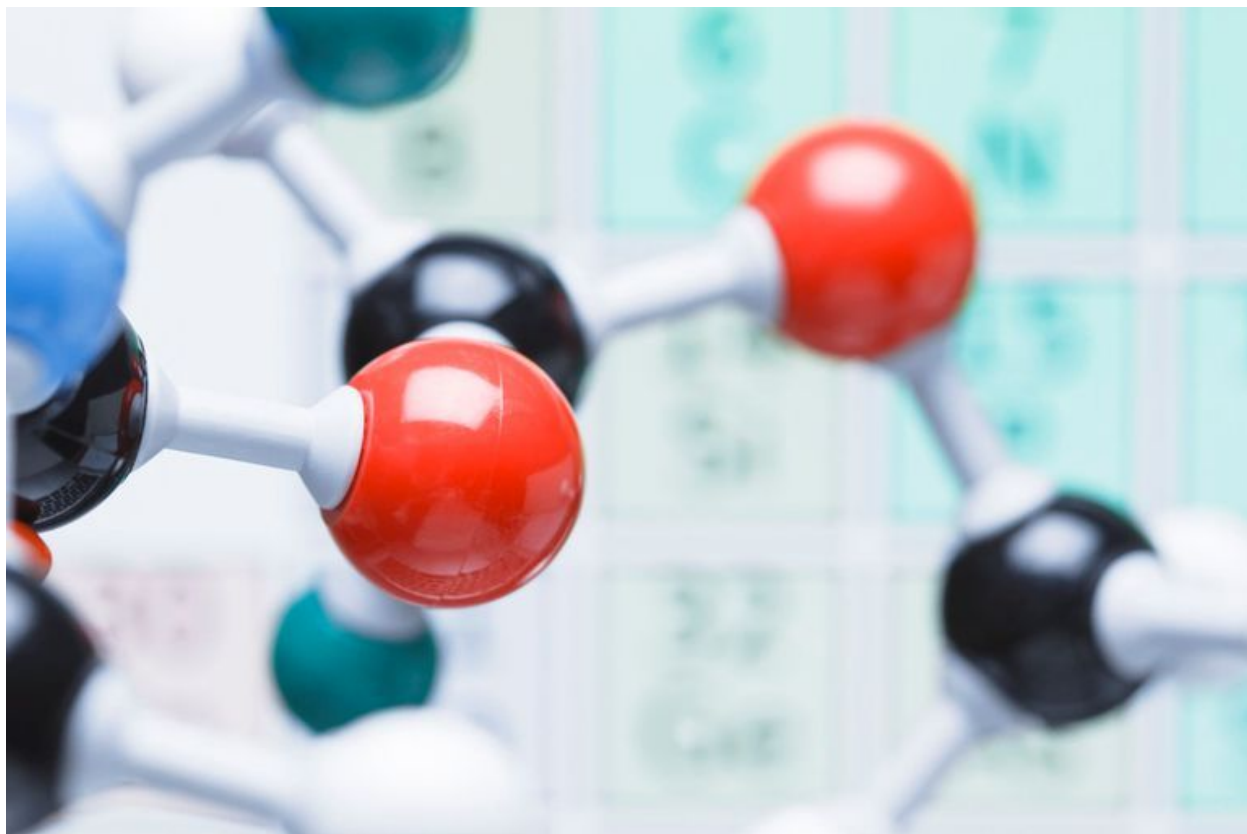

YYC Science Bowl

Chemistry Guide



Chemical Bonding



Introduction

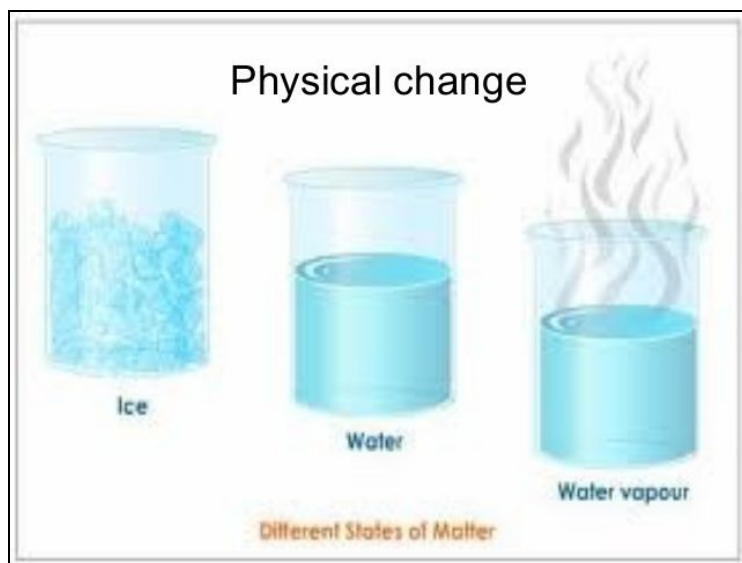
Chemistry is recognized as the study of matter, primarily with relation to electron movement within atoms and molecules. Chemists study fields ranging from the bonding of atoms to other bodies, the thermal release of energy in bonding scenarios, the speed of reaction, the properties of the resulting compounds, etc... As such, chemistry is a vast field which requires in depth understanding of its basic components to be able to progress in the subject.

Chemical and Physical Change

Chemistry deals with two types of change within molecules, its physical change and its chemical change. The difference between the two processes relates to the chemical composition of an atom, molecule, or mol of a substance at the beginning and at the end of a reaction.

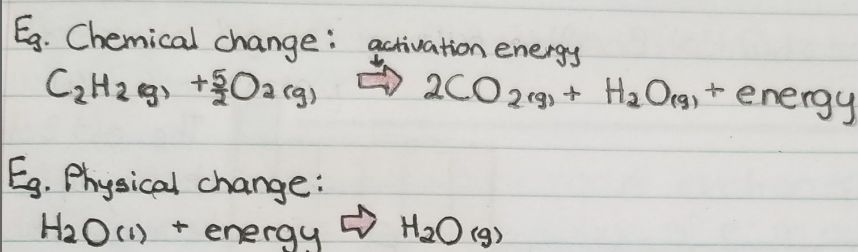
- ❑ Chemical Change → change in composition resulting in a possible change of smell, appearance, properties, etc...
- ❑ Physical change → no change in composition, but changes in: texture, colour, temperature, shape, and / or chemical state.

A physical change primarily deals with a change in physical properties, of which can be: lustre, malleability, ductility, density, viscosity, solubility, mass, and volume. Typically any changes to these properties is due to a physical change.



The process to the left is a basic model of the three (primary) states of matter, solids, liquids and gases. A transition between these states is describable as a physical change.

Chemical Change differs in that it requires bonds breaking and new bonds forming, often indicated by changes in temperature, changes in colour, odour after a reaction begins, formation of a precipitate in an aqueous solution, or the formation of gas bubbles in an aqueous solution.



Molecular and Empirical Formulas

Chemical formulas describe the makeup of chemicals in a way which can be useful to determine chemical identity. Empirical formulas deal primarily with ratios of elements in a molecule, while molecular formula formulas use discrete values of elements to describe the exact amount of atoms of an element present in a molecule.

<u>Empirical Formula (ratio)</u>	<u>Molecular Formula (true formula)</u>
CH	C_2H_2 , C_6H_6 etc...
CH_2O	$\text{C}_6\text{H}_{12}\text{O}_6$

Using these formulas, one can determine chemical makeup through knowledge of molar mass and percent composition. Note that for this competition it is assumed you know how to work with molar mass and basic mathematical ratios.

Example problem:

Urea is tested for its empirical formula, the compound results in the following:

- 36g carbon
- 12g hydrogen
- 84g nitrogen
- 48g oxygen

Using this rounded data, what is the empirical formula of urea?

Answer:

LCD = 3, \therefore 3 mol of urea

C $36\text{g} / 12\text{g/mol} = 3\text{ mol C}$ 1 mol C

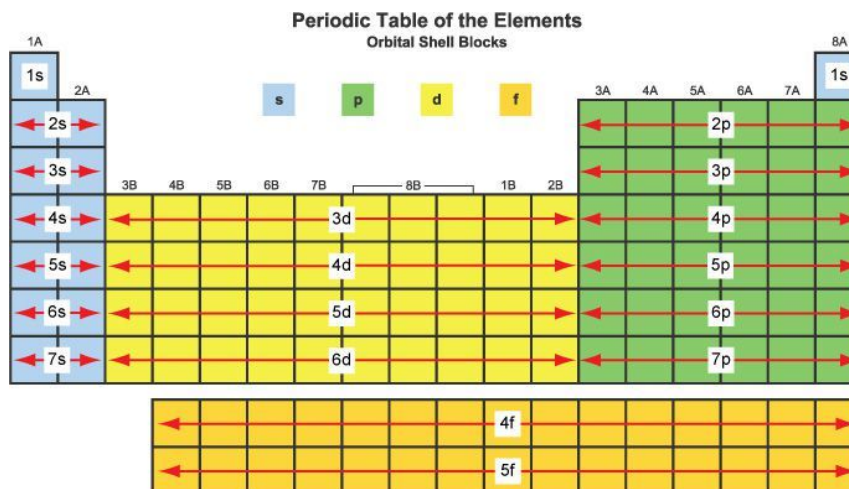
H $12\text{g} / 1\text{g/mol} = 12\text{ mol H} \rightarrow 4\text{ mol H} \rightarrow \text{CH}_4\text{N}_2\text{O}$

N $84\text{g} / 14\text{g/mol} = 6\text{ mol N}$ 2 mol N

O $48\text{g} / 16\text{g/mol} = 3\text{ mol O}$ 1 mol O

Advanced Atomic Theory

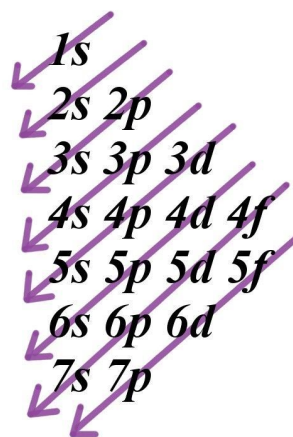
The periodic table used in high school runs until the 7th energy level, consisting of S, P, D, and F sublevels, however scientists have moved past these ideas and have theorized the existence of G orbitals and further energy levels. For the purpose of the competition, one



Energy sublevels make up each energy levels of an atom. Each energy level is separated into the periods of the periodic table, and each sublevel is separated in the table as shown

above (where blue is the S sublevel, green is P, yellow is D, and orange is F). Energy sublevels in an atom are described as being composed of orbitals. Each orbital can hold 2 electrons. S sublevels hold 1 orbital, and as such a maximum of 2 electrons, P orbitals hold 3 orbitals (up to 6 electrons), D orbitals hold 5 orbitals (10 max electrons) and lastly F orbitals hold 7 orbitals and therefore a max of 14 electrons.

Learning to name elements using SPDF theory is essential for university chemistry, and it will become helpful when dealing with hybridization, periodicity, and bonding. The element cobalt (Co_{27}) can be written as $1s^2 2s^2 2p^6 3s^2 3p^6 3d^7 4s^2$ or $[\text{Ar}]_{18} 3d^7 4s^2$. The naming system names each period 1→7 with an exception on D & F orbitals where the period 4 D orbital is named 3, and the period 6 F orbital is labeled 4. One names orbitals from left→right and shells from up→down. Nomenclature works on the basis of the table to the right, however it is easier to analyse and name on the basis of how the periodic table is set up (refer to the periodic table above).



Alternatively, one would have the name of the closest preceding noble gas, then the remaining orbital notation. To the left an oxygen example is shown for both ways, and a bromine example is shown for the noble gas alternative.

Upon this basis, one can take the electron configuration of an element and make it into an electron spin diagram (as a way to represent the opposing motion of electrons in an element's orbitals).

Ions and Excited States

Ionized substances are written similarly to regular atoms, where the difference is that electrons are removed from the highest energy orbital (therefore highest energy level, and its highest energy sublevel, where F is the highest energy, followed by D, then by P, then S). For instance:

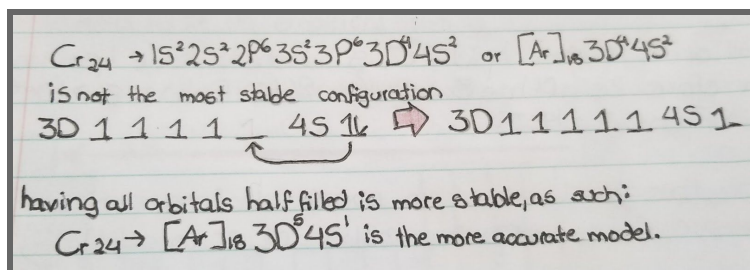
- ❑ Ca atom ground state: $[\text{Ar}]_{18} 4\text{S}^2$
- ❑ Ca atom in excited state: $[\text{Ar}]_{18} 4\text{S}^1 4\text{P}^1$ (electron from valence S orbital moves up an energy level to partly fill a P orbital)
- ❑ Ca^{2+} cation: $[\text{Ar}]_{18}$

In the example above, a calcium atom can gain enough energy to excite one of its electrons from its highest energy orbital (4S) to one above (or even higher depending on the amount of energy added). If the electron were to receive enough energy it reaches its ionization energy and as such electrons are lost, ionizing the calcium. In the Ca^{2+} cation, the calcium has reached its first and second ionization energies resulting in a loss of 2 electrons, making its model be closest to that of Argon gas, as such Ca^{2+} and Ar share electron configuration and electron spin diagrams.

Electron Configuration Exceptions and Magnetism

The reason orbitals half fill before filling in pairs is due to electron repulsion (Hund's rule, also states that unpaired electrons will all have the same spin - same arrow direction). As like charges repel, the negative electrons will do the most possible to remain as far apart as possible, and as such the most stable models of an atom are those where electrons are not paired up. For instance take Cr_{24} (chromium):

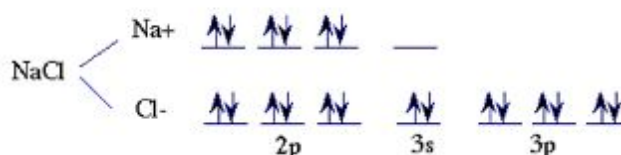
Chromium and its family will all experience a similar electron shift from an S orbital to a D orbital, and the same could occur with F orbitals if a more stable diagram exists. Another exception occurs in the family of copper, where the normal diagram of $[\text{Ar}]_{18} 3\text{D}^9 4\text{S}^2$ is replaced by the more stable $[\text{Ar}]_{18} 3\text{D}^{10} 4\text{S}^1$, as having a fully filled D with a half filled S orbital is more stable than a half filled D orbital and a full S orbital. This is due to the S orbital being further from the nucleus of the atom, and as such experiencing a weaker pull towards it, making the electrons in the outermost orbital more susceptible to ionization.



It is important to draw the electron spin diagrams as they may provide more stable alternatives to the more common electron configuration diagrams.

Being able to determine the most accurate spin model of an atom or ion allows one to predict the properties of said atom. For instance, magnetism is related to how filled the orbitals of an atom are. Paramagnetic atoms are those which have at least one half filled orbital, this results in the atom being attracted by external magnetic fields. Diamagnetic atoms are instead those who have all electrons in a paired manner, and as such repel magnets. This concept can extend to compounds, and as such can help explain the properties of molecules.

Diamagnetic: all spins are paired
(nonmagnetic)



Periodic Nature of Matter

The original periodic table of elements was made by Dmitri Mendeleev and it arranged elements on the basis of atomic mass, where as the current one arranges the elements on the basis of atomic number. By looking at the periodic table, one can gather many more

trends than just a rising number of protons in an element.

