Name ______________________

Please put answers within boxes provided.

Chemistry 342

December 8, 1998

Final Exam (3 hrs.) **Answers**

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

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

$[p+a(n/V)^2](V-nb) = nRT$ van der Waals equation of state

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

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

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

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

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

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

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 $\equiv \tfrac{1}{2}\sum m_i z_i^2$

$$\ln a_A = \Delta_{fus}H/R\left[-\frac{1}{T} + \frac{1}{T^*}\right]$$

◆◆◆

If insufficient information is provided, you may assume ideal behavior (and you must clearly state that you are doing so), provided that there is nothing in the problem that contradicts this assumption. Otherwise, you must assume that explicitly non-ideal systems are under consideration. Pace yourself with the suggested maximum times (out of total 180 min.) shown.

1. 15 min. The enthalpy of formation of HBr(g) from H_2(g) and Br_2(g) at 25°C is -9.0 kcal mol^{-1} . Assume that all diatomic gases have a constant heat capacity at constant pressure of 7.0 cal mol^{-1} K^{-1}.

(a) **Determine** what the enthalpy of formation of HBr(g) would be at 125°C.

The reaction is $\tfrac{1}{2}H_2(g) + \tfrac{1}{2}Br_2(g) = HBr(g)$

$\Delta_{rxn}H^\ominus_{298} = -9.0$ kcal mol^{-1}

There are equal number of moles of gases in reactants compared to products, so, since heat capacities of products and reactants are equal, no change in heat capacity of mixture upon reaction. Therefore, $\Delta_{rxn}H^\ominus_{125°C} = \Delta_{rxn}H^\ominus_{25°C} = -9.0$ kcal mol^{-1}

(b) If 1.0 mole of H_2 and 99.0 moles of Br_2 are exploded in an insulated bomb (of heat capacity 900 cal K^{-1}) then **calculate** the final temperature (of calorimeter and gases) if the initial temperature was 25°C.

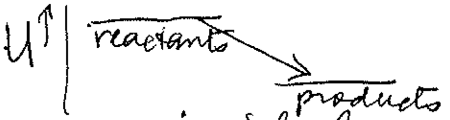
② moles HBr are formed from 1 mole H_2, 98 moles of Br_2 remain unreacted.

$\Delta H = 2(-9.0) = -18 \text{ kcal} = \Delta U + \Delta(pV)$.

But $\Delta(pV)$ = zero since equal no. of moles of gas (100) before + after reaction $\therefore \Delta U = -18$ kcal also.

$\Delta U_{rxn} = -18$ kcal

Energy is released by the reaction:



C_V of each gas is $C_p - R$ (assuming ideal gas behavior in this respect)
$= 5.0 \text{ cal mol}^{-1} \text{K}^{-1}$

$$q_V = 18 \times 10^3 \text{ cal} = \underset{\substack{\text{cal } K^{-1} \\ \text{calorimeter}}}{900}(T_f - 298) + \underset{\text{gases}}{5.0 \text{ cal mol}^{-1}\text{K}^{-1}}\underset{\text{mol}}{(100)}(T_f - 298)$$

$$(T_f - 298) = \frac{18{,}000}{900+500} = 12.8$$

$$T_f = 310.8 \text{ K}$$

2. 10 min. If a <u>small</u> amount of SO_2 is introduced into oxygen gas at 2 atm pressure, the equilibrium molar ratio of SO_3/SO_2 is found to be 10^4 at 1000°C. If this gaseous mixture is now allowed to expand to a volume nine times the original one, still at 1000°C, **calculate** what the new value of the SO_3/SO_2 ratio should be at equilibrium.

The reaction is $SO_2(g) + \frac{1}{2}O_2(g) = SO_3(g)$

$$K_p = \frac{(P_{SO_3}/1)}{\left(\frac{P_{SO_2}}{1}\right)\left(\frac{P_{O_2}}{1}\right)^{1/2}} = \frac{x_{SO_3}P/1}{x_{SO_2}\frac{P}{1}\left(x_{O_2}\frac{P}{1}\right)^{1/2}} = \frac{x_{SO_3}}{x_{SO_2}} \cdot \frac{(P/1\text{atm})^{-1/2}}{x_{O_2}^{1/2}}$$

Since O_2 is in large excess, mole fraction of O_2 is ≈ constant

At 1000°C $K_p = 10^4 \cdot \frac{(2/1\text{atm})^{-1/2}}{x_{O_2}^{1/2}}$

When volume is nine times the original, P is $\frac{1}{9}$ times the original, that is, $P = \frac{1}{9}(2 \text{ atm})$

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$$K_p = 10^4 \frac{(2/1)^{-1/2}}{x_{O_2}^{1/2}} = \frac{x_{SO_3}}{x_{SO_2}} \cdot \frac{(3/9)^{-1/2}}{x_{O_2}^{1/2}}$$

same K_p at same T

x_{O_2} same (excess

$$\therefore \frac{x_{SO_3}}{x_{SO_2}} = \frac{1}{3} \cdot 10^4$$

3. 15 min. Consider the dissociation of nitrogen tetroxide:

$$N_2O_4(g) = 2NO_2(g)$$

T = 298 K

at 25°C. The Gibbs free energies of formation at 25°C and 1 atm are:

$N_2O_4(g)$	98.296 kJ mol^{-1}
$NO_2(g)$	51.845 kJ mol^{-1}

(a) Suppose 2 moles of N_2O_4 is confined in a vessel under 2 atm pressure. **Calculate** the degree of dissociation, i.e., what fraction of the N_2O_4 dissociated?

$$\Delta G^\ominus = 2(51.845) - 1(98.296) = 5.394 \text{ kJ mol}^{-1}$$

That is, per reaction as written.

$$\Delta G^\ominus = -RT \ln K_p$$

$$\therefore K_p = \exp\frac{-5394}{8.3144(298)} = e^{-2.18} = 0.1134$$

$N_2O_4(g) = 2NO_2(g)$ Let x = moles N_2O_4 disappeared

moles $2-x$ $2x$ total moles $= (2-x) + 2x = 2+x$

mole fractions $\frac{2-x}{2+x}$ $\frac{2x}{2+x}$

partial pressures $\left(\frac{2-x}{2+x}\right) \cdot P$ $\left(\frac{2x}{2+x}\right) \cdot P$ $P = 2$ atm

$$K_p = \frac{\left(\frac{2x}{2+x} P/1\text{atm}\right)^2}{\left(\frac{2-x}{2+x} P/1\text{atm}\right)} = \frac{(2x)^2}{(2+x)(2-x)} \cdot \frac{2\text{ atm}}{1\text{ atm}} = \frac{8x^2}{4-x^2} = 0.1134$$

Solve for x $\longrightarrow$ $x = 0.236$ moles dissociated

Degree of dissociation $= \frac{x}{2} = 0.118$

2 moles to start with

(b) If 5 moles of argon are introduced and the mixture confined under 2 atm pressure, **calculate** the degree of dissociation.

