Exercises #1

1. Consider the following reaction: \( \text{CO(g)} + \text{H}_2\text{O(g)} \rightleftharpoons \text{CO}_2(g) + \text{H}_2(g) \)

   (a) In one experiment 1.0 mole of \( \text{H}_2\text{O} \) and 1.0 mole of \( \text{CO} \) are placed in a sealed flask and heated to 350\(^\circ\)C. In the second experiment 1.0 mole of \( \text{H}_2 \) and \( \text{CO}_2 \) are placed in another sealed flask of the same volume and heated to 350\(^\circ\)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 \(^{14}\text{C} \)-labeled \( \text{CO} \) molecules are introduced into the equilibrium mixture in the above reaction (without disturbing the equilibrium, will the \(^{14}\text{C} \) be found only in the \( \text{CO} \) or will some be found in the \( \text{CO}_2 \)? Explain.

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

   (i) \( \text{CH}_4(g) + \text{H}_2\text{O(g)} \rightleftharpoons \text{CO(g)} + \text{3 H}_2(g) \)

   (ii) \( \text{N}_2(g) + \text{3 H}_2(g) \rightleftharpoons 2 \text{NH}_3(g) \)

   (iii) \( (\text{NH}_4)_2\text{CO}_3(s) \rightleftharpoons \text{CO}_2(g) + 2 \text{NH}_3(g) + \text{H}_2\text{O(g)} \)

   (iv) \( \text{NH}_3(g) + \text{HCl(g)} \rightleftharpoons \text{NH}_4\text{Cl(s)} \)

   (v) \( \text{HNO}_2(aq) + \text{H}_2\text{O(l)} \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{NO}_2^-(aq) \)

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

3. An equilibrium mixture of \( \text{H}_2 \), \( \text{N}_2 \), and \( \text{NH}_3 \) gases at 500 K is found to contain the following concentrations: \([\text{H}_2]\) = 1.197 \( M \), \([\text{N}_2]\) = 0.399 \( M \), and \([\text{NH}_3]\) = 0.203 \( M \).

   (a) Determine the equilibrium constant \( K_c \) and \( K_p \) for the following reaction at 500 K.

   \[ \text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g) \]

   (R = 0.08206 \( \text{L} \cdot \text{atm} / \text{mol} \cdot \text{K} \))

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

   \[ \text{NH}_3(aq) \rightleftharpoons \frac{1}{2} \text{N}_2(g) + \frac{3}{2} \text{H}_2(g) \]

   (c) If the concentration of \( \text{N}_2 \) is increased by 1.000 \( \text{mol/L} \) in which direction will the net reaction occur to reach new equilibrium position? How would the concentrations of \( \text{H}_2 \) and \( \text{NH}_3 \) 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: \( \text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g) \) at 500 K.

<table>
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<tr>
<th>Expt. #</th>
<th>([\text{N}_2])</th>
<th>([\text{H}_2])</th>
<th>([\text{NH}_3])</th>
<th>([\text{N}_2])</th>
<th>([\text{H}_2])</th>
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<td>0.763</td>
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<td>1.123</td>
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<tr>
<td>3</td>
<td>0</td>
<td>0</td>
<td>1.000</td>
<td>0.399</td>
<td>1.197</td>
<td>0.203</td>
</tr>
</tbody>
</table>

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: \( \text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g) \).
A mixture containing 1.000 mole of \( \text{N}_2 \) and 3.000 moles of \( \text{H}_2 \) are placed in a 10.0-L reaction vessel and allowed to react at 523 K. When equilibrium is established, the concentration of \( \text{NH}_3 \) was found to be 0.0112 mol/L. What are the concentrations (in mol/L) of \( \text{N}_2 \) and \( \text{H}_2 \) at equilibrium? Calculate the equilibrium constants \( K_c \) and \( K_p \) for the above reaction at 523 K. (\( R = 0.0821 \text{ L.atm/(K.mol)} \)).

