**Problem Set 4**  (**Due Nov. 21st by 7:00 PM**)

Answers to the problems in **RED** need to be submitted through the course website.

**Review Questions. (Bonus March 31)**

1. Determine the mass of the solid formed and the final pressure in the flask when 5 grams of solid phosphorus is added to 4 L of hydrogen gas at 1.4 atm and 212 °C. During the reaction, which produces solid phosphorus pentahydride, the volume remains the constant but the temperature increases by 15 °C.
2. Draw the Lewis structure of SOCl2. From this structure, determine:
   1. The number of lone pairs on each atom.
   2. The hybridization of each atom.
   3. The molecular geometry.
   4. All intermolecular forces that will stabilize SOCl2 in condensed phases.
   5. By the way, what is a condensed phase?
3. What is electronegativity? Using what you know about electron affinity and ionization energy, explain why fluorine is the most electronegative atom.
4. Describe how you can make 3.2 L of 265 mM sodium sulfate from:
   1. Solid sodium sulfate
   2. A solution that contains 2.5 M sodium sulfate.
5. Using the information in the table below, determine the rate of a reaction where [A] = [B] = [C] = 0.25 mM

|  |  |  |  |
| --- | --- | --- | --- |
| **rate (mM/min)** | **[A] (mM)** | **[B] (mM)** | **[C] (mM)** |
| 0.5034375 | 0.5 | 0.5 | 0.1 |
| 0.0040275 | 0.1 | 0.5 | 0.1 |
| 0.00003222 | 0.1 | 0.1 | 0.1 |
| 0.0040275 | 0.1 | 0.5 | 0.5 |

**Equilibrium – make sure to report the correct units! (Bonus March 31)**

1. Calculate Kc for each of the following reactions given the equilibrium concentrations listed.
   1. CH4 (g) + H2O (g) ⇌ CO (g) + 3 H2 (g) [CH4] = 2.96 mM [H2O] = 8.04 mM

[CO] = 5.55 mM [H2] = 21.92 mM

* 1. 2 NOCl (g) ⇌ 2 NO (g) + Cl2 (g) [NOCl] = 9.64 mM [Cl2] = 4.83 mM [NO] = 2.88 mM

1. Using what you learned in Problem 6, determine Kc for each of the following reactions:
   1. NOCl (g) ⇌ NO (g) + ½ Cl2 (g)
   2. CO (g) + 3 H2 (g) ⇌ CH4 (g) + H2O (g)
2. Calculate KP for each of the reactions in problem 6 if the temperature is 250 °C.
3. For each of the following groups, determine which reaction would be expected to have the **highest** % yield:
   1. Kc = 10, Kc = 0.1, Kc = 104, Kc = 10-4
   2. Kp = 260, Kp = 0.0268, Kp = 268, Kp = 2.68 x 10-3
4. Consider the following reaction. For each set of conditions, determine the equilibrium constant.

N2 (g) + 3 H2 (g) ⇌ 2 NH3 (g)

* 1. 1 atm of each reactant is mixed together in a 1 L reaction vessel at 298.15 K. At equilibrium the final pressure is found to be 1.393 atm. Determine Kp at 298.15 K.
  2. 1 atm of each reactant is mixed together in a 1 L reaction vessel at 500 °C. At equilibrium, the total pressure is found to be 1.924 atm. Determine Kp at 500 °C.

