Inorganic chemistry

Class code

h4n6p5j

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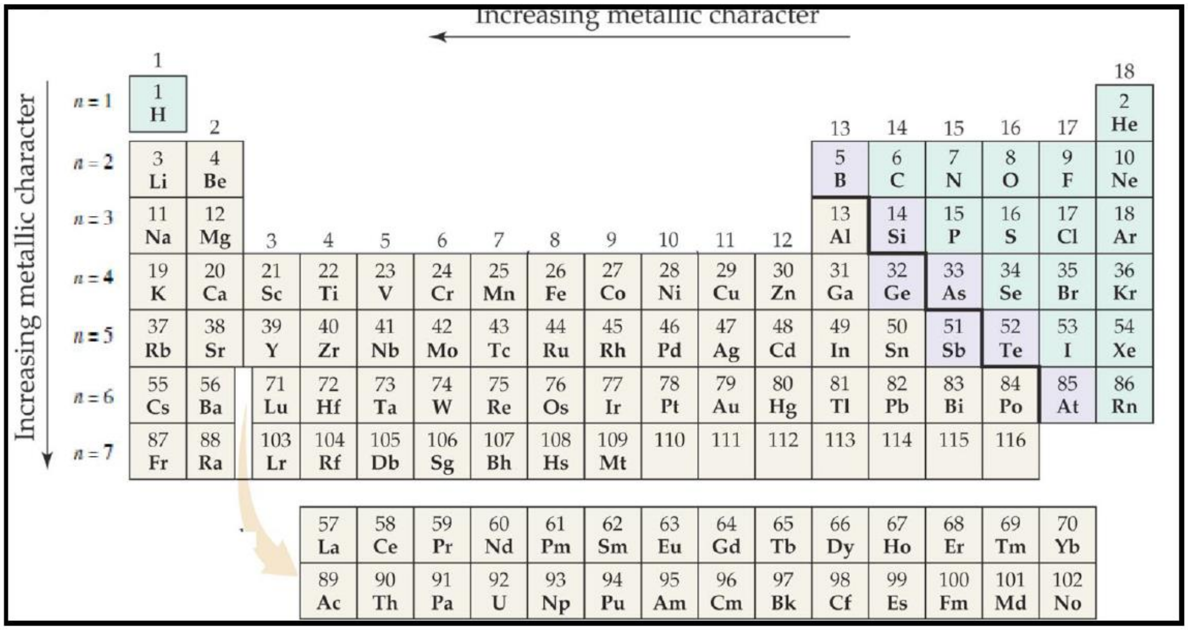

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
n = 1	1 H																	2 He
n = 2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
n = 3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
n = 4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
n = 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
n = 6	55 Cs	56 Ba	71 Lu	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
n = 7	87 Fr	88 Ra	103 Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110	111	112	113	114	115	116		

57 La	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
89 Ac	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

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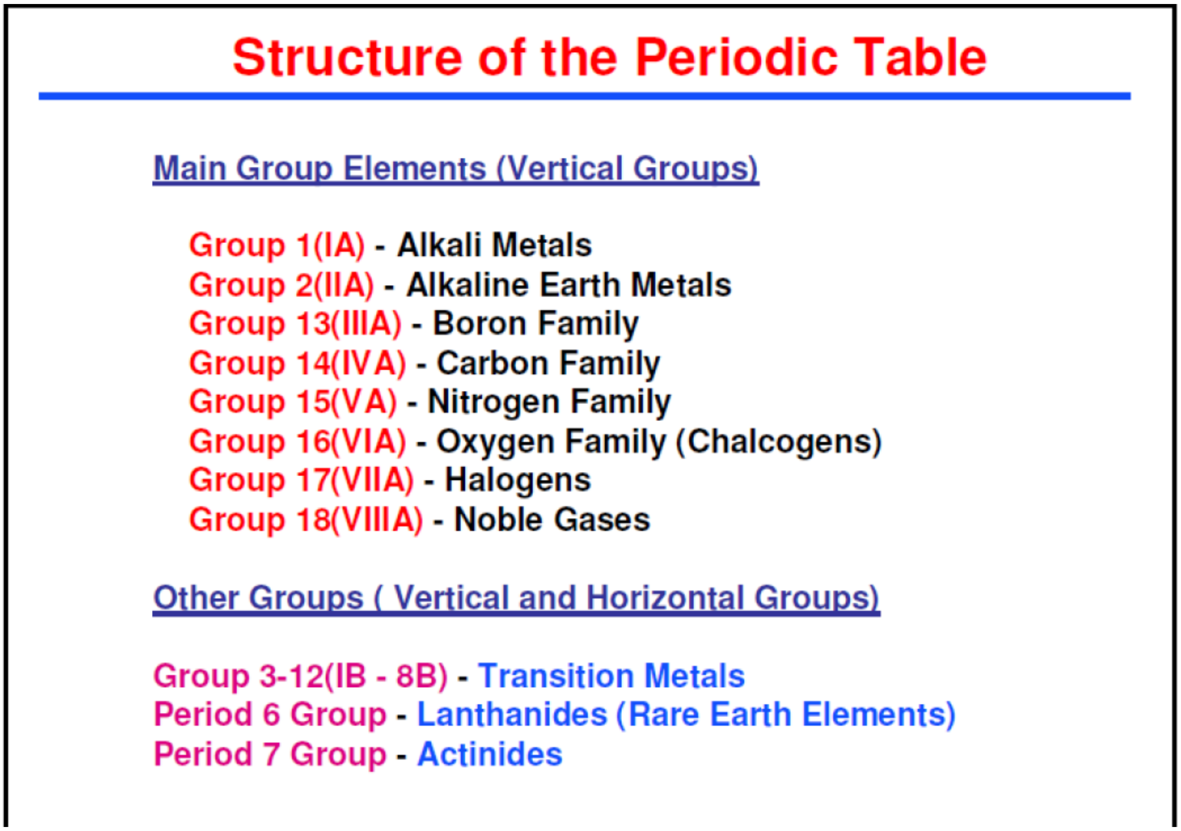


Structure of the Periodic Table

Main Group Elements (Vertical Groups)

Group 1(IA) - Alkali Metals
Group 2(IIA) - Alkaline Earth Metals
Group 13(IIIA) - Boron Family
Group 14(IVA) - Carbon Family
Group 15(VA) - Nitrogen Family
Group 16(VIA) - Oxygen Family (Chalcogens)
Group 17(VIIA) - Halogens
Group 18(VIIIA) - Noble Gases

Other Groups (Vertical and Horizontal Groups)

Group 3-12(IB - 8B) - Transition Metals
Period 6 Group - Lanthanides (Rare Earth Elements)
Period 7 Group - Actinides

Atomic Term Symbols

The Stationary States of the many-electron atom are determined by the *overall* Properties of the atom, not those of the individual electrons that exist in the atom. What are these overall properties?

- The total orbital angular momentum of the electrons, **L**
- The total spin angular momentum of the electrons, **S**
- The total angular momentum of the atom, **J**

Thus, the eigenstates of the Hamiltonian for the atom are labeled by these properties. These labels are called **Atomic Term Symbols.**

The 'definition' of the term symbol:

$\mathbf{^{2S+1}L_J}$

Note: In the symbol **L** must be replaced with its alphabetic 'code':

L=0 is S,
L=1 is P,
L=2 is D,
L=3 is F,
L=4 is G,
L=5 is H...

J is the vector sum of **L** and **S**:

J = (L+S), (L+S-1), (L+S-2), ...|L-S|

***Assigning* Term Symbols:**

The ground state of **hydrogen** atom is one electron in the lowest energy atomic orbital: the $\mathbf{1s^1}$. Therefore the total orbital angular momentum of all (one) electrons is L=l=0, and the total electron spin is S=s=1/2.

Applying the 'definition' of the term symbol results in a $\mathbf{^2S_{1/2}}$ atomic term for the ground state of the H atom. This symbol is ‗read‘: ―doublet Ess one half‖

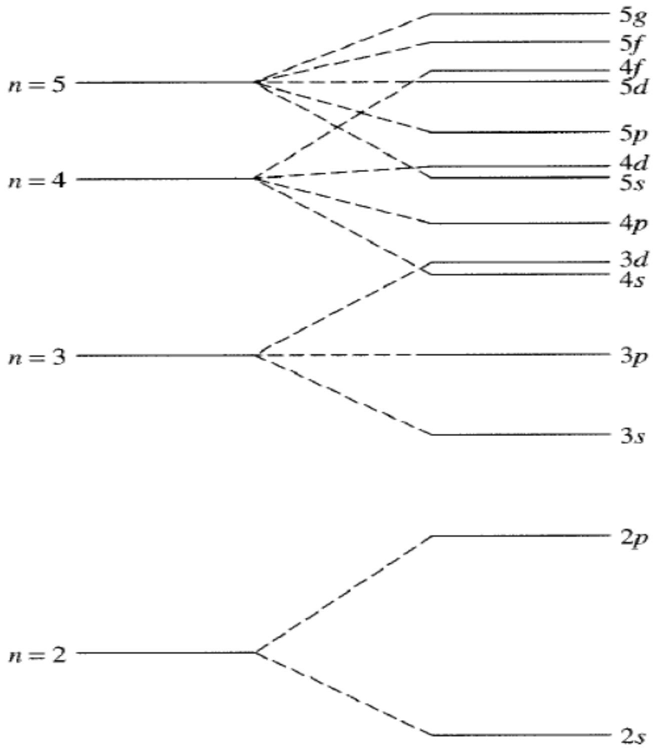
The lowest electron configuration of He is $1s^2$. The ground state of the neutral helium atom is therefore $^1S_0$ since the total orbital and spin angular momentum of this configuration is zero. In fact, any electron configuration (orbital population) that consists of any combination of closed shells or subshells will result in this (totally symmetric $\mathbf{^1S_0}$ term. Therefore, in the designation of atomic terms, the **contribution from closed subshell electrons may be neglected**.

What can‘t be neglected? The resultant angular momenta of the open-shell electrons in the atom! Because the angular momenta of each electron ***adds*** to the rest of the electrons ***vectorially***, there will, in general, be more than one possible result of this addition. It is our job to account for each and every possible way in which the properties of the electrons will sum up and sort those possibilities into those corresponding to distinct Terms (total energies; atomic Eigen states).

Shielding

In atoms with more than one electron, energies of specific levels are difficult to Predict quantitatively, but one of the more common approaches is to use the idea of **Shielding. Each electron acts as a shield for electrons farther out from the Nucleus, reducing the attraction between the nucleus and the distant electrons.** Although the quantum number *n* is most important in determining the energy, ℓ must also be included in the calculation of the energy in atoms with more than one electron.

As the atomic number increases, the electrons are drawn toward the nucleus and the orbital energies become more negative. Although the energies decrease with increasing Z, the changes are irregular because of shielding of outer electrons by inner electrons.
As a result of shielding and other more subtle interactions between the electrons, the simple order of orbitals (in order of energy increasing with increasing *n)* holds only at very low atomic number Z and for the innermost electrons of any atom. For the outer orbitals, the increasing energy difference between levels with the same *n* but different ℓ values forces the overlap of energy levels with $n = 3$ and $n = 4$, and *4s* fills before *3d.*
In a similar fashion, *5s* fills before *4d, 6s* before *5d, 4f* before *5d,* and *5f* before *6d*
(Figure *below).*



Slater formulated a set of simple rules that serve as a rough guide to this effect. He defined the effective nuclear charge Z* as a measure of the nuclear attraction for an electron. Z* can be calculated from

