

# CHEMISTRY

## ATOMIC STRUCTURE

### Subatomic Particles

**Atomic Number (Z)** – The number of protons in an atom.

**Mass Number (A)** – The number of protons and neutrons in an atom.

**Valence Electrons** – Outer electrons, determine the reactivity and chemical properties of an atom. Since they experience less electrostatic effective charge from the nucleus, they are more likely to participate in chemical interactions with other atoms.

### Atomic Weights and Isotopes

**Atomic Weight** – Grams per mole of atoms for a specific element.

**Mole** – Number of atoms or particles equal to Avogadro's Number,  $6.022 \times 10^{23}$

**Isotope** – A given sample of an element will contain approximately the same isotopic distribution as found in nature. Carbon-12 has 6 neutrons, Carbon-13 has 7 neutrons.

- **Protium** – Hydrogen-1, 1 proton, 0 neutrons
- **Deuterium** – Hydrogen-2, 1 proton, 1 neutron
- **Tritium** – Hydrogen-3, 1 proton, 2 neutrons

### Bohr's Model of Hydrogen Atoms

**Bohr's Model** – Only adequate for atoms with one electron, as he did not account for interelectron electrostatic repulsion.

**Quantum** – Discrete packet of electromagnetic radiation (energy). A quantum is the amount of energy necessary for an electron to transition between energy states and varies in amount depending on which two energy states are in question.

**Energy of an Electron** – A proton and electron completely separated have no electrostatic energy between them, or 0J. As the electron becomes closer to the nucleus (in quantum number) its energy value goes into the negative, decreasing. As an electron gets farther from the nucleus its energy approaches zero, increasing

**Ground State** – The lowest energy orbital path for an electron,  $n=1$ .

**Atomic Emission Spectra** – Used to identify elements in solid or liquid phase. When electrons move from the excited state to the ground state, energy is released in specific quanta of electromagnetic radiation. Each element is capable of different quanta (energy intervals) and so produces a unique emission spectrum, like a fingerprint.

**Atomic Absorption Spectra** – Used to identify elements in gas phase. The energy levels necessary for absorption transition are the same necessary for emission transition.

### Quantum Mechanical Model of Atoms

**Heisenberg Uncertainty Principle** – It is impossible to simultaneously determine, with perfect accuracy, the momentum and the position of an electron. The electron must be stopped (no momentum) to determine position or must be moving (no single position) to determine momentum.

**Energy State** – Position and energy of an electron, described by the quantum numbers.

- **Principal Quantum Number (n)** – The principal quantum number corresponds to the shell, and its period number. The value of 'n' may be any integer, 1 or higher. It is used in the Bohr Model. Since the Bohr Model energy is based on the square of 'n', there is a greater energy difference between lower levels (1 and 2) than there is for higher levels (3 and 4).
- **Azimuthal/Angular Momentum Quantum Number (l)** – The angular momentum quantum number refers to the number of subshells within a shell (principal number). The value of 'l' may be any integer, 0 up to 'n-1'. Note that on the periodic tables, subshells are arranged by relative energy levels, which may overlap. For instance, the 4s subshell is less energetic than the 3d subshell, which is less energetic than the 4p subshell.
  - 0 – s subshell
  - 1 – p subshell
  - 2 – d subshell
- **Magnetic Quantum Number ( $m_l$ )** – The magnetic quantum number specifies the orbital in which an electron is statistically likely to be found. The possible values of ' $m_l$ ' range from '-l' to '+l', including zero. S orbitals are spherical. P orbitals are dumbbell shaped. The orbital shapes are actually density graphs of probabilities of where electrons are likely to be.
  - s(0) subshell – one orbital: 0
  - p(1) subshell – three orbitals: -1, 0, +1
  - d(2) subshell – five orbitals: -2, -1, 0, +1, +2
- **Spin Quantum Number ( $m_s$ )** – The quantum number differentiating between the two electrons within an orbital. The possible values are '+1/2' and '-1/2'. Positive spin is also called up spin and negative spin is also called down spin. Orbitals are filled with positive spins before they are filled with negative spins.
  - **Parallel Spin** – Two positive or two negative electrons are said to have parallel spins.
  - **Hund's Rule** – Degenerate orbitals are all filled with a single positive spin electron before any are filled with a negative spin electron, so that there are a maximum number of parallel spins at all times.

**Electron Configuration** – Configuration based on quantum numbers.  $2p^4$  refers to having 4 electrons in the  $2^{nd}(p)$  subshell of the  $2^{nd}$  principal shell. One subshell fills before the next begins to fill and degenerate orbitals are filled evenly with up spin electrons before any are filled with down spin electrons. Note that atoms prefer to have full or half full subshells. Electrons may be put into or pulled out of the s orbital before being put into or pulled out of the degenerate d orbital.

**Paramagnetic** – Atoms that are slightly attracted by magnetic fields, due to unpaired electrons which align with the magnetic field. 'Para'magnetic materials will allow unpaired electrons to spin 'para'llel to the magnetic field.

**Diamagnetic** – Atoms that are slightly repelled by magnetic fields, due to all electrons being paired.

**Valence Electrons** – For the main group elements, only the 's' and 'p' electrons are in the valence shell. For transition elements, any 's' 'p' and 'f' electrons are in the valence shell.

## THE PERIODIC TABLE

### Periodic Properties of The Elements

**Effective Nuclear Charge ( $Z_{eff}$ )** – The net positive nuclear charge experienced by an electron. Lower level electrons reduce the effective electrostatic charge experienced by higher level electrons.

- **Periodic Trend** – Effective nuclear charge increases from left to right on the periodic table, as for each added proton the added electrons are in the same shell.
- **Group Trend** – Effective nuclear charge decreases from top to bottom as each new intermediate shell adds to the shielding of the nuclear charge.

**Atomic Radius** – As the effective nuclear charge increases it pulls harder on the outer electrons and atomic radius decreases. The largest element in a period is to the left and in a group is at the bottom.

- **Periodic Trend** – Increases right to left.
- **Group Trend** – Increases top to bottom.

**Ionization Potential Energy** – The energy required expel an electron from an atom. As effective nuclear charge increases, the outer electrons are held more tightly and will require more energy to be released. The *first ionization energy* is the energy required to remove the first electron from a neutral atom. Subsequent ionization energies become progressively greater.

- **Periodic Trend** – Increases left to right.
- **Group Trend** – Increases bottom to top.

**Electron Affinity** – The energy released by an atom which gains an electron. The greater the effective nuclear charge at the outer shell, the greater the energy release when an electron is gained.

- **Periodic Trend** – Increases left to right.
- **Group Trend** – Increases bottom to top.

**Electronegativity** – The measure of attraction that an atom will exert on electrons participating in a bond. Higher effective nuclear charges lead to higher attractions of bonding electrons and higher electronegativities.

- **Periodic Trend** – Increases left to right.
- **Group Trend** – Increases bottom to top.

### Types of Elements

**Metals** – Lower left side of the periodic table. Malleable, ductile, and conductive, defined by a low effective nuclear charge.

**Nonmetals** – Upper right side of the periodic table. Nonconductive. Properties vary widely.

**Metalloids** – Share characteristics of metals and nonmetals. Properties vary widely.

### The Chemistry of Groups

**Active Metals** – Highly reactive metals.

- **Alkali Metals (Group 1)** – Low effective nuclear charge, large atomic radius, easily lose electrons to react with the nonmetals.
- **Alkaline Earth Metals (Group 2)** – Low effective nuclear charge, fairly large atomic radius, easily lose electrons to react with the nonmetals.