1. If 0.20 atm H2 (g) and 3.0 atm CH4 (g) are mixed in the presence of 4 grams of carbon at the indicated temperature, determine if the reaction is at equilibrium (that is, compare Q and K). If it is not, determine if products or reactants will be formed:
   1. C (s) + 2 H2 (g) ⇌ CH4 (g) Kp = 2.69 x 103 atm-1 (at 500 °C)
   2. C (s) + 2 H2 (g) ⇌ CH4 (g) Kp = 0.4725 atm-1 (at 900 °C)
2. For each question if Problem 11, determine the total pressure at equilibrium.
3. Calculate the concentration of H3O+ that will form in each of the following reactions:
   1. 1 mM NH4+ (aq) reacts with water to form H3O+ and NH3. Kc = 3.98 x 10-10 M-1 (at 25 °C)
   2. 0.5 M H2CO3 (aq) reacts with water to form H3O+ and HCO3-1. Kc = 4.3 x 10-7 M-1 (at 25 °C)
4. For each of the following, determine if the reaction is at equilibrium. If not, determine if reactant or products will be formed to reestablish equilibrium:

2 NH3 (g) ⇌ N2 (g) + 3 H2 (g) Kp = 83.35 atm

1. Determine the vapor pressure of water (in atm.) at each temperature. Remember that the vapor pressure just another way of saying the partial pressure of water vapor.
   1. 50 °C (Kp = 92.5876 mmHg)
   2. 75 °C (Kp = 38.5630 kPa)

**Enthalpy, Entropy, and Gibbs Free Energy (Bonus April 6)**

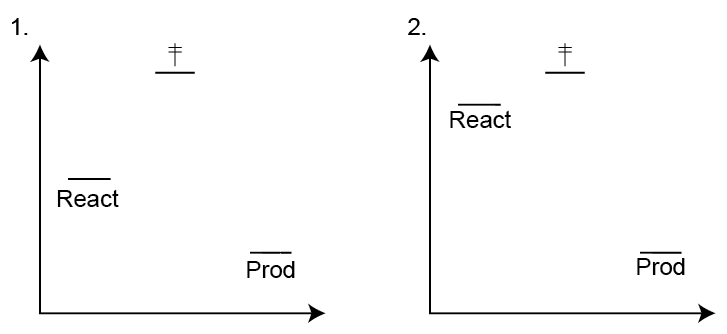
1. Consider the following reaction at equilibrium. For each of the following, determine if the equilibrium will shift toward products or reactants or if there will be no change.

Zn(s) + CO2 (g) ⇌ ZnO (s) + CO (g) Kp = 600

1. The temperature is increased in a flask that was at equilibrium.
2. The volume is decreased in a flask that was at equilibrium.
3. ZnO (s) is added to the reaction chamber.
4. Zn (s) is added to the reaction chamber.
5. Carbon monoxide is added to the chamber.
6. Carbon dioxide is added to the chamber.
7. 1 gram of Zn (s) and 1 gram of ZnO (s) is added to a flask with PCO = 850 atm and PCO2 = 2 atm
8. 1 gram of Zn (s) and 1 gram of ZnO (s) is added to a flask with PCO = 0.8 atm and PCO2 = 5 atm
9. For each change listed in Problem 16, determine if Grxn > 0, Grxn < 0, or Grxn = 0.
10. Use the [table of bond enthalpies in your textbook (Table 14.5)](http://bohr.winthrop.edu/faculty/grossoehme/link_to_webpages/courses/chem105/supp/Table14.5.pdf) to predict if each of the following reactions are enthalpically favorable. Note that these are not necessarily balanced.
11. H2O2 (l) ⇌ H2O (l) + O2 (g)
12. CCl4 (l) + H2 (g) ⇌ HCl (g) + C (s)
13. C2H2 (g) + O2 (g) ⇌ CO2 (g) + H2 (g)
14. For each reaction in Problem 18, determine if K will be larger at 100 K or 250 K.
15. Without doing any math, determine if Srxn > 0 or Srxn < 0 for each of the reactions in Problem 18. If it is not possible to determine the sign qualitatively, select “Unable to determine.” Recall that phase changes are the most important part of predicting change in entropy.
16. Using [Appendix D in your book](http://bohr.winthrop.edu/faculty/grossoehme/link_to_webpages/courses/chem105/supp/AppendixD.pdf), calculate for each of the reactions in Problem 18.
17. For each reaction below, calculate. Report you answer in kJ mol-1.
18. PCl3 (g) + Cl2 (g) ⇌ PCl5 (g) K = 1.1 x 105
19. 2 SO3 (g) ⇌ 2 SO2 (g) + O2 (g) K = 1.32 x 10-25
20. For each reaction below, calculate Grxn when the indicated concentrations are mixed together at 25 °C. Report you answer in kJ mol-1. Note that you calculated in the previous problem.
    1. PCl3 (g) + Cl2 (g) ⇌ PCl5 (g) K = 1.1 x 105 [Cl2] = 0.5 M [PCl3] = 0.1 M [PCl5] = 0.1 M
    2. 2 SO3 (g) ⇌ 2 SO2 (g) + O2 (g) K = 1.32 x 10-25 [SO3] = 8 mM [SO2] = 2 mM [O2] = 0.1 mM
21. For each of the following reactions, determine the standard reaction entropy () at 25 °C.
22. PCl5 (g) ⇌ PCl3 (g) + Cl2 (g) K = 3.03 x 10-7
23. 2 SO3 (g) ⇌ 2 SO2 (g) + O2 (g) K = 1.32 x 10-25
24. Predict which of the following will have a higher S°.
    1. S (s) vs. Se (s)
    2. H2O (l) vs. H2O (g)
    3. H2S (l) vs. H2O (l)
25. Consider the two **reaction coordinates** shown below. If the reactions are carried out under identical conditions, which of the following statements is true?
    1. K1 > K2 and k1 > k2
    2. K1 > K2 and k1 < k2
    3. K1 < K2 and k1 > k2
    4. K1 < K2 and k1 < k2

