

Inorganic pharmaceutical chemistry.

Reference:

Inorganic Medical and pharmaceutical Chemistry –
by Block Roche, Soine and Wilson.

Dr. Ishaq A. Raheem

Atomic and Molecular Structure/ Complexation

* Atomic structure:-

-Subatomic Particles:-

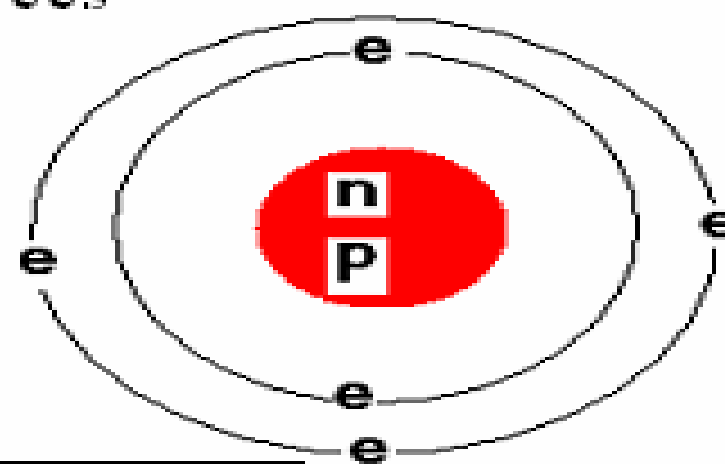
Atoms are composed of a central "nucleus" surrounded by "electrons" which occupy discrete regions of space.

The nucleus is considered to contain 2 types of stable particles which comprise most of the mass of the atom. These particles are held

within the nucleus by various "nuclear forces"

$$\text{nucleus} = \{p + n\}$$

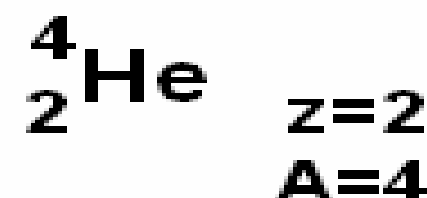
these particles include :-



particles	Charge	Mass
Neutrons (n)	(0)	1.675×10^{-24} g or 1.009 a.m.u.
Proton (p)	(+ve)	===
Electrons (e)	(--ve)	9.107×10^{-28} g or 0.0006 a.m.u. or = 1/1840 of (p)

* **The atomic number** (Z) = # of p(s) = # of e (s)

* **The Atomic Mass** (A) [Mass number] = $m_p + m_n$



* in a neutral atom the : # of p(s)(+) = # of e(s)(-)

[If not ,the atom has an overall charge and is then called an ion e.g. Na^+ (11 p,10 e) or Cl^- (17 p,18 e)]

Isotopes:- The number of neutrons in an atom can vary within small limits. For example, there are three kinds of carbon atom ^{12}C , ^{13}C and ^{14}C . They all have the same number of protons, but the number of neutrons varies.

	protons	neutrons	mass number
carbon-12	6	6	12
carbon-13	6	7	13
carbon-14	6	8	14

These different atoms of carbon are called isotopes. Isotopes are atoms which have the same atomic number but different mass numbers. They have the same number of protons but different numbers of neutrons .

Isotopic forms of a particular element differ in the number of neutrons, and, therefore, in the atomic mass, e.g.

${}^1_1\text{H}$, ${}^2_1\text{H}$ and ${}^3_1\text{H}$ are the three isotopes of hydrogen with mass numbers of 1, 2 and 3, with 0, 1 and 2 neutrons respectively, but all have 1 proton. Hydrogen-1 is the most common, there is a trace of hydrogen-2 naturally but hydrogen-3 is very unstable and is used in atomic fusion weapons.

${}^3_2\text{He}$ and ${}^4_2\text{He}$ are the two isotopes of helium with mass numbers of 3 and 4, with 1 and 2 neutrons respectively but both have 2 protons. Helium-3 is formed in

the sun by the initial nuclear fusion process. Helium-4 is also formed in the sun and as a product of radioactive alpha decay of an unstable nucleus.

Atomic Orbitals:

The early quantitative description of electronic structure came from Niels Bohr in 1913, and involved a planetary picture of the atom. Electrons were considered as particles which revolved around the nucleus in the stationary planar orbits and which had definite energies. Bohr's model involved the use of classical Newtonian mechanics, and suitably predicted the electronic spectrum of hydrogen. However, atoms with more than one electron did not yield satisfactory results.

- Bohr's theory only works for hydrogen atoms.
- Once you have more than one electron, the calculations for the electron energy and the orbit radii breakdown.
- Therefore, a new theory needed to be developed for multi-electron elements.
- Bohr's theory did make two important contributions:
 - It suggested reasonable explanation for the discrete line spectrum of the elements.
 - It introduced the idea of quantized electron energy levels (orbits)

Quantum Numbers :

The relation of a particular electron to the nucleus can be described through a series of four numbers, called the Quantum Numbers. The first three of these numbers describe the energy (Principle quantum number), shape (Angular momentum quantum number), and orientation of the orbital (magnetic quantum number). The fourth number represents the "spin" of the electron (spin quantum number).

Quantum Numbers

- The wave function contains **four** variables known as the **Quantum Numbers** which describe the size, energy, shape and position of the orbitals.
- These numbers serve as an “address” of the probable location of the electron.

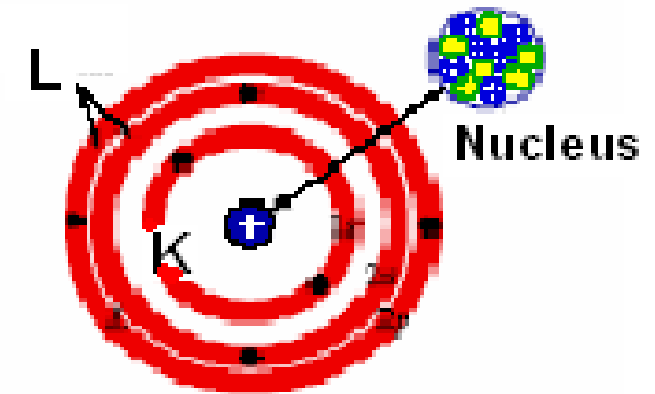
The Principle Quantum Number (n):

- provides info about the distance of the e from the nucleus.
- also called shell.
- As n increases, the orbital becomes larger & the e⁻ spends more time further from the nucleus and the energy is less negative (increase Energy)
- n is related the size and energy of the orbital.

