Unit 3 Equilibrium - Find the Center

Content Area: **Science**
Course(s): **AP Chemistry**
Time Period: **October**
Length: **6 weeks**
Status: **Published**

Transfer Skills

Chemical processes to do not all go to completion and equilibrium concepts will govern the end product and behavior of reaction systems

Enduring Understandings

Equilibrium is a physical state in which forces and changes occur in opposite and off-setting directions.

At any temperature there are infinite equilibrium positions, however only one equilibrium constant.

Acids and bases play a major role in our every day lives.

Essential Questions

What constitutes a state of dynamic equilibrium?

Why are reactant and product concentration not necessarily equal at equilibrium?

To what extent can the strengths of acids and bases be quantified?

Why is pH important?

How is it possible for a buffered solution to use up both excess acid and excess base to maintain a constant pH?

To what extent are the characteristics of all titration the same?

Content

Equilibrium constant expression, reaction quotient, LeChatelier's Principle, hydrolysis, common ion effect, Henderson-hasselbalch, solubility product constant, ion product, complex ion

Skills

Use Le Chatelier's Principle to predict the changes in equilibrium position due to changes in temperature, pressure and/or concentrations.

Calculate the numerical value for the equilibrium constant for a reaction, given experimental data.

Convert between Kp and Kc for a gaseous equilibrium.

Calculate equilibrium concentrations for a reaction, given the Keq, initial concentrations and some piece of information about the equilibrium.

Calculate the numerical value of Ksp for a chemical reaction from molar solubility, or the numerical value of molar solubility given Ksp.

Predict whether a precipitate will form when two solutions are mixed based on Ksp values and concentrations and volumes of the two solutions.

Determine the point in a titration that neutralization occurs.

Determine the pH of buffer solutions

Resources

Standards

Big Idea 2: Chemical and physical properties of materials can be explained by the structure and the arrangement of atoms, ions, or molecules and the forces between them.
Enduring understanding 2.A:
a. Matter can be described by its physical properties. The physical properties of a substance generally depend on the spacing between the particles (atoms, molecules, ions) that make up the substance and the forces of attraction among them.

2.A Learning Objectives:
LO 2.1 Students can predict properties of substances based on their chemical formulas, and provide explanations of their properties based on particle views. [See SP 6.4, 7.1]

LO 2.2 The student is able to explain the relative strengths of acids and bases based on molecular structure, interparticle forces, and solution equilibrium. [See SP 7.2, connects to Big Idea 5, Big Idea 6] Note: These learning objectives apply to essential knowledge components of 2A–2D.

Big Idea 3: Changes in matter involve the rearrangement and/or reorganization of atoms and/or the transfer of electrons.
Essential knowledge 3.B.2: In a neutralization reaction, protons are transferred from an acid to a base.
a. The amphoteric nature of water plays an important role in the chemistry of aqueous solutions, since water can both accept protons from and donate protons to dissolved species.

b. Acid-base reactions: 1. Only reactions in aqueous solutions are considered. 2. The Brønsted-Lowry concept of acids and bases is the focus of the course. 3. When an acid or base ionizes in water, the conjugate acid-base pairs can be identified and their relative strengths compared.

3.B.2 Learning Objective:
LO 3.7 The student is able to identify compounds as Brønsted-Lowry acids, bases, and/or conjugate acid-base pairs, using proton-transfer reactions to justify the identification. [See SP 6.1]

Big Idea 6: Any bond or intermolecular attraction that can be formed can be broken. These two processes are in a dynamic competition, sensitive to initial conditions and external perturbations.
Enduring understanding 6.A: Chemical equilibrium is a dynamic, reversible state in which rates of opposing processes are equal. Essential knowledge 6.A.1: In many classes of reactions, it is important to consider both the forward and reverse reaction.
a. Many readily observable processes are reversible. Examples include evaporating and condensing water, absorption of a gas, or dissolving and precipitating a salt. Relevant and interesting contexts include biological examples (binding of oxygen to hemoglobin and the attachment of molecules to receptor sites in the nose) and environmental examples (transfer of carbon between atmosphere and biosphere and transfer of dissolved substances between atmosphere and hydrosphere).

b. Dissolution of a solid, transfer of protons in acid-base reactions, and transfer of electrons in redox reactions are important examples of reversible reactions.

