Equilibrium Objectives

Equilibrium Conceptually

- I can identify what is equal at equilibrium.
- I can explain why equilibrium is considered dynamic.
    1. Characterize a system at equilibrium with respect to each of the following:
        a. The rates of the forward and reverse reactions
        b. The overall composition of the reaction mixture
- I can draw a graph and identify when a reaction has reached equilibrium and whether it favors the reactants or products at equilibrium.
    1. There is only one value of the equilibrium constant for a particular system at a particular temperature, but there is an infinite number of equilibrium positions. Explain.
- I can identify the three factors that determine whether the reaction at equilibrium will favor the reactants or the products.
    1. Is the following statement true or false? "Reactions with large equilibrium constants are very fast." Explain.
- I can explain the relationship between Gibbs free energy and equilibrium.

Equilibrium Expresssions

- I can write equilibrium expressions for reactions at equilibrium.
    1. $2\ O_3\ (g) \longleftrightarrow 3\ O_2\ (g)$
    2. $2\ NO\ (g) + Cl_2\ (g) \longleftrightarrow 2\ NOCl\ (g)$
    3. $BaSO_4\ (s) \longleftrightarrow Ba^{2+}\ (aq) + SO_4^{2-}\ (aq)$
- I can calculate the equilibrium constant, K, for a reaction at equilibrium.
    a. An aqueous solution of acetic acid is found to have the following equilibrium concentrations at 25°: $[HC_2H_3O_2] = 1.65 \times 10^{-2}$ M, $[H^+] = 5.44 \times 10^{-4}$ M, and
        i. $[C_2H_3O_2^-] = 5.44 \times 10^{-4}$ M. Calculate the equilibrium constant for the ionization of acetic acid at 25°C.
    b. $CO\ (g) + Cl_2\ (g) \longleftrightarrow COCl_2\ (g)$ $\quad K_c = 1.2 \times 10^3$ at 395°C
        i. Write the equilibrium expression.
        ii. If the equilibrium concentration of Cl_2 and $COCl_2$ are the same at 395°C, find the equilibrium concentration of CO.
- I can write and calculate K_p expressions using partial pressures instead of concentrations.
    1. A mixture of hydrogen and nitrogen in a reaction vessel is allowed to attain equilibrium. The equilibrium of gases was analyzed and found to contain 7.38 atm H_2, 2.46 atm N_2, and 0.166 atm NH_3. From these data calculate the equilibrium constant, K_p, for $N_2\ (g) + 3\ H_2\ (g) \longleftrightarrow 2\ NH_3\ (g)$.
- I can identify the two things that will change the equilibrium constant, K.
- I can predict and calculate K based on the original equation and given a new manipulated equation and the original equilbrium constant.
    a. The equilibrium constant for the reaction: $2\ NO_{(g)} + Br_{2\ (g)} \longleftrightarrow 2\ NOBr_{(g)}$ is 1.3×10^{-2} at 1000 K.
        i. Calculate the K for $2\ NOBr_{(g)} \longleftrightarrow 2\ NO_{(g)} + Br_{2\ (g)}$
        ii. Calculate the K for $NOBr_{(g)} \longleftrightarrow NO_{(g)} + \frac{1}{2}\ Br_{2\ (g)}$

- I can recall and utilize the equation needed to convert K (K_c) to K_p.
    a. $N_2\ (g) + 3\ H_2\ (g) \longleftrightarrow 2\ NH_3\ (g)$ $\quad K_c = 9.60$ at 300°C
        i. Calculate the K_p for the same reaction at 300°C.

- I can use the value calculate or given for K to determine whether the equilibrium lies towards the products or the reactants.
    1. At 900°C, K_p = 1.04 for the reaction: $CaCO_3$ (s) ⟷ CaO (s) + CO_2 (g). At a low temperature, dry ice (solid CO_2), calcium oxide and calcium carbonate are introduced into a 50.0-L reaction chamber. The temperature is raised to 900°C, resulting in the dry ice converting to gaseous CO_2. For the following mixtures, will the initial amount of calcium oxide increase, decrease, or remain the same as the system moves toward equilibrium?
        - 655 g $CaCO_3$, 95.0 g CaO, P_{CO2} = 2.55 atm
        - 780 g $CaCO_3$, 1.00 g CaO, P_{CO2} = 1.04 atm
        - 0.14 g $CaCO_3$, 5000 g CaO, P_{CO2} = 1.04 atm
        - 715 g $CaCO_3$, 813 g CaO, P_{CO2} = 0.211 atm

Reaction Quotient (Q)

- I can calculate where a reaction is at any point by solving for the reaction quotient, Q.
- I can compare Q to K and interpret which side of the reaction is favored at that point and the shift that the reaction will make to reach equilibrium.
    1. If Q is greater than K,
        (a) The reaction favor the reactant side
        (b) The reaction will favor the product side
        (c) The reaction is at equilibrium
        (d) It will shift to the side with the greater number of moles
        (e) It will shift away from the heat
    1. At 448°C, the equilibrium constant, $K_{eq,}$ for the reaction H_2 (g) + I_2 (g) ⟷ 2 HI (g) is 51. Predict how the reaction will proceed at equilibrium at 448°C if 2.0 x 10^{-2} mol HI, 1.0 mol H_2, and 3.0 x 10^{-2} mol I_2 are placed in a 2.00-L container.