$n_{total} = 5 + (2+x) \qquad P = 2\text{atm}$

$$K_p = 0.1134 = \frac{\left(\frac{2x}{7+x}\right)^2 \left(\frac{2\text{atm}}{1\text{atm}}\right)}{\left(\frac{2-x}{7+x}\right)} = \frac{8x^2}{(7+x)(2-x)}$$

Solve for x

$x = 0.408$

Degree of dissociation = $\frac{x}{2} = 0.204$

(c) If the volume of the vessel, determined by the conditions specified in (a), is kept constant, and 5 moles of argon are introduced, **calculate** the degree of dissociation.

$n_{total} = 5 + (2+x)$

$$P = 2\text{atm} \cdot \left(\frac{n_{total}}{\text{old } n_{total}}\right) = 2\text{atm}\left(\frac{7+x}{2+x_{old}}\right)$$

old n_{total} → part (a)

where $x_{old} = 0.236$

$$K_p = 0.1134 = \frac{\left(\frac{2x}{7+x}\right)^2 \left(\frac{2\text{atm}}{1\text{atm}} \; \frac{7+x}{2+x_{old}}\right)}{\left(\frac{2-x}{7+x}\right)}$$

$$0.1134 = \frac{4x^2}{2-x} \cdot \frac{2}{2+x_{old}}$$

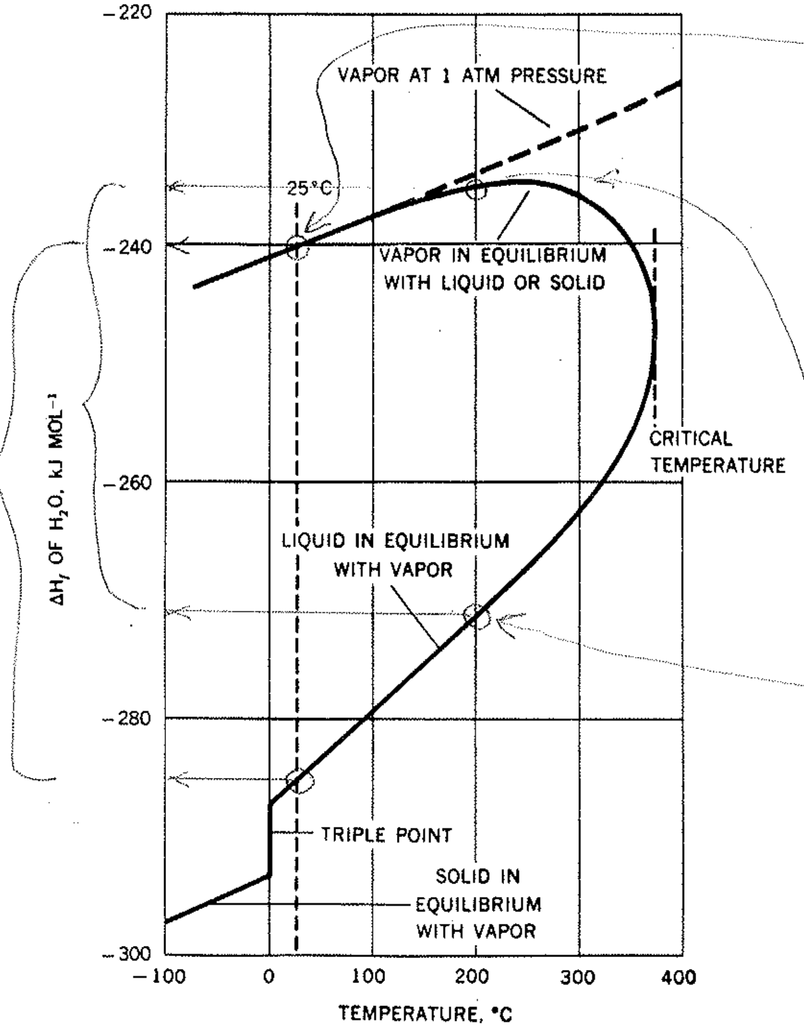
$x = 0.236$

Degree of dissociation $= \frac{x}{2} = 0.118$

Note that this is exactly the same equation to solve for x in part (a). Therefore x here is the same as in part (a)!

4. 20 min. (a) The enthalpy content of the vapor, liquid, and solid phases of water as a function of temperature is shown in the figure below:

$\Delta_{vap}H$ at 25°C, 0.0313 atm



Determine the enthalpy of formation of $H_2O(g)$ at 298 K.

Read at 25°C

$\Delta H_f \ H_2O_{(g)} = -240 \ kJ \ mol^{-1}$

Determine $\Delta_{vap}H$ of water at 200°C.

$\Delta_{vap}H = (H_{(g)} - H_{(l)})_{at\ 200°C}$

$= -235 - -270.6$

$= 35.6 \ kJ \ mol^{-1}$

(b) **Calculate** ΔH, ΔS, ΔG for the <u>conversion of liquid water at 25°C, subjected to its equilibrium vapor pressure of 0.0313 atm, to steam at 100°C and 1 atm</u>. Take the heat capacity of liquid water at 1 atm to be constant at 75.4 J K^{-1}mol^{-1} and $S^{\ominus}_{298} = 69.9$ J K^{-1} mol^{-1}. The heat capacity of water vapor at 1 atm is 30.54 + 10.29×10^{-3}T J K^{-1} mol^{-1}.