**Transition Metals** – Have high melting and boiling points and are good conductors.

Many have different possible *oxidation states*. Note that because various oxidation states can be achieved, transition metals can form hydration complexes in water, increasing their solubility.

**Halogens (Group 17)** – Very reactive nonmetals. Range from gases to liquids to solids at normal temperatures.

**Noble Gases (Group 18)** – Inert gases, no unpaired valence electrons and so they are very nonreactive.

## BONDING AND CHEMICAL INTERACTIONS

### Ionic Bonds

**Ionic Bond** – Metal/Nonmetal bond. Ionic bonds form compounds.

- **Ionic compounds** – Compounds with very high melting and boiling points due to the strength of the electrostatic force between atoms. When solid, they form crystalline structures based upon minimizing charge potentials. They dissolve readily in polar solvents and are generally conductive.

### Covalent Bonds

**Covalent Bond** – Nonmetal/Nonmetal bond. Covalent bonds form molecules, which are also compounds.

- **Covalent Compounds** – Contain discrete molecular units with relatively weak intermolecular forces holding them together. This leads to relatively low melting and boiling points.
- **Coordinate Covalent Bond** – All shared electrons are contributed by only one of the participating atoms. Common between Lewis acid/base interactions.

**Bond Order** – The number of shared electron pairs between two atoms.

- **Single Bond** – Bond order of one.
- **Double Bond** – Bond order of two.
- **Triple Bond** – Bond order of three.

**Bond Length** – The average distance between the two nuclei of atoms in a bond. As the bond order increases, the atoms are pulled closer together and bond length decreases.

**Bond Energy** – The energy absorbed to break a bond or released to form a bond, for atoms in gaseous states. As bond order increases, bond energy increases.

**Polarity** – The higher an atom's electronegativity, the greater its pull will be on any shared electrons.

- **Nonpolar Covalent Bond**
- **Polar Covalent Bond** – Dipole moment measured as a vector in Debye (Coulomb-meter) units.

**Lewis Dot Structure** – Diagram showing atoms and their respective electrons.

Particularly useful for examining potential covalent bonds.

- **Formal Charge** – The formal charge of an overall compound can be determined from the Lewis Structure for that compound. However, the formal charge underestimates the effects of electronegativity, while oxidation state estimations overestimate the effects of electronegativity. The actual distribution of electrons falls somewhere between the two extremes.
  - $\text{Formal Charge} = (\text{Valence e \#}) - (\text{Nonbonding e \#}) - 1/2(\text{Bonding e \#})$
- **Resonance Structures** – Different ways in which a compound can be arranged. The more resonance structures the more stable the compound. The stability of individual resonance structures are analyzed using formal charge. *Major Resonance Structures* will have amount and magnitude of charges minimized with negative charges only at the most electronegative atoms while *Minor Resonance Structures* will be any other possible structure. *Major Resonance Structures* are more stable and less reactive and play a larger role in the *Resonance Hybrid*.
  - **Resonance Hybrid** – The actual nature of bonds within a compound are a hybrid of the possible resonance structures.

**Valence Shell Electron Pair Repulsion Theory (VSEPR) -**

Electron Pairs	Electron Geometry	Ideal Bond Angle	Molecule Geometry
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2B0NB	Linear	180	Linear
2B1NB	Trigonal Planar	120	Bent
2B2NB	Tetrahedral	109.5	Bent
2B3NB	Trigonal Bipyramidal	90, 120, 180	Linear
3B0NB	Trigonal Planar	120	Trigonal Planar
3B1NB	Tetrahedral	109.5	Trigonal Pyramidal
3B2NB	Trigonal Bipyramidal	90, 120, 180	T Shaped
4B0NB	Tetrahedral	109.5	Tetrahedral
4B1NB	Trigonal Bipyramidal	90, 120, 180	Seesaw
5B0NB	Trigonal Bipyramidal	90, 120, 180	Trigonal Bipyramidal
5B1NB	Octahedral	90, 180	Square Pyramidal

### Atomic and Molecular Orbitals

- **Sigma Bond** – End to end overlap of orbitals, a single bond.
- **Pi Bond** – Side to side overlap of orbitals, a double or triple bond.

### The Intermolecular Forces

#### Van Der Waals Forces

- **Dispersion (London) Forces** – The weakest of all intermolecular interactions. Short lived dipoles caused by the position of electrons closer to one atom or the other at any given time. A temporary dipole may also be induced in nearby atoms or compounds. Atoms with lower effective nuclear charge at the valence level are more polarizable and are capable of slightly stronger dispersion forces.
- **Dipole-Dipole Interactions** – A fairly strong intermolecular interaction. Positive regions and negative regions of adjacent molecules will align in order to reduce electrostatic potential within the system. Dipole-dipole interactions are significant in solid and liquid phase, but almost negligible in gas phase due to the distance of molecules.
  - **Hydrogen Bonds** – A very strong electrostatic interaction that may be intermolecular or intramolecular. When hydrogen is bound to Fluorine, Oxygen, or Nitrogen, the hydrogen receives so little of the electrons that it can practically act as a lone Hydrogen. This positively charged Hydrogen can interact with nearby Fluorine, Oxygen, or Nitrogen in a particularly strong type of dipole-dipole interaction. These strong interactions lead to an increase in boiling/melting point.

**Ionic Interactions** – The extremely strong electrostatic interactions between fully polar ionic compounds. These interactions are so strong that they tend to form lattice structures that have very high melting/boiling points.

## COMPOUNDS AND STOICHIOMETRY

### Moles and Molecules

**Molecular Weight** – The sum of the atomic weights of the atoms in a covalent molecule. Measured in AMUs.

**Formula Weight** – The sum of the atomic weights of atoms in an ionic compound. Measured in grams.

**Mole** –  $6.022 \times 10^{23}$

**Molar Mass** – The mass of one mole of an atom or compound. Measured in grams/mol.

**Equivalents** – The number of moles of “electrons or protons” that some amount of a substance or molecule can contribute. Ex: one mole of HCl supplies one mole (one equivalent) of Hydrogen ions while one mole of  $\text{H}_2\text{SO}_4$  is 2 equivalent for Hydrogen ions.

**Gram Equivalent Weight** – The mass of a substance that is capable of providing one equivalent of electrons/protons.

**Normality** – A measure of concentration, equivalents/Liter. Ex: A 1 Normal solution of Hydrogen ions contains 1 mole of Hydrogen ions per Liter of solution, a 2 Normal solution contains 2 moles of hydrogen ions per liter of solution.

### Representation of Compounds

**The Law of Constant Composition** – Any sample of a compound, no matter the source, will always be composed of constant proportions of the constituent elements.

**Percent Composition by Mass** –  $(\text{mass of X in formula})/(\text{Formula weight}) \times 100\%$

### Types of Chemical Reactions

**Combination Reaction** – When there are more reactants than products. Ex:  $\text{A} + \text{B} \rightarrow \text{C}$

**Decomposition Reaction** – When there are more products than reactants. Ex:  $\text{A} \rightarrow \text{B} + \text{C}$

**Single Displacement Reaction** – An atom/ion in a compound is replaced by another ion/atom. Ex:  $\text{A} + \text{BC} \rightarrow \text{B} + \text{AC}$

**Double Displacement Reaction (Metathesis)** – Atoms from two different compounds swap places. Ex:  $\text{AB} + \text{CD} \rightarrow \text{AD} + \text{CB}$

- **Neutralization Reaction** – A specific type of metathesis where an acid and base neutralize to produce a salt. Ex:  $\text{HCl} + \text{NaOH} \rightarrow \text{NaCl} + \text{H}_2\text{O}$

### Net Ionic Equations

**Ionic Equation** – Since ions will tend to be in solution, an equation can be written in ionic form. Ex:  $\text{Zn(s)} + \text{Cu}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) \rightarrow \text{Cu(s)} + \text{Zn}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq})$

**Net Ionic Equation** – Ionic equation minus spectator ions, which are present on both sides and so can cancel each other out. Ex:  $\text{Zn(s)} + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{Cu(s)} + \text{Zn}^{2+}(\text{aq})$

### Applications of Stoichiometry

**Limiting Reactant (Reagent)** – The reactant that is used up first, thus limiting the number of times a chemical process can run.

