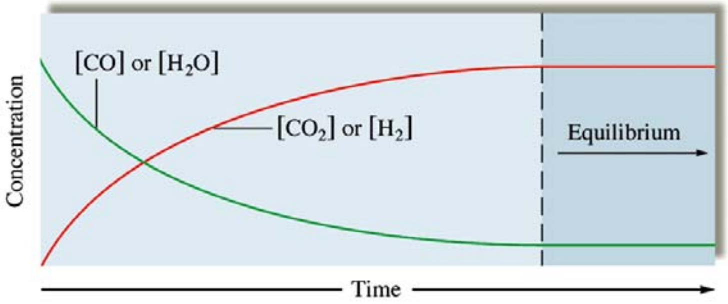
Name ________________________ **AP CHEM** __/__/__

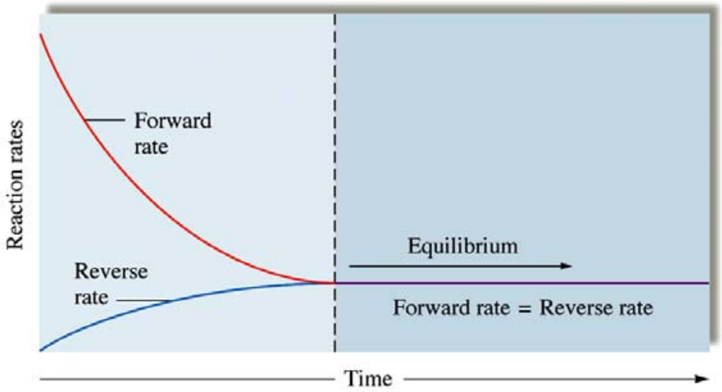
Chapter 13 Outline – Chemical Equilibrium

The Equilibrium Condition

- In stoichiometry we assumed that reactions went to completion. Most reactions do go to completion but there are many that stop far short of completion.
- Chemical equilibrium is that state where the concentrations of all reactants and products remain constant with time.
- Since no changes occur in the concentrations of reactants and products in a reaction at equilibrium, it may appear everything has stopped.
- Equilibrium is not static; it is highly dynamic and frantic on the molecular level. The reaction continues to proceed in both directions but the rate of the forward reaction is equal to the rate of the reverse reaction.
- The figure below is an profile of the progress of a reaction: $H_2O(g) + CO(g) \rightleftharpoons H_2(g) + CO_2(g)$. Note that once equilibrium is reached, the concentrations of the products and reactants do not change and neither becomes zero.



- The other graphic below represents the rates of the forward and reverse reaction for the same reaction



The Equilibrium Constant

- From their observations of many chemical reactions, two Norwegian Chemists, Cato Maximilian Guldberg (1836-1902) and Peter Waage (1833 – 1900) proposed in 1864 **the law of mass action**.
- $jA + kB \rightleftharpoons lC + mD$ would be represented as:

$$K= \frac{[C]^l\,[D]^m}{[A]^j\,[B]^k}$$

- Example: Write the mass action expression for the following equation: $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

Answer: $$K= \frac{[NH_3]^2}{[N_2]x[H_2]^3}$$

- You try: Write the equilibrium expression for the following: $4NH_3(g) + 7O_2(g) \rightleftharpoons 4NO_2(g) + 6H_2O(g)$

- The value of the equilibrium constant at a given temperature can be calculated if you know the equilibrium concentrations of the reaction components.
- Equilibrium constants are customarily given without units.
- Example: For the following equation: $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$. At a particular temperature, a scientist determined the concentration of HI to be 1.30M, H_2 to be 0.30M & I_2 to be 0.30M.
  - a. Calculate the equilibrium constant at this temperature.
  - b. Calculate the equilibrium constant for the reverse reaction.
  - c. Calculate the equilibrium constant for the following reaction $\frac{1}{2} H_2(g) + \frac{1}{2} I_2(g) \rightleftharpoons HI(g)$

a. $$\frac{[H_2] \text{ x } [I_2]}{[HI]^2} \longrightarrow \frac{[0.30] \text{ x } [0.30]}{[1.30]^2} \longrightarrow \mathbf{K_{eq} = 0.053}$$

