CH 13 HOMEWORK

a. Read CH 13
b. Review your notes.
c. Answer the following:

1. Characterize a system at equilibrium with respect to each of the following:
   (a) The rates of the forward and reverse reactions.

   The rates of the forward and reverse reactions are equal at equilibrium.

   (b) The overall composition of the reaction mixture.

   The overall composition of the reaction mixture will not change as long as the temperature is constant.

2. Is the following statement true or false? “Reactions with large equilibrium constants are very fast.” Explain.
   False - equilibrium and kinetics are independent of one another.

3. Distinguish between the terms equilibrium constant and equilibrium position.

   The equilibrium constant is a number that tells us the relative concentrations or products of reactants and products at equilibrium. An equilibrium position is a set of concentrations or pressures that satisfy the equilibrium constant expression. More than one equilibrium position can satisfy the equilibrium constant expression.

4. There is only one value of the equilibrium constant for a particular system at a particular temperature, but there are an infinite number of equilibrium positions. Explain.

   The equilibrium position depends on the initial concentration. Since there are an infinite number of initial concentrations, there are an infinite number of equilibrium positions. Each one of these equilibrium positions will give the same value for the equilibrium constant.

5. Consider the reaction:

   \[ \text{H}_2\text{O} (g) + \text{CO} (g) \leftrightarrow \text{H}_2 (g) + \text{CO}_2 (g) \]

   In one experiment, 1.00 mol H₂O (g) and 1.00 mol CO (g) are put into a flask and heated to 350°C. In a second experiment, 1.00 mol H₂ (g) and 1.00 mol CO₂ (g) are put into another flask with the same volume as the first and heated to 350°C. After equilibrium is reached, will there be any difference in the composition of the mixtures in the two flasks?

   No, it doesn’t matter from which direction the equilibrium position is reached.

   Both experiments will give the same equilibrium position since both experiments started with stoichiometric amounts of reactants and products.
6. Write the equilibrium expression (K) for each of the following gas-phase reactions:

(a) \( N_2 (g) + O_2 (g) \leftrightarrow 2 \text{NO} (g) \)
\[
K = \frac{[\text{NO}]^2}{[N_2][O_2]}
\]

(b) \( \text{SiH}_4 (g) + 2 \text{Cl}_2 (g) \leftrightarrow \text{SiCl}_4 (g) + 2 \text{H}_2 (g) \)
\[
K = \frac{[\text{SiCl}_4][\text{H}_2]^2}{[\text{SiH}_4][\text{Cl}_2]^2}
\]

7. At a given temperature, \( K = 1.3 \times 10^{-2} \) for the reaction
\( N_2 (g) + 3 \text{H}_2 (g) \leftrightarrow \frac{4}{3} \text{NH}_3 (g) \)

Calculate the values of K for the following reactions at this temperature.

(a) \( \frac{1}{3} N_2 (g) + \frac{3}{2} \text{H}_2 (g) \leftrightarrow \text{NH}_3 (g) \)
\[
K' = K^n = (1.3 \times 10^{-2})^{\frac{3}{2}} = 0.11
\]

(b) \( 2 \text{NH}_3 (g) \leftrightarrow N_2 (g) + 3 \text{H}_2 (g) \)
\[
K' = \frac{1}{K} = \frac{1}{0.013} = 76.9 = \boxed{77}
\]

(c) \( \text{NH}_3 (g) \leftrightarrow \frac{1}{3} N_2 (g) + \frac{3}{2} \text{H}_2 (g) \)
\[
K' = \left( \frac{1}{K} \right)^{\frac{3}{2}} = \left( \frac{1}{0.013} \right)^{\frac{3}{2}} = 2.8
\]

(d) \( 2 \text{N}_2 (g) + 6 \text{H}_2 (g) \leftrightarrow 4 \text{NH}_3 (g) \)
\[
K' = K^n = (0.013)^{\frac{2}{3}} = 1.7 \times 10^{-4}
\]

