Advanced Placement Chemistry at Argo Community High School

Updated 8/2022



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First Semester

Unit 01 – Atomic Structure And Properties

Topic 1.1 Moles and Molar Mass

Enduring Understanding

Calculate quantities of a substance or its relative number of particles using dimensional analysis and the mole concept Essential Knowledge

One cannot count particles directly while performing laboratory work. Thus, there must be a connection between the masses of substances reacting and the actual number of particles undergoing chemical changes.

Avogadro's number ($N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$) provides the connection between the number of moles in a pure sample of a substance and the number of constituent particles (or formula units) of that substance.

Expressing the mass of an individual atom or molecule in atomic mass units (amu) is helpful because the average atomic mass in amu of one particle (atom or molecule) or formula unit of a substance will always be numerically equal to the molar mass of that substance in grams. Thus, there is a quantitative connection between the mass of a substance and the number of particles that the substance contains.

Topic 1.2 Mass Spectroscopy of Elements

Enduring Understanding

Explore the quantitative relationship between the mass spectrum of an element and the masses of the element's isotopes Essential Knowledge

The mass spectrum of a sample containing a single element can be used to determine the identity of the isotopes of that element and the relative abundance of each isotope in nature

The average atomic mass of an element can be estimated from the weighted average of the isotopic masses using the mass of each isotope and its relative abundance

Exclusion Statement

** Interpreting mass spectra of samples containing multiple elements or peaks arising from species other than singly charged monatomic ions will not be assessed on the AP exam. **

Topic 1.3 Elemental Composition of Pure Substances

Enduring Understanding

Explain the quantitative relationship between the elemental composition by mass and the empirical formula of a pure substance

Essential Knowledge

Some pure substances are composed of individual molecules, while others consist of atoms or ions held together in fixed proportions known as a formula unit.

According to the law of definite proportions, the ratio of the masses of the constituent elements in any pure sample of that compound is always the same.

The chemical formula that lists the lowest whole number ratio of atoms of the elements in a compound is the empirical formula.

Topic 1.4 Composition of Mixtures

Enduring Understanding

Explain the quantitative relationship between the elemental composition by mass and the composition of substances in a mixture

Essential Knowledge

While pure substances contain molecules or formula units of a single type, mixtures contain molecules or formula units of two or more types, whose relative proportions can vary.

Elemental analysis can be used to determine the relative numbers of atoms in a substance and to determine its purity.

Topic 1.5 Atomic Structure and Electron Configuration

Enduring Understanding

Represent the electron configuration of an element or ions of an element using the Aufbau principle

Essential Knowledge

The atom is composed of negatively charged electrons and a positively charged nucleus that is made of protons and neutrons.

Coulomb's law is used to calculate the force between two charged particles:

EQN:
$$F_{coulombic} \propto \frac{q_1 q_2}{r^2}$$

In atoms and ions, the electrons can be thought of being in "shells (energy levels)" and "subshells (sublevels)", as described by the electron configuration. Inner electrons are called core electrons, and outer electrons are called valence electrons. The electron configuration is explained by quantum mechanics, as delineated by the Aufbau principle and exemplified in the periodic table of the elements.

The relative energy required to remove an electron from different subshells of an atom or ion or from the same subshell of different atoms or ions (ionization energy) can be estimated through a qualitative application of Coulomb's law. This energy is relative to the distance from the nucleus and the effective (shield) charge of the nucleus.

Exclusion Statement

** The assignment of quantum numbers to electrons in subshells of an atom will not be assessed on the AP chemistry exam. **

Topic 1.6 Photoelectron Spectroscopy

Enduring Understanding

Explain the relationship between the photoelectron spectrum of an atom or ion and (a) the electron configuration of the species and (b) the interactions between the electrons and the nucleus.

Essential Knowledge

The energies of the electrons in a given shell can be measured experimentally with photoelectron spectroscopy (PES). The position of each peak in the PES spectrum is related to the energy required to remove an electron from the corresponding subshell, and the height of each peak is (ideally) proportional to the number of electrons in that subshell.

Topic 1.7 Periodic Trends

Enduring Understanding

Explain the relationship between trends in atomic properties of elements and electronic structure and periodicity.

Essential Knowledge

The organization of the periodic table is based on the recurring properties of the elements and explained by the pattern of electron configurations and the presence of completely or partially filled shells (and subshells) of electrons in atoms.

Exclusion Statement

** Writing the electron configuration of elements that are exceptions to the Aufbau principle will not be assessed on the AP exam. **

Trends in atomic properties within the periodic table (periodicity) can be qualitatively understood through the position of the element on the periodic table, Coulomb's law, the shell model, and the concept of shielding/effective nuclear charge. These properties include: (a) ionization energy, (b) atomic and ionic radii, (c) electron affinity, (d) electronegativity.

The periodicity is useful to predict / estimate values of properties in the absence of data.

Topic 1.8 Valence Electrons and Ionic Compounds

Enduring Understanding

Explain the relationship between trends in the reactivity of elements and periodicity.

Essential Knowledge

The likelihood that two elements will form a chemical bond is determined by the interactions between the valence electrons and nuclei of elements.

Elements in the same column of the periodic table tend to form analogous compounds.

Typical charges of atoms in ionic compounds are governed by their location on the periodic table and the number of valence electrons.

Unit 02 Molecular and Ionic Compound Structure and Properties

Topic 2.1 Types of Chemical Bonds

Enduring Understanding

Explain the relationship between the type of bonding and the properties of the elements participating in the bond.

Essential Knowledge

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.

Valence electrons shared between atoms of similar electronegativity constitute a nonpolar covalent bond. For example, bonds between carbon and hydrogen are effectively nonpolar even though carbon is slightly more electronegative than hydrogen.

Valence electrons shared between atoms of unequal electronegativity values constitute a polar covalent bond.

- (a) The atom with a higher electronegativity will develop a partial negative charge relative to the other atom in the bond.
- (b) In single bonds, greater difference in electronegativity leads to greater bond dipoles.
- (c) All polar 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 should be designated as ionic or covalent. Generally, bonds between a metal and nonmetal are ionic, and bonds between two nonmetals are covalent. Examination of the properties of a compound is the best way to characterize the type of bonding.

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

Topic 2.2 Intramolecular Force and Potential Energy

Enduring Understanding

Represent the relationship between potential energy and distance between atoms, based on factors that influence the interaction strength.

Essential Knowledge

A graph of potential energy versus the distance between atoms is a useful representation for describing the interactions between atoms. Such graphs illustrate both the equilibrium bond length (the separation between atoms at which the potential energy is lowest) and the bond energy (the energy required to separate the atoms).

In a covalent bond, the bond length is influenced by both the size of the atom's core and the bond order (i.e. single, double, triple). Bonds with a higher order are shorter and have larger bond energies.

Coulomb's law can be used to understand the strength of interactions between cations and anions.

- (a) Because the interaction strength is proportional to the charge on each ion, larger charges lead to stronger interactions.
- (b) Because the interaction strength increases as the distance between the centers of the ions (nuclei) decreases, smaller ions lead to stronger interactions.

Topic 2.3 Structure of Ionic Solids

Enduring Understanding

Represent an ionic solid with a particulate model that is consistent with Coulomb's law and the properties of the constituent ions.

Essential Knowledge

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.

Exclusion Statement

** Knowledge of specific types of crystal structures will not be assessed on the AP exam. **

Topic 2.4 Structure of Metals and Alloys

Enduring Understanding

Represent a metallic solid and/or alloy using a model to show essential characteristics of the structure and interactions present in the substance.

