The Concept Outline

Big Idea 1: The chemical elements are fundamental building materials of matter, and all matter can be understood in terms of arrangements of atoms. These atoms retain their identity in chemical reactions.

The atomic theory of matter is the most fundamental premise of chemistry. A limited number of chemical elements exist, and the fundamental unit of the chemical identities they carry is the atom. Although atoms represent the foundational level of chemistry, observations of chemical properties are always made on collections of atoms, and macroscopic systems involve such large numbers that they are typically counted in the unit known as the mole rather than as individual atoms. For elements, many chemical and physical properties exhibit predictable periodicity as a function of atomic number. In all chemical and physical changes, atoms are conserved.

Enduring understanding 1.A: All matter is made of atoms. There are a limited number of types of atoms; these are the elements.

The concept of atoms as the building blocks of all matter is a fundamental premise of the discipline of chemistry. This concept provides the foundation for conceptualizing, interpreting, and explaining the macroscopic properties and transformations observed inside and outside the laboratory in terms of the structure and properties of the constituent materials. The concept of the mole enables chemists to relate measured masses in the laboratory to the number of particles present in a sample. These two concepts also provide the basis for the experimental determination of the purity of a sample through chemical analysis. The most important aspect of chemistry is not the memorization of the laws and definitions, but rather the ability to explain how the laws and relationships arise because of the atomic nature of matter.

Essential knowledge 1.A.1: Molecules are composed of specific combinations of atoms; different molecules are composed of combinations of different elements and of combinations of the same elements in differing amounts and proportions.

a. The average mass of any large number of atoms of a given element is always the same for a given element.

b. A pure sample contains particles (or units) of one specific atom or molecule; a mixture contains particles (or units) of more than one specific atom or molecule.

c. Because the molecules of a particular compound are always composed of the identical combination of atoms in a specific ratio, the ratio of the masses of the constituent elements in any pure sample of that compound is always the same.

d. Pairs of elements that form more than one type of molecule are nonetheless limited by their atomic nature to combine in whole number ratios. This discrete nature can be confirmed by calculating the difference in mass percent ratios between such types of molecules.

Learning Objective for EK 1.A.1:

LO 1.1 The student can justify the observation that the ratio of the masses of the constituent elements in any pure sample of that compound is always identical on the basis of the atomic molecular theory. [*See* **SP 6.1**]

Essential knowledge 1.A.2: Chemical analysis provides a method for determining the relative number of atoms in a substance, which can be used to identify the substance or determine its purity.

a. Because compounds are composed of atoms with known masses, there is a correspondence between the mass percent of the elements in a compound and the relative number of atoms of each element.

b. An empirical formula is the lowest whole number ratio of atoms in a compound. Two molecules of the same elements with identical mass percent of their constituent atoms will have identical empirical formulas.

c. Because pure compounds have a specific mass percent of each element, experimental measurements of mass percents can be used to verify the purity of compounds.

Learning Objectives for EK 1.A.2:

LO 1.2 The student is able to select and apply mathematical routines to mass data to identify or infer the composition of pure substances and/or mixtures. [*See* **SP 2.2**]

LO 1.3 The student is able to select and apply mathematical relationships to mass data in order to justify a claim regarding the identity and/or estimated purity of a substance. [*See* **SP 2.2, 6.1**]

Essential knowledge 1.A.3: The mole is the fundamental unit for counting numbers of particles on the macroscopic level and allows quantitative connections to be drawn between laboratory experiments, which occur at the macroscopic level, and chemical processes, which occur at the atomic level.

a. Atoms and molecules interact with one another on the atomic level. Balanced chemical equations give the number of particles that react and the number of particles produced. Because of this, expressing the amount of a substance in terms of the number of particles, or moles of particles, is essential to understanding chemical processes.

b. Expressing the mass of an individual atom or molecule in atomic mass unit (amu) is useful because the average mass in amu of one particle (atom or molecule) of a substance will always be numerically equal to the molar mass of that substance in grams.

c. Avogadro's number provides the connection between the number of moles in a pure sample of a substance and the number of constituent particles (or units) of that substance.

d. Thus, for any sample of a pure substance, there is a specific numerical relationship between the molar mass of the substance, the mass of the sample, and the number of particles (or units) present.

Learning Objective for EK 1.A.3:

LO 1.4 The student is able to connect the number of particles, moles, mass, and volume of substances to one another, both qualitatively and quantitatively. [*See* **SP 7.1**]

Enduring understanding 1.B: The atoms of each element have unique structures arising from interactions between electrons and nuclei.

The shell model arises from experimental data. The shell model forms a basis for understanding the relative energies of electrons in an atom. The model is based on Coulomb's law and qualitatively predicts ionization energies, which can be measured in the lab. Understanding how the shell model is consistent with the experimental data is a key learning goal for this content, beyond simple memorization of the patterns of electron configurations.

Essential knowledge 1.B.1: The atom is composed of negatively charged electrons, which can leave the atom, and a positively charged nucleus that is made of protons and neutrons. The attraction of the electrons to the nucleus is the basis of the structure of the atom. Coulomb's law is qualitatively useful for understanding the structure of the atom.

a. Based on Coulomb's law, the force between two charged particles is proportional to the magnitude of each of the two charges (q_1 and q_2), and inversely proportional to the square of the distance, r, between them. (Potential energy is proportional to q_1q_2/r.) If the two charges are of opposite sign, the force between them is attractive; if they are of the same sign, the force is repulsive.

b. The first ionization energy is the minimum energy needed to remove the least tightly held electron from an atom or ion. In general, the ionization energy of any electron in an atom or ion is the minimum energy needed to remove that electron from the atom or ion.

c. The relative magnitude of the ionization energy can be estimated through qualitative application of Coulomb's law. The farther an electron is from the nucleus, the lower its ionization energy. When comparing two species with the same arrangement of electrons, the higher the nuclear charge, the higher the ionization energy of an electron in a given subshell.

d. Photoelectron spectroscopy (PES) provides a useful means to engage students in the use of quantum mechanics to interpret spectroscopic data and extract information on atomic structure from such data. In particular, low-resolution PES of atoms provides direct evidence for the shell model. Light consists of photons, each of which has energy $E = h\nu$, where h is Planck's constant and ν is the frequency of the light. In the photoelectric effect, incident light ejects electrons from a material. This requires the photon to have sufficient energy to eject the electron. Photoelectron spectroscopy determines the energy needed to eject electrons from the material. Measurement of these energies provides a method to deduce the shell structure of an atom. The intensity of the photoelectron signal at a given energy is a measure of the number of electrons in that energy level.

e. The electronic structure of atoms with multiple electrons can be inferred from evidence provided by PES. For instance, both electrons in He are identical, and they are both roughly the same distance from the nucleus as in H, while there are two shells of electrons in Li, and the outermost electron is further from the nucleus than in H.

Learning Objectives for EK 1.B.1:

LO 1.5 The student is able to explain the distribution of electrons in an atom or ion based upon data. [*See* **SP 1.5, 6.2**]

LO 1.6 The student is able to analyze data relating to electron energies for patterns and relationships. [*See* **SP 5.1**]

Essential knowledge 1.B.2: The electronic structure of the atom can be described using an electron configuration that reflects the concept of electrons in quantized energy levels or shells; the energetics of the electrons in the atom can be understood by consideration of Coulomb's law.

a. Electron configurations provide a method for describing the distribution of electrons in an atom or ion.

b. Each electron in an atom has a different ionization energy, which can be qualitatively explained through Coulomb's law.

c. In multielectron atoms and ions, the electrons can be thought of as being in "shells" and "subshells," as indicated by the relatively close ionization energies associated with some groups of electrons. Inner electrons are called core electrons, and outer electrons are called valence electrons.

d. Core electrons are generally closer to the nucleus than valence electrons, and they are considered to "shield" the valence electrons from the full electrostatic attraction of the nucleus. This phenomenon can be used in conjunction with Coulomb's law to explain/rationalize/predict relative ionization energies. Differences in electron-electron repulsion are responsible for the differences in energy between electrons in different orbitals in the same shell.

Learning Objectives for EK 1.B.2:

LO 1.7 The student is able to describe the electronic structure of the atom, using PES data, ionization energy data, and/or Coulomb's law to construct explanations of how the energies of electrons within shells in atoms vary.
[*See* **SP 5.1, 6.2**]

LO 1.8 The student is able to explain the distribution of electrons using Coulomb's law to analyze measured energies. [*See* **SP 6.2**]

Enduring understanding 1.C: Elements display periodicity in their properties when the elements are organized according to increasing atomic number. This periodicity can be explained by the regular variations that occur in the electronic structures of atoms. Periodicity is a useful principle for understanding properties and predicting trends in properties. Its modern-day uses range from examining the composition of materials to generating ideas for designing new materials.

Although a simple shell model is not the currently accepted best model of atomic structure, it is an extremely useful model that can be used qualitatively to explain and/or predict many atomic properties and trends in atomic properties. In particular, the arrangement of electrons into shells and subshells is reflected in the structure of the periodic table and in the periodicity of many atomic properties. Many of these trends in atomic properties are important for understanding the properties of molecules, and in being able to explain how the structure of the constituent molecules or atoms relates to the macroscopic properties of materials. Students should be aware that the shells reflect the quantization inherent in quantum mechanics and that the labels given to the atomic orbitals are examples of the quantum numbers used to label the resulting quantized states. Being aware of the quantum mechanical model as the currently accepted best model for the atom is important for scientific literacy.

Essential knowledge 1.C.1: Many properties of atoms exhibit periodic trends that are reflective of the periodicity of electronic structure.

a. The structure of the periodic table is a consequence of the pattern of electron configurations and the presence of shells (and subshells) of electrons in atoms.

b. Ignoring the few exceptions, the electron configuration for an atom can be deduced from the element's position in the periodic table.

✘ *Memorization of exceptions to the Aufbau principle is* ***beyond the scope*** *of this course and the AP Exam.*

Rationale: *The mere rote recall of the exceptions does not match the goals of the curriculum revision. If given an exception on the AP Exam, students will be responsible for providing possible reasons for the exceptions based on theory.*

c. For many atomic properties, trends within the periodic table (and relative values for different atoms and ions) can be qualitatively understood and explained using Coulomb's law, the shell model, and the concept of shielding/effective nuclear charge. These properties include:

   1. First ionization energy

   2. Atomic and ionic radii

   3. Electronegativity
   4. Typical ionic charges

d. Periodicity is a useful tool when designing new molecules or materials, since replacing an element of one group with another of the same group may lead to a new substance with similar properties. For instance, since SiO_2 can be a ceramic, SnO_2 may be as well.

Learning Objectives for EK 1.C.1:

LO 1.9 The student is able to predict and/or justify trends in atomic properties based on location on the periodic table and/or the shell model. [*See* **SP 6.4**]

LO 1.10 Students can justify with evidence the arrangement of the periodic table and can apply periodic properties to chemical reactivity. [*See* **SP 6.1**]

LO 1.11 The student can analyze data, based on periodicity and the properties of binary compounds, to identify patterns and generate hypotheses related to the molecular design of compounds for which data are not supplied. [*See* **SP 3.1, 5.1**]

Essential knowledge 1.C.2: The currently accepted best model of the atom is based on the quantum mechanical model.

a. Coulomb's law is the basis for describing the energy of interaction between protons and electrons.

b. Electrons are not considered to follow specific orbits. Chemists refer to the region of space in which an electron is found as an orbital.

c. Electrons in atoms have an intrinsic property known as spin that can result in atoms having a magnetic moment. There can be at most two electrons in any orbital, and these electrons must have opposite spin.

d. The quantum mechanical (QM) model addresses known problems with the classical shell model and is also consistent with atomic electronic structures that correspond with the periodic table.

e. The QM model can be approximately solved using computers and serves as the basis for software that calculates the structure and reactivity of molecules.

✘ *Assignment of quantum numbers to electrons is* ***beyond the scope*** *of this course and the AP Exam.*

Rationale: *Assignment of quantum numbers to electrons does not increase students' conceptual understanding of quantum theory.*

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Learning Objective for EK 1.C.2:

LO 1.12 The student is able to explain why a given set of data suggests, or does not suggest, the need to refine the atomic model from a classical shell model with the quantum mechanical model. [*See* **SP 6.3**]

Enduring understanding 1.D: Atoms are so small that they are difficult to study directly; atomic models are constructed to explain experimental data on collections of atoms.

Because the experimental measurement of ionization energy provides a window into the overall electronic structure of the atom, this content provides rich opportunities to explore how scientific models can be constructed and refined in response to available data. The modern use of mass spectrometry provides another example of how experimental data can be used to test or reject a scientific model.

Essential knowledge 1.D.1: As is the case with all scientific models, any model of the atom is subject to refinement and change in response to new experimental results. In that sense, an atomic model is not regarded as an exact description of the atom, but rather a theoretical construct that fits a set of experimental data.

a. Scientists use experimental results to test scientific models. When experimental results are not consistent with the predictions of a scientific model, the model must be revised or replaced with a new model that is able to predict/explain the new experimental results. A robust scientific model is one that can be used to explain/predict numerous results over a wide range of experimental circumstances.

b. The construction of a shell model of the atom through ionization energy information provides an opportunity to show how a model can be refined and changed as additional information is considered.

Learning Objective for EK 1.D.1:

LO 1.13 Given information about a particular model of the atom, the student is able to determine if the model is consistent with specified evidence. [*See* **SP 5.3**]

Essential knowledge 1.D.2: An early model of the atom stated that all atoms of an element are identical. Mass spectrometry data demonstrate evidence that contradicts this early model.

a. Data from mass spectrometry demonstrate evidence that an early model of the atom (Dalton's model) is incorrect; these data then require a modification of that model.

b. Data from mass spectrometry also demonstrate direct evidence of different isotopes from the same element.

c. The average atomic mass can be estimated from mass spectra.