8. At high temperatures, elemental nitrogen and oxygen react with one another to form nitrogen monoxide:
\( N_2 (g) + O_2 (g) \leftrightarrow 2 \text{NO} (g) \)

Suppose the system is analyzed at a particular temperature and the equilibrium concentrations are found to be \([N_2] = 0.041 \text{ M}, [O_2] = 0.0078 \text{ M}, \text{and} [\text{NO}] = 4.7 \times 10^{-4} \text{ M}\). Calculate the value of K for the reaction.
\[
K = \frac{[\text{NO}]^2}{[N_2][O_2]} = \frac{\left(4.7 \times 10^{-4}\right)^2}{(0.041)(0.0078)} = \boxed{6.9 \times 10^{-4}}
\]
9. At a particular temperature a 2.00 L flask at equilibrium contains $2.80 \times 10^{-4}$ mol of $N_2$, $2.50 \times 10^{-5}$ mol of $O_2$, and $2.00 \times 10^{-2}$ mol $N_2O$. Calculate the value of $K$ at this temperature for the reaction:

$$2 \text{N}_2 (g) + O_2 (g) \rightleftharpoons 2 \text{N}_2\text{O} (g)$$

\[
K = \frac{[\text{N}_2\text{O}]^2}{[\text{N}_2]^2 [O_2]} = \frac{(0.01)^2}{(1.4 \times 10^{-4})(1.25 \times 10^{-5})} = 4.08 \times 10^8
\]

10. Distinguish between the terms *equilibrium constant* and *reaction quotient*.

They both have the same form. For $K$ we use equilibrium concentrations and for $Q$ we use any concentration. $Q$ is used to determine how far the reaction is from the equilibrium position.

11. The magnitude of the equilibrium constant is related to the tendency of a reaction to occur. Explain.

The magnitude of $K$ tells us whether a reaction has mostly products or reactants at equilibrium. When $K$ is large, products dominate. When $K$ is small, reactants dominate.

12. For the reaction

$$\text{H}_2 (g) + \text{Br}_2 (g) \rightleftharpoons 2 \text{HBr} (g)$$

$K_p = 3.5 \times 10^4$ at 1495K. What is the value of $K_p$ for the following reactions at 1495K?

(a) $\text{HBr} (g) \rightleftharpoons \frac{1}{2} \text{H}_2 (g) + \frac{1}{2} \text{Br}_2 (g)$

$$K_p = \left( \frac{1}{K_p^\prime} \right)^{\frac{1}{2}} = \sqrt{3.5 \times 10^4} = 5.3 \times 10^{-3}$$

(b) $2 \text{HBr} (g) \rightleftharpoons \text{H}_2 (g) + \text{Br}_2 (g)$

$$K_p = \frac{1}{K_p^\prime} = 3.5 \times 10^4 = 2.9 \times 10^{-5}$$

(c) $\frac{1}{2} \text{H}_2 (g) + \frac{1}{2} \text{Br} (g) \rightleftharpoons \text{HBr} (g)$

$$K_p = K_p^\prime = \sqrt{3.5 \times 10^4} = 187$$
13. The following equilibrium pressures at a certain temperature were observed for the reaction:

\[
2 \text{NO}_2 (g) \leftrightarrow 2 \text{NO (g)} + \text{O}_2 (g)
\]

\[
P_{\text{NO}_2} = 0.55 \text{ atm} \quad P_{\text{NO}} = 6.5 \times 10^{-5} \text{ atm} \quad P_{\text{O}_2} = 4.5 \times 10^{-5} \text{ atm}
\]

Calculate the value of the equilibrium constant \( K_p \) at this temperature.

\[
K_p = \left( \frac{P_{\text{NO}}^2 P_{\text{O}_2}}{P_{\text{NO}_2}^2} \right) = \left( \frac{(6.5 \times 10^{-5})^2}{(4.5 \times 10^{-5})} \right) = 6.3 \times 10^{-13}
\]