ΔH $(LIQ, 298K, 0.0313 atm) \xrightarrow[REV]{(1)} (GAS, 298K, 0.0313 atm) \xrightarrow[REV]{(2)} (GAS, 373, 0.0313 atm) \xrightarrow[REV]{(3)} (GAS, 373, 1 atm)$

Read from figure at ~~25~~ 25°C $\Delta H_1 = (-240 - -284) = +44 \ kJ \ mol^{-1}$

$$\Delta H_2 = \int_{298}^{373} C_p dT = \int_{298}^{373} (30.54 + 10.29 \times 10^{-3} T) dT = 30.54(373-298) + 10.29 \times 10^{-3} (\tfrac{1}{2})(373^2 - 298^2)$$

answer space continued on next page

$= 2,55 \ kJ \ mol^{-1}$

$$\Delta H_3 = \int_{0.0313}^{1} (\partial H / \partial p)_T \, dp = 0 \text{ if ideal gas}$$

$$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3 = 44 + 2.55 + 0 = 46.55 \text{ kJ mol}^{-1}$$

ΔS $$\Delta S_1 = \frac{q_{REV}}{T} = \frac{44 \times 10^3}{298} = 147.65 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$\Delta S_2 = \int_{298}^{373} \frac{C_p dT}{T} = \int_{298}^{373} \left(\frac{30.54}{T} + 10.29 \times 10^{-3}\right) dT = 30.54 \ln \frac{373}{298} + 10.29 \times 10^{-3} (373 - 298)$$
$$= 7.63 \text{ J K}^{-1} \text{mol}^{-1}$$

$$\Delta S_3 = \int_{0.0313}^{1} \left(\frac{\partial S}{\partial p}\right)_T dp = \int_{0.0313}^{1} -\left(\frac{\partial V}{\partial T}\right)_p dp \underset{\text{gas}}{\overset{\text{ideal}}{=}} \int_{0.0313}^{1} -\frac{R}{p} dp = -8.3144 \ln \frac{1}{0.0313}$$
$$= -28.80 \text{ J K}^{-1} \text{mol}^{-1}$$

$$\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3 = 147.65 + 7.63 - 28.80 = 126.48 \text{ J K}^{-1} \text{mol}^{-1}$$

ΔG $\Delta G_1 = 0$ (2 phases are at equilibrium under these conditions)

$$\Delta G_2 = \Delta H_2 - \Delta(TS) = \Delta H_2 - \{373 S^{\ominus}_{GAS,373} - 298 S^{\ominus}_{GAS,298}\}$$

given $S^{\ominus}_{LIQ,298} = 69.9 \text{ J K}^{-1} \text{mol}^{-1}$

$$S^{\ominus}_{GAS,298} = 69.9 + \Delta S_1 = 69.9 + 147.65 = 217.55 \text{ J K}^{-1} \text{mol}^{-1}$$

~~and~~ $S^{\ominus}_{GAS,373} = S^{\ominus}_{GAS,298} + \Delta S_2 = 217.55 + 7.63 = 225.18$

$$\Delta G_2 = \Delta H_2 - 373 \cdot S^{\ominus}_{GAS,\cancel{373}} + 298 S^{\ominus}_{GAS,298}$$
$$= 2550 - 373 (225.18) + 298 (217.55) = -16{,}612 \text{ J mol}^{-1}$$

$$\Delta G_3 = \int_{0.0313}^{1} V dp \underset{\text{gas}}{\overset{\text{ideal}}{=}} \int_{0.0313}^{1} RT \frac{dp}{p} = 8.3144 (373) \ln \frac{1}{.0313} = 10743 \text{ J mol}^{-1}$$

$$\Delta G = \Delta G_1 + \Delta G_2 + \Delta G_3 = 0 - 16612 + 10743 = -5868.8 \text{ J mol}^{-1}$$

or else $\Delta G = \Delta H - \Delta(TS) = \Delta H - [373 \underbrace{S^{\ominus}_{GAS,373}}_{69.9+\Delta S} - 298 \underbrace{S^{\ominus}_{LIQ,298}}_{69.9}]$

$$= 46550 - [373(69.9 + 126.48) - 298(69.9)]$$
$$= 46550 - 52419$$
$$= -5869 \text{ J mol}^{-1}$$ the same answer

5. 10 min. (a) **Derive** $(\partial[G/T]/\partial T)_p$.

$G \equiv H - TS \qquad \frac{G}{T} = \frac{H}{T} - S$

$\left(\frac{\partial[G/T]}{\partial T}\right)_p = \frac{1}{T}(\partial H/\partial T)_p + H\left(-\frac{1}{T^2}\right) - (\partial S/\partial T)_p$

$= \frac{C_p}{T} + H\left(-\frac{1}{T^2}\right) - \frac{C_p}{T} = -H/T^2$

Alternate

$(\partial[G/T]/\partial T)_p = G\left(-\frac{1}{T^2}\right) + \frac{1}{T}(\partial G/\partial T)_p$

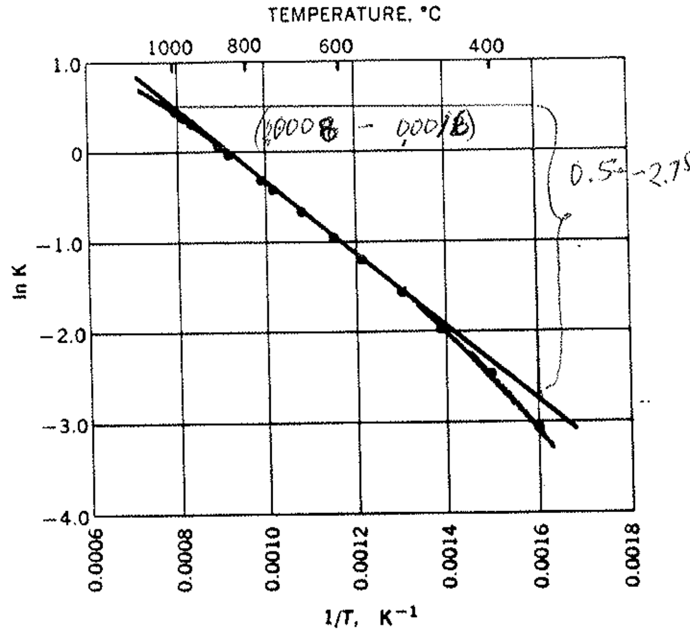
$= (H-TS)\left(-\frac{1}{T^2}\right) + \frac{1}{T}(\partial G/\partial T)_p$

But $(\partial G/\partial T)_p = -S$

$= H\left(-\frac{1}{T^2}\right) + \cancel{\frac{S}{T}} - \cancel{\frac{S}{T}}$

$= H\left(-\frac{1}{T^2}\right)$

(b) For the all-gas reaction $CO_2 + H_2 = CO + H_2O$ the temperature dependence has been measured.