Learning Objective for EK 1.D.2:

LO 1.14 The student is able to use data from mass spectrometry to identify the elements and the masses of individual atoms of a specific element. [*See* **SP 1.4, 1.5**]

Essential knowledge 1.D.3: The interaction of electromagnetic waves or light with matter is a powerful means to probe the structure of atoms and molecules, and to measure their concentration.

a. The energy of a photon is related to the frequency of the electromagnetic wave through Planck's equation ($E = h\nu$). When a photon is absorbed (or emitted) by a molecule, the energy of the molecule is increased (or decreased) by an amount equal to the energy of the photon.

b. Different types of molecular motion lead to absorption or emission of photons in different spectral regions. Infrared radiation is associated with transitions in molecular vibrations and so can be used to detect the presence of different types of bonds. Ultraviolet/visible radiation is associated with transitions in electronic energy levels and so can be used to probe electronic structure.

c. The amount of light absorbed by a solution can be used to determine the concentration of the absorbing molecules in that solution, via the Beer-Lambert law.

Learning Objectives for EK 1.D.3:

LO 1.15 The student can justify the selection of a particular type of spectroscopy to measure properties associated with vibrational or electronic motions of molecules. [*See* **SP 4.1, 6.4**]

LO 1.16 The student can design and/or interpret the results of an experiment regarding the absorption of light to determine the concentration of an absorbing species in a solution. [*See* **SP 4.2, 5.1**]

Enduring understanding 1.E: Atoms are conserved in physical and chemical processes.

The conservation of mass in chemical and physical transformations is a fundamental concept, and is a reflection of the atomic model of matter. This concept plays a key role in much of chemistry, in both quantitative determinations of quantities of materials involved in chemical systems and transformations, and in the conceptualization and representation of those systems and transformations.

Essential knowledge 1.E.1: Physical and chemical processes can be depicted symbolically; when this is done, the illustration must conserve all atoms of all types.

a. Various types of representations can be used to show that matter is conserved during chemical and physical processes.

    1. Symbolic representations

    2. Particulate drawings

b. Because atoms must be conserved during a chemical process, it is possible to calculate product masses given known reactant masses, or to calculate reactant masses given product masses.

c. The concept of conservation of atoms plays an important role in the interpretation and analysis of many chemical processes on the macroscopic scale. Conservation of atoms should be related to how nonradioactive atoms are neither lost nor gained as they cycle among land, water, atmosphere, and living organisms.

Learning Objective for EK 1.E.1:

LO 1.17 The student is able to express the law of conservation of mass quantitatively and qualitatively using symbolic representations and particulate drawings. [*See* **SP 1.5**]

Essential knowledge 1.E.2: Conservation of atoms makes it possible to compute the masses of substances involved in physical and chemical processes. Chemical processes result in the formation of new substances, and the amount of these depends on the number and the types and masses of elements in the reactants, as well as the efficiency of the transformation.

a. The number of atoms, molecules, or formula units in a given mass of substance can be calculated.

b. The subscripts in a chemical formula represent the number of atoms of each type in a molecule.

c. The coefficients in a balanced chemical equation represent the relative numbers of particles that are consumed and created when the process occurs.

d. The concept of conservation of atoms plays an important role in the interpretation and analysis of many chemical processes on the macroscopic scale.

e. In gravimetric analysis, a substance is added to a solution that reacts specifically with a dissolved analyte (the chemical species that is the target of the analysis) to form a solid. The mass of solid formed can be used to infer the concentration of the analyte in the initial sample.

f. Titrations may be used to determine the concentration of an analyte in a solution. The titrant has a known concentration of a species that reacts specifically with the analyte. The equivalence of the titration occurs when the analyte is totally consumed by the reacting species in the titrant. The equivalence point is often indicated by a change in a property (such as color) that occurs when the equivalence point is reached. This observable event is called the end point of the titration.

Learning Objectives for EK 1.E.2:

LO 1.18 The student is able to apply conservation of atoms to the rearrangement of atoms in various processes. [*See* **SP 1.4**]

LO 1.19 The student can design, and/or interpret data from, an experiment that uses gravimetric analysis to determine the concentration of an analyte in a solution. [*See* **SP 4.2, 5.1, 6.4**]

LO 1.20 The student can design, and/or interpret data from, an experiment that uses titration to determine the concentration of an analyte in a solution. [*See* **SP 4.2, 5.1, 6.4**]

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.

Transformations of matter can be observed in multiple ways that are generally categorized as either chemical or physical change. These categories can generally be distinguished through consideration of the electrostatic (Coulombic) forces that are associated with a given change at the particulate level. The strength of such forces falls along a continuum, with the strongest forces generally being chemical bonds. Chemical changes involve the making and breaking of chemical bonds. For physical changes, the forces being overcome are weaker intermolecular interactions, which are also Coulombic in nature. The shapes of the particles involved, and the space between them, are key factors in determining the nature of these physical changes. Using only these general concepts of varying strengths of chemical bonds and weaker intermolecular interactions, many properties of a wide range of chemical systems can be understood.

Learning Objectives for Big Idea 2:

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.**

Enduring understanding 2.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.

There is a relationship between the macroscopic properties of solids, liquids, and gases, and the structure of the constituent particles of those materials on the molecular and atomic scale. The properties of solids, liquids, and gases also reflect the relative orderliness of the arrangement of particles in those states, their relative freedom of motion, and the nature and strength of the interactions between them. For gases, volumetric relationships can be used to describe ideal behavior, and a conceptual understanding of that behavior can be constructed based on the atomic model and a relatively simple kinetic molecular theory (KMT).

Solutions are an important class of mixtures; of particular importance is a conceptual understanding on the molecular level of the structure and composition of a liquid solution. In addition, the energetics of solution formation can be understood qualitatively through consideration of the interactions and structure of the components before and after the creation of the solution.

Essential knowledge 2.A.1: The different properties of solids and liquids can be explained by differences in their structures, both at the particulate level and in their supramolecular structures.

a. Solids can be crystalline, where the particles are arranged in a regular 3-D structure, or they can be amorphous, where the particles do not have a regular, orderly arrangement. In both cases, the motion of the individual particles is limited, and the particles do not undergo any overall translation with respect to each other. Interparticle interactions and the ability to pack the particles together provide the main criteria for the structures of solids.

b. The constituent particles in liquids are very close to each other, and they are continually moving and colliding. The particles are able to undergo translation with respect to each other and their arrangement, and movement is influenced by the nature and strength of the intermolecular forces that are present.

c. The solid and liquid phases for a particular substance generally have relatively small differences in molar volume because in both cases the constituent particles are very close to each other at all times.

d. The differences in other properties, such as viscosity, surface tension, and volumes of mixing (for liquids), and hardness and macroscopic crystal structure (for solids), can be explained by differences in the strength of attraction between the particles and/or their overall organization.

e. Heating and cooling curves for pure substances provide insight into the energetics of liquid/solid phase changes.

Learning Objective for EK 2.A.1:

LO 2.3 The student is able to use aspects of particulate models (i.e., particle spacing, motion, and forces of attraction) to reason about observed differences between solid and liquid phases and among solid and liquid materials. [*See* **SP 6.4, 7.1**]

Essential knowledge 2.A.2: The gaseous state can be effectively modeled with a mathematical equation relating various macroscopic properties. A gas has neither a definite volume nor a definite shape; because the effects of attractive forces are minimal, we usually assume that the particles move independently.

a. Ideal gases exhibit specific mathematical relationships among the number of particles present, the temperature, the pressure, and the volume.

b. In a mixture of ideal gases, the pressure exerted by each component (the partial pressure) is independent of the other components. Therefore, the total pressure is the sum of the partial pressures.

c. Graphical representations of the relationships between P, V, and T are useful to describe gas behavior.

d. Kinetic molecular theory combined with a qualitative use of the Maxwell-Boltzmann distribution provides a robust model for qualitative explanations of these mathematical relationships.

e. Some real gases exhibit ideal or near-ideal behavior under typical laboratory conditions. Laboratory data can be used to generate or investigate the relationships in 2.A.2.a and to estimate absolute zero on the Celsius scale.

f. All real gases are observed to deviate from ideal behavior, particularly under conditions that are close to those resulting in condensation. Except at extremely high pressures that are not typically seen in the laboratory, deviations from ideal behavior are the result of intermolecular attractions among gas molecules. These forces are strongly distance-dependent, so they are most significant during collisions.

g. Observed deviations from ideal gas behavior can be explained through an understanding of the structure of atoms and molecules and their intermolecular interactions.

✘ *Phase diagrams are **beyond the scope** of this course and the AP Exam.*

***Rationale:** Phase diagrams are standard in all high school chemistry textbooks and therefore are considered prior knowledge.*

Learning Objectives for EK 2.A.2:

LO 2.4 The student is able to use KMT and concepts of intermolecular forces to make predictions about the macroscopic properties of gases, including both ideal and nonideal behaviors. [*See* **SP 1.4, 6.4**]

LO 2.5 The student is able to refine multiple representations of a sample of matter in the gas phase to accurately represent the effect of changes in macroscopic properties on the sample. [*See* **SP 1.3, 6.4, 7.2**]

LO 2.6 The student can apply mathematical relationships or estimation to determine macroscopic variables for ideal gases. [*See* **SP 2.2, 2.3**]

Essential knowledge 2.A.3: Solutions are homogenous mixtures in which the physical properties are dependent on the concentration of the solute and the strengths of all interactions among the particles of the solutes and solvent.

a. In a solution (homogeneous mixture), the macroscopic properties do not vary throughout the sample. This is in contrast to a heterogeneous mixture in which the macroscopic properties depend upon the location in the mixture. The distinction between heterogeneous and homogeneous depends on the length scale of interest. As an example, colloids may be heterogeneous on the scale of micrometers, but homogeneous on the scale of centimeters.

b. Solutions come in the form of solids, liquids, and gases.

c. For liquid solutions, the solute may be a gas, a liquid, or a solid.

d. Based on the reflections of their structure on the microscopic scale, liquid solutions exhibit several general properties:

   1. The components cannot be separated by using filter paper.
   2. There are no components large enough to scatter visible light.
   3. The components can be separated using processes that are a result of the intermolecular interactions between and among the components.

e. Chromatography (paper and column) separates chemical species by taking advantage of the differential strength of intermolecular interactions between and among the components.

f. Distillation is used to separate chemical species by taking advantage of the differential strength of intermolecular interactions between and among the components and the effects these interactions have on the vapor pressures of the components in the mixture.

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g. The formation of a solution may be an exothermic or endothermic process, depending on the relative strengths of intermolecular/interparticle interactions before and after the dissolution process.

h. Generally, when ionic compounds are dissolved in water, the component ions are separated and dispersed. The presence of ions in a solution can be detected by use of conductivity measurements.

i. Solution composition can be expressed in a variety of ways; molarity is the most common method used in the laboratory. Molarity is defined as the number of moles of solute per liter of solution.

j. Understanding how to prepare solutions of specified molarity through direct mixing of the components, through use of volumetric glassware, and by dilution of a solution of known molarity with additional solvent is important for performing laboratory work in chemistry.

✘ *Colligative properties are **beyond the scope** of this course and the AP Exam and are therefore considered prior knowledge and not directly assessed on the exam.*

✘ *Calculations of molality, percent by mass, and percent by volume are **beyond the scope** of this course and the AP Exam.*

***Rationale:** Molality pertains to colligative properties, which are considered prior knowledge and therefore molality will not be assessed on the exam.*

Learning Objectives for EK 2.A.3:

LO 2.7 The student is able to explain how solutes can be separated by chromatography based on intermolecular interactions. [*See* **SP 6.2**]

LO 2.8 The student can draw and/or interpret representations of solutions that show the interactions between the solute and solvent. [*See* **SP 1.1, 1.2, 6.4**]

LO 2.9 The student is able to create or interpret representations that link the concept of molarity with particle views of solutions. [*See* **SP 1.1, 1.4**]

LO 2.10 The student can design and/or interpret the results of a separation experiment (filtration, paper chromatography, column chromatography, or distillation) in terms of the relative strength of interactions among and between the components. [*See* **SP 4.2, 5.1, 6.4**]

Enduring understanding 2.B: Forces of attraction between particles (including the noble gases and also different parts of some large molecules) are important in determining many macroscopic properties of a substance, including how the observable physical state changes with temperature.

Chemists categorize intermolecular interactions based on the structural features giving rise to the interaction. Although there are some trends in the relative strengths of these interactions, the specific structure and size of the particles involved can play a very important role in determining the overall strength of a particular intermolecular (or intramolecular) interaction. The properties of condensed phases and of many crucial biological structures are determined by the nature and strength of these interactions. Deviation from ideal gas behavior is generally a reflection of the presence of intermolecular interactions between gas particles. Thus, in all phases, the structure of particles on the molecular level is directly related to the properties of both the particles themselves and the behavior of macroscopic collections of those molecules.

Essential knowledge 2.B.1: London dispersion forces are attractive forces present between all atoms and molecules. London dispersion forces are often the strongest net intermolecular force between large molecules.

a. A temporary, instantaneous dipole may be created by an uneven distribution of electrons around the nucleus (nuclei) of an atom (molecule).

b. London dispersion forces arise due to the Coulombic interaction of the temporary dipole with the electron distribution in neighboring atoms and molecules.

c. Dispersion forces increase with contact area between molecules and with increasing polarizability of the molecules. The polarizability of a molecule increases with the number of electrons in the molecule, and is enhanced by the presence of pi bonding.