**Excess Reactant (Reagent)** – The reactant(s) in excess, anything but the limiting reactant.

**Theoretical Yield** – The yield of a reaction expected from the balanced equation.

**Actual Yield** – The yield of a reaction measured from experimentation.

**Percent Yield** –  $(\text{Actual Yield})/(\text{Theoretical Yield}) \times 100\%$

## CHEMICAL KINETICS AND EQUILIBRIUM

### Chemical Kinetics

**Overall Reaction** – The full balanced equation, which is actually the summation of a series of *elementary reactions*. The full series of elementary reactions is known as a *reaction mechanism*.

- **Intermediate** – A species that is formed and consumed within the elementary steps of a reaction and does not appear in the overall reaction. An intermediate cannot be isolated.
- **Rate Determining Step** – The slowest elementary step in a reaction, which sets the speed of the overall reaction. All other elementary steps can be assumed to occur instantaneously.

### Reaction Rates

**Rate Law** – The rate law predicts how quickly a reaction will run. For nearly all forward, irreversible reactions, the rate is equal to the *rate constant* times the *concentration of each reactant* raised to *some power*. Note that the rate law ONLY includes the concentrations of the reactants.

Ex:  $\text{rate} = k[\text{A}]^x[\text{B}]^y$

- **Rate Constant (k)** – The rate constant is the same for any such reaction and does not change with concentration changes. However, the rate constant may change if there is a change in temperature or a change in the required activation energy.
- **Reaction Order** – The sum of the individual orders of each reactant (x, y, etc.).
  - **Reactant Orders** – The individual order of each reactant (x, y, etc.). The order of each reactant must be determined experimentally.



- **Zeroth Order Reaction** –  $(\text{Rate})=k$ , the only way to change a zeroth order reaction rate is to change the temperature or add a catalyst.
- **First Order Reaction** – A first order reaction with only one reactant depends upon the spontaneous chemical change of that reactant.
- **Second Order Reaction** – A second order reaction generally suggests the physical collision of two reacting species.
- **Higher Order Reaction** – It is practically impossible to have a third order reaction with only a single reactant as it is statistically unlikely that three particles will all collide simultaneously.
- **Mixed Order Reaction** – A reaction in which the order of a reaction is a non-integer (fraction) or in which the rate order varies over time.
  - **Broken Order Reaction** – A reaction with fractional reaction orders, as opposed to integer reaction orders.

**Equilibrium Expression** – The equilibrium expression predicts where the reactions equilibrium lies.

### **Molecular Chemical Reaction Theories**

- **Collision Theory of Chemical Kinetics** – Reacting species must collide with sufficient energy and with the proper orientation in order to react. The rate of a reaction is proportional to the number of collisions per second between reacting molecules.
- **Transition State Theory** – When molecules collide with energy equal to or greater than the activation energy, they form a *transition state*, in which the old bonds weaken and the new bonds begin to form.
  - **Transition State (Activated Complex) ( $\ddagger$ )** - A transition continuum which is in a higher energy state than either the products or reactants, allowing it to form products or revert to reactants with no further energy input. Since it is a continuum lacking a distinct identity, unlike intermediates, the transition state cannot be theoretically isolated.
  - **Enthalpy Change of the Reaction ( $\Delta H$ )** – Potential energy of the products minus potential energy of the reactants.
    - **Positive  $\Delta H$**  – Endothermic, energy is absorbed.
    - **Negative  $\Delta H$**  – Exothermic, energy is released.

### **Factors Affecting Reaction Rate**

- **Reactant Concentrations** – The greater the concentrations of reactants, the greater the number of effective collisions per unit time.
- **Temperature** – Temperature is proportional to average molecular kinetic energy, so increasing the temperature increases the average energy, potentially pushing more molecules into the activation energy range. Too high of a temperature could denature biological catalysts, in that way reducing reaction rate.
- **Medium** – The chemical makeup (aqueous or nonaqueous) as well as the physical state (solid/liquid/gas) may affect different reactions differently.

- **Catalysts** – Substances that increase the reaction rate but remain unchanged or at least return to their original state throughout the reaction. Catalysts work by providing an alternative, lower energy, pathway for the reaction. They may increase the frequency of reactant collisions, alter the relative orientation of the reactant molecules, donate electron density to the reactants, or reduce intramolecular forces within the reactant molecules.
  - **Homogeneous Catalysis** – The catalyst is in the same physical phase (solid/liquid/gas) as the reactants.
  - **Heterogeneous Catalysis** – The catalyst is in a different physical phase than the reactants.

## Equilibrium

### **Dynamic Equilibrium of Reversible Chemical Reactions**

- **Irreversible Reactions** – Reactions that can only proceed in a forward direction. These reactions run to completion, forming the maximum amount of product allowed by the limiting reagent.
- **Reversible Reactions** – Reactions that proceed in a forwards and backwards direction simultaneously, eventually the forward and reverse reaction rates will equalize and the reaction will be in equilibrium.
- **Dynamic Equilibrium** – A state in which the relative amounts of reactants and products remain equal although the forward and reverse reactions continue to run. There is a change, but no net change. At equilibrium, a systems *entropy* is at it's maximum while it's *Gibbs free energy* is at it's minimum.

### **Law of Mass Action**

- **Law of Mass Action** - Sets the forward reaction rate equal to the reverse reaction rate. For the law of mass action, the powers of each species are equal to the stoichiometric coefficients of each species in the balanced chemical formula.
  - **$K_{eq}$**  – Equilibrium constant, a combination of the forward and reverse rate constants. For a multistep process, the overall equilibrium constant is the product of the elementary step equilibrium constants.
    - **$K_c$**  – The equilibrium constant used when dealing specifically with concentrations. The concentration constant can be defined as the ratio of the forward rate constant over the reverse rate constant.
    - **$K_p$**  – The equilibrium constant used when dealing specifically with gases and pressures. Non gases are not included in the equation.
    - **$K_{sp}$**  – The equilibrium constant used when dealing with dissolving substances. Only the products are used, the concentrations of each product raised to the number of dissociated particles of each product. Reactants are not included because they are in the solid phase and pure solids and liquids are never included in the Law of Mass Action.
    - **$K_w$**  – Water autoionization equilibrium constant.

- $K_A$  – Acid dissociation equilibrium constant.
- $K_B$  – Base dissociation equilibrium constant.

### Reaction Quotient

- **Reaction Quotient** – Applies current, or initial, concentrations to the Law of Mass Action to determine in which direction a system will proceed or whether that system is already in equilibrium.

### Properties of the Law of Mass Action

- The concentrations of pure solids and liquids do not appear in the equilibrium expression, as their concentrations do not change throughout the reaction.
- The equilibrium constant is temperature dependent, as temperature changes so does the equilibrium constant.

### Le Chatelier's Principle

**Le Chatelier's Principle** – When a stress is applied to a system in equilibrium, there is a shift in the system to relieve that stress and achieve a new equilibrium.

