldsymbol{U}$, $\Delta \boldsymbol{H}$, $\Delta \boldsymbol{S}$, $\Delta \boldsymbol{G}$, q, w **are equal to zero** for the system specified. **For those which are not zero, state whether the value is positive or negative.** If information is not available to determine the sign of a non-zero value, use NA. [*Hint*: Only 4-5 NA]

(a) A non-ideal gas is taken around an irreversible cycle.

(b) At 25°C a solution is formed by mixing 0.3 mol of liquid C_6H_{14} with 0.5 mol of liquid C_7H_{16}, forming an ideal solution.

(c) H_2 and O_2 react to form H_2O inside an insulated bomb calorimeter.

(d) One mole of liquid benzene is vaporized at 80°C (its normal boiling point) and 1 atm in a canister fitted with a frictionless weightless piston and immersed in a heat reservoir that is maintained at 80°C.

(e) C_2H_6 is burned with excess oxygen inside an insulated canister fitted with a frictionless weightless piston.

(f) A reaction occurs in an electrochemical cell that has E = + 0.50 volt at constant T and p. In another experiment, E of this cell is found to have a negative temperature coefficient. No gases are involved at either electrode of this cell.

(g) Heat is withdrawn slowly at a uniform rate from a liquid-solid system at 1 atm at its eutectic temperature without any work being done.

(h) A non-ideal gas [having negative values for both $(\partial \boldsymbol{U}/\partial V)_T$ and $(\partial \boldsymbol{H}/\partial p)_T$] originally at V_1 expands isothermally into an evacuated volume so as to make its final volume equal to $3V_1$.

(i) Two ideal gases A and B each at 0.5 atm and 300 K separately occupy two glass bulbs joined by a stopcock. The stopcock is opened and all thermometer and pressure gauge readings are unchanged.

(j) Reactants in dilute aqueous solutions are combined in a open flask immersed in a thermostated bath, and an exothermic reaction occurs until chemical equilibrium is achieved. No gases are involved in this reaction.

Enter 0, +, - , or NA **into the appropriate box in the table**

	(a)	(b)	(c)	(d)	(e)	(f)	(g)	(h)	(i)	(j)
ΔT	0	0	+	0	+	0	0	0	0	0
$\Delta \boldsymbol{U}$	0	0	0	NA	-	-	-	-	0	-
$\Delta \boldsymbol{H}$	0	0	NA	+	0	-	-	+	0	-
$\Delta \boldsymbol{S}$	0	+	+	+	+	-	-	+	+	NA
$\Delta \boldsymbol{G}$	0	-	-	0	-	-	0	-	-	-
q	NA	0	0	+	0	-	-	-	0	-
w	NA	0	0	-	-	-	0	0	0	0

and on the next page, **provide a brief explanation by enumerating the key concepts that apply to each case and how you used them to arrive at** 0, +, -, NA