6.A.1 Learning Objective:
LO 6.1 The student is able to, given a set of experimental observations regarding physical, chemical, biological, or environmental processes that are reversible, construct an explanation that connects the observations to the reversibility of the underlying chemical reactions or processes. [See SP 6.2]

Essential knowledge 6.A.2: The current state of a system undergoing a reversible reaction can be characterized by the extent to which reactants have been converted to products. The relative quantities of reaction components are quantitatively described by the reaction quotient, Q.
a. Given an initial set of reactant and product concentrations, only those sets of concentrations that are consistent with the reaction stoichiometry can be attained. ICE (initial, change, equilibrium) tables are useful for determining which sets of concentration values are possible.

b. The reaction quotient, Q, provides a convenient measure of the current progress of a reaction. Q does not include substances whose concentrations are independent of the amount of substance, such as for a solid in contact with a liquid solution or with a gas, or for a pure solid or liquid in contact with a gas.

c. The value of Q (and so also K) changes when a reaction is reversed. When reactions are added together through the presence of a common intermediate, Q (and so also K) of the resulting reaction is a product of the values of Q (or K) for the original reactions.

6.A.2 Learning Objective:
LO 6.2 The student can, given a manipulation of a chemical reaction or set of reactions (e.g., reversal of reaction or addition of two reactions), determine the effects of that manipulation on Q or K. [See SP 2.2]

Essential knowledge 6.A.3: When a system is at equilibrium, all macroscopic variables, such as concentrations, partial pressures, and temperature, do not change over time. Equilibrium results from an equality between the rates of the forward and reverse reactions, at which point Q = K.
a. When equilibrium is reached, no observable changes occur in the system. 1. Reactant and product molecules are present. 2. Concentration of all species remains constant.

b. If the rate of the forward reaction is greater than the reverse reaction, there is a net conversion of reactants

to products. If the rate of the reverse reaction is greater than the forward reaction, there is a net conversion of products to reactants. An equilibrium state is reached when these rates balance, at which point the progress of reaction, Q, becomes equal to the equilibrium constant, K.

c. Comparing Q to K allows the determination of whether the reaction is at equilibrium, or will proceed toward products or reactants to reach equilibrium.

d. Equilibrium constants can be determined from experimental measurements of the concentrations of the reactants and products at equilibrium.

e. Given a single reaction, initial concentrations, and K, the concentrations at equilibrium may be predicted.

f. Graphs of concentration over time for simple chemical reactions can be used to understand the establishment of chemical equilibrium.

6.A.3 Learning Objectives:
LO 6.3 The student can connect kinetics to equilibrium by using reasoning about equilibrium, such as LeChatelier's principle, to infer the relative rates of the forward and reverse reactions. [See SP 7.2]

LO 6.4 The student can, given a set of initial conditions (concentrations or partial pressures) and the equilibrium constant, K, use the tendency of Q to approach K to predict and justify the prediction as to whether the reaction will proceed toward products or reactants as equilibrium is approached. [See SP 2.2, 6.4]

LO 6.5 The student can, given data (tabular, graphical, etc.) from which the state of a system at equilibrium can be obtained, calculate the equilibrium constant, K. [See SP 2.2]

LO 6.6 The student can, given a set of initial conditions (concentrations or partial pressures) and the equilibrium constant, K, use stoichiometric relationships and the law of mass action (Q equals K at equilibrium) to determine qualitatively and/or quantitatively the conditions at equilibrium for a system involving a single reversible reaction. [See SP 2.2, 6.4]

Essential knowledge 6.A.4: The magnitude of the equilibrium constant, K, can be used to determine whether the equilibrium lies toward the reactant side or product side.
a. For many aqueous reactions, K is either very large or very small, and this may be used to reason qualitatively about equilibrium systems.

b. Particulate representations can be used to describe the relationship between the numbers of reactant and product particles present at equilibrium, and the value of the equilibrium constant.