- **Changes in Concentration of a Reacting Species**
  - **Add Reactant** – Equilibrium shifts right, reducing reactants.
  - **Remove Reactant** – Equilibrium shifts left, producing reactants.
  - **Add Product** – Equilibrium shifts left, reducing products.
  - **Remove Product** – Equilibrium shifts right, producing products.
- **Changes in Pressure (By Changing Volume)**
  - **Add Pressure/Reduce Volume** – Equilibrium shifts towards the side with fewer moles of gas to conserve space.
  - **Remove Pressure/Add Volume** – Equilibrium shifts towards the side with more moles of gas to fill space.
- **Changes in Temperature**
  - **Exothermic Reaction/Heat as a Product**
    - **Add Heat** – Equilibrium shifts left, applying the excess heat to the reverse reaction.
    - **Remove Heat** – Equilibrium shifts right, filling the heat deficit.
  - **Endothermic Reactions/Heat as a Reactant**
    - **Add Heat** – Equilibrium shifts right, applying the excess heat to the forward reaction.
    - **Remove Heat** – Equilibrium shifts left, filling the heat deficit.

## THERMOCHEMISTRY

### Systems and Processes

#### Types of Systems

- **Isolated System** – The system cannot exchange energy or matter with the surroundings.
- **Closed System** – The system can exchange energy, but not matter with the surroundings.
- **Open System** – The system can exchange energy and matter with the surroundings.

**Process** – The process of changing energy, concentrations, temperatures, or pressures within a system.

- **Isothermal Process** – Any process that occurs with constant temperature.
- **Adiabatic Process** – Any process that occurs with constant internal energy.
- **Isobaric Process** – Any process that occurs with constant pressure.

### States and State Functions

**State** – A set of state functions (certain macroscopic properties) of a system. State functions cannot describe a process, only a specific state. Processes change one state to another.

- **State Functions**
  - Temperature (T)
  - Pressure (P)
  - Volume (V)
  - Density (p)
  - Internal Energy (E or U) – The amount of internal energy within a system. Changes in internal energy can be measured as the heat transferred into the system minus the work done by the system.  $\Delta U = Q - W$
  - Enthalpy (H)
  - Entropy (S)
  - Gibbs Free Energy (G)

### **Standard State Conditions for Thermodynamics**

- 25 degrees C / 298 Kelvin
- 1 Atmosphere / 760 mmHg

**Standard State** – The most stable form of a substance in standard state. Ex:  $O_2(g)$ ,  $H_2O(l)$ ,  $C(s)$ ,  $NaCl(s)$

### Heat

**Temperature (T)** – The state function measurement of the average kinetic energy of particles of a substance.

**Heat (Q)** – The process function that is the spontaneous transfer of energy from particles of higher energy and temperature to particles of lower energy and temperature.

- **Units** - 1 calorie = 4.184 Joules

- **Specific Heat** – The amount of energy required to raise the temperature of one gram of a substance by one degree celsius.
  - **Specific Heat of Water** – 1 calorie per gram degrees celsius.
- **Calorimetry** – The measurement of heat transfer.
  - **Constant Pressure Calorimeter** – Like a coffee cup calorimeter.
  - **Constant Volume Calorimeter** – Like a bomb calorimeter.

### Enthalpy

**Enthalpy (H)** – The state function that represents the energy state following a heat change.

**Standard Enthalpy of Formation ( $\Delta H^\circ_f$ )** – The enthalpy change resulting from the formation of one mole of a compound in standard state from its elements in standard state.

**Standard Enthalpy of Reaction ( $\Delta H^\circ_{rxn}$ )** – The enthalpy change resulting from a specific reaction occurring at standard state conditions.

**Standard Enthalpy of Combustion ( $\Delta H^\circ_{comb}$ )** -

**Hess's Law** – Enthalpy measures, like any state function, are additive.

**Bond Dissociation Energy** – The application of enthalpy and Hess's law to the formation and breaking of chemical bonds.

### Entropy

**The Second Law of Thermodynamics** – Energy spontaneously moves down its energy gradient.

**Entropy (S)** – The measure of the spontaneous dispersal of energy at a specific temperature.

### Gibb's Free Energy

**Gibb's Free Energy (G)** – The state function that combines enthalpy and entropy to determine whether a reaction will be spontaneous. The free energy is the total amount of energy available to perform useful work. Free energy is like a valley between two hills, the bottom of which is equilibrium. Any system will tend to roll down the hills to reduce free energy.

- **Spontaneous Reaction ( $-\Delta G$ )** – A reaction that reduces free energy, rolling down the hills.
- **Nonspontaneous Reaction ( $+\Delta G$ )** – A reaction that increases free energy, rolling up the hills.
- **Reaction at Equilibrium** – A reaction at equilibrium has 0 free energy, at the bottom of the valley.

$\Delta H$	$\Delta S$	Outcome
-	+	Spontaneous at all temperatures

+	-	Nonspontaneous at all temperatures
+	+	Spontaneous at high temperatures
-	-	Spontaneous at low temperatures

**Standard Free Energy ( $\Delta G^\circ_{\text{rxn}}$ )**– Free energy of a system or reaction measured under standard state conditions.

- $\Delta G^\circ_{\text{rxn}} = -RT \ln K_{\text{eq}}$ , for reactions at equilibrium, if K is less than one the reaction is spontaneous.
- $\Delta G^\circ_{\text{rxn}} = RT \ln (Q/K)$ , for reactions in progress, if (Q/K) is less than one the reaction spontaneously moves forward until equilibrium is reached. If (Q/K) is greater than one the reaction spontaneously moves backward until equilibrium is reached.

## THE GAS PHASE

### The Gas Phase

**Gaseous Phase** – Fluid phase in which molecules are far apart and move very quickly, with only very weak intermolecular attractions between them. Gases can change volume or shape to fill their container.

### **Measurements in the Gaseous Phase**

- **Pressure (P)** – 1 atm = 760 mmHg = 760 torr = 101000 Pascals
- **Volume (V)**
- **Temperature (T)**
- **Moles (n)**

### **Standard Temperature and Pressure for Gases (STP)**

- 0 degrees celsius / 273 K
- 1 atm

### Ideal Gases

**Ideal Gases** – A hypothetical gas whose molecules occupy no volume and have no intermolecular interactions/attractions with each other. Most gases behave ideal unless at very high pressures and low temperatures. In a sense, a gas behaving ideally loses its identity and behaves like any other ideal gas.

### Kinetic Molecular Theory of Gases

**Kinetic Molecular Theory** – Theory that explains the behavior of gases.

1. The volumes of gas particles are negligible compared to the container volume.
2. Gas particles exhibit no intermolecular attractions or repulsions.
3. Gas particles are in continuous, random motion, undergoing collisions with other gas particles and the container walls.

4. Collisions between gas particles are elastic, conserving momentum and kinetic energy.
5. The average kinetic energy of gas particles is directly proportional to temperature and is equal for all gas particles at that temperature, regardless of identity.

**Average Molecular Speeds** – The kinetic energy of a gas particle is directly proportional to the temperature of the gas. However, since the velocity of an individual particle at any point in time cannot be discerned, the root-mean-square speed may be calculated as an approximation of the speed that correlates with the available kinetic energy.

- $KE = \frac{1}{2} mv^2 = \frac{3}{2} kT$ , where  $k$  is the Boltzmann Constant  $1.4 \times 10^{-23} \text{ m}^2 \text{ kg s}^{-2} \text{ K}^{-1}$
- $\mu_{\text{rms}} = \sqrt{(3RT/M)}$ , where  $M$  is the molecular mass

### **Graham's Law of Effusion and Diffusion**

- **Diffusion** – The movement of gas molecules through a mixture, such as air. The kinetic molecular theory predicts that heavier gases diffuse more slowly while lighter gases diffuse quicker due to varying speeds.
- **Effusion** – The movement of gas particles under pressure from one area to another through a small opening.