	The key concepts that apply to each case	Using these key points, choose 0, +, or – using this reasoning:
(a)	***cycle* makes all** **Δ(state function) = 0**	q and W opposite signs but NA
(b)	$dT = 0$, ***ideal liquid solution* means (ΔV, ΔH, q) = 0 upon mixing**.	$\Delta T = 0$, $\Delta H = 0$, $q = 0$, $\Delta V = 0$ gives $W = 0$, $\Delta U = q+W = 0$, $\Delta S_{mixing} > 0$ since greater disorder in the mixture than in separate pure liquids, $\Delta G = \Delta H - T\Delta S = 0 - [+] = [-]$
(c)	$q = 0$, $dV = 0$, **isolated system**, **spontaneous reaction**, $\Delta n_{gas} = -1$	$\Delta T > 0$ since *adiabatic* combustion, $W=0$, $\Delta U = q_V = 0$, spontaneous, $\therefore$ $\Delta S_{isol\ sys} > 0$ and $\Delta_{\rm rxn} G < 0$ $\Delta H = \Delta U + \Delta(n_{gas}RT) = 0 + R(T_f - 1.5T_i)$ = NA
(d)	$dT = 0$, $dp = 0$, dV +, two phases are **at equilibrium** during the liq→gas transformn	$\Delta G = 0$ at equilibrium, $\Delta S > 0$ since $S_{gas} > S_{liq}$, $\Delta_{vap}H > 0$ since $H_{gas} > H_{liq}$, $q_p = \Delta H > 0$, $\Delta U = q_p - p\Delta V$ = NA
(e)	$q = 0$, $dp = 0$, $\Delta n_{gas} = +\frac{1}{2}$, dV +, **spontaneous reaction**	$\Delta T > 0$ since *adiabatic* combustion, $q = 0$, $\Delta H = q_p = 0$, $W = -p\Delta V < 0$, $\Delta U = 0+W < 0$ spontaneous, $\therefore \Delta G < 0$, $\Delta H - T\Delta S < 0$ leads to $\Delta S > 0$
(f)	$dT = 0$, $dp = 0$, $\Delta n_{gas} = 0$, $\Delta_{\rm rxn}G = -\nu F \mathrm{E} = W_{elec}$, from which: $\nu F (\partial \mathrm{E}/\partial T)_p = \Delta_{\rm rxn}S$, $\Delta_{\rm rxn}H = -\nu F \cdot \{\mathrm{E} - T(\partial \mathrm{E}/\partial T)_p\}$	From the given signs: $\mathrm{E} > 0$, $(\partial \mathrm{E}/\partial T)_p < 0$, we get $W_{elec} < 0$, $\Delta_{\rm rxn}G < 0$, $\Delta_{\rm rxn}S < 0$, $\Delta_{\rm rxn}H < 0$ $q_p = \Delta H < 0$, $\Delta U = q + W_{elec} < 0$
(g)	$dT = 0$, $dp = 0$, $W = 0$, $q < 0$, 3 phases remain **at equilibrium** at $T_{eutectic}$,	$\Delta G = 0$ at equilibrium, $\Delta U = q + W < 0$ $\Delta H = q_p < 0$, $\Delta H - T\Delta S = 0$ leads to $\Delta S < 0$
(h)	$dT = 0$, $dV > 0$, $p_{op} = 0$, spontaneous $(\partial U/\partial V)_T < 0$, $(\partial H/\partial p)_T < 0$ ideal gas $dS = C_V dT + nR\,dV/V$ $\Delta S_T = nR \int dV/V$	$dU = C_V dT + (\partial U/\partial V)_T dV = 0+(-)(+) = [-]$ $dH = C_p dT + (\partial H/\partial p)_T dp = 0+(-)(-) = [+]$ $W = 0$, $q = \Delta U - W = [-] - 0 = [-]$ spontaneous, thus $\Delta G < 0$ $\Delta S_T > 0$ (also greater space disorder)
(i)	$dT = 0$, $dp = 0$, $dV_{tot} = 0$, **spontaneous** mixing, ideal: $U=U(T)$, $H=H(T)$	$dV_{tot} = 0$ $\therefore W = 0$, $dT = 0$ $\therefore \Delta U = \Delta H = 0$ $q = \Delta U - W = 0$, no q and W $\therefore$ an isolated system, which has $\Delta S > 0$ for spontaneous change, spontaneous, $\therefore$ $\Delta G_{T,p} < 0$
(j)	$dT = 0$, $dp = 0$, $q < 0$, $\Delta n_{gas} = 0$ **spontaneous reaction**	$\Delta n_{gas} = 0$ $\therefore$ $W = 0$, $\Delta U = q+W = [-] + 0$ $\Delta H = \Delta U + \Delta(pV) = [-] + 0$ spontaneous, $\therefore$ $\Delta_{rxn}G_{T,p} < 0$ $\Delta G = \Delta H - T\Delta S$ leads to $[-] = [-] - T\Delta S$ $\therefore \Delta S$ = NA

9. These are about one-component phase diagrams:

(a) Starting from $d\boldsymbol{G} = Vdp - \boldsymbol{S}dT$ **derive the Clapeyron equation** for a pure substance in phase α and phase β coexisting in equilibrium.

$d\boldsymbol{G}_{\alpha} = V_{\alpha}dp - \boldsymbol{S}_{\alpha}dT$ for phase α $d\boldsymbol{G}_{\beta} = V_{\beta}dp - \boldsymbol{S}_{\beta}dT$ for phase α

Subtract the two equations: $d\boldsymbol{G}_{\alpha} - d\boldsymbol{G}_{\beta} = (V_{\alpha} - V_{\beta})\,dp - (\boldsymbol{S}_{\alpha} - \boldsymbol{S}_{\beta})\,dT$

For a pure substance in phase α and phase β coexisting in equilibrium, $d\boldsymbol{G}_{\alpha} = d\boldsymbol{G}_{\beta}$

$(V_{\alpha} - V_{\beta})\,dp = (\boldsymbol{S}_{\alpha} - \boldsymbol{S}_{\beta})\,dT$

$dp/dT = (\boldsymbol{S}_{\alpha} - \boldsymbol{S}_{\beta})/(V_{\alpha} - V_{\beta})$

(b) The vapor pressure of acetonitrile is changing at the rate of 0.030 atm/deg in the vicinity of its normal boiling point, which is 80°C. **Calculate the enthalpy of vaporization of acetonitrile.**