6.A.4 Learning Objective:
LO 6.7 The student is able, for a reversible reaction that has a large or small K, to determine which chemical species will have very large versus very small concentrations at equilibrium. [See SP 2.2, 2.3]

Enduring understanding 6.B: Systems at equilibrium are responsive to external perturbations, with the response leading to a change in the composition of the system. Essential knowledge 6.B.1: Systems at equilibrium respond to disturbances by partially countering the effect of the disturbance (LeChatelier's principle).
a. LeChatelier's principle can be used to predict the response of a system to the following stresses: addition or removal of a chemical species, change in temperature, change in volume/pressure of a gas phase system, and dilution of a reaction system with water or other solvent.

b. LeChatelier's principle can be used to reason about the effects a stress will have on experimentally measurable properties, such as pH, temperature, and color of a solution.

6.B.1 Learning Objectives:
LO 6.8 The student is able to use LeChatelier's principle to predict the direction of the shift resulting from various possible stresses on a system at chemical equilibrium. [See SP 1.4, 6.4]

LO 6.9 The student is able to use LeChatelier's principle to design a set of conditions that will optimize a desired outcome, such as product yield. [See SP 4.2]

Essential knowledge 6.B.2: A disturbance to a system at equilibrium causes Q to differ from K, thereby taking the system out of the original equilibrium state. The system responds by bringing Q back into agreement with K, thereby establishing a new equilibrium state.
a. LeChatelier's principle involves qualitative reasoning that is closely connected to the quantitative approach of 6.A.3.

b. Some stresses, such as changes in concentration, cause a change in Q. A change in temperature causes a change in K. In either case, the reaction shifts to bring Q and K back into equality.

6.B.2 Learning Objective:
LO 6.10 The student is able to connect LeChatelier's principle to the comparison of Q to K by explaining the effects of the stress on Q and K. [See SP 1.4, 7.2]

Enduring understanding 6.C: Chemical equilibrium plays an important role in acid-base chemistry and in solubility. Essential knowledge 6.C.1: Chemical equilibrium reasoning can be used to describe the proton-transfer reactions of acid-base chemistry.
a. The concentrations of hydronium ion and hydroxide ion are often reported as pH and pOH, respectively.

b. Water autoionizes with an equilibrium constant, Kw. For pure water, pH = pOH, and this condition is called "neutrality," or a neutral solution. At 25°C, pKw = 14, and thus pH and pOH add to 14. In pure water at 25°C, pH = pOH = 7.

c. Common strong acids include HCl, HBr, HI, $HClO_4$, H_2SO_4, and HNO_3. The molecules of strong acids completely ionize in solution to produce hydronium ions. In other words, 100 percent of the molecules of the strong acid are ionized in a solution (assuming that the concentration is not extremely high). As such, the concentration of H_3O^+ in a strong acid solution is equal to the initial concentration of the strong acid, and thus the pH of the strong acid solution is easily calculated.

d. Common strong bases include group I and II hydroxides. When dissolved in solution, strong bases completely dissociate to produce hydroxide ions. Note that some group II hydroxides are slightly soluble in water. However, 100 percent of the dissolved base is ionized.

e. Weak acid molecules react with water to transfer a proton to the water molecule. However, weak acid molecules only partially ionize in this way. In other words, only a small percentage of the molecules of a weak acid are ionized in a solution (assuming that the initial concentration is not extremely low). Thus, the concentration of H_3O^+ does not equal the initial concentration of the molecular acid, and the vast majority of the acid molecules remain un-ionized. A solution of a weak acid thus involves equilibrium between an un-ionized acid and its conjugate base. The equilibrium constant for this reaction is Ka, often reported as pKa. The pH of a weak acid solution can be determined from the initial acid concentration and the pKa. The common weak acids include carboxylic acids. The relative magnitudes of Ka's are influenced by structural factors such as bond strength, solvation, and electronegativity of the atom bonded to the labile proton.