### Ideal Gas Behavior

**Ideal Gas Law** – The law which relates pressure, volume, temperature, and moles.

- $PV = nRT$ ,  $R = .0821$

**Dalton's Law of Partial Pressures** – When multiple gases are in one container and are behaving ideally, they each act as if they are the only gas in the container and produce as much pressure as if they were the only gas. The total pressure is the sum of each partial pressure.

- $P_{\text{Total}} = P_A + P_B + P_C \dots$
- $P_A = P_T X_A$ , where  $X$  is the mole fraction of that gas
- $X_A = n_A / n_T$

### Real Gas Behavior

**Deviations due to Pressure** – As gas particles are forced closer together by higher pressures, their actual volume becomes more significant.

**Deviations due to Temperature** – As temperature decreases, kinetic energy and average velocities decrease, and attractive/repulsive intermolecular forces become more significant.

### **Van Der Waals Equation of State**

- $[P + (n^2 a / V^2)](V - nb) = nRT$ , where  $a$  is the affect of intermolecular attractions and  $b$  is the actual volume taken up by each gas particle.

## PHASES AND PHASE CHANGES

## Solids

**Solids** – The most dense condensed phase (except for in water) in which the intermolecular forces have overcome translational molecular motion and almost all kinetic energy is in the form of vibrational molecular motion. Generally, regardless of changes in pressure, solids are incompressible.

- **Solid Water** – Due to the crystalline structure of ice in the solid phase actually spreading the molecules apart slightly more than in the liquid phase, solid water is less dense than liquid water. Water is densest at 4 degrees celsius, above which kinetic energy spreads the molecules and below which crystallization spreads the molecules.

## **Molecular Arrangements of Solids**

- **Crystalline Solid** – Solids with ordered structure, such as solid water or ionic compounds. Most solids are crystalline in structure. The two most common crystalline structures are metallic crystals and ionic crystals.
  - **Metallic Crystals** – The lattice within a metallic substance.
  - **Ionic Crystals** – The lattice within an ionic substance, such as NaCl.
- **Amorphous Solid** – Solids with disordered structure, such as glass or plastic.

## **Repeating Units within Crystals**

- **Unit Cell** – The repeating unit within a crystalline lattice structure.
  - **Cubic Unit Cell**
    - **Simple Cubic** – Eight equivalent particles spaced at the eight corners of a cube. Within the cube is  $1/8^{\text{th}}$  of each particle, for a total of 1 particle per cube.
    - **Body Centered Cubic** – Eight equivalent particles spaced at the eight corners of a cube with a ninth equivalent particle in the center of the cube. Within the cube is  $1/8^{\text{th}}$  of each corner particle plus the one center particle, for a total of 2 particles.
    - **Face Centered Cubic** – Eight equivalent particles spaced at the eight corners of a cube with 6 more particles in the face of each side of the cube. Within the cube is  $1/8^{\text{th}}$  of each corner particle plus  $1/2$  of each face particle, for a total of 4 particles within the cube.

## Liquids

**Liquid** – The condensed phase that is generally less dense than the solid phase. Liquids are assumed to be incompressible like solids, but fluid like gases as they do not resist shear forces like solids do. Because of the degree of freedom of fluids, all fluids can diffuse. Furthermore, liquids near the surface layer can gain enough kinetic energy to escape into the gas phase, vaporization.

**Miscibility** – The degree to which two liquids can mix to form a solution. Miscible fluids can mix and immiscible fluids cannot.



- **Emulsion** – A fairly homogenous mixture created by the aggregation of two immiscible liquids.

### Phase Equilibria

**Phase Changes** – Any change between solid, liquid, and gas phases.

#### **Gas-Liquid Equilibrium**

- **Vaporization (Evaporation)** – The escape of high energy/velocity liquid molecules into the gaseous phase. Vaporization lowers the average kinetic energy of the molecules that remain behind.
- **Condensation** – The vapor pressure of vaporized molecules decreases the solubility of vapor in the air causing some gaseous molecules to return to the liquid phase. The vapor pressure increases as the kinetic energy of the liquid increases as more liquid molecules have the energy to vaporize.
- **Boiling Point**– At the boiling point, the average kinetic energy of the entire liquid has increased to the point that the vapor pressure of the water equals atmospheric pressure and liquid molecules can vaporize from any part of the liquid, not just at the surface.

#### **Liquid-Solid Equilibrium**

- **Fusion (Melting)** – A solid melts when enough energy is input to break the intermolecular bonds within the solid.
- **Solidification (Crystallization or Freezing)** – The transition from liquid to solid as energy escapes, allowing intermolecular forces to overpower kinetic forces.
- **Melting Point/Freezing Point** – The transition temperature between liquid/solid phases. Note that while crystalline solids have very distinct melting points, amorphous solids tend to melt over a range due to their disorganized network of intermolecular forces.

#### **Gas-Solid Equilibrium**

- **Sublimation** – The phase change from solid directly to gas.
- **Deposition** – The phase change from gas directly to solid.

**The Gibbs Function** – When any two phases are in equilibrium, the Gibbs free energy must be equal to zero.

**Heating Curves** – When a compound is heated (energy is added), the temperature rises until the melting or boiling point, at which the temperature ceases to increase as all input energy begins going towards breaking intermolecular bonds. Only once all intermolecular bonds are sufficiently broken to put the entire sample into the next phase will input energy be put towards increasing molecular kinetic energy and temperature.

### Phase Diagrams

**Phase Diagrams** – The diagram showing the temperatures and pressures at which a particular substance will be thermodynamically stable in a particular phase. These diagrams also show where equilibrium exists between two adjacent phases.

**Single Component (Compound) Diagram**

- **Lines of Equilibrium (Phase Boundaries)** – The lines on phase diagrams representing the equilibria temperatures and pressures.
- **Triple Point** – The point at which the three phase boundaries meet. At this temperature and pressure, all three phases can coexist in equilibrium.
- **Critical Point** – The far end of the phase boundary line between liquid and gas. This is the temperature and pressure above which there is no distinction between the phases. As liquid is heated its density decreases and the vapor density increases. Above the critical point, the two densities are equal and so the two phases are indistinguishable.

**Multiple Component (Compound) Diagram** – A diagram representing the varying compositions of liquid and vapor phases for a mixture of liquids/vapors with different boiling points and/or different levels of volatility. The top regression line represents vapor while the lower regression line represents liquid. There is a horizontal line through the graph representing the boiling point of the solution as a whole.

Colligative Properties

**Vapor Pressure Depression**

**Boiling Point Elevation**

**Freezing Point Depression**

**Osmotic Pressure**

## SOLUTIONS

Nature of Solutions

**Solution** – A homogenous mixture of two or more substances combined in a single phase, usually the liquid phase.

**Solute** – Dissolves in a solvent, usually the substance in a smaller amount.

**Solvent** – Solvates a solute, usually the substance in a greater amount.

**Solvation (Dissolution)** – The electrostatic interaction between solute and solvent molecules. Solvation when water is the solvent is called *hydration*.

- **Endothermic Solvation** – The new interactions are weaker than the original interactions, process favored at high temperatures.
- **Exothermic Solvation** – The new interactions are stronger than the original interactions, process favored at low temperatures.

