Chapter 15

Chemical Equilibrium

Chapter 15 suggested problems
10th Ed. - 15.x: 13, 15, 17, 19, 27, 33, 35, 37, 39, 43, 51
11th Ed. - 15.x: 13, 15, 17, 19, 27, 33, 35, 37, 39, 43, 51

Chapter Objectives

After completing this chapter, you should, *at a minimum*, be able to do the following. This information can be found in my lecture notes for this and other chapters and also in your text.

1. Correctly answer all of the questions suggested above and in the quiz for this chapter.
2. Define basic terms such as Haber process, dynamic equilibrium, chemical equilibrium, equilibrium constant, equilibrium constant expression, product favored, reactant favored, K_c, K_p, homogeneous equilibria, heterogeneous equilibria, reaction quotient, LeChatelier's principle.
3. Understand the relationship between kinetics, rates laws, and equilibrium constant expressions.
4. Understand the concept and relevance of equilibrium constants and what they convey in a general sense about chemical reactions.
5. Be able to write equilibrium constant expressions for any reaction.
6. Express the difference between K_c and K_p for a reaction and convert from one to the other.
7. Explain why the concentrations of pure solids and liquids do not appear in equilibrium constant expressions.
8. Be able to calculate equilibrium constants and to use equilibrium constants to calculate equilibrium concentrations of reactants and products.
9. Calculate reaction quotients and predict whether or not a system is at equilibrium.
10. Using LeChatelier's principle predict the effects of changes in concentration, temperature, pressure, and catalysts on a system at equilibrium.

Class Notes

I. The concept of equilibrium

   A. The Haber process: $N_{2\,(g)} + 3\ H_{2\,(g)} \rightarrow 2\ NH_{3\,(g)}$

   B. It is apparent that the reaction never goes to completion, but rather, it slows down and appears to stop; the reaction vessel contains a mixture of nitrogen, hydrogen, and ammonia

C. We know from kinetics that a reaction rate is dependent on the concentration of the reactants; as reactant concentration decreases, rate also decreases

D. In addition, a competing reaction begins and its rate increases with time: the decomposition of ammonia to form nitrogen and hydrogen

E. This simultaneous process of reactants reacting to form product, and of product reacting to form reactants, is called a dynamic equilibrium and is represented in a chemical equation with two arrows pointing in opposite directions e.g. rxt <=> prod

1. Dynamic equilibrium: "the condition in which two opposing processes are occurring simultaneously at equal rates" (BLB-10: 460)

F. As reactant concentration decreases and the rate of the forward reaction slows, and as product concentration increases and the rate of the reverse reaction increases, at some time the rates of the forward and the reverse reactions will level off and equal each other; this state is called chemical equilibrium

1. In a state of chemical eqb. $rate_f = rate_r$

G. Given the reaction rxt <=> prod at eqb. (remember that concentrations are expressed as molar concentrations)

1. $Rate_f = k_f[rxt]$
2. $Rate_r = k_r[prod]$
3. $Rate_f = rate_r$
4. $k_f[rxt] = k_r[prod]$
5. $k_f/k_r = [prod]/[rxt] = constant$

II. The equilibrium constant

A. The constant that is either the ratio of the rate constants or the ratio of product and reactant concentrations at eqb. is called the eqb. constant and is represented K_c

B. The magnitude of equilibria constants provides insight into whether the reaction is product or reactant-favored

1. If $K_c > 1$ then the product of the concentrations of products is greater than the product of the concentrations of reactants; the reaction is product favored
2. If $K_c < 1$ then the product of the concentrations of reactants is greater than the product of the concentrations of products; the reaction is reactant favored
3. The more $K_c > 1$ the more product favored the reaction
4. The more $K_c < 1$ the more reactant favored the reaction
5. Negative values of K_c never occur

C. Given the reaction: rxt <=> prod, then $K_c = k_f/k_r = [prod]/[rxt]$

D. For A + B <=> C + D

1. $Rate_f = k_f[A][B]$
2. $Rate_r = k_r[C][D]$
3. $K_c = k_f/k_r = [C][D]/[A][B]$

E. For aA + bB <=> cC + dD

1. $Rate_f = k_f[A]^a[B]^b$
2. $Rate_r = k_r[C]^c[D]^d$
3. $K_c = k_f/k_r = [C]^c[D]^d/[A]^a[B]^b$