Learning Objective for EK 2.B.1:

LO 2.11 The student is able to explain the trends in properties and/or predict properties of samples consisting of particles with no permanent dipole on the basis of London dispersion forces. [*See* **SP 6.2, 6.4**]

Essential knowledge 2.B.2: Dipole forces result from the attraction among the positive ends and negative ends of polar molecules. Hydrogen bonding is a strong type of dipole-dipole force that exists when very electronegative atoms (N, O, and F) are involved.

a. Molecules with dipole moments experience Coulombic interactions that result in a net attractive interaction when they are near each other.

   1. Intermolecular dipole-dipole forces are weaker than ionic forces or covalent bonds.

   2. Interactions between polar molecules are typically greater than between nonpolar molecules of comparable size because these interactions act in addition to London dispersion forces.

   3. Dipole-dipole attractions can be represented by diagrams of attraction between the positive and negative ends of polar molecules trying to maximize attractions and minimize repulsions in the liquid or solid state.

   4. Dipole-induced dipole interactions are present between a polar and nonpolar molecule. The strength of these forces increases with the magnitude of the dipole of the polar molecule and with the polarizability of the nonpolar molecule.

b. Hydrogen bonding is a relatively strong type of intermolecular interaction that exists when hydrogen atoms that are covalently bonded to the highly electronegative atoms (N, O, and F) are also attracted to the negative end of a dipole formed by the electronegative atom (N, O, and F) in a different molecule, or a different part of the same molecule. When hydrogen bonding is present, even small molecules may have strong intermolecular attractions.

✘ *Other cases of much weaker hydrogen bonding are* ***beyond the scope*** *of the AP Chemistry course and exam.*

Rationale: *The hydrogen bonding that occurs when hydrogen is bonded to highly electronegative atoms (N, O, and F) will be emphasized as will the electrostatic versus covalent nature of the bond. We will not include other cases of much weaker hydrogen bonding in the AP Chemistry course.*

c. Hydrogen bonding between molecules, or between different parts of a single molecule, may be represented by diagrams of molecules with hydrogen bonding and indications of location of hydrogen bonding.

d. Ionic interactions with dipoles are important in the solubility of ionic compounds in polar solvents.

Learning Objectives for EK 2.B.2:

LO 2.12 The student can qualitatively analyze data regarding real gases to identify deviations from ideal behavior and relate these to molecular interactions.
[*See* **SP 5.1, 6.5,** *connects to* **2.A.2**]

LO 2.13 The student is able to describe the relationships between the structural features of polar molecules and the forces of attraction between the particles.
[*See* **SP 1.4, 6.4**]

LO 2.14 The student is able to apply Coulomb's law qualitatively (including using representations) to describe the interactions of ions, and the attractions between ions and solvents to explain the factors that contribute to the solubility of ionic compounds. [*See* **SP 1.4, 6.4**]

Essential knowledge 2.B.3: Intermolecular forces play a key role in determining the properties of substances, including biological structures and interactions.

a. Many properties of liquids and solids are determined by the strengths and types of intermolecular forces present.
   1. Boiling point
   2. Surface tension
   3. Capillary action
   4. Vapor pressure

b. Substances with similar intermolecular interactions tend to be miscible or soluble in one another.

c. The presence of intermolecular forces among gaseous particles, including noble gases, leads to deviations from ideal behavior, and it can lead to condensation at sufficiently low temperatures and/or sufficiently high pressures.

d. Graphs of the pressure-volume relationship for real gases can demonstrate the deviation from ideal behavior; these deviations can be interpreted in terms of the presence and strengths of intermolecular forces.

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e. The structure and function of many biological systems depend on the strength and nature of the various Coulombic forces.
   1. Substrate interactions with the active sites in enzyme catalysis
   2. Hydrophilic and hydrophobic regions in proteins that determine three-dimensional structure in water solutions

Learning Objectives for EK 2.B.3:

LO 2.15 The student is able to explain observations regarding the solubility of ionic solids and molecules in water and other solvents on the basis of particle views that include intermolecular interactions and entropic effects. [*See* **SP 1.4, 6.2,** *connects to* **5.E.1**]

LO 2.16 The student is able to explain the properties (phase, vapor pressure, viscosity, etc.) of small and large molecular compounds in terms of the strengths and types of intermolecular forces. [*See* **SP 6.2**]

Enduring understanding 2.C: The strong electrostatic forces of attraction holding atoms together in a unit are called chemical bonds.

Covalent bonds, ionic bonds, and metallic bonds are distinct from (and significantly stronger than) typical intermolecular interactions. Electronegativity can be used to reason about the type of bonding present between two atoms. Covalent chemical bonds can be modeled as the sharing of one or more pairs of valence electrons between two atoms in a molecule. The extent to which this sharing is unequal can be predicted from the relative electronegativities of the atoms involved; the relative electronegativities can generally be understood through application of the shell model and Coulomb's law. The Lewis structure model, combined with valence shell electron pair repulsion (VSEPR), can be used to predict many structural features of covalently bonded molecules and ions. Ionic bonding is the phrase used to describe the strong Coulombic interaction between ions in an ionic substance. The bonding in metals is characterized by delocalization of valence electrons.

Learning Objective for EU 2.C:

LO 2.17 The student can predict the type of bonding present between two atoms in a binary compound based on position in the periodic table and the electronegativity of the elements. [*See* **SP 6.4**]

Essential knowledge 2.C.1: In covalent bonding, electrons are shared between the nuclei of two atoms to form a molecule or polyatomic ion. Electronegativity differences between the two atoms account for the distribution of the shared electrons and the polarity of the bond.

a. Electronegativity is the ability of an atom in a molecule to attract shared electrons to it.

b. Electronegativity values for the representative elements increase going from left to right across a period and decrease going down a group. These trends can be understood qualitatively through the electronic structure of the atoms, the shell model, and Coulomb's law.

c. Two or more valence electrons shared between atoms of identical electronegativity constitute a nonpolar covalent bond.

d. However, bonds between carbon and hydrogen are often considered to be nonpolar even though carbon is slightly more electronegative than hydrogen. The formation of a nonpolar covalent bond can be represented graphically as a plot of potential energy vs. distance for the interaction of two identical atoms. Hydrogen atoms are often used as an example.

   1. The relative strengths of attractive and repulsive forces as a function of distance determine the shape of the graph.

   2. The bond length is the distance between the bonded atoms' nuclei, and is the distance of minimum potential energy where the attractive and repulsive forces are balanced.

   3. The bond energy is the energy required for the dissociation of the bond. This is the net energy of stabilization of the bond compared to the two separated atoms. Typically, bond energy is given on a per mole basis.

e. Two or more valence electrons shared between atoms of unequal electronegativity constitute a polar covalent bond.

   1. The difference in electronegativity for the two atoms involved in a polar covalent bond is not equal to zero.

   2. The atom with a higher electronegativity will develop a partial negative charge relative to the other atom in the bond. For diatomic molecules, the partial negative charge on the more electronegative atom is equal in magnitude to the partial positive charge on the less electronegative atom.

   3. Greater differences in electronegativity lead to greater partial charges, and consequently greater bond dipoles.

   4. The sum of partial charges in any molecule or ion must be equal to the overall charge on the species.

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f. All bonds have some ionic character, and the difference between ionic and covalent bonding is not distinct but rather a continuum. The difference in electronegativity is not the only factor in determining if a bond is designated ionic or covalent. Generally, bonds between a metal and nonmetal are ionic, and between two nonmetals the bonds are covalent. Examination of the properties of a compound is the best way to determine the type of bonding.

Learning Objective for EK 2.C.1:

LO 2.18 The student is able to rank and justify the ranking of bond polarity on the basis of the locations of the bonded atoms in the periodic table. [*See* **SP 6.1**]

Essential knowledge 2.C.2: Ionic bonding results from the net attraction between oppositely charged ions, closely packed together in a crystal lattice.

a. The cations and anions in an ionic crystal are arranged in a systematic, periodic 3-D array that maximizes the attractive forces among cations and anions while minimizing the repulsive forces.

✗ *Knowledge of specific types of crystal structures is* ***beyond the scope*** *of this course and the AP Exam.*

Rationale: *The study of crystal structures does not strengthen understanding of the big ideas.*

b. Coulomb's law describes the force of attraction between the cations and anions in an ionic crystal.

    1. Because the force is proportional to the charge on each ion, larger charges lead to stronger interactions.
    2. Because the force is inversely proportional to the square of the distance between the centers of the ions (nuclei), smaller ions lead to stronger interactions.

Learning Objective for EK 2.C.2:

LO 2.19 The student can create visual representations of ionic substances that connect the microscopic structure to macroscopic properties, and/or use representations to connect the microscopic structure to macroscopic properties (e.g., boiling point, solubility, hardness, brittleness, low volatility, lack of malleability, ductility, or conductivity). [*See* **SP 1.1, 1.4, 7.1,** *connects to* **2.D.1, 2.D.2**]

Essential knowledge 2.C.3: Metallic bonding describes an array of positively charged metal cores surrounded by a sea of mobile valence electrons.

a. The valence electrons from the metal atoms are considered to be delocalized and not associated with any individual atom.

b. Metallic bonding can be represented as an array of positive metal ions with valence electrons drawn among them, as if the electrons were moving (i.e., a sea of electrons).

c. The electron sea model can be used to explain several properties of metals, including electrical conductivity, malleability, ductility, and low volatility.

d. The number of valence electrons involved in metallic bonding, via the shell model, can be used to understand patterns in these properties, and can be related to the shell model to reinforce the connections between metallic bonding and other forms of bonding.

Learning Objective for EK 2.C.3:

LO 2.20 The student is able to explain how a bonding model involving delocalized electrons is consistent with macroscopic properties of metals (e.g., conductivity, malleability, ductility, and low volatility) and the shell model of the atom. [*See* **SP 6.2, 7.1,** *connects to* **2.D.2**]

Essential knowledge 2.C.4: The localized electron bonding model describes and predicts molecular geometry using Lewis diagrams and the VSEPR model.

a. Lewis diagrams can be constructed according to a well-established set of principles.

b. The VSEPR model uses the Coulombic repulsion between electrons as a basis for predicting the arrangement of electron pairs around a central atom.

c. In cases where more than one equivalent Lewis structure can be constructed, resonance must be included as a refinement to the Lewis structure approach in order to provide qualitatively accurate predictions of molecular structure and properties (in some cases).

d. Formal charge can be used as a criterion for determining which of several possible valid Lewis diagrams provides the best model for predicting molecular structure and properties.

✗ *The use of formal charge to explain why certain molecules do not obey the octet rule is* ***beyond the scope*** *of this course and the AP Exam.*

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Rationale: *Explaining why certain molecules do NOT obey the octet rule is* ***beyond the scope*** *of the course. The scope of the course DOES include the use of formal charge to evaluate different structures that follow the octet rule and the limitations of using Lewis structures for molecules with odd numbers of electrons or expanded octets.*

e. The combination of Lewis diagrams with the VSEPR model provides a powerful model for predicting structural properties of many covalently bonded molecules and polyatomic ions, including the following:

   1. Molecular geometry
   2. Bond angles
   3. Relative bond energies based on bond order
   4. Relative bond lengths (multiple bonds, effects of atomic radius)
   5. Presence of a dipole moment

f. As with any model, there are limitations to the use of the Lewis structure model, particularly in cases with an odd number of valence electrons. Recognizing that Lewis diagrams have limitations is of significance.

✘ *Learning how to defend Lewis models based on assumptions about the limitations of the models is* ***beyond the scope*** *of this course and the AP Exam.*

Rationale: *Learning how to defend Lewis models does not strengthen understanding of the big ideas.*

g. Organic chemists commonly use the terms "hybridization" and "hybrid orbital" to describe the arrangement of electrons around a central atom. When there is a bond angle of 180°, the central atom is said to be sp hybridized; for 120°, the central atom is sp^2 hybridized; and for 109°, the central atom is sp^3 hybridized. Students should be aware of this terminology, and be able to use it. When an atom has more than four pairs of electrons surrounding the central atom, students are only responsible for the shape of the resulting molecule.

✘ *An understanding of the derivation and depiction of these orbitals is* ***beyond the scope*** *of this course and the AP Exam. Current evidence suggests that hybridization involving d orbitals does not exist, and there is controversy about the need to teach any hybridization. Until there is agreement in the chemistry community, we will continue to include sp,* sp^2*, and* sp^3 *hybridization in the current course.*

Rationale: *The course includes the distinction between sigma and pi bonding, the use of VSEPR to explain the shapes of molecules, and the sp,* sp^2*, and* sp^3 *nomenclature. Additional aspects related to hybridization are both controversial and do not substantially enhance understanding of molecular structure.*

h. Bond formation is associated with overlap between atomic orbitals. In multiple bonds, such overlap leads to the formation of both sigma and pi bonds. The overlap is stronger in sigma than pi bonds, which is reflected in sigma bonds having larger bond energy than pi bonds. The presence of a pi bond also prevents the rotation of the bond, and leads to structural isomers. In systems, such as benzene, where atomic p-orbitals overlap strongly with more than one other p-orbital, extended pi bonding exists, which is delocalized across more than two nuclei. Such descriptions provide an alternative description to resonance in Lewis structures. A useful example of delocalized pi bonding is molecular solids that conduct electricity. The discovery of such materials at the end of the 1970s overturned a long-standing assumption in chemistry that molecular solids will always be insulators.

i. Molecular orbital theory describes covalent bonding in a manner that can capture a wider array of systems and phenomena than the Lewis or VSEPR models. Molecular orbital diagrams, showing the correlation between atomic and molecular orbitals, are a useful qualitative tool related to molecular orbital theory.