- **Isothermic Solvation** – The new interactions are about as strong as the original interactions, enthalpy change is close to zero, this is an *ideal solution*.

**Solubility** – The maximum amount of a substance that can be dissolved in a particular solvent at a particular temperature. Solubility is a function of the Gibbs Free Energy change and so is related to enthalpy and entropy change. If the Gibbs Free Energy is negative, the solute will spontaneously dissolve and so is soluble. If the Gibbs Free Energy is positive, the solute will not spontaneously dissolve and so is insoluble.

- **Diluted Solution** – A solution in which the ratio of solute to solvent is small.
- **Concentrated Solution** – A solution in which the ratio of solute to solvent is large
- **Saturated Solution** – A solution in which the maximum amount of solute is dissolved and its dissolved state is in equilibrium with its undissolved state.
  - **Precipitant** – Solute that is in excess of the solubility limit will either come out of solution or never enter solution, precipitating into its undissolved form.
  - **Sparingly Soluble Salts** – Salts with a very small negative Gibbs Energy which are minimally soluble in water.

**Aqueous Solutions** – Solutions for which water is the solvent.

### **Solubility Rules for Aqueous Solutions**

- **Rules for Solubility**
  - Salts of Alkali Metals are soluble
  - Salts of Ammonium ( $\text{NH}_4^+$ ) are soluble
  - Chlorides, Bromides, and Iodides are soluble
    - Except with Ag, Pb, Hg
  - Salts of Sulfate ( $\text{SO}_4^{2-}$ ) are soluble
    - Except with Ca, Sr, Ba, and Pb
- **Rules for Insolubility**
  - Metal Oxides are insoluble
    - Except with Alkali Metals, CaO, SrO, and BaO
  - Hydroxides are insoluble
    - Except with Alkali Metals, Ca, Sr, and Ba
  - Carbonates ( $\text{CO}_3$ ), Phosphates ( $\text{PO}_4$ ), Sulfides ( $\text{S}^{2-}$ ), and Sulfites ( $\text{SO}_3$ ), are insoluble
    - Except with Alkali Metals and Ammonium

### Ions

### **Nomenclature**

- **-ide**
- **hypo-/-ite, hypo-/-ous**
- **-ite, -ous**
- **-ate, ic**

- per-/-ate, per-/-ic

## Common Ions

- **One Variation**
  - **Hydroxide**  $\text{OH}^-$
  - **Cyanide**  $\text{CN}^-$
  - **Permanganate**  $\text{MnO}_4^-$
  - **Acetate**  $\text{C}_2\text{H}_3\text{O}_2^-$
  - **Chromate**  $\text{CrO}_4^{2-}$
  - **Ammonium**  $\text{NH}_4^+$
- **Multiple Variations**
  - **Nitrate**  $\text{NO}_3^-$
  - **Chlorate**  $\text{ClO}_3^-$
  - **Carbonate**  $\text{CO}_3^{2-}$ 
    - **Hydrogen Carbonate**  $\text{HCO}_3^-$
  - **Sulfate**  $\text{SO}_4^{2-}$ 
    - **Hydrogen Sulfate**  $\text{HSO}_4^-$
  - **Phosphate**  $\text{PO}_4^{3-}$ 
    - **Hydrogen Phosphate**  $\text{HPO}_4^{2-}$
    - **Dihydrogen Phosphate**  $\text{H}_2\text{PO}_4^-$

**Electrolytes** – Solutes that produce ions upon dissociation, these free charges facilitate electrical conduction.

- **Strong Electrolytes** – Electrolytes which dissociate completely in water, usually strong acids/bases or compounds with highly polar covalent bonds or ionic bonds.
- **Weak Electrolytes** – Electrolytes which dissociate incompletely in water, usually weak acids/bases or compounds with nonpolar covalent bonds.
- **Nonelectrolytes** – Compounds which do not ionize at all in water, usually nonpolar gases and organic compounds.

## Concentration

### Units of Concentration

- **Percent Composition by Mass (Parts Per Hundred)**
  - $\% \text{ Comp} = (\text{solute mass}) / (\text{solution mass}) * 100\%$
- **Parts Per Million (ppm)**
  - $\text{ppm} = (\text{solute mass}) / (\text{solution mass}) * 1,000,000$
- **Mole Fraction (X)**
  - $X = (\text{moles of compound}) / (\text{moles of all compounds})$
- **Molarity (M)**
  - $M = (\text{moles of solute}) / (\text{Liters of solution})$
- **Molality (m)**
  - $m = (\text{moles of solute}) / (\text{kg of solvent})$
- **Normality (N)**

$$N = (\text{equivalents of solute}) / (\text{Liters of Solution})$$

**Dilution** – Adding solvent to a concentrated solution to make a less concentrated solution.

- $M_1V_1 = M_2V_2$
- $m_1V_1 = m_2V_2$
- $N_1V_1 = N_2V_2$

### Solution Equilibria

**Molar Solubility (M)** = (moles of solute) / (Liters of solution)

**Slightly Soluble Salt  $K_{sp}$ , M = cation, X = anion, x = molar solubility**

Salt Formula	$K_{sp}$
MX	$x^2$
$MX_2$	$4x^3$
$MX_3$	$27x^4$

### **Solid Dissolution in Liquid**

- **Higher Temperature** – Generally more soluble
- **Lower Temperature** – Generally less soluble

### **Gas Dissolution in Liquid**

- **Higher Temperature** – Generally less soluble
- **Lower Temperature** – Generally more soluble
- **Higher Pressure** – Generally more soluble
- **Lower Pressure** – Generally less soluble

**Ion Product (I.P.)** - Analogous to the reaction quotient (Q) for chemical reactions. Use the  $K_{sp}$  formula, but with initial concentrations rather than equilibrium concentrations.

- **I.P. <  $K_{sp}$**  – Reaction is not yet at equilibrium, the solution is undersaturated.
- **I.P. >  $K_{sp}$**  - Reaction is beyond equilibrium, the solution is supersaturated. Any disturbance to a supersaturated solution will cause the excess solute to precipitate.
- **I.P. =  $K_{sp}$**  - Reaction is at equilibrium, the solution is saturated.

**The Common Ion Effect** – The reduction in molar solubility of a salt when one of its constituent ions is already present in solution. This is a special case of Le Chatelier's Principle.

## ACIDS AND BASES

### Definitions

#### **Arrhenius Definition**

- **Acid** – A species which dissolves in water to produce Hydrogen ions.
  - **Arrhenius Nomenclature**
    - -ide is replaced with -ic, and the prefix hydro- is used.
    - -ite is replaced with -ous, and no prefix is used.
    - -ate is replaced with -ic, and no prefix is used.
- **Base** – A species which dissociates in water to produce an Hydroxide ion.

### **Bronsted-Lowry Definition**

- **Acid** – A species which donates Hydrogen ions.
- **Base** – A species which accepts Hydrogen ions.
- **Conjugate Acid/Base Pairs** – Bronsted Lowry acids always occur in conjugate pairs.

### **Lewis Definition**

- **Acid** – Species which accepts electron pairs.
- **Base** – Species which donates electron pairs.