The reverse reaction: $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

b. $$\frac{[HI]^2}{[H_2] \text{ x } [I_2]} \qquad \frac{[1.30]^2}{[0.30] \text{ x } [0.30]} \qquad \mathbf{K'_{eq} = 19}$$ (rounded from 18.77)

The equilibrium constant for a reverse reaction can be found by taking the reciprocal of the equilibrium constant for the forward reaction. Using the values from above: $K'_{\mathbf{reverse}} = 1 / K_{\text{forward}}$

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$K'_{\mathbf{reverse}} = 1 / 0.053$
$K'_{\mathbf{reverse}} = 19$

c. $$\frac{[HI]}{[H_2]^{1/2} \text{ x } [I_2]^{1/2}} \qquad \frac{[1.30]}{[0.30]^{1/2} \text{ x } [0.30]^{1/2}} \qquad \mathbf{K''_{eq} = 4.3}$$

Since $$\left(\frac{[HI]^2}{[H_2] \text{ x } [I_2]}\right)^{1/2} = \frac{[HI]}{[H_2]^{1/2} \text{ x } [I_2]^{1/2}} \qquad \text{Thus: } K'' = \sqrt{K'}$$

- A set of equilibrium concentrations is called an **equilibrium position**. There can be many equilibrium positions for a reaction at a certain temperature, but only one equilibrium constant for a particular system at a particular temperature.
- I think you need to try one. The following concentrations were observed for the Haber Process at 127 ºC. $[NH_3] = 3.1 \text{ x } 10^{-2}$ mol/L, $[N_2] = 8.5 \text{ x } 10^{-1}$ mol/L, $[H_2] = 3.1 \text{ x } 10^{-3}$ mol/L.
  - a. Calculate the value of K at 127 ºC for the reaction: $N_2 + 3H_2 \rightleftharpoons 2NH_3$
  - b. Calculate the equilibrium constant at 127 ºC for the reaction: $2NH_3 \rightleftharpoons N_2 + 3H_2$
  - c. Calculate the equilibrium constant at 127 ºC for the reaction: $\frac{1}{2} N_2 + \frac{3}{2} H_2 \rightleftharpoons NH_3$

Equilibrium Expressions Involving Pressures

- The ideal gas law (PV = nRT) can be derived to include concentration (n/V or moles per Volume). This formula is: P = CRT.
- In terms of partial pressure, the **equilibrium partial pressures of the gases equation** can be used. For the sample equation: $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

  $$K_P = \frac{[P_{NH3}]^2}{[P_{N2}]x[P_{H2}]^3}$$

  P represents the partial pressure of each gas.
- Example: The reaction for the formation of nitrosyl chloride: $2NO(g) + Cl_2(g) \rightleftharpoons 2NOCl$ The pressures at equilibrium were found to be: $P_{NO} = 0.60$ atm, $P_{Cl2} = 0.40$ atm and $P_{NOCl} = 2.20$ atm Calculate the K_p for the reaction.

  $$K_P = \frac{[P_{NOCl}]^2}{[P_{NO}]^2 \text{ x } [P_{Cl2}]}$$

  $K_p = 34$
- You try: Calculate K_P for the following: $2HF(g) \rightleftharpoons H_2(g) + F_2(g)$ if $P_{HF} = 775$ mm Hg, $P_{H2} = 650$ mm Hg and $P_{F2} = 480$ mm Hg
- The relationship between K_c and K_P is: $\mathbf{K_P = K_c(RT)^{\Delta n}}$ Δn = the sum of the moles of gaseous product – sum of the moles of the gaseous reactants.
- Example: Calculate the K at 25°C for the reaction $2NO(g) + Cl_2(g) \rightleftharpoons 2NOCl$ K_P (from earlier example: 34)

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

  $K = K_P / (RT)^{\Delta n}$

  $K = 34 / [(0.08206)(298)]^{-1}$

  $K = 830$
- You try: Calculate the equilibrium constant at 40.0°C for the following equation: $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ $P_{N2} = 2.11$ atm, $P_{H2} = 1.65$ atm and $P_{NH3} = 3.45$ atm

