Name ______________________

Please put answers within boxes provided.

Chemistry 342

December 8, 1998

Final Exam (3 hrs.)

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

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

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

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

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

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

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

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

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), <u>provided</u> 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 <u>maximum</u> 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 $\mathrm{mol^{-1}}$. Assume that all diatomic gases have a constant heat capacity at constant pressure of 7.0 cal $\mathrm{mol^{-1}\ K^{-1}}$.

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

(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. 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.

answer space continued on next page

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

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

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

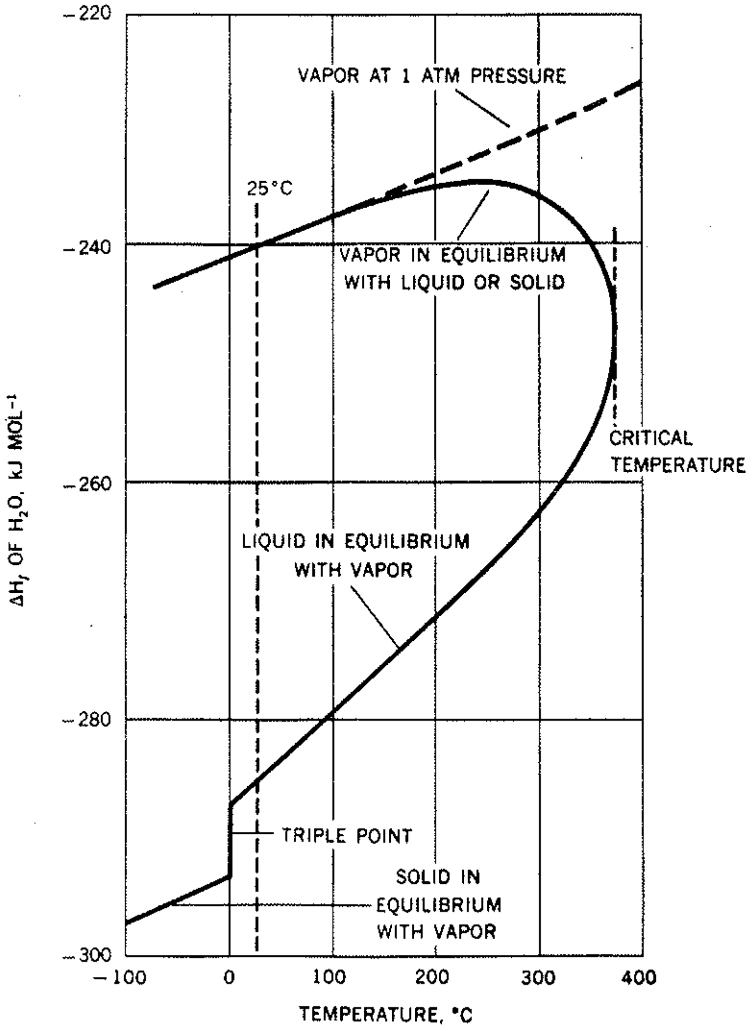
$N_2O_4(g)$	98.296 kJ mol^{-1}
$NO_2(g)$	51.845 kJ mol^{-1}

(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?

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

(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.

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:



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

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

(b) **Calculate** ΔH, ΔS , ΔG for the 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. 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 $30.54 + 10.29\times10^{-3}T$ J K^{-1} mol^{-1}.

ΔH

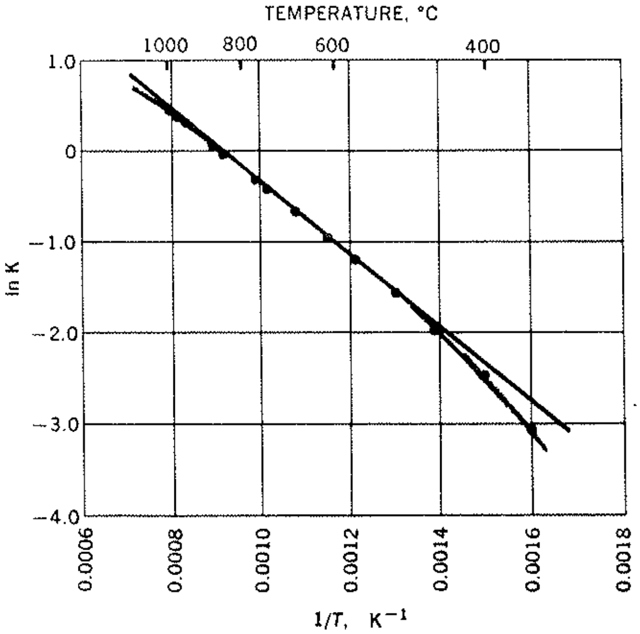
answer space continued on next page

ΔS

ΔG

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

(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.