### Properties of Acids and Bases

#### **Autoionization of Water and Hydrogen Ion Equilibria**

- **Amphoteric Species** – Species that can act as either an acid or a base, depending on the other chemicals present.
  - **Autoionization** – Amphoteric species can react with themselves to a certain extent. One water molecule donates a Hydrogen ion to another, forming one Hydronium ion and one Hydroxide ion. In this way, in pure water, the Hydroxide and Hydronium concentrations are always equal ( $10^{-7}$  mol/L each), and so the pH is 7 and the pOH is 7.
    - **Autoionization of Water** – At standard state (298K, 1atm), the *Water Dissociation Constant* ( $K_w$ ) =  $[H_3O^+][OH^-] = 10^{-14}$ . At temperatures above standard state,  $K_w$  increases due to the endothermic nature of dissociation. At temperatures below,  $K_w$  decreases.
- **pH and pOH Scales**
  - pH scale of 1-14 only valid at standard state conditions (298K, 1atm)
  - $pH = -\log [H^+]$
  - $pOH = -\log [OH^-]$
  - $pH + pOH = 14$
- **Estimating p-scale Values**

X	pX, -logX
$10^{-1}$	1
$10^{-4}$	4
$10^{-8}$	8
$10^{-12}$	12

- $\log(1) = 0$
- $\log(10) = 1$

### Strong Acids and Bases

- **Strong Acid** – An acid which completely dissociates in solution.
  - HCl
  - HBr
  - HI
  - $\text{H}_2\text{SO}_4$
  - $\text{HNO}_3$
  - $\text{HClO}_4$
- **Strong Base** – A base which completely dissociates in solution.
  - NaOH
  - KOH

### Weak Acids and Bases

- **Weak Acid** – An acid which only partially dissociates in solution.
  - **Weak Acid Dissociation Constant ( $K_A$ )** =  $[\text{H}^+][\text{A}^-]/[\text{HA}]$ 
    - Smaller  $K_A$ , weaker acid, higher pH
- **Weak Base** – A base which only partially dissociates in solution.
  - **Weak Base Dissociation Constant ( $K_B$ )** =  $[\text{B}^+][\text{OH}^-]/[\text{BOH}]$ 
    - Smaller  $K_B$ , weaker base, lower pH

### Conjugate Acid/Base Pairs

- **Conjugate Acid** – The acid formed when a base gains a proton.
- **Conjugate Base** – The base formed when an acid loses a proton.
- **Conjugate Relation** –  $K_A$  and  $K_B$  are inversely related, so if one is large the other is small (strong acids conjugate with weak bases, weak acids conjugate with strong bases).

### Salt Formation

**Neutralization Reaction** – The reaction of an acid and base which produces a salt, and usually water as well. These reactions usually run to completion and the salt may precipitate or remain in solution, depending on the specifics of the situation.

- **Strong Acid/Strong Base** – In equimolar concentrations, the acid and base completely neutralize each other, forming salt and water with a pH of 7.
- **Strong Acid/Weak Base** – In equimolar concentrations, a salt forms, but usually no water since weak acids are generally not hydroxides. The resulting solution is in the acidic pH range.
- **Weak Acid/Strong Base** – In equimolar concentrations, the salt reacts with water to form an acid and hydroxide ions. The resultant solution will have a higher hydroxide concentration than proton concentration and so will be in the basic pH range.

**Hydrolysis** – The reverse of a neutralization reaction, in which a salt combines with water to produce an acid or base.

### Polyvalence and Normality

**Acid Equivalent** – One mole of  $\text{H}^+$  (or  $\text{H}_3\text{O}^+$ ) ions.

**Base Equivalent** – One mole of  $\text{OH}^-$  ions.

**Polyvalent Substances** – Some acids/bases are polyvalent, releasing more than 1 equivalence per each mole of that substance. *Example: 1 mole of  $\text{H}_2\text{SO}_4$  can produce 2 acid equivalents (2 moles of  $\text{H}_3\text{O}^+$ ).*

- **Normality** – Normality is the number of equivalents that can be liberated from a certain concentration (moles/Liter) of a substance. *Example: 1M  $\text{H}_2\text{SO}_4$  is 2 normal. 3M  $\text{H}_2\text{SO}_4$  is 6 normal.*
- **Equivalent Weight** – The mass of a substance that can liberate 1 equivalent. *Example:  $\text{H}_2\text{SO}_4$  (MM – 98g/mol) = 2 equivalents/98grams = 1 equivalent/49 grams. Equivalent Weight = 49 grams.*

### **Common Polyvalent Acids**

- $\text{H}_2\text{SO}_4$
- $\text{H}_3\text{PO}_4$
- $\text{H}_2\text{CO}_3$

### **Common Polyvalent Bases**

- $\text{Al}(\text{OH})_3$
- $\text{Ca}(\text{OH})_2$
- $\text{Mg}(\text{OH})_2$

### Amphoteric Species

**Amphoteric (Amphiprotic)** – A species which acts like an acid in a basic environment or like a base in an acidic environment.

- **Common Amphoteric Examples**
  - Water.
  - Partially dissociated polyprotic acids.
  - Partially dissociated polyvalent bases.
  - Oxidizing/reducing agents.

### Titration and Buffers

**Titration** – Procedure used to determine the molarity of a known reactant in a solution.

A solution of known volume and unknown concentration is reacted with a solution of known volume and known concentration.

- **Acid-Base Titrations** – The most commonly tested titration type, used to determine the molarity of a known acid or base in solution.  $N_A V_A = N_B V_B$ 
  - **Equivalence Point** – The point at which the equivalents/moles of acid and base in solution are equal. In strong acid/strong base titrations, the equivalence



point is around 7 pH. Polyprotic acids/bases will have multiple equivalence points.

- **Equivalence Point Determination (2 Methods)**

1. **Graphical** – Plot “solution pH” versus “volume of added titrant”, the equivalence point is the center of the steepest slope.
  2. **Color Indicator** – A weak organic acid/base (weaker than the acid/base being titrated so it does not react until all titration acid/base has reacted), which changes color when protonated, is added. Reaction and subsequent color change marks the *end point*, which can be assumed as very close and practically equal to the equivalence point.
- **Halfway Point** – If at the equivalence point, all of the acid/base has dissociated, then at the half equivalence point only half of the acid/base has dissociated and so the ratio of conjugate acid and base is 1:1. Plugging this into the Henderson-Hasselbalch equation, at the halfway point the  $\text{pH} = \text{pK}_\text{A}$ .
- **Strong Acid/Strong Base Titration (Equivalence pH = 7)**
  - **Weak Acid/Strong Base Titration (Equivalence pH > 7)**
  - **Strong Acid/Weak Base Titration (Equivalence pH < 7)**

**Buffer Solution** – A mixture of conjugate acid and base which reacts with acids or bases to limit changes in pH.

- **Buffering Capacity** – The amount of acid/base a buffer can absorb. If the buffering capacity is exceeded, there will be a drastic change in pH/pOH.
- **Common Buffer Solutions**
  - $\text{HC}_2\text{H}_3\text{O}_2$  with  $\text{Na}^+\text{C}_2\text{H}_3\text{O}_2^-$  ( $\text{C}_2\text{H}_3\text{O}_2^-$ )
  - $\text{NH}_3$  with  $\text{NH}_4^+\text{Cl}^-$  ( $\text{NH}_4^+$ )

In acidic solutions with relatively few dissociated protons, the water ionization protons may affect pH.

## REDOX REACTIONS AND ELECTROCHEMISTRY

### Oxidation-Reduction Reactions

**Oxidation-Reduction (Redox) Reactions** – The transfer of electrons from one chemical species to another.

- **Oxidation** – The loss of electrons and subsequent increase in charge.
  - **Oxidizing Agent** – A species which accepts electrons. Oxygen is the most common oxidizing agent, hence the name. Oxidizing agents are themselves reduced in a reaction.
- **Reduction** – The gain of electrons and subsequent reduction in charge.
  - **Reducing Agent** – A species which donates electrons. Reducing agents are themselves oxidized in a reaction.

- **Law of Conservation of Charge** – Electrical charge can neither be created nor destroyed. Oxidation and Reduction are always coupled. When one occurs, so does the other.

### Assigning Oxidation Numbers

1. Oxidation number of a free element is 0.
2. Oxidation number of a monatomic ion is equal to the charge of that ion.
3. Oxidation number of group IA is +1, of group IIA is +2, of group VIIA is -1.
4. In most, but not all, compounds the oxidation number of oxygen is -2.
5. The oxidation number of Hydrogen is +1 when bonded to more electronegative species or -1 when bonded to less electronegative species (Groups IA & IIA).
6. The sum of oxidation numbers within a compound equal the overall charge on that compound.
7. \*HINT\* Conventional formula writing usually places cations first and anions second. This fact may come in handy on test day.

### Balancing Redox Reactions

- **Half-Reaction Balancing Method** – To balance a redox reaction, the number of atoms on each side as well as the sum charges on each side must be equal.
  1. Separate the 2 half reactions.
  2. Balance the atoms of each half reaction (except H and O).
    - For acidic solutions, add  $\text{H}_2\text{O}$  to balance O atoms and  $\text{H}^+$  to balance H the atoms.
    - For basic solutions, add  $\text{H}_2\text{O}$  to balance the O atoms and  $\text{OH}^-$  to balance the H atoms.
  3. Balance the charges of each half reaction by adding  $e^-$  as necessary and then multiplying each half reaction by any coefficient necessary.
  4. Add the half reactions together as in Hess' Law.

### Electrochemical Cells

**Anode** – The electrode where oxidation occurs. *AN OX*

**Cathode** – The electrode where reduction occurs. *RED CAT*

**Galvanic (Voltaic) Cell** – Nonrechargeable batteries are only galvanic cells. The redox processes within galvanic cells are always spontaneous. Since they give off energy, their inherent change in Gibbs energy is negative, resulting in spontaneity. The electromotive force is always opposite Gibbs energy, and so is positive in this instance, that is to say that electrical current runs in the opposite direction of electrons. The movement of charge (electrons) results in a conversion of electrical potential energy into kinetic energy. By separating the two half reactions and forcing the electrical movement through a conductive wire and placing electrically run components along that wire, we can harness this energy conversion.

- **Galvanic Electrodes** – Two electrodes of distinct chemical identity are placed in two separate compartments called *half cells*. The two electrodes are connected by an electrically conductive wire.
- **Half Cells** – Two separate compartments each containing a separate half of the redox reaction, either oxidation or reduction. Within both compartments is a solution of cations and anions surrounding that compartment's electrode. The half cells are connected by a *salt bridge*.
- **Salt Bridge** – A tube containing an inert salt in a gelatinous mixture. This salt is most often  $\text{KNO}_3$ . The salt can contribute ions to either half cell solution to maintain the neutrality of each solution. Without the salt bridge, each side would quickly build up a charge strong enough to counteract the EMF, halting the reaction altogether.
- **Cell Diagram** – anode|anode solution||cathode solution||cathode

**Electrolytic Cell** – The opposite of a galvanic cell, in which the movement of charge (electrons) is forcibly reversed, such as while charging a rechargeable battery. For this reason, electrolytic redox reactions are nonspontaneous, requiring an overall input of energy. The components of an electrolytic cell are the same as for a galvanic cell, except the direction of charge is reversed. The cathode of the battery is attached to an external energy source anode with higher potential, and so becomes negatively charged itself. The anode of the battery is connected to an external energy source cathode with higher potential, and so becomes positively charged itself.

- **Faraday's Constant (F)** = 100,000 Coulombs/mol  $e^-$ , or the charge carried by one mole, or one equivalent, of electrons.

**Concentration Cell** – A special type of voltaic cell, in which the components and direction of current are the same. The only difference is that both electrodes are chemically identical. A difference in ionic concentrations in each half cell results in the potential necessary to drive the reaction. Once the ionic concentrations in each half have equalized, the concentration is in equilibrium and can do no more work.

### Electrode Charge Designation

- **Negative Movement** – Electrons move from the negative electrode to the positive electrode.
- **Positive Movement (Current)** – Positive movement is always equal and opposite to negative movement, and so current moves from the positive electrode to the negative electrode.
  - **Amperes (A)** – 1 Ampere = 1 Coulomb / second

### Reduction Potentials and the Electromotive Force

**Reduction Potential** – The potential, measured in volts (V) for a chemical species to be reduced (gain electrons), the more positive the reduction potential the more likely

it is to be reduced. In a reaction, the species with the highest reduction potential will be reduced.

- **Standard Hydrogen Electrode (SHE)** – An electrode of hydrogen has an arbitrary reduction potential of zero. All other reduction potentials are set relative to that of Hydrogen.
- **Standard Reduction Potential ( $E_{\text{red}}^{\circ}$ )** - The reduction potential of a particular species, measured in volts (V), at standard state. That is 25 degrees celsius or 298 Kelvin at 1 atmosphere of pressure and in 1 Molarity concentration.
  - **Galvanic Cell (Primary Cells) Electrodes**
    - Electrode with higher reduction potential is spontaneously reduced, and so is the cathode.
    - Electrode with lower reduction potential is spontaneously oxidized, and so is the anode.
  - **Electrolytic Cell (Secondary Cell) Electrodes**
    - Electrode with higher reduction potential is nonspontaneously oxidized, and so is the anode.
    - Electrode with lower reduction potential is nonspontaneously reduced, and so is the anode.

**Electromotive Force (emf or  $E^{\circ}_{\text{cell}}$ )** – The difference in potential between two half cells. Found by subtracting the lower reduction potential from the higher reduction potential ( $E_{\text{red}}^{\circ} \text{ higherRP} - E_{\text{red}}^{\circ} \text{ lowerRP} = \text{emf}$ ) or by reversing the lower reduction potential into an oxidation potential and adding that to the higher reduction potential ( $E_{\text{red}}^{\circ} \text{ higherRP} + E_{\text{ox}}^{\circ} \text{ lowerRP} = \text{emf}$ ). \*Note\* Reduction potentials are NEVER balanced or multiplied before being combined. Technically, changing the amount of a species does not change the reduction potential of that species.

- **Voltmeter** – A device used to measure the emf of a system.
  - **Potentiometer** – A type of voltmeter which draws no current and gives more accurate readings of the potential between two electrodes.

### Thermodynamics of Redox Reactions

#### **EMF and Gibbs Free Energy**

- **Change in Gibbs Free Energy ( $\Delta G$ )** – The change in the chemical potential of a reaction, or the change in the amount of energy available in a chemical system to do work. If change of G is negative, potential energy is being spontaneously lowered. If change of G is positive, something is nonspontaneously giving the system more potential energy, which it can later use to do more work.
  - $\Delta G = -nFE_{\text{cell}}$ , for standard state conditions

#### **The Effect of Concentration on EMF**

- **Nernst Equation**

- $E_{\text{cell}} = E_{\text{cell}}^{\circ} - (RT/nF)(\ln Q)$ , for non-standard state conditions (concentrations other than 1 M), where Q is the reaction concentration quotient for the reaction at a given point in time.

### **EMF and the Equilibrium Constant ( $K_{\text{eq}}$ )**

- $\Delta G = -nFE_{\text{cell}} = -RT \ln K_{\text{eq}}$
- $-\Delta G = nFE_{\text{cell}} = RT \ln K_{\text{eq}}$ 
  - The natural log of any number less than one is negative and the natural log of any number greater than one is positive. The natural log of 1 is zero, and in this case the reaction is already at equilibrium.