CHAPTER 13 LECTURE NOTES
CHEMICAL EQUILIBRIUM

13.1 and 13.2 The Equilibrium Condition and The Equilibrium Constant

EQUILIBRIUM- NO REACTION GOES FULLY TO COMPLETION
EQUILIBRIUM IS REACHED WHEN THE RATES OF THE FORWARD AND REVERSE REACTIONS ARE EQUAL.

1. What is dynamic equilibrium ? $H_2 + I_2 \leftarrow\rightarrow 2\,HI$

rate of forward reaction = rate of reverse reaction

2. What is true about the initial rate of forward and reverse reactions in a system where only reactants are present ?

With no products to start with, the reaction is only moving forward (right / to products)

3. What is true about the rates of forward and reverse reactions at equilibrium ?

Equivalent rate (this does NOT mean equavilent concentrations)

4. Why does equilibrium occur ?

Many possibilities

5. What are some of the factors that determine the equilibrium position of a reaction ?

Concentration, state of matter, temperature, nature of the chemicals

Law of Mass Action

$$nA + mB \leftrightarrow pC + qD$$

the equilibrium constant K is given by

$$K = \frac{[C]^p[D]^q}{[A]^n[B]^m}$$

$H_2 + I_2 \leftarrow\rightarrow 2\,HI$

$$K = \frac{[HI]^2}{[H_2][I_2]}$$

K is the ratio of the forward to reverse rate constants (not the rate). Coefficients become exponents when put into the mass action expression.

1. Write the equilibrium expression for each of the following reactions:
   - a. $PCl_{5\,(g)} \leftrightarrow PCl_{3\,(g)} + Cl_{2\,(g)}$
   - b. $S_{8\,(g)} \leftrightarrow 8\,S_{(g)}$
   - c. $Cl_2O_{7\,(g)} + 8\,H_{2\,(g)} \leftrightarrow 2\,HCl_{(g)} + 7\,H_2O_{(g)}$

$$K = \frac{[PCl_3][Cl_2]}{[PCl_5]} \qquad K = \frac{[S]^8}{[S_8]} \qquad K = \frac{[HCl]^2\,[H_2O]^7}{[Cl_2O_7]\,[H_2]^8}$$

2. Calculate the equilibrium constant, K, for the following reaction at 25 °C,
$H_{2\,(g)} + I_{2\,(g)} \leftrightarrow 2\,HI_{(g)}$ if the equilibrium concentrations are $[H_2] = 0.106$ M, $[I_2] = 0.022$ M, and $[HI] = 1.29$ M

$$K = \frac{[HI]^2}{[H_2][I_2]} \qquad \frac{[1.29]^2}{[0.022][0.106]} = \underline{710}$$

3. Using the same reaction as in our previous problem (with $K = 7.1 \times 10^2$ at 25 °C), if the equilibrium concentrations of H_2 and I_2 are 0.81 M and 0.035 M respectively, calculate the equilibrium concentration of HI.

$$710 = \frac{[HI]^2}{[0.81][0.035]} \qquad [HI] = 4.49\text{ M}$$

Cross multiply and then take square root to find [HI].

4. Your textbook discusses certain conclusions regarding the value of K when you modify a balanced chemical equation. Reread that discussion. Given our balanced chemical equation and value of K from the past two problems, calculate the value of K for the following reactions.
   a. The equation is the reverse of the original.
   b. The equation is 1/3 of the original.
   c. The equation is reversed and is four times the original.

$$K = \frac{[HI]^2}{[H_2][I_2]}$$

a. K^{-1}

b. The same K value as before because both the top and the bottom would be impacted equally

c. K^{-1} $\frac{4 \times 4}{4^2}$ So, the same as a. K^{-1}

$$\frac{4.2 \times 10^{-5}}{1}$$

13.3 Equilibrium Expressions Involving Pressure

Your textbook points out that equilibria for gases can be expressed either in concentrations or in pressure terms. We use K for the equilibrium constant gotten by using concentration and K_p for that using pressures. K and K_p can be related.