Essential Knowledge

Metallic bonding can be represented as an array of positive metal ions surrounded by delocalized valence electrons (i.e. a "sea of electrons").

Interstitial alloys form between atoms of different radii, where the smaller atoms fill the interstitial spaces between the larger atoms (e.g. with steel in which carbon occupies the interstices in iron).

Substitutional alloys form between atoms of comparable radius, where one atom substitutes for the others in the lattice. (In certain brass alloys, other elements, usually zinc, substitute for copper).

Topic 2.5 Lewis Diagrams

Enduring Understanding

Represent a molecule with a Lewis diagram

Essential Knowledge

Lewis diagrams can be constructed according to an established set of principles.

Topic 2.6 Resonance and Formal Charge

Enduring Understanding

Represent a molecule with a Lewis diagram that accounts for resonance between equivalent structures or that uses formal charge to select between nonequivalent structures.

Essential Knowledge

In cases where more than one equivalent Lewis structure can be constructed, resonance must be included as a refinement to the Lewis structure. In many such cases, this refinement is needed to provide qualitatively accurate predictions of molecular structure and properties.

The octet rule and formal charge can be used as criteria for determining which of several possible valid Lewis diagrams provides the best model for predicting molecular structure and properties.

As with any model, there are limitations to the use of the Lewis structure model, particularly in cases with an odd number of electrons.

Topic 2.7 VSEPR & Hybridization

Enduring Understanding

Based on the relationship between Lewis diagrams, VSEPR theory, bond orders, and bond polarities: (a) Explain structural properties of molecules; (b) Explain electron properties of molecules

Essential Knowledge

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

Both Lewis diagrams and VSEPR theory must be used for predicting electronic and structural properties of many covalently bonded molecules and polyatomic ions, including the following: (a) molecular geometry, (b) bond angles, (c) relative bond energies based on bond order, (d) relative bond lengths [multiple bonds, effects of atomic radius], (e) presence of a dipole moment, (f) hybridization of valence orbitals of the molecule

The terms "hybridization" and "hybrid atomic orbital" are used to describe the arrangement of electrons around a central atom. When the central atom is sp hybridized, its ideal bond angles are 180°; for sp² hybridized atoms the bond angles are 120°; and for sp³ hybridized atoms the bond angles are 109.5°.

Exclusion Statement

- ** An understanding of the derivation and depiction of hybrid orbitals will not be assessed on the AP exam.**
- ** Hybridization involving d orbitals will not be assessed on the AP exam. 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. **

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 greater energy than pi bonds. The presence of a pi bond also prevents the rotation of the bond and leads to structural isomers.

Exclusion Statement

** Molecular orbital theory is recommended as a way to provide deeper insight into bonding. However, the AP exam will neither explicitly assess molecular orbital diagrams, filling of molecular orbitals, nor the distinction between bonding, nonbonding, and antibonding orbitals. **

Unit 03 Intermolecular Forces and Properties

Topic 3.1 Intermolecular Forces

Enduring Understanding

Explain the relationship between the chemical structures of molecules and the relative strength of their intermolecular forces when: (a) the molecules are of the same chemical species and (b) the molecules are of two different chemical species

Essential Knowledge

London dispersion forces are the result of the Coulombic interactions between temporary, fluctuating dipoles. London dispersion forces are often the strongest net intermolecular force between large molecules.

- (a) Dispersion forces increase with increasing contact area between molecules and with increasing polarizability of the molecules.
- (b) The polarizability of a molecule increases with an increasing number of electrons in the molecule and the size of the electron cloud. It is enhanced by the presence of pi bonding.
- (c) The term "London dispersion forces" should not be used synonymously with the term "van der Waal's forces".

The dipole moment of a polar molecule leads to additional interactions with other chemical species.

- (a) Dipole-induced dipole interactions are present between a polar molecule and nonpolar molecule. These forces are always attractive. 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) Dipole-dipole interactions are present between polar molecules. The interaction strength depends on the magnitudes of the dipoles and their relative orientation. Interactions between polar molecules are typically greater than those between nonpolar molecules of comparable size because these interactions act in addition to London dispersion forces.
- (c) Ion-dipole forces of attraction are present between ions and polar molecules. These tend to be stronger than dipole-dipole forces.

The relative strength and orientation dependence of dipole-dipole and ion-dipole forces can be understood qualitatively by considering the sign of the partial charges responsible for the molecular dipole moment, and how these partial charges interact with an ion or with an adjacent dipole.

Hydrogen bonding is a strong type of intermolecular interaction that exists when the hydrogen atoms covalently bonded to the highly electronegative atoms (N, O, and F) are 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.

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

Topic 3.2 Properties of Solids

Enduring Understanding

Explain the relationship among the macroscopic properties of a substance, the particulate-level structure of the substance, and the interaction between these particles.

Essential Knowledge

Many properties of liquids and solids are determined by the strengths and types of intermolecular forces present. Because intermolecular interactions are broken when a substance vaporizes, the vapor pressure and boiling point are directly related to the strength of those interactions. Melting points also tend to correlate with interaction strength, but because the interactions are only rearranged, in melting, the relations can be more subtle.

Particulate-level representations, showing multiple interacting chemical species, are a useful means to communicate or understand how intermolecular interactions help to establish macroscopic properties.

Due to strong interactions between ions, ionic solids tend to have low vapor pressures, high melting points, and high boiling points. They tend to be brittle due to the repulsion of like charges caused when one layer slides across another layer. They conduct electricity only when the ions are mobile, as when the ionic solid is melted or dissolved in water or another solvent.

In covalent network solids, the atoms are covalently bonded together in a three-dimensional network (e.g. diamond) or layers of two-dimensional networks (e.g. graphite). These are only formed from nonmetals: elemental (e.g diamond, graphite) or binary compounds of two nonmetals (e.g. silicon dioxide and silicon carbide). Due to the strong covalent interactions, covalent solids have high melting points. Three-dimensional network solids are also rigid and hard, because the covalent bond angles are fixed. However, graphite is soft because adjacent layers can slide past each other relatively easily.

Molecular solids are composed of distinct, individual units of covalently-bonded molecules attracted to each other through relatively weak intermolecular forces. Molecular solids generally have a low melting point because of the relatively weak intermolecular forces present between the molecules. They do not conduct electricity because their valence electrons are tightly held within the covalent bonds and the lone pairs of each constituent molecule. Molecular solids are sometimes composed of very large molecules or polymers.

Metallic solids are good conductors of electricity and heat, due to the presence of free valence electrons. They also tend to be malleable and ductile, due to the ease with which the metal cores can rearrange their structure. In an interstitial alloy, interstitial atoms tend to make the lattice more rigid, decreasing malleability and ductility. Alloys typically retain a sea of mobile electrons and so remain conducting.

In large biomolecules and polymers, noncovalent interactions may occur between different molecules or different regions of the same biomolecule. The functionality and properties of such molecules depend strongly on the shape of the molecule, which is largely dictated by noncovalent interactions.

Topic 3.3 Solids, Liquids, and Gases

Enduring Understanding

Represent the differences between solid, liquid and gas phases using a particulate-level model

Essential Knowledge

Solids can be crystalline, where the particles are arranged in a regular three-dimensional 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 overall translation with respect to each other. The structure of the solid is influenced by interparticle interactions and the ability of the particles to pack together.

The constituent particles in liquids are in close contact with each other, and they are continually moving and colliding. The arrangement and movement of particles are influenced by the nature and strength of the forces (e.g. polarity, hydrogen bonding, and temperature) between the particles.