F. Other examples

1. For Haber process: $K_c = [NH_3]^2/[N_2][H_2]^3$
2. For N_2O_4 <=> 2 NO_2: $K_c = [NO_2]^2/[N_2O_4]$

G. Implications

1. If we know the equilibrium concentrations of the various reactants and products we can calculate K_c
2. If we know K_c we can calculate equilibrium concentrations or the results of changes to the system
3. Note that is K_c is unitless
4. (BLB-10: 635)

initial and equilibrium molar concentrations of N_2O_4 and NO_2 in the gas phase at 100°C					
experiment	**$[N_2O_4]_i$**	**$[NO_2]_i$**	**$[N_2O_4]_{eqb}$**	**$[NO_2]_{eqb}$**	**K_c**
1	0.0	0.0200	0.00140	0.0172	0.211
2	0.0	0.0300	0.00280	0.0243	0.211
3	0.0	0.0400	0.00452	0.0310	0.213
4	0.0200	0.0	0.00452	0.0310	0.213

H. Equilibrium constants expressed in terms of pressure

1. For a system in which the reactants and products are gases, K can be calculated in terms of the partial pressures of the gases
2. For aA + bB <=> cC + dD: $K_c = P_C^{\ c} \cdot P_D^{\ d} / P_A^{\ a} \cdot P_B^{\ b}$
3. For each gaseous reactant and product PV = nRT,
   a. [conc] = n/V

b. P = MRT, M = molar concentration

c. $K_p = K_c(RT)^{\Delta n}$ where Δn is the sum of the difference between the number of moles of gaseous product and the number of moles of gaseous reactants

III. Heterogeneous Equilibria

A. Homogeneous and heterogeneous equilibria

1. Homogeneous equilibria: all reactants and products are in the same phase, e.g. Haber process

2. Heterogeneous equilibria: reactants and products are not in the same phase, e.g. reaction of baking soda and vinegar

B. The concentrations of pure solids and pure liquids are constant and do not change during chemical reactions

1. While a substance may be produced or consumed, the mass to volume ratio of pure solids and liquids remains constant, i.e., if a a certain mass of substance is produced, the volume of the substance will increase proportionally; if a a certain mass of substance is consumed, the volume of the substance will decrease proportionally

2. The molar concentration of pure solids and liquids is dependent on their density and molar mass

a. Water: (1000 mL / 1 L) x (1.00 g / 1 mL) x (1 mol / 18.02 g) = 55.5 M

b. Acetone: (1000 mL / 1 L) x (0.7899 g / 1 mL) x (1 mol / 58.08 g) = 13.6 M

c. Sodium chloride: (1000 cm^3 / 1 L) x (2.165 g / 1 cm^3) x (1 mol / 58.44 g) = 37.0 M

d. $PbCl_2$: (1000 cm^3 / 1 L) x (5.85 g / 1 cm^3) x (1 mol / 278.10 g) = 21.04 M

C. If a pure solid or a pure liquid is present in an equilibrium mixture, either as a reactant or as a product, its concentration is not used the equilibrium-constant expression for the reaction but is incorporated into the equilibrium constant

1. $CO_{2\,(g)} + H_{2\,(g)} \Leftrightarrow CO_{(g)} + H_2O_{(l)}$

a. $K_c = [CO] / [CO_2][H_2]$

b. $K_p = P_{CO} / P_{CO_2} P_{H_2}$

2. $SnO_{2\,(s)} + 2\ CO_{(g)} \Leftrightarrow Sn_{(s)} + 2\ CO_{2\,(g)}$

a. $K_c = [CO_2]^2 / [CO]^2$

b. $K_p = P_{CO_2}{}^2 / P_{CO}{}^2$

3. $3\ Fe_{(s)} + 4\ H_2O_{(g)}$ <=> $Fe_3O_{4\ (s)} + 4\ H_{2\ (g)}$

   a. $K_c = [H_2]^4 / [H_2O]^4$

   b. $K_p = P_{H2}{}^4 / P_{H2O}{}^4$

D. Even though they do not appear in the equilibrium-constant expression, pure solids and liquids must be present in the reaction for eqb. to be established

IV. Calculating equilibria constants

A. If the equilibrium concentrations of reactants and products are known, K_c can be calculated

1. A mixture of nitrogen and hydrogen gases is allowed to reach equilibrium at 472 °C. The eqb. mixture contained 0.1207 M hydrogen, 0.0402 M nitrogen, and 0.00272 M ammonia. What is the equilibrium constant for the Haber process at this temperature?
   $K_c = [NH_3]^2/[N_2][H_2]^3 = [0.00272]^2/[0.0402][0.1207]^3 = 0.105$

2. Nitryl chloride decomposes to form nitrogen dioxide and chlorine as follows:
   $2\ NO_2Cl_{\ (g)}$ <=> $2\ NO_{2\ (g)} + Cl_{2\ (g)}$
   At eqb. the nitryl chloride concentration is 0.00106 M, the nitrogen dioxide concentration is 0.0108 M, and the chlorine concentration is 0.00538 M. What is the value of the equilibrium constant?
   $K_c = [NO_2]^2[Cl_2]/[NO_2Cl]^2 = [0.0108]^2[0.00538]/[0.00106]^2 = 0.558$

B. If the equilibrium concentrations of reactants and products are not known they can often be deduced from reaction stoichiometry

1. A mixture of 5.000×10^{-3} moles of hydrogen and 1.000×10^{-2} moles of iodine is placed in a 5.000 L container at 448°C and allowed to come to equilibrium, at which point the concentration of the product, hydrogen iodide, is 1.87×10^{-3} M. What is K_c for this reaction?

   a. initial $[H_2] = 1.000 \times 10^{-3}$ M; initial $[I_2] = 2.000 \times 10^{-3}$ M; $H_{2\ (g)} + I_{2\ (g)}$ <=> $2\ HI_{(g)}$

   b.