f. The common weak bases include ammonia, amines and pyridines, other nitrogenous bases, and conjugate bases (defined below in g). Weak base molecules in aqueous solutions react with water molecules to produce hydroxide ions. However, only a small percentage of the molecules of a weak base in a solution ionize in this way (assuming that the initial concentration is not extremely low). Thus, the concentration of OH^- in the

solution does not equal the initial concentration of the molecular base, and the vast majority of the base molecules remain un-ionized. A solution of a weak base thus involves an equilibrium between an un-ionized base and its conjugate acid. The equilibrium constant for this reaction is Kb, often reported as pKb. The pH of a weak base solution can be determined from the initial base concentration and the pKb.

g. When an acid molecule loses its proton, it becomes a base, since the resultant ion could react with water as a base. The acid and base are referred to as a conjugate acid-base pair. The ionization constants for the acid-base pair are related to Kw, and at 25°C, pKa + pKb = 14. This relation can be used to reason qualitatively about the relative strengths of conjugate acids and bases. For example, the conjugate base of a strong acid is a much weaker base than H2O, and therefore does not react as a base in aqueous solutions.

h. The pH of an acid solution depends on both the strength of the acid and the concentration of the acid. If we compare solutions of a weak acid and of a strong acid at the same pH, we find that both solutions have the same concentration of H3O+ (aq). However, the strong acid is completely dissociated into ions in solution, whereas the weak acid is only partially dissociated into ions in solution. Thus, there are vastly more un-ionized acid molecules in the weak acid solution than in the strong acid solution at the same pH. Thus, to achieve solutions of equal pH, the weak acid solution must be a much greater concentration than the strong acid solution. If we compare solutions of a weak acid and of a strong acid of the same initial concentration, the concentration of H3O+ in the strong acid solution is much larger (and the pH thus lower) since the strong acid is 100 percent ionized.

i. Reactions of acids and bases are called neutralization reactions, and these reactions generally have K >1, and thus can be considered to go to completion. 1. For a mixture of a strong acid with a strong base, the neutralization reaction is H3O+ + OH– → H2O. The K for this reaction is 1014 at 25°C, so the reaction goes to completion. This allows the pH of mixtures of strong acids and bases to be determined from the limiting reactant, either the acid or the base. 2. When a strong base is added to a solution of a weak acid, a neutralization reaction occurs: conjugate acid + OH- → conjugate base + H2O. 3. When a strong acid is added to a solution of a weak base, a neutralization reaction occurs: conjugate base + H3O+ → conjugate acid + H2O.

j. For a weak acid solution and a strong acid solution with the same pH, it takes much more base to neutralize the weak acid solution because the initial acid concentration is much larger. The weak acid solution contains a large amount of un-ionized acid molecules. Therefore, a weak acid solution resists changes in pH for a much greater amount of added base.

k. A titration technique exists for neutralization reactions. At the equivalence point, the moles of titrant and the moles of titrate are present in stoichiometric proportions. In the vicinity of the equivalence point, the pH rapidly changes. This can be used to determine the concentration of the titrant.

l. As base is added to either a strong acid solution or a weak acid solution, the H3O+ (aq) concentration does not change much. The change in pH is less than ~1.5 for the region where 10 to 90 percent of the base needed to reach the equivalence point has been added.

m. The pKa of an acid can be determined from the pH at the half equivalence point of the titration if the equivalence point is known (i.e., the concentration of both the titrant and analyte are known).

n. For polyprotic acids, the use of titration curves to evaluate the number of labile protons is important, as well as knowing which species are present in large concentrations at any region along the curve.

o. Halfway to the equivalence point, the contents of a solution, formed by titrating a weak acid, is different from that formed by titrating a strong acid. For a strong acid, the main species in a solution halfway to the equivalence point are H3O+(aq), the anion from the acid (e.g., Cl–, NO3 –), and the cation from the base (e.g., Na+). The total positive charge is equal to the total negative charge. For a weak acid, the main species in a

solution halfway to the equivalence point are H3O+(aq), the anion from the acid (e.g., CH3COO–, F–), the cation from the base (e.g., Na+), and undissociated acid, HA. The total positive charge is equal to the total negative charge, and [HA] = [A–].

