

AP Chemistry Notes

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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 or 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 empirical 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.

$$\begin{aligned}\text{Moles of an element} &= \frac{\text{mass of sample}}{\text{AAM}} = \frac{\text{mass of sample}}{\text{Molar Mass}} \\ \text{Moles of a molecular compound} &= \frac{\text{mass of sample}}{\text{molecular mass}} = \frac{\text{mass of sample}}{\text{Molar Mass}} \\ \text{Moles of an ionic compound} &= \frac{\text{mass of sample}}{\text{formula mass}} = \frac{\text{mass of sample}}{\text{Molar Mass}}\end{aligned}$$

Once we have established how to determine the empirical and molecular formula of compounds, 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 around 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 caused 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 electromagnetic 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 idea of 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 sub-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 stated above, the orbitals represent three-dimensional areas of space in the atom where an electron may be found, 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 found. The number of nodes equals $n - 1$ for s orbitals. p orbitals are peanut shaped and have nodal planes where the electron can never be found, yet the electron can magically get from one side of the peanut to the other without ever going through the nodal plane. p orbitals have 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 smallest energy, 2s having the next smallest. There is a pretty significant complication that arises here, which can be accommodated 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 anomalies and have configurations 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 $[\text{Ne}]3s^23p^3$.

Ions are charged particles that are formed from atoms by either the loss 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 process, $E = h\nu = \text{IE} + \text{KE}$.

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 Group 2 metals imply bases are made when placed in water.

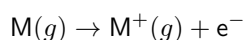
Groups 16 atoms have an electronic structure [Noble Gas] s^2p^4 . This means that they tend to gain two p electrons when they form an ion, in order to reach an inert noble gas type structure with a charge of -2.

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/

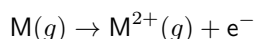
Transition metals are in the d-block of the periodic table. Transition element ions yield colorful solutions when they have unpaired electrons in the d subshell. When regarding electron configurations of the transition metals, anomalies occur at chromium and copper to minimize electron/electron repulsion. 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.



The second ionization energy is defined as the energy change accompanying



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.

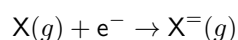
As a group is descended the atomic size increases. This is because that although there is again an increase in nuclear charge, the valence electrons enter new shells, further away from the nucleus. As a result the atomic size increases since the greater the number of shells occupied in an atom, the larger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

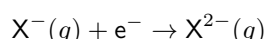
First electron affinity is defined as the energy change when one mole of electrons is added to one mole of gaseous atoms, to produce one mole of gaseous ions.



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:



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.

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 that are 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 and 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 attracted 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 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 is called the bond strength.

Since for 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 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 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 are 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 lattice 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 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.

- $\Delta EN < 0.5$: nonpolar covalent
- $0.5 \leq \Delta EN \leq 1.7$: polar covalent
- $\Delta EN > 1.7$: 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 3 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 atom 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 electric 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 around 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 or 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 one 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, although rare, of a molecular substance that can conduct electricity. Pi bonds may form only if unhybridized p orbitals remain on the bonded atom and when sp or sp² hybridization is present on the central atom, not sp³ 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 metal's atoms are replaced by another metal's 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 alloys have similar, reduced malleability and ductility to substitutional alloys 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 alloy 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.

3 Properties of Substances and Mixtures

3.1 Solids, Liquids, and Gases

3.2 Intermolecular Forces

3.3 Solubility

3.4 Properties of Solids

3.5 Kinetic Molecular Theory

3.6 Ideal Gas Law

3.7 Deviation from Ideal Gas Law

3.8 Solutions and Mixtures

3.9 Representations of Solutions

3.10 Separation of Solutions and Mixtures Chromatography

3.11 Spectroscopy and the Electromagnetic Spectrum

3.12 Photoelectric Effect

3.13 Beer-Lambert Law

4 Chemical Reactions

4.1 Introduction to Reactions

4.2 Net Ionic Equations

4.3 Representations of Reactions

4.4 Physical and Chemical Changes

4.5 Stoichiometry

4.6 Introduction to Titration

4.7 Types of Chemical Reaction

4.8 Oxidation-Reduction (Redox) Reactions

5 Kinetics

5.1 Reaction Rates

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

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

5.4 Concentration Changes Over Time

5.5 Catalysts

6 Thermochemistry

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- 6.2 Energy Diagrams**
- 6.3 Heat Transfer and Thermal Equilibrium**
- 6.4 Heat Capacity and Calorimetry**
- 6.5 Energy of Phase Changes**
- 6.6 Introduction to Enthalpy of Reaction**
- 6.7 Bond Enthalpies**
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7 Equilibrium

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- 7.2 Calculating the Equilibrium Constant, Magnitude of the Equilibrium Constant, and Calculating Equilibrium Concentrations**
- 7.3 Representations of Equilibrium**
- 7.4 Reaction Quotient and Equilibrium Constant & Reaction Quotient and Le Chatelier's Principle**
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- 7.7 Introduction to Solubility Equilibria**
- 7.8 Free Energy of Dissolution**
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- 7.10 pH and Solubility**

8 Acids and Bases

- 8.1 Introduction to Acids and Bases & pH and pOH of Strong Acids and Bases**
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- 8.3 Acid-Base Reactions and Buffers**
- 8.4 Acid-Base Titrations**
- 8.5 Molecular Structure of Acids and Bases**
- 8.6 Properties of Buffers**
- 8.7 pH and pKa & Henderson-Hasselbalch Equation**
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9 Thermodynamics and Electrochemistry

- 9.1 Introduction to Entropy & Absolute Energy and Entropy Change**
- 9.2 Gibbs Free Energy and Thermodynamic Favorability & Thermodynamic and Kinetic Control**
- 9.3 Coupled Reactions**
- 9.4 Free Energy and Equilibrium**
- 9.5 Galvanic (Voltaic) and Electrolytic Cells**
- 9.6 Cell Potential and Free Energy**
- 9.7 Cell Potential Under Nonstandard Conditions**
- 9.8 Electrolysis and Faraday's Law**