The solid and liquid phases for a particular substance typically have similar molar volume because, in both phases, the constituent particles are in close contact at all times.

In the gas phase, the particles are in constant motion. Their frequencies of collision and the average spacing between them are dependent on temperature, pressure, and volume. Because of this constant motion, and minimal effects of forces between particles, a gas have neither a definite volume nor a definite shape.

Exclusion Statement

** Understanding/interpreting phase diagrams will not be assessed on the AP exam. **

Topic 3.4 Ideal Gas Law

Enduring Understanding

Explain the relationship between the macroscopic properties of a sample of gas or mixture of gases using the ideal gas law.

Essential Knowledge

The macroscopic properties of ideal gases are related through the ideal gas law: EQN: PV = nRT.

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

EQN:
$$P_{A} = P_{total} \times X_{A}$$
, where $X_{A} = \text{moles A/total moles}$ EQN: $P_{total} = P_{A} + P_{B} + P_{C} + \dots$

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

Topic 3.5 Kinetic Molecular Theory Enduring Understanding

Explain the relationship between the motion of particles and the macroscopic properties of gases with: (a) the kinetic molecular theory (KMT), (b) a particulate model, (c) a graphical representation

Essential Knowledge

The kinetic molecular theory (KMT) relates the macroscopic properties of gases to motions of the particles in the gas. The Maxwell-Boltzmann distribution describes the distribution of the kinetic energies of particles at a given temperature.

All the particles in a sample of matter are in continuous, random motion. The average kinetic energy of a particle is related to its average velocity by the equation: $EQN: KE = \frac{1}{2} mv^2$

The Kelvin temperature of a sample of matter is proportional to the average kinetic energy of the particles in the sample.

The Maxwell-Boltzmann distribution provides a graphical representation of the energies/velocities of particles at a given temperature.

Topic 3.6 Deviation from Ideal Gas Law

Enduring Understanding

Explain the relationship among non-ideal behaviors of gases, interparticle forces, and/or volumes

Essential Knowledge

The ideal gas law does not explain the actual behavior of real gases. Deviations from the ideal gas law may result from interparticle attractions among gas molecules, particularly at conditions that are close to those resulting in condensation. Deviations may also arise from particle volumes, particularly at extremely high pressures.

Topic 3.7 Solutions and Mixtures

Enduring Understanding

Calculate the number of solute particles, volume, or molarity of solutions

Essential Knowledge

Solutions, also sometimes called homogenous mixtures, can be solids, liquids, or gases. In a solution, the macroscopic properties do not vary throughout the sample. In a heterogeneous mixture, the macroscopic properties depend on the location in the mixture.

Solution composition can be expressed in a variety of ways; molarity is the most common method used in the laboratory:

EQN: $M = n_{solute}/L_{solution}$

Topic 3.8 Representations of Solutions

Enduring Understanding

Using particulate models for mixtures: (a) Represent interactions between components; (b) Represent concentrations of components

Essential Knowledge

Particulate representations of solutions communicate the structure and the properties of solutions, by illustration of the relative concentrations of the components in the solution and drawings that show interactions among the components.

Exclusion Statement

- ** Colligative properties will not be assessed on the AP exam. **
- ** Calculations of molality, percent by mass, and percent by volume will not be assessed on the AP exam. **

Topic 3.9 Separation of Solutions and Mixtures Chromatography

Enduring Understanding

Explain the relationship between the solubility of ionic and molecular compounds in aqueous and nonaqueous solvents, and the intermolecular interactions between particles.

Essential Knowledge

The components of a liquid solution cannot be separated by filtration. They can, however, be separated using processes that take advantage of difference in the intermolecular interactions of the components.

- (a) Chromatography (paper, thin-layer, and column) separates chemical species by taking advantage of the differential strength of intermolecular interactions between and among the components of the solution (the mobile phase) and with the surface components of the stationary phase.
- (b) Distillation separates chemical species by taking advantage of the differential strength of intermolecular interactions between and among components and the effects these interactions have on the vapor pressure of the components in the mixture.

Topic 3.10 Solubility

Enduring Understanding

Explain the relationship between the solubility of ionic and molecular compounds in aqueous and nonaqueous solvents, and the intermolecular interactions between particles.

Essential Knowledge

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

Topic 3.11 Spectroscopy and the Electromagnetic Spectrum

Enduring Understanding

Explain the relationship between a region of the electromagnetic spectrum and the types of molecular or electronic transitions associated with that region.

Essential Knowledge

Differences in absorption or emission of photons in different spectral regions are related to the different types of molecular motion or electronic transition:

- (a) Microwave radiation is associated with transitions in molecular rotational levels.
- (b) Infrared radiation is associated with transitions in molecular vibrational levels.
- (c) Ultraviolet/visible radiation is associated with transitions in electronic energy levels.

Topic 3.12 Photoelectric Effect

Enduring Understanding

Explain the properties of an absorbed or emitted photon in relationship to an electronic transition in an atom or molecule.

Essential Knowledge

When a photon is absorbed (or emitted) by an atom or molecule, the energy of the species is increased (or decreased) by an amount equal to the energy of the photon.

The wavelength of the electromagnetic wave is related to its frequency and the speed of light by the equation: EQN: $c = \lambda v$. The energy of a photon is related to the frequency of the electromagnetic wave through Planck's equation (E = hv).

Topic 3.13 Beer-Lambert Law

Enduring Understanding

Explain the amount of light absorbed by a solution of molecules or ions in relationship to the concentration, path length, and molar absorptivity

Essential Knowledge

The Beer-Lambert law relates the absorption of light by a solution to three variables according to the equation: EQN: $A = \mathcal{E}bc$. The molar absorptivity \mathcal{E} describes how intensely a sample of molecules or ions absorbs light of a specific wavelength. The path length b and concentration c are proportional to the number of absorbing species.

In most experiments, the path length and wavelength of light are held constant. In such cases, the absorbance is proportional only to the concentration of absorbing molecules or ions.



Unit 04 Chemical Reactions

Topic 4.1 Introduction for Reactions

Enduring Understanding

Identify evidence of chemical and physical changes in matter

Essential Knowledge

A physical change occurs when a substance undergoes a change in properties but not a change in composition. Changes in the phase of a substance (solid, liquid, gas) or formation/separation of mixtures of substances are common physical changes.

A chemical change occurs when substances are transformed into new substances, typically with different compositions. Production of heat or light, formation of a gas, formation of a precipitate, and/or color change provide possible evidence that a chemical change has occurred.

Topic 4.2 Net Ionic Equations

Enduring Understanding

Represent changes in matter with a balanced chemical or net ionic equation: (a) for physical changes; (b) for given information about the identity of the reactants and/or product; (c) for ions in a given chemical reaction

Essential Knowledge

All physical and chemical processes can be represented symbolically by balanced equations.

Chemical equations represent chemical changes. These changes are the result of a rearrangement of atoms into new combinations; thus, any representation of a chemical change must contain equal numbers of atoms of every element before and after the change occurred. Equations thus demonstrate that mass is conserved in chemical reactions.

Balanced molecular, complete ionic, and net ionic equations are differing symbolic forms used to represent a chemical reaction. The form used to represent the reaction depends on the context in which it is being used.

Topic 4.3 Representations of Reactions

Enduring Understanding

Represent a given chemical or physical process with a consistent particulate model

Essential Knowledge

Balanced chemical equations in their various forms can be translated into symbolic particulate representations.