✗ *Other aspects of molecular orbital theory, such as recall or filling of molecular orbital diagrams, are* ***beyond the scope*** *of this course and the AP Exam.*

Rationale: *As currently covered in freshman college chemistry textbooks, molecular orbital theory is superficially taught and limited to homonuclear molecules in the second period. Algorithmic filling of such MO diagrams does not lead to a deeper conceptual understanding of bonding. The course does include the important distinction between sigma and pi bonding.*

Learning Objective for EK 2.C.4:

LO 2.21 The student is able to use Lewis diagrams and VSEPR to predict the geometry of molecules, identify hybridization, and make predictions about polarity. [*See* **SP 1.4**]

Enduring understanding 2.D: The type of bonding in the solid state can be deduced from the properties of the solid state.

In solids, the properties of the material reflect the nature and strength of the interactions between the constituent particles. For this reason, the type of bonding that predominates in a solid material, and the nature of the interactions between the particles comprising the solid, can generally be inferred from the observed macroscopic properties of the material. Properties such as vapor pressure, conductivity as a solid and in aqueous solution, and relative brittleness or hardness can generally be explained in this way.

Although recognizing the properties that can be associated with a particular type of bonding is valuable in categorizing materials, relating those properties to the structure of the materials on the molecular scale, and being able to make reasoned predictions of the properties of a solid based on its constituent particles, provides evidence of deeper conceptual understanding.

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Learning Objective for EU 2.D:

LO 2.22 The student is able to design or evaluate a plan to collect and/or interpret data needed to deduce the type of bonding in a sample of a solid. [*See* **SP 4.2, 6.4**]

Essential knowledge 2.D.1: Ionic solids have high melting points, are brittle, and conduct electricity only when molten or in solution.

a. Many properties of ionic solids are related to their structure.

   1. Ionic solids generally have low vapor pressure due to the strong Coulombic interactions of positive and negative ions arranged in a regular three-dimensional array.

   2. Ionic solids tend to be brittle due to the repulsion of like charges caused when one layer slides across another layer.

   3. Ionic solids do not conduct electricity. However, when ionic solids are melted, they do conduct electricity because the ions are free to move.

   4. When ionic solids are dissolved in water, the separated ions are free to move; therefore, these solutions will conduct electricity. Dissolving a nonconducting solid in water, and observing the solution's ability to conduct electricity, is one way to identify an ionic solid.

   5. Ionic compounds tend not to dissolve in nonpolar solvents because the attractions among the ions are much stronger than the attractions among the separated ions and the nonpolar solvent molecules.

b. The attractive force between any two ions is governed by Coulomb's law: The force is directly proportional to the charge of each ion and inversely proportional to the square of the distance between the centers of the ions.

   1. For ions of a given charge, the smaller the ions, and thus the smaller the distance between ion centers, the stronger the Coulombic force of attraction, and the higher the melting point.

   2. Ions with higher charges lead to higher Coulombic forces, and therefore higher melting points.

✗ *The study of the specific varieties of crystal lattices for ionic compounds is* ***beyond the scope*** *of this course and the AP Exam.*

Rationale: *This topic has not been part of AP Chemistry for many years and including the topic in the new course was not viewed as the best way to deepen understanding of the big ideas.*

Learning Objectives for EK 2.D.1:

LO 2.23 The student can create a representation of an ionic solid that shows essential characteristics of the structure and interactions present in the substance. [*See* **SP 1.1**]

LO 2.24 The student is able to explain a representation that connects properties of an ionic solid to its structural attributes and to the interactions present at the atomic level. [*See* **SP 1.1, 6.2, 7.1**]

Essential knowledge 2.D.2: Metallic solids are good conductors of heat and electricity, have a wide range of melting points, and are shiny, malleable, ductile, and readily alloyed.

a. A metallic solid can be represented as positive kernels (or cores) consisting of the nucleus and inner electrons of each atom surrounded by a sea of mobile valence electrons.

   1. Metals are good conductors because the electrons are delocalized and relatively free to move.

   2. Metals are malleable and ductile because deforming the solid does not change the environment immediately surrounding each metal core.

b. Metallic solids are often pure substances, but may also be mixtures called alloys.

   1. Some properties of alloys can be understood in terms of the size of the component atoms:
      — Interstitial alloys form between atoms of different radius, where the smaller atoms fill the interstitial spaces between the larger atoms. (Steel is an example in which carbon occupies the interstices in iron.) The interstitial atoms make the lattice more rigid, decreasing malleability and ductility.
      — Substitutional alloys form between atoms of comparable radius, where one atom substitutes for the other in the lattice. (Brass is an example in which some copper atoms are substituted with a different element, usually zinc.) The density typically lies between those of the component metals, as with interstitial alloys, substitutional alloys are less malleable and ductile than pure metals.

   2. Alloys typically retain a sea of mobile electrons and so remain conducting.

   3. Often the surface of a metal or alloy is changed through a chemical reaction. An example is formation of a chemically inert oxide layer in stainless steel, through reaction with oxygen in the air.

Learning Objectives for EK 2.D.2:

LO 2.25 The student is able to compare the properties of metal alloys with their constituent elements to determine if an alloy has formed, identify the type of alloy formed, and explain the differences in properties using particulate level reasoning. [*See* **SP 1.4, 7.2**]

LO 2.26 Students can use the electron sea model of metallic bonding to predict or make claims about the macroscopic properties of metals or alloys. [*See* **SP 6.4, 7.1**]

LO 2.27 The student can create a representation of a metallic solid that shows essential characteristics of the structure and interactions present in the substance. [*See* **SP 1.1**]

LO 2.28 The student is able to explain a representation that connects properties of a metallic solid to its structural attributes and to the interactions present at the atomic level. [*See* **SP 1.1, 6.2, 7.1**]

Essential knowledge 2.D.3: Covalent network solids have properties that reflect their underlying 2-D or 3-D networks of covalent bonds. Covalent network solids generally have extremely high melting points and are hard.

a. Covalent network solids consist of atoms that are covalently bonded together into a two-dimensional or three-dimensional network.

   1. Covalent network solids are only formed from nonmetals: elemental (diamond, graphite) or two nonmetals (silicon dioxide and silicon carbide).
   2. The properties of covalent network solids are a reflection of their structure.
   3. Covalent network solids have high melting points because all of the atoms are covalently bonded.
   4. Three-dimensional covalent networks tend to be rigid and hard because the covalent bond angles are fixed.
   5. Generally, covalent network solids form in the carbon group because of their ability to form four covalent bonds.

b. Graphite is an allotrope of carbon that forms sheets of two-dimensional networks.

   1. Graphite has a high melting point because the covalent bonds between the carbon atoms making up each layer are relatively strong.
   2. Graphite is soft because adjacent layers can slide past each other relatively easily; the major forces of attraction between the layers are London dispersion forces.

c. Silicon is a covalent network solid and a semiconductor.
   1. Silicon forms a three-dimensional network similar in geometry to a diamond.
   2. Silicon's conductivity increases as temperature increases.
   3. Periodicity can be used to understand why doping with an element with one extra valence electron converts silicon into an n-type semiconducting (negative charge carrying) material, while doping with an element with one less valence electron converts silicon into a p-type semiconducting (positive charge carrying) material. Junctions between n-doped and p-doped materials can be used to control electron flow, and thereby are the basis of modern electronics.

Learning Objectives for EK 2.D.3:

LO 2.29 The student can create a representation of a covalent solid that shows essential characteristics of the structure and interactions present in the substance. [*See* **SP 1.1**]

LO 2.30 The student is able to explain a representation that connects properties of a covalent solid to its structural attributes and to the interactions present at the atomic level. [*See* **SP 1.1, 6.2, 7.1**]

Essential knowledge 2.D.4: Molecular solids with low molecular weight usually have low melting points and are not expected to conduct electricity as solids, in solution, or when molten.

a. Molecular solids consist of nonmetals, diatomic elements, or compounds formed from two or more nonmetals.

b. Molecular solids are composed of distinct, individual units of covalently bonded molecules attracted to each other through relatively weak intermolecular forces.
   1. Molecular solids are not expected to conduct electricity because their electrons are tightly held within the covalent bonds of each constituent molecule.
   2. Molecular solids generally have a low melting point because of the relatively weak intermolecular forces present between the molecules.
   3. Molecular solids are sometimes composed of very large molecules, or polymers, with important commercial and biological applications.

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Learning Objectives for EK 2.D.4:

LO 2.31 The student can create a representation of a molecular solid that shows essential characteristics of the structure and interactions present in the substance. [*See* **SP 1.1**]

LO 2.32 The student is able to explain a representation that connects properties of a molecular solid to its structural attributes and to the interactions present at the atomic level. [*See* **SP 1.1, 6.2, 7.1**]

Big Idea 3: Changes in matter involve the rearrangement and/or reorganization of atoms and/or the transfer of electrons.

When chemical changes occur, the new substances formed have properties that are distinguishable from the initial substance or substances. Such chemical processes may be observed in a variety of ways, and often involve changes in energy as well. Chemical change is depicted in several ways, with the most important and informative one being the balanced chemical equation for the reaction. Because there is a large diversity of possible chemical reactions, it is useful to categorize reactions and be able to recognize the category into which a given reaction falls.

Learning Objective for Big Idea 3:

LO 3.1 Students can translate among macroscopic observations of change, chemical equations, and particle views. [*See* **SP 1.5, 7.1**]

Note: This learning objective applies to *essential knowledge* components of **3A–3C**.

Enduring understanding 3.A: Chemical changes are represented by a balanced chemical equation that identifies the ratios with which reactants react and products form.

Chemical reactions are the primary means by which transformations in matter occur. Chemical equations for reactions efficiently communicate the rearrangements of atoms that occur during a chemical reaction. Describing a chemical change can include different forms of the equation, such as molecular, ionic, and net ionic. The equation provides information about atoms, ions and/or molecules reacting (not how they react) at the particulate level, as well as quantitative information about stoichiometry at the macroscopic level. Many chemical reactions involve small whole number ratios of reactants and products as expressed by the stoichiometric coefficients of the balanced equation. Many modern materials are composed of non-stoichiometric combinations of the constituent elements.

Essential knowledge 3.A.1: A chemical change may be represented by a molecular, ionic, or net ionic equation.

a. Chemical equations represent chemical changes, and therefore must contain equal numbers of atoms of every element on each side to be "balanced."

b. Depending on the context in which it is used, there are different forms of the balanced chemical equations that are used by chemists. It is important not only to write a balanced molecular, ionic, or net ionic reaction equation, but also to have an understanding of the circumstances under which any of them might be the most useful form.

c. The balanced chemical equation for a reaction is capable of representing chemistry at any level, and thus it is important that it can be translated into a symbolic depiction at the particulate level, where much of the reasoning of chemistry occurs.

d. Because chemistry is ultimately an experimental science, it is important that students be able to describe chemical reactions observed in a variety of laboratory contexts.

Learning Objective for EK 3.A.1:

LO 3.2 The student can translate an observed chemical change into a balanced chemical equation and justify the choice of equation type (molecular, ionic, or net ionic) in terms of utility for the given circumstances. [*See* **SP 1.5, 7.1**]

Essential knowledge 3.A.2: Quantitative information can be derived from stoichiometric calculations that utilize the mole ratios from the balanced chemical equations. The role of stoichiometry in real-world applications is important to note, so that it does not seem to be simply an exercise done only by chemists.

a. Coefficients of balanced chemical equations contain information regarding the proportionality of the amounts of substances involved in the reaction. These values can be used in chemical calculations that apply the mole concept; the most important place for this type of quantitative exercise is the laboratory.

   1. Calculate amount of product expected to be produced in a laboratory experiment.

   2. Identify limiting and excess reactant; calculate percent and theoretical yield for a given laboratory experiment.

b. The use of stoichiometry with gases also has the potential for laboratory experimentation, particularly with respect to the experimental determination of molar mass of a gas.

c. Solution chemistry provides an additional avenue for laboratory calculations of stoichiometry, including titrations.

Learning Objectives for EK 3.A.2:

LO 3.3 The student is able to use stoichiometric calculations to predict the results of performing a reaction in the laboratory and/or to analyze deviations from the expected results. [*See* **SP 2.2, 5.1**]

LO 3.4 The student is able to relate quantities (measured mass of substances, volumes of solutions, or volumes and pressures of gases) to identify stoichiometric relationships for a reaction, including situations involving limiting reactants and situations in which the reaction has not gone to completion. [*See* **SP 2.2, 5.1, 6.4**]

Enduring understanding 3.B: Chemical reactions can be classified by considering what the reactants are, what the products are, or how they change from one into the other. Classes of chemical reactions include synthesis, decomposition, acid-base, and oxidation-reduction reactions.

There are a vast number of possible chemical reactions. In order to study and make predictions and comparisons concerning such a wide array of reactions, chemists have devised ways to classify them. Because of their prevalence in the laboratory and in real-world applications, two categories of reactions that are of particular importance are acid-base reactions and oxidation-reduction reactions. Also, a key contribution of chemistry to society is the creation of new materials or compounds that benefit the health and welfare of people in the community. Most often the creation of new materials or compounds can be considered as synthesis reactions, another important reaction category.

Essential knowledge 3.B.1: Synthesis reactions are those in which atoms and/or molecules combine to form a new compound. Decomposition is the reverse of synthesis, a process whereby molecules are decomposed, often by the use of heat.

a. Synthesis or decomposition reactions can be used for acquisition of basic lab techniques and observations that help students deal with the abstractions of atoms and stoichiometric calculations.

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Learning Objectives for EK 3.B.1:

LO 3.5 The student is able to design a plan in order to collect data on the synthesis or decomposition of a compound to confirm the conservation of matter and the law of definite proportions. [*See* **SP 2.1, 4.2, 6.4**]

LO 3.6 The student is able to use data from synthesis or decomposition of a compound to confirm the conservation of matter and the law of definite proportions. [*See* **SP 2.2, 6.1**]

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.