Group	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og
				58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu	
				90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr	

Atomic size for instance increases going down, but decreases from left to right of the table. To better understand this, one should be aware of the electrostatic attraction and repulsion of electrons to the nucleus and other electrons.

$Z_{\text{effective}}$ for instance is the number arising by taking an element's atomic number and subtracting the number of its non-valence electrons. The higher the resulting number, means the higher the electron attraction is to the nucleus of the atom, and as such a smaller atomic radii. For instance:

B^5	C^6	N^7	O^8	F^9	Ne^{10}
# $5p^+$	$6p^+$	$7p^+$	$8p^+$	$9p^+$	$10p^+$
$e^- 2e^-$	$2e^-$	$2e^-$	$2e^-$	$2e^-$	$2e^-$ (non-valence)
$Z_{\text{eff}} 3^+$	4^+	$5e^-$	$6e^-$	$7e^-$	$8e^-$

→ Decreasing atomic radii →

This notion of $Z_{\text{effective}}$ therefore proves that an atom's size will decrease going from left to right in the periodic table.









































Increasing atomic size downward in the periodic table can also be proven via the notion of energy levels, as an atom of energy level $n = 1$ like hydrogen is much smaller than one with $n = 2$ such as lithium (where "n" refers to the principal quantum number with regards to energy level). Note that the increase in size due to energy levels is much bigger than the relative decrease due to increasing nuclear attraction, and this effect increases further the farther electrons are from the nucleus, as an increasing electron shielding provides higher repulsion. Be aware of the possibility of exceptions however, as SPDF theory proves that all throughout the transitional metals the atomic radii trend will prove to be inconsistent.

Another Important tool when dealing with atomic radii is coulomb's law, where "F" is the attracting force (in this scenario) between the nucleus and its electrons, "q₁" and "q₂" are respectively charges which become important when calculating the melting point of molecules, and lastly the "r" value which represents the distance between the nucleus and the electrons, "k" is a constant and therefore has no impact on the fundamental ideas. By the formula, attraction increases as distance decreases, and as the charges increase in magnitude, their attraction does as well.

$$F = \frac{kq_1q_2}{r^2}$$

Size of Atoms Versus Ions

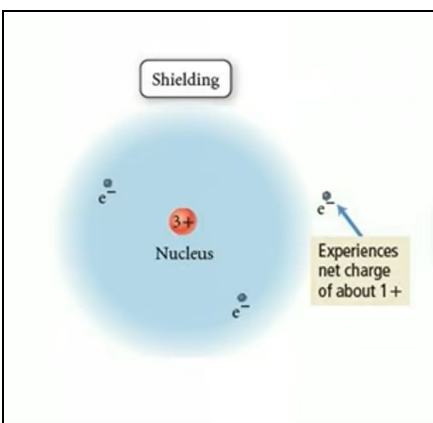
While comparing the radii of atoms is relatively simple when looking outside of the transitional metals, ions tend to complicate the trends of the periodic table. In a nutshell, cations are smaller than their atomic counterparts, and

Group 1		Group 2		Group 13		Group 16		Group 17	
Li ⁺  90	Li  134	Be ²⁺  59	Be  90	B ³⁺  41	B  82	O  73	O ²⁻  126	F  71	F ⁻  119
Na ⁺  116	Na  154	Mg ²⁺  86	Mg  130	Al ³⁺  68	Al  118	S  102	S ²⁻  170	Cl  99	Cl ⁻  167
K ⁺  152	K  196	Ca ²⁺  114	Ca  174	Ga ³⁺  76	Ga  126	Se  116	Se ²⁻  184	Br  114	Br ⁻  182
Rb ⁺  166	Rb  211	Sr ²⁺  132	Sr  192	In ³⁺  94	In  144	Te  135	Te ²⁻  207	I  133	I ⁻  206

anions are bigger than their atomic variants. This is primarily due to the result of giving and taking in electrons with relation to electron repulsion. By losing electrons, cations will end up with lower electron repulsion at the valence energy level, as such resulting in a greater net force of attraction from the nucleus to the electrons. By gaining electrons, anions will experience a greater electron repulsion, and as such a lower attractive force towards the nucleus.

With this logic in mind, the general trend for radii is that **for both atoms and ions size will increase moving down the periods of the table, atoms will decrease moving towards the noble gases, and ions will decrease moving towards the alkali metals.** This trend however does not explain particular exceptions such as why transition metals tend to stay constant in size.

Electron Shielding, Radial Probability and Penetration



Electron shielding is the phenomenon caused by inner electrons having a repulsion on outer electrons in an atom, resulting in a bigger atomic radius. Typically electron shielding will increase as one moves down the periodic table, as the addition of more electrons results in higher repulsion. In polyelectronic systems (those containing more than one electron) electron repulsion becomes a factor affecting outer electrons, causing them to feel a weaker pull from the nucleus. In essence, $Z_{\text{effective}}$ can then be seen as a way to calculate the force the nucleus puts towards outer shell electrons. By

taking atomic number of lithium (3) and subtracting its inner orbital (2 electrons), the outermost electron in its 2S orbital will experience roughly a 1+ charge. In contrast, a Li^{2+} ion will have a 3+ on its electron as there will be no electron shielding or repulsion to act on it.

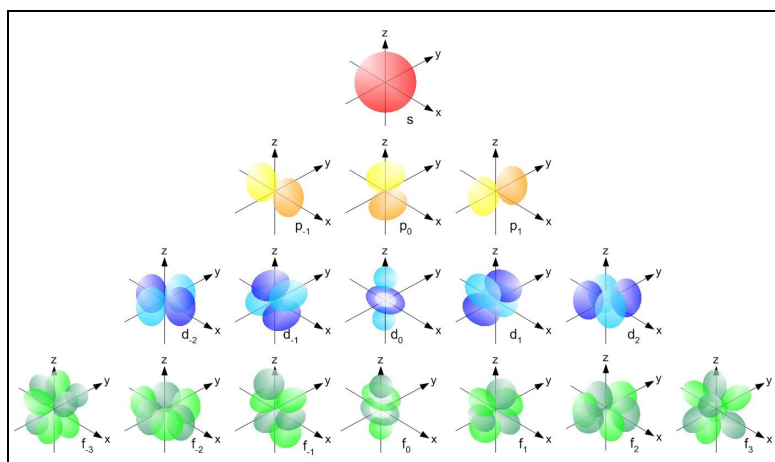
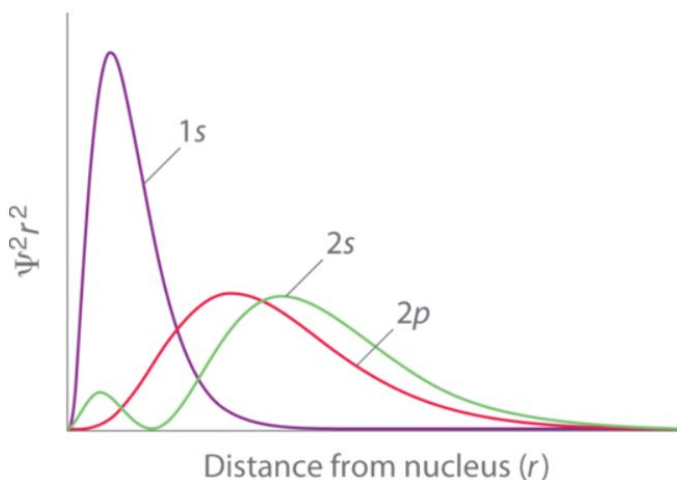
To better understand the effects of shielding on the different elements however, one needs to view the orbital model with regards to Schrödinger's equation for the hydrogen atom. The concept of radial distribution is extremely complex with regards to mathematical concepts, and as such only the basics need to be understood. Orbital theory works on the premise that electrons have a % chance to be in a particular place in a particular time, and due to quantum uncertainty along with the particle-wave nature of matter and light, it isn't possible to 100% of the time predict an electron's location. The

orbital SPDF system arose out of a wave function which describes the possible location of an electron, where the first orbital was calculated to be circular in nature with regards to the hydrogen atom. Without getting too complex, once one arrives at polyelectric molecules, the nature of radial distribution curves of 2P and 2S orbitals reveal an important concept about shielding.