14. At 25.0°C, \( K = 3.7 \times 10^9 \) for the reaction

\[
\text{CO (g) + Cl}_2 (g) \leftrightarrow \text{COCl}_2 (g)
\]

Calculate \( K_p \) at this temperature.

\[
K_p = K (RT)^{\Delta n} = (3.7 \times 10^9) \left( \frac{(0.0821)(298)}{1.5 \times 10^8} \right)^{-1}
\]

\[
= 1.5 \times 10^8
\]

15. At 1100 K, \( K_p = 0.25 \) for the reaction

\[
2 \text{SO}_2 (g) + \text{O}_2 (g) \leftrightarrow 2 \text{SO}_3 (g)
\]

Calculate \( K \) at this temperature.

\[
K = \left( \frac{(R)(T)}{\Delta n} \right) = 2.2 \times 10^{-8}
\]

16. Write the expression for \( K \) for the following reactions:

(a) \( P_4 (s) + 5 O_2 (g) \leftrightarrow P_4O_{10} (s) \)

\[
K = \frac{1}{[O_2]^5}
\]

(b) \( S_8 (s) + 8 O_2 (g) \leftrightarrow 8 SO_2 (g) \)

\[
K' = \frac{[SO_2]^8}{[O_2]^8}
\]
17. Write the expression for $K_p$ for the following reactions:

(a) $4 \text{KO}_2 (s) + 2 \text{H}_2\text{O} (g) \leftrightarrow 4 \text{KOH} (s) + 3 \text{O}_2 (g)$

$$K_p = \frac{(P_{\text{H}_2\text{O}})^2}{(P_{\text{O}_2})^3}$$

(b) $\text{CO}_2 (g) + \text{MgO} (s) \leftrightarrow \text{MgCO}_3 (s)$

$$K_p = \frac{1}{P_{\text{CO}_2}}$$

18. In a study of the reaction

$$3 \text{Fe} (s) + 4 \text{H}_2\text{O} (g) \leftrightarrow \text{Fe}_3\text{O}_4 (s) + 4 \text{H}_2 (g)$$

At 1200 K it was observed that when the equilibrium partial pressure of water vapor is 15.0 torr, the total pressure at equilibrium is 36.3 torr. Calculate the value of $K_p$ for this reaction at 1200 K. *Hint:* apply Dalton’s law of partial pressure.

$$P_{\text{H}_2\text{O}} = P_{\text{H}_2} + P_{\text{H}_2\text{O}}^0 = 36.3 \text{ torr}$$

$$P_{\text{H}_2\text{O}}^0 = 15.0 \text{ torr}$$

$$P_{\text{H}_2} = 21.3 \text{ torr}$$

$$K_p = \frac{(P_{\text{H}_2})^4}{(P_{\text{H}_2\text{O}})^4} = \frac{(0.0280263159)^4}{(0.0197368421)^4} = 4.07$$

19. The equilibrium constant, $K$, is $2.40 \times 10^3$ at a certain temperature for the reaction

$$2 \text{NO} (g) \leftrightarrow \text{N}_2 (g) + \text{O}_2 (g) \quad K = 2.40 \times 10^3 = \frac{[\text{N}_2][\text{O}_2]}{[\text{NO}]^2}$$

For which of the following sets of conditions is the system at equilibrium? For those that are not at equilibrium, in which direction will the system shift?

