Chapter 15 Chemical Equilibrium

Common Student Misconceptions

• Many students need to see how the numerical problems in this chapter are solved.
• Students confuse the arrows used for resonance and equilibrium.
• Students often have problems distinguishing between $K$ and $Q$.
• Students who have difficulty with some of the mathematical manipulations in this chapter should be directed to Appendix A of the text.
• Students often do not know (or check) whether an approximate equilibrium calculation is valid.

Lecture Outline

15.1 The Concept of Equilibrium (EOCQ’S 1,2,11,12)

• Consider colorless frozen $\text{N}_2\text{O}_4$.
  • At room temperature, it decomposes to brown $\text{NO}_2$.
  $$\text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g)$$
  • At some time, the color stops changing and we have a mixture of $\text{N}_2\text{O}_4$ and $\text{NO}_2$.
  • Chemical equilibrium is the point at which the concentrations of all species are constant.
  • Assume that both the forward and reverse reactions are elementary processes.
  • We can write rate expressions for each reaction.
    • Forward reaction: $\text{N}_2\text{O}_4(g) \rightarrow 2\text{NO}_2(g)$
      • $\text{Rate}_f = k_f[\text{N}_2\text{O}_4]$  $k_f$ = rate constant (forward reaction)
      • Reverse reaction: $2\text{NO}_2(g) \rightarrow \text{N}_2\text{O}_4(g)$
        • $\text{Rate}_r = k_r[\text{NO}_2]^2$  $k_r$ = rate constant (reverse reaction)
  • Place some pure $\text{N}_2\text{O}_4$ into a closed container.
    • As $\text{N}_2\text{O}_4$ reacts to form $\text{NO}_2$, the concentration of $\text{N}_2\text{O}_4$ will decrease and the concentration of $\text{NO}_2$ will increase.
    • Thus we expect the forward reaction rate to slow and the reverse reaction rate to increase.
    • Eventually we get to equilibrium where the forward and reverse rates are equal.
• At equilibrium:

\[ k_f[N_2O_4] = k_r[NO_2]^2 \]

• Rearranging, we get:

\[ k_f / k_r = \text{a constant} \]

• At equilibrium the concentrations of N₂O₄ and NO₂ do not change.

• This mixture is called an equilibrium mixture.

• This is an example of a dynamic equilibrium.

  • A dynamic equilibrium exists when the rates of the forward and reverse reactions are equal.
  • No further net change in reactant or product concentration occurs.
  • The double arrow \( \Leftrightarrow \) implies that the process is dynamic.

**FORWARD REFERENCES**

• Equilibria involving acids and bases will be the subject of chapters 16 and 17.

• Solubility equilibria will be discussed in Ch. 17 (section 17.4).

• The concept of equilibrium will be important throughout Ch. 19.

**15.2 The Equilibrium Constant (EOCQ’s 13-26)**

• Consider the Haber process:

\[ N_2(g) + 3H_2(g) \Leftrightarrow 2NH_3(g) \]

• It is used for the preparation of ammonia from nitrogen and hydrogen.

• The process is carried out at high temperature and pressure.

  • Ammonia is a good source of fixed nitrogen for plants.
  • Much of the NH₃ produced industrially is used as a fertilizer.

• If we start with a mixture of nitrogen and hydrogen (in any proportions), the reaction will reach equilibrium with constant concentrations of nitrogen, hydrogen and ammonia.

• However, if we start with just ammonia and no nitrogen or hydrogen, the reaction will proceed and N₂ and H₂ will be produced until equilibrium is achieved.

• No matter what the starting composition of reactants and products is, the equilibrium mixture contains the same relative concentrations of reactants and products.

  • Equilibrium can be reached from either direction.
• We can write an expression for the relationship between the concentration of the reactants and products at equilibrium.
  • This expression is based on the law of mass action.
  • For a general reaction, \( aA + bB \rightleftharpoons dD + eE \)
  • The equilibrium-constant expression is given by:

\[
K_c = \frac{[D]^d[E]^e}{[A]^a[B]^b}
\]

• Where \( K_c \) is the equilibrium constant.
• The subscript “c” indicates that molar concentrations were used to evaluate the constant.
• Note that the equilibrium constant expression has products in the numerator and reactants in the denominator.