5. Calculate K_p for the reaction: $CH_3OH_{(g)} \leftrightarrow CO_{(g)} + 2\,H_{2(g)}$

Given the equilibrium pressures as follows:

$P_{CH3OH} = 6.10 \times 10^{-4}$ atm $P_{CO} = 0.387$ atm $P_{H2} = 1.34$ atm

$$K_p = \frac{(CO)(H_2)^2}{(CH_3OH)} \qquad \frac{(0.387)(1.34)^2}{(6.10 \times 10^{-4})} = 1139$$

Converting pressure constant in concentration constants.

$K = K_p(RT)^{-\Delta n}$

Using R = 0.08206 L atm / K mol

T = 298 K

$K = 1139\,(0.0821 \times 298)^{-(3-1)}$

$K = 1.9$

Δn = 3 moles gas on products side - 1 mole gas on reactant side

13.3 Heterogeneous Equilibria

Equilibrium expressions involve concentrations (or pressures) of substances that change from initial to the equilibrium conditions. A pure substance, such as water, changes amount, but not concentrations.

THE CONCENTRATIONS OF PURE SOLIDS AND LIQUIDS REMAIN CONSTANT.

That means that pure solids and liquids can't be incorporated into the equilibrium constant. For example, the equilibrium expression for

$CaCO_{3\,\underline{(s)}} \leftrightarrow CaO_{\underline{(s)}} + CO_{2\,(g)}$ is not $K = \dfrac{[CaO][CO_2]}{[CaCO_3]}$ $K = \dfrac{1\,[CO_2]}{1}$

Rather, $[CaCO_3]$ and $[CaO]$ are constant. The amounts of each will change, but their concentration are called. Thus, we can incorporate them into our equilibrium expression. $K = [CO_2]$

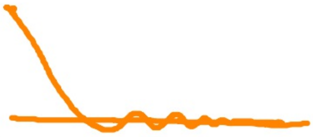
6. Write equilibrium expressions for each of the following reactions:

after a. set these up on your own

a. $Ba(OH)_{2\,(s)} \leftrightarrow Ba^{+2}_{(aq)} + 2\,OH^-_{(aq)}$
b. $NH_4NO_{2\,(s)} \leftrightarrow N_{2\,(g)} + 2\,H_2O_{(g)}$
c. $HCl_{(g)} + NH_{3\,(g)} \leftrightarrow NH_4Cl_{(s)}$
d. $Zn(OH)_{2\,(s)} + 2\,OH^-_{(aq)} \leftrightarrow Zn(OH)_4^{2-}{}_{(aq)}$
e. $CH_3CO_2H_{(aq)} \leftrightarrow H^+_{(aq)} + CH_3CO_2^-{}_{(aq)}$
f. $Al(NO_3)_{3\,(s)} + 6\,H_2O_{(l)} \leftrightarrow [Al(H_2O)_6]^{3+}_{(aq)} + 3\,NO_3^-{}_{(aq)}$

a. $K = \dfrac{[Ba^{2+}][OH^{-1}]^2}{1}$

13.3 Application of the Equilibrium Constant



Review of things that K can and cannot indicate:

- K **does not reflect how fast** a reaction goes.
- A **large value of K means that mostly products** will be present at equilibrium.
- A **small value of K means that mostly reactants** will be present at equilibrium.

The theme of this section is the use of the reaction quotient (Q). **Q predicts the direction in which the reaction will go to reach equilibrium**. You calculate Q by using the law of mass action on the **initial, not equilibrium**, concentrations (or pressures) of the reaction substances.

- If **Q is equal to K, the system is at equilibrium**.
- If **Q is greater than K**, mathematically, there is too much product present. The system will **shift to the left** to reach equilibrium.
- If **Q is less than K**, there is too much reactant present. The system will **shift to the right** to reach equilibrium.