7. When 1.000 mole of \( \text{PCl}_5 \) is introduced into a 5.000 L container at 500 K, \( 78.50\% \) of the \( \text{PCl}_5 \) dissociates to give an equilibrium mixture of \( \text{PCl}_3 \), \( \text{PCl}_3 \), and \( \text{Cl}_2 \). Calculate the values of \( K_c \) and \( K_p \) at 500 K for the following equilibrium.

\[ \text{PCl}_5(g) \rightleftharpoons \text{PCl}_3(g) + \text{Cl}_2(g), \]

8. For the equilibrium: \( \text{PCl}_3(g) \rightleftharpoons \text{PCl}_3(g) + \text{Cl}_2(g), \quad K_p = 1.42 \) at a certain temperature.
If the initial partial pressures are \( P_{\text{PCl}_5} = 3.00 \text{ atm} \), \( P_{\text{PCl}_3} = 2.00 \text{ atm} \), and \( P_{\text{Cl}_2} = 1.50 \text{ atm} \), what are the partial pressures of \( \text{PCl}_5 \), \( \text{PCl}_3 \), and \( \text{Cl}_2 \) at equilibrium?

9. The reaction: \( \text{COCl}_2(g) \rightleftharpoons \text{CO}(g) + \text{Cl}_2(g) \) has \( K_c = 1.3 \times 10^{-3} \) at a certain temperature.
If the initial concentration of \( \text{COCl}_2 \) was 0.500 M and there were initially no \( \text{CO} \) or \( \text{Cl}_2 \), what are the concentrations of \( \text{COCl}_2 \), \( \text{CO} \), and \( \text{Cl}_2 \) at equilibrium?

10. Nitrosyl bromide, \( \text{NOBr} \), decomposes according to the following equation:

\[ 2 \text{NOBr}(g) \rightleftharpoons 2\text{NO}(g) + \text{Br}_2(g) \]
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 \( \text{NOBr} \) in the equilibrium mixture is 0.46 M. (a) Calculate the concentration of \( \text{NO} \) and \( \text{Br}_2 \), respectively, at equilibrium. What is the equilibrium constant \( K_c \) for the reaction?
Exercises #2
1. The reaction: \( \text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g) \) has \( K_p = 3.6 \times 10^{-5} \) at 500 K.

A mixture contains \( \text{H}_2 \), \( \text{N}_2 \), and \( \text{NH}_3 \) 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 \( (K_c \text{ or } K_p) \) and reaction quotient \( (Q_c \text{ or } Q_p) \)?

3. Given the following equilibrium:
   \( \text{N}_2(g) + \frac{1}{2} \text{O}_2(g) \rightleftharpoons \text{N}_2\text{O}(g); \quad K_c = 2.4 \times 10^{18} \)
   \( \text{N}_2(g) + \text{O}_2(g) \rightleftharpoons 2 \text{NO}(g); \quad K_c = 4.1 \times 10^{30} \)

Calculate the equilibrium constant for the following reactions:
   (a) \( \text{N}_2\text{O}(g) + \frac{1}{2} \text{O}_2(g) \rightleftharpoons 2 \text{NO}(g); \)
   (b) \( 4 \text{NO}(g) \rightleftharpoons 2 \text{N}_2\text{O}(g) + \text{O}_2(g). \)

4. Given the equilibrium constants for the following reactions at a certain temperature,
   (a) \( \text{CO}(g) + \text{H}_2\text{O}(g) \rightleftharpoons \text{CO}_2(g) + \text{H}_2(g); \quad K_c = 1.0 \times 10^5 \)
   (b) \( \text{CO}(g) + 2 \text{H}_2(g) \rightleftharpoons \text{CH}_3\text{OH}(g); \quad K_c = 1.4 \times 10^7 \)

Calculate the equilibrium constant for the following reaction at the same temperature.
   \( \text{CO}_2(g) + 3 \text{H}_2(g) \rightleftharpoons \text{CH}_3\text{OH}(g) + \text{H}_2\text{O}(g) \)

5. The reaction: \( \text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2\text{HI}(g) \) has \( K_c = 55 \) at 350°C.

A mixture containing 1.000 mole each of \( \text{H}_2 \) and \( \text{I}_2 \) 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 \( \text{H}_2 \), \( \text{I}_2 \), and \( \text{HI} \), respectively, in the equilibrium mixture?

6. Ammonium hydrogen sulfide decomposes according to the following reaction:
   \( \text{NH}_4\text{HS}(s) \rightleftharpoons \text{NH}_3(g) + \text{H}_2\text{S}(g); \quad K_p = 0.11 \) at 250°C.