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:

W:

ΔU:

q:

ΔH:

ΔS:

ΔA:

ΔG:

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
normal melting point	-210.01°C
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
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 ↴

Temperature, K →

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

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

8. 10 min. For the reaction 2NOBr = 2 NO + 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.

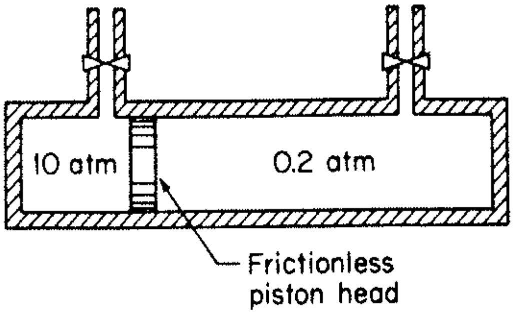
9. 15 min. Consider the following systems. In each one **calculate** the pressure p which must be applied in order that equilibrium be established between A and B at the given temperature.

A	B	Calculations here, p atm
rhombic sulfur	monoclinic sulfur	
p atm	p atm	
$\Delta_f G^\ominus = 0$	$\Delta_f G^\ominus = 0.023$ kcal mol^{-1}	
densities:		
1.5 g cm^{-3}	1.2 g cm^{-3}	

H_2 1 atm	Pd membrane allows only H_2 to pass	$H_2 + N_2$ mixture is $4N_2 : 1H_2$ p atm

pure liquid water 1 atm 298 K vapor pressure p_{H2O}*	semi-permeable membrane	0.1 mole% solution sucrose in H_2O p atm 298 K vapor pressure according to Raoult's law

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 ΔU, ΔH, and ΔS for the overall process.

ΔU:

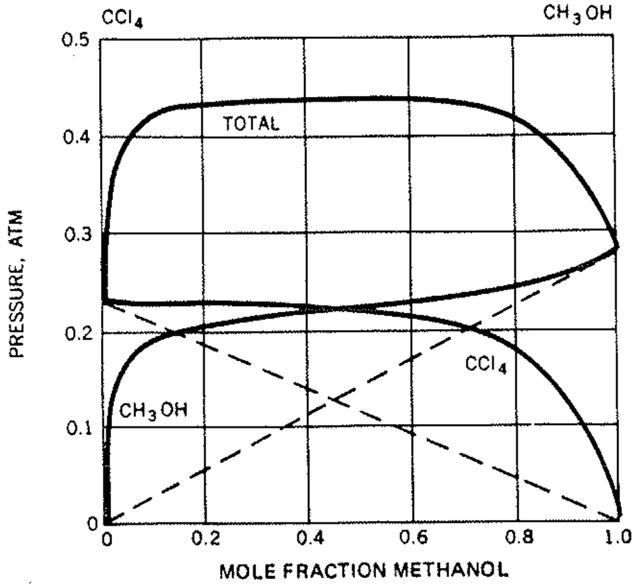
T_f:

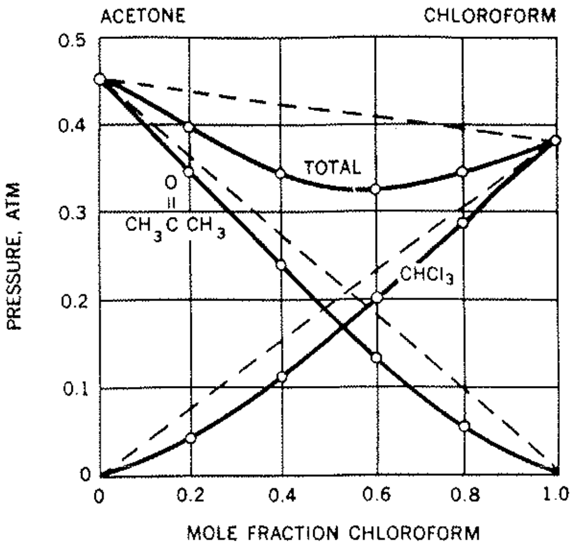
p_f:

ΔH:

ΔS:

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?

(b) What is the vapor pressure of pure liquid CCl_4?

(c) What is the Henry's law constant for $CHCl_3$ in acetone solution?

(d) What is the Henry's law constant for acetone in $CHCl_3$ solution?