✗ *Lewis acid-base concepts are* ***beyond the scope*** *of this course and the AP Exam.*

Rationale: *The definition of Lewis acids is commonly taught in a first-year high school chemistry course and is therefore considered prior knowledge. Note: The formation of complex ions and the qualitative impact on solubility are both part of the AP Chemistry course.*

3. When an acid or base ionizes in water, the conjugate acid-base pairs can be identified and their relative strengths compared.

Learning Objective for EK 3.B.2:

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**]

Essential knowledge 3.B.3: In oxidation-reduction (redox) reactions, there is a net transfer of electrons. The species that loses electrons is oxidized, and the species that gains electrons is reduced.

a. In a redox reaction, electrons are transferred from the species that is oxidized to the species that is reduced.

✗ *Language of reducing agent and oxidizing agent is* ***beyond the scope*** *of this course and the AP Exam.*

Rationale: *Understanding this terminology is not necessary for reasoning about redox chemistry.*

b. Oxidation numbers may be assigned to each of the atoms in the reactant and products; this is often an effective way to identify the oxidized and reduced species in a redox reaction.

c. Balanced chemical equations for redox reactions can be constructed from tabulated half-reactions.

d. Recognizing that a reaction is a redox reaction is an important skill; an apt application of this type of reaction is a laboratory exercise where students perform redox titrations.

e. There are a number of important redox reactions in energy production processes (combustion of hydrocarbons and metabolism of sugars, fats, and proteins).

Learning Objectives for EK 3.B.3:

LO 3.8 The student is able to identify redox reactions and justify the identification in terms of electron transfer. [*See* **SP 6.1**]

LO 3.9 The student is able to design and/or interpret the results of an experiment involving a redox titration. [*See* **SP 4.2, 5.1**]

Enduring understanding 3.C: Chemical and physical transformations may be observed in several ways and typically involve a change in energy.

An important component of a full understanding of chemical change involves direct observation of that change; thus, laboratory experiences are essential for the AP Chemistry student to develop an appreciation of the discipline. At the AP course level, observations are made on macroscopically large samples of chemicals; these observations must be used to infer what is occurring at the particulate level. This ability to reason about observations at one level (macroscopic) using models at another level (particulate) provides an important demonstration of conceptual understanding and requires extensive laboratory experience. The difference between physical and chemical change is best explained at the particulate level. Laboratory observations of temperature change accompanying physical and chemical transformations are manifestations of the energy changes occurring at the particulate level. This has practical applications, such as energy production via combustion of fuels (chemical energy conversion to thermal energy) and/or batteries (chemical energy conversion to electrical energy).

Essential knowledge 3.C.1: Production of heat or light, formation of a gas, and formation of a precipitate and/or a color change are possible evidences that a chemical change has occurred.

a. Laboratory observations are made at the macroscopic level, so students must be able to characterize changes in matter using visual clues and then make representations or written descriptions.

b. Distinguishing the difference between chemical and physical changes at the macroscopic level is a challenge; therefore, the ability to investigate chemical properties is important.

c. In order to develop the ability to distinguish experimentally between chemical and physical changes, students must make observations and collect data from a variety of reactions and physical changes within the laboratory setting.

d. Classification of reactions provides important organizational clarity for chemistry; therefore, students need to identify precipitation, acid-base, and redox reactions.

Learning Objective for EK 3.C.1:

LO 3.10 The student is able to evaluate the classification of a process as a physical change, chemical change, or ambiguous change based on both macroscopic observations and the distinction between rearrangement of covalent interactions and noncovalent interactions. [*See* **SP 1.4, 6.1,** *connects to* **5.D.2**]

Essential knowledge 3.C.2: Net changes in energy for a chemical reaction can be endothermic or exothermic.

a. Macroscopic observations of energy changes when chemicals react are made possible by measuring temperature changes.

b. These observations should be placed within the context of the language of exothermic and endothermic change.

c. The ability to translate observations made at the macroscopic level in the laboratory to a conceptual framework is aided by a graphical depiction of the process called an energy diagram, which provides a visual representation of the exothermic or endothermic nature of a reaction.

d. It is important to be able to use an understanding of energy changes in chemical reactions to identify the role of endothermic and exothermic reactions in real-world processes.

Learning Objective for EK 3.C.2:

LO 3.11 The student is able to interpret observations regarding macroscopic energy changes associated with a reaction or process to generate a relevant symbolic and/or graphical representation of the energy changes. [*See* **SP 1.5, 4.4**]

Essential knowledge 3.C.3: Electrochemistry shows the interconversion between chemical and electrical energy in galvanic and electrolytic cells.

a. Electrochemistry encompasses the study of redox reactions that occur within electrochemical cells. The reactions either generate electrical current in galvanic cells, or are driven by an externally applied electrical potential in electrolytic cells. Visual representations of galvanic and electrolytic cells are tools of analysis to identify where half-reactions occur and the direction of current flow.

b. Oxidation occurs at the anode, and reduction occurs at the cathode for all electrochemical cells.

✗ *Labeling an electrode as positive or negative is* ***beyond the scope*** *of this course and the AP Exam.*

Rationale: *The sign on the electrode is different for electrochemical and electrolytic cells, but the most important concept is that oxidation always takes place at the anode in either cell type. Labeling electrodes does not provide a deeper understanding of electrochemistry.*

c. The overall electrical potential of galvanic cells can be calculated by identifying the oxidation half-reaction and reduction half-reaction, and using a table of Standard Reduction Potentials.

d. Many real systems do not operate at standard conditions and the electrical potential determination must account for the effect of concentrations. The qualitative effects of concentration on the cell potential can be understood by considering the cell potential as a driving force toward equilibrium, in that the farther the reaction is from equilibrium, the greater the magnitude of the cell potential. The standard cell potential, Eo, corresponds to the standard conditions of $Q = 1$. As the system approaches equilibrium, the magnitude (i.e., absolute value) of the cell potential decreases, reaching zero at equilibrium (when $Q = K$). Deviations from standard conditions that take the cell further from equilibrium than $Q = 1$ will increase the magnitude of the cell potential relative to E°. Deviations from standard conditions that take the cell closer to equilibrium than $Q = 1$ will decrease the magnitude of the cell potential relative to E°. In concentration cells, the direction of spontaneous electron flow can be determined by considering the direction needed to reach equilibrium.

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✘ *The Nernst equation is* ***beyond the scope*** *of this course and the AP Exam.*

Rationale: *Qualitative reasoning about the effects of concentration on cell potential is part of the course. However, inclusion of algorithmic calculations was not viewed as the best way to deepen understanding of the big ideas.*

e. ΔG° (standard Gibbs free energy) is proportional to the negative of the cell potential for the redox reaction from which it is constructed.

f. Faraday's laws can be used to determine the stoichiometry of the redox reactions occurring in an electrochemical cell with respect to the following:
    i. Number of electrons transferred
    ii. Mass of material deposited or removed from an electrode
    iii. Current
    iv. Time elapsed
    v. Charge of ionic species

Learning Objectives for EK 3.C.3:

LO 3.12 The student can make qualitative or quantitative predictions about galvanic or electrolytic reactions based on half-cell reactions and potentials and/or Faraday's laws. [*See* **SP 2.2, 2.3, 6.4**]

LO 3.13 The student can analyze data regarding galvanic or electrolytic cells to identify properties of the underlying redox reactions. [*See* **SP 5.1**]

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Big Idea 4: Rates of chemical reactions are determined by details of the molecular collisions.

Chemical changes occur over a wide range of time scales. Practically, the manner in which the rate of change is observed is to measure changes in concentration of reactant or product species as a function of time. There are a number of possible factors that influence the observed speed of reaction at the macroscopic level, including the concentration of reactants, the temperature, and other environmental factors. Measured rates for reactions observed at the macroscopic level can generally be characterized mathematically in an expression referred to as the rate law. In addition to these macroscopic-level characterizations, the progress of reactions at the particulate level can be connected to the rate law. Factors that influence the rate of reaction, including speeding of the reaction by the use of a catalyst, can be delineated as well.

Enduring understanding 4.A: Reaction rates that depend on temperature and other environmental factors are determined by measuring changes in concentrations of reactants or products over time.

The rate of a reaction is the rate at which reactants are converted to products, and is given in terms of the change in concentrations with time. Rates of reactions span a wide range, and generally increase with reactant concentrations and with temperature. The rate may be measured by monitoring concentrations as a function of time, and the results of many experiments may be summarized with a mathematical expression known as the rate law. The rate law gives the dependence of the rate on reactant concentrations, and contains a proportionality constant called the rate constant.

Essential knowledge 4.A.1: The rate of a reaction is influenced by the concentration or pressure of reactants, the phase of the reactants and products, and environmental factors such as temperature and solvent.

a. The rate of a reaction is measured by the amount of reactants converted to products per unit of time.

b. A variety of means exist to experimentally measure the loss of reactants or increase of products as a function of time. One important method involves the spectroscopic determination of concentration through Beer's law.

c. The rate of a reaction is influenced by reactant concentrations (except in zero-order processes), temperature, surface area, and other environmental factors.

Learning Objective for EK 4.A.1:

LO 4.1 The student is able to design and/or interpret the results of an experiment regarding the factors (i.e., temperature, concentration, surface area) that may influence the rate of a reaction. [*See* **SP 4.2, 5.1**]

Essential knowledge 4.A.2: The rate law shows how the rate depends on reactant concentrations.

a. The rate law expresses the rate of a reaction as proportional to the concentration of each reactant raised to a power. The power of each reactant in the rate law is the order of the reaction with respect to that reactant. The sum of the powers of the reactant concentrations in the rate law is the overall order of the reaction. When the rate is independent of the concentration of a reactant, the reaction is zeroth order in that reactant, since raising the reactant concentration to the power zero is equivalent to the reactant concentration being absent from the rate law.

b. In cases in which the concentration of any other reactants remain essentially constant during the course of the reaction, the order of a reaction with respect to a reactant concentration can be inferred from plots of the concentration of reactant versus time. An appropriate laboratory experience would be for students to use spectrophotometry to determine how concentration varies with time.

c. The method of initial rates is useful for developing conceptual understanding of what a rate law represents, but simple algorithmic application should not be considered mastery of the concept. Investigation of data for initial rates enables prediction of how concentration will vary as the reaction progresses.

Learning Objective for EK 4.A.2:

LO 4.2 The student is able to analyze concentration vs. time data to determine the rate law for a zeroth-, first-, or second-order reaction. [*See* **SP 5.1, 6.4,** *connects to* **4.A.3**]

Essential knowledge 4.A.3: The magnitude and temperature dependence of the rate of reaction is contained quantitatively in the rate constant.

a. The proportionality constant in the rate law is called the rate constant.

b. The rate constant is an important measurable quantity that characterizes a chemical reaction.

c. Rate constants vary over many orders of magnitude because reaction rates vary widely.

d. The temperature dependence of reaction rates is contained in the temperature dependence of the rate constant.

e. For first-order reactions, half-life is often used as a representation for the rate constant because they are inversely proportional, and the half-life is independent of concentration. For example, radioactive decay processes provide real-world context.

Learning Objective for EK 4.A.3:

LO 4.3 The student is able to connect the half-life of a reaction to the rate constant of a first-order reaction and justify the use of this relation in terms of the reaction being a first-order reaction. [*See* **SP 2.1, 2.2**]

Enduring understanding 4.B: Elementary reactions are mediated by collisions between molecules. Only collisions having sufficient energy and proper relative orientation of reactants lead to products.

Reactions proceed through elementary steps involving one or more reactants. In a unimolecular reaction, collisions with other molecules activate the reactant such that it is converted into product. In bimolecular and higher-order reactions, collisions between reactants lead to formation of products, provided both the energy of the collision and the relative orientation of reactants are favorable for reaction. A successful collision can be viewed as proceeding along some single reaction coordinate. The energy profile along this reaction coordinate provides a useful construct for reasoning about the connection between the energetics of a reaction and the rate of the reaction. In particular, this profile includes the activation energy required to overcome the energy barrier between reactants and products.

Essential knowledge 4.B.1: Elementary reactions can be unimolecular or involve collisions between two or more molecules.

a. The order of an elementary reaction can be inferred from the number of molecules participating in a collision: unimolecular reactions are first order, reactions involving bimolecular collisions are second order, etc.

b. Elementary reactions involving the simultaneous collision of three particles are rare.

Learning Objective for EK 4.B.1:

LO 4.4 The student is able to connect the rate law for an elementary reaction to the frequency and success of molecular collisions, including connecting the frequency and success to the order and rate constant, respectively. [*See* **SP 7.1**, *connects to* **4.A.3, 4.B.2**]

Essential knowledge 4.B.2: Not all collisions are successful. To get over the activation energy barrier, the colliding species need sufficient energy. Also, the orientations of the reactant molecules during the collision must allow for the rearrangement of reactant bonds to form product bonds.

a. Unimolecular reactions occur because collisions with solvent or background molecules activate the molecule in a way that can be understood in terms of a Maxwell-Boltzmann thermal distribution of particle energies.

b. Collision models provide a qualitative explanation for order of elementary reactions and the temperature dependence of the rate constant.

c. In most reactions, only a small fraction of the collisions leads to a reaction. Successful collisions have both sufficient energy to overcome activation energy barriers and orientations that allow the bonds to rearrange in the required manner.

d. The Maxwell-Boltzmann distribution describes the distribution of particle energies; this distribution can be used to gain a qualitative estimate of the fraction of collisions with sufficient energy to lead to a reaction, and also how that fraction depends on temperature.

Learning Objective EK 4.B.2:

LO 4.5 The student is able to explain the difference between collisions that convert reactants to products and those that do not in terms of energy distributions and molecular orientation. [*See* **SP 6.2**]

Essential knowledge 4.B.3: A successful collision can be viewed as following a reaction path with an associated energy profile.

a. Elementary reactions typically involve the breaking of some bonds and the forming of new ones. It is usually possible to view the complex set of motions involved in this rearrangement as occurring along a single reaction coordinate.

b. The energy profile gives the energy along this path, which typically proceeds from reactants, through a transition state, to products.

c. The Arrhenius equation can be used to summarize experiments on the temperature dependence of the rate of an elementary reaction and to interpret this dependence in terms of the activation energy needed to reach the transition state.