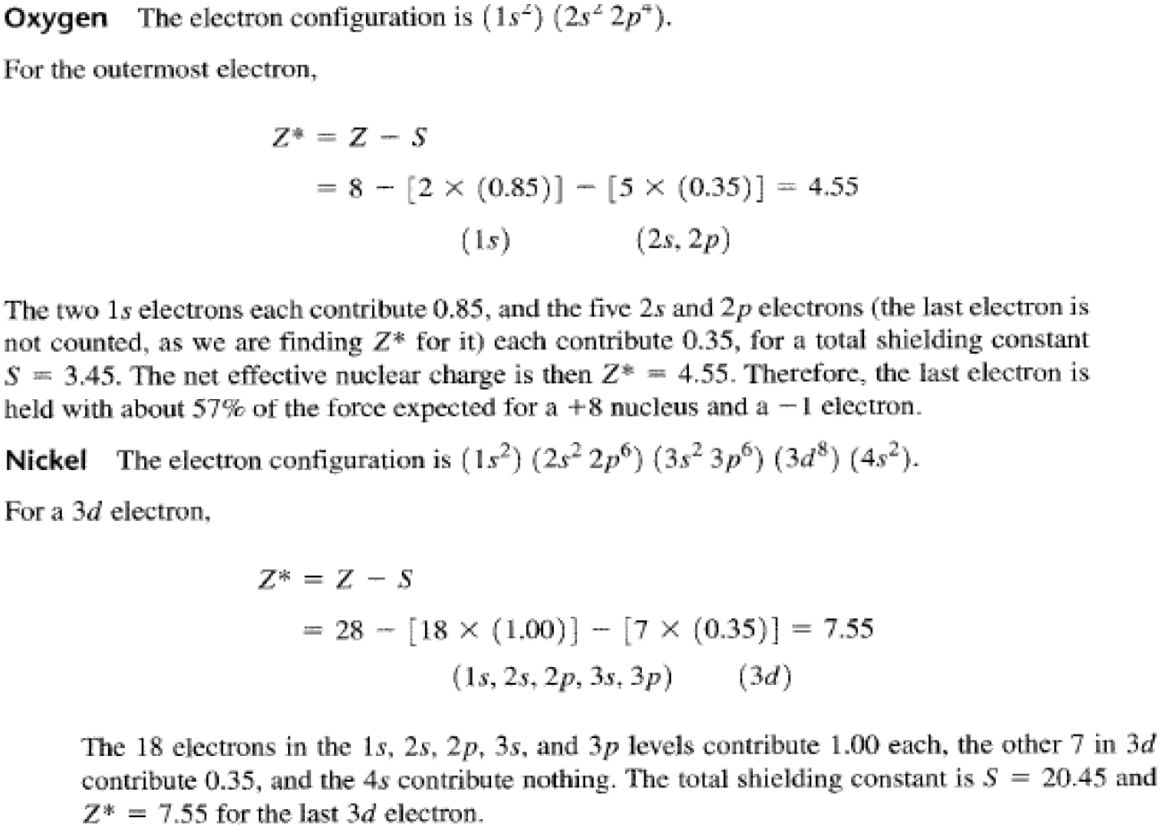
$$Z^* = Z - S$$

where Z is the nuclear charge and S is the shielding constant. The rules for determining S for a specific electron are as follows:

1. The electronic structure of the atom is written in groupings as follows:
   *(1s) (2s,2 p) (3s,3 p) (3d)(4s,4 p) (4d)(4f)(5s,5p) ···*etc .

2\. Electrons in higher groups (to the right in the list above) do not shield those in . lower groups.
3. For *ns* or *np* valence electrons:
a. Electrons in the same *ns*, *np* group contribute *0.35,* except the *1s,* where *0.30* works better.
b. Electrons in the *n - 1* group contribute *0.85.*
c. Electrons in the *n* - 2 or lower groups contribute *1.00.*
4. For *nd* and *nf* valence electrons:
a. Electrons in the same *nd* or *nf* group contribute *0.35.*
b. Electrons in groups to the left contribute *1.00.*
The shielding constant S obtained from the sum of the contributions above is subtracted from the nuclear charge Z to obtain the effective nuclear charge Z*

affecting the selected electron. Some examples follow.



Oxygen The electron configuration is $(1s^2)\ (2s^2\ 2p^4)$.

For the outermost electron,

$$\begin{aligned} Z^* &= Z - S \\ &= 8 - \underbrace{[2 \times (0.85)]}_{(1s)} - \underbrace{[5 \times (0.35)]}_{(2s,\ 2p)} = 4.55 \end{aligned}$$

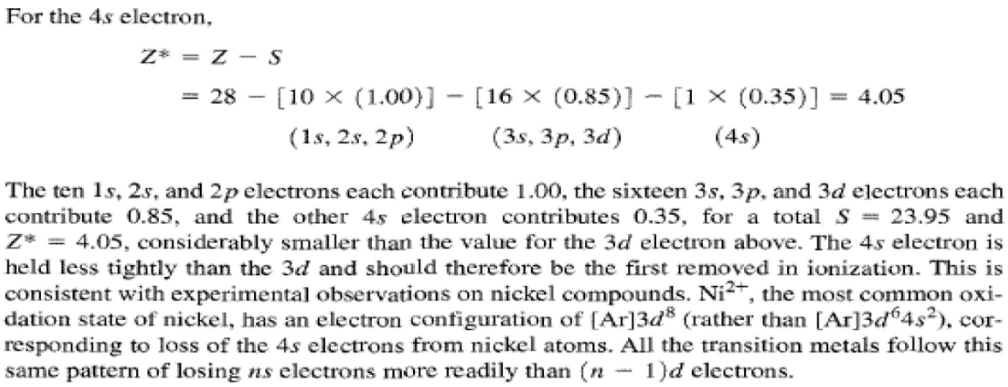
The two $1s$ electrons each contribute 0.85, and the five $2s$ and $2p$ electrons (the last electron is not counted, as we are finding Z^* for it) each contribute 0.35, for a total shielding constant $S = 3.45$. The net effective nuclear charge is then $Z^* = 4.55$. Therefore, the last electron is held with about 57% of the force expected for a +8 nucleus and a −1 electron.

Nickel The electron configuration is $(1s^2)\ (2s^2\ 2p^6)\ (3s^2\ 3p^6)\ (3d^8)\ (4s^2)$.

For a $3d$ electron,

$$\begin{aligned} Z^* &= Z - S \\ &= 28 - \underbrace{[18 \times (1.00)]}_{(1s,\ 2s,\ 2p,\ 3s,\ 3p)} - \underbrace{[7 \times (0.35)]}_{(3d)} = 7.55 \end{aligned}$$

The 18 electrons in the $1s$, $2s$, $2p$, $3s$, and $3p$ levels contribute 1.00 each, the other 7 in $3d$ contribute 0.35, and the $4s$ contribute nothing. The total shielding constant is $S = 20.45$ and $Z^* = 7.55$ for the last $3d$ electron.



For the $4s$ electron,

$$\begin{aligned} Z^* &= Z - S \\ &= 28 - \underbrace{[10 \times (1.00)]}_{(1s,\ 2s,\ 2p)} - \underbrace{[16 \times (0.85)]}_{(3s,\ 3p,\ 3d)} - \underbrace{[1 \times (0.35)]}_{(4s)} = 4.05 \end{aligned}$$

The ten $1s$, $2s$, and $2p$ electrons each contribute 1.00, the sixteen $3s$, $3p$, and $3d$ electrons each contribute 0.85, and the other $4s$ electron contributes 0.35, for a total $S = 23.95$ and $Z^* = 4.05$, considerably smaller than the value for the $3d$ electron above. The $4s$ electron is held less tightly than the $3d$ and should therefore be the first removed in ionization. This is consistent with experimental observations on nickel compounds. Ni^{2+}, the most common oxidation state of nickel, has an electron configuration of $[Ar]3d^8$ (rather than $[Ar]3d^6 4s^2$), corresponding to loss of the $4s$ electrons from nickel atoms. All the transition metals follow this same pattern of losing ns electrons more readily than $(n-1)d$ electrons.

Ionization Energy (IE) or Ionization potential(IP)

The minimum energy needed to remove an electron from a gas phase atom

Depends on

(a) Size of the atom - IE decreases as the size of the atom increases

(b) Nuclear Charge - IE increases with increase in nuclear charge

(c) The type of electron - Shielding effect

1st IE H is 1312 KJ mol^{-1}
Li is 520 KJ mol $^{-1}$

Reasons

1. Average distance of 2s electron is greater than that of 1s
2. Penetration effect
3. Electronic configuration

On moving down a group

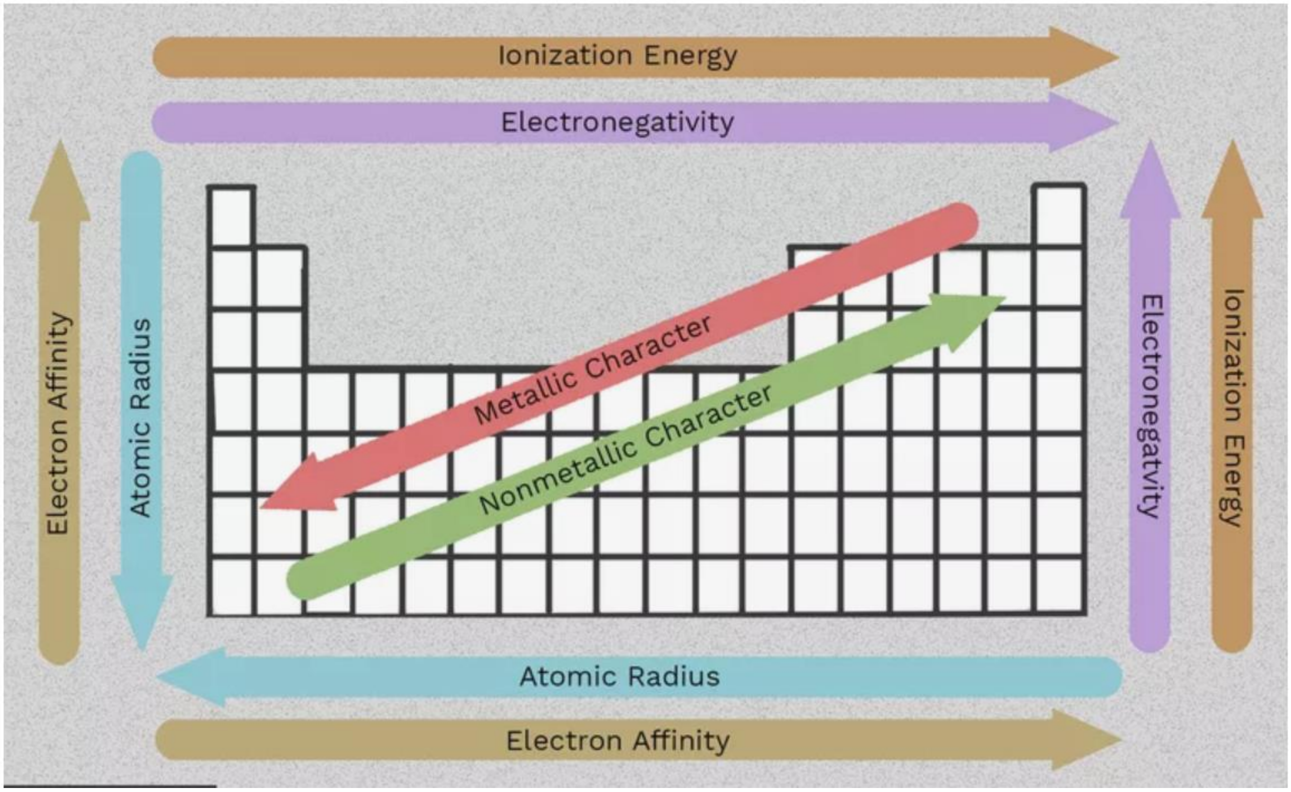
1. nuclear charge decreases
2. Z* due to screening is almost constant
3. number of shells increases, hence atomic size increases.
4. there is a increase in the number of inner electrons which shield the valence electrons from the nucleus .

