1. (6 pts) What is the equilibrium expression for the following reaction?

$S_{8(s)} + 2\ CH_{4(g)} \Leftrightarrow 2\ CS_{2(l)} + C_2H_{2(g)}$

$K_P = \mathbf{(P_{C2H2})/(P_{CH4})^2}$

2. (6 pts) Consider the following:

$I_{2(g)} \Leftrightarrow 2\ I_{(g)}$ $K_P = 6.8$ atm at 1200 K

Calculate ΔG° for the reaction.

$\Delta G^\circ = -RTlnK = -(8.3145\ J/molK)(1200\ K)\cdot ln(6.8) = -19000\ J/mol$

3. (6 pts) Again, let's look at the reaction $I_{2(g)} \Leftrightarrow 2\ I_{(g)}$. Circle the correct concluding word(s) to each statement.

a. The reaction is enthalpically _____.	~~favorable~~	**unfavorable**
b. The reaction is entropically _____.	**favorable**	~~unfavorable~~
c. The reaction will be spontaneous _____.	~~always~~ **at high temp.**	~~never~~ ~~at low temp.~~

4. (6 pts) Hydrogen and iodine react as follows:

$H_{2(g)} + I_2 \Leftrightarrow 2\ HI_{(g)}$ $K_P = 54$ at 298 K

Which way will the reaction proceed when the partial pressures of H_2 and I_2 are 0.50 atm, and the partial pressure of HI is 4.00 atm? Show your reasoning explicitly.

$Q = (4.00\ atm)^2/(0.5\ atm)(0.5\ atm) = 64$

Q > K: Reaction runs to the left, towards reactants

5. (6 pts) Consider the following equilibrium:

$3\ KAlSi_3O_{8(s)} + 12\ H_2O_{(l)} + 2\ H^+_{(aq)} \Leftrightarrow KAl_2(OH)_2[Si_3AlO_{10}]_{(s)} + 2\ K^+_{(aq)} + 6\ H_4SiO_{4(aq)}$

In <u>one</u> sentence, explain the role this reaction plays in soil formation.

The weathering of rocks leads to the formation of clays and the release of nutrient cations to the soil.

6. (6 pts) In <u>one</u> sentence, why does $Al^{3+}_{(aq)}$ have a <u>negative</u> molar entropy (S°)?

The negative molar entropy reflects the ordering of water molecules around the aluminum cation.

7. (16 pts) Nitrogen reacts with water as follows:

$N_{2(g)} + 2\ H_2O_{(g)} \Leftrightarrow 2\ NO_{(g)} + 2\ H_{2(g)}$ $K_P = 2.0 \times 10^{-8}$ atm at 800 K.

If you start with 2.0 atm of N_2 and H_2O, predict the final partial pressures of all reactants and products at equilibrium.

	P_{N2}	P_{H2O}	P_{NO}	P_{H2}
I	**2**	**2**	**0**	**0**
C	**-x**	**-2x**	**2x**	**2x**
E	**2-x**	**2-2x**	**2x**	**2x**
Actual	**2.0 atm**	**2.0 atm**	**0.02 atm**	**0.02 atm**

$K_P = (2x)^2(2x)^2/(2-x)(2-2x)^2 \approx (2x)^4/8$ if we assume 2x << 2.

$16x^4/8 = 2 \times 10^{-8}$

x = 0.01 atm

8. (10 pts) The solubility product for $PbBr_2$ is 6.6×10^{-6} M^3.

a. Write the balanced reaction that has the equilibrium constant given above.

$PbBr_{2(s)} \Leftrightarrow Pb^{2+}_{(aq)} + 2\ Br^-_{(aq)}$

b. What is the concentration of Pb^{2+} in a saturated solution of $PbBr_2$.

$K_{sp} = [Pb^{2+}][Br^-]^2 = 4s^3 = 6.6 \times 10^{-6}\ M^3$
$[Pb^{2+}] = s = 0.012\ M$

9. (12 pts) The following reaction describes the production of rust (Fe_2O_3) from metallic iron when exposed to oxygen.

$4\ Fe_{(s)} + 3\ O_{2(g)} \Leftrightarrow 2\ Fe_2O_{3(s)}$

Predict whether the thermodynamic constants listed below are **positive**, **negative** or **about zero**, and give a one sentence explanation for each of your predictions.

ΔG_{rxn}° is **Negative. Rusting of iron is a spontaneous process.**

ΔS_{rxn}° is **Negative. Seven moles go to two moles in this reaction.**

ΔH_{rxn}° is **Negative. Because the reaction is spontaneous, yet is entropically unfavorable, we know it must be favorable exothermically.**

10. (14 pts) Methanol (CH_3OH) is a liquid that boils at 65˚C and 1.00 atm pressure. The enthalpy of vaporization of methanol (ΔH_{vap}°) is 37.8 $^{kJ}/_{mol}$.

a. What is the entropy of vaporization (ΔS_{vap}°) at 65˚C?

ΔG_{vap}° = 0 at the boiling point.
$\Delta S_{vap}^{\circ} = -(\Delta G_{vap}^{\circ} - \Delta H_{vap}^{\circ})/T$ = (37800 J/mol)/338 K = 112 J/molK

b. Calculate the equilibrium constant for the vaporization of methanol at 25˚C.

Two ways to do this:

i. **$\Delta G_{vap}^{\circ} = \Delta H_{vap}^{\circ} - T\Delta S_{vap}^{\circ}$ @298**
= (37800 J/mol)-(298 K)(112 J/molK) = +4400 J/mol
K = exp(-4400 J/mol/(8.3 J/molK)(298K)) = 0.16

ii. $\ln\left(\frac{K_1}{K_2}\right) = -\frac{\Delta H^o}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$ **note that K_{338} = 1, and plug and chug to get the same answer.**

11. (12 pts) Consider a syringe that initially contains 10.0 mL of pure $NO_{2(g)}$ with an external atmospheric pressure of 1.00 atm. Upon going to equilibrium with $N_2O_{4(g)}$ the syringe volume drops to 6.0 mL. Given that result, what is the equilibrium constant (K_P) for the following reaction?

$$2\ NO_{2(g)} \Leftrightarrow N_2O_{4(g)} \quad K_P = ?$$

(Note that you do not need temperature in this problem, but if you really want, you can assume 300 K).

Initially, $V_{NO2} = 10.0$ mL
Finally, $V_{NO2} + V_{N2O4} = 6.0$ mL

By stoichiometry, $V_{NO2} + 2\ V_{N2O4} = 10.0$ mL

Solving for V_{N2O4}:

$(6.0\ mL - V_{N2O4}) + 2\ V_{N2O4} = 10.0$ mL
$V_{N2O4} = 4.0$ mL, therefore
$V_{NO2} = 2.0$ mL

$P_{N2O4} = (4.0\ mL/6.0\ mL)(1.00\ atm) = 0.67$ atm
$P_{NO2} = 0.33$ atm

$K = (.67\ atm)/(0.33\ atm)^2 = 6.0$