	$[H_2]$	**$[I_2]$**	**[HI]**
initial	1.000×10^{-3}	2.000×10^{-3}	0
change	-x	-x	+2x
eqb	1.000×10^{-3} - x	2.000×10^{-3} - x	1.87×10^{-3}

   c. If $2x = 1.87 \times 10^{-3}$ then $x = 9.35 \times 10^{-4}$

   d. $[H_2] = 1.000 \times 10^{-3} - 9.35 \times 10^{-4} = 6.5 \times 10^{-5}$

   e. $[I_2] = 2.000 \times 10^{-3} - 9.35 \times 10^{-4} = 1.065 \times 10^{-3}$

   f. $K_c = [HI]^2 / [H_2][I_2] = [1.87 \times 10^{-3}]^2 / [6.5 \times 10^{-5}][1.065 \times 10^{-3}] = 50.52$

2. Sulfur trioxide decomposes at elevated temperatures to form sulfur dioxide and oxygen according to the equation
   $2\ SO_{3\ (g)} <=> 2\ SO_{2\ (g)} + O_{2\ (g)}$. In an experiment at 1000 K the initial concentration of SO_3 was 6.09×10^{-3} M. Sometime later, once the system had reached equilibrium, it was 2.44×10^{-3} M. What is K_c at the temperature of this experiment?

   a.

	$[SO_3]$	$[SO_2]$	$[O_2]$
initial	6.09×10^{-3}	0	0
change	-2x	+2x	+x
eqb	6.09×10^{-3} - 2x	2x	x

   b. If ($6.09 \times 10^{-3} - 2x = 2.44 \times 10^{-3}$) then $x = 1.825 \times 10^{-3}$

   c. $[SO_2] = 2x = 3.65 \times 10^{-3}$

   d. $[O_2] = x = 1.825 \times 10^{-3}$

   e. $K_c = [SO_2]^2[O_2]/[SO_3]^2 = [2.44 \times 10^{-3}]^2 / [3.65 \times 10^{-3}]^2[1.825 \times 10^{-3}] = 4.08 \times 10^{-3}$

V. Applications of equilibria constants

A. Predicting the direction of reaction

1. At any point in a reaction before equilibrium is reached, if the concentrations of reactants and products at that time are substituted into the equilibrium-constant expression, a value called the reaction quotient (Q) is obtained

   a. If $Q < K_c$ then the forward reaction will occur

   b. If $Q > K_c$ then the reverse reaction will occur

   c. If $Q = K_c$ then the system is at equilibrium

2. If the concentrations of hydrogen, iodine, and hydrogen iodide in a reaction are, respectively, 5.00×10^{-3} M, 1.50×10^{-2} M, and 1.00×10^{-2} M, which way will the reaction proceed? Assume the reaction temperature is 448°C.

   a. $K_c = 50.52$; $Q = [HI]^2 / [H_2][I_2] = [1.00 \times 10^{-2}]^2 / [5.00 \times 10^{-3}][1.50 \times 10^{-2}] = 1.33$; the forward reaction will occur

3. If the concentrations of sulfur trioxide, sulfur dioxide, and oxygen in a reaction are, respectively, 2.00×10^{-3} M, 5.00×10^{-3} M, and 3.00×10^{-2} M, which way will the reaction proceed? Assume the reaction temperature is 1000 K.

   a. $K_c = 4.08 \times 10^{-3}$; $Q = [SO_2]^2[O_2]/[SO_3]^2 = [5.00 \times 10^{-3}]^2[3.00 \times 10^{-2}] / [2.00 \times 10^{-3}]^2 = 0.188$; the reverse reaction will occur

B. Predicting equilibrium concentrations

1. For the Haber process at 500°C $K_p = 1.45 \times 10^{-5}$. At equilibrium, the partial pressure of hydrogen is 0.928 atm and the partial pressure of nitrogen is 0.432 atm. What is the partial pressure of ammonia?

    a. $K_p = [NH_3]^2/[N_2][H_2]^3$; $[NH_3] = \{K_p[N_2][H_2]^3\}^{1/2} = 2.237 \times 10^{-3}$