(a) A 1.00 L flask contains 0.0240 mol NO, 2.00 mol N$_2$, and 4.00 mol O$_2$.

$$Q = \frac{(2.0)(4.0)}{(0.024)^2} = 1.38 \times 10^4 \quad Q > K \text{ reaction shifts left}$$

(b) A 2.00 L flask contains 0.0320 mol NO, 0.0620 mol N$_2$, and 4.00 mol O$_2$.

$$Q = \frac{(0.032)(2.0)}{(0.016)^2} = 2.50 \times 10^2 \quad Q < K \text{ reaction shifts right}$$

(c) A 3.00 L flask contains 0.0600 mol NO, 2.40 mol N$_2$, and 1.70 mol O$_2$.

$$Q = \frac{(0.80)(0.57)}{(0.020)^2} = 1.1 \times 10^3 \quad Q < K \text{ reaction shifts right}$$

OVER
20. The equilibrium constant, \( K \), for the reaction

\[
\text{H}_2 (g) + \text{F}_2 (g) \rightleftharpoons 2 \text{ HF} (g)
\]

Has a value of \( 2.1 \times 10^3 \) at a particular temperature. When the system is analyzed at equilibrium at this temperature, the concentrations of \( \text{H}_2 (g) \) and \( \text{F}_2 (g) \) are both found to be 0.0021 M. What is the concentration of \( \text{HF} (g) \) in the equilibrium system under these conditions?

\[
K = \frac{[\text{HF}]}{[\text{H}_2][\text{F}_2]} = 2.1 \times 10^3
\]

\[
2.1 \times 10^3 = \frac{[\text{HF}]}{(0.0021)(0.0021)}
\]

\[
[\text{HF}] = \frac{(2.1 \times 10^3)(0.0021)}{(2.1 \times 10^3)(0.0021)} = 0.096 \text{ M}
\]

21. A 1.00 L flask is filled with 2.00 mol gaseous \( \text{SO}_2 \) and 2.00 mol gaseous \( \text{NO}_2 \) and heated. After equilibrium was reached, it was found that 1.30 mol of gaseous \( \text{NO} \) was present. Assume that the reaction

\[
\text{SO}_2 (g) + \text{NO}_2 (g) \rightleftharpoons \text{SO}_3 (g) + \text{NO} (g)
\]

occurs under these conditions. Calculate the value of the equilibrium constant, \( K \), for this reaction.

\[
K = \frac{[\text{SO}_3][\text{NO}]}{[\text{SO}_2][\text{NO}_2]} = \frac{(1.30)(1.30)}{(1.70)(1.70)} = 0.941
\]

22. At a particular temperature, 12.0 mol of \( \text{SO}_3 \) is placed into a 3.0 L rigid container, and the \( \text{SO}_3 \) dissociates by the reaction

\[
2 \text{ SO}_3 (g) \rightleftharpoons 2 \text{ SO}_2 (g) + \text{O}_2 (g)
\]

At equilibrium, 3.00 mol of \( \text{SO}_2 \) is present. Calculate \( K \) for this reaction.

\[
K = \frac{[\text{SO}_2]^2}{[\text{SO}_3]^2}
\]

\[
K = \frac{(1.0)^2(1.5)}{(3.0)^2} = 0.056
\]
23. At a particular temperature, $K = 3.75$ for the reaction

$$\text{SO}_2 (g) + \text{NO}_2 (g) \rightleftharpoons \text{SO}_3 (g) + \text{NO} (g)$$

If all four gases had initial concentrations of 0.800 M, calculate the equilibrium concentrations of the gases.

$$\text{SO}_2 (g) + \text{NO}_2 (g) \rightleftharpoons \text{SO}_3 (g) + \text{NO} (g)$$