Integral Values: : n = 1, 2, 3, 4 never 0

K, L, M, N

n	shell
1	K
2	L
3	M
4	N



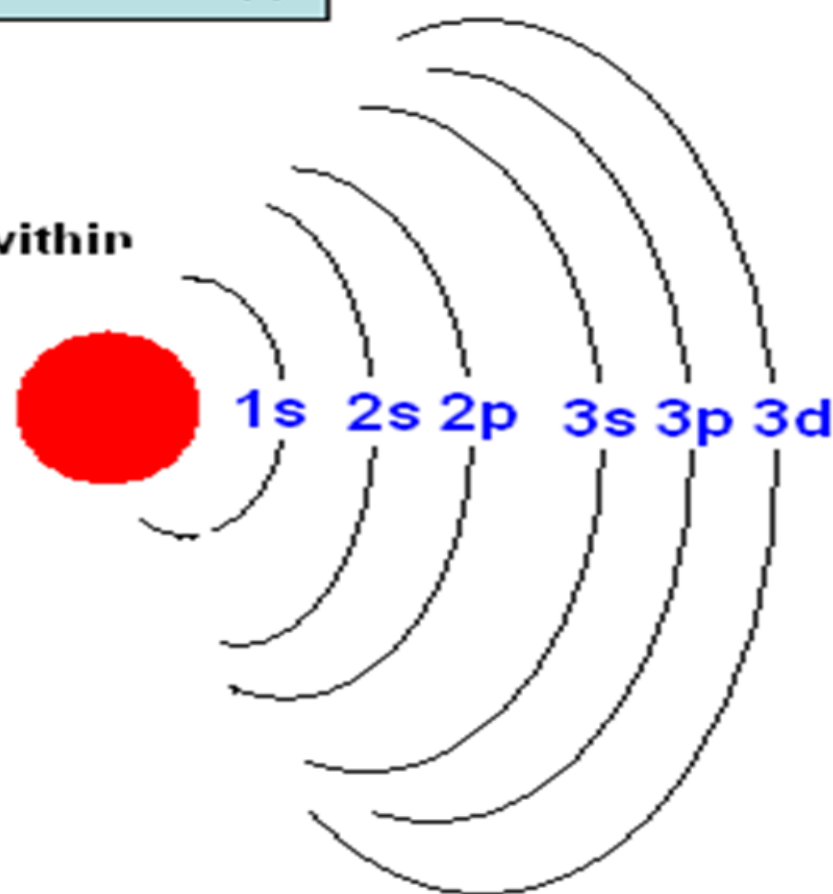
Angular-Momentum Quantum Number (l)

- sublevel (**l**)

- The angular momentum quantum no. (l) defines the 3D shape of the orbitals found within a particular shell.

Integral Values: $l = 0, 1, 2, 3, \dots, n-1$

Value of l	Letter used
0	s
1	p
2	d
3	f



The # of sublevels within a shell is equal to the principal quantum #.

Magnetic Quantum Number (m_l)

- The Magnetic Quantum Number (m_l) describes the orientation in 3D space of the sublevel, thereby denoting a specific orbital. **or**

[The value of (m_l) relates to the orientation of the orbital in space relative to the other orbitals in the atom]

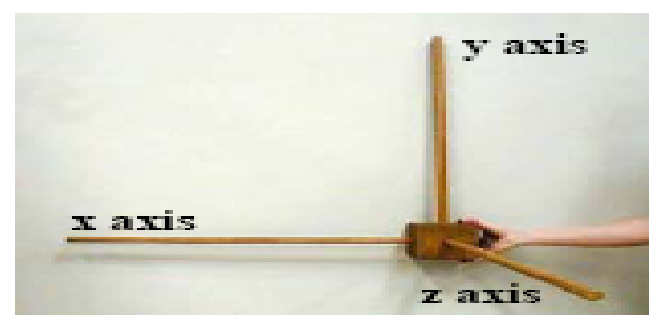
- The number of orientations (and therefore orbitals) per sublevel is determined by the equation:

$$m_l = 2l + 1$$

Integral Values: $m_l = -l, \dots, +l$

l	0 (s)	1 (p)	2 (d)	3 (f)
$2l + 1$				

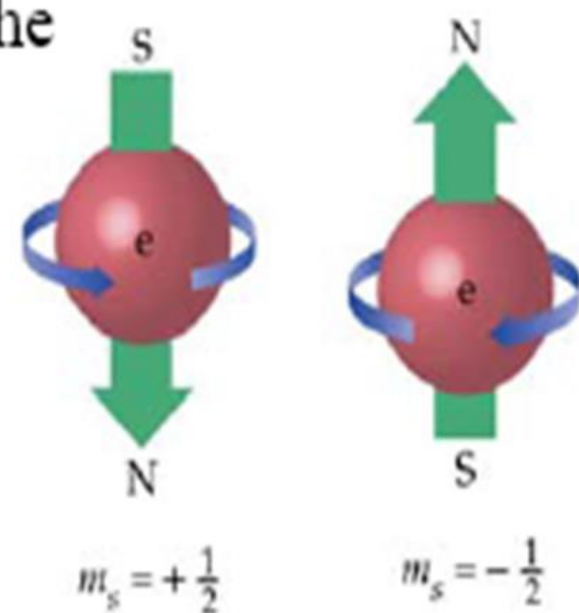
s	p			d					
<input type="text"/>	<input type="text"/>	<input type="text"/>	<input type="text"/>	<input type="text"/>	<input type="text"/>	<input type="text"/>	<input type="text"/>	<input type="text"/>	<input type="text"/>
0	-1	0	+1	-2	-1	0	+1	+2	



Spin Quantum Number (m_s)

- The *Pauli Exclusion Principle* states that no two electrons can have the same four quantum numbers
 - only two electron per orbital and they must have opposite spins

$$m_s = \pm \frac{1}{2}$$



n	l	ml	orbital	shell
1	0	0	1s	K
2	0	0	2s	L
	1	+1, 0, -1	2p	
3	0	0	3s	M
	1	+1, 0, -1	3p	
	2	+2, +1, 0, -1, -2	3d	
4	0	0	4s	N
	1	+1, 0, -1	4p	
	2	+2, +1, 0, -1, -2	4d	
	3	+3, +2, +1, 0, -1, -2, -3	4f	

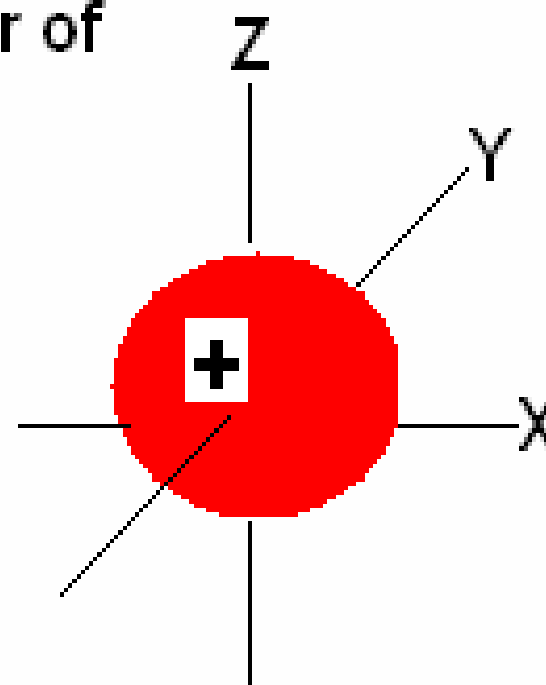
Shapes of the Orbitals

- * Each orbital has a specific shape determined by its angular momentum # (l)
- * As you increase n principle quantum # (n), n orbitals increase in size but not shape.