The temperature dependence of the equilibrium constant for the reaction $CO_2 + H_2 \rightleftarrows CO + H_2O$

Determine $\Delta_{rxn}H^\ominus$ for this reaction at 600°C

Describe the states that this $\Delta_{rxn}H^\ominus$ corresponds to.

From above $(\partial(\Delta_{rxn}G^\ominus/T)/\partial T)_p = -\Delta_{rxn}H^\ominus/T^2$ and from $\Delta_{rxn}G^\ominus = -RT\ln K$

we get $-\Delta_{rxn}H^\ominus/T^2 = -R(\partial \ln K/\partial T)_p$

If $\Delta_{rxn}H^\ominus$ constant over the T range, $d\ln K = -\frac{\Delta_{rxn}H^\ominus}{R}d\left(\frac{1}{T}\right)$

plot of ln K vs $1/T$ has a slope of $-\frac{\Delta_{rxn}H^\ominus}{R}$ at each point.

From the plot, slope $= 3.25/-0.0008 = -4062.5\ K^{-1}$

$-4062.5 = -\frac{\Delta_{rxn}H^\ominus}{8.3144} \quad \therefore \Delta_{rxn}H^\ominus = +33.78\,kJ$

$\Delta_{rxn}H^\ominus$ corresponds to gases, one mole of each, behaving ideally in the limit $P \to 0$.

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6. 30 min. Two moles of a gas that obeys the van der Waals equation of state undergoes isothermal expansion from 1 atm, 200 K to ten times its initial volume against a constant pressure of 0.1 atm. The parameters for this gas are $a = 1.4$ L^2 atm mol^{-2}, $b = 0.39$ L mol^{-1} $C_V = (5/2)R - 0.370\times10^{-3}\ T + 25.46\times10^{-7}T^2$ cal mol^{-1}K^{-1}.

For this problem, final numerical answers are not required. However, each answer must have all numbers and units such that only the operation of a simple $2. calculator is required to arrive at the numerical result. That is, 10Rln 2 is not acceptable but 10(1.987)ln 2 cal mol^{-1}K^{-1}is acceptable. Hint: Avoid $(\partial V/\partial T)_p$.

Find V_i, W, ΔU, q, ΔH, ΔS, ΔA, ΔG.

V_i: Given $\left(p + \frac{an^2}{V^2}\right)(V - nb) = nRT$

$$\left[1. + 1.4\left(\frac{4}{V_i^2}\right)\right]\left[V_i - 2(0.39)\right] = 2(.08205)(200)$$

$$V_i = 33.44 \text{ L}$$

W: $W = -\int P_{op}\,dV = -\int_{V_i}^{10V_i} 0.1 \text{ atm}\, dV = -0.1[10V_i - V_i]$

$= -0.9\,V_i$ L atm

$= -30.10$ Latm

or -728.8 cal

ΔU: We need $\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p$ rearrange to get p:

$$p = \frac{nRT}{V-nb} - a\left(\frac{n}{V}\right)^2$$

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{2R}{V-2b} \quad \therefore \left(\frac{\partial U}{\partial V}\right)_T = \frac{2RT}{V-2b} - p = \frac{4a}{V^2}$$

$$dU = \overset{\text{zero}}{C_V dT} + \left(\frac{\partial U}{\partial V}\right)_T dV = 0 + \frac{4a}{V^2}dV$$

$$\Delta U = 0 + 4a\int\frac{dV}{V^2} = 0 - 4a\left(\frac{1}{10V_i} - \frac{1}{V_i}\right) = 4(1.4)\left(\frac{0.9}{V_i}\right) \text{ L atm} = 0.1507 \text{ L atm}$$

or 3.65 cal

q: $\Delta U = q + W$

$$q = \Delta U - W = \left(4(1.4)\frac{0.9}{V_i} + 0.9V_i\right) \text{ Latm}$$

(avoid using $\left(\frac{\partial H}{\partial p}\right)_T dp$ because $\left(\partial V/\partial T\right)_p$ is too messy!

ΔH: $H = U + pV$

$$\Delta H = \Delta U + P_f V_f - P_i V_i$$

$$\Delta H = 4(1.4)\frac{0.9}{V_i} + P_f 10V_i - 1V_i \quad = \qquad \text{L atm}$$

where P_f is calculated from

$$\left[P_f + 1.4\frac{(4)}{(10V_i)^2}\right]\left[10V_i - 2(0.39)\right] = 2(0.08205)200$$

$$P_f = 0.098 \text{ atm}$$

ΔS: $dS = \left(\partial S/\partial T\right)_V \underbrace{dT}_{\text{zero here isothermal}} + \underbrace{\left(\partial S/\partial V\right)_T}_{(\partial p/\partial T)_V} dV = \underbrace{\left(\partial p/\partial T\right)_V}_{\frac{nR}{V-nb} \text{ or } \frac{2R}{V-2(.39)}} dV$

$$\Delta S = \int_{V_i}^{10V_i} \frac{2R}{V-2(.39)}\, dV = 2(1.987)\ln\frac{10V_i - 2(.39)}{V_i - 2(.39)} \quad \text{cal K}^{-1}$$

ΔA: $A \equiv U - TS$

$\Delta A = \Delta U - T\Delta S$ since isothermal

$$\Delta A = 4(1.4)\left(\frac{0.9}{V_i}\right) \times \frac{1.987 \text{ cal}}{0.08205 \text{ L atm}} - (200)(2)(1.987)\ln\frac{10V_i - 2(.39)}{V_i - 2(.39)}$$

cal

ΔG: $G \equiv H - TS$

$\Delta G = \Delta H - T\Delta S$ since isothermal

$$\Delta G = \left[4(1.4)\frac{0.9}{V_i} + P_f 10V_i - V_i\right]\frac{1.987 \text{ cal}}{0.08205 \text{ L atm}}$$