Where the X axis is distance to the nucleus, the graph to the right demonstrates the idea that in terms of proximity the 1S orbital is followed by the 2P orbital, then the 2S, etc... However the small green sector which lies before the initial rise of the red curve proposes the idea that electrons in the 2S orbital can **penetrate** the area of the 1S curve. This has to do with the idea that orbitals of different kinds (SPDF) have different shapes. Furthermore, if one were to add the small maximum to the second maximum of the 2S curve, the resulting maximum would peak before the 2P curve, as such the 2S curve

is treated as being closer to the nucleus. The idea that the 2S curve has the potential to break into the space of the 1S curve is called “**electron penetration**”, and with it one can interpret the idea of electron shielding as having a lesser effect on electrons penetrating from the 2S orbital in the area of the 1S orbital, as electrons are not exposed to repelling forces of the 1S electrons. With regards to the initial Lithium example, electrons in the 2S orbital have the ability to experience a full 3+ charge of the nucleus, however this does not always occur. Penetration makes the S orbital more stable than the other orbitals, followed by P, then D, and lastly F (within the same “n” value).

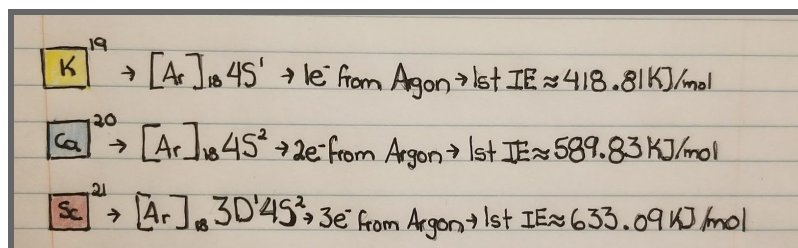
What does penetration have to do with electron shielding then? Electron shielding works with regards to electron density, and due to penetration and the particular shapes of each orbital, the shielding capabilities of orbitals differ. S orbitals have the strongest shielding since they have the highest penetration, and therefore the highest electron density,



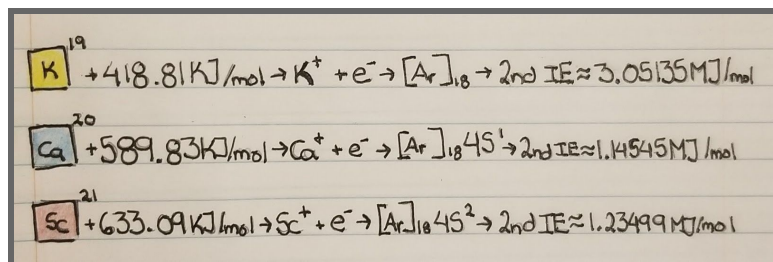
followed by P, then D, then F orbitals. This phenomenon is able to explain particular fluctuations in atomic size, especially with regards to elements involving the D and F sublevels.

Ionization Energy Trends

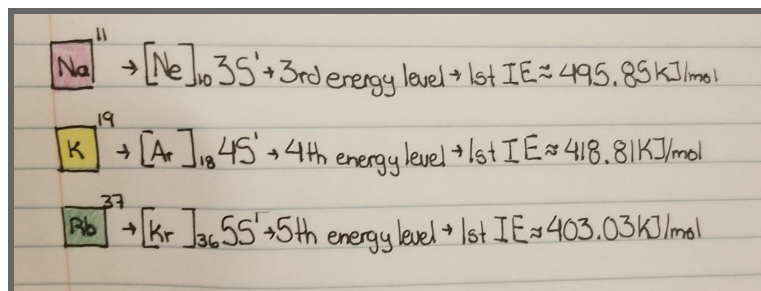
On a much simpler note, ionization energy (the energy for an element or ion to lose an electron) is another trend which can be studied in the periodic table. As a whole, ionization energy tends to be low when an element becomes more stable if it loses an electron, and high if it becomes more stable by gaining an electron. As such, metals tend to have low ionization energies, non-metals tend to have very high ionization energies, and noble gases, have the highest out of any group. Ionization energy will grow lower the closer one element is to its nearest preceding noble gas.



□ As such, normally ionization energy will tend to increase moving towards the right side of the periodic table. The first ionization energy of alkali metals will therefore be the lowest in the period.



□ After losing one electron, the leftover ions will have a similar pattern of ionization energy trends, increasing going right. The Alkali metals group however, will have a high 2nd ionization energy as their orbitals are already in the most stable form (nearest preceding noble gas).



□ Ionization energy will tend to increase going up the periods as well. This is due to a higher effective nuclear charge - due to less electron shielding - as one moves up the periodic table. As a result, Helium will have the highest first ionization energy due to it having a full valence shell, and it having no shielding to its electrons.

There are some exceptions to watch out for however, as sometimes having a set of half filled orbitals would be more stable than having a paired orbital and a couple unpaired orbitals.

Electron Affinity and Electronegativity

Electron affinity is yet another trend that is interpretable from the periodic table, and it very much opposes ionization energy.

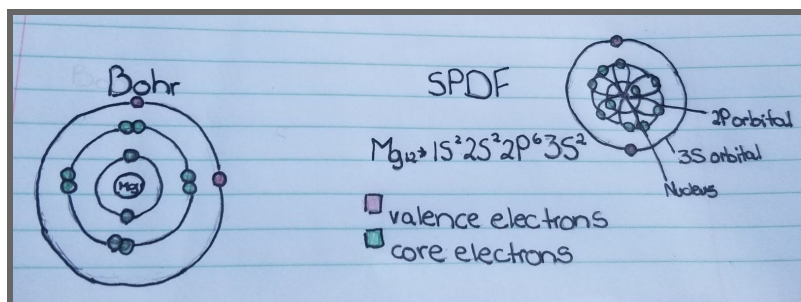
Electron affinity is referred to as the enthalpy change which occurs when an electron is absorbed by an element, therefore either the loss or gain of energy of an element due to obtaining an electron. Typically if electron affinity is negative, it is because the element can become slightly more stable, while if it is positive, gaining an electron makes the atom unstable requiring it to absorb more energy. Typically group 2

1A	2A	3A	4A	5A	6A	7A	8A
1 H -73							2 He >0
3 Li -60	4 Be >0	5 B -27	6 C -122	7 N >0	8 O -141	9 F -328	10 Ne >0
11 Na -53	12 Mg >0	13 Al -43	14 Si -134	15 P -72	16 S -200	17 Cl -349	18 Ar >0
19 K -48	20 Ca -4	31 Ga -30	32 Ge -119	33 As -78	34 Se -195	35 Br -325	36 Kr >0
37 Rb -47	38 Sr -11	49 In -30	50 Sn -107	51 Sb -103	52 Te -190	53 I -295	54 Xe >0

alkaline earth metals, and noble gases will be those with positive EAs as they would prefer to not grow in electrons. As such electron affinity increases moving right with few exceptions (previously mentioned). Electron affinity will also decrease moving down the periodic table, as electron shielding increases, resulting in a lessened pull by the nucleus with regards to electrons.

Electronegativity works in a similar manner, as it is the attraction of a bonding pair of electrons for a particular nucleus. Electronegativity is commonly measured in the Pauling scale where fluorine (the most electronegative element) is assigned the number of 4.0, and all other elements are ranked accordingly. Much like electron affinity, it increases moving up and to the right of the periodic table, however it's only exception will be with noble gases, as only in very few instances do they even attract electrons.

Advanced Bonding



Most of the topics so far have dealt with the inner electrons of elements,

however bonding (except for a few exceptions) deals primarily with the valence electrons of an element.

In chem 20 one is introduced to the bohr model of the atom, which can depict the electron structure of an atom somewhat accurately until the involvement of the 3D orbital (therefore up to calcium in the periodic table). Once D and F orbitals become involved, the layering rules of 2,8,8,etc... break down as energy levels are able to hold even more (2,8,18, 32, etc... this doesn't even account for excitation). As such, even though still slightly inaccurate, it is best to picture bonding using electron configuration. Basic bonding will still work with the use of lewis dot diagrams, however the moment one advances into the 3rd period one meets an exception to the octet rule.

Lewis Dot Diagrams, Orbitals and Octet Rule

I	II		III	IV	V	VI	VII	0
H •								He ••
Li •	Be •		B ••	C ••	N ••	O ••	F ••	Ne ••
Na •	Mg •		Al ••	Si ••	P ••	S ••	Cl ••	Ar ••
K •	Ca •		Ga ••	Ge ••	As ••	Se ••	Br ••	Kr ••
Rb •	Sr •		In ••	Sn ••	Sb ••	Te ••	I ••	Xe ••
Cs •	Ba •		Tl ••	Pb ••	Bi ••	Po ••	At ••	Rn ••

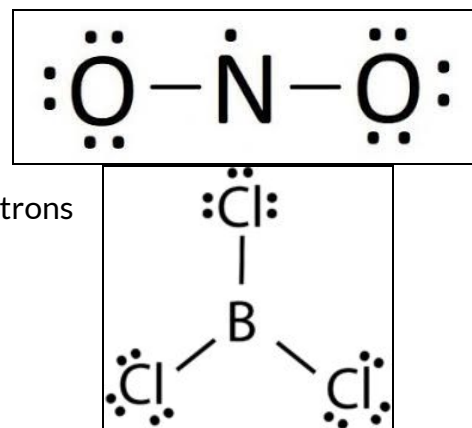
Metal
 Metalloid
 Nonmetal

Generally bonding works on the premise of the octet rule. An element is most stable when its valence shell is fully filled with 8 electrons. Lewis dot diagrams are made with the purpose to display the outer shell of an element, and as such its bonding capacity. It generally consists of an element symbol surrounded by dots in singles or pairs (bonding and lone pairs respectively), which can accurately show the bonding nature of most elements, and later on molecules (where lines represent bonding pairs, therefore 2 electrons). Lewis dot diagrams work on the basis of the octet rule, and as such they typically max out at 8 dots around a target element. There are however 3 particular violations to the octet rule which are important:

❑ Odd-electron molecules:

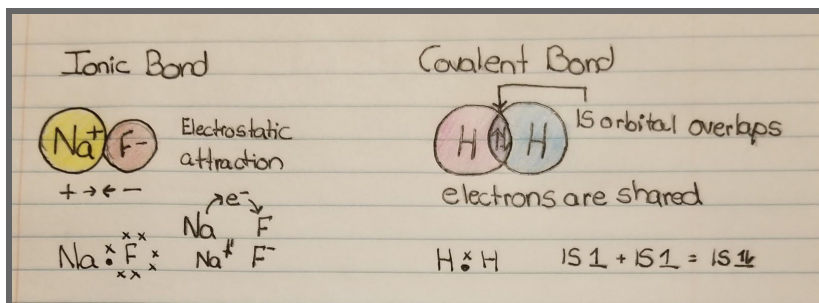
- ❑ Although few, there exist some compounds which are stable while remaining without a filled octet. For instance NO, NO₂ and ClO₂. This will occur with any species with an odd number of electrons (when speaking in terms of molecules).

❑ Electron deficient molecules:



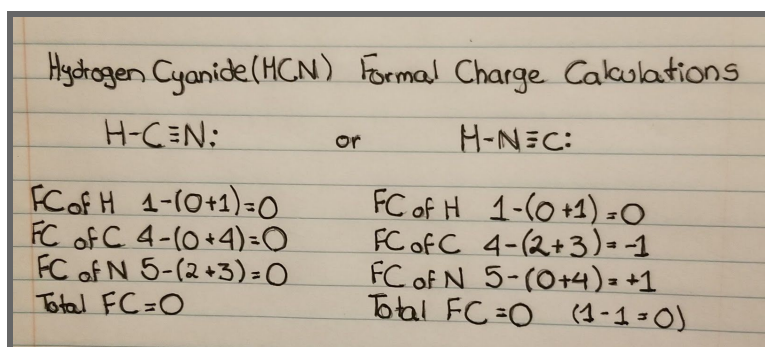
- ❑ Common examples being boron compounds, as boron will have a filled octet at 6 electrons, and beryllium which will have a filled octet at 4 electrons.
- ❑ **Expanded octet molecules** - which will be the focus of this particular topic, but will be analysed later.

When talking about covalent bonding (sharing of electrons), ions come together such that their orbitals containing unpaired electrons overlap. In contrast to covalent bonds, ionic bonds instead rely on the electromagnetic force which brings the cations and anions together. The distance between the nuclei of both bond atoms is the **bond length**, which will vary depending on the element, the type of bond, and other factors.



Formal Charge and Resonance Structures

When drawing Lewis dot diagrams of molecules, one may come across a multitude of different ways to draw particular molecules. For instance Hydrocyanic acid has two configurations shown below. In theory they both work, however one is optimal in terms of stability. Formal charge is a tool used to calculate the charge of particular atoms in a

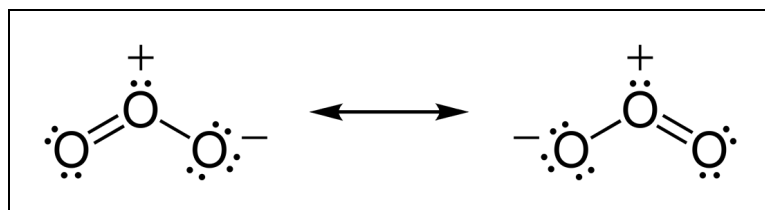


structure (assuming equal sharing of electrons in a structure). Optimally formal charge of the entire structure should equal 0 if the structure is neutral, or in the case of ion it should equal out of the ion's charge.

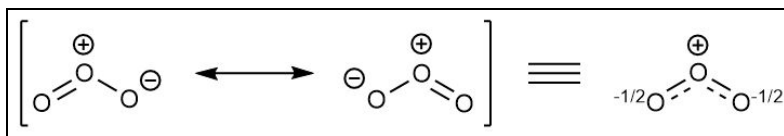
Therefore by comparing the formal charge of the two structure above (Formal charge = [#Valence electrons] - [non-bonded electrons +

number of bonds]) one can derive the left structure as being the way hydrocyanic acid actually exists (as it is more stable). A trick for comparing formal charge is to calculate [#Valence electrons of an atom] - [dots + line] in a Lewis dot diagram, as it can make it easier to picture.

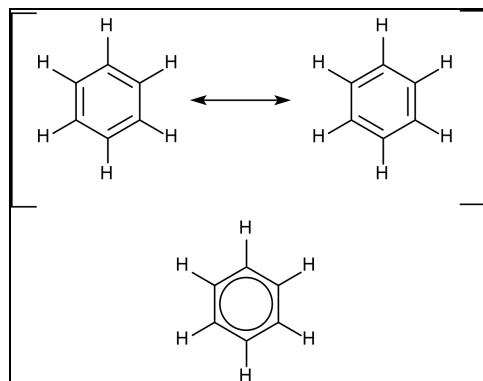
Another aspect of lewis dot diagrams arrives when introduced to the idea of double and triple bonds. There are many different ways one could even arrive at the same molecular structure, for instance there is ozone. The simple way of looking at it is that one could



move the double bond in the structure for the left side to the right side. This idea is right, however not entirely accurate, as what is being shown is actually one of the oxygens giving up its lone pairs to become bonding pairs and another taking its bonding pairs to become lone pairs, just in two different sections of the molecule. Note that the formal charge is



depicted above, and both structures of ozone will leave positive and negative ends to the molecule. A hybrid between the two molecules of ozone, or a **resonance structure** can then be drawn, which allows for the delocalization of charge across the molecule. The resonance structure allows for the idea of having the properties of a double bond, keeps the total formal charge of 0 ($1 - 0.5 - 0.5 = 0$), and is able to represent both structures. Note that instead of a double and a single bond, the resonance structure instead has 2 1.5



bonds, still adding up to the correct amount of electrons of the molecule. Scientists discovered actual resonance structures in various compounds today, as they are able to explain why molecules are more stable than one would expect (through the delocalization of charges). A famous example of this was the molecule of benzene, the delocalization of electrons across of its structure makes the molecule incredibly stable, something which goes against its lewis dot diagram as double and triple bonds tend to be reactive. The reason delocalized electrons make a

molecule more stable is that by allowing the electrons to occupy the orbitals of others, they fill their octets thereby making them less likely to react.


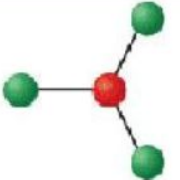
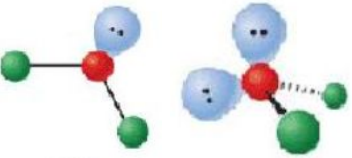
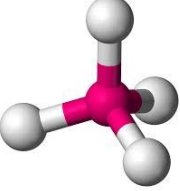
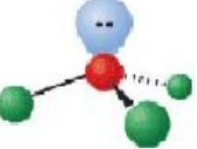
It is important to keep the following table in mind when analysing bonding structures:

<u>Single bonds</u>	<u>Double bonds</u>	<u>Triple bonds</u>
Longest bond	In between	Shortest bond

Least reactive bond	In between	Most reactive bond
Least energy	In between	Most energy

VSEPR Theory and Expanded Octets

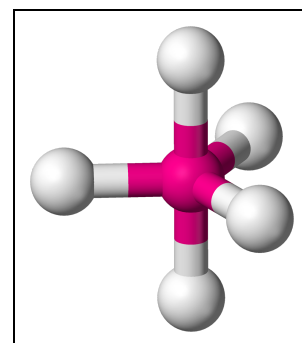
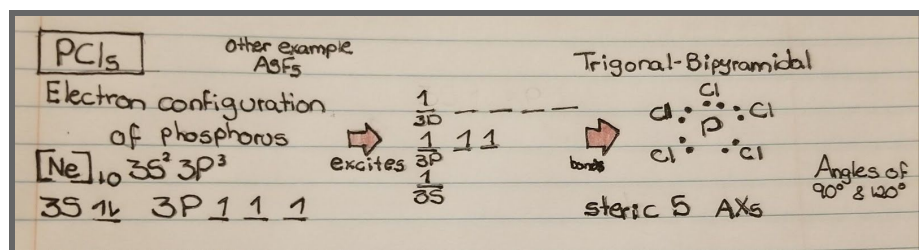
Valence Shell Electron Pair Repulsion theory or VSEPR theory is the commonly used model to predict the geometric shapes of molecules by minimizing the effects of electron repulsion of an atom's valence electrons in a molecule. VSEPR theory predicts a variety of simple shapes which do not require an expanded octet:

<u>Steric Number</u>	<u>Structure Name</u>	<u>VSEPR notation</u>	<u>Geometry</u>	<u>Ideal Bond Angles</u>	<u>Examples</u>
2	<i>linear</i>	AX_2		180°	BeH_2
3	<i>Trigonal planar</i>	AX_3		120°	BF_3
3/4	<i>Bent</i>	AX_2E Or AX_2E_2		120° for steric 3, for 109.5° for steric 4	O_3 for steric 3 and H_2O for steric 4
4	<i>Tetrahedral</i>	AX_4		109.5°	CF_4
4	<i>Trigonal Pyramidal</i>	AX_3E		109.5°	NF_3

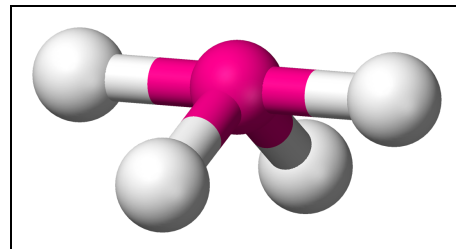
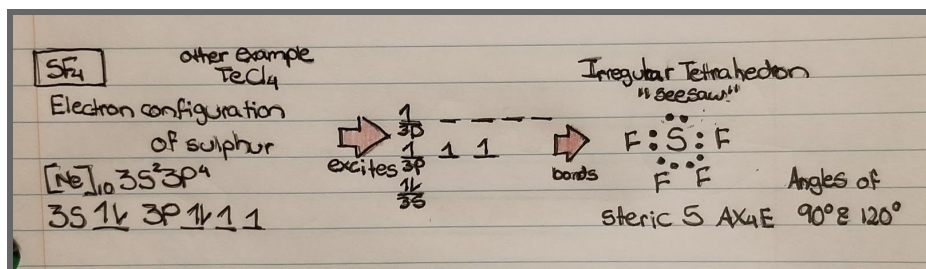
Note that in VSEPR notation X refers to a bonding pair, and E to a lone pair. Bond angles of geometric shapes holding lone pairs are approximated, for instance the bond angle of a water molecule is closer to 104.5° . This applies to expanded octet molecules as well.

All of the above mentioned geometric shapes obey the octet rule, as all (except particular examples like BeH_2 and BF_3) will have a full octet of either bonding or lone pairs. There are however molecules which have more than 8 electrons in their valence shell available for bonding, and such the **expanded octet** is the final violation of the octet rule. Here are only **some** of the possible shapes allowed by an expanded octet.

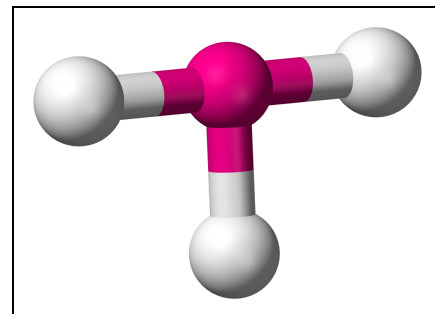
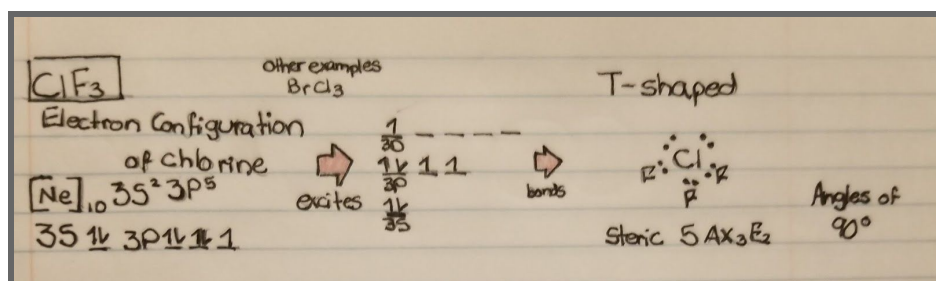
Trigonal-Bipyramidal



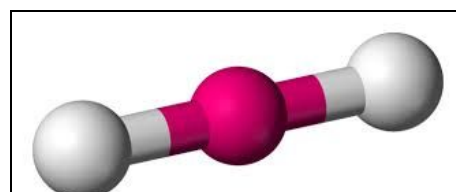
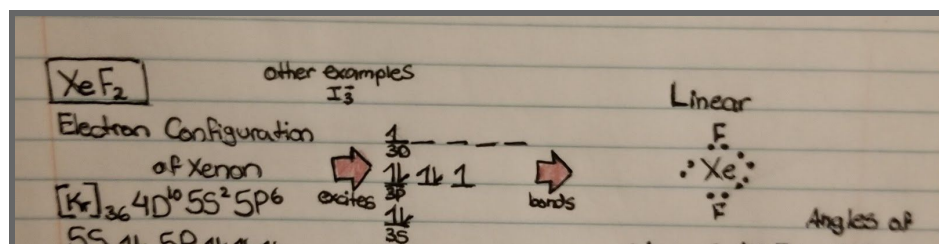
Irregular Tetrahedron - Seesaw



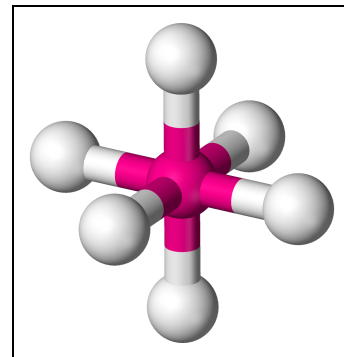
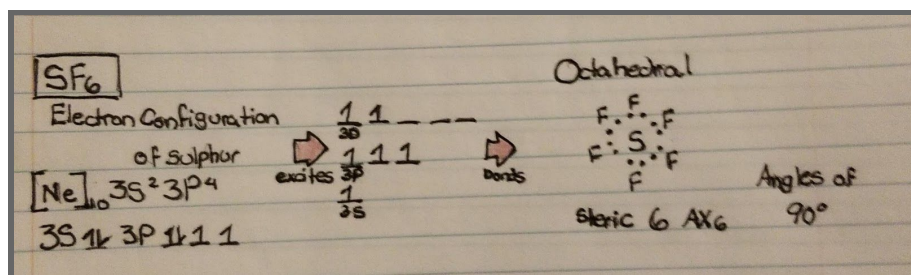
T-Shaped



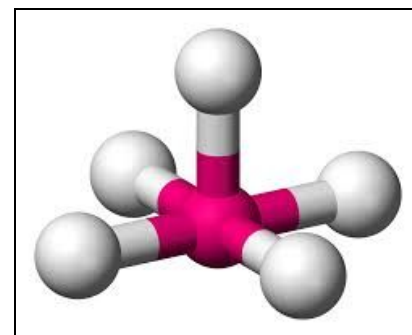
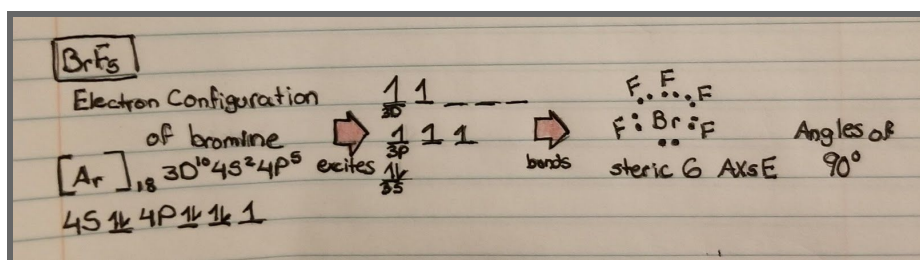
Linear



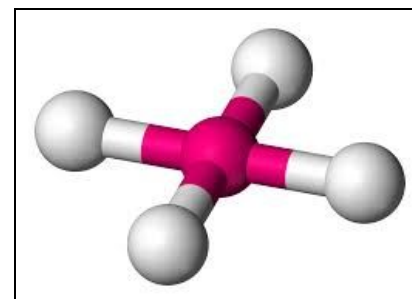
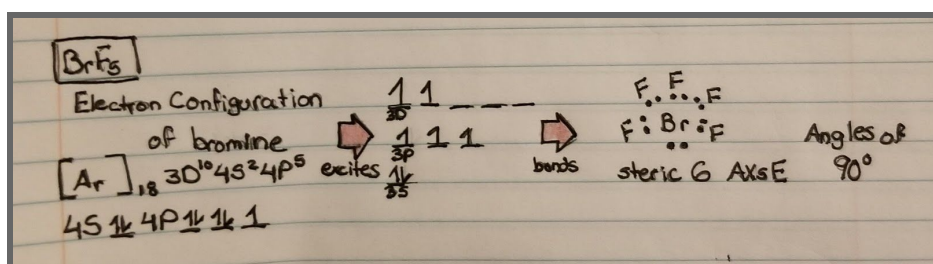
Octahedral



Square Pyramidal



Square Planar



These are many more shapes (even within steric 6), where VSEPR notation begins to be the same for multiple shapes (as there are multiple ways to arrange the same electron positioning while remaining stable). Other common examples of expanded octets can be seen within oxides, as they have a tendency to expand their octets to be able to minimize formal charges.

Intermolecular Forces

Intermolecular Forces (commonly known as IMFs) are the forces which hold molecules together (molecule to molecule), are quite useful when it comes to predicting relative melting and boiling points of substances. There are 3 IMFs to consider when comparing melting and boiling points:

❑ London Dispersion

- ❑ London dispersion forces are held by any and all molecules, and they increase with an increasing amount of total electrons. This is an electrostatic force based on momentary dipoles which form when electrons move across a molecule.

❑ Dipole-Dipole

- ❑ Dipole-Dipole forces are stronger than London dispersion, but weaker than hydrogen bonding, and they work on the basis of non-momentary polarity in a molecule. If a molecule is not symmetrical, it is nearly guaranteed to have polarity and as such have dipole-dipole forces. This works on the basis of a side of the molecule being more negative or positive relative to the other (based on electronegativity). Molecules which have lone pairs such as NH_3 (ammonia) have dipole-dipole forces as their lone pairs makes them polar (lone pairs being negative).

❑ Hydrogen Bonding

- ❑ The most complex of the forces, hydrogen bonding is also the strongest intermolecular force. It works on the basis of having really electronegative elements (particularly **Fluorine, Oxygen, and Nitrogen**) bond with hydrogen. The electronegative atom nearly pulls on hydrogen's electron so strongly it leaves the s=hydrogen unshielding, creating a highly positive end and a negative end.
- ❑ One common misconception has to do with the fact that just any electronegative element bond with hydrogen will result in a hydrogen bond. For instance Hydrogen chloride will have dipole-dipole but not hydrogen bonding, without getting too in depth, this has to do with the relative nuclear pull of the Cl nucleus in comparison to the other 3 viable elements. Due to the size of the Cl atom, poor overlap in orbitals results in poor mixing, and as such no hydrogen bonding.

As hydrogen bonding is the strongest IMF (followed by DD then LD), molecules holding all 3 forces will tend to have higher melting and boiling points as their molecules will want to stick to one another due to electrostatic attractions. This explains water's relatively high boiling point compared to other molecular compounds.

When comparing the melting and boiling points of all molecules however (not just molecular compounds), these factors cause a higher boiling points in increasing order:

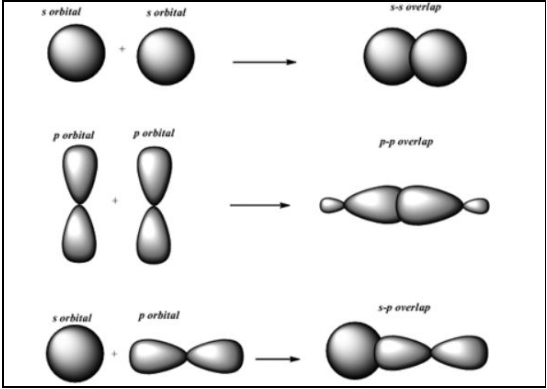
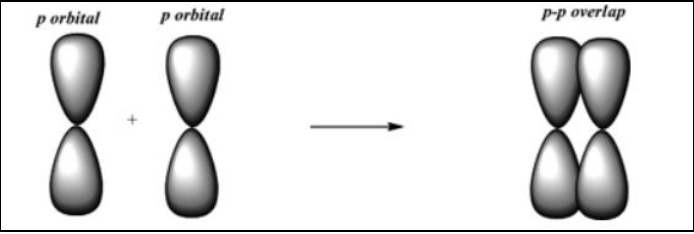
- ❑ London Dispersion
- ❑ Dipole-Dipole
- ❑ Hydrogen Bonding

- ❑ Ionic Bonding or Metallic Bonding (depending on circumstances)
- ❑ Network Covalent Bonding (due to its high number of strong covalent bonds it tends to have the highest melting and boiling points).