$l = 0$: The s Orbitals

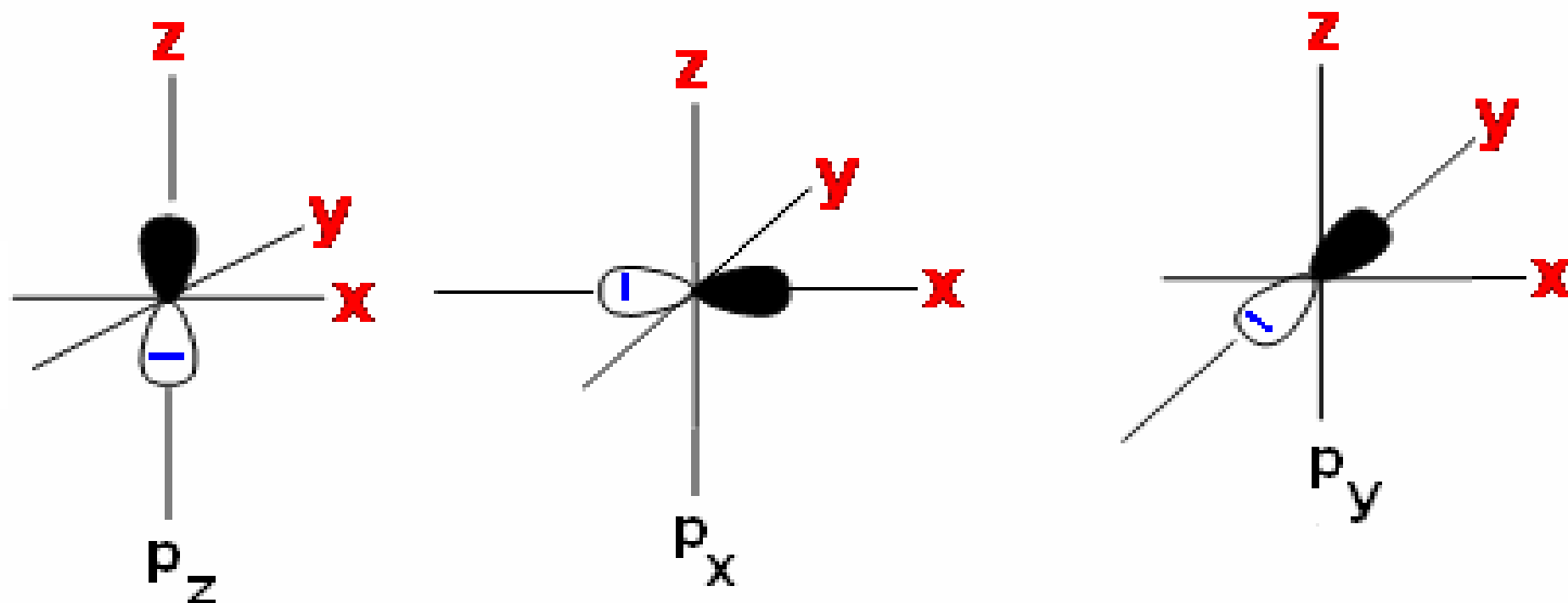
- The s orbitals are spherical, meaning the probability of finding the e^- only on distance from the nucleus, not direction.

(spherical w/ n nucleus at the center of n sphere)



$l = 1$: The p Orbitals

- The p orbitals are dumbbell shaped with their electron density concentrated in identical lobes residing on opposite sides of a nodal plane.
- This shape means that a p electron will never be found near the nucleus.
- The two lobes of a p orbital have different phases (are opposite in sign) which becomes important in bonding among atoms.
- The three orientations ($m_l = -1, 0, +1$) are 90° differentials along the x, y and z axes.
- The orbitals are designated p_x (along the x axis), p_y (along the y axis), and p_z (along the z axis)