Topic 4.4 Physical and Chemical Changes

Enduring Understanding

Explain the relationship between macroscopic characteristics and bond interactions for: (a) chemical processes and (b) physical processes

Essential Knowledge

Processes that involve the breaking and/or formation of chemical bonds are typically classified as chemical processes. Processes that only involve changes in intermolecular interactions, such as phase changes, are typically classified as physical processes.

Sometimes physical processes involve the breaking of chemical bonds. For example, plausible arguments could be made for the dissolution of a salt in water, as either a physical or chemical process, involves breaking of ionic bonds, and the formation of ion-dipole interactions between ions and solvent.

Topic 4.5 Stoichiometry

Enduring Understanding

Explain changes in the amounts of reactants and products based on the balanced chemical equation for a chemical processEssential Knowledge

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

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 involving the mole concept.

Stoichiometric calculations can be combined with the ideal gas law and calculations involving molarity to quantitatively study gases and solutions.

Topic 4.6 Introduction to Titration Enduring Understanding

Identify the equivalence point in a titration based on the amounts of the titrant and analyte, assuming the titration reaction goes to completion.

Essential Knowledge

Titrations may be used to determine the concentration of an analyte in solution. The titrant has a known concentration of a species that react specifically and quantitatively with the analyte. The equivalence point 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 endpoint of the titration.

Topic 4.7 Types of Chemical Reactions Enduring Understanding

Identify a reaction as acid-base, oxidation-reduction, or precipitation

Essential Knowledge

Acid-base reactions involve transfer of one or more protons between chemical species.

Oxidation-reduction reactions involve transfer of one or more electrons between chemical species, as indicated by changes in oxidation numbers of the involved species. Combustion is an important subclass of oxidation-reduction reactions, in which a species reacts with oxygen gas. In the case of hydrocarbons, carbon dioxide and water are products of complete combustion.

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

Exclusion Statement

** The meaning of the terms "reducing agent" and "oxidizing agent" will not be assessed on the AP exam. **

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

Precipitation reactions frequently involve mixing ions in aqueous solution to produce an insoluble or sparingly soluble ionic compound. All sodium, potassium, ammonium, and nitrate salts are soluble in water.

Exclusion Statement

** Rote memorization of "solubility rules" other than those implied will not be assessed on the exam. **

Topic 4.8 Introduction to Acid-Base Reactions

Enduring Understanding

Identify species as Bronsted-Lowry acids, bases, and/or conjugate acid/base pairs, based on proton-transfer involving those species.

Essential Knowledge

By definition, a Bronsted-Lowry acid is a proton donor and a Bronsted-Lowry base is a proton acceptor.

Only in aqueous solutions, water plays an important role in many acid-base reactions, as its molecular structure allows it to accept protons from and donate protons to dissolved species.

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

Exclusion Statement

** Lewis acid-base concepts will not be assessed on the AP exam. **

Topic 4.9 Oxidation-Reduction (Redox) Reactions Enduring Understanding

Represent a balanced redox reaction equation using half-reactions

Essential Knowledge Balanced chemical equations for redox reactions can be constructed from half-reactions.



Second Semester Unit 05 Kinetics

Topic 5.1 Reaction Rates

Enduring Understanding

Explain the relationship between the rate of a chemical reaction and experimental parameters

Essential Knowledge

The kinetics of a chemical reaction is defined as the rate at which an amount of reactants is converted to products per unit of time.

The rates of change of reactant and product concentration are determined by the stoichiometry in the balanced chemical equation.

The rate of a reaction is influenced by reactant concentrations, temperature, surface area, catalysts, and other environmental factors.

Topic 5.2 Introduction to Rate Laws

Enduring Understanding

Represent experimental data with a consistent rate law expression

Essential Knowledge

Experimental methods can be used to monitor the amounts of reactants and/or products of a reaction and to determine the rate of the reaction.

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.

The proportionality constant in the rate law is called the rate constant. The value of this constant is temperature dependent and the units reflect the overall reaction order.

Comparing initial rates of a reaction is a method to determine the order with respect to each reactant.

Topic 5.3 Concentration Changes over Time

Enduring Understanding

Identify the rate law expression of a chemical reaction using data that show how the concentration of reaction species change over time

Essential Knowledge

The order of a reaction can be inferred from a graph of concentration of reactant versus time.

If a reaction is first order with respect to a reactant being monitored, a plot of the natural log (ln) of the reactant concentration as a function of time will be linear.

If a reaction is second order with respect to a reactant being monitored, a plot of the reciprocal of the concentration of that reactant versus time will be linear.

The slopes of the concentration versus time data for zeroth, first, and second order reactions can be used to determine the rate constant for the reaction:

Zeroth order:

$$EQN: [A]_t - [A]_0 = -kt$$

First order:

EQN:
$$\ln[A]_t - \ln[A]_0 = -kt$$

Second order:

EQN:
$$1/[A]_{t} - 1/[A]_{0} = kt$$

Half-life is a critical parameter for first order reactions because the half-life is constant and related to the rate constant by the equation:

EQN: $t_{1/2} = 0.693/k$.

Radioactive decay processes provide an important illustration of first order kinetics.

Topic 5.4 Elementary Reactions

Enduring Understanding

Represent an elementary reaction as a rate law expression using stoichiometry

Essential Knowledge

The rate law of an elementary reaction can be inferred from the stoichiometry of the molecules participating in a collision.

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

Topic 5.5 Collision Model

Enduring Understanding

Explain the relationship between the rate of an elementary reaction and the frequency, energy, and orientation of molecular collisions

Essential Knowledge

For an elementary reaction to successfully produce products, reactants must successfully collide to initiate bond-breaking and bond-making events.

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

The Maxwell-Boltzmann distribution curve 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.

Topic 5.6 Reaction Energy Profile

Enduring Understanding

Represent the activation energy and overall energy change in an elementary reaction using a reaction energy profile Essential Knowledge

Elementary reactions typically involve the breaking of some bonds and the forming of new ones.

The reaction coordinate is the axis along which the complex set of motions involved in rearranging reactants to form products can be plotted.

The energy profile gives the energy along the reaction coordinate, which typically proceeds from reactants, through a transition state, to products. The energy difference between the reactants and the transition state is the activation energy for the forward reaction.

The Arrhenius equation relates the temperature dependence on the rate of an elementary reaction to the activation energy needed by molecular collisions to reach the transition state.

** Calculations involving the Arrhenius equation will not be assessed on the AP exam. **

Topic 5.7 Introduction to Reaction Mechanisms

Enduring Understanding

Identify the components of a reaction mechanism

Essential Knowledge

A reaction mechanism consists of a series of elementary reactions, or steps, that occur in sequence.

The elementary steps when combined should align with the overall balanced equation of a chemical reaction.

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

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

Exclusion Statement

** Collection of data pertaining to detection of a reaction intermediate will not be assessed on the AP exam. **

Topic 5.8 Reaction Mechanism and Rate Law

Enduring Understanding

Identify the rate law for a reaction from a mechanism in which the first step is rate limiting

Essential Knowledge

For reaction mechanisms in which each elementary step is irreversible, or in which the first step is rate limiting, the rate law of the reaction is set by the molecularity of the slowest elementary step (i.e. the rate-limiting step).

Topic 5.9 Steady-State Approximation

Enduring Understanding

Identify the rate law for a reaction from a mechanism in which the first step is not rate limiting.

Essential Knowledge

If the first elementary reaction is not rate limiting, approximations (such as steady state) must be made to determine a rate law

Topic 5.10 Multiple Step Reaction Energy Profile

Enduring Understanding

Represent the activation energy and overall energy change in a multistep reaction with a reaction energy profile

Essential Knowledge

Knowledge of the energetics of each elementary reaction in a mechanism allows for the construction of an energy profile for a multistep reaction.