6.C.1 Learning Objectives:
LO 6.11 The student can generate or use a particulate representation of an acid (strong or weak or polyprotic) and a strong base to explain the species that will have large versus small concentrations at equilibrium. [See SP 1.1, 1.4, 2.3]

LO 6.12 The student can reason about the distinction between strong and weak acid solutions with similar values of pH, including the percent ionization of the acids, the concentrations needed to achieve the same pH, and the amount of base needed to reach the equivalence point in a titration. [See SP 1.4, connects to 1.E.2]

LO 6.13 The student can interpret titration data for monoprotic or polyprotic acids involving titration of a weak or strong acid by a strong base (or a weak or strong base by a strong acid) to determine the concentration of the titrant and the pKa for a weak acid, or the pKb for a weak base. [See SP 5.1, connects to 1.E.2]

LO 6.14 The student can, based on the dependence of Kw on temperature, reason that neutrality requires [H+] = [OH–] as opposed to requiring pH = 7, including especially the applications to biological systems. [See SP 2.2, 6.2]

LO 6.15 The student can identify a given solution as containing a mixture of strong acids and/or bases and calculate or estimate the pH (and concentrations of all chemical species) in the resulting solution. [See SP 2.2, 2.3, 6.4]

LO 6.16 The student can identify a given solution as being the solution of a monoprotic weak acid or base (including salts in which one ion is a weak acid or base), calculate the pH and concentration of all species in the solution, and/ or infer the relative strengths of the weak acids or bases from given equilibrium concentrations. [See SP 2.2, 6.4]

LO 6.17 The student can, given an arbitrary mixture of weak and strong acids and bases (including polyprotic systems), determine which species will react strongly with one another (i.e., with K >1) and what species will be present in large concentrations at equilibrium. [See SP 6.4]

Essential knowledge 6.C.2: The pH is an important characteristic of aqueous solutions that can be controlled with buffers. Comparing pH to pKa allows one to determine the protonation state of a molecule with a labile proton.
a. A buffer solution contains a large concentration of both members in a conjugate acid-base pair. The conjugate acid reacts with added base and the conjugate base reacts with added acid. The pH of the buffer is related to the pKa and the concentration ratio of acid and base forms. The buffer capacity is related to absolute concentrations of the acid and base forms. These relationships can be used both quantitatively and qualitatively to reason about issues such as the ratio of acid to base forms in a given buffer, the impact of this on the buffer capacity for added acid or base, and the choice of an appropriate conjugate acid-base pair for a desired buffer pH (including polyprotic acids).

b. If [A–]/[HA] starts as 1, it is not until the ratio changes by a factor of 10 that a 1 pH unit change occurs; adding small amounts of either acid or base does not change the ratio much, so the pH changes are much smaller for buffers than unbuffered solutions.

c. Weak acids and their conjugate bases make good buffers. Strong acids and bases do not. It takes much more base to change the pH of a weak acid solution because there is a large reservoir of undissociated weak acid.

d. By comparing the pH of a solution to the pKa of any acid in the solution, the concentration ratio between

the acid and base forms of that acid (the protonation state) can be determined. For example, if pH < pKa, the acid form has a higher concentration than the base form. If pH > pKa, the base form has a higher concentration than the acid form. Applications of this relationship include the use of acid-base indicators, the protonation state of protein side chains (including acids or proteins with multiple labile protons), and the pH required for acid-catalyzed reactions in organic chemistry.

6.C.2 Learning Objectives:
LO 6.18 The student can design a buffer solution with a target pH and buffer capacity by selecting an appropriate conjugate acid-base pair and estimating the concentrations needed to achieve the desired capacity. [See SP 2.3, 4.2, 6.4]

LO 6.19 The student can relate the predominant form of a chemical species involving a labile proton (i.e., protonated/deprotonated form of a weak acid) to the pH of a solution and the pKa associated with the labile proton. [See SP 2.3, 5.1, 6.4]

LO 6.20 The student can identify a solution as being a buffer solution and explain the buffer mechanism in terms of the reactions that would occur on addition of acid or base. [See SP 6.4]

Essential knowledge 6.C.3: The solubility of a substance can be understood in terms of chemical equilibrium.
a. The dissolution of a substance in a solvent is a reversible reaction, and so has an associated equilibrium constant. For dissolution of a salt, the reaction quotient, Q, is referred to as the solubility product, and the equilibrium constant for this reaction is denoted as Ksp, the solubility-product constant.