✗ *Calculations involving the Arrhenius equation are* ***beyond the scope*** *of this course and the AP Exam.*

Rationale: *The conceptual aspects of the Arrhenius equation and the interpretation of graphs is part of the course. However, inclusion of algorithmic calculations was not viewed as the best way to deepen understanding of the big ideas.*

Learning Objective for for EK 4.B.3:

LO 4.6 The student is able to use representations of the energy profile for an elementary reaction (from the reactants, through the transition state, to the products) to make qualitative predictions regarding the relative temperature dependence of the reaction rate. [*See* **SP 1.4, 6.4**]

Enduring understanding 4.C: Many reactions proceed via a series of elementary reactions.

Many reactions proceed through a series of elementary reactions or steps, and this series of steps is referred to as the reaction mechanism. The steps of the mechanism sum to give the overall reaction; the balanced chemical equation for the overall reaction specifies the stoichiometry. The overall rate of the reaction is an emergent property of the rates of the individual reaction steps. For many reactions, one step in the reaction mechanism is sufficiently slow so that it limits the rate of the overall reaction. For such reactions, this rate-limiting step sets the rate of the overall reaction. Reaction intermediates, which are formed by a step in the reaction mechanism and then consumed by a following step, play an important role in multistep reactions, and their experimental detection is an important means of investigating reaction mechanisms.

Learning Objective for EU 4C:

LO 4.7 The student is able to evaluate alternative explanations, as expressed by reaction mechanisms, to determine which are consistent with data regarding the overall rate of a reaction, and data that can be used to infer the presence of a reaction intermediate. [*See* **SP 6.5,** *connects to* **4.C.1, 4.C.2, 4.C.3**]

Essential knowledge 4.C.1: The mechanism of a multistep reaction consists of a series of elementary reactions that add up to the overall reaction.

a. The rate law of an elementary step is related to the number of reactants, as accounted for by collision theory.

b. The elementary steps add to give the overall reaction. The balanced chemical equation for the overall reaction specifies only the stoichiometry of the reaction, not the rate.

c. A number of mechanisms may be postulated for most reactions, and experimentally determining the dominant pathway of such reactions is a central activity of chemistry.

Essential knowledge 4.C.2: In many reactions, the rate is set by the slowest elementary reaction, or rate-limiting step.

a. For reactions in which each elementary step is irreversible, the rate of the reaction is set by the slowest elementary step (i.e., the rate-limiting step).

Essential knowledge 4.C.3: Reaction intermediates, which are formed during the reaction but not present in the overall reaction, play an important role in multistep reactions.

a. A reaction intermediate is produced by some elementary steps and consumed by others, such that it is present only while a reaction is occurring.

b. Experimental detection of a reaction intermediate is a common way to build evidence in support of one reaction mechanism over an alternative mechanism.

✘ *Collection of data pertaining to 4.C.3b is* ***beyond the scope*** *of this course and the AP Exam.*

Rationale: *Designing an experiment to identify reaction intermediates often requires knowledge that is beyond the scope of a general chemistry course.*

Enduring understanding 4.D: Reaction rates may be increased by the presence of a catalyst.

Catalysts, such as enzymes in biological systems and the surfaces in an automobile's catalytic converter, increase the rate of a chemical reaction. Catalysts may function by lowering the activation energy of an elementary step in a reaction, thereby increasing the rate of that elementary step, but leaving the mechanism of the reaction otherwise unchanged. Other catalysts participate in the formation of a new reaction intermediate, thereby providing a new reaction mechanism that provides a faster pathway between reactants and products.

Essential knowledge 4.D.1: Catalysts function by lowering the activation energy of an elementary step in a reaction mechanism, and by providing a new and faster reaction mechanism.

a. A catalyst can stabilize a transition state, lowering the activation energy and thus increasing the rate of a reaction.

b. A catalyst can increase a reaction rate by participating in the formation of a new reaction intermediate, thereby providing a new reaction pathway or mechanism.

Learning Objective for EK 4.D.1:

LO 4.8 The student can translate among reaction energy profile representations, particulate representations, and symbolic representations (chemical equations) of a chemical reaction occurring in the presence and absence of a catalyst. [*See* **SP 1.5**]

Essential knowledge 4.D.2: Important classes in catalysis include acid-base catalysis, surface catalysis, and enzyme catalysis.

a. In acid-base catalysis, a reactant either gains or loses a proton; this changes the rate of the reaction.

b. In surface catalysis, either a new reaction intermediate is formed, or the probability of successful collisions is modified.

c. Some enzymes accelerate reactions by binding to the reactants in a way that lowers the activation energy. Other enzymes react with reactant species to form a new reaction intermediate.

Learning Objective for EK 4.D.2:

LO 4.9 The student is able to explain changes in reaction rates arising from the use of acid-base catalysts, surface catalysts, or enzyme catalysts, including selecting appropriate mechanisms with or without the catalyst present. [*See* **SP 6.2, 7.2**]

Big Idea 5: The laws of thermodynamics describe the essential role of energy and explain and predict the direction of changes in matter.

All changes in matter involve some form of energy change. Thus, the availability or disposition of energy plays a role in virtually all observed chemical processes. Thermodynamics provides a number of tools for understanding this key role, particularly the conservation of energy, including energy transfer in the forms of heat and work. Chemical bonding is central to chemistry, so one key concept associated with energy is that the breaking of a chemical bond inherently requires an energy input, and because bond formation is the reverse process, it will release energy. One key determinant of chemical transformations is the change in potential energy that results from changes in electrostatic forces. In addition to the transfer of energy, the thermodynamic concept of entropy is an important component in determining the direction of chemical or physical change.

Learning Objective for Big Idea 5:

LO 5.1 The student is able to create or use graphical representations in order to connect the dependence of potential energy to the distance between atoms and factors, such as bond order (for covalent interactions) and polarity (for intermolecular interactions), which influence the interaction strength. [*See* **SP 1.1, 1.4, 7.2,** *connects to* **Big Idea 2**]

Note: This learning objective applies to *essential knowledge* components of 5A–5E.

Enduring understanding 5.A: Two systems with different temperatures that are in thermal contact will exchange energy. The quantity of thermal energy transferred from one system to another is called heat.

The particles in chemical systems are continually undergoing random motion. The temperature of a system is a direct measure of the average kinetic energy associated with this random motion. When chemical systems that have different temperatures are placed in thermal contact, kinetic energy is transferred from the hotter object to the cooler object until the temperatures become equal. This transfer of kinetic energy is referred to in this course as heat transfer. An understanding of heat as the transfer of energy between a system at higher temperature and a system at lower temperature is fundamental. Many practical applications exist, such as weather prediction, design of heating and cooling systems, and regulation of the rates of chemical reactions.

Essential knowledge 5.A.1: Temperature is a measure of the average kinetic energy of atoms and molecules.

a. All of the molecules in a sample are in motion.

b. The Kelvin temperature of a sample of matter is proportional to the average kinetic energy of the particles in the sample. When the average kinetic energy of the particles in the sample doubles, the Kelvin temperature is doubled. As the temperature approaches 0 K (zero Kelvin), the average kinetic energy of a system approaches a minimum near zero.

c. The Maxwell-Boltzmann distribution shows that the distribution of kinetic energies becomes greater (more disperse) as temperature increases.

Learning Objective for EK 5.A.1:

LO 5.2 The student is able to relate temperature to the motions of particles, either via particulate representations, such as drawings of particles with arrows indicating velocities, and/or via representations of average kinetic energy and distribution of kinetic energies of the particles, such as plots of the Maxwell-Boltzmann distribution. [*See* **SP 1.1, 1.4, 7.1**]

Essential knowledge 5.A.2: The process of kinetic energy transfer at the particulate scale is referred to in this course as heat transfer, and the spontaneous direction of the transfer is always from a hot to a cold body.

a. On average, molecules in the warmer body have more kinetic energy than the molecules in the cooler body.

b. Collisions of molecules that are in thermal contact transfer energy.

c. Scientists describe this process as "energy is transferred as heat."

d. Eventually, thermal equilibrium is reached as the molecular collisions continue. The average kinetic energy of both substances is the same at thermal equilibrium.

e. Heat is not a substance, i.e., it makes no sense to say that an object contains a certain amount of heat. Rather, "heat exchange" or "transfer of energy as heat" refers to the process in which energy is transferred from a hot to a cold body in thermal contact.

f. The transfer of a given amount of thermal energy will not produce the same temperature change in equal masses of matter with differing specific heat capacities.

Learning Objective for EK 5.A.2:

LO 5.3 The student can generate explanations or make predictions about the transfer of thermal energy between systems based on this transfer being due to a kinetic energy transfer between systems arising from molecular collisions. [*See* **SP 7.1**]

Enduring understanding 5.B: Energy is neither created nor destroyed, but only transformed from one form to another.

The conservation of energy plays an important role in reasoning about the transfer of energy in chemical systems. A molecular system has energy that is a function of its current state. The energy of a system changes when the state of the system changes; for instance, when the temperature of the system changes, when a substance melts or boils, or when a chemical reaction occurs, the energy changes. Conservation of energy implies that any change in the energy of a system must be balanced by the transfer of energy either into or out of the system. This energy transfer can take the form of either heat transfer or work. Work includes all forms of energy transfer other than heat transfer. Examples of mechanical work include the expansion of a gas against a piston in engines. The change in energy associated with a chemical process is an important aspect of such processes characterizing, for instance, the amount of energy that can be obtained from a fuel system. Because the change in energy associated with a given process is proportional to the amount of substance undergoing that process, this change is best described on a per mole (or per gram) basis, as in heat capacities (for heating/cooling), enthalpies of fusion or vaporization (for physical transformations), and enthalpies of reaction (for chemical transformations). Calorimetry provides a convenient means to measure changes in energy, and thus is used experimentally to determine heat capacities or enthalpies of physical and chemical transformations.

Essential knowledge 5.B.1: Energy is transferred between systems either through heat transfer or through one system doing work on the other system.

a. Heating a cold body with a hot body is a form of energy transfer between two systems. The transfer of thermal energy is an important concept in thermodynamics.

b. An additional form of energy transfer is through work. Work is described by other scientific frameworks, such as Newtonian Mechanics or electromagnetism.

c. In this course, calculations involving work are limited to that associated with changes in volume of a gas. An example of the transfer of energy between systems through work is the expansion of gas in a steam engine or car piston. Reasoning about this energy transfer can be based on molecular collisions with the piston:

The gas is doing work on the piston, and energy is transferred from the gas to the piston.

Essential knowledge 5.B.2: When two systems are in contact with each other and are otherwise isolated, the energy that comes out of one system is equal to the energy that goes into the other system. The combined energy of the two systems remains fixed. Energy transfer can occur through either heat exchange or work.

a. When energy is transferred from system 1 to system 2, the energy transferred from system 1 is equal in magnitude to the energy transferred to system 2.

b. If a system transfers energy to another system, its energy must decrease. Likewise, if energy is transferred into a system, its energy must increase.

Learning Objectives for EK 5.B.1 and 5.B.2:

LO 5.4 The student is able to use conservation of energy to relate the magnitudes of the energy changes occurring in two or more interacting systems, including identification of the systems, the type (heat versus work), or the direction of energy flow. [*See* **SP 1.4, 2.2,** *connects to* **5.B.1, 5.B.2**]

LO 5.5 The student is able to use conservation of energy to relate the magnitudes of the energy changes when two nonreacting substances are mixed or brought into contact with one another. [*See* **SP 2.2,** *connects to* **5.B.1, 5.B.2**]

Essential knowledge 5.B.3: Chemical systems undergo three main processes that change their energy: heating/cooling, phase transitions, and chemical reactions.

a. Heating a system increases the energy of the system, while cooling a system decreases the energy. A liter of water at 50°C has more energy than a liter of water at 25°C.

b. The amount of energy needed to heat one gram of a substance by 1°C is the specific heat capacity of that substance.

c. Energy must be transferred to a system to cause it to melt (or boil). The energy of the system therefore increases as the system undergoes a solid-liquid (or liquid-gas) phase transition. Likewise, a system gives off energy when it freezes (or condenses). The energy of the system decreases as the system undergoes a liquid-solid (or gas-liquid) phase transition.

d. The amount of energy needed to vaporize one mole of a pure substance is the molar enthalpy of vaporization, and the energy released in condensation has an equal magnitude. The molar enthalpy of fusion is the energy absorbed when one mole of a pure solid melts or changes from the solid to liquid state and the energy released when the liquid solidifies has an equal magnitude.

e. When a chemical reaction occurs, the energy of the system decreases (exothermic reaction), increases (endothermic reaction), or remains the same. For exothermic reactions, the energy lost by the reacting molecules (system) is gained by the surroundings. The energy is transferred to the surroundings by either heat or work. Likewise, for endothermic reactions, the system gains energy from the surroundings by heat transfer or work done on the system.

f. The enthalpy change of reaction gives the amount of energy released (for negative values) or absorbed (for positive values) by a chemical reaction at constant pressure.