Unit 06 Thermodynamics

Topic 6.1 Endothermic and Exothermic Processes

Enduring Understanding

Explain the relationship between experimental observations and energy changes associated with a chemical or physical transformation.

Essential Knowledge

Temperature changes in a system indicate energy changes.

Energy changes in a system can be described as endothermic and exothermic processes such as the heating or cooling of a substance, phase changes, or chemical transformations.

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

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.

Topic 6.2 Energy Diagrams

Enduring Understanding

Represent a chemical or physical transformation with an energy diagram

Essential Knowledge

A physical or chemical process can be described with an energy diagram that shows the endothermic or exothermic nature of that process.

Topic 6.3 Heat Transfer and Thermal Equilibrium

Enduring Understanding

Explain the relationship between the transfer of thermal energy and molecular collisions

Essential Knowledge

The particles in a warmer body have a greater kinetic energy than those in a cooler body.

Collisions between particles in thermal contact can result in the transfer of energy. This process is called "heat transfer", "heat exchange", or "transfer of energy as heat".

Eventually, thermal equilibrium is reached as the particles continue to collide. At thermal equilibrium, the average kinetic energy of both bodies is the same, and hence, their temperatures are the same.

Topic 6.4 Heat Capacity and Calorimetry Enduring Understanding

Calculate the heat q absorbed or released by a system undergoing heating/cooling based on the amount of the substance, the heat capacity, and the change in temperature.

Essential Knowledge

The heating of a cool body by a warmer body is an important form of energy transfer between two systems. The amount of heat transferred between two bodies may be quantified by the heat transfer equation: EQN: $q = mc\Delta T$. Calorimetry experiments are used to measure the transfer of heat.

The first law of thermodynamics states that energy is conserved in chemical and physical processes.

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.

Heating a system increases the energy of the system, while cooling a system decreases the energy of the system.

The specific heat capacity of a substance and the molar heat capacity are both used in energy calculations,

Chemical systems change their energy through three main processes: heating/cooling, phase transitions, and chemical reactions.

Topic 6.5 Energy of Phase Changes

Enduring Understanding

Explain changes in the heat q absorbed or released by a system undergoing a phase transition based on the amount of the substance in moles and the molar enthalpy of the phase transition

Essential Knowledge

Energy must be transferred to a system to cause a substance to melt (or boil). The energy of the system therefore increases as the system undergoes a solid-to-liquid (or liquid-to-gas) transition. Likewise, a system releases energy when it freezes (or condenses). The energy of the system decreases as the system undergoes a liquid-to-solid (or gas-to-liquid) phase transition. The temperature of a pure substance remains constant during a phase change.

The energy absorbed during a phase change is equal to the energy released during a complementary phase change in the opposite direction. For example, the molar heat of condensation of a substance is equal to the negative of its molar heat of vaporization.

Topic 6.6 Introduction to Enthalpy of Reaction

Enduring Understanding

Calculate the heat q absorbed or released by a system undergoing a chemical reaction in relationship to the amount of the reacting substance in moles and the molar enthalpy of reaction

Essential Knowledge

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

Exclusion Statement

** The technical distinction between enthalpy and internal energy will not be assessed on the exam. **

Topic 6.7 Bond Enthalpies

Enduring Understanding

Calculate the enthalpy change of a reaction based on the average bond energies of bonds broken and formed in the reaction Essential Knowledge

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

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

Topic 6.8 Enthalpy of Formation Enduring Understanding

Calculate the enthalpy change for a chemical or physical process based on the standard enthalpies of formation.

Essential Knowledge

Tables of standard enthalpies of formation can be used to calculate the standard enthalpies of reactions:

EQN: $\Delta H^{\circ}_{\text{reaction}} = \Sigma \Delta H_{f}^{\circ}_{\text{products}} - \Sigma \Delta H_{f}^{\circ}_{\text{reactants}}$

Topic 6.9 Hess's Law

Enduring Understanding

Represent a chemical or physical process in a series of steps

Essential Knowledge

Although the concept of "state function" is not required for the course, two principles of Hess's law should be understood. First, when a reaction is reversed, the enthalpy change stays constant in magnitude, but becomes reversed in mathematical sign. Second, when two (or more) reactions are added to obtain an overall reaction, the individual enthalpy changes of each reaction are added to obtain the net enthalpy of the overall reaction.

Enduring Understanding

Explain the relationship between the enthalpy of a chemical or physical process and the sum of the enthalpies of the individual steps

Essential Knowledge

When the products of a reaction are at a different temperature than the surroundings, they exchange energy with the surroundings to reach thermal equilibrium. Thermal energy is transferred to the surroundings from the products of an exothermic reaction. Thermal energy is transferred from the surroundings to the products of an endothermic reaction.

Unit 07 Equilibrium

Topic 7.1 Introduction to Equilibrium Enduring Understanding

Explain the relationship between the occurrence of a reversible chemical or physical process, and the establishment of equilibrium, to experimental observation

Essential Knowledge

Many observable processes are reversible. Examples include evaporation and condensation of water, absorption and desorption of a gas, or dissolution and precipitation of a salt. Some important reversible chemical processes include the transfer of protons in acid-base reactions and the transfer of electrons in redox reactions.

When equilibrium is reached, no observable changes occur in the system. Reactants and products are simultaneously present, and the concentrations or partial pressures of all species remain constant.

The equilibrium state is dynamic. The forward and reverse processes continue to occur in equal rates, resulting in no net observable change.

Graphs of concentration, partial pressure, or rate of reaction versus time for simple chemical reactions can be used to understand the establishment of chemical equilibrium.

Topic 7.2 Direction of Reversible Reactions

Enduring Understanding

Explain the relationship between the direction in which a reversible reaction proceeds and the relative rates of the forward and reverse reactions

Essential Knowledge

If the rate of the forward reaction is greater than that of the reverse reaction, then there is a net conversion of reactants to products. If the rate of the reverse reaction is greater than that of the forward reaction, then there is a net conversion of products to reactants. An equilibrium state is reached when these rates are equal.

Topic 7.3 Reaction Quotient and Equilibrium Constant Enduring Understanding

Represent the reaction quotient Q_c or Q_p for a reversible reaction, and the corresponding equilibrium expressions $K_c = Q_c$ or $K_p = Q_p$

Essential Knowledge

The reaction quotient Q_c describes the relative concentration of reaction species at any time. For gas phase reactions, the reaction quotient may instead be written in terms of pressures as Q_p . The reaction quotient tends toward the equilibrium constant such that at equilibrium $K_c = Q_c$ and $K_p = Q_p$. As examples.

EQN: $K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$ and that for K_p , Q_p is

For the reaction aA + bB \leftrightarrow cC + dD, the equilibrium expression for $K_c,\,Q_c$ is

EQN:
$$K_p = \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b}$$

Exclusion Statement

- ** Conversion between K_c and K_p will not be assessed on the AP exam. **
- ** Equilibrium calculations on systems where a dissolved species is in equilibrium with that species in gas phase will not be assessed on the AP exam. **

The reaction quotient does not include substances whose concentrations (or partial pressures) are independent of the amount, such as for solids and pure liquids.

Topic 7.4 Calculating the Equilibrium Constant

Enduring Understanding

Calculate K_c or K_p based on experimental observations of concentrations or pressures at equilibrium

Essential Knowledge

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

Topic 7.5 Magnitude of the Equilibrium Constant

Enduring Understanding

Explain the relationship between very large or very small values of K and the relative concentrations of chemical species at equilibrium

Essential Knowledge

Some equilibrium reactions have very large K values and proceed essentially to completion. Others have very small K values and barely proceed at all.