b. The solubility of a substance can be calculated from the Ksp for the dissolution reaction. This relation can also be used to reason qualitatively about the relative solubility of different substances.

c. The free energy change (ΔG°) for dissolution of a substance reflects both the breaking of the forces that hold the solid together and the interaction of the dissolved species with the solvent. In addition, entropic effects must be considered. Qualitative reasoning regarding solubility requires consideration of all of these contributions to the free energy.

d. All sodium, potassium, ammonium, and nitrate salts are soluble in water.

e. A salt is less soluble in a solution that has an ion in common with the salt. This has important consequences for solubility of salts in sea water and other natural bodies of water. This phenomenon can be understood qualitatively using LeChatelier’s principle.

f. The solubility of a salt will be pH sensitive when one of the ions is an acid or base. Applications include the iron hydroxides of acid-mine drainage and the effects of acid rain on solubility of carbonates. These effects can be understood qualitatively with LeChatelier’s principle.

6.C.3 Learning Objectives:
LO 6.21 The student can predict the solubility of a salt, or rank the solubility of salts, given the relevant Ksp values. [See SP 2.2, 2.3, 6.4]

LO 6.22 The student can interpret data regarding solubility of salts to determine, or rank, the relevant Ksp values. [See SP 2.2, 2.3, 6.4]

LO 6.23 The student can interpret data regarding the relative solubility of salts in terms of factors (common ions, pH) that influence the solubility. [See SP 5.1]

LO 6.24 The student can analyze the enthalpic and entropic changes associated with the dissolution of a salt, using particulate level interactions and representations. [See SP 1.4, 7.1, connects to 5.E]

Enduring understanding 6.D: The equilibrium constant is related to temperature and the difference in Gibbs free energy between reactants and products. Essential knowledge 6.D.1: When the difference in Gibbs free energy between reactants and products (ΔG°) is much larger than the thermal energy (RT), the equilibrium constant is either very small (for $\Delta G^\circ > 0$) or very large (for $\Delta G^\circ < 0$). When ΔG° is comparable to the thermal energy (RT), the equilibrium constant is near 1.
a. The free energy change for a chemical process in which all of the reactants and products are present in a standard state (as pure substances, as solutions of 1 molar concentration, or as gases at a pressure of 1 bar, or 1 atm) is given a particular symbol, ΔG°.

b. The equilibrium constant is related to free energy by $K = e^{-\Delta G^\circ/RT}$. This relation may be used to connect thermodynamic reasoning about a chemical process to equilibrium reasoning about this process. This reasoning can be done quantitatively through numerical examples or qualitatively through estimation. For example, the thermal energy (RT) at room temperature is 2.4 kJ/mol. This sets the energy scale for relating the enthalpy and entropy changes to the magnitude of K, since when the magnitude of ΔG° is large compared to the thermal energy, then K deviates strongly from 1.

c. The relation $K = e^{-\Delta G^\circ/RT}$ provides a refinement of the statement in 5.E that processes with $\Delta G^\circ < 0$ favor products, while those with $\Delta G^\circ > 0$ favor reactants. If $\Delta G^\circ < 0$, then $K > 1$, while if $\Delta G^\circ > 0$, then $K < 1$. The phrase “favors products” in 5.E is therefore more precisely stated as $K > 1$, while “favors reactants” in 5.E is more precisely stated as $K < 1$.

d. Since K is directly related to free energy, when the magnitude of K is of primary interest, it is useful to consider whether a reaction is exergonic ($\Delta G^\circ < 0$) or endergonic ($\Delta G^\circ > 0$). (Exothermic versus endothermic is the useful distinction when the issue of interest is whether a reaction releases or consumes energy.) In many biological applications, the magnitude of K is of central importance, and so the exergonic/endergonic distinction is useful.

6.D.1 Learning Objective:
LO 6.25 The student is able to express the equilibrium constant in terms of ΔG° and RT and use this relationship to estimate the magnitude of K and, consequently, the thermodynamic favorability of the process. [See SP 2.3]