Learning Objective for EK 5.B.3:

LO 5.6 The student is able to use calculations or estimations to relate energy changes associated with heating/cooling a substance to the heat capacity, relate energy changes associated with a phase transition to the enthalpy of fusion/vaporization, relate energy changes associated with a chemical reaction to the enthalpy of the reaction, and relate energy changes to $P\Delta V$ work.
[*See* **SP 2.2, 2.3**]

Essential knowledge 5.B.4: Calorimetry is an experimental technique that is used to determine the heat exchanged/transferred in a chemical system.

a. The experimental setup for calorimetry is the following: A chemical system is put in thermal contact with a heat bath. The heat bath is a substance, such as water, whose heat capacity has been well established by previous experiments. A process is initiated in the chemical system (heating/cooling, phase transition, or chemical reaction), and the change in temperature of the heat bath is determined.

b. Because the heat capacity of the heat bath is known, the observed change in temperature can be used to determine the amount of energy exchanged between the system and the heat bath.

c. The energy exchanged between the system and the heat bath is equal in magnitude to the change in energy of the system. If the heat bath increased in temperature, its energy increased, and the energy of the system decreased by this amount. If the heat bath decreased in temperature, and therefore energy, the energy of the system increased by this amount.

d. Because calorimetry measures the change in energy of a system, it can be used to determine the heat associated with each of the processes listed in 5.B.3. In this manner, calorimetry may be used to determine heat capacities, enthalpies of vaporization, enthalpies of fusion, and enthalpies of reactions. *Only constant pressure calorimetry is required in the course.*

Learning Objective for EK 5.B.4:

LO 5.7 The student is able to design and/or interpret the results of an experiment in which calorimetry is used to determine the change in enthalpy of a chemical process (heating/cooling, phase transition, or chemical reaction) at constant pressure. [*See* **SP 4.2, 5.1, 6.4**]

Enduring understanding 5.C: Breaking bonds requires energy, and making bonds releases energy.

Chemical bonds arise from attractive interactions between negatively charged electrons and the positively charged nuclei of the atoms that make up the bond. As electrons approach a positive charge, the potential energy of a system is lowered. Therefore, having electrons shared between atoms results in the system being in a lower energy state, which can only happen if energy is somehow released. Thus, making chemical bonds releases energy. The converse is true for the opposing process. In order to break a chemical bond, energy must be put into the system to overcome the attractive interaction between the shared electrons and the nuclei of the bonded atoms. When considering chemical reactions, however, it is important to recognize that in most cases both bond breaking and bond formation occurs. The overall energy change is determinable from looking at all the energy inputs (to break bonds) and the energy outputs (from the formation of bonds). There are several ways to calculate energy changes for reactions, including traditionally used methods involving enthalpy of formation. One compelling conceptual model for this calculation is to use average bond energies or enthalpies to determine the energy change of a reaction. Many practical examples of chemistry take place in solvents (often water); thus, the determination of overall changes in energy for a reaction must include consideration of any solvent interactions with reactants and products. Energy may appear in different forms, such as potential energy or kinetic energy. In chemical systems, the stored energy is called chemical energy, and the energy of motion (translational, rotational, or vibrational) is called thermal energy. Chemical energy is the potential energy associated with chemical systems. The amount of chemical energy in a system changes when the chemicals are allowed to react. The energy transferred to or from the surroundings when a chemical system undergoes a reaction is often in the form of thermal energy.

Essential knowledge 5.C.1: Potential energy is associated with a particular geometric arrangement of atoms or ions and the electrostatic interactions between them.

a. The attraction between the electrons of one atom and the protons of another explains the tendency for the atoms to approach one another. The repulsion between the nuclei (or core electrons) explains why the atoms repel one another at close distance. The distance at which the energy of interaction is minimized is called the bond length, and the atoms vibrate about this minimum energy position.

b. A graph of energy versus the distance between atoms can be plotted and interpreted. Using this graph, it is possible to identify bond length and bond energy.

c. Conceptually, bond making and bond breaking are opposing processes that have the same magnitude of energy associated with them. Thus, convention becomes important, so we define the bond energy as the energy required to break a bond.

d. Because chemical bonding arises from electrostatic interaction between electrons and nuclei, larger charges tend to lead to larger strengths of interaction. Thus, triple bonds are stronger than double or single bonds because they share more pairs of electrons.

e. Stronger bonds tend to be shorter bonds.

Essential knowledge 5.C.2: The net energy change during a reaction is the sum of the energy required to break the bonds in the reactant molecules and the energy released in forming the bonds of the product molecules. The net change in energy may be positive for endothermic reactions where energy is required, or negative for exothermic reactions where energy is released.

a. During a chemical reaction, bonds are broken and/or formed, and these events change the potential energy of the reaction system.

b. The average energy required to break all of the bonds in the reactant molecules can be estimated by adding up the average bond energies or bond enthalpies for all the bonds in the reactant molecules. Likewise, the average energy released in forming the bonds in the products can be estimated. If the energy released is greater than the energy required, then the reaction is exothermic. If the energy required is greater than the energy released, then the reaction is endothermic.

c. For an exothermic reaction, the products are at a lower potential energy compared with the reactants. For an endothermic reaction, the products are at a higher potential energy than the reactants.

d. In an isolated system, energy is conserved. Thus, if the potential energy of the products is lower than that of the reactants, then the kinetic energy of the products must be higher. For an exothermic reaction, the products are at a higher kinetic energy. This means that they are at a higher temperature. Likewise, for an endothermic reaction, the products are at a lower kinetic energy and, thus, at a lower temperature.

e. Because the products of a reaction are at a higher or lower temperature than their surroundings, the products of the reaction move toward thermal equilibrium with the surroundings. Thermal energy is transferred to the surroundings from the hot products in an exothermic reaction. Thermal energy is transferred from the surroundings to the cold products in an endothermic reaction.

f. Although the concept of "state functions" is not required for the course, students should understand these Hess's law ideas: When a reaction is reversed, the sign of the enthalpy of the reaction is changed; when two (or more) reactions are summed to obtain an overall reaction, the enthalpies of reaction are summed to obtain the net enthalpy of reaction.

g. Tables of standard enthalpies of formation can be used to calculate the standard enthalpy of reactions. Uses should go beyond algorithmic calculations and include, for instance, the use of such tables to compare related reactions, such as extraction of elemental metals from metal oxides.

Learning Objective for 5.C.2:

LO 5.8 The student is able to draw qualitative and quantitative connections between the reaction enthalpy and the energies involved in the breaking and formation of chemical bonds. [*See* **SP 2.3, 7.1, 7.2**]

Enduring understanding 5.D: Electrostatic forces exist between molecules as well as between atoms or ions, and breaking the resultant intermolecular interactions requires energy.

The same essential interaction that forms chemical bonds, electrostatic attraction, also explains the attractive forces as non-bonded atoms draw near each other. When atoms approach each other, there is always an electrostatic attraction between the positive charges of the nucleus in each atom and the electrons of the approaching atom. When a chemical bond does not form between the two atoms, this attraction is described as an intermolecular force. For molecular systems, these intermolecular forces are understood in terms of charge distributions leading to dipoles (permanent or induced) that then attract each other. The most common categories for these interactions are (a) dipole-dipole, (b) dipole-induced dipole, and (c) induced dipole-induced dipole (dispersion) forces. Hydrogen bonding is an important, specialized form of dipole-dipole interactions. These forces may occur (a) between small molecules, (b) between different large molecules, or (c) between different regions of the same large molecule. The distinction at the particulate level between electrostatic interactions of nonbonded atoms and those of chemically bonded atoms provides the cleanest distinction between a chemical and physical process. A physical process generally involves nonbonded interactions, and a chemical process involves breaking and/or forming covalent bonds. In many systems involving large molecules (both biochemical systems and synthetic polymer systems), the nonbonded interactions play important roles in the observed functions of the systems.

Essential knowledge 5.D.1: Potential energy is associated with the interaction of molecules; as molecules draw near each other, they experience an attractive force.

a. Chemists categorize intermolecular forces in terms of the nature of the charge distributions in the molecules involved. Thus, dipole-dipole, dipole-induced dipole, and induced dipole-induced dipole (dispersion) can be defined.

b. All substances will manifest dispersion forces, and these forces tend to be larger when the molecules involved have more electrons or have a larger surface area.

c. Hydrogen bonding is a relatively strong type of intermolecular interaction that occurs when hydrogen atoms that are covalently bonded to the highly electronegative atoms (N, O, and F) are also attracted to the negative end of a dipole formed by the electronegative atom (N, O, and F) in a different molecule, or a different part of the same molecule. When hydrogen bonding is present, even small molecules may have strong intermolecular attractions.

Learning Objective for 5.D.1:

LO 5.9 The student is able to make claims and/or predictions regarding relative magnitudes of the forces acting within collections of interacting molecules based on the distribution of electrons within the molecules and the types of intermolecular forces through which the molecules interact. [*See* **SP 6.4**]

Essential knowledge 5.D.2: At the particulate scale, chemical processes can be distinguished from physical processes because chemical bonds can be distinguished from intermolecular interactions.

a. The distinction between chemical and physical processes relates to the nature of the change in molecular interactions. Processes that involve the breaking and/or formation of chemical bonds are classified as chemical processes. Processes that involve only changes in weak intermolecular interactions, such as phase changes, are classified as physical processes.

b. A gray area exists between these two extremes. For instance, the dissolution of a salt in water involves breaking of ionic bonds and the formation of interactions between ions and solvent. The magnitude of these interactions can be comparable to covalent bond strengths, and so plausible arguments can be made for classifying dissolution of a salt as either a physical or chemical process.

Learning Objective for EK 5.D.2:

LO 5.10 The student can support the claim about whether a process is a chemical or physical change (or may be classified as both) based on whether the process involves changes in intramolecular versus intermolecular interactions. [*See* **SP 5.1**]

Essential knowledge 5.D.3: Noncovalent and intermolecular interactions play important roles in many biological and polymer systems.

a. In large biomolecules, noncovalent interactions may occur between different molecules or between different regions of the same large biomolecule.

b. The functionality and properties of molecules depend strongly on the shape of the molecule, which is largely dictated by noncovalent interactions. For example, the function of enzymes is dictated by their structure, and properties of synthetic polymers are modified by manipulating their chemical composition and structure.

Learning Objective for EK 5.D.3:

LO 5.11 The student is able to identify the noncovalent interactions within and between large molecules, and/or connect the shape and function of the large molecule to the presence and magnitude of these interactions. [*See* **SP 7.2**]

Enduring understanding 5.E: Chemical or physical processes are driven by a decrease in enthalpy or an increase in entropy, or both.

One of the most powerful applications of thermodynamic principles is the ability to determine whether a process corresponding to a physical or chemical change will lie toward the reactant or product side when the process reaches a steady equilibrium state. The standard change in Gibbs free energy, $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$, is used to make this determination. If $\Delta G^\circ < 0$, then products are favored at equilibrium, and the forward process is considered to be "thermodynamically favored." Conversely, if $\Delta G^\circ > 0$, then reactants are favored at equilibrium, and the reverse process is considered to be "thermodynamically favored." Both the enthalpy change (ΔH°) and the entropy change

(ΔS°) are closely related to the structure and nature of the components of the system; for this reason, it is often possible to make qualitative determinations concerning the sign (and magnitude) of ΔG° without explicit calculation. Enthalpy changes are closely related to the relative bond energies (and relative strengths of intermolecular interactions) of the reactants and products; entropy changes are generally related to the states of the components and the number of individual particles present. In this way, the Gibbs free energy provides a framework based on molecular structure and intermolecular interactions for understanding why some chemical reactions are observed to proceed to near completion, while others reach equilibrium with almost no products being formed. Some processes that are not thermodynamically favored (for example, the recharging of a battery) can be driven to occur through the application of energy from an external source — in this case, an electrical current. Importantly, in biochemical systems, some reactions that oppose the thermodynamically favored direction are driven by coupled reactions. Thus, a cell can use energy to create order (a direction that is not thermodynamically favored) via coupling with thermodynamically favored reactions. For example, many biochemical syntheses are coupled to the reaction in which ATP is converted to ADP + phosphate.

In some cases, processes that are thermodynamically favored are not observed to occur because of some kinetic constraint; quite often there is a high activation energy to overcome in order for the process to proceed. Thus, although Gibbs free energy can be used to determine which direction of a chemical process is thermodynamically favored, it provides no information about the rate of the process, or the nature of the process on the microscopic scale.

Essential knowledge 5.E.1: Entropy is a measure of the dispersal of matter and energy.

a. Entropy may be understood in qualitative terms rather than formal statistical terms. Although this is not the most rigorous approach to entropy, the use of qualitative reasoning emphasizes that the goal is for students to be able to make predictions about the direction of entropy change, ΔS°, for many typical chemical and physical processes.

b. Entropy increases when matter is dispersed. The phase change from solid to liquid, or from liquid to gas, results in a dispersal of matter in the sense that the individual particles become more free to move, and generally occupy a larger volume. Another way in which entropy increases in this context is when the number of individual particles increases when a chemical reaction precedes whose stoichiometry results in a larger number of product species than reacting species. Also, for a gas, the entropy increases when there is an increase in volume (at constant temperature), and the gas molecules are able to move within a larger space.

c. Entropy increases when energy is dispersed. From KMT, we know that the distribution of kinetic energy among the particles of a gas broadens as the temperature increases. This is an increase in the dispersal of energy, as the total kinetic energy of the system becomes spread more broadly among all of the gas molecules. Thus, as temperature increases, the entropy increases.