Heterogeneous Equilibria

- So far we have only looked at equilibria for systems in the gas phase, where all reactants and products are gases. These are homogeneous equilibria.
- Equilibria involving more than one phase are called heterogeneous equilibria.
- If pure solids or pure liquids are involved in a chemical reaction, their concentrations are not included in the equilibrium expression for the reaction.
- Consider the following heterogeneous equilibria: $2H_2O(l) \rightleftharpoons 2H_2(g) + O_2(g)$

  Thus: $K = [H_2]^2[O_2]$ and $K_P = (P_{H2})^2(P_{O2})$

  Water is not included because it is a pure liquid.
- You try: Write the expression for K and K_P for the following process: Solid phosphorus pentachloride decomposes to form liquid phosphorus trichloride and chlorine gas.

Application of the Equilibrium Constant

- The tendency for a reaction to occur is indicated by the magnitude of the equilibrium constant. A value of K larger than 1 means that at equilibrium the reaction will consist of mostly products – the equilibrium lies to the right. A very small K value, one less than one, means that most of the system will be in the form of the reactants.
- The size of the K and the time required to reach equilibrium are not directly related. The time required to achieve equilibrium depends on reaction rate, which is determined by the size of the activation energy.
- When the reactants and products are mixed, it is useful to know whether the mixture is at equilibrium, or if not, the direction in which the system must shift to reach equilibrium. To determine the shift, the **reaction quotient, Q,** is used. The reaction quotient is obtained by applying the law of mass action using initial concentrations instead of equilibrium concentrations.
- To determine the direction a system will shift, compare the Q & K values for a reaction.
    - If $Q = K$, the reaction is already at equilibrium.
    - If $Q > K$, the system shifts to the left and more reactants are formed until equilibrium is reached.
    - If $Q < K$, the system shifts to the right and more products are formed until equilibrium is reached.
- For example: For the synthesis of ammonia at 500°C, the equilibrium constant is 6.0×10^{-2}. Determine the direction in which the system will shift to reach equilibrium in the following case: $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$. $[N_2]_0 = 1.0 \times 10^{-5}$ M, $[H_2]_0 = 2.0 \times 10^{-3}$ M, $[NH_3]_0 = 1.0 \times 10^{-3}$ M.

$$Q = \frac{[NH_3]^2}{[N_2] \times [H_2]^3}$$

$$Q = 1.3 \times 10^7$$

Since $Q > K$ the reaction shifts to the left and ammonia decomposes to form nitrogen gas and hydrogen gas.

- You try: For the synthesis of ammonia at 500°C, the equilibrium constant is 6.0×10^{-2}. Determine the direction in which the system will shift to reach equilibrium in the following case: $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$. $[N_2]_0 = 5.0$ M, $[H_2]_0 = 1.0 \times 10^{-2}$ M, $[NH_3]_0 = 1.0 \times 10^{-4}$ M.

- Calculating equilibrium pressure. Example: O_2 can be converted into ozone, O_3. If oxygen is placed in a flask and allowed to reach equilibrium at a temperature where $K_P = 0.250$. At equilibrium, the pressure of O_2 is found to be 2.25 atm. Calculate the equilibrium pressure of $O_3(g)$.

$$3O_2(g) \rightleftharpoons 2O_3(g)$$

$$K_P = \frac{(P_{O3})^2}{(P_{O2})^3}$$

$$0.250 = \frac{(P_{O3})^2}{(2.25)^3}$$

$$P_{O3} = \sqrt{2.847656}$$

$$P_{O3} = 1.69 \text{ atm}$$

- You try: $N_2O_4(g) \rightleftharpoons 2\,NO_2(g)$. Calculate the pressure of nitrogen dioxide if the $K_P = 0.133$ and the pressure of N_2O_4 is 2.48 atm.

- Example: At a certain temperature a 1.00 L flask initially contained 0.298 mol PCl_3 (g) and 8.70 x 10^{-3} mol PCl_5. After the system had reached equilibrium, 2.00 x 10^{-3} mol of $Cl_2(g)$ was found in the flask. Gaseous PCl_5 decomposes according to the reaction: $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ Calculate the equilibrium concentrations of all species and the value of K.

  Determine the initial concentration of each substance.