**Gibbs Free Energy**

**Gibbs Free Energy**



**Thermochemistry (Bonus April 13)**

1. For each of the following, determine the sign of H and state if the reaction is endothermic or exothermic.
   1. Solidification
   2. Condensation
   3. Fusion
   4. Vaporization
   5. Sublimation
2. Order each group of compounds by increasing Hfus.
   1. HF, F2, HCl, Cl2
   2. NH3, NCl3, PCl3
3. Use [table 14.3 in your book](http://bohr.winthrop.edu/faculty/grossoehme/link_to_webpages/courses/chem105/supp/Table14.3.pdf) to determine standard reaction enthalpies. Note that these equations are not necessarily balanced.
   1. C2H4 (g) 🡪 C2H2 (g) + H2 (g)
   2. HCl (g) + CH4 (g) 🡪CCl4 (l) + H2 (g)
4. Use the values you determined in problem 29 to calculate H for each of these reactions.
   1. A 2.8 L flask at 200 °C is pressurized to 2.8 atm with C2H4 (g). The % yield of the reaction is 67%.
   2. A 5.5 L flask at 212 °C is contains HCl at a pressure of 1.904 atm and CH4 at a pressure of 0.602 atm. The reaction has a 100% yield.
5. Consider a system at rest. For each pair, determine which will have a greater impact on the total internal energy of the system:
   * 1. The volume of the system changes by 0.2 L with a constant external pressure of 1 atm OR
     2. The volume of the system changes by 0.3 L with a constant external pressure of 0.75 atm
     3. The volume of the system changes by 0.5 L with a constant external pressure of 4 atm OR
     4. The volume of the system changes by 1 L with a constant external pressure of 2.5 atm
6. Starting with the information below, determine the boiling temperature of each molecule when the atmospheric pressure is exactly 1 atm. Recall that Tb occurs when pvap = 1 atm. Also recall that vapor pressure is determined from the vaporization equilibrium (liquid ⇌ gas).
   1. Ethanol has a vapor pressure of 100 mmHg at 34.9 °C and
   2. Acetone has a vapor pressure of 400 mmHg at 39.5 °C and
7. Use the following data for ethyl alcohol (CH3CH2OH) to answer the following questions:

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Tb (˚C) | Tm (˚C) | Hfusion (kJ/mol) | Hvaporization(kJ/mol) | C (solid)  J / (mol˚C) | C (liquid)  J / (mol˚C) | C (gas)  J / (mol˚C) |
| 78.3 | -117 | 5.02 | 38.57 | 111.5 | 112.4 | 87.55 |

* 1. 140 g of gaseous ethyl alcohol is cooled from the boiling point to -120 ˚C. Determine H.
  2. 360 g of ethyl alcohol is heated from 50°C to 92 ˚C. Determine H.