$dp/dT = (\boldsymbol{S}_{\mathrm{g}} - \boldsymbol{S}_{\mathrm{liq}})/(V_{\mathrm{g}} - V_{\mathrm{liq}})$. For the change (definition of normal boiling point):

$CH_3CN(\mathrm{liq}, 353\mathrm{K}, 1\ \mathrm{atm}) \rightarrow CH_3CN(\mathrm{gas}, 353\mathrm{K}, 1\ \mathrm{atm})$,

$(\boldsymbol{S}_{\mathrm{g}} - \boldsymbol{S}_{\mathrm{liq}}) = q_{REV}/T = q_{\mathrm{p}}/T = \Delta\boldsymbol{H}_{vap}/T$ and $V_{\mathrm{g}} \approx RT/p >> V_{\mathrm{liq}}$

$$dp/dT = \frac{\Delta\boldsymbol{H}_{vap}/T}{RT/p} = \frac{\Delta\boldsymbol{H}_{vap}\,p}{RT^2} \qquad \text{Thus,} \quad 0.030\ \mathrm{atm/deg} = \frac{\Delta\boldsymbol{H}_{vap} \times 1\ \mathrm{atm}}{1.987\ \mathrm{cal\ mol^{-1}\ K^{-1}}\ 353^2}$$

Solve for $\Delta\boldsymbol{H}_{vap}$

$\Delta\boldsymbol{H}_{vap} = 0.030\ \mathrm{atm\ K^{-1}} \times 1.987\ \mathrm{cal\ mol^{-1}\ K^{-1}} \times 353^2\ \mathrm{K^2}\ /1\ \mathrm{atm}$

$= 7400\ \mathrm{cal\ mol^{-1}}$

Answer: $7400\ \mathrm{cal\ mol^{-1}}$

(c) Explain whether the melting point of a solid substance A will be raised or lowered by pressure, given that solid A does not float on liquid A. **Illustrate your explanation by suitable equations.**

$dp/dT = (\boldsymbol{S}_{\mathrm{liq}} - \boldsymbol{S}_{\mathrm{solid}})/(V_{\mathrm{liq}} - V_{\mathrm{solid}})$

$\boldsymbol{S}_{\mathrm{liq}} > \boldsymbol{S}_{\mathrm{solid}}$ always. Thus, $(\boldsymbol{S}_{\mathrm{liq}} - \boldsymbol{S}_{\mathrm{solid}}) > 0$ (a positive number)

Solid A does not float on liquid A means that the density of solid A is greater than the density of liquid A at the same temperature, density=mass/volume, thus, $V_{m,liquid} > V_{m,solid}$

Thus, $(V_{m,liquid} - V_{m,solid}) > 0$(a positive number)

Therefore, $dp/dT = (+)/(+) = (+)$

so applying increasing pressure increases the melting point of the solid.

(d) For substance B the change of entropy on melting is 3 cal K^{-1} per mL of solid that melts. The melting point under 1 atm pressure is 6°C, and densities of solid and liquid are 0.90 and 0.85 g mL^{-1} respectively. **Calculate the melting point** under 10^4 atm pressure.

$dp/dT = (S_{liq} - S_{solid})/(V_{liq} - V_{solid})$

density=mass/volume.

Consider 1 mL of solid B: $m_{solid} = 0.90$ g .

This melts to a volume $V_{liq} = 0.90 \text{ g} / 0.85 \text{ g mL}^{-1} = 1.06$ mL

For every mL of solid that melts, $(V_{liq} - V_{solid}) = (1.06 - 1)$ mL $= 0.06$ mL

$(S_{liq} - S_{solid})/(V_{liq} - V_{solid}) = (3 \text{ cal K}^{-1}/0.06 \text{ mL})\times(1 \text{ L}/10^3 \text{ mL})\times(1.987 \text{ cal}/0.082057 \text{ L atm})$

$= 2050 \text{ atm K}^{-1}$

10^4 atm/2050 atm K^{-1} = 4.9 K. This is the change in the melting point compared to the normal melting point at 1 atm. Melting point at 10^4 atm is thus, 279+4.9 = 283.9 K.