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$$K = \frac{[\text{SO}_3][\text{NO}]}{[\text{SO}_2][\text{NO}_2]} = 3.75 = \frac{(8+\chi)(8+\chi)}{(8-\chi)(8-\chi)}$$

$$\frac{8+\chi}{8-\chi} = 1.936491673$$

$$8+\chi = 1.54919338 - 1.936491673\chi$$

$$0.936491673\chi = 0.549193385$$

$$\chi = 0.553182175$$

$$[\text{SO}_2] = [\text{NO}_2] = 0.8 - 0.553182175 = 0.2468178$$

$$[\text{SO}_3] = [\text{NO}] = 0.8 + 0.553182175 = 1.553182175$$

24. At a particular temperature, $K = 1.00 \times 10^2$ for the reaction

$$\text{H}_2 (g) + \text{I}_2 (g) \rightleftharpoons 2 \text{HI} (g)$$

In an experiment, 1.00 mol H$_2$ and 1.00 mol I$_2$ and 1.00 mol HI are introduced into a 1.00 L container. Calculate the concentrations of all species when equilibrium is reached.

$$\text{H}_2 (g) + \text{I}_2 (g) \rightleftharpoons 2 \text{HI} (g)$$

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$$K = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = 100 = \frac{(1+2\chi)^2}{(1-\chi)(1-\chi)}$$

$$10 = \frac{1+2\chi}{1-\chi}$$

$$10 - 10\chi = 1 + 2\chi$$

$$9 = 2\chi$$

$$\chi = 0.75$$

$$[\text{H}_2] = [\text{I}_2] = 1.00 - 0.75 = 0.25$$

$$[\text{HI}] = 1.00 + 2(0.75) = 2.50$$

OVER
25. At 2200°C, $K_p = 0.050$ for the reaction

$$\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2 \text{NO}(\text{g})$$

What is the partial pressure of NO in equilibrium with N$_2$ and O$_2$ that were placed in a flask at initial pressures of 0.800 atm and 0.200 atm, respectively?

Let $x$ be the partial pressure of NO at equilibrium.

$$\chi = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-0.05 \pm \sqrt{(0.05)^2 - 4(3.95)(-0.008)}}{2(3.95)} = 3.9 \times 10^{-2} \text{ atm}$$

$$\rho_{\text{NO}} = 2x = 3(3.9 \times 10^{-2} \text{ atm}) = 7.8 \times 10^{-2} \text{ atm}$$

26. At 35°C, $K = 1.60 \times 10^{-5}$ for the reaction

$$2 \text{NOCl}(\text{g}) \rightleftharpoons 2 \text{NO}(\text{g}) + \text{Cl}_2(\text{g})$$

Calculate the concentrations of all species at equilibrium for each of the following original mixtures:

(a) 2.00 mol pure NOCl in a 2.00 L flask

$$2 \text{NOCl}(\text{g}) \rightleftharpoons 2 \text{NO}(\text{g}) + \text{Cl}_2(\text{g})$$

Let $x$ be the partial pressure of NO at equilibrium.

$$K = \frac{[\text{NO}]^2 [\text{Cl}_2]}{[\text{NOCl}]^2} = 1.6 \times 10^{-5} = \frac{(2x)^2(x)}{(2x)^2}$$

Assume $x$ is small

$$1.6 \times 10^{-5} = \frac{4x^3}{1} = x^3$$

$$x = 0.016$$

Check: $1 - 2x = 1 - 0.032 = 0.968$

$$[\text{NO}] = 0.032 \text{ M}$$
$$[\text{Cl}_2] = 0.016 \text{ M}$$
$$[\text{NOCl}] = 1.00 \text{ M}$$
(b) 1.00 mol NOCl and 1.00 mol NO in a 1.00 L flask

\[ K = 1.6 \times 10^{-5} \]

\[
\begin{align*}
2 \text{NOCl}(g) & \rightleftharpoons 2 \text{NO}(g) + \text{Cl}_2(g) \\
I & = 1.0 \\
C & = -2\chi \\
E & = 1 + 2\chi
\end{align*}
\]

\[
K = \frac{[\text{NO}]^2 [\text{Cl}_2]}{[\text{NOCl}]^2} = 1.6 \times 10^{-5} = \frac{(1+2\chi)^2}{(1-2\chi)^2}
\]

Assume \( \chi \) is small,

\[
1.6 \times 10^{-5} \approx \frac{(1)^2}{(1)^2}
\]

\[
\chi = 1.6 \times 10^{-5}
\]