What if K = 40 but Q = 30?
How would the reaction move to achieve equilibrium?
Since Q needs to increase until Q = K, then the [products] need to increase, shift right.

7. Let's reexamine the reaction between hydrogen gas and iodine gas. The following a to e, the reaction is not at equilibrium and will shift until Q = K.

$H_{2\,(g)} + I_{2\,(g)} \leftrightarrow 2HI_{(g)}$ K = 7.1 x 10^2 at 25 °C.

Predict the direction that the system will shift in order to reach equilibrium given each of the following initial conditions:

a. Q = 427

since K = 710, the reaction would shift right to make more [HI] until Q is increased to = K.

b. Q = 1522

Q is too large and the [HI] needs to decrease (or reactants increase) to reduce the Q value until it = K.

c. $[H_2]_o$ = 0.81 M $[I_2]_o$ = 0.44 M $[HI]_o$ = 0.58 M

$$Q = \frac{(0.58)^2}{(0.81)(0.44)} = 0.94$$

This is far too small and the reaction will produce more products (shift right) until Q = K.

d. $[H_2]_o$ = 0.078 M $[I_2]_o$ = 0.033 M $[HI]_o$ = 1.35 M

Q = 710, no change would be visible

e. $[H_2]_o$ = 0.034 M $[I_2]_o$ = 0.035 M $[HI]_o$ = 1.50 M

Q is calculated to be Q = 1890, shift left towards the reactants until Q = K.

Another type of problem that you may be have is being given an initial concentrations and K and are asked to find equilibrium concentrations. When you have a large value for K, you must determine the direction of the reaction. You must compare Q to K. You must set up a table of initial and final conditions to evaluate the problem. With small values for K, the reaction will stay for to the left. Because K is small, let us assume that X is negligible.

Finding Equilibrium Concentrations!!!!

$H_{2\,(g)} + I_{2\,(g)} \leftrightarrow 2\,HI_{(g)}$ K = 7.1×10^2 at 25 °C.

8. Using the data from the previous example, calculate the equilibrium concentrations if a 5.00 L vessel initially contains 15.7 g of H_2 and 294 g of I_2.

We are going to setup a data table to help organize our thoughts. We need to do a lot of work to fill this in with data. The steps are in below.

	H_2	+	I_2	←→	2 HI
[Initial]	1.56		0.232		0
[Change]	-X		-X		+2X
[Equilibrium]	1.56 - X		0.232 - X		2X
[Final]	1.33		0.00022		0.464

1. Calculate [Initial]

$$\frac{15.7\ g\ H_2}{} \left| \frac{1\ mol\ H_2}{2.02\ g\ H_2} \right| \frac{}{5.00\ L} = 1.56\ M\ H_2$$

$$\frac{294\ g\ I_2}{} \left| \frac{1\ mol\ I_2}{253.8\ g\ I_2} \right| \frac{}{5.00\ L} = 0.232\ M\ I_2$$

There is no [HI]

2. Determine [Change] values

The reactants will be decreasing and their coefficients are both 1 so we will put in [-1x] for both. However, the product is increasing as [+2x]

3. Setup algebriac [Equilibrium]

$[H_2] = 1.56 - X$
$[I_2] = 0.232 - X$
$[HI] = 0 + 2X$

4. Setup Equilibrium expression and solve for X.

$$K = \frac{[HI]^2}{[H_2]\ [I_2]} \qquad 710 = \frac{[2X]^2}{[1.56 - X][0.232 - X]}$$

X = 1.57 or 0.23178

$$710(1.56-x)(.232-x) - 4x^2 = 0$$

$$710(0.362 - 1.792x + x^2) - 4x^2$$

$$\underset{a}{706}x^2 - \underset{b}{1272}x + \underset{c}{257} = 0$$

$$X = 1.56 \text{ or } \boxed{.232}$$

Is it safe too assume almost all of one reactant or product will always be used up?

