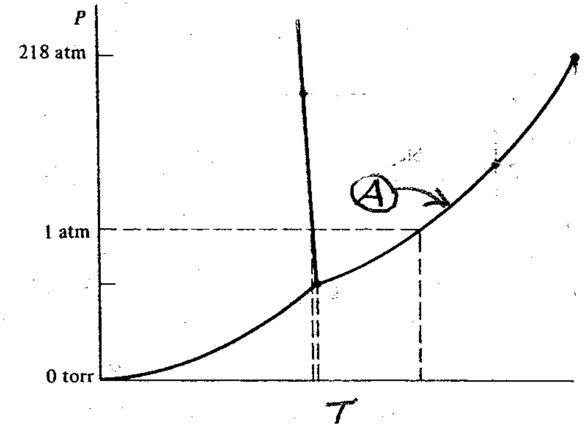
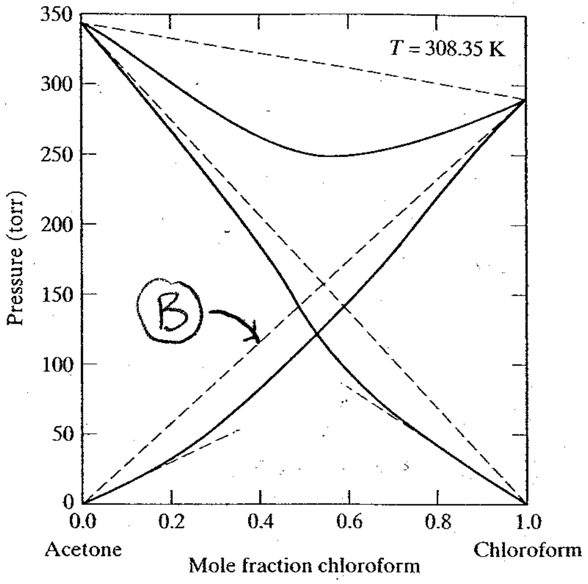
due Wed. April 13

Chemistry 342

Problem Set 9

1. In the figures on the following page, **first *write an equation* that mathematically describes the set of points that constitute each straight or curved line that is labeled with a circled letter. Then, *define unambiguously* every symbol you have used in the equation you wrote.** Examples are shown below to clarify what is required in your answers. Do not use approximate equations, unless they apply to the system in the figure.





Answers:

A : $dp/dT = (1/T)(\boldsymbol{H}_{vapor} - \boldsymbol{H}_{liquid})/(V_{vapor} - V_{liquid})$

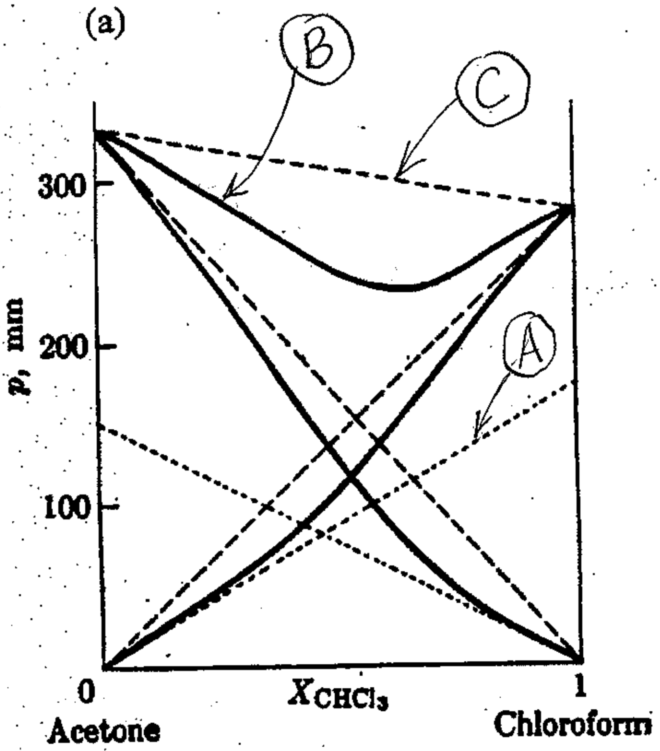
$\quad = (1/T)\Delta \boldsymbol{H}_{vaporization}/(V_{vapor} - V_{liquid})$

where p is the equilibrium vapor pressure of the liquid substance at temperature T, and $\boldsymbol{H}_{vapor}$ and $\boldsymbol{H}_{liquid}$ are the molar enthalpies of the substance in the vapor and the liquid phases, respectively, at temperature T; and V_{vapor} and V_{liquid} are the molar volumes of the vapor and liquid forms of the substance, respectively, at temperature T.