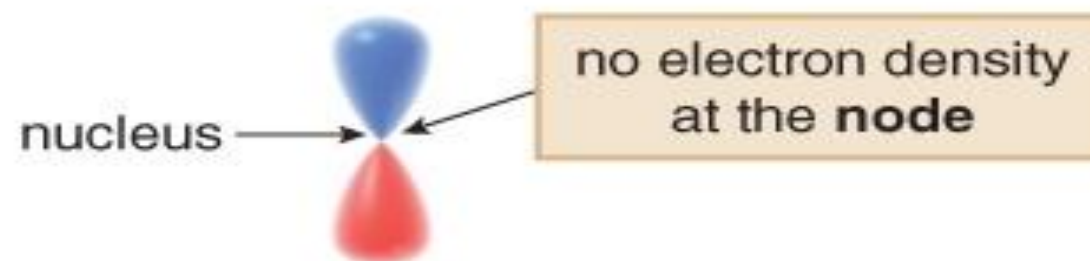


s orbital

p orbital



lower in energy



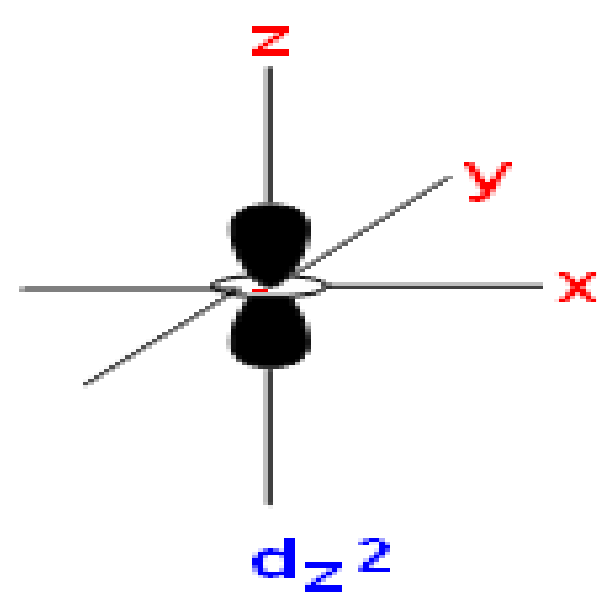
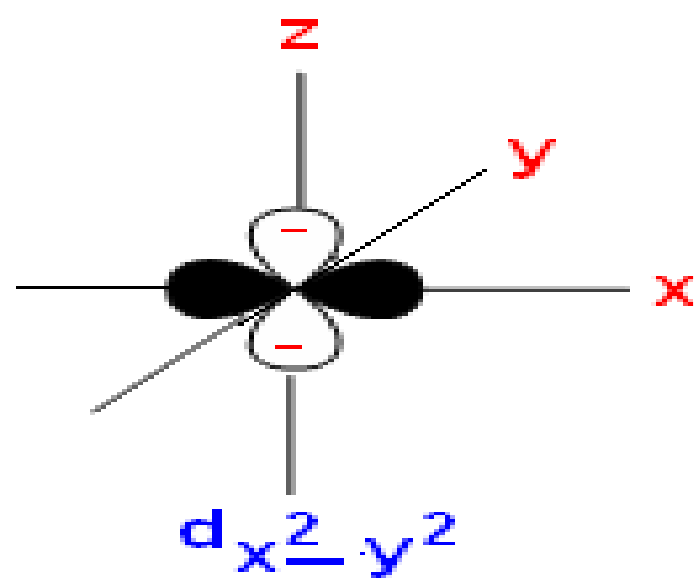
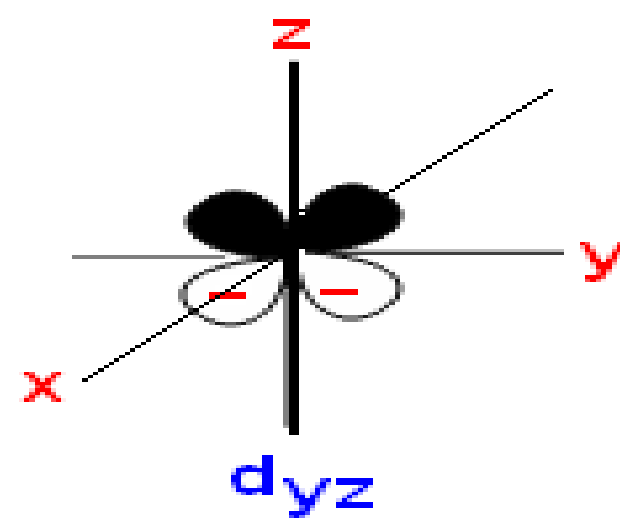
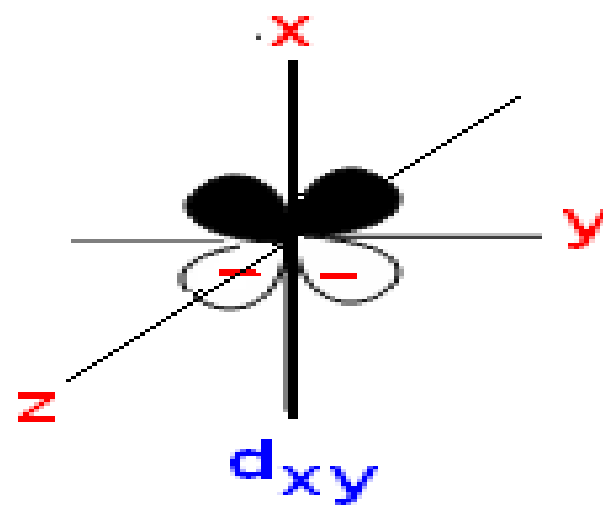
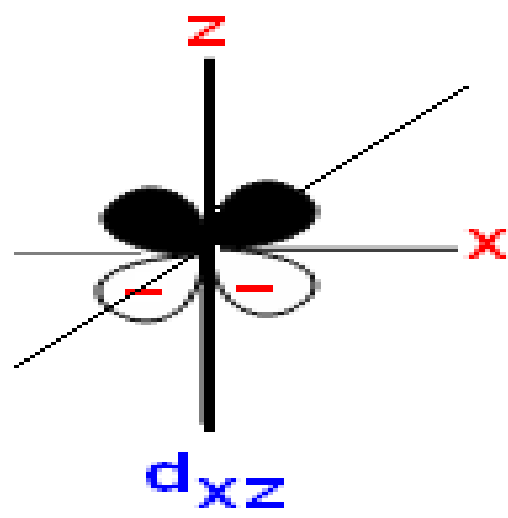
higher in energy

$l = 2$: The d Orbitals

d_{xy} d_{yz} d_{xz} $d_{x^2-y^2}$ d_{z^2}

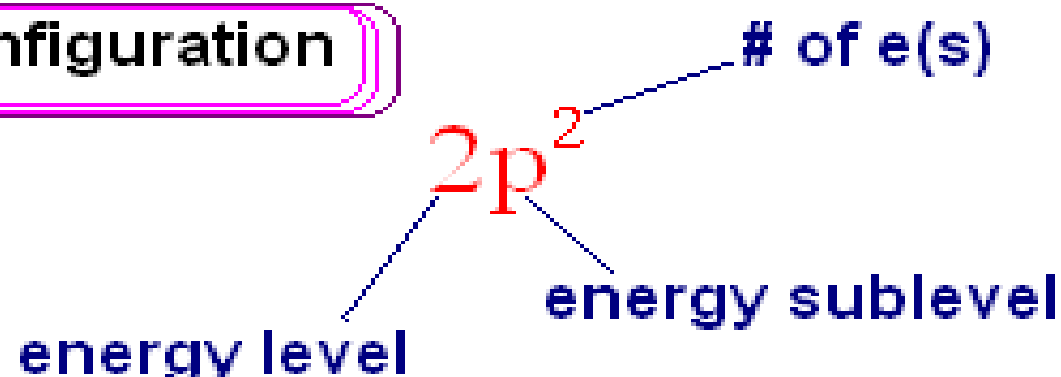


+2 +1 0 -1 -2



Electron Configurations

* structure of an atom = **Electron Configuration**
(buildup)



- Many of an element's chemical properties depend on its electron configuration
- The electron configuration of an atom is a method of writing the location of electrons by sublevel.
- The principal quantum level (n) is written first, followed by the letter designation of the sublevel (l) then a superscript with the number of electrons in the sublevel.
- There are rules for the order and manner that each sublevel is filled called the Aufbau Principle.