$$- 200(2)(1.987)\ln\frac{10V_i - 2(.39)}{V_i - 2(0.39)}$$

in cal

do not use $\Delta G = \int V dp$, because V is too messy as a function of p

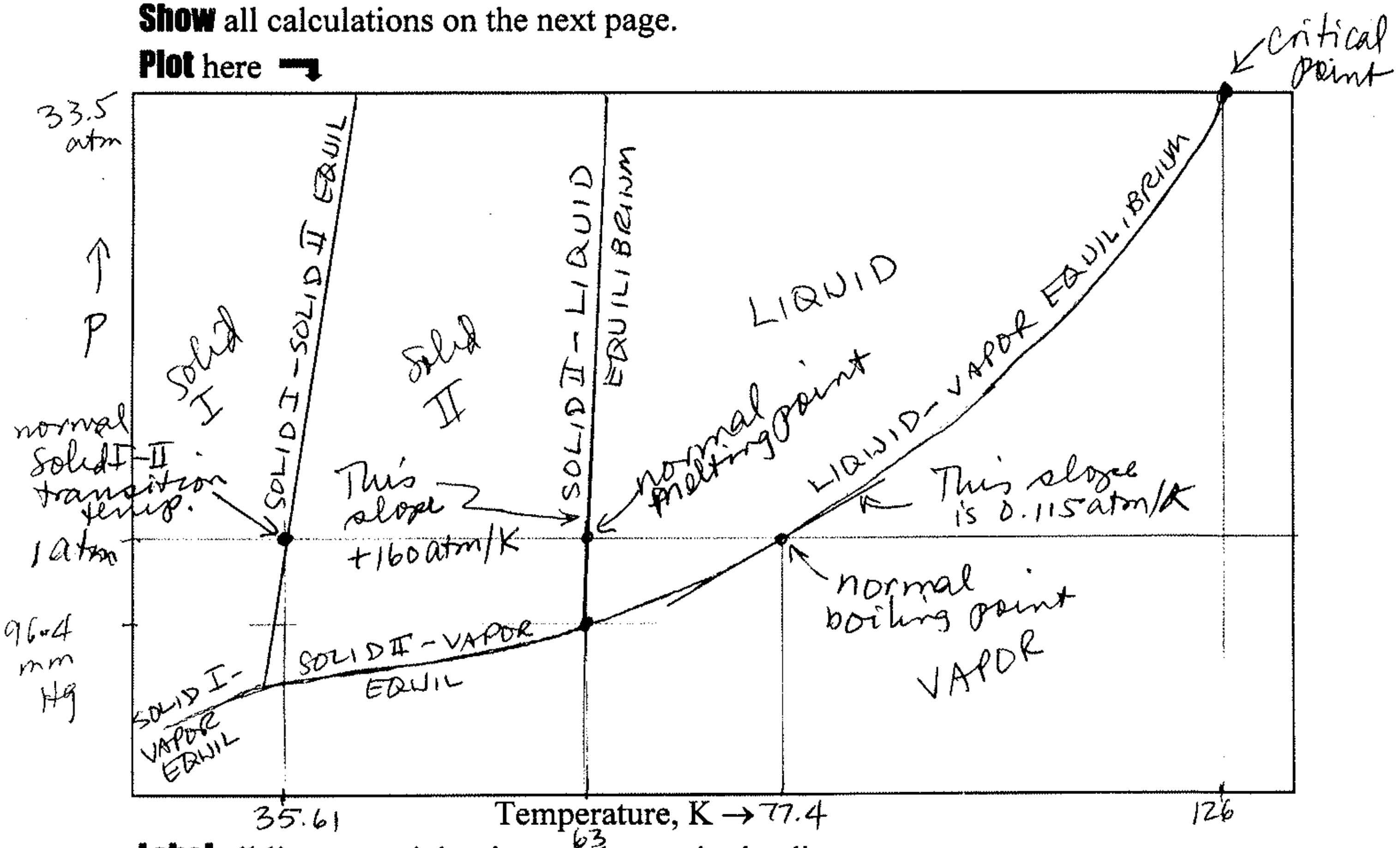
7. 15 min. Some properties of N_2 are given below:

density (0°C, 1 atm)	1.25 g L^{-1}	
normal boiling point	-195.8°C	77.4K
normal melting point	-210.01°C	63 K
vapor density (at boiling point)	4.61 g L^{-1}	
liquid density (at boiling point)	804 g L^{-1}	
solid density (at melting point)	820 g L^{-1}	
vapor pressure of solid (at melting point)	96.4 mm Hg	0.127atm
enthalpy of vaporization (at boiling point)	47.6 cal g^{-1}	
enthalpy of fusion (at melting point)	6.1 cal g^{-1}	
critical temperature	126.0 K	
critical pressure	33.5 atm	

At 1 atm there is a transition from crystalline solid II to the more closely packed crystalline solid I (which is stable at lower temperatures) at 35.61 K.

Plot specific points on the phase diagram of N_2. **Label** the numerical coordinates of all such points along the axes. **Calculate** slopes of curves from available data. **Show** all calculations on the next page.

Plot here ➡



Label all lines, special points, and areas in the diagram.

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Calculations here: (Plot *p* versus *T* on the previous page)

slopes $\frac{dp}{dT} = \frac{\Delta S}{\Delta V}$ Clapeyron eqn

Solid II - Liquid equilibrium :

At 63 K density of liquid should be slightly greater than at 77.4 K, $\gtrsim 804\ g\ L^{-1}$

If we use $804\ g\ L^{-1}$ we get the slope

$$\frac{dp}{dT} \simeq \Delta_{fus}S/(V_{liq} - V_{solid}) = \frac{6.1\ cal}{63\ K}\ \frac{0.08205}{1.987} / \left(\frac{1}{804} - \frac{1}{820}\right)$$

$$\simeq +160\ atm\ K^{-1}$$

liquid - vapor equilibrium :

At 77.4 K, $\Delta S = \Delta_{vap}H/T_b$

$$\frac{dp}{dT} = \frac{47.6}{77.4} \times \frac{0.08205}{1.987} / \left(\frac{1}{4.61} - \frac{1}{804}\right)$$

$$= 0.115\ atm\ K^{-1}$$

Solid I - solid II equilibrium :

solid I is said to be more closely-packed and more stable

$$\frac{dp}{dT} = \Delta S / \Delta V \qquad \begin{cases} \Delta S = S_{solid\ II} - S_{solid\ I} > 0 \\ \Delta V = V_{solid\ II} - V_{solid\ I} > 0 \end{cases}$$

$$\therefore \frac{dp}{dT} > 0 .$$

solid I → solid II transition point

melting point

Boiling point

Points (1 atm, 35.61 K), (1 atm, 63 K), (1 atm, 77.4 K), (33.5 atm, 126.0 K), and (0.127 atm, 63 K)

critical point

8. 10 min. For the reaction $2NOBr = 2NO + Br_2$, the equilibrium constant K_p = 0.35 and $\Delta_{rxn}H^{\ominus}$ = 15.7 kcal at 300 K. **Calculate** the equilibrium constant for this reaction at 600 K. You may consider the heat capacities of the gases to be constant in the temperature range considered here. C_p cal mol^{-1} K^{-1} = 6.3 for NOBr, 7.0 for NO, and 8.6 for Br_2.

