Chem 1B Name:_____

Chapter 13 Exercises

Exercises #1

1. Consider the following reaction: $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$

(a) In one experiment 1.0 mole of H_2O and 1.0 mole of CO are placed in a sealed flask and heated to 350°C. In the second experiment 1.0 mole of H_2 and CO_2 are placed in another sealed flask of the same volume and heated to 350°C. After equilibrium is reached in both cases, is there any difference in the composition of the mixtures in the two flasks? Explain.

(b) If some ^{14}C-labeled CO molecules are introduced into the equilibrium mixture in the above reaction (without disturbing the equilibrium, will the ^{14}C be found only in the CO or will some be found in the CO_2? Explain.

2. (A) Write the expressions for the equilibrium constant K_c for the following equilibrium systems.

(*i*) $CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3\,H_2(g)$

(*ii*) $N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$

(*iii*) $(NH_4)_2CO_3(s) \rightleftharpoons CO_2(g) + 2\,NH_3(g) + H_2O(g)$

(*iv*) $NH_3(g) + HCl(g) \rightleftharpoons NH_4Cl(s)$

(*v*) $HNO_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NO_2^-(aq)$

(B) For equations (*i*) – (*iv*), write the expressions for the equilibrium constant K_p.

3. An equilibrium mixture of H_2, N_2, and NH_3 gases at 500 K is found to contain\ the following concentrations: $[H_2] = 1.197\ M$, $[N_2] = 0.399\ M$, and $[NH_3] = 0.203\ M$.
(a) Determine the equilibrium constant K_c and K_p for the following reaction at 500 K.
($R = 0.08206\ ^{L.atm}/_{mol.K}$)

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

(b) What are the values of K_c and K_p for the given reversed reaction at 500 K?

$$NH_3(aq) \rightleftharpoons \tfrac{1}{2}\,N_2(g) + {}^{3}/_{2}\,H_2(g)$$

(c) If the concentration of N_2 is increased by 1.000 mol/L in which direction will the net reaction occur to reach new equilibrium position? How would the concentrations of H_2 and NH_3 change in the new equilibrium mixture? Will each of them increase or decrease or not change in the new equilibrium?

4. Explain the following statement: "for a given reaction at a fix temperature, there is only one value for the equilibrium constant (K_c or K_p), but there will be an infinite number of equilibrium positions."

5. Consider the following data obtained for the reaction: $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ at 500 K.

	Initial Concentration, *M*			Concentrations at Equilibrium, *M*		
Expt. #	$[N_2]$	$[H_2]$	$[NH_3]$	$[N_2]$	$[H_2]$	$[NH_3]$
1	1.000	1.000	0	0.921	0.763	0.157
2	1.000	3.000	1.000	0.938	2.816	1.123
3	0	0	1.000	0.399	1.197	0.203

Show that, at constant temperature the equilibrium constant K_c is the same regardless of the composition of the equilibrium mixture.

6. Consider the reaction: $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$.
A mixture containing 1.000 mole of N_2 and 3.000 moles of H_2 are placed in a 10.0-L reaction vessel and allowed to react at 523 K. When equilibrium is established, the concentration of NH_3 was found to be 0.0112 mol/L. What are the concentrations (in mol/L) of N_2 and H_2 at equilibrium? Calculate the *equilibrium constants* K_c and K_p for the above reaction at 523 K. (R = 0.0821 L.atm/(K.mol))

7. When 1.000 mole of PCl_5 is introduced into a 5.000 L container at 500 K, 78.50% of the PCl_5 dissociates to give an equilibrium mixture of PCl_5, PCl_3, and Cl_2. Calculate the values of K_c and K_p at 500 K for the following equilibrium.

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

8. For the equilibrium: $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$, $K_p = 1.42$ at a certain temperature.

If the initial partial pressures are $P_{PCl5} = 3.00$ atm, $P_{PCl3} = 2.00$ atm, and $P_{Cl2} = 1.50$ atm, what are the partial pressures of PCl_5, PCl_3, and Cl_2 at equilibrium?

9. The reaction: $COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g)$ has $K_c = 1.3 \times 10^{-4}$ at a certain temperature.

If the initial concentration of $COCl_2$ was 0.500 *M* and there were initially no CO or Cl_2, what are the concentrations of $COCl_2$, CO, and Cl_2 at equilibrium?

10. Nitrosyl bromide, NOBr, decomposes according to the following equation:

$$2\ NOBr(g) \rightleftharpoons 2\ NO(g) + Br_2(g)$$

A 0.64 mole sample of nitrosyl bromide is placed in an evacuated, sealed 1.00-L reaction vessel. When the reaction reaches equilibrium at a certain temperature, the concentration of NOBr in the equilibrium mixture is 0.46 *M*. (a) Calculate the concentration of NO and Br_2, respectively, at equilibrium. What is the equilibrium constant K_c for the reaction?