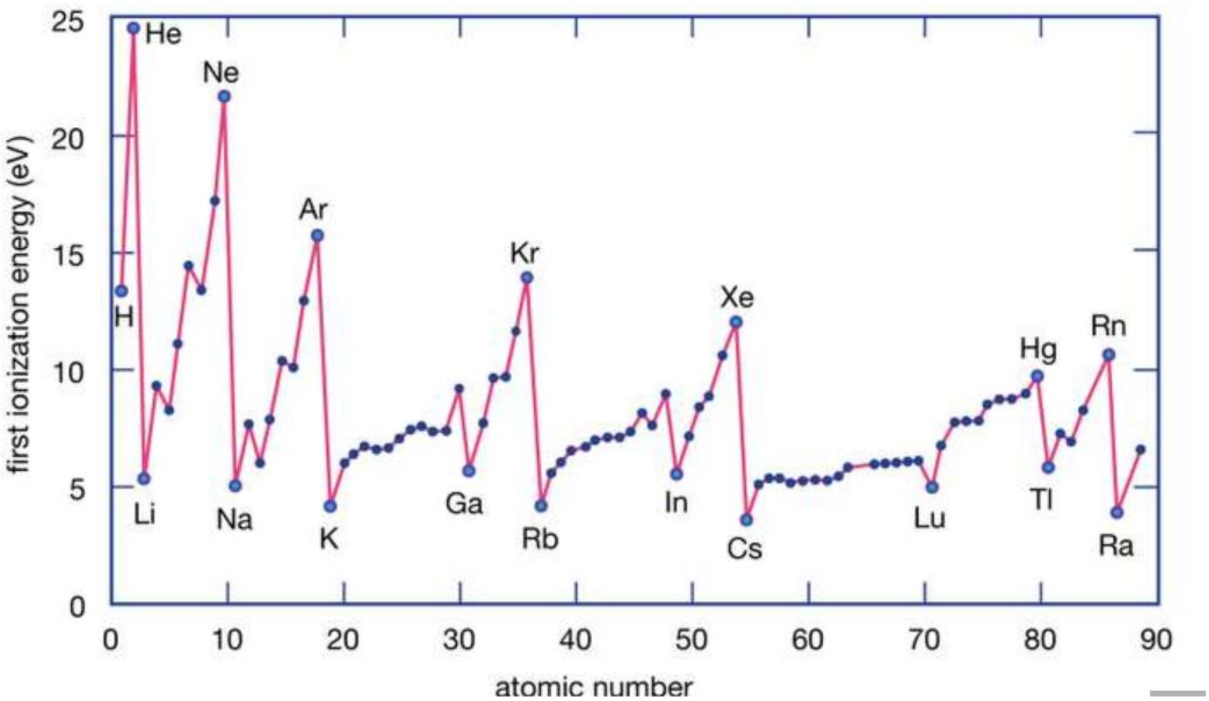
Thus IE decreases down the group

On moving across a period

1. the atomic size decreases
2. nuclear charge increases

Thus IE increases along a period


Ionization Energy
Electronegativity
Electron Affinity
Atomic Radius
Metallic Character
Nonmetallic Character
Electronegatvity
Ionization Energy
Atomic Radius
Electron Affinity

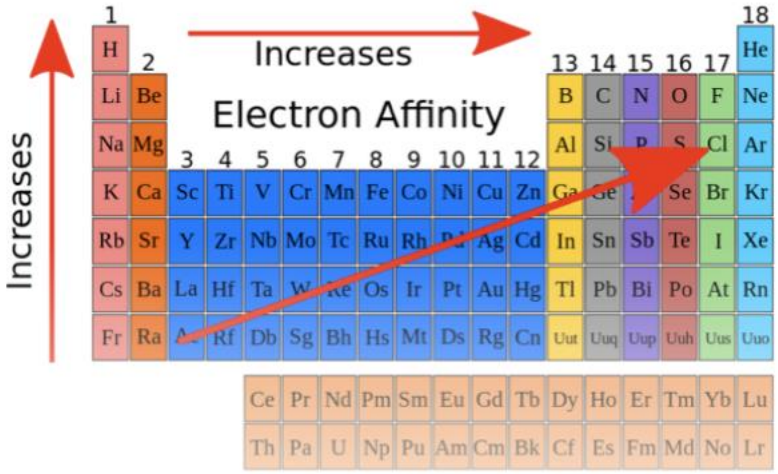


The electronegativity (EN)

The electronegativity of an element is a measure of the relative tendency of an atom to attract electrons to itself *when it is chemically combined with another atom.* Elements with high electronegativities (nonmetals) often gain electrons to form anions. Elements with low electronegativities (metals) often lose electrons to form cations.

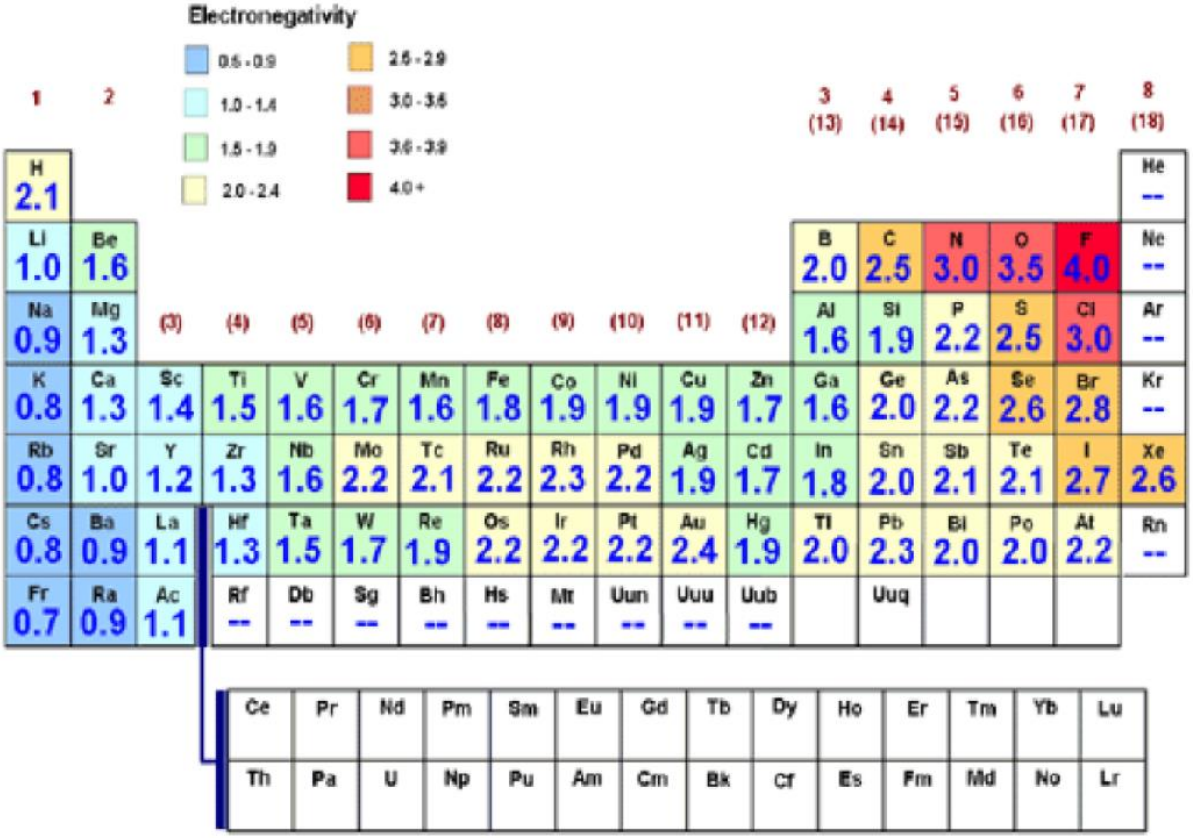
The electronegativity of fluorine (4.0) is higher than that of any other element.

This tells us that when fluorine is chemically bonded to other elements it has a greater tendency to attract electron density to itself than does any other element. Oxygen is the second most electronegative element. For the representative elements, electronegativities usually increase from left to right across periods and decrease from top to bottom within groups.



1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Uuq	Uup	Uuh	Uus	Uuo
				Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
				Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Periodic Trend: Electron Affinity



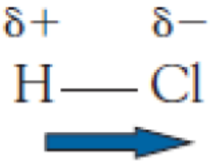
Electronegativity

🟦 0.6 - 0.9
🟦 1.0 - 1.4
🟩 1.5 - 1.9
🟨 2.0 - 2.4
🟧 2.5 - 2.9
🟧 3.0 - 3.5
🟥 3.6 - 3.9
🟥 4.0 +

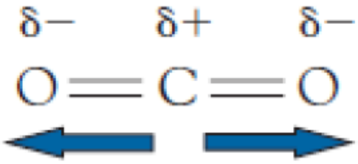
1	2	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	3 (13)	4 (14)	5 (15)	6 (16)	7 (17)	8 (18)
H 2.1																	He --
Li 1.0	Be 1.6											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	Ne --
Na 0.9	Mg 1.3											Al 1.6	Si 1.9	P 2.2	S 2.5	Cl 3.0	Ar --
K 0.8	Ca 1.3	Sc 1.4	Ti 1.5	V 1.6	Cr 1.7	Mn 1.6	Fe 1.8	Co 1.9	Ni 1.9	Cu 1.9	Zn 1.7	Ga 1.6	Ge 2.0	As 2.2	Se 2.6	Br 2.8	Kr --
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.3	Nb 1.6	Mo 2.2	Tc 2.1	Ru 2.2	Rh 2.3	Pd 2.2	Ag 1.9	Cd 1.7	In 1.8	Sn 2.0	Sb 2.1	Te 2.1	I 2.7	Xe 2.6
Cs 0.8	Ba 0.9	La 1.1	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 2.0	Pb 2.3	Bi 2.0	Po 2.0	At 2.2	Rn --
Fr 0.7	Ra 0.9	Ac 1.1	Rf --	Db --	Sg --	Bh --	Hs --	Mt --	Uun --	Uuu --	Uub --		Uuq				

Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Some useful electronegativity values are shown in above. Thus, in a molecule such as Hydrogen chloride, the bonding electrons will not be shared equally between the two Atoms. Instead, the higher Z_{eff} of chlorine will cause the bonding pair to be more Closely associated with the chlorine atom than with the hydrogen atom. As a result, There will be a permanent dipole in the molecule. This dipole is depicted in Figure below, using the dsign to indicate a partial charge and an arrow to indicate the dipole Direction.



Individual bond dipoles can act to ―can cell‖ each other. A simple example is provided by carbon dioxide, where the bond dipoles are acting in opposite directions. Hence, the Molecule does not possess a net dipole; in other words, the molecule is nonpolar



Pauling development of the concept of electronegativity in the 1930s arose from studies of bond energies, for which he used the symbol D. He considered two elements A and B and argued that, for a purely covalent bond, the A—B bond energy should be the geometric mean of the A—A and B—B bond energies. However, he found this was often not the case. He defined this difference as $\Delta_{/}$, where

$$\Delta' = \boldsymbol{D(A-B)} - \sqrt{\boldsymbol{(D(A-A)(B-B)}}$$

For example, the Cl-Cl bond has an energy of 242 kJ.mol$_{-1}$ and that of the H—H bond is 432 kJ.mol$_{-1}$. The geometric mean is 323 kJ.mol$_{-1}$, but the experimental value for the H—Cl bond energy is 428 kJ.mol$_{-1}$. Thus, $\Delta_{/}$ (H—Cl) is 105 kJ.mol$_{-1}$. Pauling ascribed this difference to an ionic contribution to the bonding, making the heterogeneous bond Stronger than the mean of the two homogeneous bonds.

Mulliken electronegativity, χ_{M}, as the average value of the ionization energy and the electron affinity of the element (both expressed in electron volts):

$$X_M = \frac{1}{2}(I + E_a)$$

Electron affinity (EA)

The **electron-gain enthalpy**, is the change in standard molar enthalpy when a gaseous atom gains an electron:

$A(g) + e^-(g) \rightarrow A^-(g)$

The greater the energy released in the process of taking up the extra electron, greater is the EA.

On moving across a period,

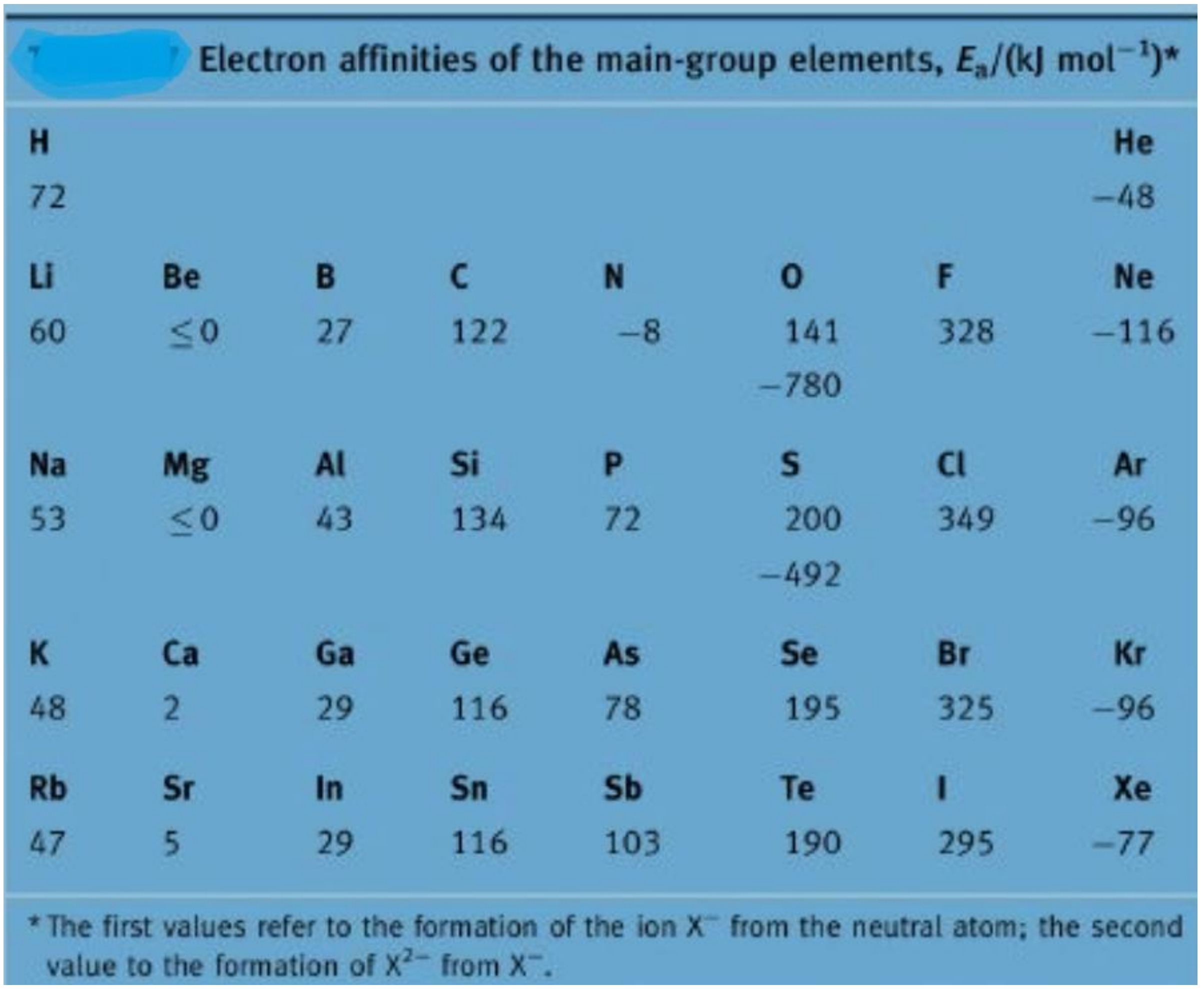
The atomic size decreases and hence the force of attraction exerted by the nucleus on the electrons increases. Consequently, the atom has a greater tendency to attract additional electron i.e., its electron affinity increases.

