# Worksheet 7

February 15th, 2022

Collaborations are encouraged and students must report all collaborators on each assignment. All external sources (websites, books) must be cited. An *extra credit* (*EC*) problem will be available per assignment. Please submit a completed homework on-time to receive *EC* and no partial *EC* (all parts must be correct) will be given out. Additional problems are listed at the end of each assignment. This week's assignment is due *Tuesday, Feb 22nd at 10:00am.*

1. (4 pts) **Entropy** The following is a molecular visulization of a system undergoing a spontaneous change. Determine from the picture whether entropy increases or decreases during the process. Account for the spontaneity of the process in terms of the entropy changes in the system and the surroundings. The therometers show the temperature of the system.
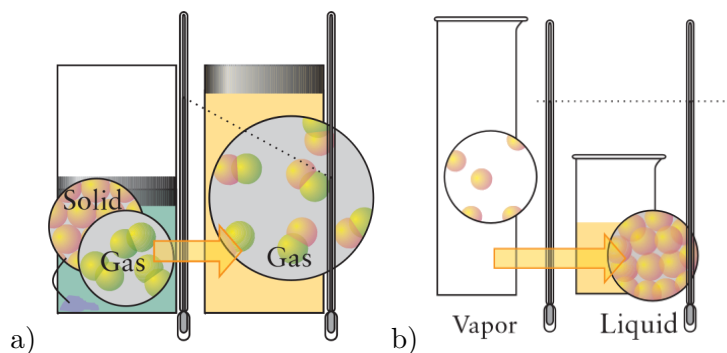
2. (2 pts) **Equilibrium and Law of Mass Action** Write the equilibrium constant expression for the following reaction:

$$NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$$

At 100°C, the equilibrium constant is 0.1513. What is the equilibrium partial pressure of $NH_3(g)$ if the partial pressure of $H_2S(g)$ is 4.57 atm. Report to 3 significant figures.

3. (6 pts) **Relating Free Energy and Equilibrium Constant** Supposed a reaction is given by:

$$aA + bB \rightleftharpoons cC + dD$$
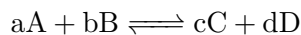
where a, b, ... are the coefficients and A, B, ..., C, D are the reactants and products.

(a) Derive the equation that relates the free energy of reaction (ΔG_r) and the equilibrium constant K as seen in lecture. Define all variables. *Hint:* $G(P) = G^\circ + nRT \ln \frac{P}{P^\circ}$.

(b) Using the equation in (a), at what temperature is the following reaction at equilibrium?

$$CO(g) + H_2O(g) \rightleftharpoons H_2(g) + CO_2(g) \quad K = 9.6175 \times 10^4$$
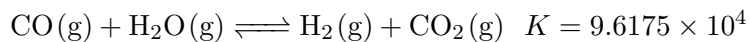
4. (4 pts) **Subtitued Benzene** There are three different substituted benzene compounds with the formula $C_6H_4F_2$.

(a) Draw the lewis structures of the three compounds.

(b) Assume that the benzene rings pack similarly into their crystal lattices. If the positions of the H and F atoms are statistically disordered in the solid state, which isomer will have the *least* molar entropy?

5. (7 pts) **Air Pollutants** Sulfur trioxide SO_3 and nitrogen oxide NO can react in the atmosphere as follows:

$$SO_3\,(g) + NO\,(g) \rightleftharpoons SO_2\,(g) + NO_2\,(g).$$
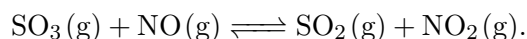
(a) Predict the effect of the following changes to the amount of NO_2 when the reacton has come to equilibrium in a stainless steel bulb equipped with entrants for chemicals

1. the amount of NO increases

2. the SO_2 is removed by condensation

3. the pressure is tripled by pumping in helium

(b) For each scenario in part (a), describe the "driving force" in terms of the thermodynamic quantities. *Hint:* Recall the lectures in week 6.

(c) Given that at a certain temprature $K = 6.0 \times 10^3$, calculate the amount (in moles) of NO that must be added to a 1.00 L vesssel containing 0.245 mol SO_3(g) to form 0.240 mol SO_2(g) at equilibrium. Report to 3 significant figures.

6. (6 pts) **Van't Hoff Equation** The Van't Hoff equation is often used in thermodynamics to show the equilibrium constant K dependence on temperature T.

$$\ln K = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \tag{1}$$

Using Eqn. 1, determine the ΔS° and ΔH° for the following reaction:

$$NH_3(g) + ClF_3(g) \rightleftharpoons HF(g) + N_2(g) + Cl_2(g)$$
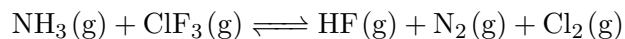
Report to 3 significant figures. Here are the following equilibrium partial pressures P of each gas species X at various T. *Hint:* Create a scatter plot.

Table 1: Equilibrium partial pressure $P(X)$ in bar at various T in °C

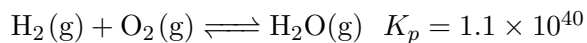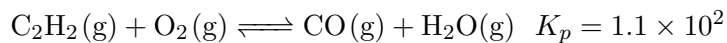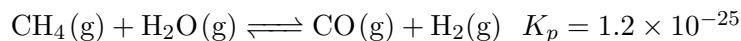| Partial Pressure	Temperature				
	10°C	100°C	300°C	900°C	1800°
P(N$_2$)	0.370	0.470	0.731	0.831	0.882
P(Cl$_2$)	0.253	0.389	0.579	0.619	0.676
P(HF)	0.290	0.450	0.612	0.568	0.600
P(NH$_3$)	0.215	0.352	0.490	0.530	0.580
P(ClF$_3$)	0.120	0.215	0.514	0.540	0.606

7. (4 pts) In a sealed 1.75 L vessel at 250°C, equilibrium is established between $PCl_5(g)$ and its dissociation products, $PCl_3(g)$ and $Cl_2(g)$. The quantities found at equilibrium are 0.562g PCl_5, 1.950g PCl_3, and 1.007g Cl_2. What is the value of K_c and K_p for the reaction. Report to 4 significant figures.

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

8. (4 pts) *Extra Credit:* Determine K_c at 300K for the unbalanced equation

$$CH_4(g) \rightleftharpoons C_2H_2(g) + H_2(g)$$
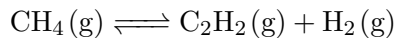
Report to 2 significant figures and given the following data

$$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + H_2(g) \quad K_p = 1.2 \times 10^{-25}$$
$$C_2H_2(g) + O_2(g) \rightleftharpoons CO(g) + H_2O(g) \quad K_p = 1.1 \times 10^2$$
$$H_2(g) + O_2(g) \rightleftharpoons H_2O(g) \quad K_p = 1.1 \times 10^{40}$$

Optional Additional Problems: Ch. 15 - odd problems 21 - 49