Evaluating \( K_c \)
• The value of \( K_c \) does not depend on initial concentrations of products or reactants.
  • Consider the reaction:

\[ \text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g) \]

\[
K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]}
\]

• The equilibrium constant is given by:
• The value of this constant (at 100 °C) is 6.50 (regardless of the initial concentrations of \( \text{N}_2\text{O}_4(g) \) or \( \text{NO}_2(g) \)).
• The equilibrium expression depends on stoichiometry.
  • It does not depend on the reaction mechanism.
  • The value of \( K_c \) varies with temperature.
• We generally omit the units of the equilibrium constant.

**Equilibrium Constants in Terms of Pressure, \( K_p \)
• When the reactants and products are gases we can write an equilibrium expression using partial pressures rather than molar concentrations.
• The equilibrium constant is \( K_p \) where “p” stands for pressure.
For the reaction: \[ aA + bB \rightleftharpoons dD + eE \]

\[ K_p = \frac{(P_D)^d}{(P_A)^a(P_B)^b} \]

They can be interconverted using the ideal gas equation and our definition of molarity:

\[ PV = nRT \]  thus \[ P = \frac{n}{V}RT \]

- If we express volume in liters the quantity \( \frac{n}{V} \) is equivalent to molarity.
- Thus the partial pressure of a substance, \( A \), is given as:

\[ P_A = \frac{n_A}{V}RT = [A]RT \]

- We can use this to obtain a general expression relating \( K_c \) and \( K_p \):

\[ K_p = K_c(RT)^\Delta n \]

- Where \( \Delta n = (\text{moles of gaseous products}) - (\text{moles of gaseous reactants}) \).
- The numerical values of \( K_c \) and \( K_p \) will differ if \( \Delta n = 0 \).

**FORWARD REFERENCES**

- Various equilibrium constants: \( K_a, K_b, K_w, K_{sp} \) will be used throughout chapters 16 and 17, and later in select end-of-chapter problems in chapters 19 and 20.
- \( K_p \) and \( K_c \) will be revisited in Ch. 19 (section 19.7).
- Haber process will be further discussed in Ch. 22 (sections 22.2 and 22.7).

### 15.3 Interpreting and Working with Equilibrium Constants (EOCQ’S 13 - 20)

**The Magnitude of Equilibrium Constants**

- The equilibrium constant, \( K \), is the ratio of products to reactants.
  - Therefore, the larger \( K \) the more products are present at equilibrium.
  - Conversely, the smaller \( K \) the more reactants are present at equilibrium.
    - If \( K >> 1 \), then products dominate at equilibrium and equilibrium lies to the right.
    - If \( K << 1 \), then reactants dominate at equilibrium and the equilibrium lies to the left.
The Direction of the Chemical Equation and $K$
- An equilibrium can be approached from either direction.
- Consider the reaction: $N_2O_4(g) \rightleftharpoons 2NO_2(g)$
  - The equilibrium constant for this reaction (at 100°C) is:

$$K_c = \frac{[NO_2]^2}{[N_2O_4]} = 0.212$$

- However, when we write the equilibrium expression for the reverse reaction, $2NO_2(g) \rightleftharpoons N_2O_4(g)$
- The equilibrium constant for this reaction (at 100°C) is:

$$K_c = \frac{[N_2O_4]}{[NO_2]^2} = 4.72$$

- The equilibrium constant for a reaction in one direction is the reciprocal of the equilibrium constant of the reaction in the opposite direction.

Relating Chemical Equations and Equilibrium Constants
- The equilibrium constant of a reaction in the reverse direction is the inverse of the equilibrium constant of the reaction in the forward direction.
- The equilibrium constant of a reaction that has been multiplied by a number is the equilibrium constant raised to a power equal to that number.
- The equilibrium constant for a net reaction made up of two or more steps is the product of the equilibrium constants for the individual steps.

15.4 Heterogeneous Equilibria (EOCQ’S 25 - 26)
- Equilibria in which all reactants and products are present in the same phase are called homogeneous equilibria.
- Equilibria in which one or more reactants or products are present in a different phase are called heterogeneous equilibria.
- Consider the equilibrium established when solid lead(II) chloride dissolves in water to form a saturated solution:

$$\text{PbCl}_2(s) \rightleftharpoons \text{Pb}^{2+}(aq) + 2\text{Cl}^-(aq)$$

- Experimentally, the amount of Pb$^{2+}$ and Cl$^-$ does not depend on the amount of PbCl$_2$.
  - Why?
- The concentration of a pure solid or pure liquid equals its density divided by its molar mass.
- Neither density nor molar mass is a variable.
  - Thus the concentrations of solids and pure liquids are constant.
  - For the dissolution of PbCl$_2$:
    \[ K_c = [\text{Pb}^{2+}][\text{Cl}^-]^2 \]
- If a pure solid or pure liquid is involved in a heterogeneous equilibrium, its concentration is not included in the equilibrium constant expression.
- Note: Although the concentrations of these species are not included in the equilibrium expression, they do participate in the reaction and must be present for an equilibrium to be established!
- Other common examples of heterogeneous equilibria include:
  - systems involving solids and gases.
  - Example: CaCO$_3$(s) ⇌ CaO(s) + CO$_2$(g)
    \[ K_c = [\text{CO}_2] \text{ and } K_p = P_{CO_2} \]
  - systems where the solvent is involved as a reactant or product and the solutes are present at low concentrations.
  - Example: H$_2$O($l$) + CO$_3^{2-}$(aq) ⇌ OH$^-$ (aq) + HCO$_3^-$ (aq)
    \[ K_c = [\text{OH}^-][\text{HCO}_3^-] / [\text{CO}_3^{2-}] \]
  - Here the concentration of water is essentially constant and we can think of it as a pure liquid.

**FORWARD REFERENCES**
- Solubility equilibria will be discussed in detail in Ch. 17.
- Exclusion of pure liquids and solids from equilibrium expressions will be revisited in Ch. 19.

**15.5 Calculating Equilibrium Constants (EOCQ’s 27-34)**

- Proceed as follows:
  - Tabulate initial and equilibrium concentrations (or partial pressures) for all species in the equilibrium.
  - If an initial and an equilibrium concentration is given for a species, calculate the change in concentration.
  - Use the coefficients in the balanced chemical equation to calculate the changes in concentration of all species.
  - Deduce the equilibrium concentrations of all species.
  - Use these to calculate the value of the equilibrium constant.

**FORWARD REFERENCES**
- Methods of finding equilibrium constants from thermodynamic or electrochemical will be discussed in Ch. 19 and Ch. 20, respectively.
15.6 Applications of Equilibrium Constants (EOCQ’s 35-50)

Predicting the Direction of Reaction

• For a general reaction: \( aA + bB \leftrightharpoons dD + eE \)
• We define \( Q \), the reaction quotient, as:
\[
Q = \frac{[D]^d [E]^e}{[A]^a [B]^b}
\]
• Where \([A]\), \([B]\), \([D]\), and \([E]\) are molarities (for substances in solution) or partial pressures (for gases) at any given time.
• We can compare \( Q_e \) to \( K_c \) or \( Q_p \) to \( K_p \):
  • If \( Q = K \), then the system is at equilibrium.
  • If \( Q < K \), then the forward reaction must occur to reach equilibrium.
  • If \( Q > K \), then the reverse reaction must occur to reach equilibrium.
  • Products are consumed, reactants are formed.
  • \( Q \) decreases until it equals \( K \).

Calculating Equilibrium Concentrations

• The same steps used to calculate equilibrium constants are used to calculate equilibrium concentrations.
• Generally, we do not have a number for the change in concentration.
  • Therefore, we need to assume that \( x \) mol/L of a species is produced (or used).
• The equilibrium concentrations are given as algebraic expressions.

FORWARD REFERENCES

• \( Q \) will be used in Ch. 19 (section 19.7) to determine Gibb’s free energy change at nonstandard conditions.
• \( Q \) will be used in Ch. 20 (section 20.6) to determine cell EMF at nonstandard conditions (Nernst Equation).

15.7 Le Châtelier’s Principle (EOCQ’s 51-56)

• Consider the Haber process: \( N_2(g) + 3H_2(g) \leftrightharpoons 2NH_3(g) \)
  • As the pressure increases, the amount of ammonia present at equilibrium increases.
  • As the temperature increases, the amount of ammonia at equilibrium decreases.
  • Can this be predicted?
• Le Châtelier’s principle: if a system at equilibrium is disturbed by a change in temperature, a change in pressure, or a change in the concentration of one or more components, the system will shift its equilibrium position in such a way as to counteract the effects of the disturbance.
Change in Reactant or Product Concentration

