PROBLEM SET 5

1) a) Find the equilibrium constant at 298 K for the reaction PCI_5 \rightarrow PCI_3 + CI_{2(g)}

b) Find the total pressure if $0.001 \text{ mol of } PCI_5$ is placed in a vessel with a volume of 20 L at 298 K and allowed to equilibrate. Assume ideal gas behavior.

- 2) a) Find ΔH° , ΔG° and K_{p} at 298 K for $I_{2(g)} \rightarrow 2I_{(g)}$
 - b) Assume ΔH^{o} constant find temperature at which $K_{p}=1$
 - c) Assume ΔH^{o} constant find K_{p} at 1000 K.
 - d) Assume ΔCp constant find K_p at 1000 K.

3) A certain gas mixture held at 395 K has the following initial pressures. $P(Cl_2) = 351.4$ torr, $P(COCl_2) = 0$. At equilibrium total pressure is 439.5 torr is held constant. Find K at 395 K for

 $\text{CO} + \text{Cl}_2 \rightarrow \text{COCl}_2$

4) For the ideal gas reaction $PCI_5 \rightarrow PCI_3 + CI_{2(g)}$

State whether equilibrium shifts to the right or left when each of the following changes is made in an equilibrium mixture at 25 $^{\circ}$ C

- a) T is decreased at constant P
- b) V is decreased at constant T
- c) Some PC15 is removed at constant T and V
- d) $He_{(g)}$ is added at constant T and V
- e) He_(g) is added at constant T and P

5) For 2 CO $_{(g)}$ + O_{2(g)} \rightarrow 2 CO_{2(g)} assume ideal gas behavior and ΔG^{o}_{298} = -514.382 kj/mol and ΔH^{o}_{T} (kj/mol) = -565.968 + 0.0015(T-298) + 2.85*10⁻⁶(T²-298²)+1448((1/T)-(1/298)) Find an expression for lnK_p(T) and calculate K_p at 1000 K for this reaction.

6) Suppose 1.0 mol of CO₂ and 1.0 mol of COF₂ are placed in a very big vessel at 25°C and a catalyst for the gas phase reaction $2 \text{ COF}_2 \leftrightarrow \text{CO}_2 + \text{CF}_4$ is added. Find the equilibrium amounts. $\Delta \text{G}^{\circ}_{298} = -35 \text{ kj/mol}$

7) For the ideal gas reaction $N_2 + 3H_2 \leftrightarrow 2$ NH₃ suppose 1 mol of N_2 and 3 mol of H₂ react at constant T and P, no other gases are present initially. Let x be the number of moles of N_2 that have reacted when equilibrium is reached. (x = ϵ_{eq})

Show that, X=1-[1-s/(s+4)]^{1/2}, s= $(27 \text{ K}_p)^{1/2} \text{ P/P}^*$

8) Nitrogen trioxide dissociates according to the reaction

$$N_2O_{3(g)} \leftrightarrow NO_{2(g)} + NO_{(g)}$$

When one mole of $N_2O_{3(g)}$ is held at 25 °C and 1 bar total pressure until equilibrium is reached, the extent of reaction is 0.30. What is $\Delta_r G^o$ for this reaction at 25 °C?

9) Calculate the molar Gibbs energy of butane isomers for extents of reaction of 0.2, 0.4, 0.6 and 0.8 for the reaction **n-butane = isobutene** at 1000 K and 1 bar.

At 1000 K $\Delta_r G^{\circ}(n-butane)=270 \text{ kJ/mol}, \Delta_r G^{\circ}(n-butane)=276.6 \text{ kJ/mol}$

Make a plot and show that the minimum corresponds to the equilibrium extent of reaction.

10) At 250 °C, PCl₅ is 80 % dissociated at a pressure of 1.013 bar, and so K=1.80. What is the extent of reaction at equilibrium after sufficient nitrogen has been added at constant pressure to produce a nitrogen partial pressure of 0.9 bar? The total pressure is maintained at 1 bar.