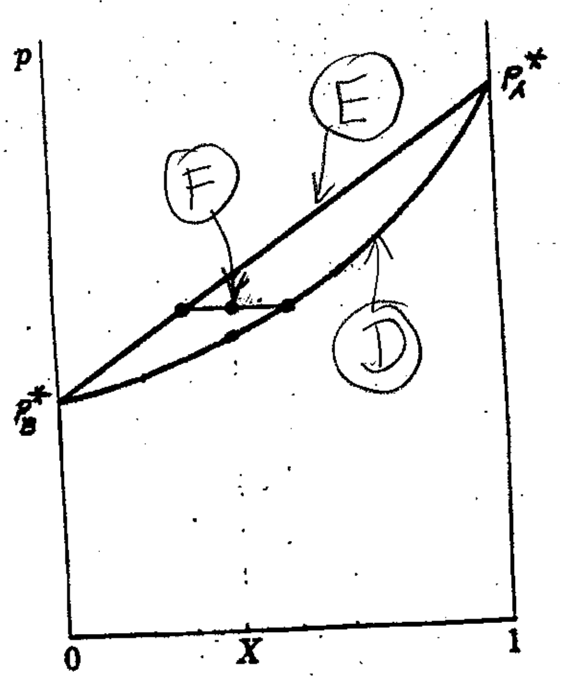
B : $p = x_{chloroform}\, p^*_{chloroform}$

where, at temperature T = 308.35 K, $p^*_{chloroform}$ is the equilibrium vapor pressure of pure liquid chloroform; p would have been the partial pressure of chloroform in the vapor in equilibrium with the liquid solution of chloroform and acetone, in which $x_{chloroform}$ is the mole fraction of chloroform in the liquid solution at temperature T = 308.35 K, if the liquid solution had been an ideal solution.

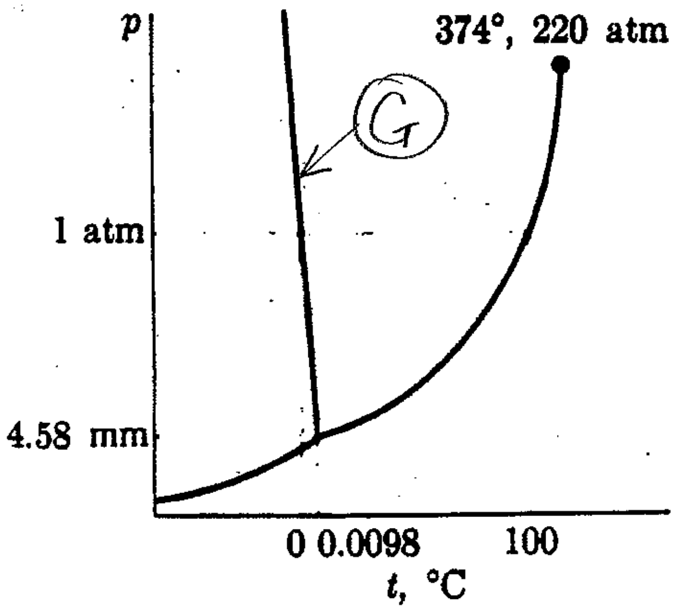
(a)


B
C
A
300
200
100
p, mm
0
X_CHCl3
1
Acetone
Chloroform

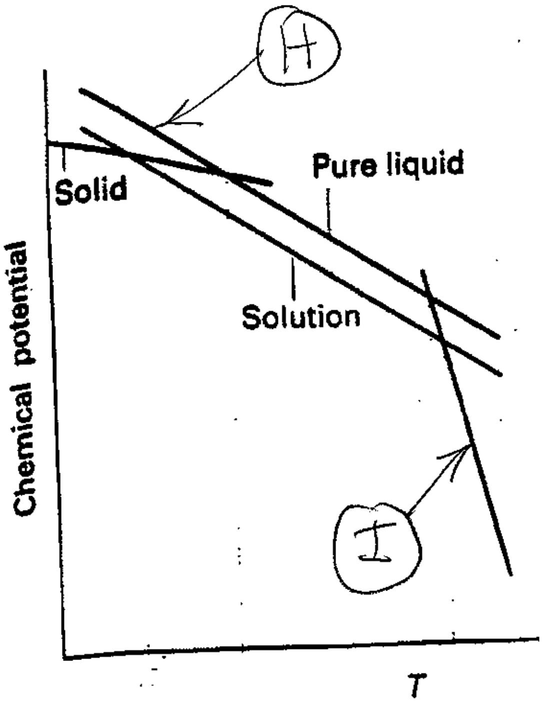
(b)