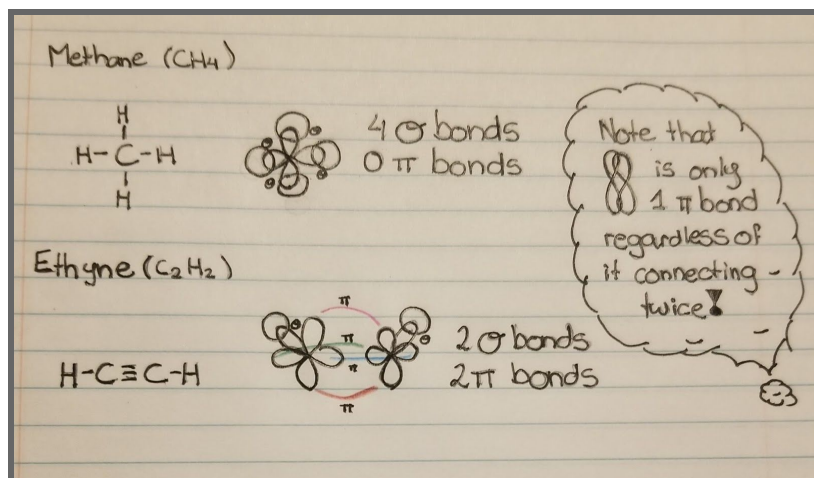
Hybridization - Orbital Mixing

Sigma and Pi Bonds

Without diving too deep, there exist two particular types of bonds which are very important in terms of visualizing bonding structure. Sigma bonds (σ) occur in between two S orbitals, between two hybrids, between an “S” and a “P” orbital, and when the heads of two “P” orbitals overlap (headon). Pi bonds are those where two “P” orbitals meet and overlap sideways such that meet at both ends of the orbital.

Possible Sigma Bonds	Possible Pi Bonds
 <p>The diagram illustrates three types of sigma bond formation:</p> <ul style="list-style-type: none"> s-s overlap: Two spherical s orbitals overlap head-on to form a single elongated lobe. p-p overlap: Two dumbbell-shaped p orbitals overlap head-on to form a single elongated lobe. s-p overlap: A spherical s orbital overlaps head-on with a dumbbell-shaped p orbital to form a single elongated lobe. 	 <p>The diagram illustrates pi bond formation:</p> <ul style="list-style-type: none"> p-p overlap: Two dumbbell-shaped p orbitals overlap sideways (parallel to each other) to form two separate lobes, one above and one below the horizontal axis.

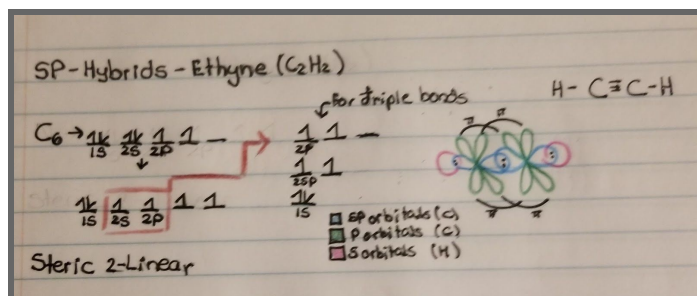
In terms of bonding, a single bond is interpreted as being a sigma bond, making sigma bonds the strongest type of bonding. Double bonds consist of one sigma bond and one pi bond, and triple bonds being the most unstable consist of a sigma and two pi bonds.



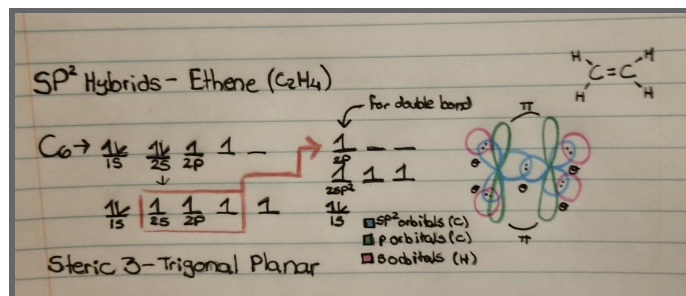
Valence Bond Theory and Hybridization

A bond is formed when an electron pair is shared by overlapping orbitals and as such potential energy is lowered. These overlapping orbitals can be either pure or hybrids, where hybrid orbitals come from orbital mixing - having new shapes and directions. The bonds formed would either be sigma or pi bonds (single, double or triple depending on the number of electrons and their configurations). Lone pairs are also able to occupy both pure and hybridized orbitals.

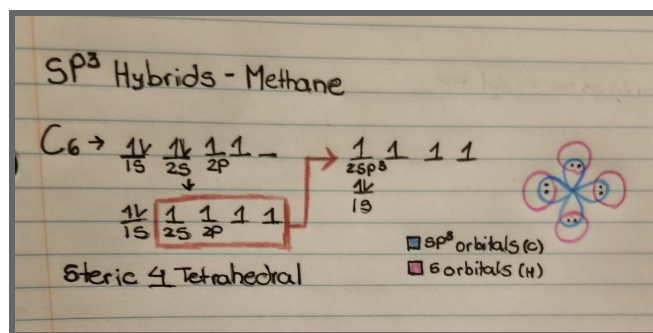
When mixing orbitals, the combination determines the number and energy of the resultant hybrid, such that the sum of the standard orbitals (pure) results in the number of hybrid orbitals. Note that the energy of the hybrid would be an inbetween of what is being mixing, for instance sp^3 orbitals would have higher energy than s orbitals but lower energy than p orbitals. Electrons in hybrid orbitals still obey Hund's rule (electrons will half-fill orbitals before pairing, and lone electrons will have the same spin).



SP Hybridization - Steric 2

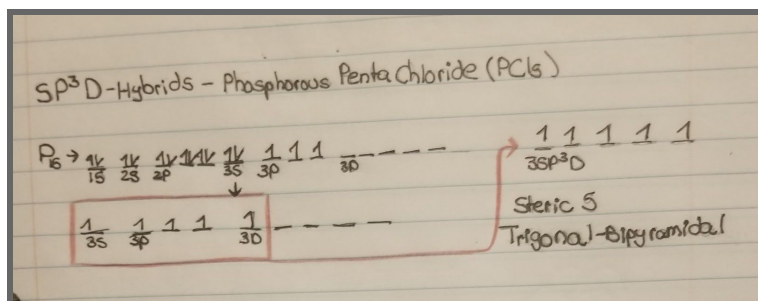


SP² Hybridization - Steric 3

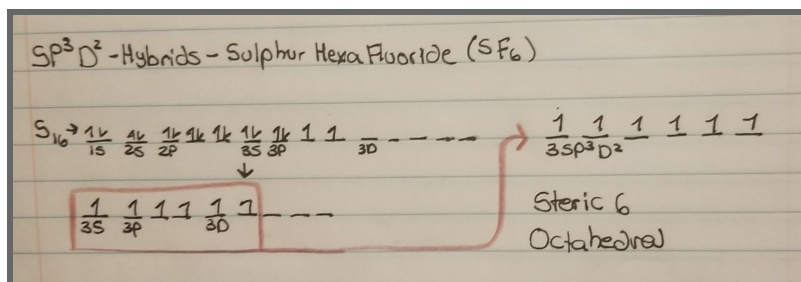


SP³ Hybridization - Steric 4

There are also hybrids for the expanded octets, however due to the sheer quantity of them (Steric 5-12), only Steric 5 and 6 need to be known.



SP³D Hybridization - Steric 5



SP³D² Hybridization - Steric 6