AP Chemistry Notes

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Contents

1 Atomic Structure and Properties

1.1 Elemental Composition of Pure Substances & Composition of Mixtures

AP Topics: 1.3 and 1.4

An element is defined as a substance that cannot be broken down into other substances by chemical means. Any single element consists of only one type of atom. The elements are displayed on the periodic table.

A compound is formed when a number of these elements bond together. Compounds always have a fixed composition of atoms. For example, the water molecule always contains two hydrogen atoms bonded to one oxygen atom, and always has the formula H_2O. When the ratio of each type of atom is fixed within a compound, so is the ratio of the masses of the atoms. If that ratio changes, then the chemical formula changes, and the substance is no longer water. All pure substances are either elements are compounds.

Unlike a pure substance, a mixture has varying composition and is made up of a number of pure substances. Mixtures are either:

- Homogeneous - uniform composition throughout a given sample but with a composition and properties that vary from one sample to another. All solutions are homogeneous mixtures.
- Heterogeneous - separate, distinct regions within the sample with a composition and properties that vary from one part of the mixture to another.

Compounds can only be separated by a chemical change whereas mixtures can be separated by a physical change.

Each element has several numbers displayed on the periodic table. Atomic numbers are typically printed above the symbol and the average atomic masses are printed below the element symbol.

The chemical formula of a compound shows the exact ratio of the atoms of the elements that are present in the compound. The numbers of each element are recorded using a subscript to the right of the element symbol.

To determine the percentage by mass composition of an individual element within a compound, simply express the mass of each element as a percentage of the total mass of the compound.

The empirical formula of a compound is the simplest whole number ratio of the atoms of each element in that compound. Entirely different and unrelated compounds, with entirely different molecular formulas, may have the same empirical formula.

Empirical formulas can be calculated from mass data. Here are the four steps:

- Take the percentage of each element present in the compound and assume a sample mass of 100 g, thus converting the $\%$'s to a mass in g of each element.
- Find the atomic mass of each element on the periodic table. Divide the mass in grams by the atomic mass, giving the moles.
- Find the smallest number of moles calculated, and divide all the results of the calculations by that number.
- The results should be in a convenient whole number ratio and gives the empirical formula.

Once the empirical formula has been established, and given further appropriate data, the molecular formulas of a compound can be calculated. The molecular formula tells us exactly how many atoms of each element are present in the compound rather than just the simplest whole number ratio. The molecular formula is a multiple of the empeirical formula.

To find the molecular formula it is necessary to know the molar mass or average atomic mass of the compound.

1.2 Moles and Molar Mass

AP Topic: 1.1

In chemistry, amounts of substances are measured in a quantity called moles. The mole is a standard number of particles and is defined as the amount of any substance that contains the same number of particles as there are C^{12} atoms in 12 g of the C^{12} isotope.

The actual number of particles in a mole, known as the Avogadro's constant, is found to be 6.022×10^{23} particles per mole, and has the unit mol^{-1}. For example, 12 g of carbon atoms contains one mole of C^{12} atoms.

Since the mass of an atom is so very tiny, we often use a certain unit to express the mass of an individual atom. That unit is the atomic mass or amu.

The average atomic masses of atoms shown on the periodic table can be used to determine the molar masses of compounds by simple summation.

The molecular/formula mass or molar mass is found by adding all of the individual AAM's together in one molecule of a molecular compound or one formula unit of an ionic compound.

We can apply the following relationships to calculate the numbers of moles of any element or compound.

$$\text{Moles of an element} = \frac{\text{mass of sample}}{\text{AAM}} = \frac{\text{mass of sample}}{\text{Molar Mass}}$$

$$\text{Moles of a molecular compound} = \frac{\text{mass of sample}}{\text{molecular mass}} = \frac{\text{mass of sample}}{\text{Molar Mass}}$$

$$\text{Moles of an ionic compound} = \frac{\text{mass of sample}}{\text{formula mass}} = \frac{\text{mass of sample}}{\text{Molar Mass}}$$

Once we has established how to determine the empirical and molecular formula of compunds, we can bring those formulas together in chemical equations that summarize chemical reactions. Since individual formulas are molar ratios of atoms, then balanced chemical equations are molar ratios of compounds. If we can calculate the moles of any one substance in a chemical reaction from its mass, then, by ratio, we can find the moles of any other substance in the balanced equation.

1.3 Mass Spectroscopy of Elements

AP Topic: 1.2

Average atomic mass is defined as the weighted average of the masses of all the atoms in a normal isotopic sample of the element based upon the scale where 1 mole of atoms of the C^{12} isotope has a mass of exactly 12.00 g.

Elements occur in nature as a number of different isotopes. Atoms with the same number of protons and electrons, but different numbers of neutrons are called isotopes. Most elements have at least two stable isotopes. This leads to the modification of the postulate in Dalton's atomic theory that claimed all atoms of a given element were identical.

Since it is the electrons in atoms that affect the chemical properties of a substance, isotopes of the same element have the same chemical properties.

All periodic tables have average atomic masses that are not integers. The non-integer values mean that there is more than one isotope of that element that exist in nature.

A simple calculation can be applied to calculate the average atomic mass when considering all of the isotopes present in a natural sample.

$$\text{Average atomic mass} = \frac{\sum(\%\text{of each isotope})(\text{atomic mass of each isotope})}{100}$$

Mass spectroscopy is used to detect isotopes and provide evidence for their existence. In the simplest of terms, a machine known as a mass spectrometer uses an ionizing beam of electrons to analyze a sample of an element by turning atoms into positive ions. The resulting individual ions are then sorted by mass. Since a sample of a single element can contain atoms with different numbers of neutrons, we can expect a number of distinct ions of different masses in the spectrum.

A typical mass spectrum contains relative intensity plotted on the y-axis and shows the abundance of each isotope. The mass/charge ratio is plotted on the x-axis and is equivalent to the mass of each isotope.

1.4 Atomic Structure and Electron Configuration

AP Topic: 1.5

The Rutherford model of the atom, where a dense nucleus containing positive protons is surrounded by negative electrons, is based aroudn the attraction between the oppositely charged protons and electrons, and is governed by Coulomb's Law. Coulomb's law states that the force between two charged particles, q_1 and q_2 is inversely proportional to the square of the distances between them.

$$F \propto \frac{q_1 q_2}{r^2}$$

When q_1 and q_2 have the same sign, the force is repulsive, and when they are of opposite signs, the force is attractive, like charges repel and opposite charges attract.

Bohr adapted Rutherford's model and suggested that electrons could only travel in fixed orbits or shells around the nucleus.

Using a device called a spectroscope, it was found that gaseous elements emitted electromagnetic radiation when heated. The light that was emitted consisted of discrete packets of energy, and each element emitted a unique pattern of radiation. It was discovered that the release of radiation was cuased by electrons in the atom absorbing energy and being promoted to a shell further away from the nucleus.

When the electron falls back to its original, lowest energy shell, it releases the energy that it absorbed when it was promoted to the higher energy shell. This release of energy creates a line in the spectrum. Note that an electron in an atom remains in its lowest energy state unless otherwise disturbed.

Since the shells are in fixed positions, the difference in energies between them, is also fixed. This gives a unique and identifiable pattern for each element. This, of course, would be an emission brightline spectrum: the spectrum of bright lines that is provided by a specific emitting substance as it loses energy and return to its ground state.

Absorption spectra can also be created: a graph of display relating how a substance absorbs electromagnetic radiation as a function of wavelength.

Sometimes an electron may gain sufficient energy to completely overcome the force of attraction from the nucleus and it may be ejected from the atom. The energy required to achieve this is called the ionization energy.

The models that suggested that the electron was a discrete particle, and that there were only strictly defined fixed orbits in which electrons travelled did not explain several of the observed properties of the atom and electrons. Works by Bohr, and new marrying classical physics and new quantum ideas suggested that the electron also had some wave-like characteristics. The description of the electron in this wave-particle duality can be briefly touched upon. First some vocab:

- Electromagnetic radiation: radio waves/television/microwaves, IR, visible light, UV, X-rays, gamma rays
- Wavelength, λ: length between two successive crests
- Frequency, ν: number of waves that pass a fixed point in a second
- Amplitude: maximum height of a wave as measured from the axis of propagation
- Nodes: points of zero amplitude; always occur at $\lambda/2$ for sinusoidal waves
- Velocity: speed of the wave. All EM radiation travels at the speed of light, $c = 2.998 \times 10^8$ m/s

$$c = \lambda\nu$$

Notice that λ and ν are inversely proportional. When one is large, the other is small.

Depending on the value of the frequency and the value of the wavelength, the radiation will fall somewhere in the electromagnetism spectrum.

Schrodinger developed the wave idea for atoms and electrons and solved wave equations to make predictions about where an electron may actually be found in an atom. The result of all this work, coupled with the Heisenberg uncertainty principle led to the quantum mechanical model of the atom of that we have today, which led to the ide aof three dimensional probability maps of where any one electron may be found at any point in time within each of the shells. In summary, we can only calculate the probability of finding an electron within a given space.

The three dimensional probability maps predicted by Schrodinger are known as orbitals and they describe the likely positions of electrons within the atom. Using the Rutherford/Bohr model as the basis, the maximum number of electrons present in each shell is given by $2(n)^2$, where n is the shell number.

Each shell is further divided into subshells. The number of sub-shells that are possible within any given shell is equal to the shell number, and the sub-shells are given the letters s, p, d, f. The first sub-shell in any shell is an s sub-shell, the second is a p sub-shell, the third is a d sub-shell and the fourth is an f sub-shell.

Each sub-shell is further divided into orbitals. The s, p, d, and f sube-shells are split into 1, 3, 5, and 7 orbitals respectively, and each orbital can hold a maximum of two electrons.

The Pauli Exclusion Principle says that all of the electrons in any single atom must be unique, so if a pair of electrons are in the same orbital as one another, since their shell, sub-shell, and orbital are all the same, they must be distinguished by another method. This is achieved by giving the electrons an intrinsic property known as spin. Two electrons in the same orbital are given opposite spins, often denoted as a pair of arrows, one pointing up, and one pointing down.

As states above, the orbitals represent three-dimensional areas of space in the atom. where an electron may be foud, and the s, p, d, and f orbitals all have different shapes. s orbitals are spherical shaped, with one possible orientation on each shell.

Keep in mind there is no sharp boundary beyond which the electrons are never found. These shapes describe the most probable regions in space where an electron in that orbital is likely to be foud. The number of nodes equals equals $n - 1$ for s orbitals. p orbitals are peanut shaped and have nodal planes where the electron can never be foud, yet the electron can magically get from one side of the peanut to the other without ever going through the nodal plane. p orbitals haev 3 possible orientations on each shell.

d orbitals are double peanut shaped, with two nodal planes slicing through the nucleus. d orbitals have 5 possible orientations on each shell.

f orbitals have more complicated shapes, with three nodal planes slicing through the nucleus and 7 possible orientations on each shell.

Let's discuss the Aufbau Process for filling orbitals.

First, find out how many electrons are present.

Second, fill out the lowest energy orbitals first. The orbitals have ascending energies with 1s having the the smallest energy, 2s having the next smallest. There is pretty significant complication that arises here, which can be accomodated by considering the 4s orbital as having a slightly lower energy than the 3d orbitals, and assuming that the 4s orbital is filled before the 3d orbitals. Similarly, it is helpful to assume the 5s and 4d orbital have the same relationship.

Lastly, Hund's Rule of maximum multiplicity states that if there is more than one orbital with the same energy, then one electron is placed into each orbital before any pairing takes place. All orbitals in the same sub-shell have a similar energy, for example, all three 2p orbitals have the same energy and are therefore degenerate. As a result, if there are three electrons to be placed into the three 2p orbitals, then one electron enters the first 2p orbital, one enters the second, and one enters the third, before any are paired in the x, y, or z.

We can also modify the periodic table by moving hydrogen and helium into groups 1 and 2, respectively.

The period number shows the shell number, the block shows the type of orbital. Then you can add one electron for each element until the orbital, then sub-shell, and ultimately the shell, is full. Record the configuration in the format; shell number, block, number of electrons.

Note that Cr and Cu are anomalis and have confugirations ending 4s3d^5 and 4s3d^{10} respectively.

Rather than writing the full electron configuration as previously, the noble gas method can be employed. In this method, the electron configuration is determined by writing the previous noble gas in square brackets, and then filling the orbitals as before. For example phosphorous is [Ne]3s^{2}3p^3.

Ions are charged particles that are formed from atoms by either the los or gain of electrons; positive ions are formed by losing electrons, negative ions are formed by gaining electrons. The magnitude of the charge denotes how many electrons have been lost or gained. In each case, the electrons are either removed or added to the outermost shell meaning that when forming positive ions, d block elements lose their outer s electrons before any d electrons. In order to find the electron configuration of an ion, simply start with the electron configuration of the atom, and either remove or add electrons from there.

You should be familiar with one other method of displaying electron configurations called the orbital notation. In orbital notation, each orbital is represented by a box or horizontal line and the electrons are represented by atoms.

1.5 Photoelectron Spectroscopy

AP Topic: 1.6

Using high-energy ultraviolet or X-ray photons, it is possible for electrons in an electron to absorb sufficient energy for them to overcome their attraction for the nucleus and to be ejected from the atom. This is called the photoelectric effect. By analyzing the electrons that are ejected in this way, photoelectron spectroscopy is used gather data about the specific electronic structure of the atom. The photons used to eject electrons that have energy from the following relationship:

$$E = h\nu$$

Where h is Planck's constant and ν is frequency.

These energies exceed the ionization energy and as a result not only are the electrons able to overcome the attraction of the nucleus and are ejected from the atom, but they also gain kinetic energy. To summarize this pocess, $E = h\nu = \text{IE} + \text{KE}$.

In a PES plot, the energy associated with each sub-shell is plotted on the x-axis (in units of MJ mol^{-1}), and the relative number of electrons is plotted on the y-axis. A higher peak means a greater number of electrons. Coulomb's law predicts that electrons that are further away from the nucleus are easiest to remove, and therefore have the lowest energy. The innermost electrons, basically those other than the valence electrons are called the core electrons.

If we are given tables of successive ionization energies, the large jump in the data in this table would show in that large jump, that electron would be extremely difficult to remove and it should be assumed that that electron is a core electron. In other words, it has a higher ionization energy.

Because ionization energy is associated with only removing the outermost, least tightly held electron, it is not possible to determine the second ionization energy until the first electron has been removed. As such, the first electron is removed from a neutral atom, and the second and subsequent electrons from positive ions.

However, when considering PES, any electron can be removed at any time, and in each case the electron will be removed from the same species hence the observed PES energy will be the same for all electrons in a given subshell. This is why a single peak is associated with all of the electrons in any given subshell, but multiple ionization energies are associated with the same subshell.

Paramagnetic species are those that are attracted by a magnet and are created when unpaired electrons are present in an atom. Diamagnetic species are slightly repelled by magnets and occur when all electrons are paired.

Isoelectronic species have the same electronic configuration. As a result, they must be distinguished by some other means, such as the number of protons present.

1.6 Periodic Trends & Valence Electrons and Ionic Compounds

AP Topic: 1.7 & 1.8

The chemical and physical properties of the elements and their compounds are very dependent upon their outermost electron configurations. When the elements are arranged in the periodic table in order of ascending atomic number, a regular change in the outermost electronic configuration is observed. In turn, a regular variation of properties is also observed. This is called periodicity.

Thus, as a period is traversed, certain regular repeatable patterns can be observed which lead to the ability to make predictions about the unknown properties of elements and their compounds. This ability to predict the behavior of elements and compounds is crucial in the design of new materials.

Additionally, elements that are in the same group have similar outer electronic configurations and often behave in a similar manner to one another.

All atoms of the noble gases (Group 18) have their outer s and p orbitals filled. We will see later that these atoms require very large amounts of energy to form ions, so much in fact, that they are considered relatively inert and do not tend to form ions or many compounds.

Group 1 atoms have an electronic structure of [Noble Gas]s^1. This means that they tend to lose the s electron when they form an ion, leaving behind an inert noble gas type structure. This explains why Group 1 elements tend to only form $+1$ ions. Group 1 metals are the most reactive metal family.

Group 2 atoms have an electronic structure of [Noble Gas]s^2. This means they tend to lose the two s electrons when they form an ion, leaving behind an inert noble gas type structure. This explains why Group 2 elements tend to only form $+2$ ions. Note the names of both Group 1 and Gruop 2 metals imply bases are made when placed in water.

Groups 16 atoms have an electronic structure [Noble Gas]s^2p^4. This means that they tend to gain two p electrons when they form an ion, in order to reach an inert noble gas type structure with a charge of -2.

Group 17 atoms have an electronic structure [Noble Gas]s^2p^5. This means that they tend to gain one p electron when they form an ion in order to reach an inert noble gas type structure with a charge of -1/

Transition metals are in the d-block of the periodic table. Transition element ions yield colorful solutions when they have unpaired electrons in the d subshell. When regarding electron configurations of the transition metals, anomalies occur at chrmoium and copper to minimize electron/electron repulsion. It is all about lowering energy by minimizing electron repulsion. Transition elements form variably charged ions.

When metals and non-metals undergo chemical reactions they are generally trying to achieve a more stable state. As we have seen above, they do this by either losing electrons or gaining electrons.

The first ionization energy is formally defined as the energy required to remove one mole of electrons from one mole of gaseous atoms to produce one mole of gaseous ions.

$$\mathrm{M}(g) \rightarrow \mathrm{M}^{+}(g) + \mathrm{e}^{-}$$

The second ionization energy is defined as the energy change accompanying

$$\mathrm{M}(g) \rightarrow \mathrm{M}^{2+}(g) + \mathrm{e}^{-}$$

Ionization energies are often measured in units of kJ mol^{-1}. They have positive values indicating that energy must be "put in" in order to remove electrons. A positive energy change is described to be endothermic.

The magnitude of the ionization energy is determined by the attraction of the positive nucleus for the negative electrons that are being removed and the force of attraction is dependent upon two factors:

- The nuclear charge.
- The shielding effect of the inner electrons. Shielding is related to the distance of the electrons from the nucleus; the greater the distance the shell is from the nuclear charge, the smaller the attraction.

As a period is traversed from left to right, the first ionization energy of the elements will steadily increase. This is because the nuclear charge increases but the electrons are being removed from the same quantum shell, experiencing no extra distance from the nucleus, and are therefore held more strongly.

As a group is descended the first ionization energy of the elements will decrease because the valence electrons are in new shells, further away from the nucleus, and experience more shielding due to the core electrons, are are therefore held less strongly.

It is possible to remove more than one electron from a single atom and it is found that removing a subsequent electron is progressively more difficult. This is because once an electron has been removed, the remaining electrons experience a reduced mutual repulsion. They move slightly closer to the nucleus and as a result become slightly more attracted to the nucleus. This makes them more difficult to remove and each subsequent ionization energy increases. In addition, once one electron has been lost from the atom, subsequent electrons are being removed from a now positive species.

As a period is traversed left to right, the atomic size decreases. This is because the nuclear charge increase and the subsequent electrons enter the same shell, experiencing no extra shielding from inner electrons are are therefore attracted more tightly.

As a group is descended the atomic size increases. This is because that although there is again an increase in nuclear charge, the valence electrons enter new shells, further away from the nucleus. As a result the atomic size increases since the greater the number of shells occupied in an atom, the larger the atom.

When an atom loses electrons to form a cation, the remaining electrons will experience less mutual repulsion and as a result they are drawn closer than they were in the atom, and the cation is smaller than the parent atom. It is also true to say when a cation is formed, an atom loses a complete valence shell of electrons which has the effect of decreasing the size of the cationic species compared to the parent atom.

When an atom gains electrons to form an anion, the extra electrons that have been added to form the anion tend to repel one another. This has the effect of slightly enlarging the new anionic species.

Note that isoelectronic species may be compared by considering the number of protons present.

First electron affinity is defined as the energy change when one mole of electrons is added to one mole of gaseous atoms, to produce one mole of gaseous ions.

$$\mathsf{X}(g) + \mathsf{e}^- \rightarrow \mathsf{X}^=(g)$$

First electron affinity values are exothermic, showing that energy is released when an electron is added to a gaseous atom.

In general, first electron affinities become less negative down a group, since the electrons are being added to shells that are further from the nucleus, and hence they are pulled toward the nucleus with a decreasing strength amount of Coulombic attraction.

The second electron affinity is defined as the energy change accompanying:

$$\mathsf{X}^-(g) + \mathsf{e}^- \rightarrow \mathsf{X}^{2-}(g)$$

Electronegativity is defined as the ability of an atom within a covalent bond to attract electrons to itself. Therefore, it is not technically an atomic trend, it is a bonding trend. In summary, excluding the noble gases, electronegativity increases across a period, and decreases down a group.

We have seen that ionization energy decreases down a group, so using this assumption we can assume that Group 1 and 2 elements will increase in reactivity when their ionization energies decrease.

To summarize this section, remember when explaining periodic trends we must use effective nuclear charge, distance from the nucleus, shielding electrons, and the minimization of electron/electron repulsions.

Problems

1. Three samples of sodium chloride are analyzed and found to contain differing percentages by mass of chlorine. What does this information, alone, tell us about the three samples?
2. A hydrocarbon is found to be 7.690% H and 92.31% C by mass. Calculate its empirical formula.
3. How many moles of $CuBr_2$ are there in 0.522 g of copper(II) bromide?
4. Does $^{40}_{19}K$ and $^{40}_{18}Ar$ represent a pair of isotopes?
5. If the two isotopes of gallium, ^{69}Ga and ^{71}Ga occur in the respective percentages of 62.1 and 37.9, calculate the average atomic mass of gallium atoms.
6. Naturally occurring chlorine molecules, Cl_2, have masses of 70, 72, and 74. They occur in the percentages 56.25%, 37.50%, and 6.250% respectively. Use this data to calculate the average atomic mass of chlorine atoms and to find the relative abundance of ^{35}Cl and ^{37}Cl isotopes.
7. The brilliant red colors seen in fireworks are due to the emission of light with wavelengths around 650 nm when strontium salts such as $Sr(NO_3)_2$ and $SrCO_3$ are heated. Calculate the frequency of red light of wavelength 6.50×10^2 nm.
8. Write the electronic configuration of Al^{3+} using the noble gas core method.
9. Which peak in the spectrum for neon will have the greatest intensity?
10. Define the term 'first ionization energy' and state the two factors which influence its magnitude.
11. Arrange the following species in order of increasing size: Ar, K^+, Ca^{2+}. S^{2-}, Cl^-.
12. The first ionization energy for phosphorus is 1060 kJ/mol, and that for sulfur is 1005 kJ/mol. Why?
13. Predict the trend in radius for the following ions: Be^{2+}, Mg^{2+}, Ca^{2+}, and Sr^{2+}.

2 Compound Structure and Properties

2.1 Types of Chemical Bonds, Intramolecular Force and Potential Energy, and Structure of Ionic Solids

AP Topic: 2.1, 2.2, & 2.3

An electron cloud diagram can be thought of as a probability map of where an electron may be found at any one time.

When two atoms join together with a covalent bond, a pair of electrons is shared between the atoms. Each atom within a covalent bond has a property known as electronegativity.

Elements that have electronegativities thata re different but very similar are usually considered to be equally shared.

When one atom has a much higher electronegativity than the other, then the electrons are attracted toward the more electronegative atom, leading to an electron cloud distortion annd a re-distribution of electron cloud density.

The creation of opposite charges at either end of the molecule is called a dipole, and the bond is said to be polar covalent in this case. With a diagram with no creation of opposite charges, the bond is said to be nonpolar covalent.

The presence of dipoles, and the intermolecular Coulombic attraction between them, determines the type of intermolecular forces present in covalently bonded compounds. In turn, the type of intermolecular forces present can greatly influence the properties of the compound.

Most compounds are covalently bonded, especially carbon compounds. In covalent bonding, electrons are shared between atoms to once again achieve full s and p subshells, this time by joining together and sharing valence electrons. When they do so they form discrete molecules. Molecular formulas are given in the true ratios of atoms. One shared pair of electrons represents a single covalent bond; two shared pairs represent a double bond. These bonds usually occur between atoms that are non-metals. Unlike ionic substances, which tend to be solids at room temperature, covalent substances may exist in any state of matter at room temperature, but melt at low temperatures. These substances are nonconductors of electricity.

Atoms are ttracted to one another when the outer electrons of one atom are electrostatically attracted to the nuclei of another atom. The attraction between two atoms makes them increasingly stable, giving lower and lower potential energies.

However, as the atoms continue to approach one another and get increasingly close, there comes a point at which the two nuclei will start to repel one another. As they start to repel one another the potential energy is raised, and the two atoms become less stable.

A happy medium is reaches at a distance where the forces of attraction and repulsion result in the lowest potential energy. The distance is called the bond length, and the potential energy at that point is called the bond strength.

Since for forces of attraction that stablize atoms when they bond are attractions between electrons and nuclei, the greater the number of electrons involved, the stronger the attraction and as such, triple covalent bonds tend to be stronger than double bonds, and double bonds tend to be stronger than single bonds. Shorter bonds also tend to be stronger than longer ones.

Ionic bonding involves the transfer of electrons between atoms to form ions.

Atoms have equal numbers of protons and electrons and consequently have no overall charge. When atoms lose or gain electrons, the proton/electron numbers are unbalanced causing the particles to become charged. These charged particles are called ions. Since metals have a tendency to lose electrons to form positive ions, and nonmetals the opposite, the ionic bond is usually formed between metal and nonmetal. These strong electrostatic forces are between the charged particles are called ionic bonds. The stronger ionic bonds are formed between ions that are small and highly charged.

The ions present in an ionic solid are held rigidly in fixed positions in a giant, 3-D lattice. Ionic formulas the given in the simplest ratio of elements. These rigid structures mean that ionic compounds are not malleable or ductile and tend to be brittle.

The strong bonds in the lattie gives ionic solids high melting and boiling points and low volatility and subsequently low vapor pressures.

Ionic substances can only conduct electricity when molten or in solution, since in the solid the ions are rigidly held and cannot move.

When an ionic solid dissolves, the polar water molecules are attracted to the oppositely charged ions, and penetrate the lattice attaching themselves to the ions. The process is called hydration, and the ions are said to be hydrated. The ions become free to move when they are hydrated, and the solution will be a good conductor of electricity. Since a non-polar solvent will not be attracted to the ions in an ionic solid, the ionic bonds holding the solid together are not broken and the solid will not dissolve.

The hydration process increases the entropy (see Unit 9).

There are some following cutoffs that are somewhat arbitrary, make sure to keep in mind that bond polarity is relative.

- $\Delta\text{EN} < 0.5$: nonpolar covalent
- $0.5 \leq \Delta\text{EN} \leq 1.7$: polar covalent
- $\Delta\text{EN} > 1.7$: ionic

To recap, bonds are attractive forces that hold groups of atoms together within a molecule or crystal lattice and make them function as a unit. Bonding relates to physical properties such as melting point, hardness, and electrical and thermal conductivity as well as solubility characteristics. The system is achieving the lowest possible energy state by bonding. Energy is released when a bond is formed, therefore, it requires energy to break a bond.

Like inter bonding, intra bonding is based upon Coulombic attraction, but the attractions here are relatively very strong, making intra bonds much stronger than intermolecular forces. Recall Coulomb's Law describes forces interacting between static electrically charged particles:

$$F = k_e \left(\frac{q_1 q_2}{r^2}\right)$$

The force of attraction between the charges is attractive if the charges have opposite signs and repulsive if like-signed. Coulomb's Law can also be used to calculate the energy of an ionic bond

$$E = 2.31 \times 10^{-19}\,\text{J} \cdot \text{nm} \left(\frac{q_1 q_2}{r^2}\right)$$

There will be a negative sign on the energy once calculated. This indicates an attractive force so that the ion pair has lower energy than the separated ions. You can also use Coulomb's Law to calculate the repulsive forces between like charges.

2.2 Lewis Diagrams

AP Topic: 2.5

Lewis structures use dots to represent valence electrons in atoms when they form molecules. Lewis structures are very useful when predicting molecular shape of molecular geometry. As discussed, when atoms form molecules they share electrons to achieve full s and p subshells. Since 2 electrons are required to fill the s subshell and 6 electrons fill the p subshell, an octet of electrons is the goal. There are some exceptions to the octet rule:

- Hydrogen can handle at most 2 electrons. Be only has 4 valence electrons. Boron has 6 valence electrons.

- Expanded octets can only happen if the central element has d-orbitals which means it is from the third period or greater and can thus be surrounded by more than four valence pairs in certain compounds.
- A few stable compounds contain an odd number of valence electrons and cannot obey the octet rule.

To draw Lewis Structures:

1. Calculate the total number of valence shell electrons.

2. In a species with more than two atoms, decide which atom is the central atom. Use one pair of electrons to form a covalent bond between the terminal atoms that are bonded to the central atom.

3. Arrange the remaining electrons to complete the octets of the terminal atoms and then place any remaining electrons on the central atom.

4. If the central atoms lacks an octet, form multiple bonds by converting non-bonding electrons from terminal atoms into bonding pairs.

5. One bonding pair of electrons represents one covalent bond that in turn can be represented by a single line. Double bonds share two pairs of electrons, represented by two lines and triple bonds share three pairs of electrons, represented by three lines.

6. Any electron pairs that occur in the valence shell of an atom but do not form a bond with another atom are called nonbonding electrons or lone pairs or an unshared pair.

Occasionally when drawing a Lewis structure you may encounter a molecule with a central atom that does not have a complete octet of electrons surrounding it. The central atom in this case would be considered electron deficient. It can make up the octet by forming bonds with other compounds that have non-bonding pairs of electrons. This type of bond is called a dative or coordinate bond. These bonds are in all coordination compounds and Lewis acids/bases.

Bonds can be polar while the entire molecule isn't and vice versa. The dipole moment is a separation of charge within the molecule that is a product of the size of the charge and the distance of separation. One way for a molecule to be polar is for the bonds within the molecule to be polar and the dipoles that are present do not cancel out due to symmetry. The dipole moment can be indicated by an arrow that points toward the negative charge center with the tail of the arrow indicating the positive charge center. Molecules that have a lone pair of electrons on the central atom tend to be polar. Polar molecules will align themselves with an electric field or in the absence of an electron field, with each other.

2.3 VSEPR and Bond Hybridization

AP Topic: 2.7

The shapes of covalently bonded molecules and ions can be determined by considering the number of electron pairs aroudn the central atom. The electron pairs repel one another and try to get as far apart as possible. This theory is called Valence Shell Electron Pair Repulsion theory of VSEPR. There are some standard shapes for specific numbers of electron pairs and some simple deviations from this theory when non-bonding pairs are present around the central atom.

A non-bonding pair of electrons will repel more strongly than a bonding pair. When comparing molecular geometries, it can be seen that this has the effect of altering the bond angles. Also, molecules will have different shapes if they have the same total number of electron pairs around the central atom, but where the total is made up of different combinations of bonding and lone pairs of electrons on the central atom. Note that multiple lone pairs will be arranged with maximum separation within the molecule, which also plays a role in molecular geometry.

When considering a polyatomic molecule the question of shape must be accounted for. Outer shell, atomic orbitals of the central atoms in Lewis structures are said to hybridize or undergo hybridization. Hybrid orbitals are a blending of atomic orbitals to create an orbital of intermediate energy.

The type of hybridization present in a species is quite simple to predict. By considering the total number of electron pairs around the central atom, one can determine the total number of orbitals that need to be present, since each electron pair needs on orbital. So, by taking, one s, and as many p orbitals as required, one can determine the correct number of orbitals needed, and hence the hybridization.

Whenever a double or triple bond is formed, the first bond is always a sigma bond. All bonds after that are considered to be pi bonds. Pi bonds lead to delocalized electron clouds via the overlap of unhybridized p orbitals, giving rise to the potential for some electron movement, and for the occasional occurrence, althought rare, of a molecular substance that can conduct electricity. Pi bonds may form only if unhybridized p orbitals remaing on the bonded atom and when sp or sp^2 hybridization is present on the central atom, not sp^3 hybridization.

There is another approach used to explain bonding in molecules. Where simple Lewis and VSEPR models fail to account for the observed behavior of molecules, another more complex theory must be used.

One such example is the unexpected paramagnetic behavior of oxygen. Its bonding can be explained using molecular orbital theory which describes covalent bonds in terms of the combination of individual atomic orbitals to form molecular orbitals rather than the independent overlap of the individual atomic orbitals.

Molecular orbital theory takes into account the idea that electrons and the positive nucleus of one atom strongly perturb or change the spatial distribution of the other atom's valence electrons. A new orbital is needed to describe the distribution of the bonding electrons.

2.4 Resonance and Formal Charge

AP Topic: 2.6

When drawing a Lewis structure that involves multiple bonds, it may be possible to draw several different Lewis structures. For these structures, the best or correct structure lies in the formal charge.

The formal charges of each atom within a structure can be calculated by:

Formal charge on an atom within a lewis structure is equal to the number of valence electrons around that atom in the free atom minus the number of nonbonding electrons around that atom in Lewis structure minus half of the number of bonding electrons around that atom in Lewis structure

Formal charges show the most likely distribution of charge.

To determine which structure in a set of possible structures is most likely, choose the structure with atoms that have formal charges of zero, and/or formal charges with absolute values as low as possible, and/or keep any negative formal charges on the most electronegative atoms.

If a multiple bond is created between two atoms, the bond length observed will be shorter than the corresponding single bond. This is because a double bond is stronger than a single bond and hence pulls the atoms closed together. A triple bond is correspondingly shorter and stronger than a double bond. Multiple bonds increase the electron density between two nuclei and therefore decrease the nuclear repulsions while enhancing the nucleus to electron density attractions - either way, the nuclei move closer together and the bond length decreases. Bond order is simply the number of bonding electron pairs shared by two atoms; fractional bond orders will exist when resonance structures exist for a compound.

2.5 Structure of Metals and Alloys

AP Topic: 2.4

A metal's structure can be considered to be a close packed lattice of positive atoms/ions surrounded by a "sea" of moving, delocalized electrons. These electrons and their movement cause metals to be good conductors of electricity. The close packed atoms/ions make them good conductors of heat.

The metallic bond is the electrostatic attraction between the positive and negative charges. The flexibility of these bonds makes metals malleable & ductile.

An alloy is a mixture of metals. There are two types of alloys:

- Substitutional alloy - where one metals' atoms are replaced by another metals' atoms. In these cases the metal atoms are usually of similar radius. Alloys of this type are less malleable and ductile than the pure metals, and have densities that typically lay between the densities of the component metals. Substitutional alloys are harder than the pure metal because the substituted atoms distort the lattice.

- Interstitial alloy - additional, smaller atoms of a different element fill the spaces in the metallic lattice. Interstitial allows have similar, reduced malleability and ductility to substitutional allows since the presence of the smaller atoms make the structure more rigid and less flexible.

In both cases the sea of electrons is maintained and the alloys remain good conductors. In some cases, the surface of the allow or metal may take on a different property than the remainder of the solid, due to an oxide layer forming, following reaction with oxygen in the air.

Problems

1. Order the following bonds according to polarity: H-H, O-H, Cl-H, S-H, and F-H.
2. Draw a lewis diagram for PCl_6^-
3. Predict the molecular structure of the sulfur dioxide molecule. Is this molecule expected to have a dipole moment?
4. Draw a lewis structure for SO_2. Identify the number of bonding & lone pairs around the central atom and predict the bond angles.
5. How is the xenon atom in XeF_4 hybridized? What is its electron geometry? What is its molecular geometry? What are the bond angles? Is the molecule polar or nonpolar?

3 Properties of Substances and Mixtures

3.1 Solids, Liquids, and Gases

AP Topic: 3.3

All matter has two distinct characteristics. It has mass and it occupies space.

Solids have a definite shape and definite volume. The particles in a solid are packed tightly together and only vibrate gently around fixed positions.

Liquids have no shape of their own but take the shape of their container. A liquid has a definite volume. The particles in a liquid are free to move.

Gases have neither a definite shape nor volume. The particles in a gas spread apart filling all the space of the container avaliable to them.

Solids fall broadly into two categories; crystalline, where a regular, ordered, repeatable 3-D structure of particles if found, or amorphous, where the arrangement of particles is not regular or ordered. However, in both cases, the particles in the solid have very little energy and move very little in relation to one another.

Liquids have some properties

- Fluidity: liquids have the ability to flow. Gases are also fluid.
- Viscosity: the measure of the resistance to flow. Molecules with large intermolecular forces have greater viscosity but viscosity also increases with molecular complexity. Viscosity decreases with increasing temperature.
- Buoyancy: the upward force a liquid exerts on an object

Modeling a liquid is difficult. Like solids, liquids have particles that are very close together, but unlike solids the particles in liquids are constantly moving and colliding with one another, have significantly greater energy, and move a lot in relation to one another. Liquids have both strong intermolecular forces and quite a bit of motion.

Since solids and liquids tend to have their particles very close together, their volumes are often very similar.

Since, in a gas, the particles possess enough energy to overcome any intermolecular forces and hence move around completely freely and with large spaces between them, a liquid represents particles in an intermediate state between the extremely ordered and low energy state of a solid, and the extremely disordered and high energy state of a gas. Solids have very strong IMFs and next to no motion.

Gases will be described later in this chapter.

If you consider the solid, liquid, and gas state of one particular substance, in most cases teh solid is more dense than liquid which is more dense than gas.

An exception to this is water. Ice floats meaning that ice is less dense than liquid water.

All of the properties of solids and liquids such as viscosity, surface tension, hardness, etc., are dependent upon how the particles that make up the solid or liquid are arranged, and the extent of the attractions between those particles.

Since the different states of matter have particles with differing energies, converting between them requires a change in energy. The changes in energy associated with phase changes can be quantified in heating and cooling curves. You should know that matter can change from one phase to another by adding or removing energy and there are six phase changes.

Phase changes that require energy (also known as endothermic)

- Melting: solid to liquid
- Vaporization: liquid to gas, occurs when molecules have enough energy to escape the pull of the other molecules
- Sublimation: solid to gas

Phase changes that release energy (exothermic)

- Condensation: gas to liquid
- Freezing: liquid to solid
- Deposition: gas to solid

A phase diagram represents phases of matter as a function of temperature and pressure.

There is some vocab related to phase diagrams

- Triple Point - the point on a phase diagram that shows the temperature and pressure combinations at which all the phases exist at equilibrium
- Critical Temperature - temperature above which the vapor cannot be liquefied
- Critical Pressure - pressure required to liquefy at the critical temperature
- Critical Point - critical temperature and pressure coodinates

Each phase boundary represents an equilibrium set of pressure and temperature conditions.

3.2 Intermolecular Forces

AP Topic: 3.1

Now it is time to consider the forces that condense matter. The forces that hold one molecule to another molecule are referred to as intermolecular forces (IMFs). These forces arise from unequal distribution of the electrons in the molecule and the electrostatic attraction between oppositely charged portions of molecules. IMFs are the forces between molecules.

Physical properties such as melting points, boiling points, vapor pressures, etc. can be attributed to the strength of the intermolecular attractions present between molecules. The lower the boiling point or vapor pressure of melting point, the weaker the intermolecular attractions. When the intermolecular forces of two different substances are similar, the substances tend to be miscible.

Inter bonding is based on the Coulombic attractions between opposite charges, but since the individual charges are usually relatively small, inter bonding is a relatively weak attraction when compared to intra bonding.

The presence of dipoles, and the intermolecular Coulombic attraction between them, determines the type of intermolecular forces present in covalently bonded compounds. In turn, the type of intermolecular forces present can greatly influence the properties.

Londin Dispersion Forces (LDF's) are small electrostatic forces that are caused by the movement of electrons within the covalent bonds of molecules that would otherwise have no permanent dipole. As one molecule approaches another the electrons of one or both are temporarily displaced owing to their mutual repulsion. This movement causes small, temporary dipoles to be set up on the surface of the particles, which then attract one another. These attractions are called London Dispersion Forces, and exist between all atoms and molecules. Without these forces, we could not liquefy covalent gases of solidify covalent liquids.

London dispersion forces increase with surface area and with the polarizability of the atom or molecule. Polarizability in turn increases with increases number of electrons. In short, larger molecules with larger surface areas have more electrons, which have greater polarizability. This leads to more London dispersion forces, greater attractions and therefore higher boiling points.

On descending group 18 the atoms of the elements get bigger, have more electrons and larger surface areas. This increases the London dispersion forces between them, making them more difficult to separate and increasing their boiling points.

When molecules that have permanent dipoles come together, they will arrange themselves so that the negative and the positive ends of the molecule attract one another.

Molecules eventually align in order to find the best compromise between attraction and repulsion. The attractions are called dipole-dipole. Compounds exhibiting dipole-dipole IMFs have higher melting and boiling points than those exhibiting weaker IMFs.

A similar intermolecular, electrostatic force is created when a polar molecule approaches a nonpolar molecule and induces a dipole in it. This is called a dipole induced dipole interaction. The polar molecule induces a temporary dipole in the nonpolar molecule. Larger molecules are more polarizable than smaller molecules since they contain more electrons. Larger molecules are more likely to form induced dipoles.

A third force involving dipoles is when a polar molecule interacts with an ion. This is called an ion-dipole force.

Each of these forces that include dipoles all rely on the Coulombic attaction between opposite charges.

Hydrogen is an exceptional element in that when it forms a covalent bond its electron is held to one side of the nuecleus leaving the other side completely exposed. Any approaching negatively charged group can get very close to the hydrogen nucleus and this produces an unexpectedly large electrostatic attraction. These electrostatic attractions are exaggerated when H is bonded to a more electronegative element that is small enough to allow significant intermolecular interaction. Such intermolecular, electrostatic attractions are a special type of dipole-dipole force called hydrogen bonds. This is typically the strongest IMF. The unique physical properties of water are due to the fact that it exhibits hydrogen bonding between separate water molecules. As a result of these attractions, water has a high boiling point, high specific heat, and many other unusual properties.

The occurrence of hydrogen bonds has two important consequences

- It gives substances containing them unusually high boiling points
- Substances containing them tend to be more viscous

Both are explained by the increased attraction betweem molecules caused by hydrogen bonding, making it more difficult to separate them.

3.3 Solubility

AP Topic: 3.10

When the intermolecular forces of two substances are similar, the substances tend to be miscible. Ionic substances tend to be attracted to and dissolve in polar substances such as water. Nonpolar substances tend to dissolve in nonpolar solvents.

The important thing to remember here is this. In order for any solute to dissolve in any solvent, solute-solute and solvent-solvent attractions must be broken, and solute-solvent attractions must be made. It is the combination of these factors that determines if a solute will dissolve in any particular solvent, and only when the solute-solvent interactions are relatively strong compared to other attractions, will the solute dissolve.

Consider a liquid in a sealed container. Even if the liquid is beliw its boiling point a few of the molecules will possess enough energy to overcome the intermolecular forces holding them together and escape into the vapor phase above the liquid. The weaker the intermolecular forces between the molecules, the easier this process will be and the more molecules will enter the vapor phase. This causes a relatively high vapor pressure. So, in summary, weak intermolecular forces cause liquids to have low boiling points, they are said to be volatile and will have high vapor pressures, and vice-versa.

Vapor pressure increases significantly with temperature. Increasing the temperature increases the kinetic energy which facilitates escape and the speed of the escapees. They bang into the sides of the container with more frequency and more energy. More molecules can attain the energy needed to overcome the IMFs in a liquid at a higher temperature since the kinetic energy increases.

In general, as molar mass increases, vapor pressure decreases, because as molecules increase in molar mass, they also increase in number of electrons. As the number of electrons increase, the polarizability of the molecule increases so more induced dipole-induced dipole or dispersion forces exist, causing stronger attractions to form between molecules. This decreases the number of molecules that escape and thus lowers the vapor pressure.

In the body of a liquid, all of the particles experience forces in three dimensions around them. This results in no net forces on these particles. However, these particles that are at the surface of the liquid, have no particles above them, and as such they arep ulled with a net force into the body of the liquid. This cohesion between particles of liquid, causes the liquid to contract to the smallest possible size and creates an internal pressure at the surface that can resist and external pressure. This is why it is possible to float very small objects with higher density than water, on the surface of water, and why water tends to bead into droplets. High surface tension indicates stronger IMFs.

If a liquid is placed into a very thin tube, the combination of cohesive forces within the liquid itself and adhesive forces between the liquid and the walls of the tube, can add up to overcome the force of gravity, and the liquid can be drawn up the tube without an external force being applied. The narrower the tube, the more the surface area of the glass, the higher the column of water climbs. The weight of the column sets the limit for the height achieved.

Both surface tension and capillary action rely upon the strength of interparticular attraction between the liquid particles.

In order for a substrate to interact with an enzyme, an intermolecular attraction must exist. In proteins, the primary, secondary, tertiary, and quaternary structures will lead to different three dimensional shapes that, depending on their orientation, may be attracted to polar water molecules or repelled.

3.4 Properties of Solids

AP Topic: 3.2

There are two broad categories for solids: crystalline and amorphous.

Crystalling solids have molecules packed together in a regular, repeating way. They are arranged in an orderly, geometric, three dimensional structure. The smallest repeating part of a crystalline structure is called a unit cell.

Molecular solids are discrete covalently bonded molecules at each of its lattice points. Units are molecules, held together by intermolecular forces using hydrogen bonds, dipole-dipole, or dispersion forces. Molecular solids are made from non-metals. Characterized by strong covalent bonding within the molecule yet weak forces between the molecules; therefore they tend to have low melting points and do not conduct electricity. Most are not solid at room temperature.

Atomic solids are where atoms of the substrance are located at the lattice points. Unit particles are atoms. They vary from being soft with very low melting points to being very hard with very high melting points and from being poor to excellent conductors.

Covalent network solids are composed of strong directional covalent bonds that are best viewed as one "giant molecule". The elements of group 14 can make four covalent bonds, and as such allow them to bond together in large, continuous networks.

Pure semiconductors like silicon are generally poor conductors of electricity, but when 'doped' the conductivity increases and can be controlled. WHen the doping is carried out with an element that has an extra valence electron compared to silicon, an n-type conductor is produced.

Conversely, when the doping is carried out with an element that has one less valence electron compared to silicon, a p-type conductor is produced. Disrupting the valence shells of the silicon atoms in this manner effectively allows electrons to flow, and the previous insulator becomes a good conductor. The boundaries between p and n are called p-n junctions, and the control of electrons through these junctions forms the basis of electronics.

Metallic solids have atoms that are surrounded by delocalized valence electrons. Metals are characterized by high thermal and electrical conductivity, malleability, and ductility. These properties are explained by the non directional covalent bonding found in metallic crystals. It is difficult to separate atoms, but easy to move them provided they stay in contact with each other. Melting points and hardness varies widely.

A metal's structure can be considered to be a close packed lattice of positive ions surrounded by a "sea" of moving, delocalized electrons. These electrons and their movement cause metals to be good conductors of electricity. The close packed ions make them good conductors of heat.

Noble gases can form atomic solids with very low melting and boiling points.

Ionic solids contain ions at the points of the lattice that describe the structure of the solid. Each ion in an ionic solid is surrounded by ions of the opposite charge in a 3D crystal lattice. This network gives ionic solids hardness. This structure also means that ionic compounds are not malleable or ductile and tend to be brittle, since when the ordered structure is disrupted, like charges repel, and the solid splits paart. Ion-ion Coulombic forces are the strongest of all attractive forces. "IMFs" usually implies covalently bonded substances, but can include ionically bonded substances as well. Ionic bonds can be considered both an intra bond and an inter bond.

In the ionic structure the lattice of ions is held together by strong electrostatic interactions between them. The strong bonds give ionic solids high melting and boiling points and low volatility and subsequently low vapor pressures.

Ionic substances can only conduct electricity when molten or in solution, since in the solid the ions are rigidly held and cannot move.

When an ionic substance dissolves, the polar water molecules are attracted to the oppositely charged ions, and penetrate the lattice attaching themselves to the ions. The process is called hydration, and the ions are said to be hydrated. The ions become free to move when they are hydrated, and the solution will be a good conductor of electricity. Since a nonpolar solvent will not be attracted to the ions in an ionic solid, the ionic bonds holding the solid together are not broken and the solid will not dissolve.

Amorphous solids have particles that are not arranged in a regular repeating pattern. Amorphous means "without shape".

Intermolecular forces are especially important in large, biochemical and organic molecules. These intermolecular forces of attraction can occur within a single molecule, or between two separate molecules. When occurring within a single molecule, the physical shape and properties of these molecules can be significantly affected.

3.5 Kinetic Molecular Theory

AP Topic: 3.5

All substances have three phases: solid, liquid, or gas. Substances that are solids or liquids under room conditions may also exist as gases, often referred to as vapors. Many of the properties of gases differ from those of solids and liquids.

- Gases are made up of particles that have large amounts of energy .
- A gas has no definite shape or volume, and will expand to fill as much space as possible.
- As a result of the large amount of empty space in a volume of gas, each molecule of a gas behaves largely as though other molecules were absent.
- Gases are easily compressed.
- Gases will mix completely with any other gas.
- Gases exert pressure on their surroundings.

Pressure is the force acting on an object per unit area.

The SI unit of pressure is Pascal.

- 1 Pa = 1 N/m^2
- 1 N = 1 kg·m/s^2

Gravity exerts a force on Earth's atmosphere. A column of air 1 m^2 in the cross section extending to the top of the atmosphere exerts a force of 10^5N. Thus the pressure of that column of air is 100 kPa.

Atmospheric pressure is measured with a barometer. If a tube is completely filled with mercury and inverted into a container of mercury open to the atmosphere, the mercury will rise until the pressure due to the mass of the mercury column is the same as atmospheric pressure. Standard atmospheric pressure is the pressure required to support 760 mm of Hg in a column.

$$1.00\text{atm} = 760.\text{mmHg} = 760.\text{torr} = 1.0325 \times 10^5\text{Pa} = 101.325\text{kPa}$$

In the laboratory, the pressures of gases not open to the atmosphere are measured using a manometer. A manometer consists of a bulb of gas attached to a U-tube containing Hg. If the U-tube is closed, then the pressure of the gas is the difference in the height of a liquid. If the U-tube is open to the atmosphere, a correction needs to be added

- If $\text{P}_{\text{gas}} < \text{P}_{\text{atm}}$ then $\text{P}_{\text{gas}}+\text{P}_{\text{h}} = \text{P}_{\text{atm}}$
- If $\text{P}_{\text{gas}} > \text{P}_{\text{atm}}$ then $\text{P}_{\text{gas}} = \text{P}_{\text{atm}} = \text{P}_{\text{h}}$

Pressure is exerted when gas particles collide with the walls of any container it is held in.

Kinetic molecular theory was developed to explain gas behavior. The five postulates are:

1. Gases are composed of tiny particles whose size is negligible compared to the average distance between them. This means that the volume of the actual, individual molecules in a gas can be assumed to be negligible compared to the volume of the container, and therefore the total volume that the gas fills is almost all empty space. The observation that gases are compressible is consistent with the assumption that the actual gas particles have a small volume compared to the total volume.

2. Gas particles move randomly, in straight lines, in all directions and at various speeds.

3. The forces of attraction or repulsion between two gas particles are negligible, except when they collide.

4. When gas particles collide with one another, the collisions are elastic. The collisions with the walls of the container create the gas pressure. Elastic collisions is consistent with the observation that gases, when left alone in a container, do not appear to lose energy and do not spontaneously convert to a liquid.

5. The average kinetic energy of a gas particle is proportional to the Kelvin temperature, and as a result, all calculations involving gases should be carried out with temperatures converted to K.

These assumptions do have some limitations. Real gas particles do attract one another to some extent and can stick to one another and are able to sometimes condense to form a liquid.

3.6 Ideal Gas Law

AP Topic: 3.4

Boyle's law states that, at constant temperature, pressure is inversely proportional to volume. This means that as pressure increases, volume decreases, and vice versa.

$$\text{PV} = \text{a constant}$$

A plot of V versus P is a hyperbola. Similarly, a plot of V versus 1/P is a straight line through the origin.

In terms of KMT, if the volume is increased, the gas particles collide with the walls of the container less often and the pressure is reduced. The process of breathing also illustrates Boyle's Law.

If we know the volume and pressure of a gas at a given temperature, and then volume or pressure is changed, Boyle's law allows us to calculate the new volume or pressure by applying the simple relationship:

$$\text{P}_1\text{V}_1 = \text{P}_2\text{V}_2$$

P_1 and V_1 are the original condictions and P_2 and V_2 are the new conditions.

Boyle's Law has been tested over three centuries. It holds true only at low pressures. An ideal gas is expected to have a constant value of PV.

Charles' law states that, at constant pressure, volume is directly proportional to absolute temperature. This means the volume of a gas increases with increasing temperature, and vice versa. A plot of V versus T is a straight line.

$\frac{V}{T} = \text{constant}$

In terms of KMT, if the temperature is increased, then the gas particles gain kinetic energy, move around more, and occupy more space.

Charles's law allows us to calculate the new volume or temperature by applying the simple relationship

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

Avogadro's law states that, at constant temperature and pressure, volume is directly proportional to the number of moles of gas present. This means that the volume of a gas increases with increasing number of moles, and vice versa.

$$\frac{V}{n} = \text{a constant}$$

In terms of KMT, as more moles of a gas are placed into a container, if conditions of temperature and pressure are to remain the same, the gas must occupy a larger volume.

The relationship between the two is below

$$\frac{V_1}{n_1} = \frac{V_2}{n_2}$$

Gay-Lussac's law states that, at constant volume, pressure is directly proportional to temperature. This means that tempearture increases with increasing pressure, and vice versa.

$$\frac{P}{T} = \text{a constant}$$

In terms of KMT, if the temperature of a gas is raised, then the particles will have more energy, the collisions with the walls of the container will occur with a greater force, and the pressure will increase.

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

Combining the equations of the gas laws above, gives

$$\frac{P_1V_1}{n_1T_1} = \frac{P_2V_2}{n_2T_2}$$

If the number of moles of gas in an experiment is constant, then the expression becomes

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

The combination of laws above leads to the formulation of the ideal gas law. Most gases obey this law at temperatures above 273 K and at pressures of 1.00 atm or lower. An ideal gas has particles that are assumed to have negligible volume when compared to the total volume, and particles that do not attract one another.

$$\text{PV} = \text{nRT}$$

R is the universal gas constant and is equal to 0.0821 L atm K^{-1} mol^{-1} when P is measured in atm and V is measured in L.

This equation is useful because it can be manipulated to include other variables. For example we can find a relationship with molar mass and density

$$MM = \frac{DRT}{P}$$

Since gas molecules are so far apart, we assume they behave independently. Dalton observed that the total pressure of a mixture of gases equals the sum of the pressures that each would exert if present alone. Partial pressure is the pressure exerted by a particular component of a gas mixture.

$$\mathrm{P_{total} = P_1 + P_2 + P_3 \ldots}$$

Assuming ideal behavior, the equation can be simplified to

$$P_{\text{total}} = n_{\text{total}} \left(\frac{RT}{V} \right)$$

Additionally, if $\mathrm{n_1}$ is the number of moles of gas 1 exerting a partial pressure $\mathrm{P_1}$, then

$$\mathrm{P_1 = X_1 P_{total}}$$

Where $\mathrm{X_1}$ is the mole fraction of gas 1 = $\mathrm{n_1/n_{total}}$

It is common to synthesize gases and collect them by displacing a volume of water. To calculate the amount of gas produced, we must correct for the partial pressure of the water vapor

$$\mathrm{P_{total} = P_{gas} + P_{water}}$$

The vapor pressure of water varies with temperature.

In statistics, the Maxwell-Boltzmann distribution is a particular probability distribution. It was first defined and used in physics for describing particle speeds in idealized gases. A particle speed probabilty distribution indicates which speeds are moe likely: any single particle will have a speed selected randomly from the distribution, and is more likely to be within one range of speeds than another. The distribution depends on the temperature of the system and the mass of the particle.

Keep in mind the Maxwell-Boltzmann distribution applies to an ideal gas. In real gases, there are various effects that can make their speed distribution different from the Maxwell-Boltzmann form.

Note that although absolute temperature of a gas is a measure of the average kinetic energy, some molecules will have less or more KE than the average. There is a spread of individual energies of gas molecules in any sample of gas. As the temperature increases, the average KE of the gas molecules increases. As KE increases, the velocity of the gas molecules increases.

The root mean square speed (u_{rms}) of the velocities of gas particles is the square root of the averages of the squares of the speeds of all the particles at a particular temperature.

$$u_{rms} = \sqrt{\frac{3RT}{MM}}$$

Note u_{rms} is the speed of a gas molecule having average KE. Average KE is related to u_{rms}

$$\mathrm{KE} = \frac{1}{2}\mathrm{m}u_{rms}^2$$

where m is the mass of the molecule.

The effect of an increased volume at constant temperature is that as V increases at constant T, the average KE of the gas remains constant, meaning that u_{rms} is a constant. However, V increases, so the gas molecules have to travel further to hit the walls of the container so P decreases.

The effect of an increased temperature at constant volume is that if T increases, the average KE Of the gas molecules will increase so there are more collisions with the container walls. The change in momentum in each collision increases so P increases.

Effusion is the process in which a gas escapes from one vessel to another by passing through a very small opening

Diffusion is the process in which a homogeneous mixture is formed by the random mixing of two different gases.

Graham's law of effusion and diffusion states that the rate of effusion or diffusion of two gases is inversely proportional to the square roots of their respective densities and molecular masses

$$\frac{\text{Rate of effusion of A}}{\text{Rate of effusion of B}} = \sqrt{\frac{\text{density of B}}{\text{density of A}}} = \sqrt{\frac{\text{MM of B}}{\text{MM of A}}}$$

Ligher gas particles effuse and diffuse at higher rates than heavier gas particles.

- Diffusion is faster for lighter gas molecules
- Diffusion is significantly slower than the u_{rms} speed.
- Diffusion is slowed by collision
- The average distance traveled by a gas molecule between collisions is called the mean free path. It would be very erratic if we could monitor the path of a single molecule.

Imagine a solution, in a closed container. with a gas filling the space above it.

At higher pressures, more gas molecules strike the surface of the solution and enter the solvent, meaning the concentration of the gas dissolved in the solvent is greater.

Gas solubility usually decreases with increase in temperature of the solution, since the gas particles have more energy, and can escape from the solvent, meaning less gas is dissolved in solution.

3.7 Deviation from Ideal Gas Law

AP Topic: 3.6

At high pressures and low temperatures gas particles come close enough to one another to make two postulates of the kinetic molecular theory invalid.

- The assumption that gases are composed of tiny particles whose size is negligible compared to the average distance between them begins to fail. When the gas is pressurized into a small space the gas particles size becomes more significant compared to the total volume.
- The assumption that the forces of attraction or repulsion between two particles in a gas are very weak of negligible begins to fail. Low temperature means less energy, so the particles are attracted to one another more.

Under these conditions, gases are said to behave non-ideally, or like real gases. There are two consequences.

1. When gases are compressed to high pressures, the size of the gas particles is no longer negligible compared to the total space occupied by the gas. Therefore, the observed total volume occupied by the gas under these real conditions is artificially large since the gas particles are now occupying a significant amount of that total volume.

2. The actual pressure of a gas is lower than one would expect when assuming there were no attractive forces between the particles. Because, in a real gas, the particles are attracted to one another, they collide with the walls with less force, and the observed pressure is less than in an ideal gas.

These corrections lead to the Van der Waals equation. You do not need to know this equation, but you should know how to relate the relative sizes of a and b to the deviations above.

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

Small, nonpolar molecules also behave more ideally than large, polar molecules.

3.8 Solutions and Mixtures

AP Topic: 3.7

Solutions are homogeneous mixtures that are composed of a solute and a solvent.

- Solute: component in lesser concentration
- Solvent: component in greater concentration

Solubility is the maximum amount of material that will dissolve in a given amount of solvent at a given temperature to produce a stable solution. In other words, the solution is saturated.

There are some factors affecting solubility.

First, molecular structure.

Second, pressure. The solubility of a gas increases with increasing temperature. Henry's Law states that the amount of gas dissolved in a solution is directly proportional to the pressure of the gas above the solution. Henry's Law is obeyed best for dilute solutions of gases that don't dissociate or react with the solvent.

$$C = kP$$

Where P is the partial pressure of the gaseous solute above the solution, k is a constant, and C is the concentration of dissolved gas.

Increasing pressure has very little effect on the solubility of liquids and solids.

Third, temperature. The solubility of a gas in water always decreases with increasing temperature.

The dissolving of a solid occurs more rapidly with an increase in temperature, but the amount of solid may increase or decrease with an increase in tempearture. It is very difficult to predict what this solubility may be - experimental evidence is the only sure way.

- The amount of solute what will dissolve usually increases with increasing temperature since most solution formation is endothermic.
- Solubility generally increases with temperature if the solution process is endothermic.
- Solubility generally decreases with temperature if the solution process is exothermic.

Molarity is the number of moles of solute per liter of solution and is tempearture dependent. The liquid solvent can expand and contract with changes in temperature. Most molar solutions are made at 25°C, so this point is subtle and picky, but important nonetheless. In relatively low molarity solutions, there are small numbers of solute particles compared to the number of solvent particles, and in relatively high molarity solutions there are relatively large numbers of solute particles compared to the number of solvent particles.

$$M = \frac{\text{moles of solute}}{\text{liters of solution}}$$

Mass percent is the percent by mass of the solute in the solution.

$$\text{Mass Percent} = \frac{\text{grams of solute}}{\text{grams of solution}} \times 100$$

Mole fraction is the ratio of the number of moles of a given component to the total number of moles present.

$$\text{Mole Fraction} = X_a = \frac{n_a}{n_a + n_b + \ldots}$$

Molality is the number of moles of solute per kilogram of solvent and is not temperature dependent.

$$m = \frac{\text{moles of solute}}{\text{kilograms of solvent}}$$

Often solutions are prepared by adding water to more concentrated tools. Calculations involving dilution problems involve three steps.

1. Calculate the number of moles present in the final, diluted solution, by applying moles = (concentration)(volume).
2. Calculate the volume the starting, more concentrated solution that supplies this number of moles by applying moles = (concentration)(volume).

3. The volume of water that must be added to the concentrated solution is simply the difference between the volume of the final, diluted solution and the volume of the concentrated solution.

In practical terms, the use of highly accurately graduated glassware is required.

- A graduated measuring pipet is used to measure volumes for which a volumetric pipet is not avaliable.
- A volumetric or transfer pipet gives one and only one measurement but is mighty accurate.

This can be summarized with the dilution formula

$$M_1V_1 = M_2V_2$$

When diluting a concentrated acid or base, it is often found that combining water and the acid or base is a very exothermic process. In some cases this energy can be very significant and may even cause the water present to turn into the gaseous state. As the steam leaves the system, it can cause a spray of concentrated acid or base and represents a significant safety hazard. In order to minimize this hazard, it is vital to always add acid to water, and not water to acid.

The dilution sequence of adding a relatively small amount of acid to a relatively large volume of water ensures that the heat generated is kept to a minimum, and that acid remains in the presence of as much water as possible until it reaches the desired dilution. This will minimize the risks of accidents.

You may be asked to prepare a standard solution using a solid solute. This is a solution whose concentration is accurately known. To do so, mass an appropriately calculated amount of solid and place it in a volumetric flask. Add only enough distilled or deionized water to dissolve the solid and swirl to completely dissolve the solid. Then add more water, filling to the mark on the flask. Secure the stopper and invert the flask a few times to ensure even distribution of the solute throughout the solution. If you dump solid into 1.00 L of water you are neglecting the space the solid will occupy and your molar concentration will not be correct.

When a solute is dissolved in a solvent, the attractive forces between solute and solvent particles are great enough to overcome the attractive forces within the pure solvent and within the pure solute. The solute becomes solvated. When the solvent is water, the solute is hydrated.

- Substances with similar types of intermolecular forces dissolve in each other.
- Water dissolves many salts because the stronger ion-dipole attractions water forms with the ions of hte salt are very similar to the strong attractions between the ions themselves.
- Oil does not dissolve in water. Oil is immiscible in water because that any weak dipole-induced dipole attractions that form between oil and water cannot overcome the stronger dipole-dipole hydrogen bonding that water molecules have for each other.

The enthalpy change associated with the formation of a solution can be negative or positive.

Enthalpy of hydration is more negative for small ions and highly charged ions.

Some heats of solution are positive. The reasion that the solute dissolves is that the solution process greatly increases the entropy which overrides the cost of the small positive heat of solution. This makes the process spontaneous. The solution process involves two factors; the change in heat and the change in entropy, and the relative magnitude of these two factors determine whether a solute dissolves in a solvent.

3.9 Representations of Solutions

AP Topic: 3.8

Solutions may be represented by particulate diagrams where properties of the solution such as concentration and interparticle interactions can be illustrated.

3.10 Separation of Solutions and Mixtures Chromatography

AP Topic: 3.9

Solutions can be gases, liquids, or solids. For a liquid solution the solute can be a gas, liquid, or a solid. In solutions the solute size is very tiny. Like a solution, a colloid is a mixture of two separate substances, but where the solute particles are larger in size than molecules. If the particle size exceeds 1000 nm, the mixture becomes a suspension. These particle size distinctions mean that a mixture can appear homogeneous or heterogeneous depending on the scale on which it is observed.

Liquid solutions, by definition, cannot be separated into their components using a filter paper and have no particles large enough to scatter visible light. Two methods that can be used to separate such solutions are chromatography and distillation.

All chromatography techniques involving a moving phase and a stationary phase. In the most common applications of paper chromatography, the paper is the stationary phase and the solvent is the moving phase. When the solution mixture is exposed to the two phases, each component of the mixture will have a greater or lesser affinity for the stationary or moving phase. If a component of the mixture has a high affinity for the mobile phase, it will move with the moving phase and travel a relatively long distance on the chromatogram. A component with less affinity for the mobile phase, or only a larger affinity for the stationary phase, will not move as far. The different distances of travel mean that the components of the mixture are physically separated.

It is possible to apply a quantitative analysis to the chromatogram by calculating a R_f value for each component of the mixture.

$$R_f = \frac{\text{Distance traveled by component of mixture}}{\text{Distance traveled by solvent}}$$

The distance travelled by the solvent is determined by measuring the distance from the baseline, and the maximum distance than the solvent has travelled, known as the solvent front.

Distillation is a simple separation technique based upon differences in boiling point of two components of a liquid mixture. The boiling point of the individual components of a mixture depends upon the intermolecular attractions between the particles of that component.

3.11 Spectroscopy and the Electromagnetic Spectrum

AP Topic: 3.11

Spectroscopy is the study of the interaction of electromagnetic radiation and matter. Absorption spectroscopy involves a sample being exposed to radiation of varying types, and then observing what happens as the sample interacts with the radiation. Spectroscopy is classified based on the energy of the radiation source used - different energies of light probe for different kinds of information about a sample.

Ultraviolet and visible light are used when we want to know more about molecules or metal ions, when the sample is in an aqueous solution. You can probe the purity or concentration of samples, or whether the substance contains pi-bonds.

Infrared spectroscopy is used when you want to know about molecules, mostly those with covalent bonds, when the sample is in a solution or a solid. When covalent bonds are exposed to infrared radiation they absorb that energy and tend to bend, stretch and vibrate. The interaction with the IR is unique for each type of bond, so IR spectroscopy can be used to distinguish between compounds that have different types of covalent bonds.

Molecular rotations can be caused by the use of microwaves, and can be used to determine the chemical composition and structure of molecules.

3.12 Photoelectric Effect

AP Topic: 3.12

Albert Einstein was a fan of Max Planck's work and proposed that all EM radiation, not just the UV region that Planck focused on, could be viewed as a stream of "particles" called photons. This explained the photoelectric effect, whereby light bombarding the surface of a metal ejects electrons.

- Energy is quantized.
- Energy can only occur in discrete units called quanta.

- EM radiation exhibits both wave and particle properties.
- Keep in mind, the more massive the object, the smaller its associated wavelength and vice versa.

Whether the type of radiation, the neergy absorbed or emitted by the matter is governed by two equations.

$$c = \lambda\nu$$

Where c is the speed of light, λ is wavelength, and ν is frequency.

$$\text{E} = h\nu$$

Where E is energy, h is Planck's constant, and ν is frequency.

Note that there is a minimum amount of energy that can be gained or lost by an atim, and all energy gained or lost must be some integer multiple, n, of that minimum. The lost minimum energy change, hν is called a quanta of energy. Think of it as a "packet" of energy equal to $h\nu$

$$\Delta\text{Energy} = n(h\nu)$$

Where h is the proportionality constant. This ν is the lowest frequency that can be absorbed or emitted by the atom. There is no such thing as a transfer of E in a fraction of a quantum, only in whole numbers of quanta.

3.13 Beer-Lambert Law

AP Topic: 3.13

The Beer-Lambert law is used to relate the concentrations of colored solutions to the amount of visible light they absorb. The amount of absorbance is calculated using the formula

$$A = \epsilon bc$$

Where A is absorbance, ϵ is molar absorptivity, b is path length, and c is concentration.

When absorbance measurements are made at a fixed wavelength, in a cell of constant path length, both a and b are constant, and the absorbance, A, will be directly proportional to c. If a solution of a compound obeys the Beer-Lambert law, a plot of absorbance versus concentration gives a straight line with slope ab. The y-intercept is zero. One can use the graph to read corresponding concentrations and absorption values.

A plot of absorption against wavelength can be used to determine the exact color of a solution. The point at which the greatest absorption is observed can be used to determine, via a color wheel, which wavelength is being reflected and therefore the color of the solution. The color that is observed is due to the wavelengths of light that the sample did not absorb. A color wheel can be used to relate absorbed and transmitted colors, the transmitted color being the complementary color of the absorbed light.

Althought theoretically the spectrophotometer can be used at a number of different wavelengths, because of the limitation of the electronics, the optimum wavelength is where the absorbance is highest. Performing the experiment at the point of highest absorbance offers at least two advantages. Firstly, Beer's law linear relationship between concentration and absorbance is likely to hold around this point, and secondly, when diluting the solution in order to investigate other lower concentrations it is likely that if one starts at a point of maximum absorbance that the absorbance will still remain significant and therefore detectable at the lower concentrations.

Problems

1. The boiling point of HCl is -85°C. The boiling point of chlorine, Cl_2 is -34°C. Discuss the differences in the boiling points of these substances in terms of the intermolecular forces present.
2. A vessel connected to an open-end manometer is filled with gas to a pressure of 0.835 atm. The atmospheric pressure is 755 torr. (a) In which arm of the manometer will the level of mercury be higher? (b) What is the height difference between the two arms?
3. The pressure on a 411 mL sample of gas is decreased from 812 mmHg to 790 mmHg. What will the new volume of the gas be?
4. A gas has a volume of 0.572 L at 35.0°C and 1.00 atm pressure. What is the temperature inside a container where this gas has a volume of 0.535 L at 1.00 atm?
5. If 2.11 g of neon gas occupies a volume of 12.0 L at 28.0°C. What volume will 6.58 g of neon occupy under the same conditions?
6. A gas exerts a pressure of 900 mmHg at 20°C. What temperature would be required to lower the pressure to 1.00 atm?
7. A sample of aluminum chloride weighing 0.100 g was vaporized at 350.°C and 1.00 atm pressure to produce 19.2 mL of vapor. Calculate a value for the molar mass of aluminum chloride.
8. Ammonium nitrite decomposes upon heating to form N_2 gas and water: $NH_4NO_2(s) \rightarrow N_2(g) + 2H_2O(g)$. When a sample of ammonium nitrite is decomposed in a test tube, 511 mL of N_2 gas is collected over water at 26° and 745 torr total pressure. How many grams of NH_4NO_2 were decomposed? The vapor pressure of water at 26°C is 25.2 torr.
9. What can be said about the u_{rms} of a gas in relation to its molar mass and in relation to its temperature?
10. The electrolyte in automobile lead storage batteries is a 3.75 M sulfuric acid solution that has a density of 1.230 g/mL. Calculate the mass percent and molality of the sulfuric acid.
11. The blue color in fireworks is often achieved by heating copper(I) chloride (CuCl) to about 1200°C. Then the compound emits blue light having a wavelength of 450 nm. What is the increment of energy that is emitted at 4.50×10^2 nm by CuCl?

4 Chemical Reactions

4.1 Introduction to Reactions

AP Topic: 4.1

If some aspect of the physical state of matter is altered, but the chemical composition remains the same, then the change is considered to be a physical change. The most common physical changes are changes of state.

In a chemical change, which is often called a chemical reaction, the atoms of a substance are rearranged to form new susbtances. A chemical change requires that the new substance or substances formed have a different chemical composition to the original substance or substances. Chemical changes are often accompanied by observable changes.

Evidence for chemical change can manifest itself in a number of ways. One might see a precipitate form, experience a change of energy in the form of light or heat, observe a color change, see the formation of a gas, or observe an electrical current, all of which suggest that a chemical reaction has taken place. Such changes are sometimes called driving forces.

4.2 Net Ionic Equations

AP Topic: 4.2

Chemical equations are a shorthand method used to illustrate what happens during a chemical reaction. Reactants react to produce the products. There can be a number of steps to writing an equation.

1. Write down the equation in words.
2. Fill in the correct formulas for all the substances.
3. Balance the equation using coefficients.

Balancing the equation can be tricky and requires practice. It involves the following steps.

1. Ensure the correct formulas are being used for all the reactants and products.
2. Balance each element in turn, remembering to multiply parentheses out carefully.
3. When balancing, only place numbers in front of whole formulas. Do not change the formulas of any of the reactants or products or add any extra formulas. The numbers that appear in front of each formula are called the stoichiometric coefficients. They have an extremely important role to play in calculations since they give the reacting ratio.

Lastly, add state symbols; (s) for solid, (l) for liquid, (g) for gas and (aq) for aqueous. State symbols are not always necessary or relevant, and should be applied on a case by case basis.

Many qualitative and quantitative chemical reactions are carried out in an aqueous solution. Water is a convenient medium since it is a cheap and readily avaliable solvent, that many solids dissolve in. When dealing with aqueous solution, we often take the molecular equations seen in the previous section, and create further nuances. To consider these other ways of representing equations, we have to think about a few aspects of chemicals in solution.

Ionic solutions can be identified by their ability to conduct electricity. If a large number of ions are present in a solution, then the solution will be an excellent conductor of electricity. Such a substance is completely ionized and is a strong electrolyte. All soluble ionic compounds, but very few molecular compounds, are strong electrolytes.

If the ionic solution conducts electricity only weakly, there are likely to be a few ions present. Such a substance is partially ionized, and is a weak electrolyte.

Non-electrolytes have no ions present in solution and therefore cannot conduct electricity. Such a substance is not ionized and is a nonelectrolyte. Most molecular compounds are either nonelectrolytes or weak electrolytes.

In order to understand what is happening as substances interact with water, we can use ionic equations to show the degree of ionization taking place.

Strong electrolytes are completely dissociated into ions.

Both cations and anions, when surrounded by water, are said to be hydrated.

Weak electrolytes are only partially dissociated into a few ions.

Non-electrolytes are not ionized at all, and therefore there are no ions present.

When a chemical reaction is shown in its ionic form, it may be possible to simplify it to what is known as a net ionic equation.

In general the following points are useful

- Learn common ions.
- Where appropriate, all compounds that produce ions in solution should be written in their ionic form and spectator ions should be ignored.
- Balance equations with lowest possible whole numbers.
- There is no requirement to use state symbols.
- Ions have charges.

4.3 Representations of Reactions

AP Topic: 4.3

The law of conservation of mass is a crucial and fundamental part of chemistry. You are expected to relate this idea in terms of symbolic representations as well as particulate representations. No matter how the chemical or physical process is represented in an equation, it can be translated into a particulate diagram where symbols can be used to represent the equation. It is very important to consider the conservation of mass. All particles that were present at the start of the reaction are present at the end.

4.4 Physical and Chemical Changes

AP Topic: 4.4

Evidence for chemical change cna manifest itself in a number of ways. One might see a precipitate form, experience a change of energy in the form of heat or light, observe a color change, see the formation of a gas, or observe an electrical current, all of which suggest that a chemical reaction has taken place. Such changes are sometimes call driving forces.

In all cases it is vital to distinguish between physical change and chemical change. If there is only an interruption in the intermolecular forces then the change should be seen as physical, but if there is a rearrangement of the intra bonds, then the change is chemical.

Some changes, such as the dissolution of salt in water, are more difficult to characterize as being physical of chemical, since both intra bonds are broken, and intermolecular attractions are broken between the solvent molecules, before ion-dipole forces are created when the ions are surrounded by water molecules.

4.5 Stoichiometry

AP Topic: 4.5

We have already seen how moles of an element or compound can be calculated and how the moles of a solution can be calculated.

The calculation and use of moles are of enormous importance in chemistry, since if we know the number of moles of a substance that is present in a reaction, and we know a balanced chemical equation, it is possible to calculate the moles of another substance present in the equation. Use the following:

1. Write a correct and balanced equation.
2. Find the number of moles present by using a moles relationship for one substance.
3. Use the stoichiometric coefficients in the balanced equation to find the reacting ratio of the moles. Use this relationship to find the number of moles of the unknown substance.
4. Re-apply a moles relationship for the unknown substance.

The stoichiometric coefficients are the numbers that are used to balance the chemical reaction and provide the reacting ratio of the moles of the substances. Stoichiometry is the study of quantities of materials consumed and produced in chemical reactions. A balanced chemical equation that shows the molar ratios can be used to make predictions about other substances within the equation.

We have seen previously how Avogadro's law states that equal volumes of all gases at constant temperature and pressure will contain equal numbers of moles. The volume of one mole of any gas is called its molar volume, and can be calculated using the ideal gas equation.

We can state that 1 mole of any ideal gas at standard temperature and pressure (STP) occupies a volume of 22.4 L.

When all the reactants in a chemical reaction are completely consumed, then the reactions are said to be in stoichiometric proportions. On other occasions, it may be that only one particular reactant is completely used up. This happens when one reactant is in excess. The reactant that is completely consumed is called the limiting reactant, and it is what determines the quantities of products that form.

In all chemical reactions, the yield of the product will be less than 100%. The yield is usually less than 100% since the reactants are often not pure, some of the product is lost during purification, the reaction may be reversible and/or side reactions may give by-products. The % yield can be calculated, and is thought of as a guide to the efficiency of the reaction. The higher the % yield, the greater the efficiency.

$$\%\text{Yield} = \left(\frac{\text{actual yield of product}}{\text{theoretical yield of product}}\right) \times 100$$

Compounds that contain carbon and hydrogen only, when burned completely in oxygen, will yield only carbon dioxide and water. Analysis of the mass of CO_2 and H_2O produced can be used to determine the empirical formula of the substance in question. This method assumes that all the carbon in CO_2 originated from the carbon in the original compound, and all the hydrogen in the water originated from the hydrogen in the original compound. The method is a variation of the steps outlined earlier to determine empirical formulas, as follows.

1. Calculate the moles of CO_2 produced. Since there is one carbon atom in one molecule of CO_2, this is also the number of moles of C atoms present in the original compound.
2. Calculate the moles of H_2O produced. Since there are two hydrogen atoms in one molecule of H_2O, multiply this number by two to calculate the number of moles of H atoms present in the original compound.
3. Calculate the masses of C and H atoms present in the combusted sample by multiplying the moles of each by their molar masses.
4. If there is another element present in the combusted substance, then calculate its mass by subtracting the mass of C and H from the total mass of the combusted sample. Turn the mass of element into moles by dividing by the appropriate molar mas.
5. Find the smallest number of moles calculated and divide all the numbers of moles by that number. This gives the molar ratio.
6. The results from #5 should be in a convenient ratio, and give the empirical formula.
7. If necessary, use the molar mass to turn the empirical formula into a molecular formula.

Hydrates are formula units with water associated with them. The water molecules are incorporated into the solid structure. Strong heating will drive off the water as a vapor. When the water is completely removed, the salts are said to be anhydrous.

4.6 Introduction to Titration

AP Topic: 4.6

Chemical reactions are often carried out between substances that are in solution. Solutions consist of a solute dissolved in a solvent, usually water. The concentration of a solution can be measured in terms of the number of grams of the solute that has been dissolved in a particular volume of the solution, or more usually, in terms of the number of moles of the solute in a particular volume of the solution. Typical units are mol/L and is referred to as molarity.

$$\text{Moles} = (\text{concentration})(\text{volume})$$

Titration is the name given to the experimental method of analysis that utilizes concentrations of solutions. As above, if we know a balanced chemical equation and can calculate the moles of one substance, then by ratio we will know the moles of other substances, and we can use that data to calculate an unknown concentration. We need to use a substance with the known concentration that specifically reacts with the solution of unknown concentration.

If no solid is formed in a reaction, we can use a indicator that changes color at the equivalence point. The observable event that occurs at the equivalence point is called the end point. Volumetric analysis is a technique for determining the amount of a certain substance by doing a titration.

4.7 Types of Chemical Reaction

AP Topic: 4.7

There are millions of possible chemical reactions. Classification schemes for chemical reactions are just a way to try to simplify thinking about them.

A double replacement/displacement is a reaction where two ions are switched in two compounds to form two new compounds.

$$\text{AB} + \text{CD} \rightarrow \text{AD} + \text{CB}$$

These often involve acids, bases, and salts, but not necessarily. No changes in oxidation numbers occur. All double replacement reactions have a driving force that removes a pair of ions from solution.

- Precipitation. A precipitate is an insoluble substance formed by the reaction of two aqueous substances. Two ions bond together so strongly that water cannot pull them apart.
- Formation of a gas. Gas may form directly or from the decomposition of a product.
- Formation of a molecular/covalent substance. When a molecular substance is formed, ions are removed from solution.

Acids have formulas that begin with H and have a hydrogen ion that they donate in reactions.

Bases are formulas that end in OH except for ammonia.

A salt is a compound formed when the hydrogen ion(s) in an acid have been replaced by metal ions or the ammonium ion.

A simple redox reaction is a reaction involving the transfer of electrons. In these reactions an oxidizing agent will cause the oxidation of another compound and in the process, itself will be reduced and vice-versa. Oxidation numbers change from the reactant side to the product side of the equation in a redox reaction.

- Single replacement are reactions where an element reacts with a compound.
- Combustion is a reaction with oxygen.
- Synthesis and composition are when a reaction with elements and/or compounds combine together to form one product or a single reactant is heated and splits up. Synthesis and decomposition are opposite of one another.

A non-simple redox reaction is a reaction involving the transfer of electrons. In these reactions an oxidizing agent will cause the oxidation of another compound and in the process, itself will be reduced and vice-versa. Oxidation numbers change from the reactant side to the product side of the equation in a redox reaction.

An oxidizing agent is one that promotes oxidation. Oxidizing agents achieve this by accepting electrons themselves, and in the process, they become reduced.

A reducing agent is one that promotes reduction. Reducing agents achieve this by donating electrons themselves, and in the process, they become oxidized.

In general, nonmetals tend to be good oxidizing agents since they tend to gain electrons and metals tend to be good reducing agents since they tend to give up electrons.

- If a reaction takes place in acid solution it means that H^+ ions are reactants and water will be one of the products.
- If a reaction takes place in basic solution it means OH^- are present and water is one of the products.
- Elements in their highest oxidation states can only be reduced and elements in their lowest oxidation states can only be oxidized.
- Disproportionation is simultaneous oxidation and reduction of one species.

Hydrolysis is a reaction with water.

- Hydrides of groups 1 and 2 release hydrogen gas and produce the correspondong hydroxide.
- Strong acids will donate H^+ in aqueous solution.

Transition metal chemistry is a reaction involving transition metal ions in aqueous solution either undergoing ligand exchange or the destruction of complexes with acids. A ligand is an ion or molecule attached to a metal atom by coordinate bonding. A coordinate bond is a covalent bond in which both electrons come from the same atom.

- Aluminum and zinc can act like transition metal ions and form complexes.
- Most first row transition metal complexes exist in solution as hexaaqua ions although the water molecule ligands are often omitted.

Regardless of the type of reaction, these are steps you should follow when asked to write a net ionic equation:

1. Write a complete, balanced equation with states of matter.
2. Split aqueous ionic or strong acids into ions. Include the charges and make sure the equation remains balanced in mass and charge.
3. Cancel out any ions that appear split and identical on both sides of the equation. Double check that the net ionic equation is balanced in both mass and charge. Rewrite the equation with the spectator ions removed.

4.8 Introduction to Acid-Base Reactions

AP Topic: 4.8

Acids and bases can be identified in many ways but the most useful way at this stage is the Bronsted-Lowry definition.

It states that an acid is a substance that donates hydrogen ions in aqueous solution and a base is a substance that accepts hydrogen ions in aqueous solution.

Water can act as both an acid and a base and is called amphoteric behavior.

Conjugate acid and base pairs are related by a difference of a hydrogen ion on either side of the equation.

A strong acid or base undergoes complete ionization.

Conjugate pairs with a very strong component in a pair will always be accompanied by a equally weak partner.

Weak acids and weak bases have very little ionization and equilibria are set up with the equilibria laying heavily on the left hand side or the undisassociated form.

One of the most important reactions of acids and bases is their ability to neutralize with one another. A neutralization reaction takes place when the hydrogen ions in an acidic solution react with the hydroxide ions and form a basic solution to form water. This makes neutralization reactions a special type of double replacement reaction. The other product of a simple neutralization in a salt. Basically

$$\text{ACID} + \text{BASE} \rightarrow \text{SALT} + \text{WATER}$$

4.9 Oxidation-Reduction (Redox) Reactions

AP Topic: 4.9

Oxidation & reduction can be defined in a number of ways, one of which is in terms of electrons.

Oxidation is a loss of electrons and reduction is a gain of electrons.

If, during a reaction the oxidation number of an element becomes more positive, then the element has been oxidized. Reduction causes a reduction of oxidation number.

Oxidation number is the number of electrons that an atom loses, or tends to lose, when it is involved in a redox reaction. If the atom gains, or tends to gain electrons, then the oxidation number is negative, and vice-versa. If there is no change in the number of electrons, then it has not taken part in a redox reaction. In the case of a simple ion the oxidation number of the species is equal to the ionic charge. In the case of covalent compounds the oxidation number may be regarded as the charge that the species would develop if the compound were fully ionic. There are reults that simplify the process of assigning oxidation numbrs.

1. The oxidation number of an element when uncombined is always zero.
2. The sum of the oxidation numbers on a neutral substance is always zero.
3. In an ion, the sum of the oxidation numbers of any elements present equals the ionic charge.
4. Some elements very common oxidation numbers in their compounds; Group 1 is always +1; group 2 is always +2; F is always -1; O almost always -2; H almost always +1
5. In binary compounds with metals, the group 17 elements are -1; group 16 are -2; and group 15 are -3

Disproportionation is a reaction where there is a simultaneous oxidation and reduction of one species.

Synthesis is a reaction where a single product is formed by the reaction of simpler materials, often its elements, but sometimes by compounds. These reactions are in the general form: $A + B \rightarrow AB$.

Decomposition is a reaction where a single reactant, a compound, is broken down into simpler substances. These reactions are in the general form $AB \rightarrow A + B$. Decomposition is the reverse of a synthesis reaction.

Single replacement is a reaction where an atom or ion in a compound is displaced by an atom or ion of another element. The general form is $A + BC \rightarrow AC + B$

Some metals will react with water, some with acids, some with both, and some with neither. Predictions can be made about the reactions that will and will not happen using the activity series.

Metals are arranged according to their ability to displace hydrogen, the most reactive at the top of the activity series.

- All metals above hydrogen in the series will displace it from an acid.
- All metals below hydrogen will not displace it from an acid or water.
- A metal relatively high in the series will displace one below it from a solution of its ions but the reverse process is not possible.

Combustion is a reaction where a compound or element burns in oxygen. The products of such a reaction are simply oxides of that which is combusted.

Very often this ia hydrocarbon that reacts with oxygen to form carbon dioxide and water and a large amount of energy.

Some ionic compounds are very soluble in water while are less so. A precipitation reaction occurs when certain cations and certain anions combine to form insoluble compounds. By definition, these compounds do not dissolve in water, and form insoluble solids, or precipitates. In order to study these reactions, it is necessary to be aware of the solubility rules.

Using the solubility rules, it becomes possible to make predictions about precipitation reactions.

A reaction wheere there is rearrangement of both cation anion pairs can be classified as a double replacement reaction. Note that not all double replacement reactions result in a solid precipitate being formed.

The formation of colored precipitates and other qualitative tests are an important tool in aqueous chemistry.

Gravimetric analysis involves the addition of a substance to an aqueous solution that causes the formation of a solid. The substance that is added is specifically chosen to react with the analyte.

When no more precipitate forms, we can be confident that the analyte has been totally consumed, and this is the point at which the stoichiometric molar ratio has been achieved. After their formation, such solids are usually removed from solutions by filtering, washing, and drying. Gravimetric analysis is separating the precipitate by filtration.

And finally, a note about how to balance redox reactions by the half reaction method.

1. Divide the equation into oxidation and reduction half reactions.
2. Balance all elements besides hydrogen and oxygen.
3. Balance O's by adding H_2O's to the appropriate side of each equation.
4. Balance H's by adding H^+.
5. Balance the charge by adding electrons.
6. Multiply the half reactions to make the number of moles of electrons equal for both half-reactions.
7. Cancel out any common terms and recombine the two half reactions.
8. If basic, neutralize any excess H^+ by adding the same number of OH^- to each side of the balanced equation.

Problems

1. Write a balanced equation for Carbon + oxygen → carbon monoxide
2. Describe any observations that you might reasonably expect to make during the reaction between hydrogen gas and oxygen gas to form water.
3. Discuss the change in forces and bonds when water decomposes into its elements.
4. A sample of copper(II) sulfate pentahydrate with a mass of 8.512 g is dissolved in enough water to make 500.0 mL of solution. A 25.00 mL portion completely reacts with 20.00 mL of 0.1702 mol L^{-1} solution of iodine ions. In what molar ratio do Cu^{2+} and iodide ions react?
5. Hydroxides can be used to neutralize acids. What volume of 1.00 M NaOH, would be required to completely neutralize 25.0 mL of 2.00 M HCl?
6. Calculate the molas mass of a gas that is formed when 0.120 g of its liquid is vaporized, at a temperature of 50.0°C, and occupies a volume of 38.0 mL at atmospheric pressure.
7. Sulfur and chlorine react with the equation below. If 202 g of sulfur are allowed to react with 303 of Cl_2 in the reaction, what is the limiting reactant? What is the mass of product that will be produced? What mass of the excess reactant will be left over?

   $$S(s) + 3Cl_2(g) \rightarrow SCl_6(l)$$

8. Aluminum will react with oxygen gas according to the equation below. In one such reaction, 23.4 g of Al are allowed to burn in excess oxygen. 39.3 g of alumnium oxide are formed. What is the percentage yield?

   $$4Al + 3O_2 \rightarrow 2Al_2O_3$$

9. When 4-ketopentenoic acid is analyzed by combustion, it is found that a 0.3000 g sample produces 0.579 g of CO_2 and 0.142 g of H_2O. The acid contains only carbon, hydrogen, and oxygen. What is the empirical formula of the acid?
10. A sample of the hydrated salt $CoCl_2 \cdot xH_2O$, with a mass of 11.73 g, is heated to drive off the water of crystallization, cooled, and reweighed until constant mass (6.410 g) is achieved. Calculate the value of x.
11. Hydroxides can be used to neutralize acids. It is found an indicator changes color at the precise moment that 44.0 mL of NaOH has been added to 25.0 mL of 2.00 mol L^{-1} HCl in a titration. Use these data to calcualte the concentration of NaOH.
12. Write the net ionic equation for when hydrogen sulfide gas is bubbled through a solution of silver nitrate and what would be the expected pH of the solution at the end of the reaction?
13. Write the net ionic equation when magnesium metal is added to a solution of iron(III) chloride.
14. Write the net ionic equation for when concentrated hydrochloric acid is added to solid manganese(IV) oxide.
15. Write the net ionic equation for when gaseous hydrogen chloride is bubbled into water.
16. Write type of bond is formed between the ligand and the central transition metal in complexes?
17. Write the net ionic equation when excess dilute nitric acid is added to a solution containing tetraaminecadium(II) ions.
18. Acetic acid is refluxed with ethanol and a catalyst for several hours. Write the net ionic equation.
19. Identify the acid, base, conjugate acid, and conjugate base:

$$\mathrm{HBr} + \mathrm{NH_3} \rightarrow \mathrm{NH_4^+} + \mathrm{Br^-}$$

20. Write a whole formula, ionic, and net ionic equation for the neutralization reaction between aqueous solutions of potassium hydroxide and sulfuric acid.
21. Write an overall reaction for the formation of aluminum oxide, then write two half equations to identify the redox process.
22. After a reaction where metal magnesium is placed in a crucible and heated strongly in air until it has been completely oxidized by oxygen in the air, what do you predict will happen to the mass of the crucible and its contents?
23. Iodate ions react with iodide ions according to the equation below. A sample of sodium iodate with a mass of 0.311 g is dissolved in water and made up to 250. mL. 25.0 mL portions are added to KI that has been dissolved in sulfuric acid. The resultant iodine is titrated against sodium thiosulfate, the average volume being 12.5 mL. Calculate the molarity of the thiosulfate solution.

$$\mathrm{IO_3^-(aq)} + 5\mathrm{I^-(aq)} + 6\mathrm{H^+(aq)} \rightarrow 3\mathrm{I_2(aq)} + 3\mathrm{H_2O(l)}$$

24. Hydrated ammonium iron(II) sulfate crystals have the formula, $(NH_4)_2SO_4 \cdot FeSO_4 \cdot xH_2O$. 8.325 g of the salt was dissolved in 250.0 mL of acidified water. A 25.00 mL portion of thie solution was titrated with potassium manganate(VII) solution of concentration at 0.4180 M. A volume of 2.250 mL was required. Calculate the value of x.
25. Predict if a reaction takes place between $AlCl_3(aq)$ + LiOH(aq).
26. A solid of unknown composition contains some chloride ions. A 0.182 g sample of the solid is dissolved in water and the cloride ions dissolve to produce an aqueous solution. The solution has a large amount of aqueous silver ions added to it until no more precipitate can be formed. After filtering, washing, and drying, it is found that 0.287 g of the precipitate is produced in the reaction. Calculate the mass percentage of chloride ions in the original sample.
27. Potassium dichromate ($K_2Cr_2O_7$) is a bright orange compound that can be reduced to a blue-violet solution of Cr^{3+} ions. Under certain conditions, $K_2Cr_2O_7$ reacts with ethyl alcohol, (C_2H_5OH) as shown below. Balance this equation using the half-reaction method.

$$\mathrm{H^+(aq)} + \mathrm{Cr_2O_7^{2-}(aq)} + \mathrm{C_2H_5OH(l)} \rightarrow \mathrm{Cr^{3+}(aq)} + \mathrm{CO_2(g)} + \mathrm{H_2O(l)}$$

5 Kinetics

5.1 Reaction Rates

AP Topic: 5.1

Many factors can influence the rate of a chemical reaction. Each factor must have a discernible ffect on the microscopic collisions that lead to a chemical reaction.

Some molecules react in a hurry; others react very slowly. Each factor must have a discernible effect on the microscopic collisions that lead to a chemical reaction.

- Physical state matters a great deal.
- Chemical identity. What exactly is reacting? Usually ions of opposite charge react very rapidly. Also, the more bonds between reacting atoms in a molecule, the slower the reaction rate. Why? More energy is required to separate the molecule into its "bits". Substances with strong bonds will react much more slowly.

Increasing the reactants concentration by putting more reactants into the same space increases the collision frequency of the particles, leading to a faster rate of reaction. A similar effect is observed when increasing the pressure in a gaseous reaction.

Adding an inert gas has no effect on the rate of the reaction since it is not in the reaction mechanism.

A rise in temperature will result in an increased rate of reaction. The faster molecules move, the more likely they are to collide and the more energetic the collisions become. Consider the Maxwell-Boltzmann distribution plot of energies. The area underneath the curve represents the total number of molecules.

When a solid reacts, only the particles on the surface of the solid are avaliable for reaction. If the solid is broken up into smaller pieces, its surface area gets larger and more particles are avaliable for collision, therefore the reaction rate increases.

Catalysts also affect the rate of reaction and are discussed in more detail later. Unlike other participants in a chemical reaction, a catalyst is not consumed, therefore it can be used again and again. A catalyst may participate in multiple chemical transformations. The effect of a catalyst may vary due to the presence of other substances known as inhibitors or promoters.

- A catalyst is a substance that changes the rate of reaction by altering the reaction pathway. Most catalysts work by decreasing the activation energy needed for the reaction to proceed, therefore, more collisions are successful and the reaction rate is increased.
- Remember, the catalyst is not part of the chemical reaction and is not used up during the reaction. Usually, the catalyst participates in the rate-determining or slowest step.
- Catalysts may be homogeneous or heterogeneous catalysts. A homogeneous catalyst is in the same phase as the reactants. A heterogeneous catalyst is in a different phase than the reactants. Heterogeneous catalysts offers the advantage and products are readily separated from the catalyst, and heterogeneous catalysts are often stable and degrade much slower than homogeneous catalysts.

Homogeneous catalysts actually appear in the rate law because their concentration affects the reaction.

5.2 Elementary Reactions, Collision Model, Reaction Energy Profile, and Multistep Reaction Energy Profile

AP Topic: 5.4, 5.5, 5.6, 5.10

Chemical reactions can occur at significantly different speeds or rates. The rate of a reaction can be determined by either monitoring the change in concentration of reactants over time, or alternatively, monitoring the change in concentration of products over time.

The basis for the study of the speed or rate of chemical reactions is collision theory. Collision theory tells that a reaction will only take place if three conditions are met.

1. The reactants come into contact.
2. The collision occurs with a certain minimum energy, known as the activation energy.
3. The collision has the correct molecular orientation. This means that the reactants must collide in a certain physical, three-dimensional orientation for the reaction to take place.

If reactants do not collide, or collide with energies lower than the activation energy, or collide without the correct molecular orientation, then no reaction will occur. These collisions are described as unsuccessful, that is, they do not lead to a chemical reaction and the reactants remain unchanged.

All chemical reactions take place via a series of elementary steps. An elementary step is a reaction that forms products in a single step, with only one transition state and no intermediates. An energy profile can be used to show the progress of a reaction from reactants, through a transition state and then on to products. Reactants with energies closer to the transition state at the beginning will have lower activation energies, and therefore faster rates of reaction.

Elementary steps can fall into one of three categories, but all successful collisions are still subject to the criteria of sufficient energy and correct oriention.

1. They can be unimolecular - single species reacts to form products when a rearrangement occurs, activating a reactant molecule. These are called first order reactions. Rearrangements are cuased by collisions between reactant species and solvent or 'background' molecules.
2. They can be bimolecular - two species collide to form products. These are called second order reactions.
3. They can be trimolecular - three species collide and react to form products. These are called third order.

The fewer the molecules involved in the elementary reaction, the more likely it is that one of the collisions will be in the correct orientation, meaning that with increasing molecularity, the changes of correctly orientated collisions goes down. In fact, trimolecular reactions are relatively rare, since they involve the need for all three species to be simultaneously in the same area of space, and colliding with the correct energy and orientation - in terms of probability, this is relatively unlikely.

In all situations, if the concentration of the reactants is increased, there will be a greater frequency of collisions, and the greater the chances of successful collisions.

If we string together a series of elementary steps we get a more complicated reaction, but the more complex reaction is actually only a series of simple, elementary ones.

5.3 Introduction to Rate Law, Introduction to Reaction Mechanisms, Reaction Mechanism and Rate Law, and Steady-State Approximation

AP Topic: 5.2, 5.7, 5.8, 5.9

The speed of a reaction is expressed in terms of its "rate" which is equal to some measurable quantity that is changing with time.

The rate of a chemical reaction is measured by the decrease in concentration of a reactant or an increase in the concentration of a product in a unit of time. Generally speaking:

$$\text{Rate} = \frac{\text{change in concentration of a species}}{\text{time interval}} = \frac{\Delta[reactants]}{t}$$

When writing rate expressions, they can be written in terms of reactant disappearance or product appearance. Rate if not a constant, it changes with time. Graphing the data of an experiment will show an average rate of reaction.

Instantaneous Reaction Rate is simply the "rate at a given instant of time".

To determine the value of the rate at a particular instant of time, known as the instantaneous rate, simply compute the slope of the line tangent to the curve at that point in time.

Relative Reaction Rate is expressed as the change in concentration of a reactant per unit time or $\frac{\Delta[A]}{\Delta\text{time}}$.

You should focus either on the disappearance of reactants or the appearance of products.

- Rate of Δ of a reactant is always negative.
- Rate of Δ of a product is always positive.

Also, the word relative refers to terms that relate to each other in the context of a given chemical system.

Reactions are reversible. So far, we've only considered the forward reaction. The reverse is equally important. When the rate of the forward is equal to the rate of the reverse, we have equilibrium. To avoid this complication we will discuss reactions soon after mixing, before things get too messy. We will deal with initial reaction rates, so we will not worry too much about the buildup of products and how that starts up the reverse reaction.

The sequence of elementary steps that make up a complex, chemical reaction is known as the mechanism. Each step will either be a relatively fast one, or a relatively slow one, but the overall rate of the complex, chemical reaction is only dependent upon the slowest elementary step. For this reason, the slowest step is known as the rate determining step.

In order to study reaction rates we need to convert qualitative elementary steps into quantitative entities. This is achieved by the use of a rate equation or rate law. All rate equations take the general form,

$$\text{Rate} = \text{k}[\text{A}]^x[\text{B}]^y[\text{C}]^z$$

where k is the rate constant and x, y, and z are the orders with respect to the concentrations of reactants A, B, and C. The order with respect to a given reactant is the power to which the concentration of that reactant is raised to in the rate equation. The overall order of the complex, chemical reaction is the sum of the individual orders.

Since only the reactants that appear in the rate-determining step are ones that affect the rate, it is only these reactants that ever appear in the rate equation, and vice-versa.

- Zero order: The change in concentration of reactant has no effect on the rate. General form: Rate = k.
- First order: Rate is directly proportional to the reactants concentration. General form: Rate = k[A].
- Second order: Rate is quadrupled when [rxt] is doubled, increases by a factor of 9 when [rxt] is tripled, etc. General form: Rate = $\text{k}[\text{A}]^2$ or k[A][B].
- Fractional orders are rare but exist too.
- k is most definitely temperature dependent and must be evaluated by experimenet.

Units of the rate constant depend on the order of the rate law

- Zero order: k has units of M/time
- First order: k has units of 1/time
- Second order: k has units of 1/(M·time)

Note:

1. It is not possible to deduce anything about the order of a reaction from the stoichiometry of the balanced equation that describes the complete, complex, chemical reaction. As such, orders must be determined experimentally or from experimental data.

   However, it is possible to deduce orders from the stoichiometry of the balanced equation that describes the slowest elementary step in the mechanism and the stoichiometric number of a substance that appears in the slow step is the power that the concentration of that substance is raised to in the rate equation.

2. Units and magnitude of the rate constant are important.

3. A reactant that has no effect on the rate is said to have an equal order of zero. It has no effect on the rate and since any number raised to the power of zero is equal to 1, it can be omitted from the rate equation.
4. Orders can be fractional.
5. In all valid mechanisms the sum of the individual elementary steps must add up to the overall, complex, chemical reaction.
6. An intermediate is formed in one elementary step during the overall reaction, but is then used up in a subsequent elementary step. When an intermediate is found in a rate determining step and therefore in a rate equation, it is usually replaced. The experimental detection of an intermediate can be one way to choose one proposed mechanism over another.
7. If a substance is present at the beginning of a reaction and present in the same form at the end of the reaction, it can be identified as a catalyst.

   Catalysts can appear in rate equations since their concentrations are often more easily determined than intermediates.
8. A reaction that is second order, and has a rate equation of Rate = k[A][B], can sometimes be carried out with a very large concentration of one of the reactants compared to the other. When this occurs, as the reaction proceeds, the reactant with very large concentration will effectively have a "constant" concentration. As a result, and if [B]>>>>[A], then the rate law can be written as Rate = k[A], and is known as a pseudo first order reaction. Situations like this can be treated simply as first order reactions.

What we've explored thus far is termed differential rate law of simply rate law. It's the method we use when the data presented is concentration and rate data. If the data presented in concentration and time data, we need a new method. So there are two types of rate laws which implies two different approaches are needed.

- Differential rate law - data table contains concentration and rate data. Use table logic or ugly algebra to determine the orders of reactants and the value of the rate constant, k.
- Integrated rate law - data table contains concentration and time data. Use graphical methods to determine the order of a given reactant. The value of the rate constant k is equal to the absolute value of the slope of the best fit line which is decided by performing 3 linear regressions and analyzing the regression correlation coefficient r.

5.4 Concentration Changes Over Time

AP Topic: 5.3

Let's discuss plotting the concentration of a reactant [reactant] against time.

Set up your axes so that time is always on the x-axis. Plot the concentration of the reactant on the y-axis of the first graph. Plot the netural log of the concentration on the y-axis of the second graph and the reciprocal of the concentration on the y-axis of the third graph. You are in search of linear data! If you set the graphs in this order, the y-axis variable leads to 0, 1, 2 orders for that constant.

In zero order, k is negative slope, in first order, k is negative slope, and in second order, k is the slope.

You can now easily solve for either time or concentration once you know the order of the reactant. Just remember y = mx + b. Choose the set of variables that gave you the best straight line and insert them into place of x and y in the generalized equation for a straight line. "A" is reactant A and A_0 is the initial concentration of reactant A at time zero.

In zero order: $[A] = -kt + [A_0]$
In first order: $\ln[A] = -kt + \ln[A_0]$
In second order: $1/[A] = -kt + 1/[A_0]$

Also recognize that |slope| = k, since the rate constant is never negative. If you are asked to write the rate expressoin it is simply Rate = $k[A]^{\text{order you determined from analyzing the graphs}}$

Graphing Calculator Tutorial:

- Set up your calculator so that time is always in L1.

- Use L2, L3, and L4 to display the y-variables. Remember the list for what is placed on the y-axis is alphabetical. L1 is time, L2 is concentration, L3 is natural log of concentration, and L4 is reciprocal concentration.

Half-life is defined as the time required for one half of one of the reactants to disappear. You probably remember dealing with half-life in the context of ^{14}C and using it to approximate the age of fossils and such. We will focus on half-life for first order reactions only.

Another way of looking at graphs to determine reaction orders is to use the definition of rate expressed below. Using that expression, and plotting reactant concentration vs time, the slope of such a graph will equal the rate.

$$\text{Rate} = \frac{\text{decrease in concentration of reactant}}{\text{time}}$$

Integrated rate laws for reactions with more than one reactant must still be determined by experiment. We use a technique called swamping.

We must flood the reaction vessel with high concentrations of all but one reactant and perform the experiment. The reactants at high concentrations stay the same. By doing this, the rate is now dependent on the concentration of the little guy since the big guys aren't changing. We can now rewrite the rate as a pseudo-rate-law and k' is a pseudo-rate-constant.

The Arrhenius equation relates rate constants, activation energy, and temperature together, and can take multiple formats. Three common ones are shown below:

$$\text{k}=\text{Ae}^{\text{-Ea/RT}}, \qquad \ln \text{k} = \left(\frac{\text{Ea}}{\text{R}}\right)\left(\frac{1}{\text{T}}\right) + \ln \text{A}, \qquad \ln\left(\frac{\text{k}_1}{\text{k}_2}\right) = \left(\frac{\text{Ea}}{\text{R}}\right)\left(\frac{1}{\text{T}_2} - \frac{1}{\text{T}_1}\right)$$

There is one more form of the Arrhenius equation that is used to quantitatively describe how orientation factor might affect a rate constant.

$$\text{k} = \text{pAe}^{\text{-Ea/RT}}$$

p is the orientation factor and is equal to 1 for the simplest required orientations, through to numbers that are many hundreds of thousands of times smaller for more complicated reactions that require more intricate and precise orientations in order for collisions to be successful. In short, the bigger the p value, the easier the required orientation, the larger the rate constant and the faster the reaction.

5.5 Catalysts

AP Topic: 5.11

Catalysts function by lowering the activation energy of an elementary step in a reaction mechanism, and by providing a new and faster reaction mechanism.

Types of catalysts:

1. Acid Base - A reactant will either lose or gain a H^+, forming a new intermediate, and as a result the reaction rate is changed. The catalytic reaction may be acid-specific, as in the case of decomposition of the sugar sucrose into glucose and fructose in sulfuric acid.
2. Surface - A surface catalyst is often a metal, working in a gaesous reactant environment. The gas molecules can be adsorbed onto the surface of the metal where a number of things can occur.

   Another effect of adsorbing the gases onto a metal surface is that effectively their concentration is increased. Putting more gas molecules into a smaller area concentrates them, and a higher concentration means more collisions and a faster reaction.

   There are usually four steps with surface catalysis.

   - Adsorption and activation of the reactants.
   - Migration of the adsorbed reactants on the surface.
   - Reaction of the adsorbed substances.

- Escape, or desorption, of the products.

Catalytic converters are also hetergeneous catalysts.

3. Enzyme - Enzymes are complex protein molecules that act as biological catalysts. They have many active sites on them, which interact with substrate molecules, and lower the activation energy for the biological process. Originally thought of as a 'lock and key' model, where only specific substrates and enzymes would fit together and work, the induced fit mechanism suggests that both enzymes and substrates are more flexible in their structures to allow a single enzyme to interact with more than one substrate. Their shape is mostly determined by IMFs, which are very temperature sensitive. Altering the pH or heating the enzyme easily disrupts the IMFs and causes the enzyme to denature.

   Other enzymes will react with the substrate to form a completely new intermediate with a lower energy for the transition state.

Problems

1. Write the relative rates of change in concentration of the reactants and products for the following reaction.
$$4\text{PH}_3(\text{g}) \rightarrow \text{P}_4(\text{g}) + 6\text{H}_2\text{g}$$
2. Identify the catalyst and the intermediate in the following mechanism:
$$\begin{aligned} \text{Step 1:} \quad & \text{SO}_2 + \text{V}_2\text{O}_5 \rightarrow \text{SO}_3 + \text{V}_2\text{O}_4 \\ \text{Step 2:} \quad & \text{V}_2\text{O}_4 + \frac{1}{2}\text{O}_2 \rightarrow \text{V}_2\text{O}_5 \end{aligned}$$
3. Calculate the rate constant for a first-order reaction with a half life of 20.0 minutes. How much time is required for this reaction to be 75% complete?
4. The rate constant for the first order transformation of cyclopropane to propene is $5.40 \times 10^{-2}\text{hr}^{-1}$. What fraction of the cyclopropane remains after 51.2 hours? What fraction remains after 18.0 hours?
5. Given a balanced equation for the reaction of the gases nitrogen dioxide and fluorine
$$2\text{NO}_2(\text{g}) + \text{F}_2(\text{g}) \rightarrow 2\text{NO}_2\text{F}(\text{g})$$
   The experimentally determined rate law is $\quad \text{Rate} = \text{k}[\text{NO}_2][\text{F}_2]$.

   A suggested mechanism for the reaction is
$$\begin{aligned} \text{NO}_2 + \text{F}_2 \rightarrow \text{NO}_2\text{F} + \text{F} \quad & \text{Slow} \\ \text{F} + \text{NO}_2 \rightarrow \text{NO}_2\text{F} \quad & \text{Fast} \end{aligned}$$
   Is this an acceptable mechanism? That is, does it satisfy the two requirements? Justify your answer.

6 Thermochemistry

6.1 Endothermic and Exothermic Processes

AP Topic: 6.1

Energy is the ability to do work or produce heat; the sum of all potential and kinetic energy in a system is known as the internal energy of the system.

- Potential energy - energy by virtue of position. In chemistry this is usually energy stored in bonds. When bonded atoms are separated, the PE is raised because energy must be added to overcome the coulombic attraction between each nucleus and the shared electrons.
- When atoms bond, the above mentioned coulombic attraction results in energy being released thus the system has a subsequently lower PE.
- Kinetic energy - energy of motion. KE is proportional to Kelvin temperature; kinetic energy depends on the mass and the velocity of the object: $KE = 1/2\ mv^2$.
- Units of Energy:
  - calorie: amount of heat needed to raise the temperature of 1.00 g of water 1.00°C.
  - kilocalorie: 1000 calories and the food label calorie with a capital C.
  - joule: SI unit of energy; 1 cal = 4.184 J

Law of Conservation of Energy - You may know it as "energy is never created nor destroyed" which implies that any change in energy of a system must be balanced by the transfer of energy either into or out of the system. This means that the energy of the universe is constant and is known as the First Law of Thermodynamics.

Mnay reactions and changes involve either the absorption or release of energy in the form of heat. We describe these as either endothermic or exothermic.

During these endothermic and exothermic reactions, energy is transferred either from or to the surroundings.

System - the part of the world that you are studying. This might be a beaker containing salt, water and a thermometer, or it could be just the salt that is dissolving. It is important to always define the system when looking at a problem.

Surroundings - everything else around the system. This might be the air, the tabletop, and your hands holding the beaker, or it might include the water, beaker, thermometer, etc.

The universe is the system and surroundings together. Heat or work is always transferred between the system and the surroundings. Therefore, energy (system) = -energy (surroundings), or if not work is done the heat lost is equal to the heat gained, $q_{sys} = -q_{surr}$.

Heat, q - Two systems with different temperatures that are in thermal conduct will exchange thermal energy, the quantity of which is called heat. This transfer of energy in a process transfers heat because of the temperature difference but, remember, temperature is not a measure of energy, it just reflects motion of particles.

With increased Kelvin temperature of particles, comes increased kinetic energy - the higher the Kelvin temperature of particles, the more they move.

$$\text{KE per molecule} = 1/2\ mv^2$$

As the Kelvin temperature approaches 0 K, the average kinetic energy of the particles also approaches zero.

The average kinetic energy of the particles in a high temperature system is greater than the average kinetic energy of particles in a low temperature system.

When two systems that are at different temperatures come into thermal contact with one another, energy is transferred from the hotter one to the cooler one, until the temperatures of each are equal. At this point, the avearge kinetic energy of the particles of each system becomes the same, and a single, intermediate temperature is achieved.

The transfer of energy is called heat or 'heat transfer' - heat is not a substance, rather it is the transfer of energy. When the two systems are at the same temperature, there is no further transfer of heat and a thermal equilibrium is reached.

In addition to the thermal transfer of energy that takes place when a hot body comes into contact with a cold body, energy can also be transferred via work.

$$\Delta E = q + w$$

Most commonly in chemistry, we think of work in terms of gases and their expansion and contraction. Consider a gas inside a piston.

As the gas expands, the particles collide with the piston and energy is transferred from the gas to the piston. The work done by the gas on the piston can be quantitatively assessed. By considering the volume change of the gas, and the external pressure P that the gas is working against, it can be calculated via

$$w = -P\Delta V$$

As the gas expands it does work on the piston, energy is transferred to the piston and the piston moves. Because of conservation of energy, any energy lost by one system, must be gained in equal magnitude by the other system. In this work scenario, energy flows from one system to the other. Keep in mind,

- If the system is pushing on the surroundings and expanding a piston, then the work is negative.
- If the surroundings are pushing on the system and compressing a piston, then the work is positive.

In endothermic processes:

- Heat is absorbed by the system from the surroundings.
- This includes the phase changes - melting, vaporization, and sublimation.
- These usually involve changes involving breaking/separation.

In exothermic processes:

- Heat is released from the system to the surroundings.
- It includes the phase changes - freezing, condensation, and deposition.
- Changes that involve forming bonds or IMFs.

When a solution forms, there are three processes that take place. By combining all three processes, you can determine if the dissolution overall is an endothermic or exothermic process.

1. The solvent must expand by overcoming its intermolecular forces. This is an endothermic process.
2. The solute must expand by overcoming its intermolecular forces. This is an endothermic process.
3. The solute and solvent must recombine. This process is exothermic.

6.2 Energy Diagrams

AP Topic: 6.2

An endothermic reaction occurs when

- Energy is absorbed by the system from the surroundings
- The products are higher in potential energy than the reactants
- The temperature of the surroundings usually decreases if heat is transferred

An exothermic reaction occurs when

- Energy is released from the system into the surroundings
- The products are lower in potential energy than the reactants
- The temperature of the surroundings usually increases if heat is transferred

The difference in the energy of the products and energy of the reactants is called the enthalpy of reaction, or heat of reaction, and is represented as Δ_{rxn}, with units of kJ/mol$_{\text{rxn}}$.

$$\Delta^{\circ}_{\text{reaction}} = \sum \Delta H^{\circ}_{\text{f products}} \text{-} \sum \Delta H^{\circ}_{\text{f reactants}}$$

The sign for ΔH is:

- Positive for endothermic reactions.
- Negative for exothermic reactions.

On the reaction energy diagram,

- ΔH is labeled as the difference between the energies of the products and reactants.
- Activation energy, E_a is the energy needed to start the reaction, used to break bonds or intermolecular forces in the reactants. The E_a of the forward reaction is labeled as the difference between the reactants and the peak of the graph.

Catalysts are added to reactions to increase the reaction rate. They are not consumed in the reaction. Some catalysts provide an alternative pathway with lower activation energies.

Note: ΔH_{rxn} is not changed by a catalyst.

6.3 Heat Transfer and Thermal Equilibrium

AP Topic: 6.3

Recall that when two substances at different temperatures are in contact with each other, heat is always transferred from the hotter substance to the colder one. If eventually the two substances reach the same temperature, thermal equilibrium has been reached. When two substances are at the same temperature, the particles in the substances have the same average kinetic energy.

6.4 Heat Capacity and Calorimetry

AP Topic: 6.4

Calorimetry is the experimental technique used to measure energy changes in a chemical system. The usual process for calorimetry involves a chemical reaction being put into thermal contact with a heat bath. There are three factors that contribute to the amount of heat, q, transferred; they are the mass of the object, the specific heat capacity, and the change in temperature.

Specific heat capacity is defined as the amount of energy required to raise 1 g of a substance by 1°C and the experiment is carried out at constant pressure. Constant pressure is achieved by using open containers. Different substances have different values of c_p. The fact that is it a unique value for any particular substance means that the transfer of an identical amount of energy to the same mass of two different substances will not result in the same temperature change of the two substances.

- Specific heat capacity, c - the energy require to raise the temperature by 1 degree, [J/°C]
- Molar heat capacity - same as above but specific to one mole of substance, [J/mol K] or [J/mol°C]
- Specific heat of water (liquid state) = 4.184 J/g°C (or 1.00 cal/g°). Water has one of the highest specific heats known! This property makes life on earth possible and regulates earth's temperature year round.

The amount of energy transferred (q) can be related to the temperature change of a substance (ΔT) by the equation below, where m = mass and c = specific heat capacity.

$$q = m\ c\ \Delta T$$

If the temperature of the heat bath goes up, then the chemical reaction must have released energy. If the temperature of the heat bath goes down, then the chemical reaction must have absorbed energy. In each case, the 'system' is the chemical reaction, and the heat bath represents the 'surroundings'.

We can apply conservation of energy, and assuming that there are no energy losses, the magnitude of the energy lost or gained by the chemical reaction, must be equal to the magnitude of the energy gained or lost by the heat bath. Since these processes will be either exothermic or endothermic, then we can write

$$q_{system} = -q_{surroundings} \quad \text{or} \quad -q_{system} = q_{surroundings}$$

where the negative sign acts in order to show that the processes are of the same magnitude, but are different in direction of heat flow.

6.5 Energy of Phase Changes

AP Topic: 6.5

Chemical systems change their energy through three main processes: heating/cooling, phase transitions, and chemical reactions. We have seen that we can use $q = m\ c\ \Delta T$ to calculate the heat transferred when a temperature change occurs, or in other words, when there is a change in the kinetic energy of the particles. But during a phase change, there is no change in temperature. Rather, the energy transferred is used to change the position of the particles relative to one another. In order words, the potential energy is changing during a phase change. This is shown as the plateaus on the heating or cooling curve. Notice that the segment for boiling is longer than the segment for melting. This is because separating liquid particles to form a gas requires more energy than separating molecules from their solid state to liquid state.

Since the temperature is constant during a phase change, we need to use a different formula to calculate the heat transferred during a phase change as follows:

$$q = m\ (\text{or } n)\ \Delta H_{\text{fusion or vaporization}}$$

where ΔH_{fusion} is "heat of fusion" or "molar heat of fusion" and is a constant, depending on the substance being considered.

In summary, energy is either being used to change the temperature, but not the phase, or it is being used to change the phase but not the temperature. A plateau represents a stage when two phases are in equilibrium with one another, and a phase change is occurring.

Note: During a phase change use: $q = \text{mol}\ (\Delta H)$ and in a single phase use: $q = m\ c\ \Delta\ T$

If a curve goes from right to left, you can call the heating curve a cooling curve.

Do not neglect to consider the sign of q, as it denotes the direction of the heat being transferred.

6.6 Introduction to Enthalpy of Reaction

Enthalpy, H - flow of energy at constant pressure when two systems are in contact. Every substance is said to have a heat content or enthalpy. Most reactions involve an enthalpy change, ΔH°, where

$$\Delta H^\circ = \sum \Delta H^\circ_{f\ \text{PRODUCTS}} - \sum \Delta H^\circ_{f\ \text{REACTANTS}}$$

The formula above holds only when we are dealing with enthalpies of formation, ΔH_f, so be careful with its use. This equation is sometimes referred to as the "big mama" equation.

- Enthalpy of reaction - amount of heat released or absorbed by a chemical reaction at constant pressure in kJ/mol_{rxn}
- Enthalpy of fusion - heat absorbed to melt 1 mole of solid to liquid at the melting point in kJ/mol_{rxn}
- Enthalpy of vaporization - heat absorbed to vaporize or boil 1 mole liquid to vapor at the boiling point in kJ/mol_{rxn}

- Standard conditions - you already know about STP, but recall that the T in STP is 0°C and humans are not happy lab workers when it is that cold. So think of standard conditions as standard lab conditions which are 1 atm of pressure, 25°C and if solutions are involved, their concentrations are 1.0 M.

Enthalpy of a reaction can be calculated from several sources including:

- Stoichiometry
- Calorimetry
- Tables of standard values
- Hess's LawBond energies

Note at constant pressure, $\Delta H = q$.

6.7 Bond Enthalpies

AP Topic: 6.7

Recall from Unit 2, if a multiple bond is created between two atoms the bond length observed will be shorter than the corresponding single bond. This is because a double bond is stronger than a single bond and hence pulls the atoms closer together. A triple bond is correspondingly shorter and stronger than a double bond. Multiple bonds increase the electron density attractions - either way, the nuclei move closer together and the bond length decreases. Evidence for the "one and one third" bond order in the carbonate ion is that all the bonds are found to be the same length, not the different lengths that one would expect to find if a combination of double and single bonds were present. Bond order is simply the number of bonding electron pairs shaired by two atoms; fractional bond orders will exist when resonance structures exist for a compound.

Bond length is determined by nature striving for a lower energy state; it will be the distance between the two nuclei where energy is a minimum between the two nuclei. When two atoms approach each other, two "bad" things happen: electron/electron repulsion and proton/proton repulsion. One "good" thing happens: proton/electron attraction. When the attractive forces offset the repulsive forces, the energy of the two atoms decreases and a bond is formed.

As states previously, one of the ways that the energy change in a reaction can be calculated is by using bond energies, aka bond dissociation energies (BDEs). Here are some things to keep in mind:

- Breaking bonds is always endothermic. The converse is also true.
- Bond energies are determined from atoms in the gas phase; they are averages within ±10%.
- When calculating reaction energies from bond energies, bonds in reactants are broken while bonds in products are formed; energy released is greater than energy absorbed in exothermic reactions and the converse is also true.
- Note this is "backwards" from the thermodynamics "big mama" equation, because of that misconception again: it takes energy to break bonds, not to make bonds.

To recap, atoms are attracted to one another when the outer electrons of one atom are electrostatically attracted to the nuclei of an atom. The attraction between two atoms makes them increasingly stable, giving lower and lower potential energies.

However, as the atoms continue to approach one another and get increasingly close, there comes a point at which the two nuclei will start to repel one another. As they start to repel one another the potential energy is raised, and the two atoms become less stable.

A happy medium is reached at a distance where the forces of attraction and repulsion result in the lowest potential energy. The distance is called the bond length, and the potential energy at that point the bond strength.

Since the forces of attraction that stabilize atoms when they bond are attractions between electrons and nuclei, the greater the number of electrons involved, the stronger the attraction and as such, triple covalent bonds tend to be stronger than double bonds, and double bonds stronger than single bonds. Shorter bonds also tend to be stronger than longer ones.

In order to break a bond, energy must be put in.

When making a bond, energy is released.

The energy change in a reaction can be calculated by first summing the energy required to break each of the bonds in the reactants, then summing the energy released when making each of the bonds in the products, and then subtracting the two values. Always draw the molecules so you can determine the number and type of each of the bonds present.

$$\Delta H = \sum \text{Bond Energies}_{\text{broken}} - \sum \text{Bond Energies}_{\text{formed}}$$

6.8 Enthalpy of Formation

AP Topic: 6.8

Standard Enthalpy of Formation, ΔH°_f is defined as the enthalpy change when one mole of a substance is formed from its elements, in their standard states. Note that the enthalpy of formation for any one element in its standard state is zero.

Use the equation shown to calculate the enthalpy of any reaction given enthalpies of formation.

$$\Delta H^\circ = \sum \Delta H^\circ_{f\,\text{PRODUCTS}} - \sum \Delta H^\circ_{f\,\text{REACTANTS}}$$

6.9 Hess's Law

AP Topic: 6.9

Hess's Law states that the enthalpy change during a reaction depends only on the nature of the reactants and products and is independent of the route taken. In order words, enthalpy is independent of the reaction pathway. If you can find a combination of chemical equations that add up to give you the desired overall equation, you can also sum up the ΔH's for the individual reactions to get the overall ΔH_{rxn}. To use it, we need to consider enthalpy changes beyond those of formation.

Standard Enthalpy of Combustion, ΔH°_c is the enthalpy change when one mole of a substance is completely burned in oxygen. Note that combustion reactions yield oxides of that which is combusted.

It is useful to remember that compounds containing some combination of carbon, hydrogen, and oxygen, when completely burned in air, produce carbon dioxide and water only. The combustion of other reactants may require other knowledge or intelligent guesswork to determine the products of that combustion.

Occasionally, not all enthalpy of formation values are found in the table of thermodynamic data. For most substances, it is not impossible to go into a lab and directly synthesize a compound from its free elements. The heat of formation for the substance must be calculated by working backwards from its heat of combustion.

The process of ionic bond formation can be broken down into a number of states. For example, in the formation of sodium chloride there are twoo possible routs;

1. A single step process (Enthalpy change = standard enthalpy of formation of NaCl)
2. A multi-step process involving five separate changes:
    - Atomization of sodium
    - Ionization of sodium
    - Dissociation of chlorine molecules
    - Formation of gaseous chloride ions from gaseous chlorine atoms
    - Bring together the gaseous ions

By assuming a compound is essentially 100% ionic, it is possible to calculate a theoretical value for the lattice enthalpy. In some cases the theoretical values agree very closely with the experimental values, but not always.

Where the match is poor, the idea of a completely ionic bond is incorrect. The differences are caused by polarization, and the ionic bond taking on a degree of covalent character. This is another example where the idea of a slidincg scale of bond type if a useful one.

A Born-Haber cycle diagram can be constructed from these data. Often, positive values are denoted as going upwards, negative values as going downwards, but you may see the cycle represented in almost any orientation.

If you see a chemical reaction with a ΔH in units of kJ/mol associated with it, it is reasonable to ask the question, "moles of what"? The question is an important one, since in the reaction, there are likely to be a number of different reactants and products.

Problems

1. A balloon is being inflated to its full extent by heating the air inside it. In the final stages of this process, the volume of the balloon changes from 4.00×10^6L to 4.50×10^6L by the addition of 1.3×10^8J of energy as heat. Assuming the balloon expands against a constant pressure of 1.0 atm, calculate ΔE for the process.
2. A solution of ammonium nitrate was created by dissolving 5.02 grams of ammonium nitrate in 100.0 mL of water at 22.3°C. After forming the solution, the temperature was 17.3°C. Was the dissolution process endothermic or exothermic?
3. When 39.0 grams of copper metal at 92.5°C is dropped into 200. mL of water at 25.0°C, the two substances reach thermal equilibrium. Which substance has particles with the greatest average speed?
4. Propane is the gas that is commonly used in gas drills. A sample of propane with a mass of 44.0 g is completely burned in oxygen and in the process it releases 2002 kJ of energy. This chemical reaction is brought into contact with a water bath, and the transfer of energy from the reaction to the water takes place.

   Assuming the specific heat capacity of water to be 4.200 J g^{-1} K^{-1}, and that in such an experiment 100% of the energy generated by burning the propane is transferred to the water causing the water temperature to increase, calculate the change in temperature of 20.00 kg of water.
5. 50.0 mL of 0.500 M HCl was added to 50.0 mL of 0.500 M NaOH. The initial temperature of the solutions was 19.8°C. The reaction below occurred:

   $$\text{HCl(aq)} + \text{NaOH(aq)} \rightarrow \text{NaCl(aq)} + \text{H}_2\text{O(l)}$$

   The final temperature of the mixture was 26.3°C.

   What is the heat of reaction per mole of NaOH?
6. Upon adding solid potassium hydroxide pellets to water the following reaction takes place:

   $$\text{KOH (s)} \rightarrow \text{KOH(aq)} + 43 \text{ kJ/mol}$$

   What is the enthalpy change for the dissolution of 14.0 g of KOH?
7. Without doing any calculations, determine the enthalpy change for the reaction

   $$\text{CH}_3\text{CH}_2\text{OH} + \text{CH}_3\text{COOH} \rightarrow \text{CH}_3\text{CO}_2\text{CH}_2\text{CH}_3 + \text{H}_2\text{O}$$
8. All elements are assigned a value of ΔH_f° equal to zero. Why?
9. Write an equation to represent the standard enthalpy of combustion of Al(s)
10. Calculate the standard enthalpy of combustion of 2-propanol, given the following data:

    Enthalpies of combustion for C(graphite) = -393 kJ mol^{-1} and H_2(g) = -286 kJ mol^{-1}. Enthalpy of formation of 2-propanol = -318 kJ mol^{-1}.
11. The enthalpy of formation of hexane is -199 kJ and the enthalpy of formation of 1-hexene is -73 kJ. Would calculating the ΔH using Hess's Law or in average bond energy terms be more accurate?

7 Equilibrium

7.1 Introduction to Equilibrium & Direction of Reversible Reactions

AP Topic: 7.1, 7.2

Many chemical reactions and processes are reversible.

Many of these processes and reactions will be accompanied by some kind of observable event that will allow you to see that the process is reversible. Reversible reactions are usually indicated by double arrows, $\rightleftharpoons$.

A dynamic equilibrium exists in a reversible chemical reaction when the rate of the forward reaction is equal to the rate of the reverse reaction. For a reaction to reach equilibrium, a finite amount of time must elapse.

At the beginning of a reversible reaction the reactant concentrations are high, and as a result the rate of the forward reaction is also high. At this point this point the product concentrations are low, and the rate of the backward reaction is low.

As the reaction proceeds, the reactant concentrations will fall, and the rate of the forward reaction will begin to decrease. As the product concentrations increase, the rate of the backward reaction will increase. The point at which the rates of forward and backward reaction are the same is when equilibrium will have been established. At this point, since reactants and products are being converted to one another at the same rate, their concentrations do not change.

Once the equilibrium has been established, a sudden introduction of reactants would result in a sudden dramatic increase of the forward reaction rate. After the spike in forward rate, a new, constant forward reaction rate will be established. The same effect can be observed in the reverse reaction rate when a product is introduced.

Whether the reaction lies far to the right or to the left depends on three factors.

- Initial concentrations
- Relative energies of reactants and products
- Degree of organization of reactants and products

When equilibrium has been achieved, on a macroscopic scale it appears that the reaction has 'stopped'. Closer inspection on the microscope reveals that it is in fact occurring. When equilibrium has been established there are both products and reactants present in the reaction mixture. If those products and reactants have observable differences, the reaction mixture will often appear as a combination of the two.

7.2 Calculating the Equilibrium Constant, Magnitude of the Equilibrium Constant, and Calculating Equilibrium Concentrations

AP Topic: 7.4, 7.5, 7.7

Consider the equilibrium below, where a, b, c and d are stoichiometric coefficients of substances A, B, C and D respectively.

$$\text{aA (aq)} + \text{bB (aq)} \rightleftharpoons \text{cC (aq)} + \text{dD (aq)}$$

The equilibrium constant (K_c) is constant at a given temperature. For the previous reaction at equilibrium, at a given temperature:

$$\text{Kc} = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Where [] represents the equilibrium concentrations in molarity. K_c has no units.

Note that K_c values do not include values for pure solids or pure liquids, since their concentrations are considered constant and as such are incorporated into the constant.

- K_c is used for concentration
- K_p is used for partial pressure

When $K > 1$, the reaction favors the products at equilibrium.

When $K < 1$, the reaction favors the reactants at equilibrium.

RICE is an acronym for the general steps for solving equilibrium problems.

- Set up a "RICE" table R = write a balanced reaction

  I = fill in the initial concentrations

  C = determine the change that is taking place in terms of x

  E = express the equilibrium concentrations in terms of x
- Set up the equilibrium expression and set it equal to its value, if given.
- Celebrate if you are given equilibrium concentrations - skip down to the "E" line and fill them in. You may be asked to work backwards to determine the "change" in equilibrium
- If you are given a K value, then use it to solve for x and use x to calculate the equilibrium concentrations.

  Hints:
  - Look for very small K values, "x" may be negligible.
  - If "x" is large enough to impact the equilibrium values, then you must subtract it from the initial concentration.
  - If none of the initial concentrations are zero, then Q must be calculated first to determine the direction of the shift before following the above general steps.

The magnitude of K can give a quantitative guide to the amount of products and reactants in any given equilibrium mixture. Very large K values indicate a large amount of products, so the reaction essentially "go to completion". Very small K values indicate large numbers of reactants, so the reactions hardly proceed at all.

7.3 Representations of Equilibrium

AP Topic: 7.8

Equilibrium constants for gaseous reactions are usually found in terms of the partial pressures of the components of the mixture. Partial pressures may be given, or if not, can be calculated using

$$\text{Partial Pressure of A} = (\text{mole fraction of A})(\text{Total Pressure})$$

$$\text{Mole fraction of A} = \frac{\text{moles of A}}{\text{total moles}}$$

When a homogeneous gaseous equilibrium is established it is possible to express the equilibrium constant for the reaction in one of two ways, either in terms of concentrations as a Kc value, or in terms of partial pressure as a Kp value. It is often helpful to use the two terms interchangeably and this can be achieved using the expression

$$Kp = Kc(RT)^{\Delta n}$$

Δn is the stoichiometric number of moles of gaseous products minus the stoichiometric number of moles of gaseous reactants

Note when $\Delta n = 0$, Then $K_c = K_p$.

7.4 Reaction Quotient and Equilibrium Constant & Reaction Quotient and Le Chatelier's Principle

AP Topic 7.3, 7.10

When equilibrium is in the process of being established, we can use the reaction quotient, Q, to determine to what extent the reaction has proceeded. Considering the equilibrium from earlier,

$$\text{aA (aq)} + \text{bB (aq)} \leftrightharpoons \text{cC (aq)} + \text{dD (aq)}$$

$$Q = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

It may seem that Q is essentially the same as K, and it is, but the difference being that K is the ratio of products to reactants when equilibrium has been established, and Q is the same ratio at any other point. This allows us to make predictions about what a reaction will do, with any given set of conditions, in order to establish the equilibrium position, and convert Q to K.

- When $K < Q$ then there are too many products in the reactant mixture, and the equilibrium must shift backwards, to the reactant side, in order to reduce the product to reactant ratio and lower Q to a point where $Q = K$.
- When $K > Q$ then there are too many reactants in the reaction mixture, and the equilibrium must shift forwards, to the product side, in order to increase the product to reactant ratio and raise Q to a point where $Q = K$.
- When $K = Q$, equilibrium has been established and there will be no more further observable changes.

7.5 Properties of the Equilibrium Constant

AP Topic: 7.6

It is helpful to be aware of the possible different formats that K and Q could take under circumstances that appear very similar. When a reversible reaction is written in the opposite direction, the new equilibrium constant is equal to the reciprocal of the original equilibrium constant; if a reaction is "halved" or "doubled", then the original equilibrium constant must be square rooted or squared respectively in order to find the new equilibrium constant.

7.6 Introduction to Le Chatelier's Principles

AP Topic: 7.9

Le Chatelier's principle states that in any equilibrium system, when a stress is placed upon the system, such as a change in temperature, pressure or concentration, then there is a shift in the position of the equilibrium to oppose that stress. This shift occurs because the stress will cause Q (or if it is a temperature stress, K) to change,, and the equilibrium will have to shift in order to bring Q back into numerical agreement with K.

It should be noted that since a catalyst causes no change in Q or K, it therefore causes no shift in the equilibrium, but that a catalyst does increase the rates of both the forward and backward reactions, and therefore the rate that equilibrium is established.

Increasing the total pressure in the reaction vessel by adding an inert gas has no effect on the partial pressures of the gases in the equilibrium system, so no change in Q results, so no shift occurs.

We can rationalize a change in K with increased temperature, by considering the energy profiles in each type of reaction. For an exothermic forward reaction, the activation energy of the forward reaction is lower than the activation energy of the endothermic, backward reaction; for an endothermic forward reaction, the activation energy of the forward reaction is larger than the activation energy of the exothermic backward reaction. In short, the endothermic direction always has the larger activation energy in an equilibrium system.

Coupling this knowledge with the fact that an increase in temperature causes a larger increase in the rate of reaction of those reactions with larger activation energies, we can conclude that an increase in temperature causes the rate of the endothermic reaction in an equilibrium system to be increased more than the rate of the exothermic reaction. This means that increasing temperature will always shift an equilibrium system in the endothermic direction. For exothermic forward reactions, that means backward, to give more reactants and smaller K's, and for endothermic forward reactions that means forward, to give more products and larger K's.

In electrochemistry, predictions about how the voltage of an electrochemical cell will change if the conditions are not standard are discussed. That explanation uses a "pseudo" Le Chatelier argument. We can also explain the changes in voltage under non-standard conditions by using "Q versus K", and that is the preferred argument.

7.7 Introduction to Solubility Equilibria

AP Topic: 7.11

You should remember that all sodium, potassium, ammonium and nitrate salts are completely soluble in water. Soluble is defined as "greater than 3 grams dissolving in 100 mL of water". We call everything else "insoluble", even if a good bit of it does dissolve. So "insoluble" is not an absolute term. Even "insoluble" salts dissolve to some degree, and these slightly soluble salts establish a dynamic equilibrium with the hydrated cations and anions in solution.

K_{sp} is defined as the product of the equilibrium concentrations of the constituent ions raised to their stoichiometric coefficients. The smaller the value of K_{sp} then the smaller the number of ions that have gone into solution, and therefore the less soluble the compound is in water. The concentration of ions that have gone into solution is usually expressed in terms of molar solubility, the number of moles of a solute in a 1.0 L of a saturated solution. However, solubility may be expressed as the number of grams of a solute in 1.0 L of a saturated solution. Obviously, these two terms have different definitions, and as such it is occasionally necessary to convert solubility values to molar solubility values, before using them in K_{sp} expressions.

With some knowledge of the reaction quotient, Q, you can determine whether a precipitate will form and what concentrations of ions are required to begin the precipitation of an insoluble salt.

- If $K_{sp} > Q$, the system is not at equilibrium (unsaturated).
- If $K_{sp} = Q$, the system is at equilibrium (saturated).
- If $K_{sp} < Q$, the system is not at equilibrium (supersaturated).

Precipitates form when the solution is supersaturated.

Metal-bearing ores often contain the metal in the form of an insoluble salt, and, to complicate matters, the ores often contain several such metal salts. To selectively precipitate only one type of metal ion, the metal salts can be dissolved to obtain the metal ions and then concentrated in some manner.

Relative solubilities of sparingly soluble salts can be deduced by comparing values of K_{sp}, but be careful! These comparisons can only be made for salts having the same ratio of cations to anions. For example AgCl and $BaSO_4$ are a good pair to compare in this manner since their ratios of ions is 1:1, and their Q/K expressions are both $K = x^2$. The larger K will result in the larger square root of K, hence the larger x value, and hence the greater solubility.

However, such a comparison is not necessarily so easy with salts that have different ratios of ions.

Finally, don't forget that solubility changes with temperature. Some substances become less soluble in cold water while others increase in solubility.

The formation of complex ions can often dissolve otherwise insoluble salts. Often as the complex ions forms, the solubility equilibrium shifts to the right and causes the insoluble salt to become more soluble.

7.8 Free Energy of Dissolution

AP Topic: 7.14

The relative thermodynamic favorability of the dissolution of a salt is determined by the sign of ΔG. As we will see later, ΔG and ΔG° depend on both enthalpy and entropy. The enthalpy change for dissolution is dependent upon three, independent factors;

1. The separation of the solute particles from one another.
2. The separation of the solvent particles from one another.
3. The interaction between the solute particles and the solvent particles.

In addition to enthalpy changes, we also need to consider entropy changes. When a solute dissolves, entropy increases.

It is the cumulative effects of enthalpy and entropy factors that determine the value of G°, and ultimately the thermodynamic favorability of any dissolution process.

7.9 Common-Ion Effect

AP Topic: 7.12

If a solution contains two dissolved substances that share a common ion, then the solubility of a salt becomes a more complex matter to determine. Experiments show that the solubility of any salt is always less in the presence of a common ion.

7.10 pH and Solubility

AP Topic: 7.13

When one of the ions in a salt can act as an acid or base, pH can influence solubility.

In general, insoluble inorganic salts containing anions derived from weak acids tend to be soluble in solutions of strong acids.

Salts are not soluble in strong acid if the anion is the conjugate base of a strong acid!

Problems

1. Write the expressions for K and K_p for the process of deep blue solid copper(II) sulfate pentahydrate being heated to drive off water vapor to form white solid copper(II) sulfate.
2. K for the reaction below has a value of 55 at a certain, given temperature. Calculate the number of moles of HBr present in an equilibrium mixture that contains 3.0 moles of hydrogen gas and 0.45 moles of bromine vapor at this temperature.
$$H_2(g) + Br_2(g) \rightleftharpoons 2HBr(g)$$
3. Sulfur dioxide and oxygen were mixed in the molar ratio 2:1 and allowed to reach equilibrium at a total pressure of 4.45 atm. At this point, 28.0% of the sulfur dioxide was converted into sulfur trioxide. Calculate K_p for the reaction.
4. For the synthesis of ammonia at 500°C, the equilibrium constant is 6.0×10^{-2}. Predict which direction the system will go when $[NH_3]_0 = 1.0 \times 10^{-4}$M, $[N_2]_0 =$ 5.0M and $[H_2]_0 = 1.0 \times 10^{-2}$M.
5. The following equilibrium concentrations were observed for the Haber process at 127°C:
$$[NH_3] = 3.1 \times 10^{-2} \text{ mol/L}$$
$$[N_2] = 8.5 \times 10^{-1} \text{ mol/L}$$
$$[H_2] = 3.1 \times 10^{-3} \text{ mol/L}$$
Calculate the value of the equilibrium constant at 127° for the reaction given by the equation:
$$\tfrac{1}{2}N_2(g)+\tfrac{3}{2}H_2(g) \rightleftharpoons NH_3(g)$$
6. Assume that gaseous hydrogen iodide is synthesized from hydrogen gas and iodine vapor at a temperature where the equilibrium constant is 1.00×10^{-2}. Suppose HI at 5.000×10^{-1} atm, H_2 at 1.000×10^{-2} atm, and I_2 at 5.000×10^{-3} atm are mixed in a 5.000-L flask. Calculate the equilibrium pressures of all species.

7. Predict the shift in equilibrium position that will occur when the volume is reduced The preparation of liquid phosphorus trichloride by the reaction:

$$P_4(s)+6Cl_2(g)\rightleftharpoons 4PCl_3(l)$$

8. A solution is prepared by adding 750.0 mL of 4.00×10^{-3}M $Ce(NO_3)_3$ to 300.0 mL of 2.00×10^{-2}M KIO_3. Will $Ce(IO_3)_3$ ($K_{sp} = 1.9 \times 10^{-10}$) precipitate from this solution?
9. A solution is prepared by mixing 150.0 mL of 1.00×10^{-2}M $Mg(NO_3)_2$ and 250.0 mL of 1.00×10^{-1}M NaF. Calculate the concentrations of Mg^{2+} and F^- at equilibrium with solid MgF_2 ($K_{sp} = 6.4 \times 10^{-9}$).
10. Purely in terms of Q and K, explain why barium sulfate is less soluble in a solution of sodium sulfate than it is in water.
11. The solubility product of $Pb(OH)_2$ is 1.2×10^{-15}. Find the molar solubility of a saturated solution of $Pb(OH)_2$ and find the molar solubility of $Pb(OH)_2$ in a solution of pH = 11.00. Explain the changes in the molar solubility of $Pb(OH)_2$.

8 Acids and Bases

8.1 Introduction to Acids and Bases & pH and pOH of Strong Acids and Bases

AP Topic: 8.1, 8.2

Acids can be defined in terms of proton (H^+) transfer, their strength in terms of ionization, and how they can be sorted into acid-base conjugate pairs.

An acid is a substance that donates hydrogen ions in aqueous solution.

A base is a substance that accepts hydrogen ions in aqueous solution.

The ability of water to act as both an acid and a base is an important concept to grasp, and is called amphoteric behavior.

An acid is a substance that dissolves in water to produce hydronium ions.

A base is a substance that dissolves in water to produce hydroxide ions.

Conjugate acid and base pairs are related by a difference of a hydrogen ion on either side of the equation.

Recall that there are seven strong acids: HCl, HBr, HI, HNO_3, H_2SO_4, $HClO_3$, and $HClO_4$, and there are eight strong bases: LiOH, NaOH, KOH, RbOH, CsOH, $Ca(OH)_2$, $Sr(OH)_2$, and $Ba(OH)_2$. A strong acid or base undergoes complete ionization.

Weak acids and weak bases, on the other hand, have very little ionization and equilibria are set up with the equilibria laying heavily on the left hand side.

The acid ionization constant is written as K_a.

$$\text{Percent ionization} = \frac{[H_3O^+]\text{equilibrium}}{[HA]\text{initial}} \times 100\%$$

Percent ionization is a measurement of the extent of ionization of an acid. However, percent ionization is dependent on both the strength of the acid or base and the initial concentration. If acids are of equal concentration, the weaker acid will have a lower percent ionization. If two samples of the same acid are of different concentrations, the solution of lower concentration will have a higher percent ionization.

It should be noted that the concentration of H_3O^+ and OH^- are dependent upon two separate factors. First, the strength of the acid or base, and secondly, the amount of water present. As such, it is possible to have a dilute, strong acid, and to have a concentrated, weak acid that have the same hydronium concentration, and therefore the same pH value. Do not confuse concentration for strength.

The pH scale is used to indicate the relative acidity or basicity of an aqueous solution. There is a common misconception that that acid-base pH scale ranges from 0 to 14; however you can have values that are less than 0 and greater than 14. Acids have pHs less than 7, bases have pHs greater than 7, and 7 on the scale is considered to be neutral, although we will see later how this can vary. Both pH and pOh are defined in a similar manner:

$$\text{pH} = \text{-log}[H_3O^+]$$

$$\text{pOH -log}[OH^-]$$

In the case of strong acids and bases, the dissociation is complete, and therefore the concentration of the H_3O^+ ions or OH^- ions can be determined directly from the stoichiometric ratio in the balanced equation and the concentration of acid or base.

$$14 = \text{pH} + \text{pOH}$$

An equilibrium constant can also be written for water.

$$K_w = [H_3O^+][OH^-]$$

Like all equilibrium constants, K_w is temperature dependent. At 298 K, $K_w = 1 \times 10^{-14}$. Only about 2 in a billion water molecules are ionized at any instant. Since pure H_2O will have equal concentrations of H_3O^+ (aq) and OH^- (aq), then under these conditions, we can find that the pH of pure water at 298 K is 7.

From the K_w equation we can find that

$$pK_w = 14 = pH + pOH$$

It should be carefully noted that at other temperatures, K_w will have values other than 1×10^{-14}. As such, at temperatures other than 298 K, pure water may not have a pH = 7, but it will still be considered neutral, since in pure water $[H^+]$ will always equal $[OH^-]$; neutrality is dependent on the equal contractions of these ions as opposed to a pH of 7. In short, in any solution at any temperature

- If $[H^+] = [OH^-]$, the solution is neutral.
- If $[H^+] > [OH^-]$, the solution is acidic.
- If $[H^+] < [OH^-]$, the solution is basic.

At 298 K, the K_a and K_b of an acid-base conjugate pair are related thus:

$$K_w = 1 \times 10^{-14} = (Ka)(Kb)$$

Logging both sides we get

$$pKw = 14 = pKa + pKb$$

8.2 Weak Acid and Base Equilibria

AP Topic: 8.3

Calculating pH of weak acids involves setting up an equilibrium. It helps to start by writing the balanced equation, setting up the acid equilibrium expression, defining initial concentrations, changes, and final concentration in terms of x, substituting values and variables into the K_a expression, and solving for x. In other words, use the RICE table method.

Often the -x term in a K_a expression can be neglected. That simplifies the math tremendously since you are not spared the tedium of having to use the quadratic formula. How do you know when to neglect x? Look at the original concentration and compare it to $100K_a$ (or $100K_b$ if you are dealing with a weak base). If the initial concentration is large by comparison, you can neglect subtracting the x term.

Because weak acids only partially dissociate, it is not possible to go directly to pH = $-\log[H_3O^+(aq)]$ from the concentration of the acid.

We can derive the following expressions.

$$Ka = \frac{[H_3O^+][A^-]}{[HA]}$$

Often written as

$$Ka = \frac{[H_3O^+]^2}{[HA]}$$

Note that the stronger the acid, the higher the value of K_a. Also,

$$pKa = -\log Ka$$

Note that the stronger the acid, the lower the value of pK_a. K_a and pK_a are inversely related.

For a weak base, dissociation is incomplete.

It is similar to a weak acid expression.

$$Kb = \frac{[OH^-][NH_4^+]}{[NH_3]}$$

Written often as

$$Kb = \frac{[OH^-]^2}{[NH_3]}$$

and

$$pKb = \text{-log } Kb$$

Note that when using RICE tables with weak bases, x represents $[OH^-]$, not $[H^+]$ as with weak acids. Taking the negative log of x will give you the pOH not the pH. Also note that the major species in any solution of a weak acid or base will be the undisassociated form.

8.3 Acid-Base Reactions and Buffers

AP Topic: 8.4

When strong acids and bases react, they do so to create water.

When the moles of base are equal to the moles of acid, neutralization has occurred. When adding unequal amounts of strong acids and strong bases together, all of the limiting reagent will be neutralized and the pH of the resulting solution is determined by the excess reagent, using the pH and pOH formulas.

A crucial part of the application of buffer solutions has been the appreciation that buffer solutions are inadvertently produced when mixing weak acids and bases. A buffer is a solution containing relatively high concentrations of a conjugate acid-base pair and is discussed further, but if a small amount of strong acid or base is added to a buffer solution, the buffer solution resists changes to the pH. When a weak acid and a strong base are mixed there are three possible combinations.

1. If the weak acid is in excess, then the resulting solution is a buffer solution. The Henderson-Hasselbalch equation can be used to determine the pH of the resulting solution.

   $$pH = pKa + \log\frac{[A^-]}{[HA]}$$

2. If the strong base is in excess, then the pH of the resulting solution will be calculated from the molarity of the solution formed from the excess moles of the base divided by the total volume of the solution. This is similar to the strong acid with a strong base as shown previously.
3. If the weak acid and strong base are equimolar, then the solution is at the equivalence point, where the weak acid has been neutralized by the strong base, but an equivalent number of moles of the salt has been formed. The pH of the resulting solution will be determined by the conjugate base of the weak acid.
   - Use a RICE table to find the equilibrium concentration of OH^-.
   - Determine the equilibrium constant for the conjugate base, $K_b = K_w/K_a$
   - Use the moles of the conjugate base and the total volume to find the initial molarity

When a strong acid and a weak base react there are also three possibilities.

1. If the weak base is in excess, then the resulting solution is a buffer solution and you should use the Henderson-Hasselbalch equation to determine the pH of the resulting solution.
2. If the strong acid is in excess, then the pH of the resulting solution will be calculated from the molarity of the solution formed from the excess moles of the hydronium ion divided by the total volume of the solution.
3. If the weak base and strong acid are equimolar, then the reaction is at its equivalence point; the mole of the acid and base are equal. The pH at the equivalence point when a strong acid and a weak base are reacting is determined by the conjugate acid of the weak base.
   - Use a RICE table to find the equilibrium concentration of the H_3O^+.
   - Start by calculating the initial molarity of the weak conjugate acid by using the mole of the conjugate acid and the total volume.
   - Then complete the RICE table establishing equilibrium

8.4 Acid-Base Titrations

AP Topic: 8.5

Titration is an experimental technique used to perform a neutralization reaction. Accurately graduated glassware is used in a quantitative manner to analyze acid-base reactions. Typically a known concentration of a base is added to an unknown concentration of an acid, or vice versa. The volume of both solutions is measured and used to calculate the unknown concentration.

In a titration, as a base or an acid is added to an acid or base respectively, there is very little change in pH, and a pH change of less than approximately 1.5 is expected up to the point that 90% of the acid or base has been neutralized. This is the buffering region that will be discussed further. When the moles of titrant are in the exact stoichiometric proportion with the titrate/analyte, then the equivalence point has been reached. At this point there is a rapid change in pH.

These changes can be summarized using a titraiton curve which plots pH against the volume of titrant added. The shape of the titration curve differs based on the identity of the titrant and the analyte; factors to consider are the strength of the acid and the base, the number of hydrogen ions/hydroxide ions that will dissociate, and the concentrations of the acid and the base.

Note that when looking at a titration curve, the inflection point corresponds to the equivalence point. WHen a strong acid and a strong base react the equivalence point will be at pH = 7. When a strong base is added to a weak acid, the pH at the equivalence point will be above pH = 7, because as the weak acid is neutralized, its conjugate base is formed, causing the solution to be basic. We can also use this titration curve to determine the pKa of the weak acid. The pKa is equal to the pH at half the equivalence point. This is because at this half equivalence point there are equal concentrations of conjugate acid and base, because half of the initial concentration of the acid will have been neutralized, and will have formed the conjugate base.

Most acid-base titrations involve the addition of one colorless solution to another colorless solution with no obvious, observable reaction taking place. Since in an acid-base titration we need to find the equivalence point in order to apply the stoichiometric ratio and then calculate the unknown concentration, we need a method of determining when the equivalence point has been reached. We do this with the aid of indicators, a chemical that changes colors at various pHs. Indicators are often weak, organic acids, where the ionized and the unionized form have different colors. Usually 1/10 of the initial form of the indicator must be changed to the other form before a new color is apparent. Since you typically only add a drop or two of the indicator to the analyte, indicators have very little effect on overall pH of interest. In practice, an indicator will change color over a small, given range of pH.

Again, the equivalence point is located in the middle of the vertical portion of the titration curves. We need to choose an indicator that changes color at a pH value as close to the equivalence point as possible. This observable color change of the indicator is called the end point, and it should correspond to the equivalence point as closely as possible. So using the titration plots, suitable indicators can be chosen.

Strong acid - Strong base: most indicators

Weak acid - Strong base - Phenolphthalein

Strong acid - Weak base - Methyl orange

The useful range of an indicator is usually its pKa ± 1. When choosing an indicator, determine the pH at the equivalence point of the titration and then choose an indicator with a pKa close to that.

For a weak acid-weak base titration there is no sharp change in pH at the equivalence point, therefore no indicator will change color sharply at the end-point, therefore no indicator is suitable. A pH meter can be used to determine the end-point in weak acid-weak base titrations.

Acids with more than one ionizable hydrogen will ionize in steps. These polyprotic acids will have multiple equivalence points, and produce a titration curve with multiple, vertical portions. On the titration curve below, a diprotic acid is being titrated with a strong base. We recognize it as diprotic because there are two inflection points. These two points correspond with the equivalence point for each of the protons being donated. We can determine the pKa for each of these protons being donated by using the half equivalence point pH method. Because there are multiple protons reacting, the two protons will be donated sequentially, instead of both at the same time. This is demonstrated through a diprotic acid having two different pKa values. Each dissociation has its own Ka value, but the first dissociation is the greatest.Subsequent dissociations will have much smaller equilibrium constants. As each H^+ is removed, the remaining acid gets weaker and therefore has a smaller Ka. As the negative charge on the acid increases it becomes more difficult to remove the positively charged proton. Looking at the Ka values of polyprotic acids, it is obvious that only the first dissociation will be important in determining the pH of the solution for all acids except sulfuric acid. Because sulfuric acid is a strong acid in its first dissociation and a weak acid in its second, we need to consider both if the concentration is more dilute than 1.0 M.

As noted earlier, careful analysis of titration curves shows that the equivalence point is not necessarily at pH = 7. This is due to the fact that salts are not always neutral. Some salts do form neutral solutions, but others react with water to form acidic or basic solutions. The reaction is called salt hydrolysis.

- Strong acid and Strong base - pH at equivalence point is 7
- Strong base and Weak acid - pH is greater than 7 at equivalence point
- Strong acid and Weak base - pH is less than 7 at equivalence point
- Weak acid and weak base -
  - If Kb for the anion ¿ Ka for the cation then basic at equivalence point
  - If Ka for the cation ¿ Kb for the anion then acidic at equivalence point
  - If Ka is approximately equal to Kb then neutral at equivalence point

8.5 Molecular Structure of Acids and Bases

AP Topic: 8.6

The structure and bonding that exist in acids and bases can influence their strength.

The chemical structures of acids controls their relative strength. Bond length, bond strength, and electronegativities of atoms in the compound all play a role in the degree to which a Bronsted-Lowry acid will dissociate in solution.

THere is a trend that an acid strength increases for binary acids down a group of the periodic table. In this case, bond length and strength appears to play the major role. The trend suggests that longer and weaker H-X bonds result in a relatively stronger acid than an acid with a shorter and stronger bond.

An oxyacid is a ternary acid with one ore more oxygens in its structure. Generally, the more oxygen present in the polyatomic ion of an oxyacid the stronger its acid within that group. This is because the H of the acid is bound to an oxygen and not any other nonmetal present. Oxygen is very electronegative and attracts the electrons of the O-H bond toward itself. If you add more oxygens, then the effect is magnified and there is an increasing electron density in the region of the molecule that is opposite the H. The added electron density weakens the bond, thus less energy is required to break the bond and the acid dissociates more readily, which we describe as “strong”.

The relative strength of a carboxylic acid depends upon the stability of the anion that is forms, when it loses its labile. If the anion is relatively stable, then it will form in solution, and the process the acid will tend to donate H^+ ions, making the acid relatively strong. Remember the smaller the pKa, the stronger the acid. It is also found that when you compare strengths of halogen-substituted caboxylic acids, the numebr of chlorine atoms present increases the strength of the acid, because the highly electronegative Cl atoms attract electron density away from the COO^- part of the anion, therefore increasing its stability.

Fluorine is the most electronegative halogen, so carboxylic acids containing fluorine tend to be the strongest.

Nitrogenous bases are substances that contain nitrogen and have the properties of bases.

Note that the vast majority of acids/bases are weak.

If you are given a mixture of weak acids, only the acid with the largest Ka value will contribute an appreciable $[H^+]$. Determine the pH based on this acid and ignore any others.

8.6 Properties of Buffers

AP Topic: 8.8

A buffer solution is one that resists change in pH when either a small amount of acid or base is added to it. Usually a buffer solution is made from a weak acid and one of its salts or from a weak base and one of its salts.

The process of "mopping up" added base and acid allow the pH to remain relatively unchanged. Note that pure water has no buffering capacity; acids and bases added to water directly affect the pH of the solution.

All buffer solutions mayb e solved with the following equation to lessen confusion:

$$[\mathrm{H}^+] = \mathrm{K}_a \frac{[\mathrm{Acid}]}{[\mathrm{Base}]}$$

Recall from previous discussions that the addition of an ion present in a system causes the equilibrium to shift away from the common ion. It is best to explain the common ion effect in terms of the reaction quotient versus the equilibrium constant.

The addition of a salt containing a common anion to a solution of a weak acid makes the solution less acidic.

8.7 pH and pKa & Henderson-Hasselbalch Equation

AP Topic: 8.7, 8.9

While RICE tables are always an option, a shortcut way to calculate the pH of a buffer solution is with the Henderson-Hasselbalch equation. This involves the pKa or pKb of the weak acid or base and the ratio of the concentrations of each component. To calculate the pH of an acidic buffer use this version of the Henderson-Hasselbalch equation:

$$\mathrm{pH} = \mathrm{pKa} + \log\left(\frac{[\mathrm{salt}]}{[\mathrm{acid}]}\right)$$

Use this version for a basic buffer:

$$\mathrm{pOH} = \mathrm{pKb} + \log\left(\frac{[\mathrm{salt}]}{[\mathrm{base}]}\right)$$

and then remember that 14 = pH + pOH applies for any solution. Note that you can use mole instead of molarity in the log ratio of each equation.

Since the pKa or pKb is fixed for a weak acid or base, if the concentration of the components are changing but remain in the same ratio, the pH of the buffer will not change. However, changing the concentrations of the components does affect the capacity of the buffer. Optimum buffering occurs when $[\mathrm{HA}] = [\mathrm{A}^-]$ and the pKa of the weak acid used should be as close as possible to the desired pH of the buffer system.

A little knolwedge of logarithms can go a long way here. Considering the acid version of the Henderson-Hasselbalch equation, it can be seen that if the pH of a buffer solution is greater than the pKa of the acid, then the salt concentration must be greater than the acid concentration. When the pH is less than the pKa, the opposite is true.

At the point the concentrations of salt and acid or salt and base are equal, the pH = pKa, or the pOH = pKb.

Using the relationship between the pH and pKa of a solution that is a buffer allows us to make qualitative and quantitative assessments of which component of the buffer is present in the greatest concentration. We can compare the pH to the pKa to determine which species is predominant at a certain pH, or use the ratio of components to determine the pH.

The Henderson-Hasselbalch equation needs to be used cautiously. A Ka or Kb problem requires a greater understanding of the factors involved and can always be used instead of the Henderson-Hasselbalch equation. This equation is only valid for solutions that contain weak, monoprotic acids and their salts or weak bases and their salts. The buffered solution cannot be too dilute and the Ka/Kb cannot be too large.

As the base is gradually added to the weak acid, some of the weak acid is neutralized, and the result is the salt of the weak acid and water. Because not all of the weak acid has been neutralized, it is still present in solution alongside the salt. This combination in a solution is a buffer solution, and its pH can be calculated by using a RICE table to determine the remaining concentration of the weak acid and the new concentration of the salt. Then applu the Henderson-Hasselbalch equation. Alternatively you can use the following:

$$[H^+] = K_a \frac{(mol_{WA}) - mol_{base}}{(mol_{WB}) + mol_{base}}$$

As the acid is gradually added to the weak base, some of the weak base is neutralized, and the result is the salt of the weak base and water. Because not all of the weak base has been neutralized, it is still present in solution alongisde the salt. This combination in solution is a buffer solution, and its pOH can be calculated by using a RICE table to determine the remaining concentration of the weak base and the new concentration of the salt. Then apply the Henderson-Hasselbalch equation. Alternatively you can use the following:

$$[H^+] = K_a \frac{mol_{WA} + mol_{acid}}{(mol_{WB}) - mol_{acid}}$$

8.8 Buffer Capacity

AP Topic: 8.10

The capacity of a buffer is defined as its ability to continue to react with any extra acid or base that is added to it without a significant change in pH. The higher the concentrations of the components of a buffer, the more acid or base it can absorb in the reactions above, and the higher its capacity. Note that if we change the concentrations of each component of a buffer the capacity will change, but if the ratio of the components remain the same, according to the Henderson-Hasselbalch equation, the pH will not change.

Problems

1. In the following reaction label the acid, base, conjugate acid, and conjugate base.

   $$\mathrm{HBr + NH_3 \rightarrow NH_4^+ + Br^-}$$

2. Calculate the pH of a solution made by dissolving 2.00 g of KOH in H_2O to a total volume of 250. mL.
3. Which solution has the lowest pH, 0.0010 M potassium hydroxide, KOH, or 0.0010 M calcium hydroxide, $Ca(OH)_2$?
4. Calculate the K_a of a solution of 0.250 M of a weak acid with a pH of 5.11.
5. Calculate the K_b of a solution of 0.250 M of a weak base with a pH of 9.12.
6. What is the pH of a solution composed of 500.0 mL of 0.250 M sodium hydroxide, NaOH, and 400.0 mL of 0.200 M hydrochloric acid, HCl?
7. The pK_a of hydrozoic acid, HN_3, is 4.72. It reacts with water according to the reaction below:

   $$\mathrm{HN_3\ (aq) + H_2O\ (l) \rightleftharpoons N_3^-\ (aq) + H_3O^+(aq)}$$

   Calculate the pH of a solution formed from 100.0 mL of 0.900 M HN_3 and 50.0 mL of 0.300 M NaOH.
8. Calculate the pH of a 5.0 M H_3PO_4 solution and the equilibrium concentrations of the species H_3PO_4, $H_2PO_4^-$, $HPO4^{2-}$, and PO_4^{3-}.
9. Predict whether an aqueous solution of $Al_2(SO_4)_3$ will be acidic, basic, or neutral with appropriate equations.
10. How do you account for the difference in the pK_a of acetic acid (CH_3COOH, 4.76) and fluoroacetic acid (CH_2FCOOH, 2.59)?
11. Determine the $[H_3O^+]$ and $[C_2H_3O_2^-]$ in 0.100 M $HC_2H_3O_2$. The K_a for acetic acid is 1.8×10^{-5}.
12. Ethanoic acid has a pK_a of 4.75. Find the pH of the solution that results from the addition of 40.0 mL of 0.040 M NaOH to 50.0 mL of 0.075 M ethanoic acid.
13. Calculate the pH of the solution that results when 0.10 mol gaseous HCl is added to 1.0 L of the buffered solution that contains 0.25 M NH_3 ($k_b = 1.8 \times 10^{-5}$) and 0.40 M NH_4Cl.

14. Three buffers were created from using a weak acid, HA (pK_a = 3.20) and LiA.
    - Buffer X = 1.00 moles of HA + 0.50 moles of LiA dissolved to form 1.00 L of solution.
    - Buffer Y = 0.50 moles of HA + 1.00 moles of LiA dissolved to form 1.00 L of solution.
    - Buffer Z = 2.00 moles of HA + 4.00 moles of LiA dissolved to form 1.00 L of solution.

    Which buffer will be best at resisting a change to the pH when an acid is added?

9 Applications of Thermodynamics

9.1 Introduction to Entropy & Absolute Energy and Entropy Change

AP Topic: 9.1, 9.2

Remember enthalpy, H, the heat content of a system? One might assume that a reaction with a negative ΔH would always proceed since the products have a lower enthalpy than the reactants and are more stable. However, this is not necessarily so. If a reaction has a very high energy of activation then it will not occur and is described as kinetically stable or under kinetic control. In these circumstances it is possible that a reaction that one might predict as being highly likely, produces little or no products.

Similarly, one might assume that a reaction with a positive ΔH will never proceed since the products have a higher enthalpy than the reactants and are less stable. However, some endothermic reactions do proceed.

The degree of disorder or dispersal of energy in a reaction is caleld the entropy and is given the symbol, S.

Entropy is closely related to probability. The key concept is that the more ways a particular state can be achieved, the greater the likelihood of finding that state. In English...nature spontaneously proceeds toward the states that have the highest probability of existing.

A pure, perfect crystal at 0 K is assigned an absolute entropy = 0, that is to say it is completely 'organized' or completely 'ordered'. The absolute entropies of substances in the real world are measured relative to that, and as such all have values that are greater than zero. The state, temperature, number of particles and volumes of gases are all important factors in entropy, and we find thatl

- absolute entropy of solids < absolute entropy of liquids <<< absolute entropy of gases
- absolute entropy of a small number of particles is less than the absolute entropy of a large number of similar particles
- absolute entropies of gases with smaller volumes are less than the absolute entropies of gases with larger volumes, since the ones with larger volumes have more space to be disordered in
- entropy increases with increasing temp since particles can move around more and are more dispersed

A couple of other hints for predicting the entropy of a system based on physical evidence:

- The greater the dispersal of matter and/or energy in a system, the larger the entropy.
- When a pure solid or liquid dissolves in a solvent, the entropy of the substance increases. (Carbonates are an exception.)
- When a gas molecule escapes from a solvent, the entropy increases.
- Entropy generally increases with increasing molecular complexity since there are more moving electrons.

In short, ΔS is positive when dispersal/disorder increases and ΔS is negative when dispersal/disorder decreases.

The change in entropy (ΔS°) in a reaction can be calculated from tables of standard values by subtracting the sum of the absolute values of the entropy of the reactants from the sum of the absolute entropies of the produts. Units of entropy are usually J/(mol$_{rxn}$·K)

$$\Delta S^\circ_{REACTION} = \sum S^\circ_{PRODUCTS} - \sum S^\circ_{REACTANTS}$$

The zeroth law of thermodynamics: If substance A is in thermal equilibrium with substance B and substance B is in thermal equilibrium, then A is also in thermal equilibrium with substance C.

The first law of thermodynamics: Energy can never be created nor destroyed. Therefore, the energy of the universe is constant.

The second law of thermodynamics: the universe is constantly increasing the dispersal of matter and energy. In order words, disorder always increases.

The third law of thermodynamics: the the entropy of a perfect crystal at 0 K is zero. There are not a lot of perfect crystals out there, so entropy values are rarely ever zero. This means the absolute entropy of a substance can then be determined at any temperature higher than zero K.

Phase changes occur at constant temperature and represent a system which is also in equilibrium.

$$\Delta S^\circ = \frac{\text{heat transferred}}{\text{temperature at which change occurs}} = \frac{q}{T} = \frac{-\Delta H}{T}$$

- where the heat supplied or evolved is divided by temperature in Kelvin
- The actual significance of whether the phase change is endothermic or exothermic is really dependent on the temperature at which the process occurs.

Usually chemists are concerned with calculating the entropy change for a system. However, it is possible to calculate the entropy change of the surroundings using the previous equation.

There is also the following relationship:

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$$

Whether a reaction will occur spontaneously may be determined by looking at the ΔS of the universe.

- If $\Delta S_{\text{universe}}$ is positive, then the reaction is thermodynamically favorable.
- If $\Delta S_{\text{universe}}$ is negative, then the reaction is not thermodynamically favorable.

9.2 Gibbs Free Energy and Thermodynamic Favorability & Thermodynamic and Kinetic Control

AP Topic: 9.3, 9.4

Luckily, chemists can get around having to determine the entropy change of the universe by defining and using a new thermodynamic quantity called Gibbs free energy. Enthalpy and entropy are brought together in the Gibbs-Helmholtz free energy equation, where all values refer to the system of interest.

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

Notes:

1. In order to apply this equation, all reactants and products in an equilibrium mixture must be present and in their standard states. A temperature should be stated.
2. Entropy values tend to be given in units that involve J, whereas enthalpy values tend to be given in units that involve kJ. Therefore, it is very important to remember that a conversion of one unit to match the other is often required.

The calculation of ΔG is what ultimately decides whether a reaction is thermodynamically favored or not. All thermodynamically favored chemical reactions have a value for ΔG° that is negative.

We can summarize the possible sign combinations of ΔH°, ΔS° and ΔG°.

- H: positive, S: positive, G: negative at high temperatures and positive at low temperatures
- H: positive, S: negative, G: always positive
- H: negative, S: positive, G: always negative
- H: negative, S: negative, G: negative at low temperatures and positive at high temperatures

A value for the change in standard Gibbs free energy in a reaction can also be calculated in much the same manner as ΔH° and ΔS°, by using the following:

$$\Delta G^\circ = \sum G^\circ_{f\ \text{PRODUCTS}} \text{ - } \sum G^\circ_{f\ \text{REACTANTS}}$$

If ΔG° is positive then the reaction is not thermodynamically favored, and if $\Delta G^\circ = 0$, then the reaction is favored equally in both the forward and backward directions. Both ΔH°_f and $\Delta G^\circ_f = 0$ for elements in their standard state and both beat units of kJ mol^{-1}. You must look up S° values rather than them being zero as well. Only a perfect diamond at absolute zero has a S° value of 0.

Yet another method for determining ΔG° for a "new" reaction is to use Hess's Law of Summation. It works exactly the same as in enthalpy calculations; arrange a series of chemical equations for which you know the $\Delta G^\circ_{\text{rxn}}$ to obtain the "goal equation". If you need to reverse an equation, then you change the sign of $\Delta G^\circ_{\text{rxn}}$ and cross off common moles of substances as you sum the equations to deliver the goal equation. If you double an equation to obtain the goal, double the value of $\Delta G^\circ_{\text{rxn}}$; if you halve a reaction, halve the value of $\Delta G^\circ_{\text{rxn}}$ for that reaction, etc.

9.3 Coupled Reactions

AP Topic: 9.6

A reaction with a positive ΔG° can be forced to occur by applying energy from an external source. Three such examples will be considered here.

1. Using electricity in the process of electrolysis.
2. Using light to overcome a highly endothermic ionization energy.
3. The coupling of a thermodynamically unfavorable reaction to a favorable one where intermediates are common throughout a series of reactions, and taken together the reactions combine to form an overall reaction with a favorable, negative ΔG°.

The process of combining non-thermodynamically favored and thermodynamically favored reactions to produce an overall thermodynamically favored reaction is called coupling.

9.4 Free Energy and Equilibrium

AP Topic: 9.5

Using the given temperature and equilibrium constant, K, for a reaction:

$$\Delta G^\circ = -RT \ln K$$

Remember two things:

1. That K has a range of magnitudes that is massive, from incredibly tiny numbers to incredibly massive numbers, but K will always be positive.
2. That ΔG° has a range of magnitude that tends to be more narrow than those of K, but that ΔG° can be either positive or negative.

Large magnitude negative values for ΔG° will lead to large magnitude values for K. Large values of K show that reactions are thermodynmically favored, with many products compared to reactants at equilibrium.

When the value of ΔG° is close to zero that will lead to values for K that are close to 1. Such values of K show that reactions are close to having reactants and products equally favored at equilibrium.

Large magnitude positive values for ΔG° will lea to small magnitude values for K. Small values of K show that reactions are thermodynamically unfavored, with many reactants compared to products at equilibrium.

We have see earlier how ΔG° can be influenced by temperature, but there is one more thing to consider. ΔG° also assumes standard conditions of 1 atm for gases and 1 M for solutions. This means that when conditions differ from those standard values, a new ΔG value applies. In some cases, not only does the magnitude of ΔG change, but the sign will change too, causing a previously non-favored reaction to become favorable, and vice-versa. There is an equation which allows the calculation of such things, namely

$$\Delta G = \Delta G^\circ + RT \ln Q$$

You should understand that initial conditions, outside of standard ones, might cause a favored reaction to actually produce very few products, and non-favored one to actually produce products.

Also note that it is not true to assume that if ΔG is large and negative, the process must proceed at a measurable rate.

9.5 Galvanic (Voltaic) and Electrolytic Cells

AP Topic: 9.7

Electrochemistry is the study of the interchange of chemical and electrical energy. Electrochemistry involves two main types of electrochemical cells:

- Galvanic (voltaic) cells - which are thermodynamically favorable chemical reactions
- Electrolytic cells - which are thermodynamically unfavorable and require an external electron source

When a metal is placed in a solution containing its own ions, a reversible reaction is set up.

So, whenever, an element is placed in contact with a solution containing its own ions, an electric charge will develop on the metal or, in the case of a non-metal, on the inert conductor placed in solution. The charge is called the electrode potential and the system is called a half-cell. The sign and size of the charge will depend on the relative ability of the element to lose or gain electrons when compared to the hydrogen half-cell. In order to make meaningful comparisons it is necessary to stipulate a set of standard conditions under which the electrode potential of a given half-cell is measured.

The Standard Electrode Reduction Potentials of a hallf-cell, E°, is defined as the electrode potential of a half-cell, measured relative to a standard hydrogen electrode, which has a value of 0.00 V, under standard conditions of 298 K, gases at a pressure of 1.0 atm, and solutions at concentrations of 1.0 M.

The practical use of the hydrogen half-cell for determining E° values suffers from at least two problems.

- It is difficult and time consuming to set up the hydrogen half-cell.
- It is fragile and non-portable.

These electrode potentials can be tabulated to show the relative tendency for each species to gain electrons. The more positive values can be thought of as being more likely to gain negative electrons, and the more negative values can be thought of as being more likely to lose negative electrons.

Note that the Standard Reduction Potential table can also be used as an activity series. Metals having less positive reduction potentials are more active and will replace metals with more positive potentials.

Species that appear at the top of the series gain electrons most readily and therefore have the most positive E° values, are easily reduced and are the best oxidizing agents.

Species that appear at the bottom of the series lose electrons most readily and therefore have the most negative E° values, are easily oxidized and are the best reducing agents.

A galvanic or voltaic cell is the apparatus for generating electrical energy from a spontaneous oxidation-reduction or redox reaction. Oxidation is loss of electrons; reduction is gain of electrons. Connecting two half-cells that have different electrode potentials forms a galvanic cell. A salt bridge connects the two half-cells.

Parts of a Galvanic/Voltaic Cell:

- Anode - the electrode where the oxidation occurs. After a period of time, the anode may appear to be smaller as it falls into solution.
- Cathode - electrode where reduction occurs. After a period of time, it may appear larger, due to ions from solution plating onto it.
- Inert electrodes - used when a gas is involved or ion to ion involved; made of Pt or graphite.
- Salt bridge - used to maintain electrical neutrality; usually in a U-shaped tube filled with agar that has a neutral salt dissolved into it before it gels, or the bridge may be replaced with a pourous disk/cup. The salt bridge could also be made from a piece of filter paper soaked in a suitable ionic solution, often KCl (aq) or KNO_3(aq). The ionic soultion used in the salt bridge must not interfere with the two half cells. The salt bridge allows the transfer of ions to each electrode. Ions will flow from the salt bridge into the electrode solutions in order to balance the charge.
- Wire - transfers electrons from the anode to the cathode; connected to the voltmeter.
- Voltmeter - measures the cell potential in volts. Note: $1\ V = 1\ J/C$. Also note that some energy is lost as heat which keeps the voltmeter reading a tad lower than the actual or calculated voltage.

Digital voltmeters have less resistance, or you could ue a potentiometer to eliminate error introduced by resistance.

A kind of shorthand for representing galvanic cells exists, called a cell diagram, where

anode metal — anode ion —— cathode ion — cathode metal

Line notation has a number of standard features;

- The oxidized species is placed on the left hand side - this is the anode
- The reduced species is placed on the right hand side - this is the cathode
- The vertical line represents the phase boundary present in each electrode
- The double vertical line represents the salt bridge connecting the two electrodes
- Different species in the same phase are separated by a comma
- The presence of an inert conductor may also be shown inside parentheses.

The EMF or E°_{cell} is the voltage measured when no current is being drawn from the cell and is determined using a high resistance voltmeter. E°_{cell} can be calculated with the following steps:

1. Decide which element is being oxidized or reduced using the table of reduction potentials. Once again, the metal with the more positive reduction potential gets to be reduced. So, it stands to reason that the other metal is oxidized.
2. Write both equations as is from the chart with their associated voltages.
3. Reverse the equation that will be oxidized and change the sign of its voltage. This is now $E^\circ_{oxidation}$ not $E^\circ_{reduction}$.
4. Balance the two half reactions by making the number of electrons cancel. Do not multiply voltage values. A volt is equivalent to a joule/coulomb, which is a ratio. Doubling the numerator and denominator of a ratio does not change the overall value of the ratio.
5. Add the two half reactions and the voltages together to determine the cell potential.

$$E^\circ_{cell} = E^\circ_{oxidation} + E^\circ_{reduction}$$

Batteries are galvanic cells that can be connected in series. The cell potentials add together to give a total voltage.

Electrolysis is the process in which electrical energy is used to force a non-spontaneous redox reaction to occur, so in that respect it is the exact opposite of an voltaic/galvanic cell (battery). It is extremely important to draw a distinction between galvanic/voltaic discussed prior to this section, and electrolysis cells discussed in this section. Important differences between a voltaic cell and an electrolytic cell:

- A voltaic cell is thermodynamically favorable and an electrolytic cell is not and thus is forced to occur by using an electron pump or battery or any type of DC power source.
- A voltaic cell is separated into two half cells to generated electricity; an electrolytic cell occurs in a single container
- A voltaic cell is a battery; an electrolytic cell needs a battery
- Anode as oxidation and cathode as reduction still apply but the polarity of the electrodes is reversed. The cathode is negative and the anode is positive. However the electrons still flow from the anode to the cathode.
- An electrolytic cell usually uses inert electrodes.

When water is present, you'll need to figure out if the ions from the salt are reacting or the water is reacting. You can always look at a standard reduction potential table to determine this, but as a rule of thumb:

- No alkali or alkaline earth metals will be reduced in an aqueous solution.
- No polyatomic ions will be oxidized in an aqueous solution.

Electrolytic cells are used to produce pure forms of elements from mined ores, which includes purifying copper for use in wiring, producing aluminum from the Hall-Heroult process, and separating sodium and chlorine using a Downs cell.

Electrolytic cells are also used for electroplating, which applies a thin layer of an expensive metal to a less expensive metal for structural or cosmetic reasons. Pure gold is 24 carat and very soft; a 24-carat gold ring would bend easily, so a stronger structure metal can be electroplated with gold to produce a sturdy version of a gold ring. If you see a car with a chrome bumper, it has been electroplated.

Nature has a way of returning metals to their natural states, which is often their ore. We call this process corrosion. It involves the oxidation of the metal, which causes it to lose its structural integrity and attractiveness. This is particularly troublesome when structural steel corrodes. The main component of steel is iron; about 20% of the iron and steel produced annually is used to replace rusted metal. Thin oxide coatings are often applied to protect the base metals from oxidizing. Another method to combat corrosion is called cathode protection, whereby a "sacrifical anode" piece of metal is applied, such as a bar of titanium attached to the hull of a ship. The Ti in salt water then acts as the anode and is oxidized instead of the steel hull, extending the life of the vessel.

Electrolysis is also used to recover metals through the passage of a direct electric current through an ionic substance that is either molten or dissolved in a suitable solvent, resulting in chemical reactions at the electrodes and separation of materials.

9.6 Cell Potential and Free Energy

AP Topic: 9.8

It is time to combine thermodynamics and electrochemistry, along with a bit of physics.

- The work that can be accomplished when electrons are transferred through a wire depends on the "push" or emf which is defined in terms of a potential difference between two points in the circuit.

$$\text{emf[V]} = \epsilon = \frac{\text{work[J]}}{\text{charge[C]}}$$

- Thus one joule of work is produced when one coulomb of charge is transferred between two points in the circuit that differ by a potential of one volt.
  - If work flows out of the system, it is assigned a negative sign.
  - When a cell produces a current, the cell potential is positive and the current can be used to do work; therefore ϵ and work have opposite signs.
    - Faraday, F - the charge on one mole of electrons = 96,485 coulombs.
    - q = # of moles of electrons × F
  - For a process carried out at constant temperatures and pressure, w_{max} is equal to ΔG. Therefore the relationship between Gibbs Free Energy and the E° is summarized by the expression.

$$\Delta G^\circ = -nFE^\circ$$

Where F = Faraday constant = 96485 J V^{-1} mol^{-1}, and n = number of moles of electrons transferred. Coupling this with the expression,

$$\Delta G^\circ = -RT\ln K$$

We can derive

$$E^\circ = \frac{RT}{nF}\ln K$$

At a temperature of 298 K, and substituting for R and F, the expression can be simplified to

$$E^\circ = \frac{0.0257}{n}\ln K$$

Analyzing the possible combinations for K, E, and G, we can see

- When K>1, E is positive, and G is negative - At equilibrium, products favored, thermodynamically favored in forward direction

- When K = 1, E is 0, and G is 0 - At equilibrium, reactants and products approximately equally favored
- When K<1, E is negative, and G is positive - At equilibrium, reactants favored, thermodynamically favored in backward direction.

Avoid the misconception that if $\Delta G>0$, the proecess cannot occur. External sources of energy can be used to drive change in these cases.

9.7 Cell Potential Under Nonstandard Conditions

AP Topic: 9.9

All of the calculations we have seen so far assume that conditions are “standard”. When conditions are not “standard”, different voltages than those predicted by the standard reduction potentials will be generated in cells. In order to make qualitative predictions about the changes that these non-standard condutions cause, there are two ways to make a valid prediction; in order to make a quantitative prediction, there is only one way.

1. Using only the reaction quotient, Q.

   A ratio of product concentrations to reactant concentrations at any point in a reaction is called the reaction quotient.

   In addition to concentrations of solutions, partial pressures of gases must also be included in Q, but any pure solids or liquids are not included. Under standard conditions, all concentrations are 1.0 M and all gas pressures are 1 atm, so by necessity Q = 1. Under circumstances where the ratio of the concentrations and partial pressures computes to something other than 1, we must have non-standard conditions.

   What do values of $Q\neq 1$ mean for the cell voltage? Qualitatively we can think of Q thus;

   - When Q = 1, the potential difference between the two half-cells causes electrons to flow from one to the other, and this the driving force for the reaction. Under these “standard” conditions, the cell voltage is described as having the “standard” value and can be calculated with standard reduction potentials.
   - When Q<1, relatively large concentrations of reactants and/or relatively small concentrations of products are present. This combination increases the driving force for the reaction, and the cell voltage is found to be greater than the standard value.
   - When Q>1, relatively large concentrations of products and/or relatively small concentrations of reactants are present. This combination decreases the driving force for reaction, and the cell voltage is found to be less than the standard value.

2. Using the reaction quotient and comparing it to the equilibrium constant

   Batteries eventually ‘die’, that is to say, the redox reaction in a cell is continually making its way toward a voltage of zero. In batteries, a voltage of zero corresponds to the equilibrium position. When the equilibrium has been achieved, a ratio of product concentrations to reactant concentrations is called the equilibrium constant.

   Note Q can be calculated at any point during the reaction, and K is onl calculated once equilibrium has been established. In redox reactions, the “end” will be achieved when large amounts of products have been produced, and very few reactants are left. At this point, the voltage in the cell is zero. Since at the beginning of the reaction Q = 1 and voltage is standard, then

   - any change in conditions that makes Q larger than 1 means that we are closer to K, closer to equilibrium, and closer to a voltage of zero
   - any change in conditions that makes Q smaller than 1 means that we are further from K, further from equilibrium, and further from a voltage of zero

The Nernst equation is used to calculate the actual voltage in a non-standard cell. Commonly it takes one of two forms.

$$E_{cell} = E^\circ - \left(\frac{RT}{nF}\right)\ln Q$$
$$E_{cell} = E^\circ - \left(\frac{0.0592}{n}\right)\log Q$$

The first version is used if both the temperature and concentrations/partial pressures are nonstandard. The second version can only be used if only the concentration/partial pressures have changed, but the temperature is still standard.

- When $Q = 1$ the voltage is standard.
- When $Q<1$, the voltage is larger than under standard conditions.
- When $Q>1$, the voltage is smaller than under standard conditions.

A concentration cell is set up when each half-cell has the same metal electrode present, but the solutions of the metal ions are of differing concentrations. With such a concentration difference, electrons flow from the half-cell with the lower ion concentration, to the half-cell with the higher ion concentration. Since electrons are flowing, there is a current and a cell is set up.

The electrons flow to the cell with the higher concentration of metal ions, where reduction takes place, and in the process the ion concentration is lowered since the ions are converted to the solid metal. Since the lower concentration half-cell is losing electrons, the metal electrode in that cell dissolves, producing more metal ions, and the ion concentration is increased.

With the ion concentration increasing in the lower concentration half-cell, and decreasing the higher concentration half-cell, eventually the two cells will reach a point where the concentration of metal ions is the same in each half-cell, and the electrons will no longer flow. An equilibrium has been established. In short, in concentration cells, electrons always flow in order to make (and until), the concentrations of the two half-cells have a potential difference of zero. Such cells generally produce quite small voltages and calculations can only be carried out with the use of Nernst Equation.

9.8 Electrolysis and Faraday's Law

AP Topic: 9.10

The amount of a substance produced in an electrolytic cell can be calculated using Faraday's law. Faraday's law states that the amount of a substance being oxidized or reduced at each electrode during electrolysis is directly proportional to the amount of electricity that passes through the cell. One method to calculate the number of Faradays passed in the electrolysis is by using these expressions;

Firstly, calculate the amount of charge in coulombs that has been passed.

$$q = It$$

Where q is the amount of charge, I is the current in amps, and t is the time in seconds.

Secondly, convert couloumbs to Faradays.

$$\text{Number of Faradays} = \text{Charge in couloumbs} \times \frac{1\ \text{Faraday}}{96485\text{Coulombs}}$$

Then, use the stoichiometry of the electrode process to determine the mass of product formed at the electrode, remembering that a process that produces one mole of product by the transfer of one mole of electrons will require one Faraday to product that one mole, and that a process that produces one mole of product by the transfer of two moles of electrons will require two Faradays to produce that one mole, etc., as described as Faraday's constant, F.

$$F = 96485 \text{ coulombs per mole of electrons}$$

Luckily, a balanced redox half reaction gives the moles of electrons per mole of substance and molar mass gives the number of grams per mole.

When the number of Faradays is less than the required stoichiometric amount demanded by the half-reaction, a ratio should be applied.

Problems

1. Which has a greater entropy - a flexible soft metal or a rigid solid?
2. Calculate the thermodynamic boiling point of $H_2O(l) \rightarrow H_2O$ (g) given that

$$\Delta H_{vap} = +44 \text{ kJ/mol}_{rxn} \qquad \Delta S_{vap} = 118.8\text{J/(K}\cdot\text{mol}_{rxn})$$

3. For the reaction $2CO(g) + O_2(g) \rightarrow 2CO_2(g)$, the ΔG° for the reaction is -257.2 kJ/mol$_{rxn}$. Calculate the equilibrium constant at 25°C.
4. Using a standard reduction potentials table, write cell diagrams for the combination of electrodes for Fe^{2+}/Fe^{3+} and hydrogen.
5. A galvanic cell is based on the reaction

$$MnO_4^-(aq) + H^+(aq) + ClO_3^- \rightarrow ClO_4^-(aq) + Mn^{2+}(aq) + H_2O(l)$$

   Give the balanced cell reaction and calculate E° for the cell.
6. Calculate the cell voltage for the galvanic cell that would utilize silver metal and involve iron(II) ion and iron (III) ion. Draw a diagram of the galvanic cell for the reaction and label completely.
7. Explain whether the following reaction is thermodynamically favorable.

$$Cu^{2+}(aq) + Fe(s) \rightarrow Cu(s) + Fe^{2+}(aq)$$

8. Using the table of standard reduction potentials, predict whether 1 M HNO_3 will dissolve gold metal to form a 1 M Au^{3+} solution.
9. If the reaction $Zn(s) + Cu^{2+}(aq) \rightarrow Cu(s) + Zn^{2+}(aq)$ is carried out using solutions that are 5.0 M Zn^{2+} and 0.3 M Cu^{2+} at 298 K, predict the effect on the voltage of the cell, when compared to the voltage generated under standard conditions.
10. For the oxidation-reduction reaction

$$S_4O_6^{-2}(aq) + Cr^{2+}(aq) \rightarrow Cr^{3+}(aq) + S_2O_3^{-2}(aq)$$

   Balance the redox reaction and calculate E° and K at 25°C.
11. How long must a current of 5.00 A be applied to a solution of Ag^+ to produce 10.5 g silver metal?
12. An acidic solution contains the ions Ce^{4+}, VO_2^+ and Fe^{3+}. Give the order of oxidizing ability of these species and predict which one will be reduced at the cathode of an electrolytic cell at the lowest voltage.