

*Chapter 15*  
*Chemical Equilibrium*

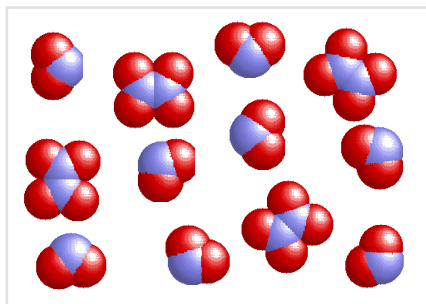
- Chemical reactions can reach a state of dynamic equilibrium.
- Similar to the equilibrium states reached in evaporation of a liquid in a closed container or the dissolution of a solid to form a saturated solution.
- Use a double arrow to indicate the process is dynamic and reversible.

*Analogy to Chemical Equilibrium*

- Two yards with a lemon tree on the border. Older and younger person throwing lemons back and forth.

*15.1 The Concept of Equilibrium*

- At equilibrium, both reactants and products are present simultaneously.
- $2\text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_4$



*Equilibrium*

- Chapter 19:  $\Delta G^\circ = -RT \ln K$
- Relationship arises from a minimization of the free energy.
- Chapter 14 considered changes in concentration with time. For a reversible reaction, we must consider the rates in both directions.
- Forward rate decreases because [reactant] decreases; reverse rate increases because [product] increases.

*Butane Isomerization*

- butane  $\rightleftharpoons$  isobutane
- $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 \rightleftharpoons \text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$

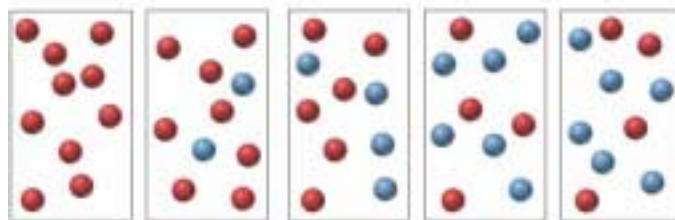
*Rates at Equilibrium*

- Reactant concentrations decrease, and product concentrations increase until they become constant at a state of equilibrium. Reaction continues in both directions, but at the same rate so there is no net change in concentration.
- $\text{Rate}_f = k_f[\text{butane}]$
- $\text{Rate}_r = k_r[\text{isobutane}]$
- At equilibrium,  $\text{Rate}_f = \text{Rate}_r$
- Rates at Equilibrium

- $k_f[\text{butane}] = k_r[\text{isobutane}]$  at equilibrium
- $k_f/k_r = [\text{isobutane}]/[\text{butane}] = K_c$
- where  $K_c$  is the equilibrium constant expressed in terms of concentrations
- No matter how complex the rate laws for the forward and reverse reactions, they always combine to give the simple equilibrium constant expression, with  $K_c = k_f/k_r$

### Sample Problem

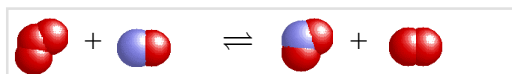
- At which point does this system reach a state of equilibrium?



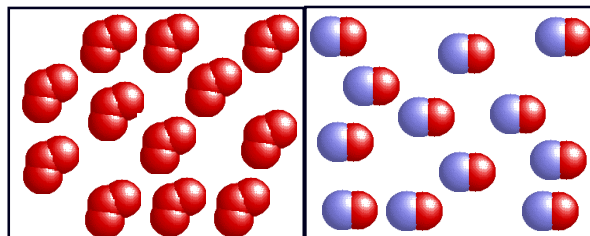
### 15.2 The Equilibrium Constant

- A reaction reaches the same position of equilibrium (at a given temperature), described by  $K_c$ , no matter what the starting conditions.
- $aA + bB \rightleftharpoons cC + dD$
- $K_c = [C]^c[D]^d/[A]^a[B]^b$
- Omit pure solids and liquids from this expression.
- To determine  $K_c$ , use  $k_f/k_r$ , or measure equilibrium concentrations and substitute into the  $K_c$  expression.
- Write the equilibrium constant expressions ( $K_c$ ) for the following reactions:
- $\text{CO(g)} + 3\text{H}_2\text{(g)} \rightleftharpoons \text{CH}_4\text{(g)} + \text{H}_2\text{O(g)}$
- $2\text{NH}_3\text{(g)} \rightleftharpoons \text{N}_2\text{(g)} + 3\text{H}_2\text{(g)}$
- $2\text{Na(s)} + \text{Cl}_2\text{(g)} \rightleftharpoons 2\text{NaCl(s)}$

### Molecular Picture of Equilibrium



- If  $K = 25$ , draw a molecular picture that shows what the system will look like when it reaches equilibrium.