  $Cl_2 = 0$
  $PCl_3 = 0.298$ mol / 1.00 L = 0.298 M
  $PCl_5 = 8.70 \times 10^{-3}$ mol / 1.00 L = 8.70 x 10^{-3} M

  Since there was no original chlorine and at equilibrium there was 2.00 x 10^{-3} mol, we can assume that the PCl_5 decreased by 2.00 x 10^{-3} moles and PCl_3 increased by 2.00 x 10^{-3} moles. Use this fact to determine the concentration at equilibrium

  First convert moles to M. 2.00 x 10^{-3} moles / 1.00 L = 2.00 x 10^{-3} M
  $Cl_2 = 0 + 2.00 \times 10^{-3} = 2.00 \times 10^{-3}$ M
  $PCl_3 = 0.298$ M + 2.00 x 10^{-3} = 0.300 M
  $PCl_5 = 8.70 \times 10^{-3}$ M - 2.00 x 10^{-3} = 6.70 x 10^{-3} M

  Plug it in to the mass action expression to find K.

  $K = (2.00 \times 10^{-3})(0.300) / 6.70 \times 10^{-3}$
  $K = 8.96 \times 10^{-2}$

- Your turn: A 1.00 L flask was filled with 2.00 mol gaseous SO_2 and 2.00 mol gaseous NO_2 are heated. After equilibrium was reached, it was found that 1.30 mol gaseous NO was present. Assume that the reaction: $SO_2(g) + NO_2(g) \rightleftharpoons SO_3(g) + NO(g)$ occurs under these conditions. Calculate the value of the equilibrium constant, K, for this reaction.

- Calculating Equilibrium Concentrations Using ICE. Example: Carbon monoxide reacts with steam to produce carbon dioxide and hydrogen. At 700 K the equilibrium constant is 5.10. Calculate the equilibrium concentrations of all species if 2.00 mol of each component is mixed in a 1.000 L flask.

Find Molarity of each substance: 2.00/1.000 = 2.00 M
Since Kc > 1 the reaction will shift to the right. Products will increase by a value of x and reactants will decrease by a value of x.

Reaction	CO	H_2O	CO_2	H_2
Initial	2.00 M	2.00 M	2.00 M	2.00 M
Change	-x	-x	+x	+x
Equilibrium	2.00 – x	2.00 – x	2.00 + x	2.00 + x
Answer	1.23	1.23	2.77	2.77

$$\frac{5.10}{1} = \frac{[2.00+x][2.00+x]}{[2.00-x][2.00-x]} \rightarrow \quad \frac{5.10}{1} = \frac{[2.00+x]^2}{[2.00-x]^2} \rightarrow \quad \frac{\sqrt{5.10}}{1} = \frac{[2.00+x]}{[2.00-x]} \rightarrow$$

$$\frac{2.26}{1} = \frac{[2.00+x]}{[2.00-x]} \rightarrow \qquad 4.52 - 2.26\,x = 2.00 + x \rightarrow 2.52 = 3.26\,x \rightarrow x = 0.773$$

Insert into ICE Chart.

- You try: Assume that the reaction for the formation of gaseous hydrogen fluoride from hydrogen and fluorine has an equilibrium constant of 1.15×10^2 at a certain temperature. In a particular experiment 4.000 moles of each component was added to a 1.750 L flask. Calculate the concentration of all species.

Note that most systems we deal with have small equilibrium constants. If the equilibrium constant is small, mathematical simplifications can be made. See below. Worked in class. Please copy.
Example: Gaseous NOCl decomposes to form the gases NO & Cl_2. At 35ºC the equilibrium constant is 1.6×10^{-5}. In an experiment in which 1.0 mol NOCl is placed in a 2.0 L flask, what are the equilibrium concentrations?

Le Chatelier's Principle

Le Chatelier's Principle was devised by French Chemist Henri Le Chatelier (1850-1936). **It states that when a system is at equilibrium and it is subjected to a stress, it will shift its equilibrium point to relieve the stress**. The way a system responds to certain stresses is outlined below:

I. Addition or Removal of Reactant or Product

- If a reactant is added, the reaction shifts to the right & increases the concentration of the products.
- If a product is added, the reaction shifts to the left & increases the concentration of the reactants.
- If a reactant is removed, the reaction shifts to the left & decreases the concentration of the products.
- If a product is removed, the reaction shifts to the right & decreases the concentration of the reactants.