Answer: melting point = 283.9 K

10. These questions are about non-ideal behavior.

(a) A particular non-ideal solution of A and B has a normal boiling point at 60°C. For this solution, at this temperature, the activity coefficients of A and B are 1.3 and 1.6 respectively, with activity definition chosen to be that of the rational system. The activity of A is 0.6 and the vapor pressure of pure liquid A is 400 mm Hg. **Calculate** for the liquid solution and the vapor phase which is in equilibrium with the liquid solution at 60°C the following: and place the **final answers into the table**

actual vapor pressure of A above the solution	240 mm Hg
mole fraction of A in the liquid solution	0.46
activity of B in the liquid solution	0.86
actual vapor pressure of B above the solution	520 mm Hg
mole fraction of A in the vapor	0.31
vapor pressure of pure liquid B	610 mm Hg

Place your calculations and reasoning in this space:

The actual vapor pressure of A above the solution is $a_A \bullet p^*_A = 0.6 \bullet 400$ mm Hg = 240 mm Hg

Since activity = activity coefficient × mole fraction, $a_A = \gamma_A \bullet x_A$, then $0.6 = 1.3 \bullet x_A$; gives $x_A = 0.46$

This means $x_B = (1 - x_A) = 0.54$; $a_B = \gamma_B \bullet x_B = 1.6 \bullet 0.54 = 0.86$

Since the solution boils (**reaches a vapor pressure of 760 mm Hg**) at 60°C, then

760 mm Hg = 240 + p_B , which gives p_B = 520 mm Hg .

Thus we find $520 = a_B \bullet p^*_B = 0.86 \bullet p^*_B$; Solving for p^*_B we get 610 mm Hg.

The mole fraction of A in the vapor is thus 240/760 = 0.31

(b) The thermodynamic solubility product for PbF_2 is 4×10^{-9}. Including activity coefficient effects where they are not negligible, **calculate the solubility** (call it S) of PbF_2 in (1) water, (2) 0.1 M NaF, (3) 0.1 M HCl [You may neglect activity coefficient effects in this last case, but recognize that HF is a weak acid and is only 1% dissociated at a pH of 1.]

(1) In water: $PbF_{2(s)} = Pb^{2+}_{(aq)} + 2F^{-}_{(aq)}$

If at first we neglect any activity coefficient effects: If S is the solubility of PbF_2 in mol L^{-1}, then $K_{sp} = 4\times10^{-9} \approx (S)(2S)^2$ leads to $S \approx 1\times10^{-3}$, just like you did in Freshman Chemistry.

The Debye-Huckel limiting value for the mean ionic activity coefficient for water at 25°C as the solvent, $\ln \gamma_{\pm} = -z_{+}z_{-}I^{1/2}\,(1.17223)$ where ionic strength $I \equiv \tfrac{1}{2}\sum m_i z_i^2$

Here, $I \equiv \tfrac{1}{2}\sum m_i z_i^2 = \tfrac{1}{2}[(1\times10^{-3})(2^2) + (2\times10^{-3})(1^2)] = 3\times10^{-3}$

$\ln \gamma_{\pm} = -z_{+}z_{-}I^{1/2}\,(1.17223) = -(2)(1)(3\times10^{-3})^{1/2}\,(1.17223)$; solve for $\gamma_{\pm}$; $\gamma_{\pm} = 0.88$ for Pb^{2+}, F^-

Since the solution is sufficiently dilute in the ions, we can use just this limiting value for our calculation in water: $4\times10^{-9} = K\gamma \times K_M = (0.88)^3(S)(2S)^2$ Solve for S; gives $S = 1.3\times10^{-3}$ mol L^{-1}.

Answer: $S = 1.3\times10^{-3}$ mol L^{-1}

(2) In 0.1 M NaF, **the ionic strength is dominated by the ions from the completely soluble and completely dissociated NaF:** $I \equiv \tfrac{1}{2}\sum m_i z_i^2 = \tfrac{1}{2}[(0.1)(1^2) + (0.1)(1^2)] = 0.1$, compared to which, the miniscule amount provided by the dissolving PbF_2 can be neglected.

$\ln \gamma_{\pm} = -z_{+}z_{-}I^{1/2}\,(1.17223) = -(2)(1)(0.1)^{1/2}\,(1.17223)$; solve for $\gamma_{\pm}$; $\gamma_{\pm} = 0.479$ for Pb^{2+}, F^-

In $4\times10^{-9} = K\gamma \times K_M = (0.479)^3(S)(0.1+2S)^2$ we can neglect 2S compared to 0.1 solve for S; gives $S = 3.64\times10^{-6}$ mol L^{-1}.

Answer: $S = 3.64\times10^{-6}$ mol L^{-1}

(3) In 0.1 M HCl, the protons from the complete dissociation of HCl captures 0.1 M of F^- ions forming molecular HF, a weak acid, which then dissociates only to the extent of 1%. Thus, of the 2S F^- ions resulting from solubility of PbF2, **only 1% remain in the form of free F^- ions**, that is, only 0.02S. We were told to neglect activity coefficient effects in this case. The solubility is now given by

$4\times10^{-9} \approx (S)(0.02S)^2$ leads to $S \approx 0.0216$ mol L^{-1}

Answer: $S = 0.0216$ mol L^{-1}