Equilibrium Calculations using ICE

- I can calculate the equilibrium constant given initial concentrations and the concentration of a reactant at equilibrium.
- I can calculate the equilibrium concentrations of ALL species given initial concentrations and the equilibrium constant.

- I can correctly use the 5% rule when applicable and prove that it is acceptable through calculation.

YOU DID LOTS OF PRACTICE!

(A) In class worksheet – ICE worksheet

(B) Book problems – Problem Set 3

(C) Extra practice problems???

1) The reaction H_2 (g) + I_2 (g) ⟷ 2 HI (g) is carried out at 690 K with the following initial concentrations: [H_2] = 1.000 x 10^{-3} M; [I_2] = 2.000 x 10^{-3} M; [HI] = 0.000 M. When the reaction reaches equilibrium, [HI] = 1.880 x 10^{-3} M. Calculate the equilibrium constant for this reaction.

2) PCl_5 (g) undergoes the following dissociation reaction at 500°C:

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

1.000 mole of PCl_5 is placed in a 2.000-L container. At equilibrium, 19.04% of the PCl_5 molecules have dissociated. Calculate the equilibrium constant for this reaction.

3) A 255.8 g sample of HI is placed in a 2.000 L container at 690 K. Using the information from problem 1 and a manipulation of K, calculate the concentrations of H_2, I_2, and HI at equilibrium.

4) At a certain temperature, the reaction 2 N_2 (g) + O_2 (g) ⟷ 2 N_2O (g) has an equilibrium constant, K_c = 2.0 x 10^{-13}. A 3.00-L container at this temperature contains 0.150 moles of N_2 and 0.270 moles of O_2 initially. Calculate the equilibrium concentrations of all species.

5) At 523 K, the reaction PCl_5 (g) ⟷ PCl_3 (g) + Cl_2 (g) has an equilibrium constant K_P = 78.3. A 0.150 mole sample of PCl_5 is placed in a 5.00-L container and allowed to come to equilibrium. Calculate the ***total*** pressure in the container.

Le Châtelier's Principle

- I can define/explain Le Châtelier's principle.
- I can explain how the equilibrium shifts with a change in concentration and explain the effect on the concentration/amount of a given reactant/product and the constant, K.
- I can explain how the equilibrium shifts with a catalyst and explain the effect on the concentration/amount of a given reactant/product and the constant, K.

- I can explain how the equilibrium shifts with a change in <u>temperature</u> and explain the effect on the concentration/amount of a given reactant/product and the constant, K.
- I can explain how the equilibrium shifts with a change in <u>pressure</u> and explain the effect on the concentration/amount of a given reactant/product and the constant, K.
- I can explain how the equilibrium shifts with a change in <u>volume</u> and explain the effect on the concentration/amount of a given reactant/product and the constant, K.

  - For the system $2\ SO_2(g) + O_2(g) \leftrightarrows 2\ SO_3(g)$ which is exothermic
    - Predict the effect of each of the following changes on the value of the equilibrium constant.
      - decreasing the volume of the system?
      - adding oxygen to the equilibrium mixture?
      - raising the temperature of the system?
      - decreasing the pressure of the system?
      - adding a catalyst?
    - Predict the effect of each of the following changes on the number of moles of SO_3 at equilibrium.
      - decreasing the volume of the system?
      - adding oxygen to the equilibrium mixture?
      - raising the temperature of the system?
      - decreasing the pressure of the system?
      - adding a catalyst?
    - Predict the effect of each of the following changes on the rate of forward reaction.
      - decreasing the volume of the system?
      - adding oxygen to the equilibrium mixture?
      - raising the temperature of the system?
      - decreasing the pressure of the system?
      - adding a catalyst?

<u>Ksp Lecture 1</u>

- I can explain what is occurring at equilibrium in a Ksp problem.
- I can write Ksp expressions for ionic compounds.
  - The Ksp expression for silver phosphate is:
  - Write the Ksp expression for the dissolution of copper (II) hydroxide.
- I can solve for Ksp given the molar solubility of a substance.

- In a saturated solution of $Zn(OH)_2$ at 25 C, the value of $[OH^-]$ is 2.0×10^{-6}M. What is the value of the solubility-product constant, Ksp, for $Zn(OH)_2$ at 25°C?
- I can solve for the molar solubility of a substance given Ksp.
  - The molar solubility of BaF_2 in water at 25°C is 7×10^{-4}. What is the Ksp for barium fluoride?
- I can compare two solutes that have the same # of ions and determine relative solubility.
- I can compare two solutes that have different # of ions and determine relative solubility.
  - Which of the following compounds has the <u>lowest</u> solubility in mol/L in water?
    a) $Al(OH)_3$ Ksp = 2.0×10^{-32}
    b) CdS Ksp = 1.0×10^{-28}
    c) $PbSO_4$ Ksp = 1.3×10^{-8}
    d) $Sn(OH)_2$ Ksp = 3.0×10^{-27}
    e) MgC_2O_4 Ksp = 8.6×10^{-5}
  - Zinc oxalate, ZnC_2O_4 and lead fluoride, PbF_2, have the same Ksp value at 25°C, 2.7×10^{-8}. What can be concluded from this information?