Learning Objective for EK 5.E.1:

LO 5.12 The student is able to use representations and models to predict the sign and relative magnitude of the entropy change associated with chemical or physical processes. [*See* **SP 1.4**]

Essential knowledge 5.E.2: Some physical or chemical processes involve *both* a decrease in the internal energy of the components ($\Delta H° < 0$) under consideration *and* an increase in the entropy of those components ($\Delta S° > 0$). These processes are necessarily "thermodynamically favored" ($\Delta G° < 0$).

a. For the purposes of thermodynamic analysis in this course, the *enthalpy* and the *internal energy* will not be distinguished.

b. The phrase "thermodynamically favored" means that products are favored at equilibrium ($K > 1$).

c. Historically, the term "spontaneous" has been used to describe processes for which $\Delta G° < 0$. The phrase "thermodynamically favored" is used here to avoid misunderstanding and confusion that can occur because of the common connotation of the term "spontaneous," which students may believe means "immediately" or "without cause."

d. For many processes, students will be able to determine, either quantitatively or qualitatively, the signs of both $\Delta H°$ and $\Delta S°$ for a physical or chemical process. In those cases where $\Delta H° < 0$ and $\Delta S° > 0$, there is no need to calculate $\Delta G°$ in order to determine that the process is thermodynamically favored.

e. As noted below in 5.E.5, the fact that a process is thermodynamically favored does not mean that it will proceed at a measurable rate.

f. Any process in which both $\Delta H° > 0$ and $\Delta S° < 0$ are **not** thermodynamically favored, ($\Delta G° > 0$) and the process *must* favor reactants at equilibrium ($K < 1$). Because the signs of $\Delta S°$ and $\Delta H°$ reverse when a chemical or physical process is reversed, this must be the case.

Learning Objective for EK 5.E.2:

LO 5.13 The student is able to predict whether or not a physical or chemical process is thermodynamically favored by determination of (either quantitatively or qualitatively) the signs of both ΔH° and ΔS°, and calculation or estimation of ΔG° when needed. [*See* **SP 2.2, 2.3, 6.4,** *connects to* **5.E.3**]

Essential knowledge 5.E.3: If a chemical or physical process is not driven by *both* entropy and enthalpy changes, then the Gibbs free energy change can be used to determine whether the process is thermodynamically favored.

a. Some exothermic reactions involve decreases in entropy.

b. When $\Delta G^\circ > 0$, the process **is not** thermodynamically favorable. When $\Delta G^\circ < 0$, the process **is** thermodynamically favorable.

c. In some reactions, it is necessary to consider both enthalpy and entropy to determine if a reaction will be thermodynamically favorable. The freezing of water and the dissolution of sodium nitrate in water provide good examples of such situations.

Learning Objective for EK 5.E.3:

LO 5.14 The student is able to determine whether a chemical or physical process is thermodynamically favorable by calculating the change in standard Gibbs free energy. [*See* **SP 2.2,** *connects to* **5.E.2**]

Essential knowledge 5.E.4: External sources of energy can be used to drive change in cases where the Gibbs free energy change is positive.

a. Electricity may be used to cause a process to occur that is not thermodynamically favored. Useful examples are charging of a battery and the process of electrolysis.

b. Light may also be a source of energy for driving a process that in isolation is not thermodynamically favored. Useful examples are as follows:

   1. The photoionization of an atom, because although the separation of a negatively charged electron from the remaining positively charged ion is highly endothermic, ionization is observed to occur in conjunction with the absorption of a photon.

   2. The overall conversion of carbon dioxide to glucose through photosynthesis, for which $6\ CO_2(g) + 6\ H_2O(l) \rightarrow C_6H_{12}O_6(aq) + 6\ O_2(g)$ has $\Delta G^\circ = +2880\ kJ/mol_{rxn}$,

yet is observed to occur through a multistep process that is initiated by the absorption of several photons in the range of 400–700 nm.

c. A thermodynamically unfavorable reaction may be made favorable by coupling it to a favorable reaction, such as the conversion of ATP to ADP in biological systems. In this context, coupling means the process involves a series of reactions with common intermediates, such that the reactions add up to produce an overall reaction with a negative $\Delta G°$.

Learning Objectives for EK 5.E.4:

LO 5.15 The student is able to explain how the application of external energy sources or the coupling of favorable with unfavorable reactions can be used to cause processes that are not thermodynamically favorable to become favorable. [*See* **SP 6.2**]

LO 5.16 The student can use Le Chatelier's principle to make qualitative predictions for systems in which coupled reactions that share a common intermediate drive formation of a product. [*See* **SP 6.4,** *connects to* **6.B.1**]

LO 5.17 The student can make quantitative predictions for systems involving coupled reactions that share a common intermediate, based on the equilibrium constant for the combined reaction. [*See* **SP 6.4,** *connects to* **6.A.2**]

Essential knowledge 5.E.5: A thermodynamically favored process may not occur due to kinetic constraints (kinetic vs. thermodynamic control).

a. Many processes that are thermodynamically favored do not occur to any measurable extent, or they occur at extremely slow rates.

b. Processes that are thermodynamically favored, but do not proceed at a measurable rate, are said to be under "kinetic control." High activation energy is a common reason for a process to be under kinetic control. The fact that a process does not proceed at a noticeable rate does not mean that the chemical system is at equilibrium. If a process is known to be thermodynamically favored (through qualitative and/or quantitative analysis of $\Delta H°$ and $\Delta S°$), and yet it is not occurring at a measurable rate, then the conclusion is that the process is under kinetic control.

Learning Objective for EK 5.E.5:

LO 5.18 The student can explain why a thermodynamically favored chemical reaction may not produce large amounts of product (based on consideration of both initial conditions and kinetic effects), or why a thermodynamically unfavored chemical reaction can produce large amounts of product for certain sets of initial conditions. [*See* **SP 1.3, 7.2,** *connects to* **6.D.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.

Many processes in nature, including large numbers of chemical reactions, are reversible, i.e., these processes can proceed in either direction. Chemical reactions can be reversible at the atomic or molecular level. When opposing processes occur at the same rate, a stable but dynamic state called equilibrium is established. The expression for the equilibrium constant, K, is a mathematical expression that describes the equilibrium state associated with a chemical change. An analogous expression for the reaction quotient, Q, describes a chemical reaction at any point, enabling comparison to the equilibrium state. A wide range of equilibrium constants is possible; of particular significance are those that arise from acid-base chemistry, particularly as embodied in biochemical systems where the value of K is such that significant amounts of both reactants and products are present. Equilibrium states can be perturbed in a variety of ways, and the response to such a perturbation is predictable.

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

A collection of molecules undergoing a reversible reaction can adopt a number of configurations that are constrained by the stoichiometry and that can be ordered by the extent to which the reactants have been converted to products. As reactants are converted to products, the reactant concentrations drop; thus, the rate of the forward reaction decreases. Simultaneously, the product concentrations increase and the rate of the reverse reaction increases. At some intermediate point, the concentrations of reactants and products are such that the rates of the forward and reverse reactions balance, and there is no net conversion between reactants and products. A system that has reached this state is at chemical equilibrium. The relative proportions of reactants and products at equilibrium is specified by the equilibrium constant, K, which may be used both quantitatively (to predict concentrations at equilibrium) and qualitatively (to reason about the relative amounts of reactants and products present at equilibrium).

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 for EK 6.A.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. [*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.

Learning Objective for EK 6.A.2:

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.

Learning Objectives for EK 6.A.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. [*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.

Learning Objective for EK 6.A.4:

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.

Chemical equilibrium is a dynamic state in which the rates of the forward and reverse reactions are equal. A change in conditions, such as addition of a chemical species, change in temperature, or change in volume, can cause the rate of the forward and reverse reactions to fall out of balance. Such a change is called a stress on the system. The system is then temporarily out of equilibrium, and there is a net conversion between reactants and products until a new equilibrium state is established. This net conversion is referred to as a shift of the chemical reaction. Le Chatelier's principle provides a convenient means to reason qualitatively about the direction of the shift in an equilibrium system resulting from various possible stresses.

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 pH, temperature, and color of a solution.

Learning Objectives for EK 6.B.1:

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. [*See* **SP 1.4, 6.4**]

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. [*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. Le Chatelier's principle involves qualitative reasoning that is closely connected to the quantitative approach of 6.A.3.

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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 for EK 6.B.2:

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*. [*See* **SP 1.4, 7.2**]

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

The proton-exchange reactions of acid-base chemistry are reversible reactions that reach equilibrium quickly, and much of acid-base chemistry can be understood by applying the principles of chemical equilibrium. Most acid-base reactions have either large or small *K*, and so qualitative conclusions regarding the equilibrium state can often be drawn without extensive computations. The dissolution of a solid in a solvent is also a reversible reaction that often reaches equilibrium quickly, and so can be understood by applying the principles of chemical equilibrium.

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, K_w. For pure water, pH = pOH, and this condition is called "neutrality," or a neutral solution. At 25°C, $pK_w = 14$, 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 K_a, often reported as pK_a. The pH of a weak acid solution can be determined from the initial acid concentration and the pK_a. The common weak acids include carboxylic acids. The relative magnitudes of K_a'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 K_b, often reported as pK_b. The pH of a weak base solution can be determined from the initial base concentration and the pK_b.

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 K_w, and at 25°C, $\mathrm{p}K_a + \mathrm{p}K_b = 14$. 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 H_2O, 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 H_3O^+ (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 H_3O^+ 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.

   i. For a mixture of a strong acid with a strong base, the neutralization reaction is $H_3O^+ + OH^- \rightarrow H_2O$. The K for this reaction is 10^{14} 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.

   ii. When a strong base is added to a solution of a weak acid, a neutralization reaction occurs: conjugate acid + $OH^- \rightarrow$ conjugate base + H_2O.

   iii. When a strong acid is added to a solution of a weak base, a neutralization reaction occurs: conjugate base + $H_3O^+ \rightarrow$ conjugate acid + H_2O.

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 $H_3O^+(aq)$ 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 pK_a 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.

✘ *Numerical computation of the concentration of each species present in the titration curve for polyprotic acids is **beyond the scope** of this course and the AP Exam.*

Rationale: *Such computations for titration of monoprotic acids are within the scope of the course, as is qualitative reasoning regarding what species are present in large versus small concentrations at any point in titration of a polyprotic acid. However, additional computations of the concentration of each species present in the titration curve for polyprotic acids may encourage algorithmic calculations and were not viewed as the best way to deepen understanding of the big ideas.*

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 $H_3O^+(aq)$, the anion from the acid (e.g., Cl^-, NO_3^-), 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 $H_3O^+(aq)$, the anion from the acid (e.g., CH_3COO^-, 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 $[HA] = [A^-]$.

Learning Objectives for EK 6.C.1:

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, 6.4,** *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 pK_a for a weak acid, or the pK_b for a weak base. [*See* **SP 5.1, 6.4,** *connects to* **1.E.2**]

LO 6.14 The student can, based on the dependence of K_w 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 pK_a allows one to determine the protonation state of a molecule with a labile proton.

The pH of an aqueous solution is determined by the identity and concentration of the substance that is dissolved in water. The value of the pH 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 acid-base systems, pH 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 pH so that the addition of an acid or base does not change the pH (e.g., amino acids and proteins in the body — the blood maintains a relatively constant pH).

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 pK_a 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).

✘ *Computing the change in pH resulting from the addition of an acid or a base to a buffer is **beyond the scope** of this course and the AP Exam.*

***Rationale:** Algorithmic calculations of pH changes are not viewed as the best way to deepen understanding of the big ideas.*

✘ *The production of the Henderson-Hasselbalch equation by algebraic manipulation of the relevant equilibrium constant expression is **beyond the scope** of this course and the AP Exam.*

***Rationale:** Reasoning about the protonation states of weak acids in solution and the functioning of buffers is within the scope of the course. However, since the Henderson-Hasselbalch equation is merely a rearrangement of the law of mass action for a weak acid, inclusion of its derivation was not viewed as the best way to deepen understanding of the big ideas.*

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.

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d. By comparing the pH of a solution to the pK_a 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 $pH < pK_a$, the acid form has a higher concentration than the base form. If $pH > pK_a$, 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.

Learning Objectives for EK 6.C.2:

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 pK_a 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 K_{sp}, the solubility-product constant.

b. The solubility of a substance can be calculated from the K_{sp} 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.

✘ *Memorization of other "solubility rules" is* ***beyond the scope*** *of this course and the AP Exam.*

Rationale: *Memorization of solubility rules does not deepen understanding of the big ideas.*

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 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 Le Chatelier's principle.

✘ *Computations of solubility as a function of pH are* ***beyond the scope*** *of this course and the AP Exam.*

Rationale: *Computations of solubility as a function of pH do not deepen understanding of the big ideas.*

✘ *Computations of solubility in such solutions are* ***beyond the scope*** *of this course and the AP Exam.*

Rationale: *Computations of solubility in such solutions do not deepen understanding of the big ideas.*

Learning Objectives for EK 6.C.3:

LO 6.21 The student can predict the solubility of a salt, or rank the solubility of salts, given the relevant K_{sp} 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 K_{sp} 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, 6.4**]

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.

The magnitude of the equilibrium constant, K, specifies the relative proportion of reactants and products present at equilibrium. This is directly related to the change in Gibbs free energy associated with the reaction, $\Delta G°$. The species that have the lower free energy (reactants versus products) have larger relative concentrations at equilibrium. For both reactants and products to be present with significant concentrations at equilibrium, i.e., for K to be near 1, the magnitude of $\Delta G°$ must be roughly equivalent to the thermal energy (RT).

Essential knowledge 6.D.1: When the difference in Gibbs free energy between reactants and products ($\Delta G°$) is much larger than the thermal energy (RT), the equilibrium constant is either very small (for $\Delta G° > 0$) or very large (for $\Delta G° < 0$). When $\Delta G°$ 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, $\Delta G°$.

b. The equilibrium constant is related to free energy by $K = e^{-\Delta G°/RT}$. 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 $\Delta G°$ is large compared to the thermal energy, then K deviates strongly from 1.

c. The relation $K = e^{-\Delta G°/RT}$ provides a refinement of the statement in 5.E that processes with $\Delta G° < 0$ favor products, while those with $\Delta G° > 0$ favor reactants. If $\Delta G° < 0$, then $K > 1$, while if $\Delta G° > 0$, 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 ($\Delta G° < 0$) or endergonic ($\Delta G° > 0$). (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.

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Learning Objective for EK 6.D.1:

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**]