Check: \( 1 - 2(1.6 \times 10^{-5}) = .999967 \approx 1 \)

\[
[\text{NOCl}] = 1.0 \ M \\
[\text{NO}] = 1.0 \ M \\
[\text{Cl}_2] = 1.6 \times 10^{-5} \ M
\]

(c) 2.00 mol NOCl and 1.00 mol Cl\(_2\) in a 1.00 L flask

\[ K = 1.6 \times 10^{-5} \]

\[
\begin{align*}
2 \text{NOCl}(g) & \rightleftharpoons 2 \text{NO}(g) + \text{Cl}_2(g) \\
I & = 2.0 \\
C & = -2\chi \\
E & = 2 - 2\chi
\end{align*}
\]

\[
K = \frac{[\text{NO}]^2 [\text{Cl}_2]}{[\text{NOCl}]^2} = 1.6 \times 10^{-5} = \frac{(2\chi)^2}{(2 - 2\chi)^2}
\]

Assume \( \chi \) is small,

\[
1.6 \times 10^{-5} \approx \frac{4\chi^2}{4}
\]

\[
1.6 \times 10^{-5} = \chi^2
\]

\[
\chi = 0.004
\]

Check: \( 2 - (2)(0.004) = 1.992 \approx 2 \)

\[
[\text{NOCl}] = 2.0 \ M \\
[\text{NO}] = 0.008 \ M \\
[\text{Cl}_2] = 1.0 \ M
\]
27. Suppose the reaction system

\[ \text{UO}_2 \text{(s)} + 4 \text{HF (g)} \leftrightarrow \text{UF}_4 \text{(g)} + 2 \text{H}_2\text{O (g)} \]

has already reached equilibrium. Predict the effect that each of the following changes has on the equilibrium position. Tell whether the equilibrium will shift to the right, will shift to the left, or will not be affected.

(a) Additional \text{UO}_2 \text{(s)} is added to the system.

\textit{No effect}

(b) The reaction is performed in a glass reaction vessel; \text{HF (g)} attacks and reacts with glass.

\textit{Shift left}

(c) Water vapor is removed.

\textit{Shift right}

28. An important reaction in the commercial production of hydrogen is

\[ \text{CO (g)} + \text{H}_2\text{O (g)} \leftrightarrow \text{H}_2 \text{(g)} + \text{CO}_2 \text{(g)} \]

How will this system at equilibrium shift in each of the following five cases?

(a) Gaseous carbon dioxide is removed.

\textit{Shift right}

(b) Water vapor is added.

\textit{Shift right}

(c) The pressure is increased by adding helium gas.

\textit{No effect}

(d) The temperature is increased (the reaction is endothermic).

\textit{Shift right}

(e) The pressure is increased by decreasing the volume of the container.

\textit{No effect}
29. In which direction will the position of the equilibrium

\[ 2 \text{HI (g)} \leftrightarrow \text{H}_2 (g) + \text{I}_2 (g) \]

be shifted for each of the following changes?

(a) \( \text{H}_2 (g) \) is added.

**Shift left**

(b) \( \text{I}_2 (g) \) is removed.

**Shift right**

(c) \( \text{HI (g)} \) is removed.

**Shift left**

(d) some \( \text{Ar (g)} \) is added.

**No effect**

(e) The volume of the container is doubled.

**No effect**

(f) The temperature is decreased (the reaction is exothermic).

**Shift right**

30. The reaction to prepare methanol from hydrogen and carbon monoxide is

\[ \text{CO (g)} + 2 \text{H}_2 (g) \leftrightarrow \text{CH}_3\text{OH (g)} \]

is exothermic. If you wanted to use this reaction for the production of methanol commercially, would high or low temperatures favor a maximum yield? Explain your answer.

**Low temperatures favor a maximum yield.**