If 5.10 g of \( \text{NH}_4\text{HS}(s) \) is placed in a sealed 5.0-L container, what is the partial pressure of \( \text{H}_2\text{S}(g) \) when the reaction reaches equilibrium at 250°C? How many grams of \( \text{NH}_4\text{HS}(s) \) remains at equilibrium?
7. The decomposition of solid ammonium carbamate, \( \text{NH}_4(\text{CO}_2\text{NH}_2) \), to gaseous ammonia and carbon dioxide is an endothermic reaction.

\[
\text{NH}_4(\text{CO}_2\text{NH}_2)(s) \rightleftharpoons 2 \text{NH}_3(g) + \text{CO}_2(g)
\]

(a) When a solid sample of \( \text{NH}_4(\text{CO}_2\text{NH}_2)(s) \) 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 \( \text{NH}_3 \) and \( \text{CO}_2 \), 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 \( \text{NH}_3 \) in the flask once equilibrium is re-established? Briefly explain your answer.

(i) Adding \( \text{CO}_2 \)  
(ii) Adding solid \( \text{NH}_4(\text{CO}_2\text{NH}_2) \)  
(iii) Removing \( \text{CO}_2 \)

(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:

\[
\text{N}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{NO}(g); \quad \Delta H^\circ = 180 \text{ kJ}
\]

(a) At constant temperature, does the equilibrium amount of nitric oxide increase, decrease, or stay 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.

\[
\text{CH}_4(g) + \text{H}_2\text{O}(g) \rightleftharpoons \text{CO}(g) + 3\text{H}_2(g); \quad \Delta H^\circ = 206 \text{ kJ}
\]

Use the Le Chatelier’s principle to explain how each of the following changes will alter the amount of \( \text{H}_2 \) gas at equilibrium.

(a) CO is removed from the equilibrium mixture.

(b) Water vapor is removed

(c) \( \text{CH}_4 \) 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) $\text{CH}_4(g) + \text{H}_2\text{O}(g) \rightleftharpoons \text{CO}(g) + 3 \text{H}_2(g)$;
   $$K_c = \frac{[\text{CO}][\text{H}_2]^3}{[\text{CH}_4][\text{H}_2\text{O}]}$$

   (ii) $\text{N}_2(g) + 3 \text{H}_2(g) \rightleftharpoons 2 \text{NH}_3(g)$;
   $$K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$$

   (iii) $(\text{NH}_4)\text{CO}_3(s) \rightleftharpoons \text{CO}_2(g) + 2 \text{NH}_3(g) + \text{H}_2\text{O}(g)$;
   $$K_c = [\text{CO}_2][\text{NH}_3]^2[\text{H}_2\text{O}]$$

   (iv) $\text{NH}_3(g) + \text{HCl}(g) \rightleftharpoons \text{NH}_4\text{Cl}(s)$;
   $$K_c = \frac{1}{[\text{NH}_3][\text{HCl}]}$$

   (v) $\text{HNO}_2(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{NO}_2^-(aq)$;
   $$K_c = \frac{[\text{H}_3\text{O}^+][\text{NO}_2^-]}{[\text{HNO}_2]}$$

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

   (i) $K_p = \frac{(P_{\text{CO}})(P_{\text{H}_2})^3}{(P_{\text{CH}_4})(P_{\text{H}_2\text{O}})}$;
   (ii) $K_p = \frac{(P_{\text{NH}_3})^2}{(P_{\text{N}_2})(P_{\text{H}_2})^3}$;
   (iii) $K_p = (P_{\text{CO}})(P_{\text{NH}_3})^2(P_{\text{H}_2\text{O}})$

   (iv) $K_p = \frac{1}{(P_{\text{N}_2})(P_{\text{HCl}})}$;
   (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. $[\text{N}_2] = 0.0944 \text{ M}; [\text{H}_2] = 0.2832 \text{ M}; [\text{NH}_3] = 0.0112 \text{ M}; K_c = 0.0585; K_p = 3.18 \times 10^{-5}$

7. $K_c = 0.573; K_p = 23.5$

8. $P_{\text{PCl}_5} = 2.76; P_{\text{PCl}_3} = 2.24; P_{\text{Cl}_2} = 1.74 \text{ atm}$

9. $[\text{COCl}_2] = 0.492 \text{ M}; [\text{CO}] = [\text{Cl}_2] = 8.1 \times 10^{-3} \text{ M}$; 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. $P_{H_2S} = 0.33 \text{ atm}; 3.13 \text{ g}$

7. (a) $P_{NH_3} = 0.077 \text{ atm (59 torr)}; P_{CO_2} = 0.039 \text{ atm (29 torr)}; K_p = 2.3 \times 10^{-4}$; 
   (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 $P_{NH_3}$ nor $P_{CO}$; 
   (v) Both $NH_3$ and CO increase; equilibrium shifts right – $P_{NH_3} \& P_{CO}$ 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.