p
p_A*
E
F
D
p_B*
0
X
1

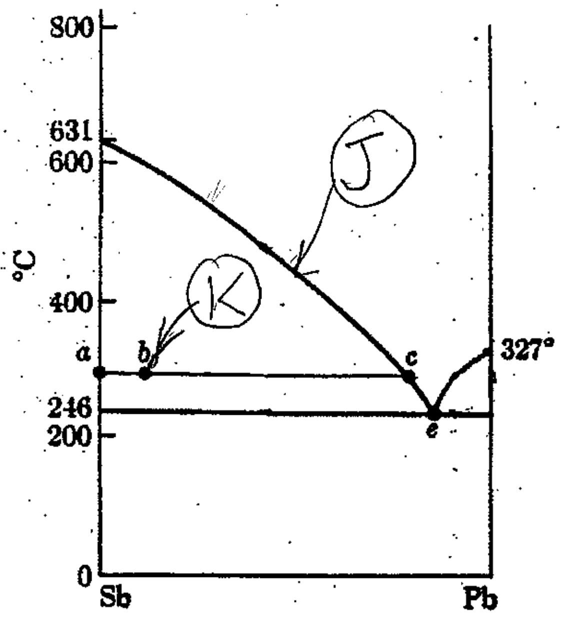
(c)


p
374°, 220 atm
G
1 atm
4.58 mm
0 0.0098
100
t, °C

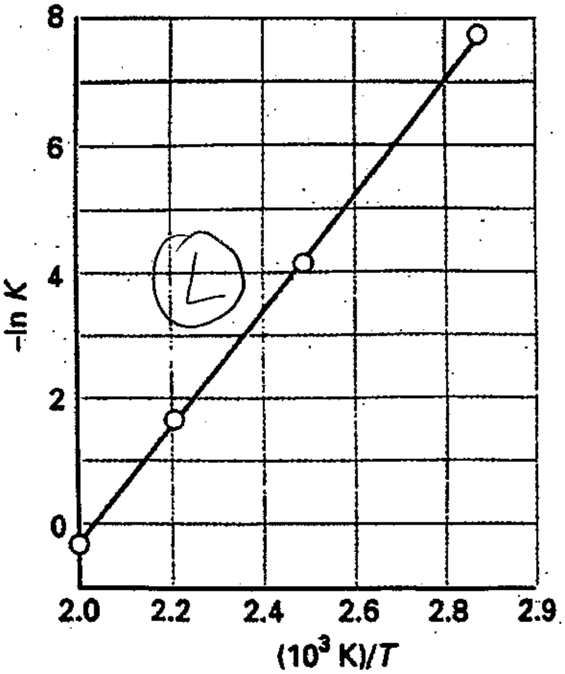
(d)


H
Solid
Pure liquid
Solution
Chemical potential
I
T

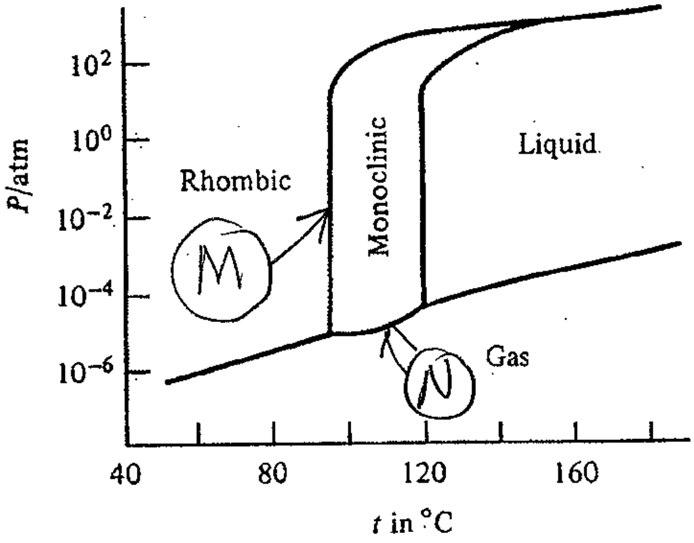
(e)