1. Consider the data in Problem 33.
2. Calculate the standard entropy of fusion for ethyl alcohol at its melting temperature.
3. Calculate the standard entropy of vaporization for ethyl alcohol at its boiling temperature.
4. For each pair of molecules, determine which will take more energy to break the indicated bond.
   1. Compare N-N bonds: N2H4 vs. N2H2
   2. Compare O-O bonds: O2 vs. H2O2
5. In your own words, please define each of these terms, in context of our discussions thermodynamics, and discuss why they are important:
   1. Total internal energy
   2. First Law of Thermodynamics
   3. Enthalpy
   4. Work

**Concepts**

You don’t need to submit an answer for these, but you need to know what they are and why they are important!

1. Draw a reaction coordinate and label it with all important energy levels. What does each energy change mean?
2. What is activation energy and how can it decreased?
3. Why are rate constants condition dependent?
4. What are 3 ways to change the rate of a reaction?
5. What are two ways that you can make a reaction more favorable (i.e. make G more negative)?
6. True or False: Equilibrium occurs when a reaction has stopped.
7. What circumstances can make a spontaneous reaction appear to not occur?
8. Under what conditions are G and G° equal?
9. In your own words (and equations if you prefer), please define the following concepts.
10. Spontaneous Reaction.
11. Second Law of Thermodynamics
12. Third Law of Thermodynamics
13. Standard Molar Entropy
14. Standard Gibbs Free Energy of Formation ()
15. The relationship between and G.

Answers to black problems:

|  |  |
| --- | --- |
| 6. 2.46 x 10-3 M2  8. 4.527 atm2  10. 737.88 atm-2  12. PH2 = 0.0339 atm, pCH4 = 3.083 atm. Ptot = 3.1229 atm  14. a. Q = 83.4. K = Q, so the reaction is at equilibrium  16. a Reactants, c. No change e. Reactants g. Products  18. a. H = -218 kJ mol-1. Exothermic, so favorable.  b. H = 470 kJ mol-1. Endothermic, so not favorable.  20. a. S > 0 0 gas 🡪 1 gas and 2 molecules 🡪 3 molecules  b. S > 0 2 gas 🡪 4 gas and 3 molecules 🡪 5 molecules  22. a. -28.77 kJ mol-1  24. a. 170 J mol-1K-1  27. a. exothermic c. endothermic d. endothermic  29. 175 kJ mol-1  31. The second one (more U from work)  33. -200.15 kJ  35. = 32.15 J mol-1K-1 | 7. 0.0207 M1/2  9. Kc = 104  11. K > Q, so products formed.  13. [H3O+] = 6.31 x 10-7 M (did you consider using the shortcut?)  15. pH2O = 0.1218 atm  17. a. Grxn > 0 c. Grxn = 0, e. Grxn > 0, f. Grxn < 0  19. a. K100 > K250 b. K250 > K100  21. a. G = -233.4 kJ mol-1, H = -196 kJ mol-1  S = 126 J mol-1K-1  a. G = -315.9 kJ mol-1, H = -241 kJ mol-1  S = 276.5 J mol-1K-1  23. a. -27.05 kJ mol-1  25. Se (s) because it’s bigger  28. a. F2 < Cl2 < HCl < HF  30. 23.68 kJ  32. 356.03 K (or 82.9 °C)  34. N2H2 |