Chem 1B Name:_____

Chapter 13 Exercises

Exercises #2

1. The reaction: $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ has $K_p = 3.6 \times 10^{-5}$ at 500 K.

   A mixture contains H_2, N_2, and NH_3 such that their partial pressures are 2.76 atm, 0.92 atm, and 0.16 atm, respectively. Determine if it is at equilibrium? If not, predict in which direction will the net reaction occur to reach equilibrium?

2. What is the difference between *equilibrium constant* (K_c or K_p) and *reaction quotient* (Q_c or Q_p)?

3. Given the following equilibrium:

   $N_2(g) + ½\ O_2(g) \rightleftharpoons N_2O(g)$; $K_c = 2.4 \times 10^{-18}$

   $N_2(g) + O_2(g) \rightleftharpoons 2\ NO(g)$; $K_c = 4.1 \times 10^{-30}$

   Calculate the equilibrium constant for the following reactions:

   (a) $N_2O(g) + ½\ O_2(g) \rightleftharpoons 2\ NO(g)$;

   (b) $4\ NO(g) \rightleftharpoons 2\ N_2O(g) + O_2(g)$.

4. Given the equilibrium constants for the following reactions at a certain temperature,

   (a) $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$; $K_c = 1.0 \times 10^5$

   (b) $CO(g) + 2\ H_2(g) \rightleftharpoons CH_3OH(g)$; $K_c = 1.4 \times 10^7$

   Calculate the equilibrium constant for the following reaction at the same temperature.

   $CO_2(g) + 3\ H_2(g) \rightleftharpoons CH_3OH(g) + H_2O(g)$

5. The reaction: $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ has $K_c = 55$ at 350°C.

   A mixture containing 1.000 mole each of H_2 and I_2 is introduced into an evacuated 1.00-L reaction vessel and sealed. When the reaction reaches equilibrium at 350°C, what are the molar concentrations of H_2, I_2, and HI, respectively, in the equilibrium mixture?

6. Ammonium hydrogen sulfide decomposes according to the following reaction:

   $NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$; $K_p = 0.11$ at 250°C.

   If 5.10 g of $NH_4HS(s)$ is placed in a sealed 5.0-L container, what is the partial pressure of $H_2S(g)$ when the reaction reaches equilibrium at 250°C? How many grams of $NH_4HS(s)$ remains at equilibrium?

7. The decomposition of solid ammonium carbamate, $NH_4(CO_2NH_2)$, to gaseous ammonia and carbon dioxide is an endothermic reaction.

$$NH_4(CO_2NH_2)(s) \rightleftharpoons 2\ NH_3(g) + CO_2(g)$$

(a) When a solid sample of $NH_4(CO_2NH_2)(s)$ is introduced into an evacuated flask at 25°C, the total pressure of the gas at equilibrium is 0.116 atm. What are the partial pressures of NH_3 and CO_2, respectively, and the equilibrium constant K_p at 25°C?

(b) Given that the decomposition reaction is at equilibrium, how would the following changes affect the total quantity of NH_3 in the flask once equilibrium is re-established? Briefly explain your answer.

(*i*) Adding CO_2 (*ii*) Adding solid $NH_4(CO_2NH_2)$ (*iii*) Removing CO_2

(*iv*) Adding nitrogen gas (*v*) Increasing the total volume (*vi*) Increasing the temperature

8. Nitric oxide, a significant air pollutant, is formed from the reaction of nitrogen and oxygen at high temperature, such as in an automobile engine. The reaction is endothermic:

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g); \qquad \Delta H^o = 180\ kJ$$

(a) At constant temperature, does the equilibrium amount of nitric oxide increase, decrease, or stays the same if pressure is increased as a result of volume compression? Explain.

(b) Would more nitric oxide be formed if the engine block becomes overheated? Explain.

9. The commercial production of hydrogen gas by steam-reformation of methane gas involves an endothermic reaction represented by the following equation.

$$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g); \quad \Delta H^o = 206\ kJ$$

Use the Le Chatelier's principle to explain how each of the following changes will alter the amount of H_2 gas at equilibrium.

(a) CO is removed from the equilibrium mixture.

(b) Water vapor is removed

(c) CH_4 gas is removed

(d) CO is added

(e) Argon gas is added, which causes the total pressure to increase.

(f) The equilibrium mixture is transferred into a larger vessel.

(g) A catalyst is added to the equilibrium mixture.

(h) The temperature of the equilibrium mixture is increased

Answers:

Exercise #1

1. (a) Compositions of both mixtures are the same. For a given equation, there is only one value of the equilibrium constant *K* at a given temperature, regardless how the reaction occurs. System contains equal moles of products and reactants. If initial moles of reactants and products are the same in both mixtures, their compositions at equilibrium are also the same to yield same value of *K*.