*Equilibrium Constants in Terms of Pressure*

- For gases, we can also use  $K_p$ , with amounts expressed as partial pressures.
- By definition,  $K_c$  and  $K_p$  have no units.
- $K_p = K_c (RT)^{\Delta n_{\text{gas}}}$  (from the ideal gas law)
- We will work primarily with  $K_c$  and concentrations.
- $K$  can be manipulated in much the same way as other thermodynamic functions, such as Gibbs free energy.

*Manipulation of K and Equilibrium Equations*

- Multiply reaction coefficients by a constant, raise all concentrations and  $K$  to the power of that constant.
- Reverse the reaction, invert  $K$  and its expression.
- Add two equations, multiply their  $K$  values.

*Manipulation of K*

- $2\text{H}_2\text{O} \rightleftharpoons 2\text{H}_2 + \text{O}_2$
- $K_1 = [\text{H}_2]^2[\text{O}_2]/[\text{H}_2\text{O}]^2$
- $\text{H}_2\text{O} \rightleftharpoons \text{H}_2 + 1/2\text{O}_2$
- $K_2 = K_1^{1/2} = ([\text{H}_2]^2[\text{O}_2]/[\text{H}_2\text{O}]^2)^{1/2} = [\text{H}_2][\text{O}_2]^{1/2}/[\text{H}_2\text{O}]$
- $2\text{H}_2 + \text{O}_2 \rightleftharpoons 2\text{H}_2\text{O}$
- $K_3 = K_1^{-1} = ([\text{H}_2]^2[\text{O}_2]/[\text{H}_2\text{O}]^2)^{-1} = [\text{H}_2\text{O}]^2/[\text{H}_2]^2[\text{O}_2]$
- Add the two reactions to get a third reaction. What is the value of  $K$  for the third reaction?
- $\text{CO} + 3\text{H}_2 \rightleftharpoons \text{CH}_4 + \text{H}_2\text{O} \quad K = 4$
- $\text{CH}_4 + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{OH} + \text{H}_2 \quad K = 0.005$
- $\text{CO} + 2\text{H}_2 \rightleftharpoons \text{CH}_3\text{OH} \quad K = ?$
- $K = 4 \times 0.005 = 0.02$  since the third equation is the sum of the first two.
- What is  $K$  for double the first reaction?
- $2\text{CO} + 6\text{H}_2 \rightleftharpoons 2\text{CH}_4 + 2\text{H}_2\text{O} \quad K = ?$
- $K = (4)^2 = 16$

*Free Energy and Equilibrium*

- Can get  $K$  from  $\Delta G^\circ$ :
- $\Delta G^\circ = -RT \ln K$
- $K = e^{-\Delta G^\circ/RT}$
- $R = 8.314 \text{ J/mol K}$ ,  $\Delta G^\circ$  in  $\text{J/mol}$ ,  $T$  in  $\text{K}$
- $K$  tells us how far toward products the position of equilibrium lies.
- $\Delta G = 0 \quad K = Q$  equilibrium
- $\Delta G < 0 \quad K > Q$  spontaneous forward
- $\Delta G > 0 \quad K < Q$  spontaneous reverse

*Free Energy and Equilibrium*

- $\Delta G = \Delta G^\circ + RT \ln Q$
- $\Delta G = 0$ ,  $K = Q$ , equilibrium,  $\text{Rate}_f = \text{Rate}_r$
- $\Delta G < 0$ ,  $K > Q$ ,  $Q$  increases until it equals  $K$  due to the forward reaction being faster than the reverse reaction,  $\text{Rate}_f > \text{Rate}_r$
- $\Delta G > 0$ ,  $K < Q$ ,  $Q$  decreases due to faster reverse reaction,  $\text{Rate}_f < \text{Rate}_r$