Topic 7.6 Properties of the Equilibrium Constant

Enduring Understanding

Represent a multistep process with an overall equilibrium expression, using the constituent K expressions for each individual reaction

Essential Knowledge

When a reaction is reversed, K is inverted.

When the stoichiometric coefficients of a reaction are multiplied by a factor c, K is raised to the power c.

When reactions are added together, the K of the resulting overall reaction is the product of the K's for the reactions that were summed.

Since the expressions for K and Q have identical mathematical forms, all valid algebraic manipulations of K also apply to Q.

Topic 7.7 Calculating Equilibrium Concentrations

Enduring Understanding

Identify the concentrations or partial pressures of chemical species at equilibrium based on the initial conditions and the equilibrium constant

Essential Knowledge

The concentrations or partial pressures of species at equilibrium can be predicted given the balanced reaction, initial conditions, and the appropriate K.

Topic 7.8 Representations of Equilibrium

Enduring Understanding

Represent a system undergoing a reversible reaction with a particulate model

Essential Knowledge

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

Topic 7.9 Introduction to Le Chatelier's Principle

Enduring Understanding

Identify the response of a system at equilibrium to an external stress, using Le Chatelier's principle

Essential Knowledge

Le Chatelier's principle can be used to predict the response of a system to stresses such as addition or removal of a chemical species, change in temperature, change in volume/pressure of a gas-phase system, or dilution of a reaction system.

Le Chatelier's principle can be used to predict the effect that a stress will have on experimentally measurable properties such as pH, temperature, and color of a solution.

Topic 7.10 Reaction Quotient and Le Chatelier's Principle

Enduring Understanding

Explain the relationships between Q, K, and the direction in which a reversible reaction will proceed to reach equilibrium Essential Knowledge

A disturbance to a system at equilibrium causes Q to differ from K, thereby taking the system out of equilibrium. The system responds by bringing Q back into agreement with K, thereby establishing a new equilibrium state.

Some stresses, such as changes in concentration, cause a change in Q only. A change in temperature causes a change in K. In either case, the concentration or partial pressures of species redistribute to bring Q and K back into equality.

Topic 7.11 Introduction to Solubility Equilibria

Enduring Understanding

Calculate the solubility of a salt based on the value of K_{sp} for the salt

Essential Knowledge

The dissolution of a salt is a reversible process whose extent can be described by K_{sp} , the solubility-product constant.

The solubility of a substance can be calculated from the K_{sp} for the dissolution process. This relationship can also be used to predict the relative solubility of different substances.

The solubility rules can be quantitatively related to K_{sp} , in which K_{sp} values > 1 correspond to soluble salts.

Topic 7.12 Common-Ion Effect

Enduring Understanding

Identify the solubility of a salt, and/or the value of K_{sp} for the salt, based on the concentration of a common ion already present in solution

Essential Knowledge

The solubility of a salt is reduced when it is dissolved into a solution that already contains one of the ions present in the salt. The impact of this "common-ion effect" on solubility can be understood qualitatively using Le Chatelier's principle or calculated from the K_{sp} for the dissolution process.

Topic 7.13 pH and Solubility

Enduring Understanding

Identify the qualitative effect of changes in pH on the solubility of a salt

Essential Knowledge

The solubility of a salt is pH sensitive when one of the constituent ions is a weak acid or base. These effects can be understood qualitatively using Le Chatelier's principle.

Exclusion Statement

** Computations of solubility as a function of pH will not be assessed on the AP exam. **

Topic 7.14 Free Energy of Dissolution

Enduring Understanding

Explain the relationship between the solubility of a salt and changes in the enthalpy and entropy that occur in the dissolution process

Essential Knowledge

The free energy change (ΔG^o) for dissolution of a substance reflects a number of factors: the breaking of the intermolecular interactions that hold the solid together, the reorganization of the solvent around the dissolved species, and the interaction of the dissolved species with the solvent. It is possible to estimate the sign and relative magnitude of the enthalpic and entropic contributions to each of these factors. However, making predictions for the total change in the free energy of dissolution can be challenging due to the cancellations among the free energies associated with the three factors cited.

Unit 08 Acids and Bases

Topic 8.1 Introduction to Acids and Bases

Enduring Understanding

Calculate the value of pH and pOH, based on K_w, and the concentration of all species present in a neutral solution of water Essential Knowledge

The concentrations of hydronium ion and hydroxide ion is often reported as pH and pOH, respectively:

EQN:
$$pH = -log[H_3O^+]$$

EQN: $pOH = -log[OH^-]$

The term "hydrogen ion" and "hydronium ion" and the symbols $H^+_{(aq)}$ and $H_3O^+_{(aq)}$ are often used interchangeably for the aqueous ion of hydrogen. Hydronium ion and $H_3O^+_{(aq)}$ are preferred, but $H^+_{(aq)}$ is also accepted on the AP exam.

Water autoionizes with an equilibrium constant K_w:

EQN:
$$K_{...} = [H_2O^+][OH^-] = 1.0 \times 10^{-14} \text{ at } 25^{\circ}\text{C}$$

In pure water, pH = pOH is called a neutral solution. At 25°C, p $K_w = 14.0$ and thus pH = pOH = 7.

EQN:
$$pK_{...} = 14 = pH + pOH$$
at 25°C

The value of K_w is temperature dependent, so the pH of pure, neutral water will deviate from 7.0 at temperatures other than 25°C.

Topic 8.2 pH and pOH of Strong Acids and Bases

Enduring Understanding

Calculate pH and pOH based on concentrations of all species in a solution of a strong acid or a strong base

Essential Knowledge

Molecules of a strong acid (e.g. HCl, HBr, HI, HClO₄, H_2SO_4 , and HNO₃) will completely ionize in aqueous solution to produce hydronium ions. 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.

When dissolved in solution, strong bases (e.g. group I and II hydroxides) completely dissociate to produce hydroxide ions. As such, the concentration of OH⁻ in a strong base solution is equal to the initial concentration of the strong base, and thus the pOH (and pH) of the strong base solution is easily calculated.

Topic 8.3 Weak Acid and Base Equilibria

Enduring Understanding

Explain the relationship among pH, pOH, and concentrations of all species in a solution of a monoprotic weak acid or weak base

Essential Knowledge

Weak acids react with water to produce hydronium ions. However, molecules of a weak acid will only partially ionize this way. In other words, only a small percentage of the molecules of a weak acid are ionized in a solution. Thus, the concentration of H_3O^+ is much less than the initial concentration of the molecular acid, and the vast majority of the acid molecules remain un-ionized.

A solution of a weak acid 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 :

EQN:
$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

EQN:
$$pK_a = -\log K_a$$

Weak bases react with water to produce hydroxide ions in solution. However, ordinarily just a small percentage of the molecules of a weak base in solution will ionize in this way. Thus, the concentration of OH⁻ in the solution does not equal the initial concentration of the base, and the vast majority of the base molecules remain un-ionized.

A solution of a weak base involves 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 :

EQN:
$$K_b = \frac{[OH^-][HB^+]}{[B]}$$

$$EQN: pK_b = -\log K_b$$

The percent ionization of a weak acid (or base) can be calculated from its pK_a (pK_b) and the initial concentration of the acid (base).

Topic 8.4 Acid-Base Reactions and Buffers

Enduring Understanding

Explain the relationship among the concentrations of major species in a mixture of weak and strong acids and bases Essential Knowledge

When a strong acid and a strong base are mixed, they react quantitatively in a reaction represented by the equation:

$$H^{+}_{(aq)} + OH^{-}_{(aq)} \rightarrow H_{2}O_{(1)}$$
.