   (b) Carbon-14 will appear in both CO and CO_2; equilibrium is a dynamic state – forward and reversed reactions continue at equilibrium.

2. (a) Write the expressions for the equilibrium constant K_c for the following equilibrium systems.

   (*i*) $CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3\,H_2(g)$; $K_c = \dfrac{[CO][H_2]^3}{[CH_4][H_2O]}$

   (*ii*) $N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$; $K_c = \dfrac{[NH_3]^2}{[N_2][H_2]^3}$

   (*iii*) $(NH_4)_2CO_3(s) \rightleftharpoons CO_2(g) + 2\,NH_3(g) + H_2O(g)$; $K_c = [CO_2][NH_3]^2[H_2O]$

   (*iv*) $NH_3(g) + HCl(g) \rightleftharpoons NH_4Cl(s)$; $K_c = \dfrac{1}{[NH_3][HCl]}$

   (*v*) $HNO_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NO_2^-(aq)$; $K_c = \dfrac{[H_3O^+][NO_2^-]}{[HNO_2]}$

   (b) For equations (*i*) – (*iv*), write the expressions for the equilibrium constant K_p.

   (*i*) $K_p = \dfrac{(P_{CO})(P_{H2})^3}{(P_{CH_4})(P_{H_2O})}$; (*ii*) $K_p = \dfrac{(P_{NH_3})^2}{(P_{N_2})(P_{H_2})^3}$; (*iii*) $K_p = (P_{CO})(P_{NH3})^2(P_{H2O})$

   (*iv*) $K_p = \dfrac{1}{(P_{N_2})(P_{HCl})^3}$; (*v*) $K_p = 1$ (no gas)

3. (a) $K_c = 0.0602$; $K_p = 3.58 \times 10^{-5}$; (b) $K_c = 4.08$; $K_p = 167$

4. At constant temperature the values of K_c and K_p are fixed (constant), but chemical compositions at equilibrium can vary.

5. #1: $K_c = 0.0603$; #2: $K_c = 0.0602$; #3: $K_c = 0.0602$

6. $[N_2] = 0.0944\ M$; $[H_2] = 0.2832\ M$; $[NH_3] = 0.0112\ M$; $K_c = 0.0585$; $K_p = 3.18 \times 10^{-5}$

7. $K_c = 0.573$; $K_p = 23.5$

8. $P_{PCl5} = 2.76$; $P_{PCl3} = 2.24$; $P_{Cl2} = 1.74$ atm

9. $[COCl_2] = 0.492\ M$; $[CO] = [Cl_2] = 8.1 \times 10^{-3}\ M$;

10. $K_c = 0.014$

Exercise #2

1. $Q_p = 1.3 \times 10^{-3}$; net reaction is to the left.

2. K_c value is calculated using concentrations measured when the system is at equilibrium. For a given reaction the value is constant at a given temperature. Q_c value is calculated using concentrations that are not necessarily at equilibrium; the value is not constant as it depends on the compositions of the mixture at any particular point during the reaction. If $Q_c = K_c$, the system has reached equilibrium, otherwise it is not.

3. (a) $K_c = 1.7 \times 10^{-12}$; (b) $K_c = 3.4 \times 10^{23}$

4. $K_c = 1.4 \times 10^{2}$

5. $[H_2] = [I_2] = 0.21\ M$; $[HI] = 1.6\ M$

6. $P_{H2S} = 0.33$ atm; 3.13 g

7. (a) $P_{NH3} = 0.077$ atm (59 torr); $P_{CO2} = 0.039$ atm (29 torr); $K_p = 2.3 \times 10^{-4}$;

   (b) (*i*) NH_3 decreases; equilibrium shifts left;
   (*ii*) No change; solid concentration is constant regardless of quantity;
   (*iii*) NH_3 increases; equilibrium shifts right;
   (*iv*) No change; N_2 not part of system – does not affect P_{NH3} nor P_{CO};
   (*v*) Both NH_3 and CO increase; equilibrium shifts right – P_{NH3} & P_{CO} drop when volume expands;
   (*vi*) Both NH_3 and CO increase; equilibrium shift right – endothermic reaction favors high T.

8. (a) NO stays the same; equilibrium does not shift left or right – equal # of gas moles on both sides;

   (b) Yes; equilibrium shifts right – reaction is endothermic.

9. (a) H_2 increases; equilibrium shifts right;
   (b) H_2 decreases; equilibrium shift left;
   (c) H_2 decreases; equilibrium shifts left;
   (d) H_2 decreases; equilibrium shifts left;
   (e) No change on H_2; Argon not part of system – Partial pressures of equilibrium mixture not affected;
   (f) H_2 increases; volume expands, partial pressures drop, $Q_p < K_p$, and equilibrium shifts right.
   (g) No change in equilibrium and no change on H_2;
   (h) H_2 increases; equilibrium shifts right – endothermic reaction favors high temperature.