$\Delta G^{\ominus} = -RT \ln K_p$ From Prob. 5 $\left(\frac{\partial(\Delta G^{\ominus}/T)}{\partial T}\right)_p dT = -\frac{\Delta H^{\ominus}}{T^2} dT$

$\frac{\partial(\Delta G^{\ominus}/T)}{\partial T} dT = -R\, d \ln K_p = -\frac{\Delta H^{\ominus}}{T^2} dT$

$d \ln K_p = \frac{\Delta H^{\ominus}(T)}{R} \frac{dT}{T^2}$ First find $\Delta_{rxn} H^{\ominus}$ as a function of T

$\Delta H^{\ominus}_T = \Delta H^{\ominus}_{300K} + \int_{300K}^{T} [2(7.0) + 8.6 - 2(6.3)]\, dT$

$= 15.7 \times 10^3 \text{ cal} + 10.0\,(T - 300) \text{ cal}$

$\int d \ln K_p = \ln\left[\frac{(K_p)_{600K}}{(K_p)_{300K}}\right] = \frac{1}{R} \int_{300K}^{600K} \frac{[15.7 \times 10^3 + 10.0(T-300)]}{T^2} dT$

$\ln\left[\frac{(K_p)_{600K}}{0.35}\right] = \frac{1}{1.987}\left\{-\left(\substack{15.7\\+3}\right)\times 10^3\left(\frac{1}{600} - \frac{1}{300}\right) + 10 \ln \frac{600}{300}\right\}$

$+31.167 \qquad + 6.93$

$= 19.17$

$(K_p)_{600K} = 7.43 \times 10^7$

9. 15 min. Consider the following systems. In each one **calculate** the pressure p which must be applied to B <u>in order that equilibrium be established between A and B at the given temperature</u>.

A		**B**	Calculations here, p atm
rhombic sulfur p atm $\Delta_f G^\ominus = 0$ densities: 1.5 g cm^{-3}		monoclinic sulfur p atm $\Delta_f G^\ominus = 0.023$ kcal mol^{-1} 1.2 g cm^{-3}	$\mu^A = \mu^B$ $\mu^{rhom}_{(1atm)} + V_{rhom}dp = \mu^{mono}_{(1atm)} + V_{mono}dp$ $0 + \int_{1atm}^{p}\frac{32}{1.5\times10^3}dp = 0.023 + \int_{1atm}^{p}\frac{32}{1.2\times10^3}dp$ rearrange 0.023×10^3 cal mol^{-1} $= \left(\frac{32}{1.5\times10^3} - \frac{32}{1.2\times10^3}\right)(p-1)\times\frac{1.987}{.08205}$ Solve for p
H_2 1 atm $P_{H_2} = 1$atm	Pd mem brane allows only H_2 to pass	$H_2 + N_2$ mixture is $4N_2 : 1H_2$ p atm $x_{H_2} = 0.20$ $P_{H_2} = 0.20p$	$\mu^A_{H_2} = \mu^B_{H_2}$ $\mu^\ominus_{H_2(1atm)} = \mu^\ominus_{H_2}(1atm) + RT\ln\frac{0.2p}{1}$ $0.2p = 1$, $p = 5$ atm
pure liquid water 1 atm 298 K vapor pressure p_{H2O}*	semi-permiable mem-brane	$x_{sucrose} = 0.001$ 0.1 mole% solution sucrose in H_2O p atm 298 K vapor pressure according to Raoult's law	$\mu^A_{H_2O}$ in pure liq $= \mu^B_{H_2O}$ in solution $\mu^\ominus_{vap,\,1atm} + RT\ln\frac{P^*_{H_2O}}{1atm} = \mu^\ominus_{vap,\,1atm} + RT\ln\frac{x_{H_2O}P^*_{H_2O}}{1atm} + \int_{1atm}^{p}V_m dp$ $\cancel{RT\ln\frac{P^*_{H_2O}}{1atm}} = RT\ln x_{H_2O} + \cancel{RT\ln\frac{P^*_{H_2O}}{1atm}} + \int_1^p V_m dp$ $-RT\ln x_{H_2O} = V_m(p-1)$

$V_m(H_2O) = 0.018$ L mol^{-1}

$\ln x_{H_2O} \approx \ln(1-0.001)$

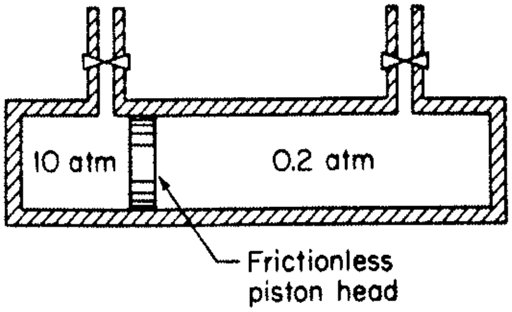
≈ -0.001

$+0.08205(298)(0.001) = 0.018(p-1)$

solve for $(p-1) = 1.358$

$p = 2.358$ atm

10. 10 min. 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 Δ***U***, Δ***H***, and Δ***S*** for the overall process.