The pH of the resulting solution may be determined from the concentration of excess reagent.

When a weak acid and a strong base are mixed, they react quantitatively in a reaction represented by the equation:

$$HA_{(aq)} + OH^{-}_{(aq)} \leftrightarrow A^{-}_{(aq)} + H_2O_{(l)}$$

If the weak acid is in excess, then a buffer solution is formed, and the pH can be determined from the Henderson-Hasselbalch (H-H equation). If the strong base is in excess, then the pH can be determined from the moles of excess hydroxide ion and the total volume of solution. If they are equimolar, then the (slightly basic) pH can be determined from the equilibrium represented in the equation:

$$A^{-}_{(aq)} + H_2O_{(l)} \leftrightarrow HA_{(aq)} + OH^{-}_{(aq)}$$
.

When a weak base and a strong acid are mixed, they will react quantitatively in a reaction represent by the equation:

$$B_{(aq)} + H_3O^+_{(aq)} \leftrightarrow HB^+_{(aq)} + H_2O_{(l)}$$

If the weak base is in excess, then a buffer solution is formed, and the pH can be determined from the H-H equation. If the strong acid is in excess, then the pH can be determined from the moles of excess hydronium ion and the total volume of solution. If they are equimolar, then the (slightly acidic) pH can be determined from the equilibrium represented in the equation:

$$HB^+_{(aq)} + H_2O_{(l)} \leftrightarrow B_{(aq)} + H_3O^+_{(aq)}$$
.

When a weak acid and a weak base are mixed, they will react in an equilibrium state whose reaction may be represented by the equation:

$$HA_{(aq)} + B_{(aq)} \leftrightarrow A^{-}_{(aq)} + HB^{+}_{(aq)}$$
.

Topic 8.5 Acid-Base Titrations

Enduring Understanding

Explain results from the titration of a mono- or polyprotic acid or base solution, in relation to the properties of the solution and its components

Essential Knowledge

An acid-base reaction can be carried out under controlled conditions in a titration. A titration curve, plotting pH against the volume of titrant added, is useful for summarizing results from a titration.

At the equivalence point, the number of moles of titrant added is equal to the number of moles of analyte originally present. This relationship can be used to obtain the concentration of the analyte. This is the case for titrations of strong acids/bases and weak acids/bases.

For titrations of weak acids/bases, it is useful to consider the point halfway to the equivalence point, that is, the half-equivalence point. At this point, there are equal concentrations of each species in the conjugate acid-base pair, for example, for a weak acid $[HA] = [A^-]$. Because $pH = pK_a$ when the conjugate acid and base have equal concentrations, the pK_a can be determined from the pH at the half-equivalence point in a titration.

For polyprotic acids, titration curves can be used to determine the number of acidic protons. In doing so, the major species present at any point along the curve can be identified, along with the pK_a associated with each proton in a polyprotic acid.

Exclusion Statement

** Computation of the concentration of each species present in the titration curve for polyprotic acids will not be assessed on the AP exam. **

Topic 8.6 Molecular Structure of Acids and Bases

Enduring Understanding

Explain the relationship between the strength of an acid or base and the structure of the molecule or ion

Essential Knowledge

The protons in a molecule that will participate in acid-base reactions, and the relative strength of these protons, can be inferred from the molecular structure.

- (a) Strong acids (such as HCl, HBr, HI, HClO₄, H₂SO₄, and HNO₃) have very weak conjugate bases that are stabilized by electronegativity, inductive effects, resonance, or some combination thereof.
- (b) Carboxylic acids are one common class of weak acid.
- (c) Strong bases (such as group I and II hydroxides) have very weak conjugate acids.
- (d) Common weak bases include nitrogenous bases such as ammonia as well as carboxylate ions.
- (e) Electronegative elements tend to stabilize the conjugate base relative to the conjugate acid, and so increase acid strength.

Topic 8.7 pH and pK_a

Enduring Understanding

Explain the relationship between the predominant form of a weak acid or base in solution at a given pH and the pK_a of the conjugate acid or the pK_b of the conjugate base

Essential Knowledge

The protonation state of an acid or base (i.e. the relative concentrations of HA and A^-) can be predicted by comparing the pH of a solution to the pK_a of the acid in that solution. When solution pH < pK_a, the acid form has a higher concentration than the base form. When solution pH > pK_a, the base form has a higher concentration than the acid form.

Acid-base indicators are substances that exhibit different properties (such as color) in their protonated versus deprotonated state, making that property respond to the pH of a solution.

Topic 8.8 Properties of Buffers

Enduring Understanding

Explain the relationship between the ability of a buffer to stabilize pH and the reactions that occur when an acid or a base is added to a buffered solution

Essential Knowledge

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. These reactions are responsible for the ability of a buffer to stabilize pH.

Topic 8.9 Henderson-Hasselbalch Equation

Enduring Understanding

Identify the pH of a buffer solution based on the identity and concentrations of the conjugate acid-base pair used to create the buffer

Essential Knowledge

The pH of the buffer is related to the pK_a of the acid and the concentration ratio of the conjugate acid-base pair. This relation is a consequence of the equilibrium expression associated with the dissociation of a weak acid, and is described by the Henderson-Hasselbalch equation. Adding small amounts of acid or base to a buffered solution does not significantly change the ratio of [A⁻] / [HA] and thus does not significantly change the solution pH. The change in pH on addition of acid or base to a buffered solution is therefore much less than it would have been in the absence of the buffer:

EQN:
$$pH = pK_a + log \frac{[A^-]}{[HA]}$$

Topic 8.10 Buffer Capacity

Enduring Understanding

Explain the relationship between the buffer capacity of a solution and the relative concentrations of the conjugate acid and conjugate base components of the solution

Essential Knowledge

Increasing the concentration of the buffer components (while keeping the ratio of these concentrations constant) keeps the pH of the buffer the same but increases the capacity of the buffer to neutralize added acid or base.

When a buffer has more conjugate acid than base, it has a greater buffer capacity for addition of added base than acid. When a buffer has more conjugate base than acid, it has a greater buffer capacity for addition of added acid than base.

Unit 09 Applications of Thermodynamics

Topic 9.1 Introduction to Entropy

Enduring Understanding

Identify the sign and relative magnitude of the entropy change associated with chemical or physical processes

Essential Knowledge

Entropy increases when matter becomes more dispersed. For example, the phase change from solid to liquid or from liquid to gas results in a dispersal of matter as the individual particles become freer to move and generally occupy a larger volume. Similarly, 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. For reactions involving gas-phase reactants or products, the entropy generally increases when the total number of moles of gas-phase products is greater than the total number of moles of gas-phase reactants.

Entropy increases when energy is dispersed. According to kinetic molecular theory (KMT), the distribution of kinetic energy among the particles of a gas broadens as the temperature increases. As a result, the entropy of the system increases with an increase in temperature.

Topic 9.2 Absolute Entropy and Entropy Change

Enduring Understanding

Calculate the entropy change for a chemical or physical process based on the absolute entropies of the species involved in the process

Essential Knowledge

The entropy change for a process can be calculated from the absolute entropies of the species involved before and after the process EQN: $\Delta S_{reaction}^{o} = \Sigma S_{products}^{o} - \Sigma S_{reactants}^{o}$

Topic 9.3 Gibbs Free Energy and Thermodynamic Favorability

Enduring Understanding

Explain whether a chemical or physical process is thermodynamically favorable based on an evaluation of ΔG^{o}

Essential Knowledge

The Gibbs free energy change for a chemical or physical process in which all the reactants and products are present in a standard state (as pure substances, as solutions of 1.0 M concentration, or as gases at a pressure of 1.0 atm) is given the symbol ΔG° .

