Name:______________________________________

First three letters of last name

Chemistry 342

Second Exam

March 18, 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 J = 1 kg m^{-2} s^{-2} 1 atm = 101325 Pa

$(p + n^2a/V^2)(V\text{-nb}) = nRT$

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

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

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

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

	score
1	
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1. Consider a perfect gas contained in a cylinder and separated by a frictionless adiabatic piston into two sections $\mathcal{A}$ and $\mathcal{B}$. All changes in $\mathcal{B}$ are isothermal, that is a thermostat surrounds $\mathcal{B}$ to keep its temperature constant. There is 2.00 mol of the gas in each section. Initially $T_{\mathcal{A}} = T_{\mathcal{B}} = 300$ K, $V_{\mathcal{A}} = V_{\mathcal{B}} = 2.00$ L. Heat is added to section $\mathcal{A}$ and the piston moves to the right <u>reversibly</u> until the final volume of section $\mathcal{B}$ is 1.00 L .

Calculate the work done by the gas in section $\mathcal{A}$. Calculate for the gas in each section: $\Delta \boldsymbol{U}$, q, $\Delta \boldsymbol{S}$, $\Delta \boldsymbol{A}$, $\Delta \boldsymbol{H}$, $\Delta \boldsymbol{G}$.

Calculate $\Delta \boldsymbol{S}$ of the total system and its surroundings.

Assume $C_V = 20$ J K^{-1} mol^{-1} .
Ideal: $C_p = 28.3144$ J K^{-1} mol^{-1} .

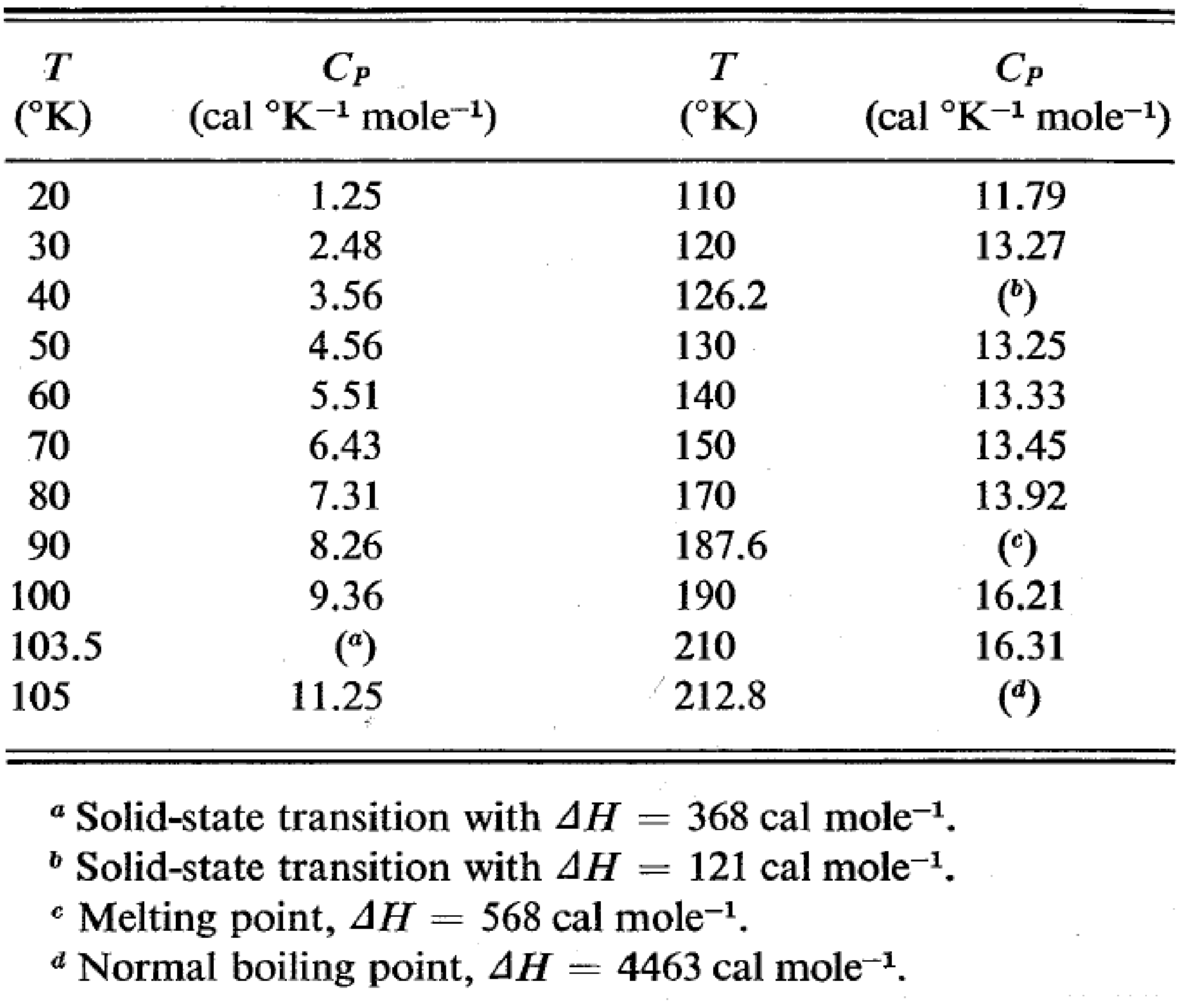
space for sketch:

	section $\mathcal{A}$	*section $\mathcal{B}$*
initial *V,T, p*		
final *V,T, p*		

W		
Δ***U***		
q		
Δ***S***		

ΔA		
ΔH		
ΔG		
ΔS_{system}		
$\Delta S_{\text{surrounds}}$		

2. The following data were obtained for hydrogen sulfide in 1936.



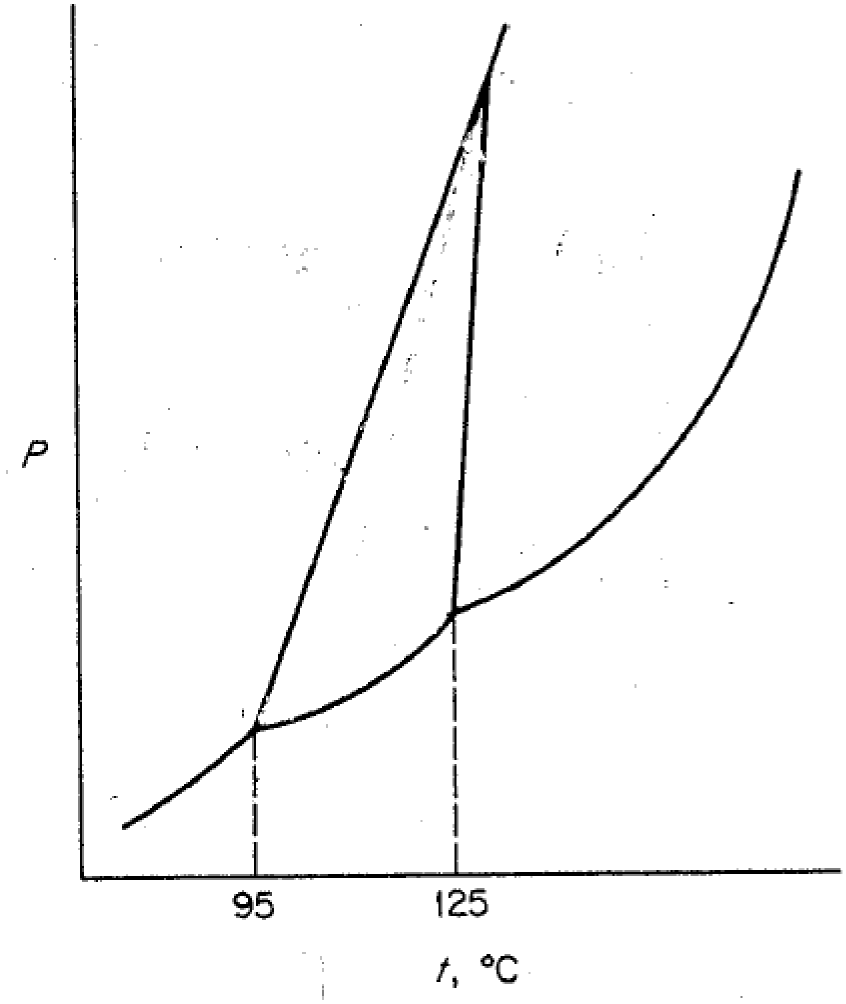
T (°K)	C_P (cal °K^{-1} mole^{-1})	T (°K)	C_P (cal °K^{-1} mole^{-1})
20	1.25	110	11.79
30	2.48	120	13.27
40	3.56	126.2	(b)
50	4.56	130	13.25
60	5.51	140	13.33
70	6.43	150	13.45
80	7.31	170	13.92
90	8.26	187.6	(c)
100	9.36	190	16.21
103.5	(a)	210	16.31
105	11.25	212.8	(d)

[a] Solid-state transition with ΔH = 368 cal mole^{-1}.
[b] Solid-state transition with ΔH = 121 cal mole^{-1}.
[c] Melting point, ΔH = 568 cal mole^{-1}.
[d] Normal boiling point, ΔH = 4463 cal mole^{-1}.

Below 20 K the heat capacity obeys the law $C_p = aT^3$.
Calculate the absolute entropy of hydrogen sulfide gas at 1 atm and 212.8 K.

3. Assume that a gas obeys the equation $p(V\text{-}b) = RT$, where b is a constant, independent of T and p. Derive an expression for the fugacity of a real gas as a function of T and p, starting from $d\boldsymbol{G} = Vdp - \boldsymbol{S}dT$. Apply the derived equation to this particular equation of state.

4. The *p* versus *t* °C phase diagram for sulfur is shown below: (Possible phases are rhombic crystalline, monoclinic crystalline, liquid, and gas, and the stable form of the element is rhombic.)



(a) On the figure given above, identify all the areas, points, and lines (curved or straight) with the correct phase descriptions (i.e., which phases are present).

(b) Where more than one phase is present, derive the Clapeyron equation that describes the constraint that links the pair of variables *p* and *T*, i.e., the equation that describes the area, line or point (where you have placed an identifying mark such as A, B, C, D, E, …) Use explicit symbols and define each of the symbols you use.

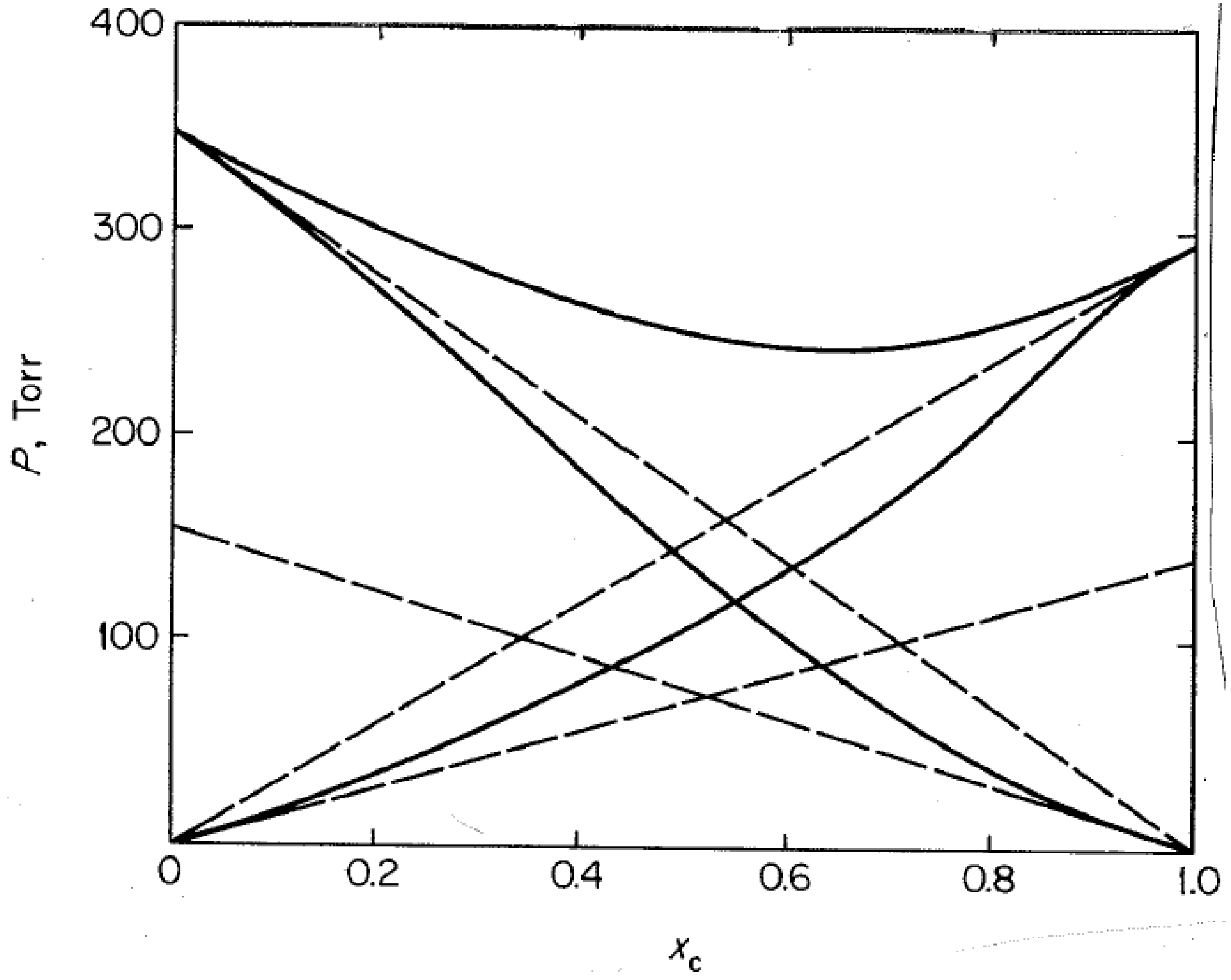
A

B

C etc.

(c) Where more than two phases are present, provide the equations that have to be solved for a unique set of coordinates (*T*, *p*). Again, unless already defined in part (b), define each of the symbols you use.

5. The vapor pressures over a liquid solution of acetone and chloroform are described by the graph below, where the x axis reads from 0 to 1 in mole fraction of chloroform.



Find the numerical values and attach the proper units to each number:

the vapor pressure of pure chloroform	
the vapor pressure of pure acetone	
the Henry's Law constant of acetone dissolved in chloroform	
the Henry's Law constant of chloroform dissolved in acetone	
partial pressure of acetone in the vapor over a liquid solution having 40 mole per cent acetone	
total vapor pressure of a solution containing 20 mole per cent acetone	
mole fraction of acetone in the vapor over a liquid solution which is 20 mole per cent acetone	

Use this space for computations, if any are required beyond reading numbers off the graph.

6. Consider the following system: Pure liquid A has a vapor pressure equal to p_A^* at 300 K while pure liquid B has a vapor pressure equal to p_B^* at 300 K. The molecules of type A have an electric dipole moment equal to 3.2 debye and are capable of forming 1 hydrogen bond per molecule. On the other hand, B molecules do not have a dipole moment at all. B molecules have a greater electric polarizability than A molecules but are incapable of forming hydrogen bonds. ***Use only this information to answer the following.*** For some of the questions, quantitative results will have to wait until we have studied colligative properties. ***Which of the following are likely to be true (select all correct ones) about the vapor pressures, boiling temperatures, and compositions of this system?***

A $p_A^* < p_B^*$ at 300 K
B $p_A^* \approx p_B^*$ at 300 K
C $p_A^* > p_B^*$ at 300 K
D $T_{b,A}^* < T_{b,B}^*$ at 1 atm
E $T_{b,A}^* \approx T_{b,B}^*$ at 1 atm
F $T_{b,A}^* > T_{b,B}^*$ at 1 atm

For a 50-50 mol % solution of A and B:

G $p_{total} < \frac{1}{2}(p_A^* + p_B^*)$ at 300 K
H $p_{total} = \frac{1}{2}(p_A^* + p_B^*)$ at 300 K
I $p_{total} > \frac{1}{2}(p_A^* + p_B^*)$ at 300 K
J $p_A < p_A^*$ at 300 K
K $p_A > \frac{1}{2}p_A^*$ at 300 K
L the vapor pressure of A exceeds that given by Raoult's law
M the vapor pressure is depressed compared to that predicted by Raoult's law
N $T_b > T_{b,B}^*$ at 1 atm
O $T_b > T_{b,A}^*$ at 1 atm
P $T_b < \frac{1}{2}(T_{b,A}^* + T_{b,B}^*)$ at 1 atm
Q $T_b = \frac{1}{2}(T_{b,A}^* + T_{b,B}^*)$ at 1 atm
R $T_b > \frac{1}{2}(T_{b,A}^* + T_{b,B}^*)$ at 1 atm
S mole fraction of A in the vapor $< \frac{1}{2}$
T mole fraction of A in the vapor $= \frac{1}{2}$
U mole fraction of A in the vapor $> \frac{1}{2}$
V mole fraction of A in the vapor $< p_A/(p_A + p_B)$
W mole fraction of A in the vapor $= p_A/(p_A + p_B)$
X mole fraction of A in the vapor $> p_A/(p_A + p_B)$
Y mole fraction of A in the vapor $< p_A^*/(p_A^* + p_B^*)$
Z mole fraction of A in the vapor $= p_A^*/(p_A^* + p_B^*)$
Σ mole fraction of A in the vapor $> p_A^*/(p_A^* + p_B^*)$
Φ fractional distillation leads to pure A in the pot and pure B coming off the distillation column
Δ fractional distillation leads to pure B in the pot and pure A coming off the distillation column
Ω fractional distillation leaves a constant-boiling mixture of A and B in the pot

Circle the letters corresponding to all the correct answers in the boxes below:

A	B	C	D	E	F	G	H	I	J	K	L	M	N	O
P	Q	R	S	T	U	V	W	X	Y	Z	∑	Φ	Δ	Ω

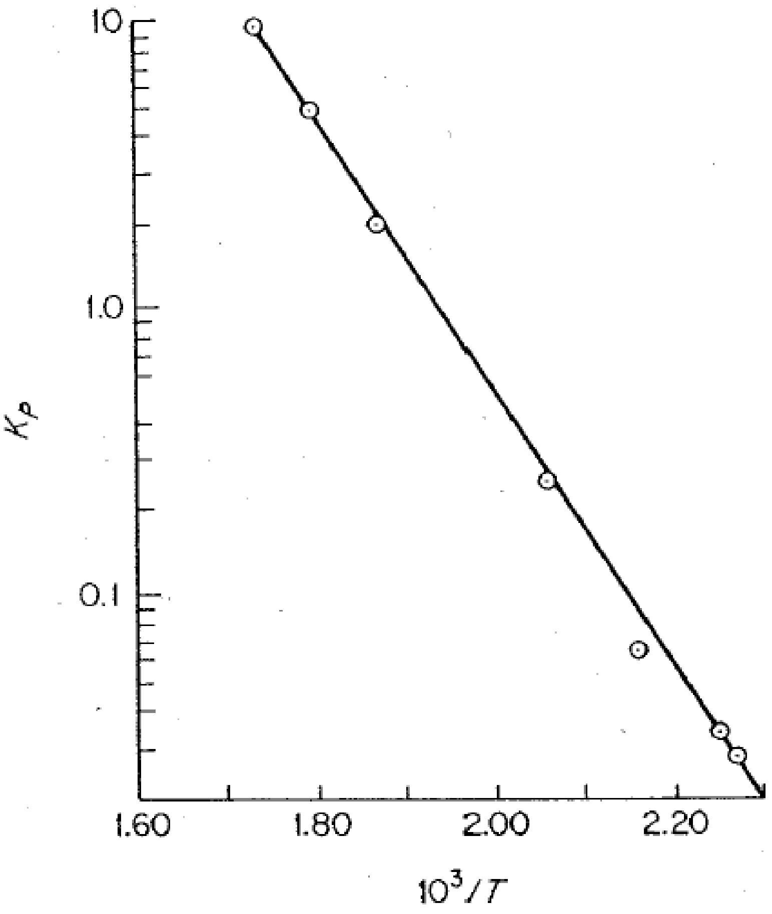
7. The variation with temperature of K_p for the gas-phase equilibrium

$$PCl_5(g) = PCl_3(g) + Cl_2(g)$$

has been measured and is shown below, in table and graphical form. Reading the plot carefully, we see that $K_p = 10$ at $1/T = 1.73\times10^{-3}\ K^{-1}$ and $K_p = 0.1$ for $1/T = 2.15\times10^{-3}\ K^{-1}$.

The $PCl_5 = PCl_3 + Cl_2$ *Equilibrium*

T (°K)	α	K_P (atm)
439	0.124	0.0269
443	0.196	0.0329
462	0.244	0.0633
485	0.431	0.245
534	0.745	1.99
556	0.857	4.96
574	0.916	9.35
613	0.975	40.4



(a) Derive an equation that will provide a determination of the $\Delta \boldsymbol{H}_{rxn}°$ for this chemical reaction in the temperature range shown.
[HINT: Start with the definition of ***G***. Also take a hint from the plot that (1/T) is a convenient explicit factor to include in your derivation. Assume that each gas behaves ideally, so that K_p can be written in pressures rather than in fugacities. Later in the course, we will consider 'true' equilibrium constants in terms of fugacities.]

Derivation here:

(b) Apply your equation to the data to find the numerical value of $\Delta \boldsymbol{H}_{\text{rxn}}°$. Here, ° means the standard state, 1 atm, of course.

Calculations here:

8. Consider the following systems. In each case calculate the pressure which must be applied to $\mathcal{B}$ in order that equilibrium be established between $\mathcal{A}$ and $\mathcal{B}$ at the given temperature.

$\mathcal{A}$	$\mathcal{B}$	Calculations for *p*, atm

(a)

rhombic sulfur density 1.5×10^3 g L^{-1} $\Delta \boldsymbol{G}^\circ_f = 0$ *p* atm	monoclinic sulfur density 1.2×10^3 g L^{-1} $\Delta \boldsymbol{G}^\circ_f = 0.023$ kcal mol^{-1} *p* atm	

(b) ***This Pd membrane allows only H_2 to pass***

↓

H_2 (g) 1 atm	$N_2(g) + H_2(g)$ $4N_2 : 1H_2$ mixture *p* atm	

(c) ***This semi-permeable membrane allows only H_2O to pass***

↓

pure liquid H_2O 1 atm vapor pressure p_w*	0.1 mole percent solution of sucrose in H_2O vapor pressure according to Raoult's law *p* atm	