-No, only when K is extreme. 710 heavily favors the products, so almost all of one of the reactants will be gone.

-If K was extremely small, the reverse could be assumed.

-If K isn't too extreme you will need to go through the steps.

13.3 Solving Equilibrium Problems

At the beginning of this section, your textbook presents a "Procedure for Solving Equilibrium Problems". You may follow that procedure, however, you must always think about what assumptions can make your problem solving easier and then test the validity of your assumptions.

9. The reaction between nitrogen and oxygen to form nitric oxide has a value for the equilibrium constant at 2000 K of K = 4.1×10^{-4}. If 0.50 moles of N_2 and 0.86 moles of O_2 are put in a 2.0 L container at 2000 K, what would the equilibrium concentrations of all species be?

$$N_{2\,(g)} + O_{2\,(g)} \leftrightarrow 2\,NO_{(g)}$$

[Initial]	0.25	0.43	0
[Change]	-X	-X	+2X
[Equilbrium]	0.25 - X	0.43 - X	2X
[Final]	0.247	0.427	0.00656

$$4.1 \times 10^{-4} = \frac{[2X]^2}{[0.25 - X][0.43 - X]}$$

X = 0.00328 M

Almost no change in reactants because K is very small.

10. Sulfurous acid dissociates in water as follows: $H_2SO_{3\,(aq)} \leftrightarrow H^+_{(aq)} + HSO_{3\,(aq)}^-$ If $[H_2SO_3]_o$ = 1.50 M and $[H^+] = [HSO_3^-]$ = 0 M, calculate the equilibrium concentrations of all species at 25 °C if $K = 1.20 \times 10^{-2}$ for this reaction.

	H_2SO_3	$\leftarrow\rightarrow$	H^+	+	HSO_3^-
[Initial]	1.50		0		0
[Change]	- X		+X		+X
[Equilbrium]	1.50 - X		X		X
[Final]	1.37		0.13		0.13

$$1.20 \times 10^{-2} = \frac{[X][X]}{[1.50 - X]}$$

X = 0.13 M

$$0 = ax^2 + bx + c$$

$$\frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

13.3 LeChatelier’s Principle

Le Chatelier’s Principle: “If a change is imposed on a system at equilibrium the position of the equilibrium will shift in a direction that tends to reduce the change.”

11. Nitrogen gas and oxygen gas combine at 25 °C in a closed container to form nitric oxide as follows: Heat + $N_{2\,(g)} + O_{2\,(g)} \leftrightarrow 2\,NO_{(g)}$

$\Delta H = +\,1.81$ kJ Endo $K_p = 3.3 \times 10^{30}$

What would be the effect on the direction of equilibrium if the following changes are made to the system ?

a. N_2 is added
b. He is added
c. the container is made larger
d. the system is cooled

a - Q would be to low, shift toward the products to achieve K

b - neither

c - both sides impacted equally since both sides have 2 moles of gas in the balanced equation, no change

This implies that if the moles were not equal a shift would occur, dependant upon which side was impacted the most. 2A + B --> C inc Volume shift left

d - toward reactants bc it is endo to make products and exo to make reactants

12. The combination of hydrogen gas and oxygen gas to give water vapor can be expressed by $2 H_{2\,(g)} + O_{2\,(g)} \leftrightarrow 2 H_2O_{(g)}$ + heat $\Delta H = -484$ kJ
Predict the effect of each of the following changes to the system on the direction of equilibrium.

a. H_2O is removed as it is being generated
b. H_2 is added
c. the system is cooled

a - Shift toward products to increase Q until it equals K, if water continues to be removed the reaction will continue until all of one reactant is used up.
b - Because the extra [H_2] would decrease Q the reaction would shift toward products to increase Q until = K
c. As T is changed the K value changes. Shifting can be predicted by looking at the Enthalpy. This is Exothermic to the products, so decreasing the temperature will shift the reaction toward the products even more. SHIFT RIGHT