Aufbau Principle

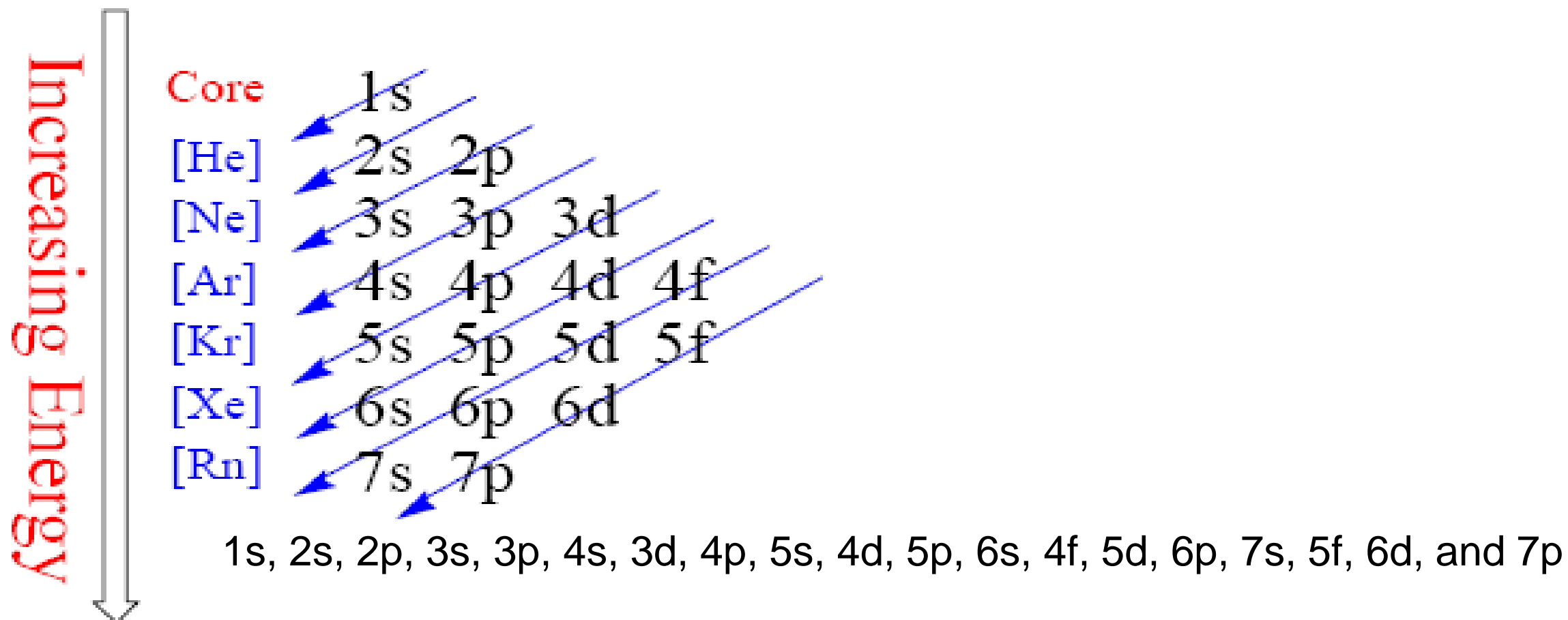
Pauli Exclusion Principle: No two electrons in an atom can have the same quantum numbers (n, l, m_l, m_s).

Hund's Rule: When filling orbitals in the same sublevel, maximize the number of parallel spins (so fill then pair!).

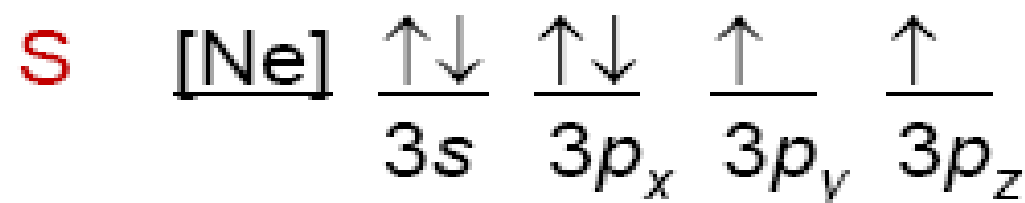
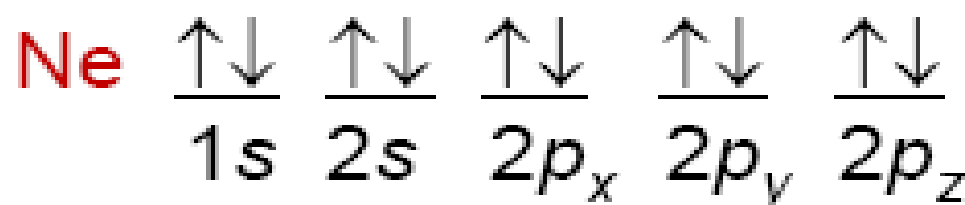
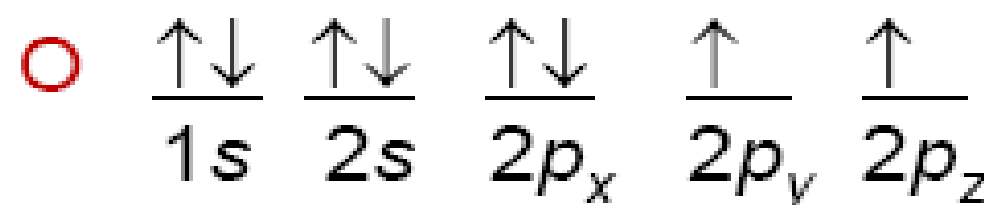
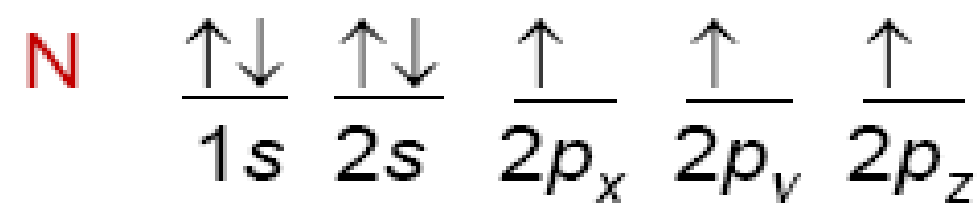
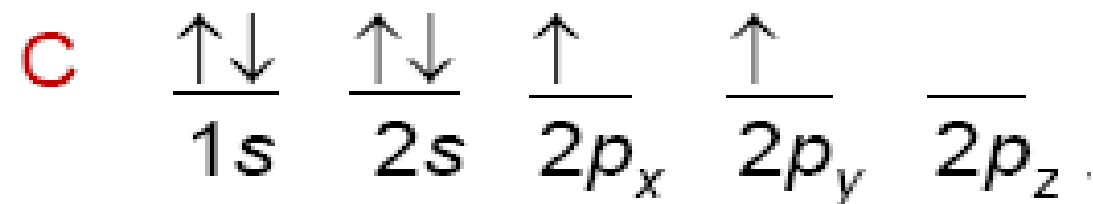
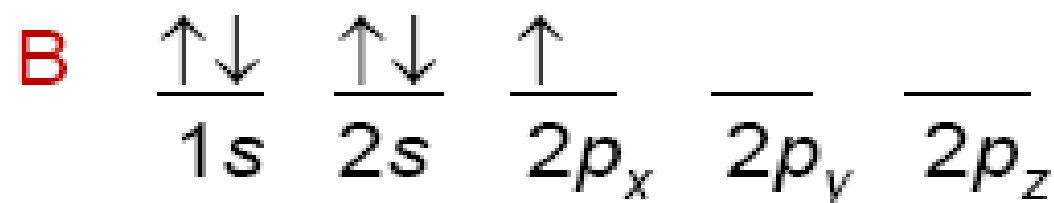
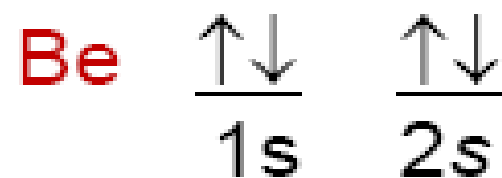
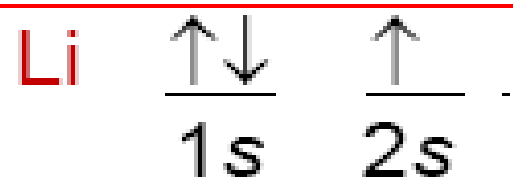
Rules of Aufbau Principle:

1. Lower n orbitals fill first. **(lower energy orbital then higher)**
2. Each orbital holds two electrons; each with different m_s .
3. Half-fill degenerate orbitals before pairing electrons. [\bar{w} orbitals have \wedge same energy i.e. $2p_x, 2p_y, 2p_z$, singly & \bar{w} parallel spins]

A schematic representation of the order in which orbitals are filled is shown:

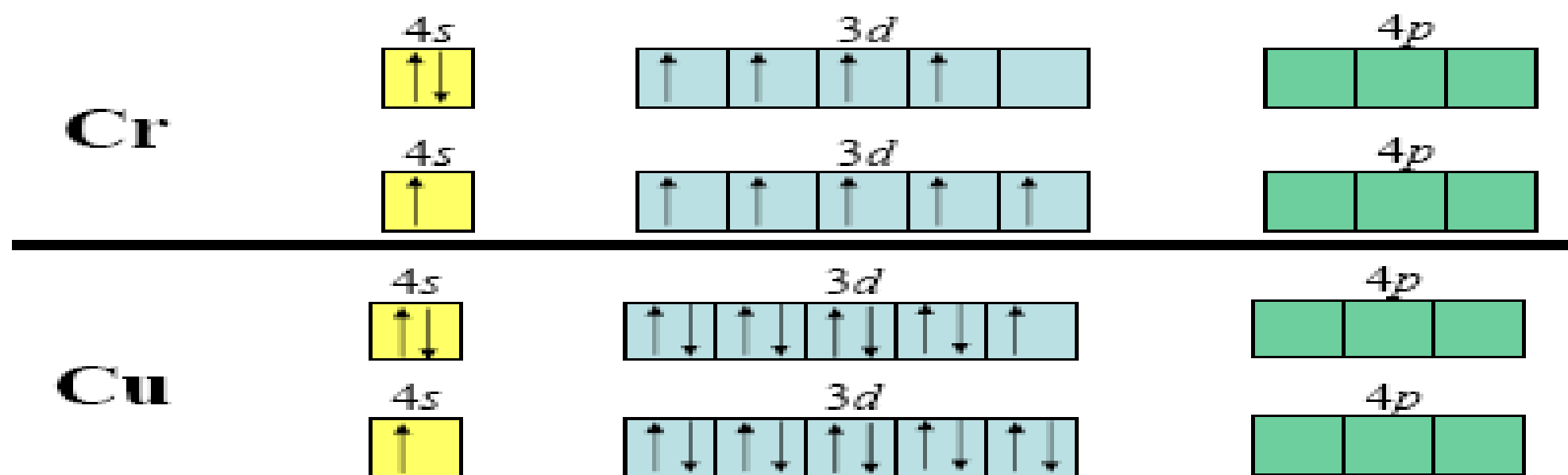


Writing Electron Configurations



Exceptions to the Filling Order

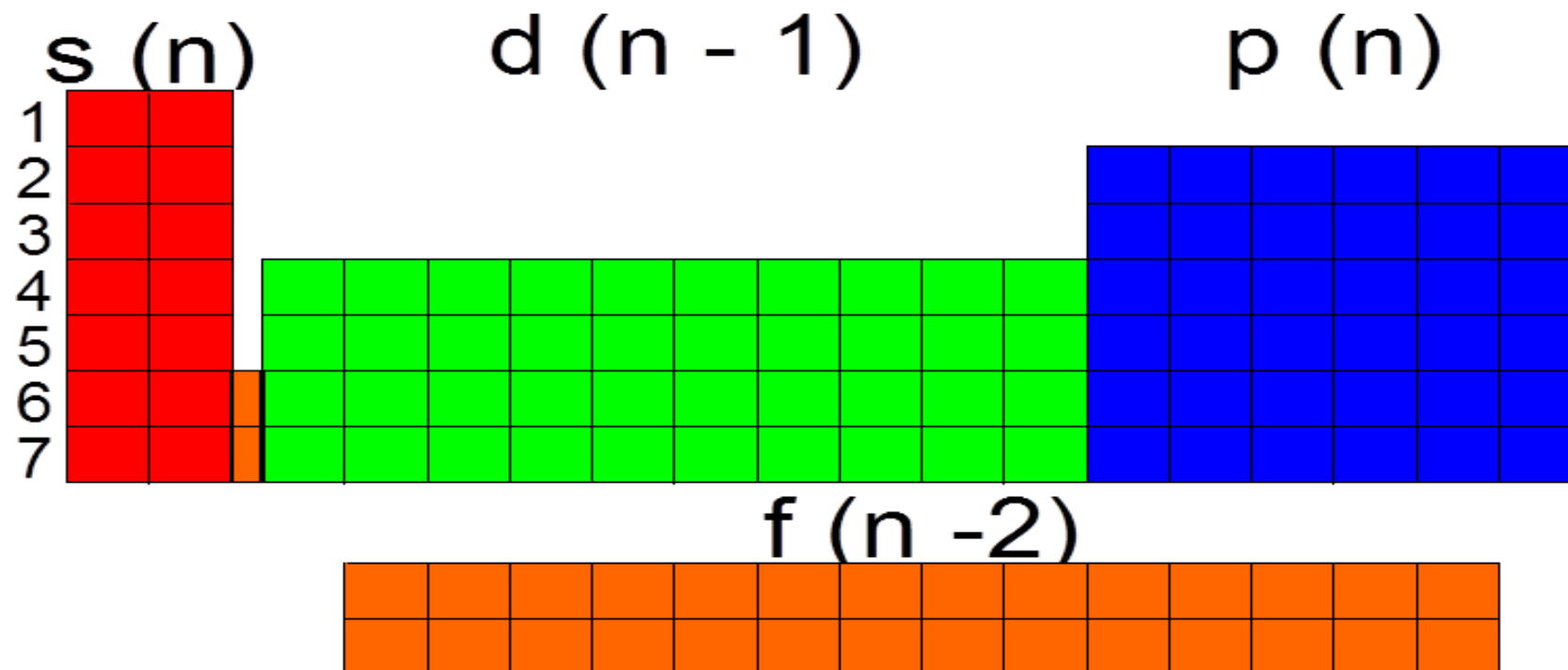
- When filling the d sublevel, exceptions occur for the chromium (Cr) and copper (Cu) families:



Sample Exercise :

- Why can't an electron have the following quantum numbers:
 - (a) $n = 2, l = 2, m_l = 1$
 - (b) $n = 3, l = 0, m_l = 3$
 - (c) $n = 5, l = -2, m_l = 1$
- Give orbital notations for electrons with the following quantum numbers:
 - (a) $n = 2, l = 1, m_l = 1$
 - (b) $n = 4, l = 3, m_l = -2$
 - (c) $n = 3, l = 2, m_l = -1$
- Give the electron configurations for sulfur(S)($Z=16$), cadmium(Cd) ($Z=48$) and radium(Ra)($Z=88$)

Periodic table arrangement



the quantum theory helps to explain the structure of the periodic table.
 $n - 1$ indicates that the d subshell in period 4 actually starts at 3 ($4 - 1 = 3$).

Ionization: process of losing one or more e(s) by chemical or physical means.



Positive ion (cation)

is distinctly different from Aufbau in that is based in physical reality.

Periodic Law:

Periodic table was suggested by Russian chemist Mandeleeff and German chemist Lothar Meyer.

They recorded data depend on periodic relationship based on A.w. of elements.

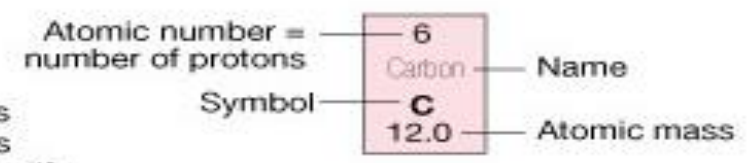
But today it know that properties of elements r based on outer or valence shell electronic str.

*There are 8 grp. Corresponding to fill s & p orbitals.
having $n = \#$ of period

Periodic Table of the Elements

Group	Periodic Table of the Elements																VIII A	
Period	IA	IIA	Transitional metals										IIIA	IVA	VA	VIA	VIIA	VIIIA
1	1 Hydrogen H 1.0																	2 Helium He 4.0
2	3 Lithium Li 6.9	4 Beryllium Be 9.0											5 Boron B 10.8	6 Carbon C 12.0	7 Nitrogen N 14.0	8 Oxygen O 16.0	9 Fluorine F 19.0	10 Neon Ne 20.2
3	11 Sodium Na 23.0	12 Magnesium Mg 24.3											13 Aluminum Al 27.0	14 Silicon Si 28.1	15 Phosphorus P 31.0	16 Sulfur S 32.1	17 Chlorine Cl 35.5	18 Argon Ar 39.9
4	19 Potassium K 39.1	20 Calcium Ca 40.1	21 Scandium Sc 45.0	22 Titanium Ti 47.9	23 Vanadium V 50.9	24 Chromium Cr 52.0	25 Manganese Mn 54.9	26 Iron Fe 55.8	27 Cobalt Co 58.9	28 Nickel Ni 58.7	29 Copper Cu 63.5	30 Zinc Zn 65.4	31 Gallium Ga 69.7	32 Germanium Ge 72.6	33 Arsenic As 74.9	34 Selenium Se 79.0	35 Bromine Br 79.9	36 Krypton Kr 83.8
5	37 Rubidium Rb 85.5	38 Strontium Sr 87.6	39 Yttrium Y 88.9	40 Zirconium Zr 91.2	41 Niobium Nb 92.9	42 Molybdenum Mo 95.9	43 Technetium Tc (98)	44 Ruthenium Ru 101.1	45 Rhodium Rh 102.9	46 Palladium Pd 106.4	47 Silver Ag 107.9	48 Cadmium Cd 112.4	49 Indium In 114.8	50 Tin Sn 118.7	51 Antimony Sb 121.8	52 Tellurium Te 127.6	53 Iodine I 126.9	54 Xenon Xe 131.3
6	55 Cesium Cs 132.9	56 Barium Ba 137.3	57* Lanthanum La 138.9	72 Hafnium Hf 178.5	73 Tantalum Ta 181.0	74 Tungsten W 183.9	75 Rhenium Re 186.2	76 Osmium Os 190.2	77 Iridium Ir 192.2	78 Platinum Pt 195.1	79 Gold Au 197.0	80 Mercury Hg 200.6	81 Thallium Tl 204.4	82 Lead Pb 207.2	83 Bismuth Bi 209.0	84 Polonium Po (209)	85 Astatine At (210)	86 Radon Rn (222)
7	87 Francium Fr (223)	88 Radium Ra 226.0	89** Actinium Ac (227)	104 Rutherfordium Rf (261)	105 Dubnium Db (262)	106 Seaborgium Sg (266)	107 Bohrium Bh (264)	108 Hassium Hs (269)	109 Meitnerium Mt (268)	110 Ununnilium Uun (271)	111 Ununium Uuu (272)	112 Ununbium Uub (277)		114 Ununquadium Uuq (289)				

- Major essential elements
- Minor essential elements
- Not believed essential for life



Modern name	Latin name	Symbol
Copper	Cuprium	Cu
Iron	Ferrum	Fe
Potassium	Kalium	K
Sodium	Natrium	Na

*	58 Cerium Ce 140.1	59 Praseodymium Pr 140.9	60 Neodymium Nd 144.2	61 Promethium Pm (145)	62 Samarium Sm 150.4	63 Europium Eu 152.0	64 Gadolinium Gd 157.3	65 Terbium Tb 158.9	66 Dysprosium Dy 162.5	67 Holmium Ho 164.9	68 Erbium Er 167.3	69 Thulium Tm 168.9	70 Ytterbium Yb 173.0	71 Lutetium Lu 175.0
**	90 Thorium Th 232.0	91 Protactinium Pa 231.0	92 Uranium U 238.0	93 Neptunium Np (237)	94 Plutonium Pu (244)	95 Americium Am (243)	96 Curium Cm (247)	97 Berkelium Bk (247)	98 Californium Cf (251)	99 Einsteinium Es (252)	100 Fermium Fm (257)	101 Mendelevium Md (258)	102 Nobelium No (259)	103 Lawrencium Lr (262)

Properties within a group of elements are generally the same .