- If a chemical system is at equilibrium and we add or remove a product or reactant, the reaction will shift so as to reestablish equilibrium.
  - For example, consider the Haber process again:
    \[ \text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g) \]
  - If H\(_2\) is added while the system is at equilibrium, \(Q < K\).
    - The system must respond to counteract the added H\(_2\) (Le Châtelier’s principle).
      - That is, the system must consume the H\(_2\) and produce products until a new equilibrium is established.
      - Therefore, [H\(_2\)] and [N\(_2\)] will decrease and [NH\(_3\)] will increase until \(Q = K\).
  - We can exploit this industrially.
    - Suppose that we wanted to optimize the amount of ammonia we formed from the Haber process.
    - We might flood the reaction vessel with reactants and continuously remove product.
    - The amount of ammonia produced is optimized because the product (NH\(_3\)) is continuously removed and the reactants (N\(_2\) and H\(_2\)) are continuously being added.

Effects of Volume and Pressure Changes

- Consider a system at equilibrium.
  - If the equilibrium involves gaseous products or reactants, the concentration of these species will be changed if we change the volume of the container.
    - For example, if we decrease the volume of the container, the partial pressures of each gaseous species will increase.
    - Le Châtelier’s principle predicts that if pressure is increased, the system will shift to counteract the increase.
      - That is, the system shifts to remove gases and decrease pressure.
      - An increase in pressure favors the direction that has fewer moles of gas.
  - Consider the following system: \(\text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g)\)
    - An increase in pressure (by decreasing the volume) favors the formation of colorless N\(_2\)O\(_4\).
    - The instant the pressure increases, the concentration of both gases increases and the system is not at equilibrium.
    - The system changes to reduce the number moles of gas.
    - A new equilibrium is established.
• The mixture is lighter in color.
• Some of the brown NO\textsubscript{2} has been converted into colorless N\textsubscript{2}O\textsubscript{4}(g)
• In a reaction with the same number of moles of gas in the products and reactants, changing the pressure has no effect on the equilibrium.
• In addition, no change will occur if we increase the total gas pressure by the addition of a gas that is not involved in the reaction.

**Effect of Temperature Changes**
• The equilibrium constant is temperature dependent.
• How will a change in temperature alter a system at equilibrium?
  • It depends on the particular reaction.
  • For example, consider the endothermic reaction:
    \[
    \text{Co(H}_2\text{O)}_6^{2+}(aq) + 4\text{Cl}^-(aq) \rightleftharpoons \text{CoCl}_4^{2-}(aq) + 6\text{H}_2\text{O(l)} \quad \Delta H > 0
    \]
    • Co(H\textsubscript{2}O\textsubscript{6})\textsuperscript{2+} is pale pink and CoCl\textsubscript{4}\textsuperscript{2–} is a deep blue.
    • At room temperature, an equilibrium mixture (light purple) is placed in a beaker of warm water.
      • The mixture turns deep blue.
      • This indicates a shift toward products (blue CoCl\textsubscript{4}\textsuperscript{2–}).
      • This reaction is endothermic.
      • For an endothermic reaction (\(\Delta H > 0\)), heat can be considered as a reactant.
        • Thus, adding heat causes a shift in the forward direction.
    • The room-temperature equilibrium mixture is placed in a beaker of ice water.
      • The mixture turns bright pink.
      • This indicates a shift toward reactants (pink Co(H\textsubscript{2}O\textsubscript{6})\textsuperscript{2+}).
      • In this case, by cooling the system we are removing a reactant (heat).
      • Thus, the reaction is shifted in the reverse reaction.
    • A change in temperature causes a change in the value of \(K\).
      • If we increase the temperature of an endothermic reaction, \(K\) increases.
      • If we increase the temperature of an exothermic reaction, \(K\) decreases.

**The Effect of Catalysts**
• A catalyst lowers the activation energy barrier for the reaction.
  • Therefore, a catalyst will decrease the amount of time needed to reach equilibrium.
  • A catalyst *does not* effect the composition of the equilibrium mixture.

**FORWARD REFERENCES**
• Le Châtelier's principle versus percent ionization will be mentioned in Ch. 16 (sections 16.6).
• Le Châtelier’s principle will be brought up in the common ion effect in Ch. 17 (sections 17.1 and 17.3).
• Le Châtelier’s principle versus solubility will be discussed in Ch. 17 (section 17.5).
• Predictions of the equilibrium shifts will be made in Ch. 19 (section 19.7).
• Haber process will be further discussed in Ch. 22 (sections 22.2 and 22.7).