ΔU: $\Delta U = q + w$ outer walls are rigid $\therefore w = 0$
insulated $\therefore q = 0$

$\therefore \quad \Delta U = 0$

T$_f$: $dU = C_v dT + \underbrace{(\partial E/\partial V)_T}_{\text{zero, ideal gas given}} dV$

$\Delta U = \int C_v dT \rightarrow 0 = \frac{3}{2}R \cdot (T_f - T_i) \quad \therefore T_f = T_i = 298\ K$

p$_f$: $V_f = \frac{2RT}{p_f} = \frac{RT}{10} + \frac{RT}{0.2} \quad \therefore \frac{2}{p_f} = \frac{1}{10} + \frac{1}{0.2}$ or $p_f = 0.392$

pressure same on both sides

ΔH: $dH = C_p dT + \underbrace{\left(\frac{\partial H}{\partial p}\right)_T}_{\text{zero, ideal gas}} dp$

since $dT = 0$
$\Delta H = 0$

ΔS: constant T this expt, $\Delta S = \frac{q_{REV}}{T} = \frac{\Delta U - W_{REV}}{T} = \frac{0 - W_{REV}}{T}$

$\Delta S = \frac{1}{T}\left\{\int p_{gas}^{left} dV + \int p_{gas}^{right} dV\right\} = \int^{left} \frac{R\,dV}{V} + \int^{right} \frac{R\,dV}{V} = R\left\{\ln\left(\frac{V_f}{V_i}\right)_{left} + \ln\left(\frac{V_f}{V_i}\right)_{right}\right\}$

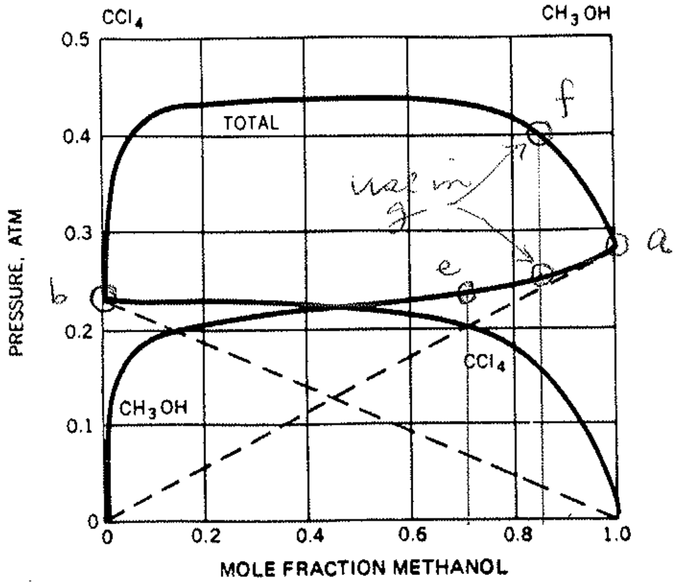
$= R\left(\ln\frac{10}{.392} + \ln\frac{0.2}{.392}\right)$

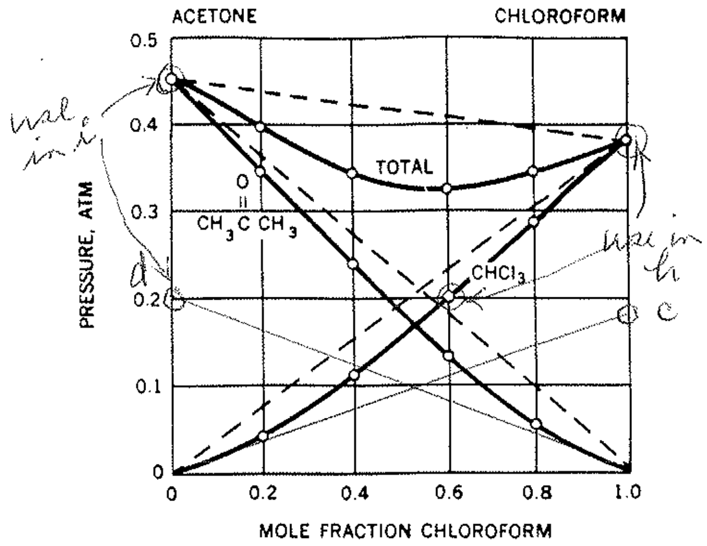
or else $dS = \frac{C_p}{T} dT + \left(\frac{\partial S}{\partial p}\right)_T dp = -\left(\frac{\partial V}{\partial T}\right)_p dp = -\frac{R}{p} dp$

$\Delta S = -R\left\{\ln\frac{p_f}{p_i}^{left} + \ln\frac{p_f}{p_i}^{right}\right\} = -R\left\{\ln\frac{0.392}{10} + \ln\frac{0.392}{0.2}\right\}$

$= 21.3\ J K^{-1}$

11. 5 min. Here are examples of two liquid solutions at 35°C:

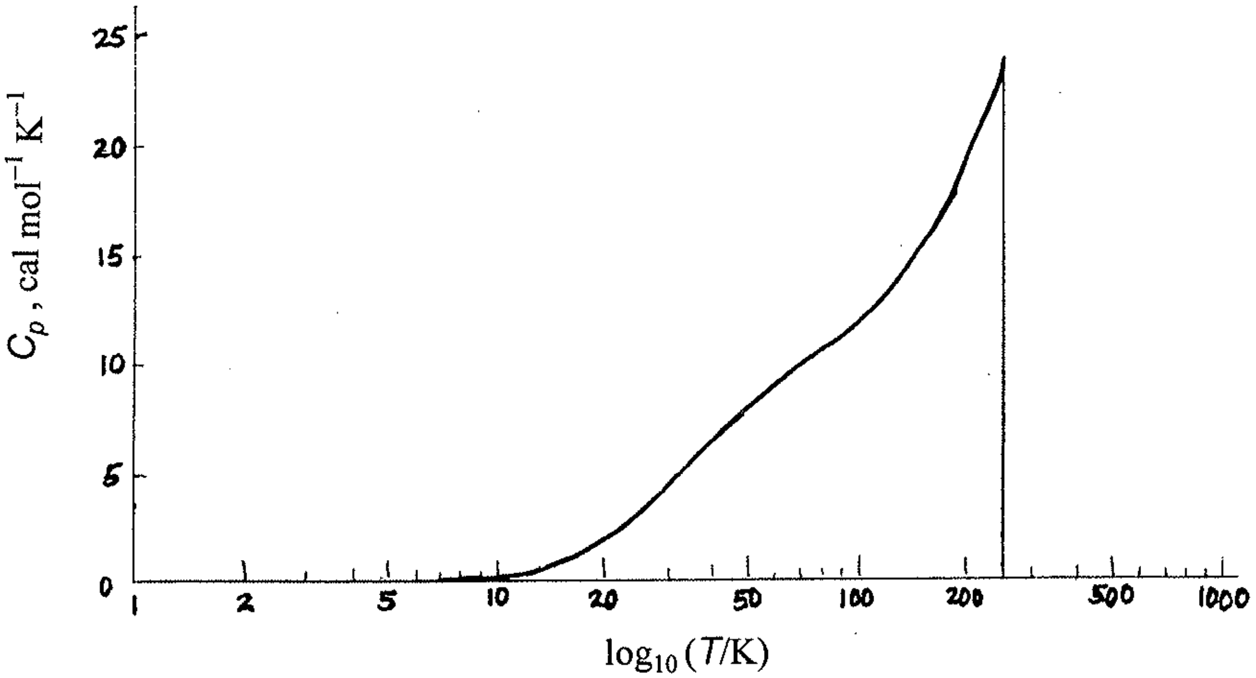




From the graphical data above, **provide the answers** (to two significant digits and with units) to the following questions:

(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 $x_{CCl4} = 0.15$?	$\frac{0.25}{0.40} = 0.625$
(h) What is $(\mu_i - \mu_i^{\ominus})$ for $i = CHCl_3$ in a liquid solution of $x_{CHCl3} =$ 0.60 in acetone at 35°C? $= RT \ln P_i/P_i^*$	$8.3144(308)\ln \frac{0.20}{0.38}$ $-1643.7\ J\,mol^{-1}$
(i) What is the activity coefficient for acetone in a liquid solution which is nearly zero molefraction 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 $a_i = K_i x_i/P_i^*$ $\therefore \gamma_i = a_i/x_i = K_i/P_i^* =$	$\gamma_{acet} = K_{acet}/P^*_{acet}$ $= 0.20/0.45$ $= 0.444$

12. 15 min. The plot of C_p vs. $\log_{10} T$ is shown below for solid benzene at 1 atm.



The area under the curve (shown above) up to 250 K is obtained graphically to be equal to 30 in the units shown. From 200 K to 250 K the molar heat capacity at constant pressure of solid benzene is given by the function: $4.0 + 0.08T$ cal mol^{-1} K^{-1}. For the process

$$C_6H_6\,(s, 200\text{ K}, 1\text{ atm}) \rightarrow C_6H_6\,(s, 250\text{ K}, 1\text{ atm})$$

determine ΔH, ΔS, ΔG.

ΔH $dH = (\partial H/\partial T)_p dT + (\partial H/\partial p)_T dp$; $dp = 0 \therefore dH = C_p dT$

$$\int dH = \Delta H = \int_{200\text{ K}}^{250} (4.0 + 0.08T)\,dT = 4.0(250-200) + \frac{0.08}{2}(250^2 - 200^2)$$

$$= 1100 \text{ cal mol}^{-1}$$

ΔS $dS = (\partial S/\partial T)_p dT + (\partial S/\partial p)_T dp$; $dp = 0 \therefore dS = \frac{C_p}{T} dT$

$$\int dS = \Delta S = \int_{200\text{ K}}^{250} \frac{C_p}{T} dT = \int_{200}^{250} \left(\frac{4.0}{T} + 0.08\right) dT = 4.0 \ln\frac{250}{200} + 0.08(250-200)$$

$$= 4.89 \text{ cal mol}^{-1}\text{ K}^{-1}$$

ΔG $\Delta G \equiv \Delta H - \Delta(TS) = \Delta H - (250 S^{\ominus}_{250} - 200 S^{\ominus}_{200})$

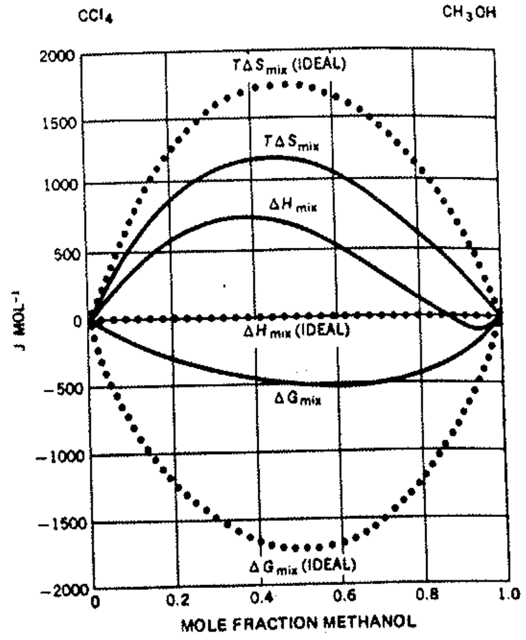
$$= \Delta H - 250 S^{\ominus}_{250} + 200 \overset{\text{from above}}{(S^{\ominus}_{250} - \Delta S)} = \underbrace{\Delta H}_{1.1\times10^{3}} - 50 S^{\ominus}_{250} + 200(4.89)$$

$$S^{\ominus}_{250} = S_{0K} + \int_0^{250} C_p\, d\ln T = 0 + 2.303 \underbrace{\left(\int_0^{250} C_p\, d\log_{10} T\right)}_{\text{given } 30 \text{ cal mol}^{-1}\text{K}^{-1}} = 69.09 \text{ cal mol}^{-1}\text{K}^{-1}$$

$$\therefore \Delta G = 1.1\times10^{3} \text{ cal mol}^{-1} - 50(69.09) \text{ cal mol}^{-1} - 200(4.89) \text{ cal mol}^{-1}$$

$$\doteq -3332 \text{ cal mol}^{-1}$$

13. 5 min. Shown at the right are the thermodynamic changes for the formation of 1 mole of a CCl_4-CH_3OH solution at 25°C.



Write the explicit (in terms of CH_3OH and CCl_4) equations which express the dotted curves for $\Delta_{mix}G$ and $T\Delta_{mix}S$.

$\Delta_{mix}G = \underset{\text{J}}{8.3144}(298)[X_{CH_3OH} \ln X_{CH_3OH} + (1 - X_{CH_3OH}) \ln(1 - X_{CH_3OH})]$

$T\Delta_{mix}S = -8.3144(298)[X_{CH_3OH} \ln X_{CH_3OH} + (1 - X_{CH_3OH}) \ln(1 - X_{CH_3OH})]$

In two sentences **explain** the deviations of the experimental values (solid curves) from the dotted ones:

Interactions between CH_3OH and CH_3OH are stronger than those between CH_3OH and CCl_4. Mixing tends to break up the CH_3OH-CH_3OH association and a positive $\Delta_{mix}H$ indicates energy is required to break them up.