*Predict direction of shift to reach equilibrium*

- $\text{CO(g)} + 3\text{H}_2\text{(g)} \rightleftharpoons \text{CH}_4\text{(g)} + \text{H}_2\text{O(g)}$   $K = 4$   
 $2 \text{ M} \quad 1 \text{ M} \quad 0.5 \text{ M} \quad 0.5 \text{ M}$
- $Q = (0.5)(0.5)/(2)(1)^3 = 0.125$
- Since  $Q < K$ , reaction will proceed in the forward direction to reach equilibrium.
- $\text{CO(g)} + 3\text{H}_2\text{(g)} \rightleftharpoons \text{CH}_4\text{(g)} + \text{H}_2\text{O(g)}$   $K = 4$   
 $0.2 \text{ M} \quad 0.1 \text{ M} \quad 1.0 \text{ M} \quad 1.0 \text{ M}$
- What is the direction of shift to equilibrium?
- Reverse since  $Q = 5000$

*15.3 Heterogeneous Equilibria*

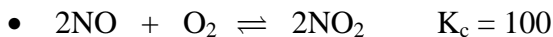
- The concentrations of pure solids and liquids are constant, so they do not show up in the equilibrium expression.

*15.4 Calculating Equilibrium Constants*

- Proceed as follows:
- Tabulate initial and equilibrium concentrations (or partial pressures) given.
- If an initial and equilibrium concentration is given for a species, calculate the change in concentration.
- Use stoichiometry on the change in concentration line only to calculate the changes in concentration of all species.
- Deduce the equilibrium concentrations of all species.
- Usually, the initial concentration of products is zero. (This is not always the case.)
- When in doubt, assign the change in concentration a variable.
- $2\text{NO}_2\text{(g)} \rightleftharpoons \text{N}_2\text{O}_4\text{(g)}$
- At equilibrium,  $[\text{N}_2\text{O}_4] = 0.00212 \text{ M}$  and  $[\text{NO}_2] = 0.100 \text{ M}$ . What is the value of  $K_c$ ?
- $K_c = 0.212$
- No matter what the starting concentrations, at a given temperature, a reaction will always have the same value of the equilibrium constant.

*15.5 Applications of Equilibrium Constants*

- How do we do stoichiometric calculations when the reaction doesn't go to completion?
- Simplest case: One unknown equilibrium concentration. Just rearrange and solve for the unknown.



$$0.010 \text{ M} \quad ? \text{ M} \quad 0.0010 \text{ M}$$

$$\bullet \quad K = \frac{[\text{NO}_2]^2}{[\text{NO}]^2[\text{O}_2]} = 100 = \frac{(0.0010)^2}{(0.010)^2 [\text{O}_2]}$$

$$\bullet \quad [\text{O}_2] = 0.00010 \text{ M}$$



$$0.50 \text{ M} \quad ? \text{ M} \quad 0.10 \text{ M} \quad 0.25 \text{ M}$$

• What is the concentration of H<sub>2</sub> at equilibrium?

$$\bullet \quad [\text{H}_2] = 0.50 \text{ M}$$

### *Approach for Solving Equilibrium Problems*

- Write a balanced chemical equation.
- Select one of the concentration changes and call it x.
- Use the stoichiometry to determine all the concentration changes in terms of x.
- Make a table containing the substances, their initial concentrations, their changes in concentration, and their equilibrium concentrations (calculated from C<sub>o</sub> and x). (ICE table)
- Write the equilibrium constant expression.
- Insert the equilibrium concentration expressions from the table into the equilibrium constant expression.
- Solve the equation for x, applying any possible simplifications (perfect squares or dropping terms when small).
- Check simplifications for validity (5% error is tolerable). If not valid, return to step 7 and do not use the simplification.
- Substitute the value of x into the expressions for the equilibrium concentrations and determine their values.
- Use the equilibrium concentrations to calculate the reaction quotient, and compare it to the equilibrium constant to verify the accuracy of the answers.

### *Typical Problem: Known Initial Concentrations*



$$1.00 \quad 1.00 \quad 0 \text{ M} \quad \text{initial concentrations}$$

• Make table of concentrations:

• Substance:	N <sub>2</sub>	H <sub>2</sub>	NH <sub>3</sub>
• Initial Conc.:	1.00	1.00	0.00
• Change:	-x	-3x	+2x
• Equil. Conc.:	1.00 - x	1.00 - 3x	2x

$$\bullet \quad K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = \frac{(2x)^2}{(1.00 - x)(1.00 - 3x)^3} = 2.5 \times 10^{-5}$$

• Assume  $3x \ll 1.00$  and  $x \ll 1.00$  to simplify

- $\frac{(2x)^2}{(1.00)(1.00)^3} = 2.5 \times 10^{-5}$
  - $2x = (2.5 \times 10^{-5})^{1/2} = 5.0 \times 10^{-3}$
  - $x = 2.5 \times 10^{-3}$
  - Check assumptions:  $1.00 - 3x = 0.9925$ , so assumption was valid (less than 5% difference)
  - $[\text{NH}_3]_{\text{eq}} = 2x = 5.0 \times 10^{-3} \text{ M}$
  - $[\text{N}_2]_{\text{eq}} = 1.00 - x = 0.9975 \text{ M}$
  - $[\text{H}_2]_{\text{eq}} = 1.00 - 3x = 0.9925 \text{ M}$
  - Check calculations:
  - $Q = (5.0 \times 10^{-3})^2 / (0.9975)(0.9925)^3 = 2.6 \times 10^{-5}$
  - $K = 2.5 \times 10^{-5}$
  - These are close to equal, so the calculations were correct.
- $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3 \quad K_c = 2.5 \times 10^{-5}$   
 0.100 0.100 0 M initial concentrations
  - What are the equilibrium concentrations?

*What if the assumptions fail?*

- The most common assumption is that  $x \ll C_0$
- If this assumption is not correct, the equation in  $x$  becomes more complex. The most difficult situation that we meet is generally one in which the equation can be rearranged into a quadratic equation in  $x$ :
- $ax^2 + bx + c = 0$
- The solution to this equation is:  $x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$

*Quadratic Example*

- $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2 \quad K_c = 4.00$   
 1.00 2.00 0.00 0.00 M
- What are the equilibrium concentrations?
- Substance: CO H<sub>2</sub>O CO<sub>2</sub> H<sub>2</sub>
- Initial Conc: 1.00 2.00 0.00 0.00
- Change: -x -x +x +x
- Equil Conc: 1.00 - x 2.00 - x +x +x
- $K_c = [\text{CO}_2][\text{H}_2] / [\text{CO}][\text{H}_2\text{O}] = 4.00$

*Quadratic Example Solution*

- $(x)(x) / (1.00 - x)(2.00 - x) = 4.00$
- Assume  $x \ll 1.00$ ,  $x \ll 2.00$
- $x^2 / (1.00)(2.00) = 4.00$
- $x^2 = 8.00$
- $x = 2.83$ , so the assumption was bad.

- $(x)(x)/(1.00 - x)(2.00 - x) = 4.00$
- $(x)(x) = 4.00 (1.00 - x)(2.00 - x)$
- $x^2 = 8.00 - 12.00x + 4.00 x^2$
- $3.00x^2 - 12.00 x + 8.00 = 0$

$$x = \frac{12.00 \pm \sqrt{(12.00)^2 - 4(3.00)(8.00)}}{2(3.00)}$$

- $x = 0.845$
- $[\text{CO}_2] = [\text{H}_2] = x = 0.845 \text{ M}$
- $[\text{CO}] = 1.00 - x = 0.155 \text{ M} = 1.155 \text{ M}$
- $Q = 0.845 \times 0.845 / 0.155 \times 1.155 = 3.99$ , which is a good match to  $K = 4.00$ , so the calculations were correct.
- $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2 \quad K_c = 4.00$   
 $0.100 \quad 0.200 \quad 0.00 \quad 0.00 \text{ M}$
- What are the equilibrium concentrations?

#### *Product Present Initially*

- The procedure remains the same if any product is in the mixture initially. The only difference will be in the value of the initial concentration. It is also possible that reaction will occur in the reverse direction, in which case  $x$  will have a negative value.
- $\text{PCl}_5 \rightleftharpoons \text{PCl}_3 + \text{Cl}_2 \quad K_c = 0.00900$   
 $1.00 \quad 0.0100 \quad 0.500 \text{ M}$  initial concentrations
- What are the equilibrium concentrations?

### 15.6 LeChatelier's Principle

- If we place a stress on a system at equilibrium, the system will respond by shifting to a new equilibrium position in such a way as to remove that stress.
- Stresses:
  - change reactant concentration
  - change product concentration
  - change pressure
  - change volume
  - add an inert gas (no effect)
  - add reactant or product
  - change temperature
  - add a catalyst (no effect)

#### *Effect of Concentration Changes*

- $\text{CO(g)} + 3\text{H}_2\text{(g)} \rightleftharpoons \text{CH}_4\text{(g)} + \text{H}_2\text{O(g)}$
- $K_c = [\text{CH}_4][\text{H}_2\text{O}]/[\text{CO}][\text{H}_2]^3$
- Add  $\text{CO(g)}$ ,  $Q < K$ , net forward reaction occurs until  $Q = K$ , removing some  $\text{CO(g)}$
- Add  $\text{CH}_4\text{(g)}$ ,  $Q > K$ , net reverse reaction occurs until  $Q = K$ , thereby removing some  $\text{CH}_4\text{(g)}$

- Add CaO(s) to remove H<sub>2</sub>O(g),  $Q < K$ , forward reaction occurs to form some H<sub>2</sub>O(g)

*Change in Reactant Concentration*

- $N_2 + 3H_2 \rightleftharpoons 2NH_3$
- Add H<sub>2</sub> to system at equilibrium

*Effect of Pressure*

- Increase pressure by decreasing volume; same as increasing all concentrations by a constant factor.
- An increase in pressure shifts the equilibrium in the direction that has the fewer number of gas molecules.
- If  $\Delta n_{\text{gas}} = 0$ , there is no change in the position of equilibrium.
- No effect if there are no gases in the system.
- $2CO_2(g) \rightleftharpoons 2CO(g) + O_2(g)$
- Which direction will the equilibrium shift if pressure is increased?

*Effect of Pressure Increase*

- Which direction does the equilibrium shift?
- $2NO_2(g) \rightleftharpoons N_2O_4(g)$

*Effect of Pressure*

- $CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$
- $K_c = \frac{[CH_4][H_2O]}{[CO][H_2]^3}$
- Change the volume of the mixture to 1/2 the original value. All the concentrations then increase by a factor of 2.
- Before the change,  $Q = K$
- After the change,  $Q = K \times (2)(2)/(2)(2)^3 = K/4$
- $Q < K$  because the reactant change was greater than the product change and the equilibrium will shift towards products.

*Effect of Pressure*

- Volume decrease causes a pressure increase, which results in a shift in equilibrium in the direction that has fewer gas molecules, which leads to a pressure decrease.
- Changing pressure with an inert gas has no effect because that gas is not involved in the reaction.

*Effect of Temperature*

- The effect depends on whether the reaction is exothermic or endothermic. The effect results from a change in the value of  $K$  with temperature.
- $\Delta G^\circ = -RT \ln K$
- $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -RT \ln K$
- $\ln K = \Delta S^\circ/R - \Delta H^\circ/RT$
- For two temperatures,
- $\ln (K_2/K_1) = \Delta H^\circ/R(1/T_1 - 1/T_2)$
- Sign of  $\Delta H^\circ$  determines whether  $K$  increases or decreases as temperature increases.



- If  $T_2 > T_1$ ,  $(1/T_1 - 1/T_2) > 0$
- If  $\Delta H^\circ > 0$ ,  $\ln(K_2/K_1) > 0$  and  $K_2 > K_1$ , so the equilibrium shifts towards products .
- If  $\Delta H^\circ < 0$ ,  $\ln(K_2/K_1) < 0$  and  $K_2 < K_1$ , so the equilibrium shifts towards reactants.
- $\text{CO} + 3\text{H}_2 \rightleftharpoons \text{CH}_4 + \text{H}_2\text{O} \quad \Delta H^\circ = -206.2 \text{ kJ}$
- Which direction does the equilibrium shift if the temperature is increased?
- Towards reactants because  $K$  gets smaller.
- We can also *imagine* that heat is a reactant or product. If temperature is increased, the amount of heat is increased. The reaction will shift in such a way as to remove some of the added heat.
- Effect of increase in  $T$ ?
- $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3 + \text{heat} \quad \Delta H^\circ = -92 \text{ kJ}$
- Higher temperature causes a shift towards reactants.
- $2\text{H}_2\text{O} + \text{heat} \rightleftharpoons 2\text{H}_2 + \text{O}_2 \quad \Delta H^\circ = 484 \text{ kJ}$
- Higher temperature causes a shift towards products.

#### *Effect of Catalysts*

- A catalyst has no effect on the position of equilibrium because it affects the forward and reverse rates equally. It doesn't change  $\Delta G^\circ$ , so it can't change  $K$ .