(e) What is the partial vapor pressure of CH_3OH in a solution with $x_{CH3OH} = 0.70$?

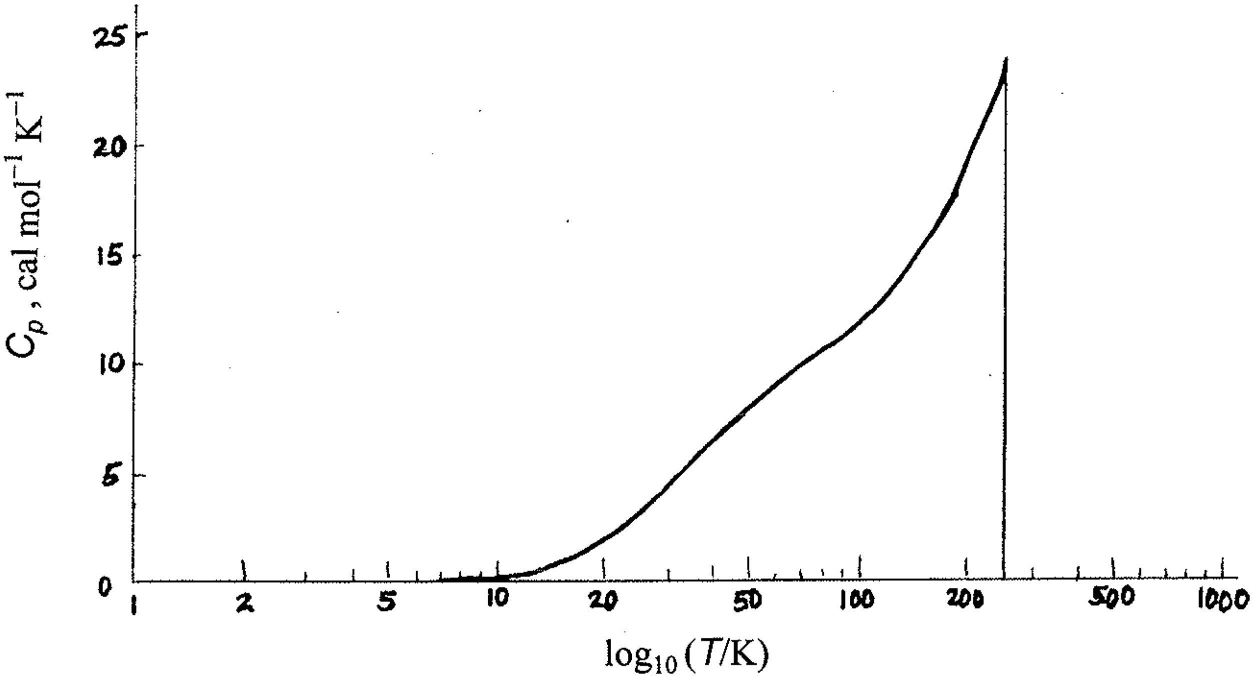
(f) What is the total vapor pressure of a solution of CH_3OH in CCl_4 with $x_{CCl4} = 0.15$?

(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 $x_{CCl4} = 0.15$?

(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?

(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?

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

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

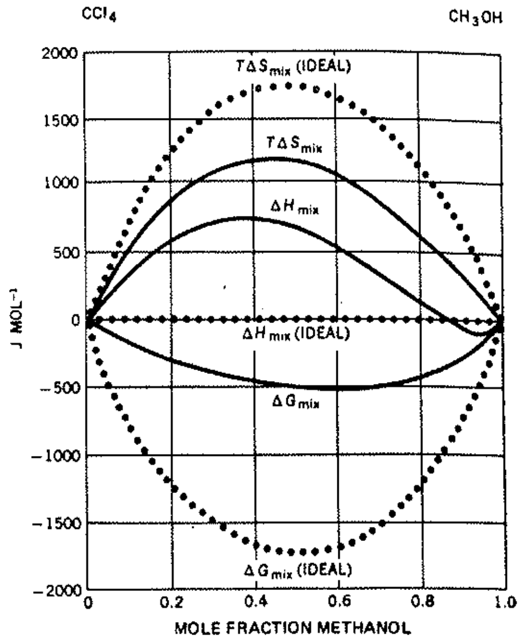
determine ΔH, ΔS, ΔG.

ΔH

ΔS

ΔG

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

$\Delta_{mix}G =$

$T\,\Delta_{mix}S =$

In two sentences **explain** the deviations of the experimental values (solid curves) from the dotted ones in this specific system.: