Name:____

First three letters of last name

Chemistry 342

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

$(p + n^2 a/V^2)(V - nb) = nRT$

For water: $\Delta_{fus}\boldsymbol{H} = 6003\ \mathrm{J\ mol^{-1}}$ or $80\ \mathrm{cal\ g^{-1}}$; heat capacities liquid, solid: 1 and 0.5 $\mathrm{cal\ g^{-1}\ K^{-1}}$

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

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

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

$[T_f/T_i]^{C_V/R} = [V_i/V_f]$ 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: $\ln \gamma_{\pm} = -z_+ z_- I^{1/2} (e^2/10\varepsilon k_B T)^{3/2} \{2\pi\rho N_{Avog}\}^{1/2}$

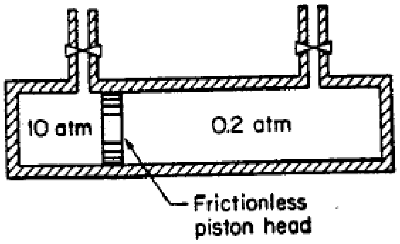
for water at 25°C as the solvent, $\ln \gamma_{\pm} = -z_+ z_- I^{1/2} (1.17223)$

ionic strength $\equiv \frac{1}{2}\sum m_i z_i^2$

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

	score
1	
2	
3	
4	
5	
6	
7	
8	
9	
10	

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.

Answer: ΔU_{tot} =

Answer: p_f = left side =, p_f right side =

Answer: T_f left side =, T_f right side =

Answer: ΔH_{tot} =

Answer: ΔS =

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, $\Delta \boldsymbol{U}$, and $\Delta \boldsymbol{H}$ in cal for steps A and B, and for the cycle.

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

State	p, atm	T, K	V, L
1			
2			
3			

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

	A	B	C	overall
q				
w				

Δ***U***				
Δ***H***				

Write your final numerical answers in the tables below:

Changes	*q*	*w*	Δ***U***	Δ***H***
step A				
step B				
step C				
overall				

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

q
ΔU
ΔH
ΔS
ΔG

ΔA

Write the numerical answers and units in this table:

w	q	ΔU	ΔH	ΔS	ΔG	ΔA

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 g^{-1} K^{-1}

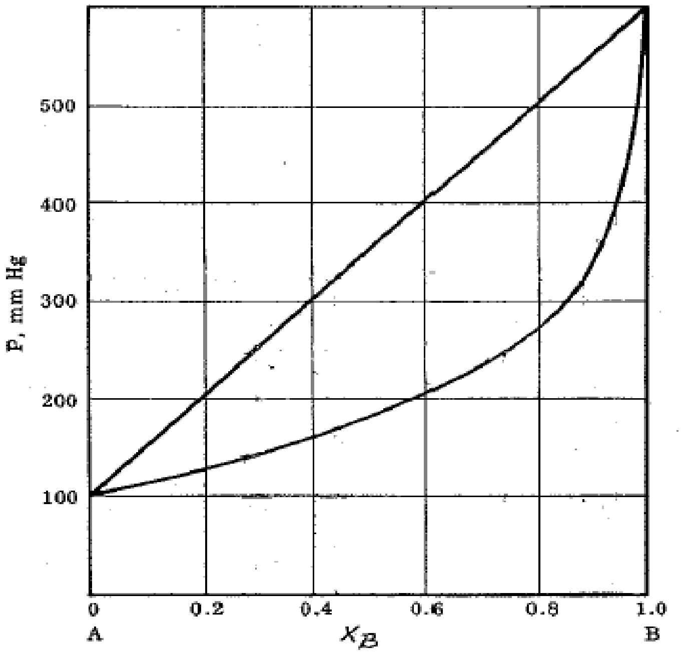
Answer	

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.

Answers, mm Hg	A:	B:

(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:



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.

Answers, mole % A	liquid:	vapor:

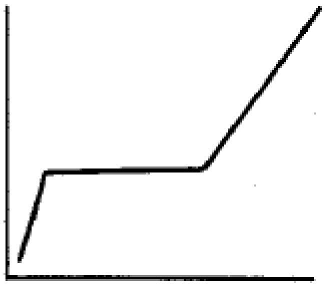
In a second experiment, 2 moles of a liquid solution of $x_A = 0.4$ is evaporated in an open container at a constant temperature of 80°C until the total vapor pressure falls to 80% of its initial value. **What is the final liquid composition**, and roughly **how many moles of liquid remain** after the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

Answers, liquid:	x_A=	moles=

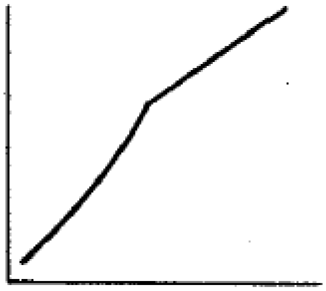
(c) Two moles of a 50 mole % solution of propyl alcohol in ethyl alcohol is distilled until the normal boiling point of the solution rises to 90°C. The condensate is allowed to accumulate in a cooled receiver and, after being mixed to insure uniformity, its vapor pressure is found to be 1,066 mm Hg when 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.