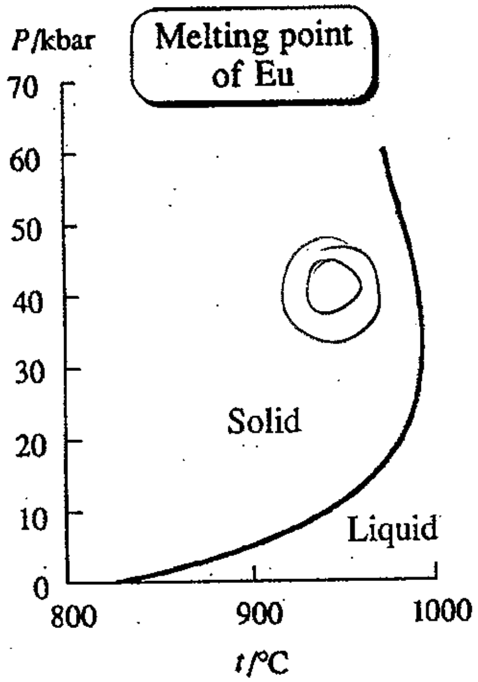
(f)



(g)

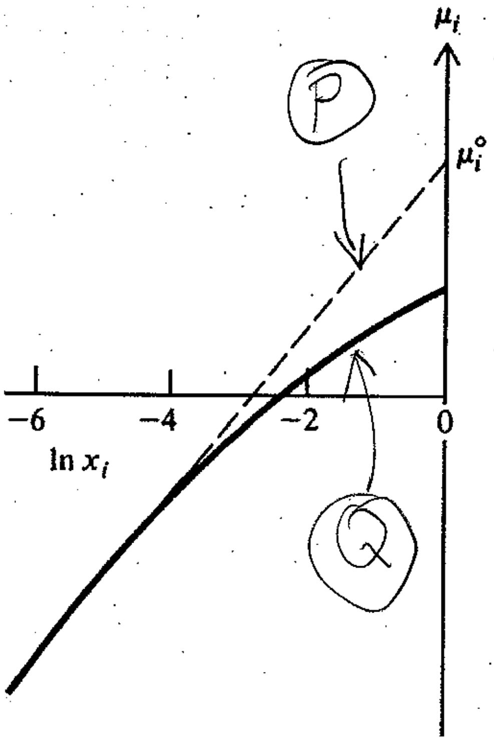


(h)



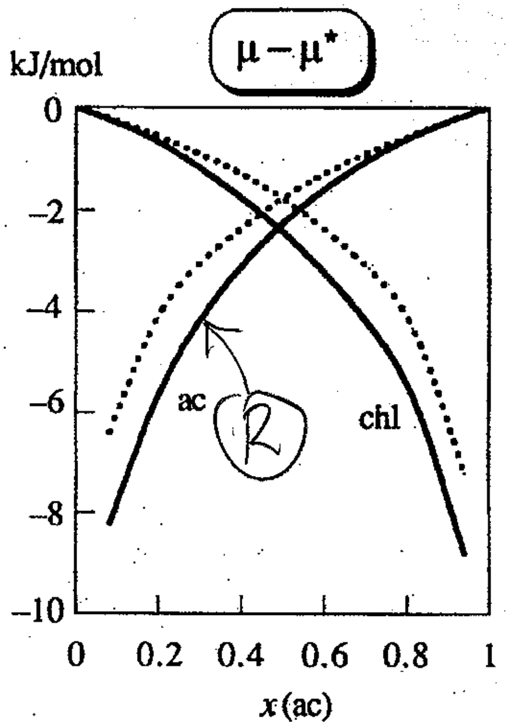
Part of the sulfur phase diagram. The vertical scale is logarithmic.

(i) for a typical non-electrolyte solute



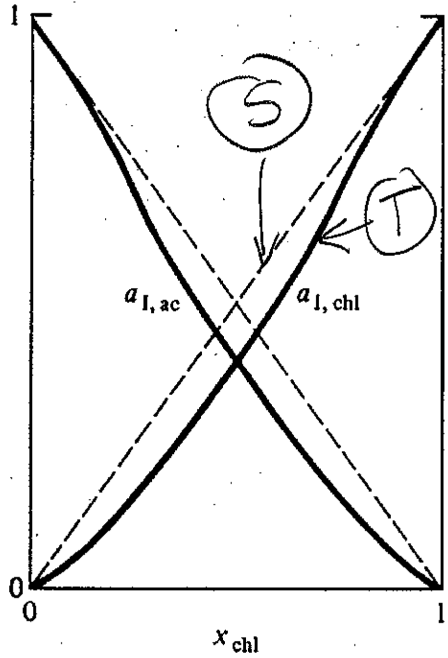
for a typical nonelectrolyte solute.