EA values of metals are low while those of non-metals are high.

Halogens have high electron affinities. This is due to their strong tendency to gain an additional electron to change into the stable ns^2np^6 configuration

On moving down a group

The atomic size increases and therefore, the effective nuclear attraction decreases and thus electron affinity decreases.



[redacted] Electron affinities of the main-group elements, $E_a/(\mathrm{kJ\ mol^{-1}})$*

H							**He**
72							−48
Li	**Be**	**B**	**C**	**N**	**O**	**F**	**Ne**
60	≤0	27	122	−8	141 −780	328	−116
Na	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**	**Ar**
53	≤0	43	134	72	200 −492	349	−96
K	**Ca**	**Ga**	**Ge**	**As**	**Se**	**Br**	**Kr**
48	2	29	116	78	195	325	−96
Rb	**Sr**	**In**	**Sn**	**Sb**	**Te**	**I**	**Xe**
47	5	29	116	103	190	295	−77

* The first values refer to the formation of the ion X^- from the neutral atom; the second value to the formation of X^{2-} from X^-.

Ionic Compounds

The Ionic Bond

there are two ways of looking at bonding: the interaction between charged species (ionic bonding) and the equal sharing of electron density (covalent bonding). In this section, we examine the ionic bond.

Properties of Ionic Substances

1) Ionic solids conduct electricity poorly, but when melted or dissolved are good electrical conductors. When molten or in solution, ions are free to move and charge can be transported. In a solid lattice, ions are locked into place so there is no way to move charge.

2) Ionic compounds have high melting points. Ionic and covalent bonds are both strong, but unlike covalent bonds, ionic bonds are not directed at only one other atom. Instead all anions, particularly those close by, are attracted to a given cation and *vice versa*. The result is extended arrays of ions that are held strongly together.
3) Ionic compounds tend to be hard and brittle. Again, this arises from ionic interactions.
4) Ionic compounds are frequently soluble in solvents with large dielectric constants. These solvents are quite polar and the dipoles are electrostatically attracted to the ions. If the solvation energy is greater than the attraction of the ions in the crystal, the crystal dissolves. Ionic compounds rarely dissolve in non-polar solvents because the ion-solvent attraction is weak and hence the solvation energy is small.

Occurrence of Ionic Bonding

Ionic bonds tend to occur for the cations of Group IA, IIA, some IIIA elements, and low oxidation states for some other elements (transition metals, Pb^{2+}, Sn^{2+}). Anions that engage in ionic bonding are largely limited to the halide ions, some chalcogen anions, and nitride ion. Why? Because the energy cost of the reaction is not

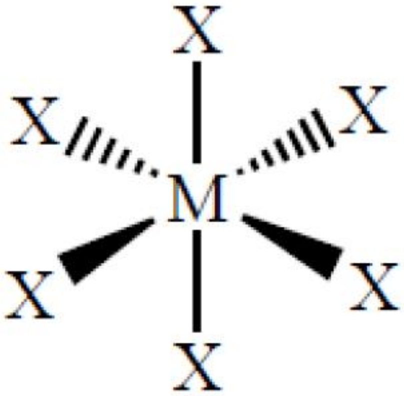
very great. Metals in high oxidation states tend to bond covalently. Thus, $MoCl_6$ has considerable covalent character in the Mo-Cl bonds.

Lattice Energy U

Consider the salt MX which crystallizes in the sodium chloride lattice. The equation that describes the energy of interaction between two ions is:

$$E_c{}' = \frac{Z^+ Z^- e^2}{4\pi\varepsilon_0 r}$$

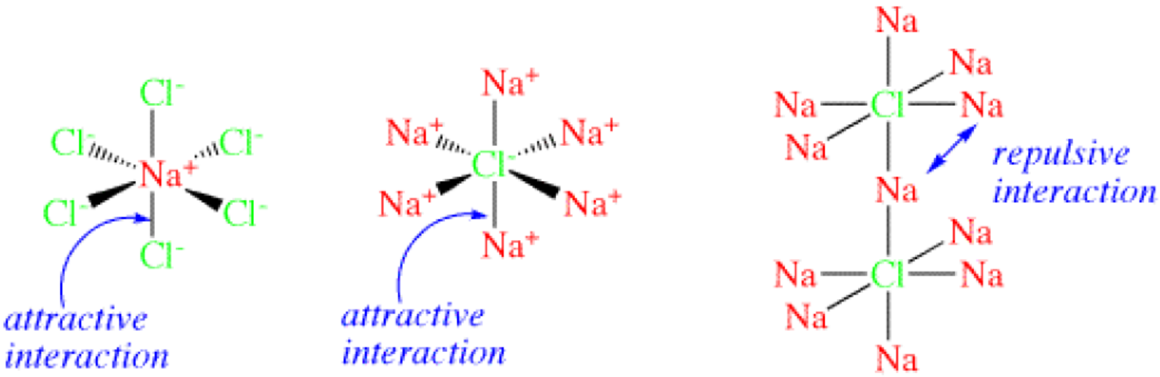
where Z_+, Z_- = ionic charges, e = electron charge, ε = permittivity of a vacuum, and r = separation of the particles.
Note that $E_c{}'$ is always negative (favorable) for ions with opposite charges. It is always positive for ions possessing the same charge. Now each cation is not attracted to just one anion, but all anions near it. It is also repelled by all other cations near it. Let's look at NaCl (MX) as an example:



Each Na+ is attracted to nearby 6 Cl- ions, so that the force of attraction felt by Na+ is 6 times larger than expected for a single attraction.

$$Ec = Ec' \left(\frac{6}{1}\right)$$

where 1 is arbitrary distance (that is, assume the M-X distance is 1). However there is another Na+ for each pair of Cl- ions that repels the Na+ (total of 12) at a distance of √ 2 away.



Thus, the total attraction is reduced $Ec = Ec' \left[\frac{6}{1} - \frac{12}{\sqrt{2}}\right]$.

When additional interactions are taken into account, this equation will continue to Expand until it eventually forms an infinite series that mathematically converges. The total Columbic attraction is written:

$$Ec' = \frac{AZ^{+} Z^{-} e^{2}}{4\pi\varepsilon_0 r}$$

Where A is the Madelung constant

$$A = \frac{6}{1} - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \cdots \text{ for the NaCl structure}$$

The Madelung constant is completely geometrical, so there is a different Madelung constant for each crystal type. The total Coulombic attraction, thus, depends on the number of charges, the signs of the charges, the distance of separation between the charges, and the arrangement of those charges in space.

Repulsive Energy

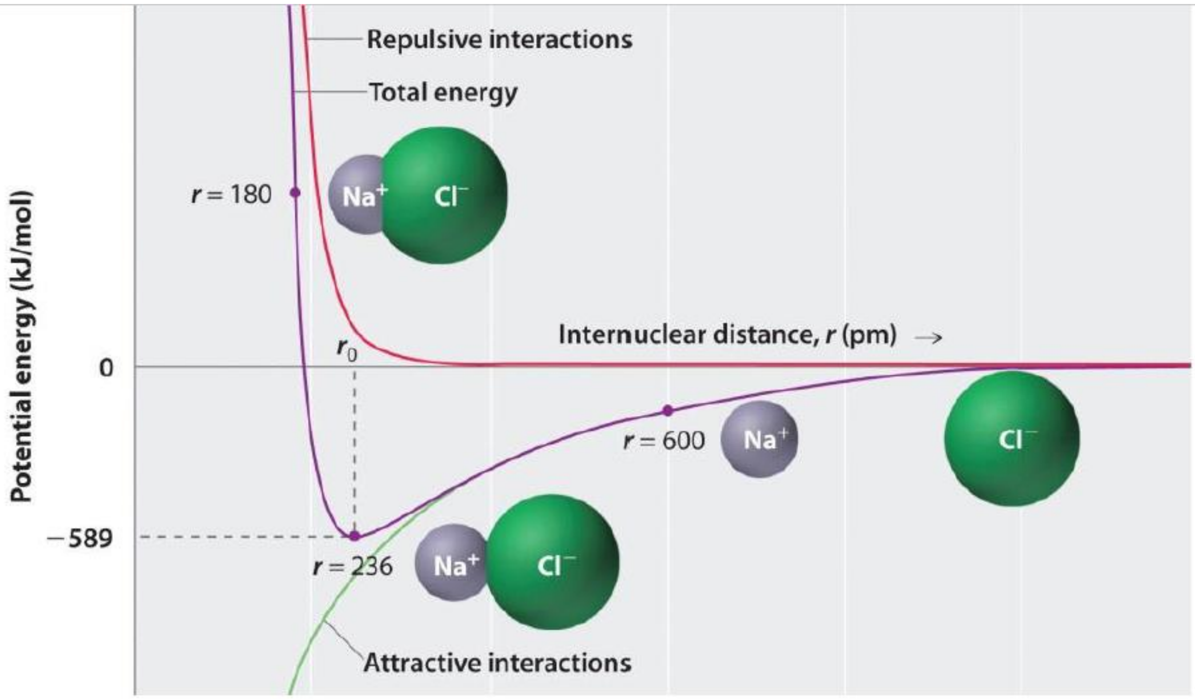
Now the coulombic interaction equation suggests that the attractive energy continually decreases (becomes more favorable) as the particles get closer. However since the ions are not point charges, at very small distances a repulsive energy develops that increases rapidly. The repulsion comes from the interaction of the core electrons of the two ions. This repulsive energy is of the form:

$$\boldsymbol{E_R = B/r^n} \qquad \text{where } E_R > 0$$

B = constant , n = Born number ,related to molecular compressibility, therefore ,the total lattice energy for a mole of compound is:

$$U = Ec + E_R = \frac{AZ^+ Z^- e^2}{4\pi\varepsilon_0 r} + \frac{NB}{r^n}$$

This is the Born-Landé equation. (N = Avogardro‘s number= 16.02 X 10^{23} mol^{-1})



The Born-Landé equation accounts for >95% of the crystal lattice energy. The equation simplifies to:

$$U_0 = \frac{ANZ^+ Z^- e^2}{4\pi\varepsilon_0 r_0}\left(1 - \frac{1}{n}\right)$$

U_0 = energy minimum, r_0 = equilibrium distance

For NaCl

$A = 1.74756$

$Z_1 = 1$, $Z_2 = -1$

$e = 1.602 \times 10^{-19}$C

$\pi = 3.142$

$\varepsilon_0 = 8.854 \times 10^{-12}\ C^2.J^{-1}.m^{-1}$

$r_0 = rNa^+ + rCl^- = 2.81\ x10^{-10}$ m

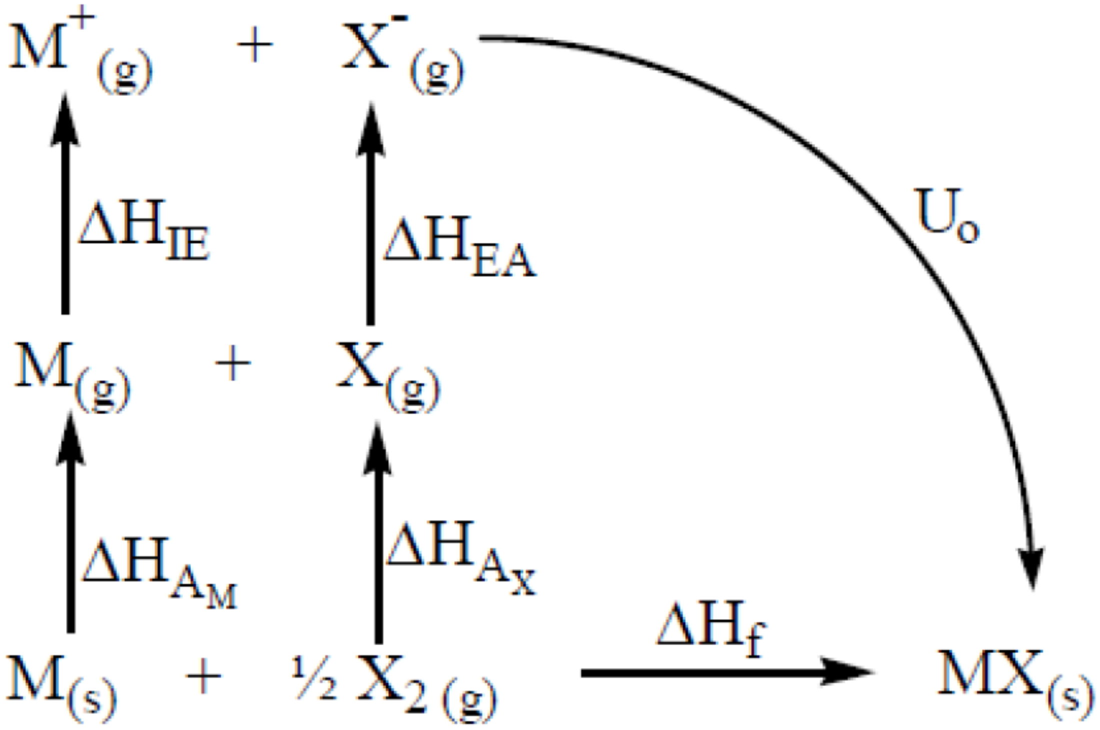
$n = (nNa^+ + nCl^-)/2 = (7+9)/2 = 8$

$U_0 = -751.$ kJ/mol but experimental $U_0 = 770$ kJ/mol

These equations account for 90-98% of the total energy of the system, depending on geometry and particular ions. So why cover this? After all, lattice energies are known for most salts. There are two reasons. First is to demonstrate that the lattice energy is simply a geometric property of the crystal lattice and because it allows us to examine why a particular set of ions crystallizes in one lattice, but not a different one. But to study this, we must first discuss the Born-Haber cycle.

Born-Haber Cycle

The Born-Haber cycle shown below explained of formation one mole of ionic compound from its starting elements.



Uo = lattice energy ΔHIE = ionization energy
ΔHf = heat of formation ΔHEA = electron affinity
ΔHAM = heat of atomization, includes sublimation energy, gaseous bond energies
ΔHAX = heat of atomization, includes appropriate terms for the anion
Thus, from Hess' Law:
ΔHf = ΔHAM + ΔHIE + ΔHAX + ΔHEA + Uo

Of these, only the lattice energy, U_o, cannot be measured. It is calculated from the previous equation. Of the measured terms listed in the Born-Haber cycle, ΔHAM, ΔHAX, and ΔHIE are always energetically unfavorable. ΔHIE is very unfavorable and ΔHEA can be. ΔHEA is favorable for monoanions and unfavorable for all higher anions.

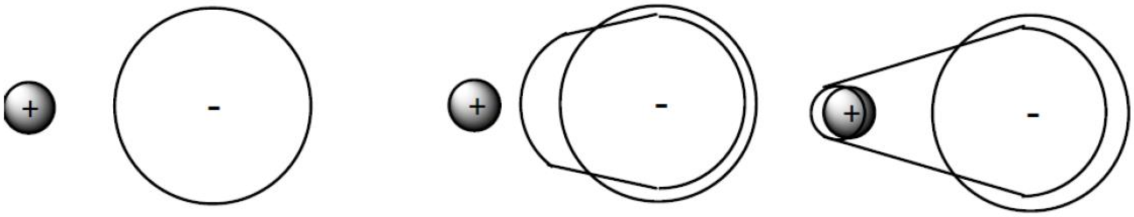
Thus for a favorable heat of formation, the lattice energy must be a large negative (favorable) number. Hence, ionic compounds form because of very favorable lattice energies.

The Born-Haber cycle allows new compounds to be evaluated. Knowing the ΔH_{AM}, ΔH_{AX}, and ΔH_{IE}, and ΔH_{EA} for any two substances, and calculating U_o, allows ΔH_f to be estimated for the salt they would form. This is important because it allows you to predict the stability of a compound before you attempt to prepare it for the first time.

Polarization and Covalency

―Ionic‖ compounds tend to have a considerable covalent contribution to their bonding when they contain *polarizing cations.*

Polarizing cations = cations capable of distorting the anion‘s electron cloud towards the cation:



No polarization. Idealized ionic bond.

Anion is polarized. (Cation may be slightly polarized.) Some covalent character.

Anion and cation are both polarized. Covalent bond.

Kasimir Fajans introduced "nonpolar character" as a perturbation on ionic bonds. The effects of covalent *vs* ionic character on the physical properties of compounds can be subtle. *Normally*, ionic compounds are higher melting, higher boiling, more water soluble, less soluble in nonpolar solvent and have higher electrical conductivity in the melt than covalent substances. These rules of thumb are useful but not infallible here. Remember that quartz, SiO_2, is a very covalent network solid with a melting point of 1710 °C, higher than many salts (mp KCl = 770°C). The high melting or boiling point of a covalent solid simply reflects the fact that there are more, or stronger, covalent bonds in the solid than in the liquid or gas phase for that solid.

Increasing covalency will often lower the melting point of a "salt", MX, by stabilizing discrete MX molecules in the melt.

Fajan’s Rules

1. Covalent character increases with **decreasing cation size** or **increasing cation**

charge. The high charge density of small and/or highly charged cations is able to exert a powerful polarizing effect which distorts the electron cloud around the anion. Compare NaCl (mp 800 °C) with $CaCl_2$ (mp 772 °C; charge effect) and KI (mp 686 °C) with LiI (mp 449°C; size effect).

2. The electrons of larger, more negatively charged anions are more loosely held because they are more shielded from the nuclear charge. Thus, these anions are more easily polarized by cations. Compare LiBr with Li_3P (charge effect), and LiF (mp 845 °C) with LiI (mp 449°C; size effect).

3. Covalent character is greater for cations with a **non-noble gas electron configuration** (i.e., 18-electron, pseudo-noble-gas cations) than for cations with a true noble-gas configuration (8- electron cations). This effect mostly shows up in transition-metal and post-transition metal cations in which one or more d-electrons ineffectively shield the outer electrons, or the electrons of an adjacent ion, from the nuclear charge. Thus, for two ions of similar size and charge, a transition metal ion with a $(n-1)d^x ns^0$ configuration will be more polarizing and more polarizable than an alkali or alkaline earth metal with a noble gas configuration, $(n-1)s^2 (n-1)p^6 ns^0$. Compare CuCl (mp 430°C, Cu^+ is $3d^{10} 4s^0$, r = 0.91 Å) with NaCl (mp 800 °C, Na^+, $2s^2 2p^6$, r = 1.16 Å) and $HgCl_2$ (mp 276 °C, Hg^{2+} is $4f^{14} 3d^{10}$, r = 116 Å) with $CaCl_2$ (mp 782 °C, Ca^{2+} is $3s^2 3p^6$, r = 114Å).

Hydration of Ions or Solubility of ionic compounds

- Ionic solids are usually soluble in water because the dipole on water interacts with the ionic charges

* Negative end of the dipole coordinates to the cation

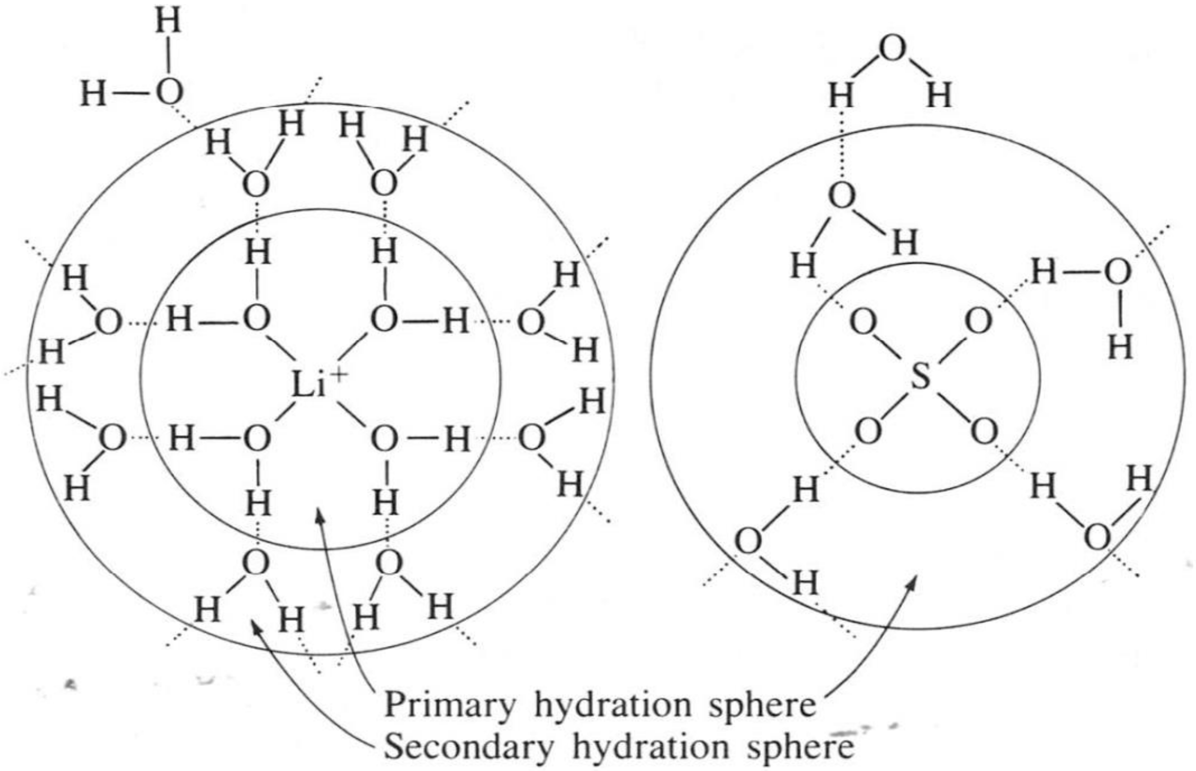
* Strength of interaction increases with decreasing cation size and increasing charge

* Strong coordination may lead to the formation of *hydrates* Ion

$$\begin{tikzcd}
MX(c) \arrow[r, "U_0"] \arrow[dr, "L"'] & M^{+}(g) \arrow[d, "\Delta H_{M^{+}}"] & + & X^{-}(g) \arrow[d, "\Delta H_{X^{-}}"] \\
 & M^{+}(\text{solv.}) & + & X^{-}(\text{solv.})
\end{tikzcd}$$

$$L = \Delta H_{M^{+}} + \Delta H_{X^{-}} + U_0$$

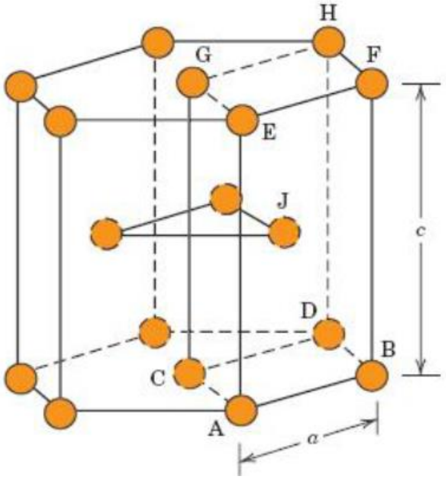
L= Enthalpy of solution
ΔH= Hydration enthalpy

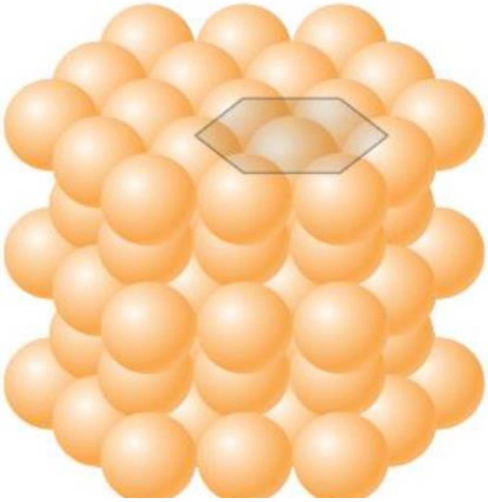


Hydrated Li^{+} and SO_4^{2-} ions.

Structure of metal crystals

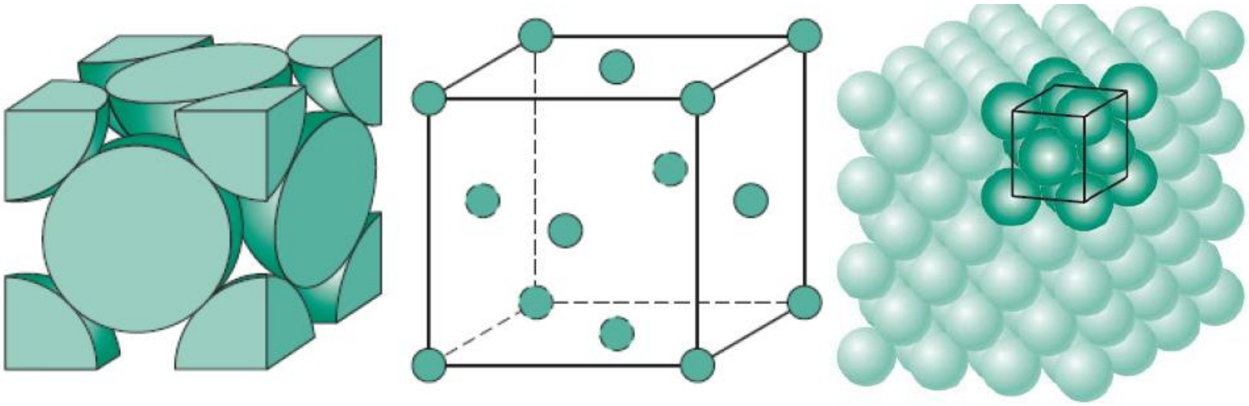
Hexagonal Close-Packed (HCP)





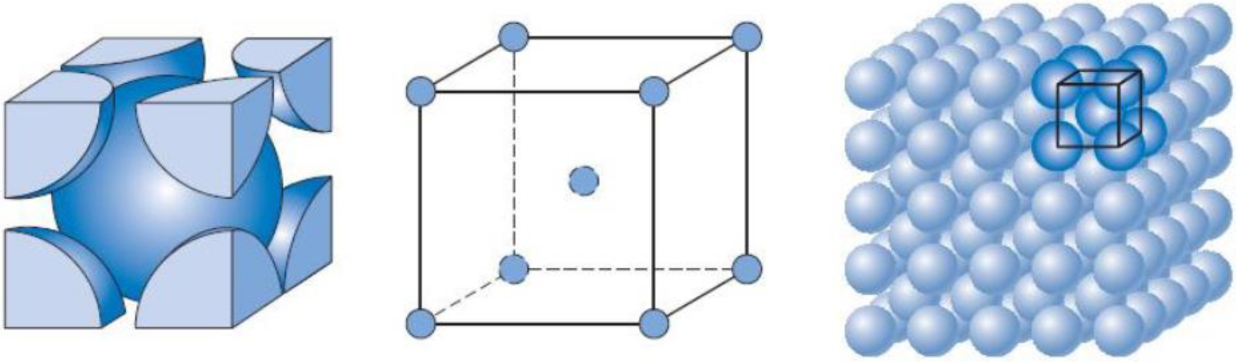
HCP structure has a hexagonal unit cell. The top and bottom faces consist of six atoms that form regular hexagons and surround a single atom in the center. Another plane that provides three additional atoms is situated between the top and bottom planes.
Familiar metals: Mg, Ti, Zn

Face-Centered Cubic (FCC)
FCC structure has a cubic unit cell with atoms located at each of the corners and the centers of all the cube faces.
Familiar metals:
Cu, Al, Ag, Au



Body-Centered Cubic (BCC)
BCC structure has a cubic unit cell with atoms located at all eight corners and a single atom at the cube center.

Familiar metals:
Cr, Fe, W



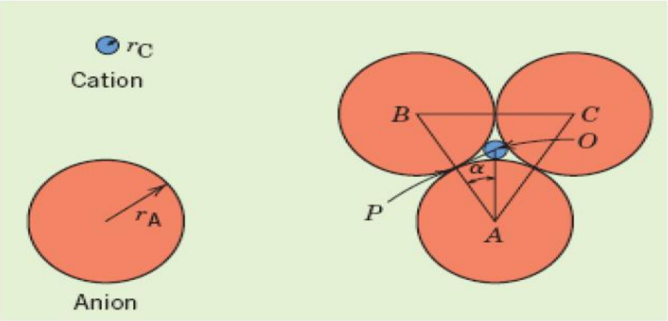
Correlation between coordination number and the cation-anion radius ratio

The coordination number is related to the cation–anion radius ratio. For a specific Coordination number, there is a critical or minimum ratio for which this cation–anion contact is established; this ratio may be determined from pure geometrical Considerations.

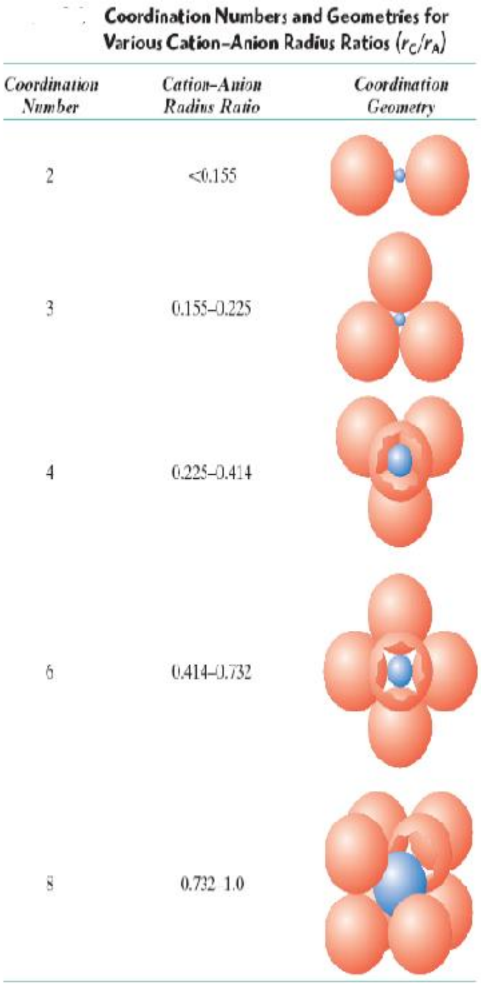
Example 1-Show that the minimum cation-to-anion radius ratio for the coordination number 3 is 0.155.

Solution

For this coordination, the small cation is surrounded by three anions to form an equilateral triangle as shown below—triangle ABC; the centers of all four ions are coplanar.



Triangle APO



Coordination Numbers and Geometries for Various Cation–Anion Radius Ratios (r_C/r_A)

Coordination Number	Cation–Anion Radius Ratio	Coordination Geometry
2	<0.155	
3	0.155–0.225	
4	0.225–0.414	
6	0.414–0.732	
8	0.732–1.0	

Example2-Show that the minimum cation-to-anion radius ratio for the coordination number 4 is 0.225.

Solution

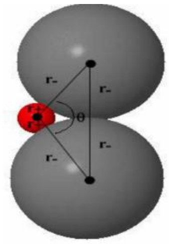
The figure opposite shows part of the ZnS structure in which the Zn^{2+} ion is surrounded by 4 S^{2-} ions.

The distance from the centre of the tetrahedron to the corner, d, is:

$d = r_+ + r_-$

To get as close to the cation as possible, the anions must touch along the edge of the tetrahedron. This distance, a, is

$\frac{r_+}{r_-} = 0.225$

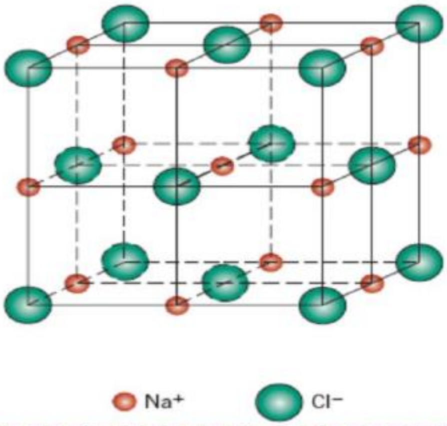


AX-type crystal structures

Some of the common ceramic materials are those in which there are equal numbers of cations and anions.

These are often referred to as AX compounds, where A denotes the cation and X the anion.

❒ Rock Salt Structure (NaCl)
❒ Cesium chloride structure(CsCl)
❒ Zinc Blende Structure(ZnS)



A unit cell for NaCl structure

Rock Salt Structure (NaCl)

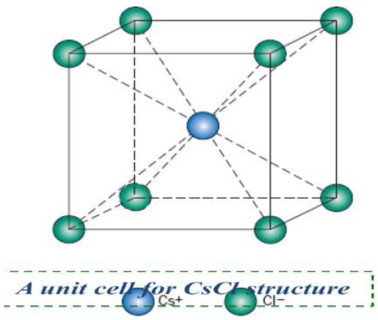
Coordination number (cations & anions): 6

$r_+/r_-=0.414\sim0.732$

The rock salt crystal structure may be thought

of as two interpenetrating FCC lattices, one composed of the cations, the other of anions.
NaCl, MgO, MnS, LiF, FeO

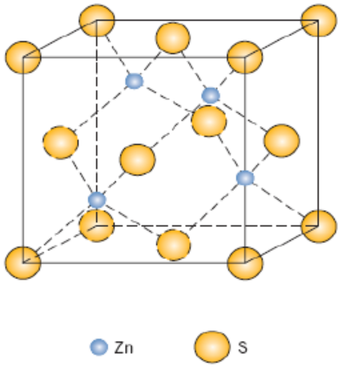
Cesium Chloride Structure
Coordination number: 8
The anions are located at each of the corners of a cube, whereas the cube



A unit cell for CsCl structure

center is a single cation. Interchange of anions with cations produces the same crystal structure.

Zinc Blende (ZnS)Structure
Coordination number: **4**, *All ions are tetrahedrally coordinated.* All corner and face positions of the cubic cell are occupied by S atoms, while the Zn atoms fill interior tetrahedral positions. Vise versa.



A unit cell for ZnS structure

. Covalent Compounds

Lewis Structures

General Rules for Drawing Lewis Structures

1. All valence electrons of the atoms in Lewis structures must be shown.
2. Generally electrons are paired. Unpaired electrons are observed in odd electron molecules such as NO and NO_2.
3. Generally each atom acquires eight electrons in its valence shell (**octet rule**)except hydrogen acquires only two electrons.
4. Multiple bonds (double and triple bonds) can be formed by C, N, O, P, and S.
5. **Hydrogen atoms are terminal atoms.** Hydrogen can accommodate a maximum of two electrons in its valence shell. It can therefore only make one bond to one other atom. There are only very few exceptions to this rule (for example, diborane, B_2H_6).
6. **Central atoms** are generally less electronegative then terminal atoms. For example, HCN is more stable than HNC because carbon is less electronegative then nitrogen. Carbon atoms are generally central atoms. Oxygen has a relatively high electronegativity and is observed to be a terminal atom in many molecules. In alcohols, the –O–H group is attached to a carbon and even though hydrogen is less electronegative it must be a terminal atom. Also, in peroxides such as hydrogen peroxide, H_2O_2, the oxygen atoms are in the center (H–O–O–H).
7. In drawing Lewis structures for relatively small molecules and polyatomic ions, the structures tend to be more stable when they are compact and symmetrical rather than extended chains of atoms.

Calculation of number of bonds in covalent molecules

EXAMPLE: Write the Lewis structure for CH_2O where carbon is the central atom.

Step 1: Determine the total number of **Electrons available**(A) for bonding. Because only valence electrons are assumed to be involved in bonding we need to determine the total number of valence electrons.

Total number of valence electrons:

Electrons available

CH_2O	C	Group 4	4
	2 H	Group 1	2(1) = 2
O		Group 6	6
			12

There are 12 electrons available for bonding.

Step 2: Determine the number of **Electrons needed** by each atom.

Electrons needed

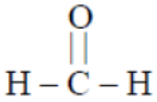
C	needs	8	8
2 H	each H needs 2		2(2) = 4
O	needs 8		8
			20

More electrons are needed then there are available. Atoms therefore make bonds by sharing electrons. Two electrons are shared per bond.

# of bonds = (# of electrons needed - # of electrons available) / 2 = (20 – 12) / 2 = 4 bonds.

Draw 4 bonds between the atoms. Carbon is indicated to be the central atom. This means all the other atoms are bound to carbon. To fill its valence shell, carbon can make 4 bonds, each of the hydrogen atoms can make one bond and oxygen can make two bonds. Remember that carbon, oxygen and nitrogen can form multiple bonds (double and triple bonds).

Step 3: Use remaining electrons to fill valence shell for each atom. All atoms need 8 electrons to fill their valence shell(**octet rule**), except hydrogen needs only 2 electrons to fill its valence shell. For CH_2O there are 4 bonds, and 2 electrons per bond.

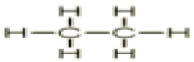
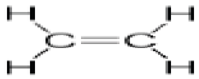


$H-\overset{\overset{O}{||}}{C}-H$

Both the carbon and oxygen atoms have 8 electrons; each hydrogen atom has 2 electrons.

Most atoms in the second period obey the **octet rule** except for boron and beryllium; these can be electron deficient in compounds. Why can atoms in the third row expand their octet? For example, sulfur, the central atom in SF_6, has 12 electrons around it, exceeding the octet rule.

Other examples

C_2H_6	C_2H_4	C_2H_2
Needed:	**Needed:**	**Needed:**
2C= 2(8) = 16	2C= 2(8) = 16	2C= 2(8) = 16
6H = 6(2) = 12	4H = 4(2) = 8	2H = 2(2) = 4
Total Needed = 28	**Total Needed = 24**	**Total Needed = 20**
Available:	**Available:**	**Available:**
2C = 2(4) = 8	2C = 2(4) = 8	2C = 2(4) = 8
6H = 6(1) = 6	4H = 4(1) = 4	2H = 2(1) = 2
Total Available = 14	**Total Available=12**	**Total Available=10**
Number of bonds:	Number of bonds:	Number of bonds:
Shared = N – A	Shared = N – A	Shared = N – A
Shared = 28 - 14 = 14	**Shared = 24 - 12 = 12**	**Shared = 20-10=10**
#bonds = shared/2	#bonds = shared/2	#bonds = shared/2
		

$COCl_2$

The number of needed and available electrons is :

Needed:

1C = 1(8) = 8

2Cl = 2(8) = 16

1O = 1(8) = 8

Total Needed = 32

Available:

1C = 1(4) = 4

2Cl = 2(7) = 14

1O = 1(6) = 6

Total Available = 24

Number of bonds:

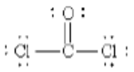
Shared = N – A

Shared = 32 - 24 = 8

#bonds = shared/2

#bonds = 4 bonds

electrons remaining = # electrons available – # electrons used in bonds = 24 – 4(2) = 16



NO$_3$

-

For structures with a charge (like -1 in this case), you add or subtract extra electrons to or from the available pool. For negative charges, we add electrons.

For positive charges, we subtract electrons.

Needed:

1N= 1(8) = 8

3O = 3(8) = 24

Total Needed = 32

Available:

1N= 1(5) = 5

3O = 3(6) = 18

-1 charge = 1(1) = 1

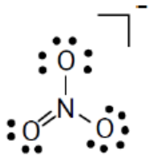
Total Available = 24

# of bonds: N – A/2

= 32 - 24 = 8/2

#bonds = 4 bonds

electrons remaining = # electrons available – # electrons used in bonds = 24 – 4(2) =16



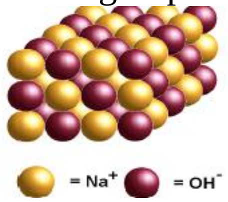
Exceptions to the Octet Rule

The Lewis structures rules do not always work! Attempt the next compounds and give a reason for why the steps broke down for each example.

NaOH

Reason:

Although the Lewis structure guidelines would be helpful for the -OH group, NaOH is Ionic and we would represent it as a lattice structure rather than a line drawing (Na does not share any electrons with the OH group and vice-versa).



$RnCl_2$

Reason:

Expanded Valence. Too many available electrons. electrons.

$BeCl_2$

Reason:

Incomplete Valence Too few available Beryllium only needs 4 electrons.

$RnCl_2$

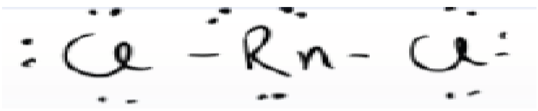
Needed:
2Cl = 2(8) = 16
1Rn = 1(10) = 10
Total Needed = 26

Available:
2Cl = 2(7) = 14
1Rn = 1(8) = 8
Total Available = 22
Number of bonds:
Shared = N – A
Shared = 26 - 22 = 4
#bonds = shared/2
#bonds = 2 bond??

$BeCl_2$

Needed:
2Cl = 2(8) = 16
1Be = 1(4) = 4
Total Needed = 20

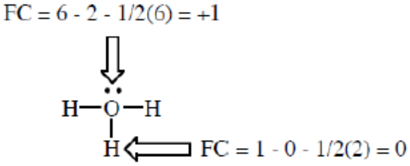
Available:
2Cl = 2(7) = 14
1Be = 1(2) = 2
Total Available=16
Number of bonds:
Shared = N – A
Shared = 20-16 = 4
#bonds = shared/2
#bonds = 2!



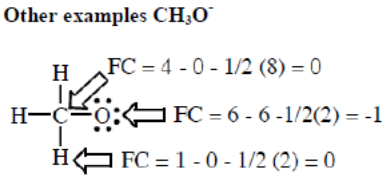
Assigning Formal Charge on Atoms In Compounds

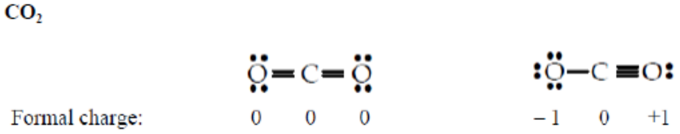
Formal charge is calculated using this formula:
FC = GN - UE - 1/2 BE

Where:
FC = formal charge
GN = periodic table group number (number of valence electrons in free, nonbonded atom)
UE = number of unshared electrons
BE = number of electrons shared in covalent bonds.
Thus for hydronium ion:



The formal charge on hydrogen is calculated as follows. Hydrogen has one valence electron (GN = 1), no unshared electrons (UE = 0) and two shared electrons in the oxygen-hydrogen covalent bond (BE = 2). Thus the calculated formal charge on hydrogen is zero. Because each hydrogen atom in this molecule is identical, each hydrogen atom has the same formal charge of zero. *Any hydrogen bearing one covalent bond always has a formal charge of zero.*
The formal charge on oxygen is calculated as follows. Oxygen has six valence electrons (GN = 6), two unshared electrons in one lone pair (UE = 2), and six shared electrons in three oxygen-hydrogen covalent bonds (BE = 6). Thus the calculated formal charge on oxygen is +1. This indicates the oxygen atom bears the majority of the positive charge of this ion.





In the left hand structure of CO_2 all the formal charges are zero and this structure is favored over the right hand structure.
Note that the formal charges on the atoms must add up to zero for molecules that are Neutral

For ionic compounds, the formal charges on the atoms must add up to the charge on the ion. For example, for NO_3^-, the formal charge on the nitrogen and oxygen atoms must add up to –1. Draw the Lewis structures and the resonance structures for NO_3^-.
The negative charge generally resides on the more electronegative atom.
Also note that fluorine is the most electronegative element in the periodic table.

Fluorine wants an electron to complete its octet and shares one electron in single bonds in covalent compounds. Fluorine generally does not make double bonds.
Fluorine is not willing to share more than one electron and with a double bond the formal charge on fluorine would be +1. A+1 formal charge on the most electronegative atom is generally not observed.

Resonance Structures

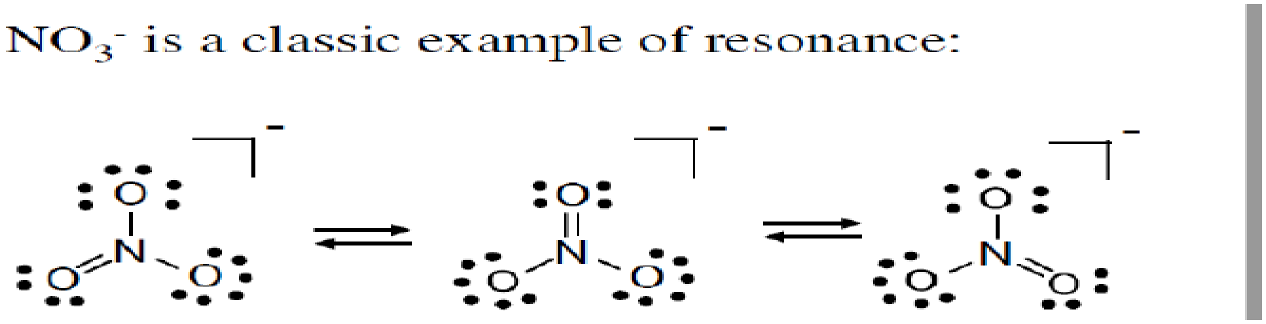
- We have assumed up to this point that there is only one correct Lewis structure.
- But, there are systems for which more than one Lewis structure is possible:

Different atomic linkages: **Structural Isomers**
Same atomic linkages, different bonding: **Resonance**

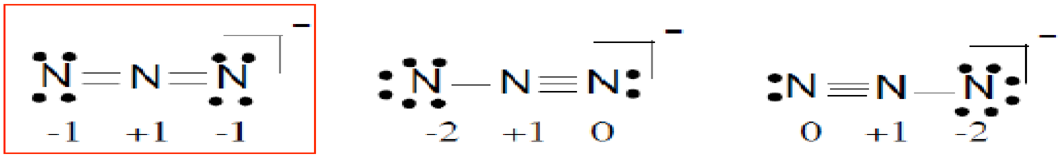
Meaning of resonance structures

- Resonance structures are needed because Lewis dot representation is too simplified
- Needed when the molecular orbitals (wavefunctions) of the bonding electrons extend across more than two atoms.

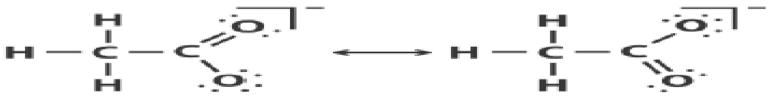
Important:
The molecule does not go back and forth between the resonance structures.


NO_3^- is a classic example of resonance:

N_3^-



Another example $CH_3CO_2^-$



Acetate ion, $CH_3CO_2^-$

Valence bond theory(VBT)

The valence-bond concept builds on the Lewis proposal that bonding results from electron pairing between neighboring atoms. The Lewis approach was put into a quantum mechanical context and then the results (the valence-bond concept) were refined by **Linus Pauling**. The concept is used much less now than it used to be but is still employed by some chemists. The valence-bond method can also be applied to the bonding in transition metal compounds.

The principles of the valence-bond method can be summarized in a series of statements:

1. A covalent bond results from the pairing of unpaired electrons in neighboring atoms.

2. The spins of the paired electrons must be antiparallel (one up and one down).

3. To provide enough unpaired electrons in each atom for the maximum bond formation, electrons can be excited to fill empty orbitals during bond formation.

4. The shape of the molecule results from the directions in which the orbitals of the central atom point.

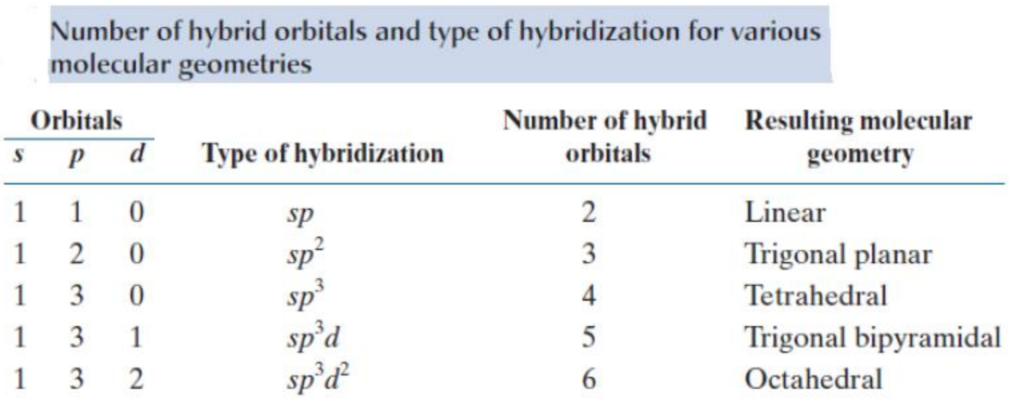
Orbital Hybridization

The orbital hybridization concept asserts that the wave functions of electrons in atomic orbitals of an atom (usually the central atom of a molecule) can mix together during bond formation to occupy hybrid atomic orbitals. According to this approach, electrons in these hybrid orbitals are still the property of the donor atom. If the wave functions of an *s* orbital and one or more *p* orbitals are combinedSuch hybrid orbitals are given the symbols *sp*, sp^2, and sp^3 depending on whether the wave functions of one, two, or three *p* orbitals are ―mixed in‖ with the *s* orbital wave function. These hybrid orbitals are oriented in a particular direction and should overlap more with the orbitals of another atom than do those of a spherical *s* orbital or of a two-lobed *p* orbital.

A greater overlap means that the wave functions of the two atoms will mix better and form a stronger covalent bond. The number of hybrid orbitals formed will equal the sum of the number of atomic orbitals that are involved in the mixing of wave functions. Like *s* and *p* orbitals, *d* orbitals can also be mixed in, although theoretical chemists now contend that *d* orbitals play a minimal role in covalent bonding. Nevertheless, for our simplistic bonding approach, it is often useful to propose *d* orbital involvement to account for the shapes of molecules where the central atom has more than four neighbors. The number of atomic orbitals used, the symbol for the hybrid orbital, and the geometry of the resulting molecule are all listed in Table below.

أمثلة	الشكل الهندسي	عدد المزدوجات الألكترونية الاتأصرية	عدد المزدوجات الألكترونية التأصرية	نوع التهجين	
$BeCl_2$	Linear	0	2	SP	2
BCl_3	Trigonal planer	0	3	SP^2	3
CH_4	Tetrahedral	0	4	SP^2	3
NH_3	Trigonal pyramidal	1	3	SP^3	4
H_2O	Bent - V - shaped	2	2	SP^3	4
$SnCl_2$	Bent - V - shaped	1	2	SP^3	4
HF	Linear	3	1	SP^3	4
PCl_5	Trigonal bi pyramidal	0	5	SP^3d	5
$TeCl_4$	Tetrahedral distorted	1	4	SP^3d	5

5	SP^3d	3	2	T - Shaped	ClF_3
5	SP^3d	2	3	Linear	XeF_2
6	SP^3d^2	6	0	Octahedral	SF_6
6	SP^3d^2	5	1	Square based pyramid هرم مربع القاعدة	IF_5, BrF_5
6	SP^3d^2	4	2	Square planer	XeF_4
7	SP^3d^3	7	0	Pentagonal bi pyramidal	IF_7



Number of hybrid orbitals and type of hybridization for various molecular geometries

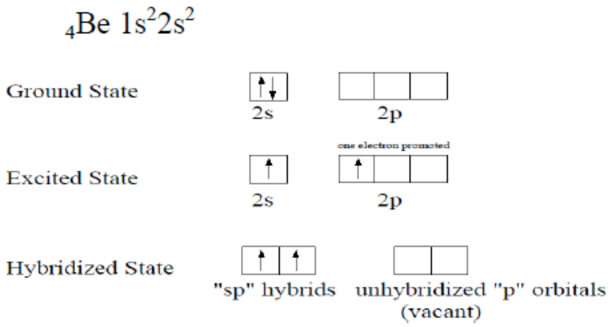
Orbitals			Type of hybridization	Number of hybrid orbitals	Resulting molecular geometry
s	*p*	*d*			
1	1	0	sp	2	Linear
1	2	0	sp^2	3	Trigonal planar
1	3	0	sp^3	4	Tetrahedral
1	3	1	sp^3d	5	Trigonal bipyramidal
1	3	2	sp^3d^2	6	Octahedral

sp hybridization (2 hybrid orbitals)

Looking at the orbital diagram for the valence shell of Beryllium in $BeCl_2$, it shows a pair of electrons in the 2s subshell. However, in order for Be to form two covalent bonds (see Lewis Structure, below), it clearly must have two **single** electrons in each of two orbitals. We theorize then, that an electron is "promoted" just prior to bonding into the 2p subshell.

Although this "promotion" does explain how Beryllium could form two bonds, it doesn't explain why the bonds appear to be identical when examined. Since the bonds were seemingly constructed using an "s" orbital and a "p" orbital, they should be different...yet they are not. The theory of "hybridization" implies that the two orbitals involved actually "melt" into two equivalent "hybrid" orbitals of identical shape and size. These "hybrid" orbitals are responsible for the two sigma bonds in $BeCl_2$ and are referred to as the "sp" hybrids.

The orbital diagrams below show the **"ground state"** before bonding, the **"excited state"** where the 2s electron has been promoted to the 2p, and the **"hybridized state"** where the two single electrons now reside in equivalent orbitals. Note that any leftover "p" orbitals are referred to as "unhybridized orbitals". These unhybridized orbitals are used to form any double or triple (Pi) bonds in a molecule and ***since this structure shows no multiple bonding, these unhybridized orbitals are vacant.*** It should be noted that the "sp" hybrid orbitals will arrange themselves in a **linear geometry**.



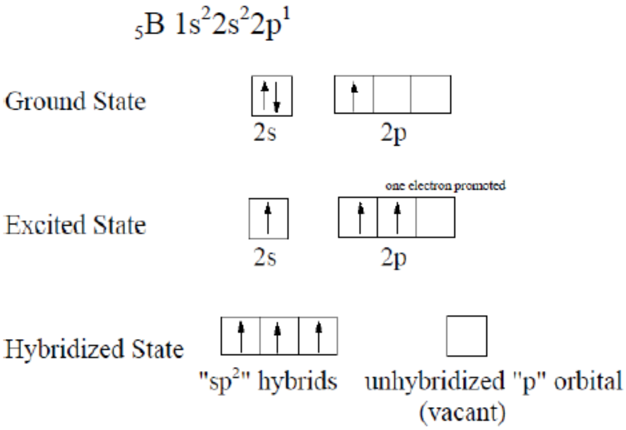
liner Geometry

sp_2 Hybridization (3 hybrid orbitals)

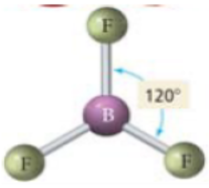
Looking at the orbital diagram for Boron in BF_3, we see three valence electrons....two in the 2s subshell and one in the 2p. But again, in order for Boron to form three covalent bonds as seen in its Lewis Structure, it must provide three **single** electrons in three separate orbitals. The promotion of an electron to the 2p subshell just prior to bonding is represented below as the "excited" state of the Boron as it begins to bond.

Since examination of the sigma bonds in BF_3 reveals that they too are identical, it is assumed that hybridization of the s orbital and two of the p orbitals occurs providing three hybrids of identical shape, size and energy.

It should be noted that these three sp_2 hybrids would arrange themselves as far apart as possible forming a **trigonal planar electron arrangement.**



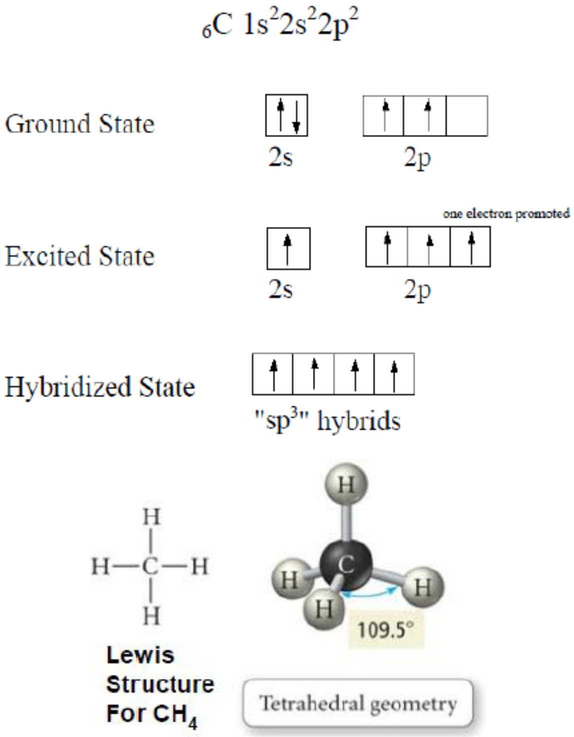
trigonal planner geometry



sp_3 hybridization (4 hybrid orbitals)

In the case of methane CH_4, the ground state of carbon reveals a pair of electrons in the 2s and two single electrons in the 2p. This is not consistent with the need for four single electrons required to form the four bonds with the hydrogens, so again, electrons

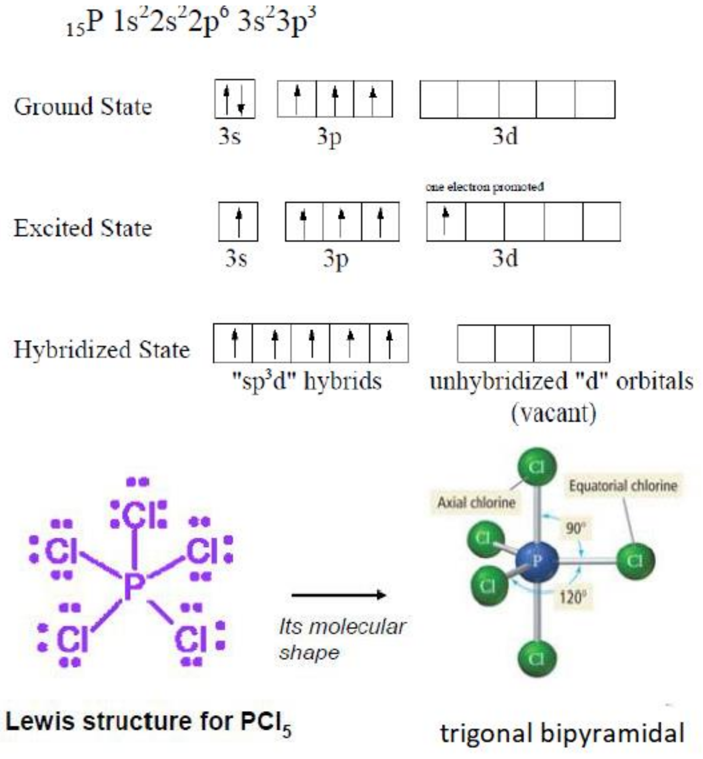
are promoted into the p subshell just prior to bonding.
These four atomic orbitals (the s orbital and all three p orbitals) apparently hybridize into four equivalent molecular orbitals referred to as the sp^3 hybrids. These four orbitals arrange themselves in a **tetrahedral geometry** in order to minimize repulsion effects.



Expanded Octets sp^3d hybridization (5 hybrid orbitals)

In order to have an expanded octet, the central atom of the molecule must have at least three shells of electrons in order to accommodate more than eight electrons in its valence shell. It isn't until we reach the third main shell that the "d" sublevel exists to provide enough orbitals for an expanded octet.
For example, PCl_5, has a ground state showing two electrons in the 3s sublevel and three single electrons in the 3p sublevel. Note that there is a vacant 3d sublevel available for the promotion of electrons. The promotion of electrons that occurs just

prior to bonding in PCl_5 provides five single electrons for the five P-Cl bonds, but requires the use of one of the "d" orbitals to do so.
Once the electrons are promoted, hybridization of the s orbital, three p orbitals and one d orbital into five equivalent molecular orbitals gives us the sp^3d hybrids responsible for the bonding in PCl_5. These five hybrid orbitals will adopt a **trigonal bipyramidal geometry** in order to get as far from each other as possible.



Phosphorus must provide five hybrid orbitals to form the five sigma bonds seen in its Lewis Structure. This requires the use of one of its "d" orbitals.

sp^3d^2 hybridization (6 hybrid orbitals)

An examination of the ground state of sulfur in SF_6 reveals a pair of electrons in the 3s, a pair and two single electrons in the 3p and a vacant 3d sublevel. It is presumed that just prior to bonding, promotion of the electrons occurs in such a way as to provide the six single electrons necessary to provide the six bonding sites for the fluorines. So, the "Excited" state shows that the electrons promoted will reside in the first two available "d" orbitals.

These six occupied atomic orbitals apparently hybridize into six equivalent molecular orbitals known as the sp^3d^2 hybrids. These six hybrid orbitals will arrange themselves in an **octahedral geometry**