The equilibrium value(K) remains the same whenever a reactant or product is added or removed from the system.

II. Temperature Changes

- In an endothermic reaction, an increase in temperature shifts right and increases the concentration of the products.
- In an exothermic reaction, an increase in temperature shifts left and increases the concentration of the reactants.
- In an endothermic reaction, a decrease in temperature shifts left and decreases the concentration of the products.
- In an exothermic reaction, a decrease in temperature shifts right and decreases the concentration of the reactants.

Since an increase in the concentration of the reactants means a decrease in the concentration of the products, and vice versa, changes in temperature do affect equilibrium. Because the equilibrium value is a measure of the concentration of the products divided by the concentration of the reactants, an increase in the concentration of the products means an increase in the equilibrium value(K) and an increase in the concentration of the reactants means a decrease in the equilibrium value(K).

III. Pressure Changes

Changes in pressure only affect gaseous substances.

- An increase in pressure will shift the equilibrium to where there are fewer moles of gas and increase the concentrations of the molecules on that side of the equation.
- A decrease in pressure will shift the equilibrium to where there are more moles of a gas and increase the concentrations of the molecules on that side of the equation.

Like changes in temperature, changes in pressure do affect equilibrium. An increase in the concentration of the products means an increase in the equilibrium value(K). An increase in the concentration of the reactants means an decrease in the equilibrium value(K).

IV. Catalysts

Catalysts only speed up a reaction and do not affect the concentration of the reactants or products or the equilibrium value.

Complete the following charts by writing LEFT, RIGHT or NONE for the equilibrium shift and INCREASES, DECREASES or STAYS THE SAME for the concentrations of the reactants, products and equilibrium value(K).

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) + 92.0\ kJ$

Stress	Equilibrium Shift	$[N_2]$	$[H_2]$	$[NH_3]$	K
1. Add N_2		-----			
2. Add H_2			-----		
3. Add NH_3				-----	
4. Remove N_2		-----			
5. Remove H_2			-----		
6. Remove NH_3				-----	
7. Increase Temperature					
8. Decrease Temperature					
9. Increase Pressure					
10. Decrease Pressure					

$2SO_3(g) + heat \rightleftharpoons 2SO_2(g) + O_2(g)$

Stress	Equilibrium Shift	$[SO_3]$	$[SO_2]$	$[O_2]$	K
11. Add SO_3		-----			
12. Add O_2				-----	
13. Add SO_2			-----		
14. Remove SO_3		-----			
15. Remove O_2				-----	
16. Remove SO_2			-----		
17. Increase Temperature					
18. Decrease Temperature					
19. Increase Pressure					
20. Decrease Pressure					

$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq) + heat$

Stress	Equilibrium Shift	[AgCl]	$[Ag^+]$	$[Cl^-]$	K
21. Add AgCl		-----			
22. Add $AgNO_3$			-----		
23. Add HCl				-----	
24. Increase Temperature					
25. Decrease Temperature					
26. Increase Pressure					
27. Decrease Pressure					

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

Stress	Equilibrium Shift	$[PCl_5]$	$[PCl_3]$	$[Cl_2]$	K
28. Add Cl_2				-----	
29. Add PCl_3			-----		
30. Add PCl_5		-----			
31. Increase Temperature					
32. Decrease Temperature					
33. Increase Pressure					
34. Decrease Pressure					

$2NO(g) \rightleftharpoons N_2(g) + O_2(g)$ + heat

Stress	Equilibrium Shift	[NO]	$[N_2]$	$[O_2]$	K
35. Remove NO		-----			
36. Remove N_2			-----		
37. Remove O_2				-----	
38. Decrease Temperature					
39. Increase Temperature					
40. Decrease Pressure					
41. Increase Pressure					

42. Define Le Chatelier's Principle.

43. What is(are) the only stress(es) that can affect the equilibrium value(K)?

44. How do catalysts affect the concentrations of reactants and products?