<u>Ksp Lecture 2</u>

- I can explain what the common ion effect does to solubility and calculate a Ksp problem that involves common ions.
  - Calculate the molar solubility of AgBr (Ksp = 5.6×10^{-13}) in 0.0030 M $AgNO_3$ solution.
  - Calculate the solubility of $Sn_3(PO_4)_2$ (Ksp = 4.2×10^{-36}) in (a) pure water and (b) 0.30 M Na_3PO_4.
- I can calculate Q for a dissolution process and determine whether a precipitate is made by comparing the value to Ksp, explaining why this is the case.
  - Will Ag_2SO_4 precipitate when 100.0 mL of 0.050 M $AgNO_3$ is mixed with 10.0 mL of 0.050 M Na_2SO_4? (K_{sp} Ag_2SO_4 = 3.1×10^{-8})
  - A solution contains 2.0×10^{-4} M Ag^+ and 1.5×10^{-3} M Pb^{2+}. If NaI is added, will AgI (Ksp = 8.3×10^{-17}) or PbI_2 (Ksp = 7.9×10^{-9}) precipitate first? What concentration of I^- is needed to initiate the precipitation?

<u>MORE REVIEW PROBLEMS IF YOU WANT SOME.....</u>

1. At 450°C ammonia gas decomposes into hydrogen and nitrogen gases. An experiment starts by placing 2.25 moles of ammonia in a 3.00 L container and heating it to 450°C. At equilibrium there are 0.522 moles of ammonia. Based on this information determine the final concentration of each gas and the K_c of the reaction.

   a. What is the K_c of the reaction: $1/2\ N_2 + 3/2\ H_2 \longleftrightarrow NH_3$?

b. What is the K_p of the reaction?

2. 0.88 moles of N_2O_5(g) was placed in a sealed 1.00 L vessel. Calculate the equilibrium concentration of N_2O_5. NO_2, and O_2 and the equilibrium constant after equilibrium has been reached by 65.0% of the N_2O_5 decomposing.

   a. Does the equilibrium favor the reactants or the products?

3. The equilibrium constant for the dissociation of iodine is 3.76 at 1000 K. Suppose 1.00 mol of iodine is placed in a 2.00 L flask at 1000 K. What are the concentrations of diatomic iodine and the iodine atom at equilibrium?

   a. What is the effect on the number of moles of I_2 if:
      - The volume of the system is increased? _____
      - A sample of argon gas is added? _____

4. Sulfuryl chloride, SO_2Cl_2, is a highly reactive gaseous compound. When heated, it decomposes as follows: $SO_2Cl_2(g) <====> SO_2(g) + Cl_2(g)$ This decomposition is endothermic. A sample of 3.509 grams of SO_2Cl_2 is placed in an evacuated 1.00-liter bulb and the temperature is raised to 375 K.
      - What would be the pressure in atmospheres in the bulb if no dissociation of the SO_2Cl_2(g) occurred?
      - When the system has come to equilibrium at 375 K, the total pressure in the bulb is found to be 1.43 atmospheres. Calculate the partial pressures of SO_2, Cl_2, and SO_2Cl_2 at equilibrium at 375 K.
      - Give the expression for the equilibrium constant (either K_p or K_c) for the decomposition of SO_2Cl_2(g) at 375 K. Calculate the value of the equilibrium constant you have given.
      - If the temperature were raised to 500 K, what effect would this have on the equilibrium constant? Explain briefly.

5. At a particular temperature, K = 2.0×10^{-6} for the reaction: $2\ CO_{2\,(g)} \longleftrightarrow 2\ CO_{(g)} + O_{2\,(g)}$. If 2.0 mol of CO_2 was initially placed in a 5.0 L container, find the equilibrium concentrations of all species.

ADDITIONAL PRACTICE PROBLEMS - Ksp

6) The solubility of silver sulfide is 8.0×10^{-17} M. Determine the Ksp of this salt.

7) Calculate the solubility of nickel (II) hydroxide with a Ksp=1.6×10^{-16}.

8) Calculate the Ksp for bismuth (III) sulfide, which has a solubility of 1.0×10^{-15} M at 25°C.

9) What is the solubility of the aluminum and hydroxide ions at 25°C if the Ksp for aluminum hydroxide is 3.0×10^{-34}?

10) Calculate the solubility of LaF_3 (Ksp = 2.00×10^{-19}) in grams per Liter in:

i. pure water
ii. 0.010 M KF solution
iii. 0.050 M $LaCl_3$ solution

11) Will $AgIO_3$ precipitate when 20.0 mL of 0.010 M $AgNO_3$ is mixed with 10.0 mL of 0.015 M $NaIO_3$ (Ksp of $AgIO_3$ is 3.1×10^{-8})?