(j) acetone-chloroform solutions at 35° C.

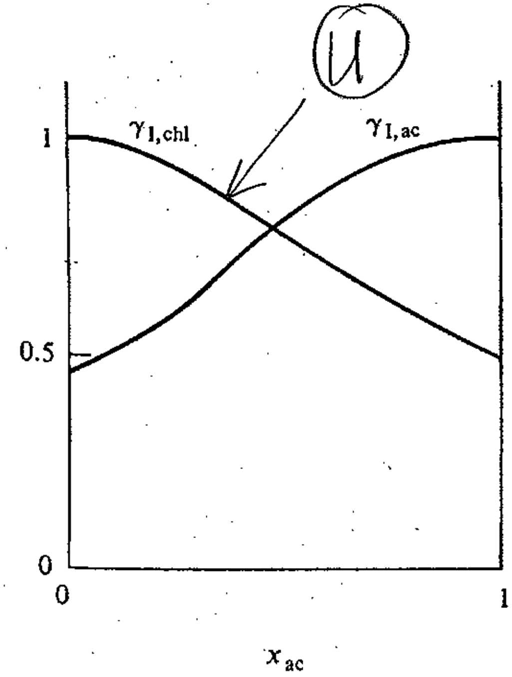


acetone–chloroform solutions at 35°C and 1 atm.

(k)



(l)

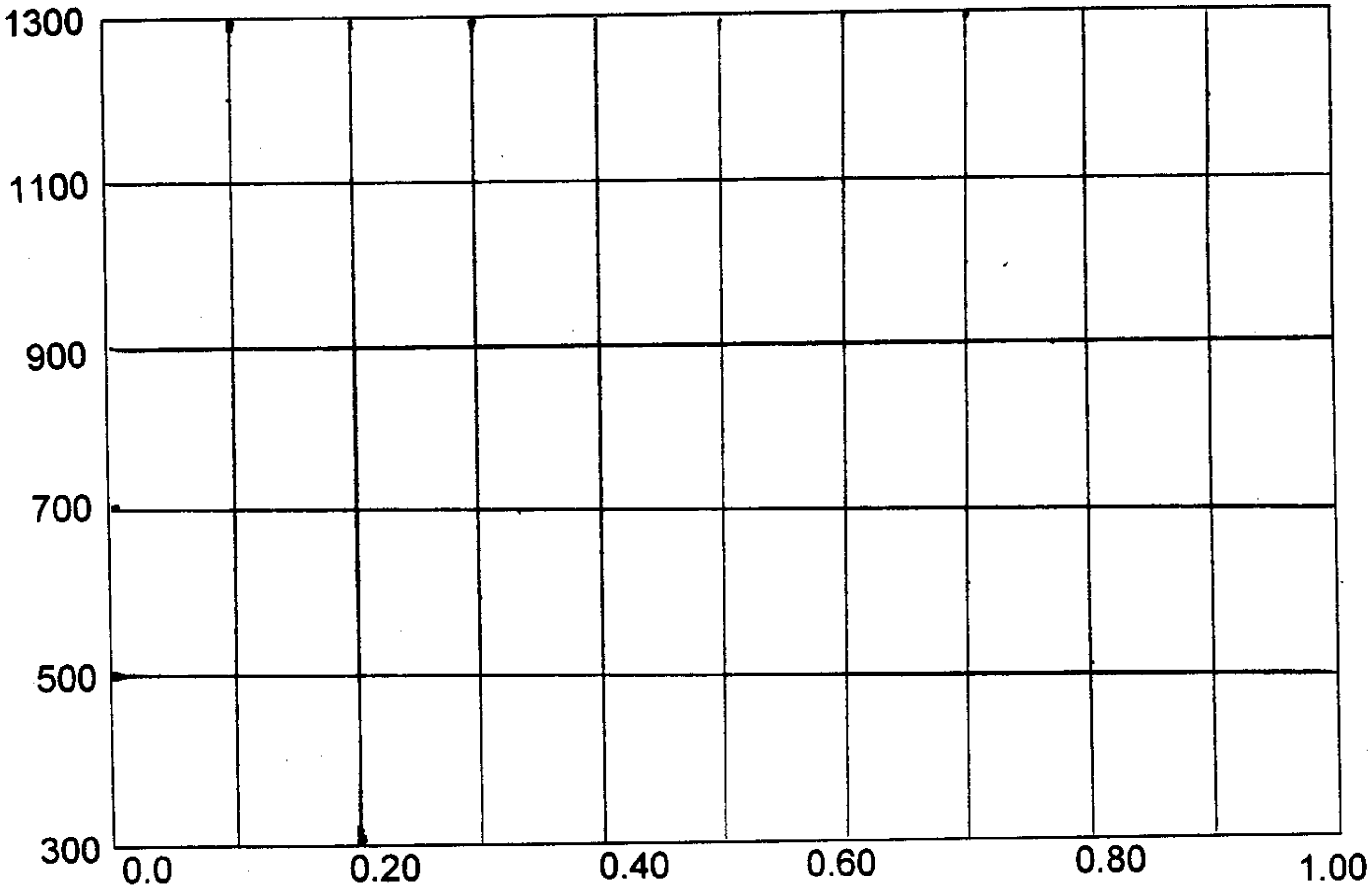


acetone-chloroform solutions at 35°C

2. The table below gives the break and halt (plateau in the cooling curve) temperatures found in the cooling curves of two metals A and B. Construct a phase diagram consistent with the data of these curves. Label the regions of the diagram, stating what phases and substances are present. Give the probable formula of any compounds that form

x_B	break, t °C	first halt, t °C	second halt, t °C
0.0		1100	
0.10	1060	700	
0.20	1000	700	
0.30	940	700	400
0.40	850	700	400
0.50	750	700	400
0.60	670	400	
0.70	550	400	
0.80		400	
0.90	450	400	
1.00		500	

For uniformity, use the graph below



3. If a small 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.

4. 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.

5. 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.

6 and 7. Nitrogen dioxide is an orange gas known to achieve equilibrium with its colorless dimer in a reaction as follows:

$$2NO_2(g) \rightarrow N_2O_4(g)$$

You may use data in Appendix A of your textbook for this problem. You may assume that Dalton's law of partial pressures holds for this mixture.

Both gases are non-ideal. First (Part I, call it Prob. **6**) let us assume that each is an ideal gas, do the problem, then (Part II, call it Prob. **7**) do the problem again with the following equation of state

$$pV = RT + B_1(T)p + B_2(T)\,p^2/RT$$

where $B_1(T) = b - a/RT$ and $B_2(T) = b^2$.

For $NO_2(g)$ $a = 5.354$ L^2 bar mol^{-2}, $b = 0.04424$ L mol^{-1}, for $N_2O_4(g)$ $a = 6.550$ L^2 bar mol^{-2}, $b = 0.05636$ L mol^{-1}. The heat capacities are

$$C_p = 6.37 + 1.01\times10^{-2}T - 3.405\times10^{-6}T^2 \quad \text{cal mol}^{-1}\text{ K}^{-1} \text{ for } NO_2(g)$$

$$C_p = 10.719 + 2.86\times10^{-2}T - 8.726\times10^{-6}T^2 \quad \text{cal mol}^{-1}\text{ K}^{-1} \text{ for } N_2O_4(g)$$

The questions are as follows:

(a) Determine ΔH^o for the reaction at 298.15 K and 1 bar of pressure. Determine $\Delta\mu^o$ for the reaction at 298.15 K

(b) Calculate f/p where f is fugacity for $NO_2(g)$ at 298.15 K for $p = 1$ to 400 bar. Do the same for $N_2O_4(g)$. Plot the results vs. p.

(c) Obtain the values K_p and K_c for the reaction at 298.15 K.

(d) Obtain ΔH^o for the reaction as a function of T from 298.15 K to 1000 K.

(e) Obtain expressions for K_p and K_c for the reaction as a function of T. Make a plot of K_p and K_c versus $(1/T)$ from 298.15 K to 1000 K.

(f) One mole of $NO_2(g)$ is initially placed in a sealed rigid container having a volume equal to 2.0 L. Obtain an expression for the equilibrium concentration of $N_2O_4(g)$ as a function of temperature. Make a semi-log plot of this concentration vs. T from 298.15 K to 1000 K.

(g) For the situation described in (f), obtain the mole fraction of $N_2O_4(g)$ present at equilibrium as a function of total pressure over the range $p = 1$ to 400 bar. Make a plot of this mole fraction vs. p for $p = 1$ to 400 bar.