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

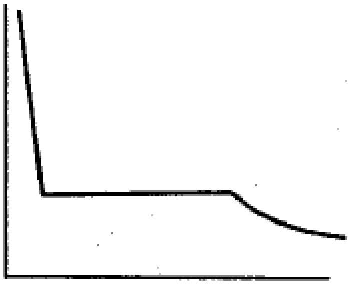
6. It takes a three dimensional plot of p versus V versus T to show the complete behavior of a substance. If one of these three variables is kept constant, a plot of the other two is possible. One thus has isotherms (p versus V or V versus p, with T constant), *isobars* (T versus V or V versus T, with 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.**



(a)



(b)



(c)

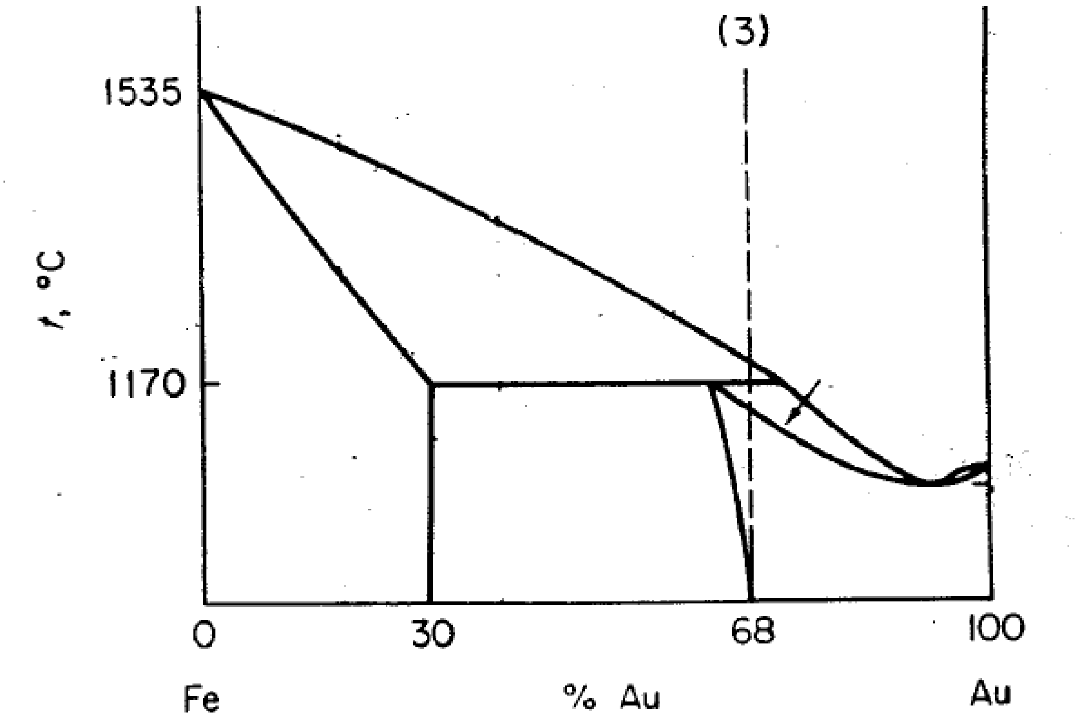
Write the explanation for your choices here:

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 ΔU and ΔH of metal in kJ. (Assume the compression occurs at a constant pressure of 10^5 atm.)

Numerical Answer: ΔU =

Numerical Answer: ΔH =

(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.



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										
$\Delta \boldsymbol{U}$										
$\Delta \boldsymbol{H}$										
$\Delta \boldsymbol{S}$										
$\Delta \boldsymbol{G}$										
q										
W										

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)		
(b)		
(c)		
(d)		
(e)		
(f)		
(g)		
(h)		
(i)		
(j)		

9. These are about one-component phase diagrams:

(a) Starting from $dG = Vdp - SdT$ **derive the Clapeyron equation** for a pure substance in phase α and phase β coexisting in equilibrium.

(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.**

Answer: .

(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.**

(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.

Answer: melting point =

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	
mole fraction of A in the liquid solution	
activity of B in the liquid solution	
actual vapor pressure of B above the solution	
mole fraction of A in the vapor	
vapor pressure of pure liquid B	

Place your calculations and reasoning in this space:

(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)

Answer: S =

(2)

Answer: S =

(3)

Answer: S =