The standard Gibbs free energy change for a chemical or physical process is a measure of thermodynamic favorability. Historically, the term "spontaneous" has been used to describe processes for which $\Delta G^o < 0$. The phrase "thermodynamically favored" is preferred so that common misunderstandings (equating "spontaneous" as "suddenly" or "without cause") can be avoided. When $\Delta G^o < 0$ for the process, it is said to be thermodynamically favored.

The standard Gibbs free energy change for a chemical or physical process may also be determined from the standard Gibbs free energy of formation of the reactants and products.

EQN:
$$\Delta G_{reaction}^{\circ} = \Sigma \Delta G_{f\ products}^{\ \circ} - \Sigma \Delta G_{f\ reactants}^{\ \circ}$$

In some cases, it is necessary to consider both enthalpy and entropy to determine is a process will be thermodynamically favored. The freezing of water and the dissolution of sodium nitrate are examples of such phenomena.

Knowing the values of ΔH^o and ΔS^o for a process at a given temperature allows ΔG^o to be calculated directly:

EQN:
$$\Delta G^{\circ} = \Delta H^{\circ} - T \Delta S^{\circ}$$

In general, the temperature conditions for a process to be thermodynamically favored ($\Delta G^o \le 0$) can be predicted from the signs of ΔH^o and ΔS^o as shown in the table below:

ΔH°	ΔS°	Symbols	$\Delta G^{ m o}$ $<$ 0 , favored at:
< 0	>0	<>	all T
>0	< 0	><	no T
>0	>0	>>	high T
< 0	< 0	<<	low T

In cases where $\Delta H^o < 0$ and $\Delta S^o > 0$, no calculation of ΔG^o is necessary to determine that the process is thermodynamically favored ($\Delta G^o < 0$). In cases where $\Delta H^o > 0$ and $\Delta S^o < 0$, no calculation of ΔG^o is necessary to determine that the process is thermodynamically unfavored ($\Delta G^o > 0$).

Topic 9.4 Thermodynamic and Kinetic Control

Enduring Understanding

Explain, in terms of kinetics, why a thermodynamically favored reaction might not occur at a measurable rate

Essential Knowledge

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

Processes that are thermodynamically favored, but do not proceed at a measurable rate, are 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 thermodynamically favored, and yet does not occur at a measurable rate, it is reasonable to conclude that the process is under kinetic control.

Topic 9.5 Free Energy and Equilibrium

Enduring Understanding

Explain whether a process is thermodynamically favored using the relationships between K, ΔG°, and T

Essential Knowledge

The phrase "thermodynamically favored" ($\Delta G^o < 0$) means that the products are favored at equilibrium (K > 1).

The equilibrium constant is related to the free energy by the equations: EQN: $K = e^{-\Delta G^{\circ}/RT}$ and EQN: $\Delta G^{\circ} = -RT \ln K$.

Connections between K and ΔG^o can be made qualitatively through estimation. When ΔG^o is near zero, the equilibrium constant will be close to 1. When ΔG^o is much larger or much smaller than RT, the value of K deviates strongly from 1.

Processes with $\Delta G^{o} < 0$ favor products (i.e. K > 1) and those with $\Delta G^{o} > 0$ favor reactants (i.e. K < 1).

Topic 9.6 Coupled Reactions

Enduring Understanding

Explain the relationship between external sources of energy or coupled reactions and their ability to drive thermodynamically unfavorable processes

Essential Knowledge

An external source of energy can be used to make a thermodynamically unfavorable process occur. Examples include: (a) electrical energy to drive an electrolytic cell or charge or battery; (b) light to drive the overall conversion of carbon dioxide to glucose in photosynthesis.

A desired product can be formed by coupling a thermodynamically unfavorable reaction that produces that product to a favorable reaction (e.g. the conversion of ATP to ADP in biological systems). In the coupled system, the individual reactions share one or more common intermediates. The sum of the individual reactions produces an overall reaction that achieves the desired outcome and has $\Delta G^o < 0$.

Topic 9.7 Galvanic (Voltaic) and Electrolytic Cells

Enduring Understanding

Explain the relationship between the physical components of an electrochemical cell and the overall operational principles of the cell

Essential Knowledge

Each component of an electrochemical cell (electrodes, solution in the half-cells, salt bridge, voltage/current measuring device) plays a specific role in the overall functioning of the cell. The operational characteristics of the cell (galvanic vs. electrolytic, direction of electron flow, reactions occurring in each half-cell, change in electrode mass, evolution of gas at an electrode, ion flow through the salt bridge) can be described at both the macroscopic and particulate levels.

Galvanic, sometimes called voltaic, cells involve a thermodynamically favored reaction, whereas electrolytic cells involve a thermodynamically unfavored reaction. Visual representations of galvanic and electrolytic cells are tools of analysis to identify where half-reactions occur and in what direction current flows.

For all electrochemical cells, oxidation occurs at the anode and reduction occurs at the cathode.

Exclusion Statement

** Labeling an electrode as positive or negative will not be assessed on the AP exam. **

Topic 9.8 Cell Potential and Free Energy

Enduring Understanding

Explain whether an electrochemical cell is thermodynamically favored, based on its standard cell potential and the constituent half-reactions within the cell

Essential Knowledge

Electrochemistry encompasses the study of redox reactions that occur within electrochemical cells. The reactions are either thermodynamically favored (resulting in a positive voltage) or thermodynamically unfavored (resulting in a negative voltage and requiring applied potential for the reaction to proceed).

The standard cell potential of electrochemical cells can be calculated by identifying the oxidation and reduction half-reactions and their respective standard cell potentials.

 ΔG° (standard Gibbs free energy change) is proportional to the negative of the cell potential for the redox reaction from which it is constructed. Thus, a cell with a positive E° involves a thermodynamically favored reaction, and a cell with a negative E° involves a thermodynamically unfavored reaction: EQN: $\Delta G^{\circ} = -nFE^{\circ}$

Topic 9.9 Cell Potential Under Nonstandard Conditions

Enduring Understanding

Explain the relationship between deviations from standard cell conditions and changes in the cell potential

Essential Knowledge

In a real system under nonstandard conditions, the cell potential will vary depending on the concentrations of the active species. The cell potential is a driving force toward equilibrium; the farther the reaction is from equilibrium, the greater the magnitude of the cell potential.

Equilibrium arguments such as Le Chatelier's principle do not apply to electrochemical sytems, because the systems are not at equilibrium.

The standard cell potential E° 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.

Algorithmic calculations using the Nernst equation are insufficient to demonstrate an understanding of electrochemical cells under nonstandard conditions. However, students should qualitatively understand the effects of concentration on cell potential and use conceptual reasoning, including the qualitative use of the Nernst equation to solve problems: EQN: $E = E^{\circ} - (RT/nF) \ln Q$

Topic 9.10 Electrolysis and Faraday's Law

Enduring Understanding

Calculate the amount of charge flow based on changes in the amounts of reactants and products in an electrochemical cell Essential Knowledge

Faraday's laws can be used to determine the stoichiometry of the redox reaction occurring in an electrochemical cell with respect to the following: (a) number of electrons transferred, (b) mass of material deposited on or removed from an electrode, (c) current, (d) time elapsed, (e) charge of ionic species: EQN: I = q/t.