2. At 500 K the decomposition of phosphorus pentachloride to phosphorus trichloride and chlorine gas has a K_p value of 0.497. At equilibrium the partial pressures of PCl_5 and PCl_3 are 0.860 atm and 0.350 atm respectively. What is the partial pressure of chlorine at equilibrium?

    a. $PCl_{5\,(g)} \Leftrightarrow PCl_{3\,(g)} + Cl_{2\,(g)}$

    b. $K_p = [PCl_3][Cl_2]/[PCl_5]$; $[Cl_2] = K_p[PCl_5]/[PCl_3] = 1.221$ atm

3. At 448°C the equilibrium constant for the reaction of hydrogen and iodine is 50.52. If the starting concentrations of hydrogen and iodine are 1.000 M and 2.000 M respectively, what are the equilibrium concentrations of hydrogen, iodine, and hydrogen iodide?

    a. $H_{2\,(g)} + I_{2\,(g)} \Leftrightarrow 2\,HI_{(g)}$

    b.

	$[H_2]$	**$[I_2]$**	**[HI]**
initial	1.000	2.000	0
change	-x	-x	+2x
eqb	1 - x	2 - x	2x

    c. $K_c = [HI]^2 / [H_2][I_2] = [2x]^2 / [1 - x][2 - x] = 50.52$

    d. Must use quadratic equation to solve for x; x = 2.323 and 0.935

    e. Since when x = 2.323 negative equilibrium concentrations result, it is a nonsense answer and is not used

    f. $[H_2] = 1.000 - 0.935 = 0.065$ M

    g. $[I_2] = 2.000 - 0.935 = 1.065$ M

    h. $[HI] = 2 \times 0.935 = 1.870$ M

    i. Proof: $K_c = [1.870]^2 / [0.065][1.065] = 50.52$

4. The decomposition of phosphorus pentachloride has an equilibrium constant value in terms of pressure of 0.497 at 500 K. If the starting pressure of PCl_5 is 1.66 atm what are the equilibrium partial pressures of the reactants and products?

    a. $PCl_{5\,(g)} \Leftrightarrow PCl_{3\,(g)} + Cl_{2\,(g)}$

    b.

	$[PCl_5]$	$[PCl_3]$	$[Cl_2]$
initial	1.66	0	0
change	-x	+x	+x
eqb	1.66 - x	x	x

c. $K_p = [PCl_3][Cl_2]/[PCl_5] = [x][x]/[1.66 - x]$

d. Must use quadratic equation to solve for x; x = 0.693 and -1.190

e. Since when x = -1.190 negative equilibrium concentrations result, it is a nonsense answer and is not used

f. $[PCl_5] = 1.66 - 0.693 = 0.967$

g. $[PCl_3] = 0.693$

h. $[Cl_2] = 0.693$

i. Proof: $K_p = [PCl_3][Cl_2]/[PCl_5] = [0.693][0.693]/[0.967] = 0.497$

VI. LeChatelier's principle

A. A system at equilibrium is stable (i.e., at an energy minima). If the system is disturbed the system will shift so as to minimize the effects of the disturbance and restore equilibrium (return to a lower energy state)

1. Concentration effects

a. Example: $N_2 + 3\ H_2 \Leftrightarrow 2\ NH_3$ and the effects of various concentration changes on the equilibrium

b. Increase in [rxt]: forward reaction

c. Increase in [prod]: reverse reaction

d. Decrease in [rxt]: reverse reaction

e. Decrease in [prod]: forward reaction

2. Temperature effects

a. If a reaction is endothermic or exothermic, LeChatelier's principle explains how changes in temperature effect the reaction

b. Exothermic: heat is treated as a product

i. Heat added: reverse reaction

ii. Heat removed: forward reaction

c. Endothermic: heat is treated as a reactant

i. Heat added: forward reaction

ii. Heat removed: reverse reaction

   d. Examples

      i. $CH_4 + 2\ O_2 <=> CO_2 + 2\ H_2O$ + heat

      ii. heat + $2\ NOCl_{(g)} <=> 2\ NO_{(g)} + Cl_{2(g)}$

3. Pressure effects

   a. Pressure changes that result from changing the partial pressure of a reactant or product gas cause the same effect as a concentration change

   b. Pressure changes that are caused by a volume change

      i. Volume decreases result in increases in the concentration of gaseous species; the equilibrium shifts in the direction of the fewest number of moles of gas

      ii. Volume increases result in decreases in the concentration of gaseous species; the equilibrium shifts in the direction of the greater number of moles of gas

      iii. If there are equal number of moles of gases on the reactant and product sides of the equation, a volume change will not affect the equilibrium

   c. Inert gases may change the total pressure of the system but since they do not affect the partial pressures of reactant and product gases they do not affect the equilibrium

4. Catalysts affect the rate of reaction but do not influence the composition of the equilibrium, i.e., K_c remains the same

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