Unit 6: Thermodynamics

Content Area: **Science**
Course(s): **AP Chemistry**
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Big Idea 6

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

Enduring understanding 6.A: Chemical equilibrium is a dynamic, reversible state in which rates of opposing processes are equal.

Essential knowledge 6.A.1

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.

Learning Objective 6.1

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.

Essential knowledge 6.A.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.

Essential knowledge 6.A.3

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 .

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.

Learning Objective 6.3

LO 6.3 The student can connect kinetics to equilibrium by using reasoning about equilibrium, such as Le Chatelier's principle, to infer the relative rates of the forward and reverse reactions.

Learning Objective 6.4

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.

Learning Objective 6.5

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.

Learning Objective 6.6

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.

Essential knowledge 6.A.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.

Learning Objective 6.7

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.

Enduring understanding 6.B

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

Essential knowledge 6.B.1: Systems at equilibrium respond to disturbances by partially countering the effect of the disturbance (Le Chatelier's principle).

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

Learning Objective 6.8

LO 6.8 The student is able to use Le Chatelier's principle to predict the direction of the shift resulting from various possible stresses on a system at chemical equilibrium.

Learning Objective 6.9

LO 6.9 The student is able to use Le Chatelier's principle to design a set of conditions that will optimize a desired outcome, such as product yield.

Essential knowledge 6.B.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. Le Chatelier'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.

Learning Objective 6.10

LO 6.10 The student is able to connect Le Chatelier's principle to the comparison of Q to K by explaining the

effects of the stress on Q and K.

Enduring understanding 6.C

Enduring understanding 6.C: Chemical equilibrium plays an important role in acid-base chemistry and in solubility.

Essential knowledge 6.C.1

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 and , respectively.

b. Water autoionizes with an equilibrium constant, . For pure water, , and this condition is called "neutrality," or a neutral solution. At , , and thus and add to 14. In pure water at , .

c. Common strong acids include , and . 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 in a strong acid solution is equal to the initial concentration of the strong acid, and thus the 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 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 , often reported as . The of a weak acid solution can be determined from the initial acid concentration and the . The common weak acids include carboxylic acids. The relative magnitudes of 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 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 , often reported as . The of a weak base solution can be determined from the initial base concentration and the .

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 , and at , . 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 , and therefore does not react as a base in aqueous solutions.

h. The 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 , we find that both solutions have the same concentration of
. 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 . Thus, to achieve solutions of equal , 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 in the strong acid solution is much larger (and the 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 , and thus can be considered to go to completion.
i. For a mixture of a strong acid with a strong base, the neutralization reaction is . The K for this reaction is at , so the reaction goes to completion. This allows the of mixtures of strong acids and bases to be determined from the limiting reactant, either the acid or the base.
ii. When a strong base is added to a solution of a weak acid, a neutralization reaction occurs:
iii. When a strong acid is added to a solution of a weak base, a neutralization reaction occurs:
j. For a weak acid solution and a strong acid solution with the same , 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 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 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 concentration does not change much. The change in is less than for the region where 10 to 90 percent of the base needed to reach the equivalence
point has been added.
m. The of an acid can be determined from the 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 , the anion from the acid (e.g., ,), and the cation from the base (e.g.,). 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 , the anion from the acid (e.g., ,), the cation from the base (e.g.,), and undissociated acid, . The total positive charge is equal to the total negative charge, and .

Learning Objective 6.11

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.

Learning Objective 6.12

LO 6.12 The student can reason about the distinction between strong and weak acid solutions with similar values of , including the percent ionization of the acids, the concentrations needed to achieve the same , and the amount of base needed to reach the equivalence point in a titration.

Learning Objective 6.13

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 for a weak acid, or the for a weak base.

Learning Objective 6.14

LO 6.14 The student can, based on the dependence of on temperature, reason that neutrality requires as opposed to requiring , including especially the applications to biological systems.

Learning Objective 6.15

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 (and concentrations of all chemical species) in the resulting solution.

Learning Objective 6.16

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 and concentration of all species in the solution, and/or infer the relative strengths of the weak acids or bases from given equilibrium concentrations.

Learning Objective 6.17

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) and what species will be present in
large concentrations at equilibrium.

Essential knowledge 6.C.2

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. The of an aqueous solution is determined by the identity and concentration of the substance that is dissolved in water. The value of the is an important feature of the solution because it characterizes the relative tendency of the solution to accept a proton from an acid added to the solution, or to donate a proton to a base that is added. For acidbase systems, characterizes the relative availability of protons, much as temperature characterizes the relative availability of kinetic energy in the environment. It is often desirable to use a solution as an environment that maintains a relatively constant so that the addition of an acid or base does not change the (e.g., amino acids and proteins
in the body — the blood maintains a relatively constant).
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 of the buffer is related to the 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 (including polyprotic acids).

b. If starts as 1, it is not until the ratio changes by a factor of 10 that a 1 unit change occurs; adding small amounts of either acid or base does not change the ratio much, so the 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 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 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 , the acid form has a higher
concentration than the base form. If , 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 acidcatalyzed reactions in organic chemistry.

Learning Objective 6.18

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.

Learning Objective 6.19

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 of a solution and the associated with the labile proton.

Learning Objective 6.20

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.

Essential knowledge 6.C.3

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 , the solubility-product constant.
b. The solubility of a substance can be calculated from the 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 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 Le Chatelier's principle.
f. The solubility of a salt will be 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 Le Chatelier's principle.

Learning Objective 6.21

LO 6.21 The student can predict the solubility of a salt, or rank the solubility of salts, given the relevant values.

Learning Objective 6.22

LO 6.22 The student can interpret data regarding solubility of salts to determine, or rank, the relevant values.

Learning Objective 6.23

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

Learning Objective 6.24

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.

Enduring understanding 6.D

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

Essential knowledge 6.D.1: When the difference in Gibbs free energy between reactants and products is much larger than the thermal energy , the equilibrium constant is either very small or very large . When 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, .

b. The equilibrium constant is related to free energy by . 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 at room temperature is . This sets the energy scale for relating the enthalpy and entropy changes to the magnitude of K, since when the magnitude of is large compared to the thermal energy, then K deviates strongly from 1.

c. The relation provides a refinement of the statement in 5.E that processes with favor products, while those with favor reactants. If , then , while if , then . The phrase "favors products" in 5.E is therefore more precisely

stated as , while "favors reactants" in 5.E is more precisely stated as .

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 or endergonic . (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.

Learning Objective 6.25

LO 6.25 The student is able to express the equilibrium constant in terms of and and use this relationship to estimate the magnitude of K and, consequently, the thermodynamic favorability of the process.

Resources

Powerpoint -

Chemical Equilibrium

Entropy, Free Energy, and Equilibrium

Electrochemistry

Assessments

https://docs.google.com/document/d/1wR7bQF-8AQoRrt0g4C3hKja0yjwDjC9_BiAmONWbTcI/edit?usp=sharing

Modifications

https://docs.google.com/document/d/1ODqaPP69YkcFiyG72fIT8XsUIe3K1VSG7nxuc4CpCec/edit