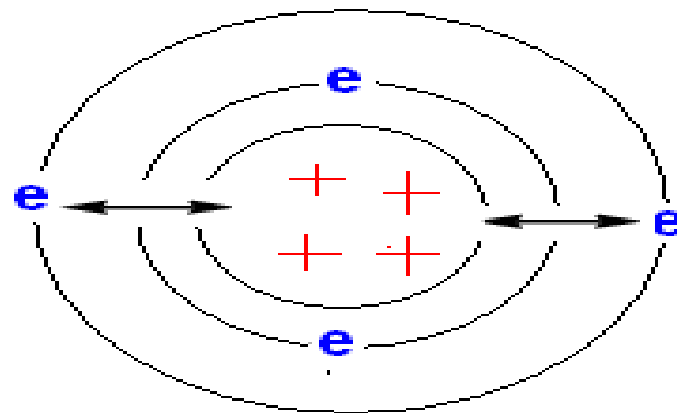
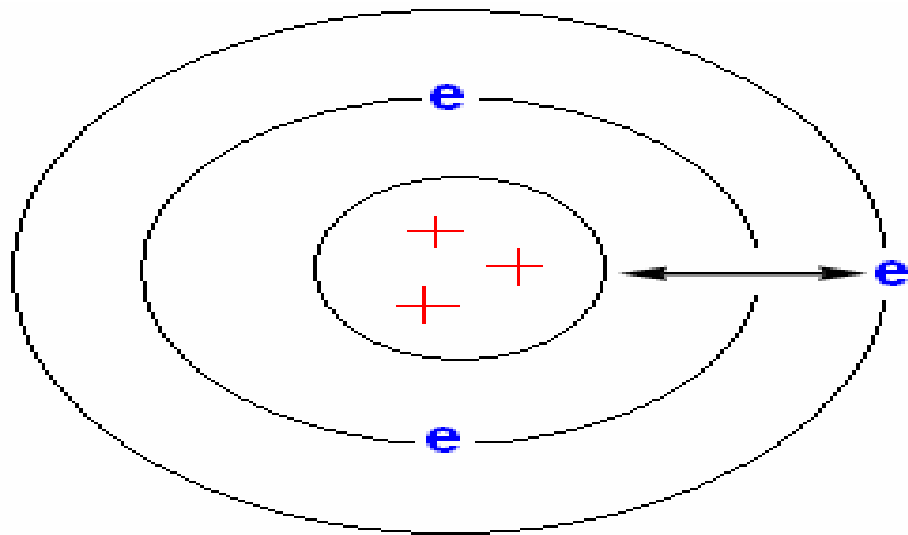
* the major differences include in quantitative.

Ionization energy: amount of energy to remove e from gaseous atom .

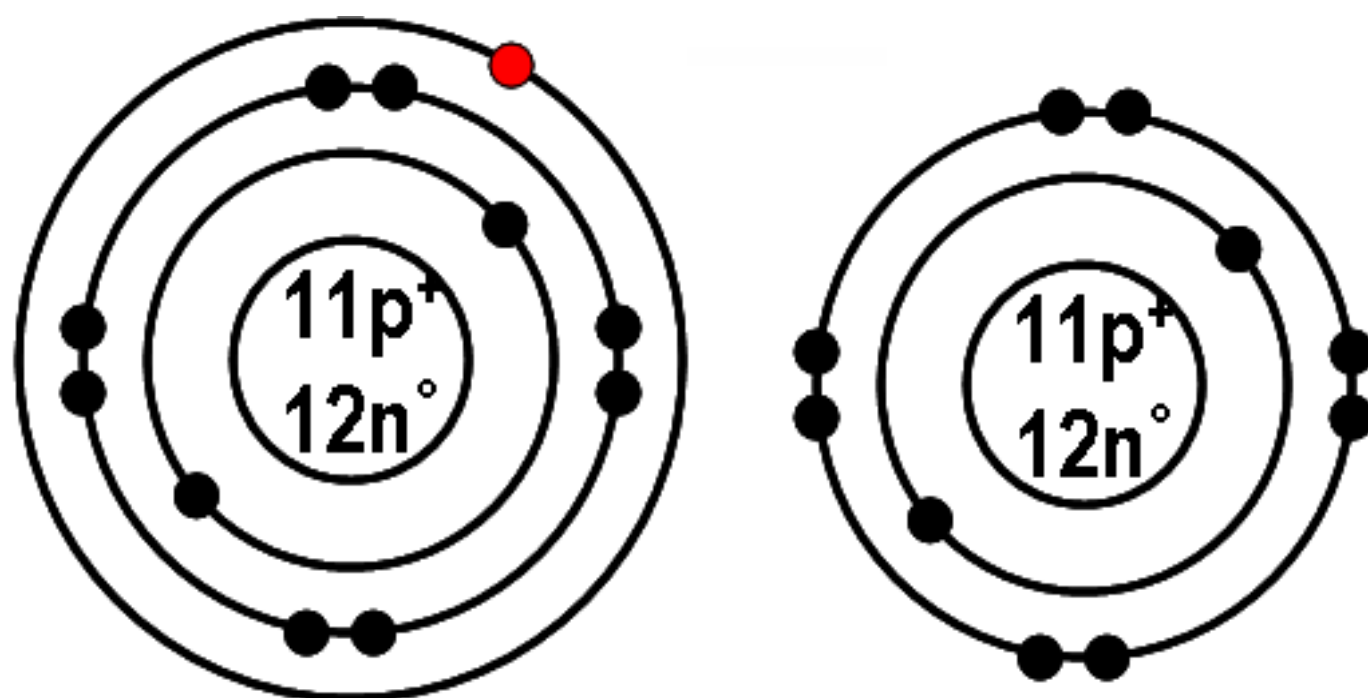
In period(row) -----ionization energy increase when move from left to right but it contrast in grp. It decrease with descending in grp.(when increase)

*** Atomic radius:

* period-----decrease Atomic radius wn going from left to right(increase A.#, n value constant) .b more p in the nucleus -
-----higher electrical force pulls e(s) closer to nucleuse



grp. -----increase Atomic radius down the grp.or by increase n value(increase atomic #). b valence e(s) r at higher E. levels and not bonund as tightly to the nucleus b they r shield(pushes away) by other e(s) in inner levels.



Electronegativity: the ability of an atom in a molecule to attract shared e(s) to itself.

** any **period** -----**increase** electronegativity from left to right.

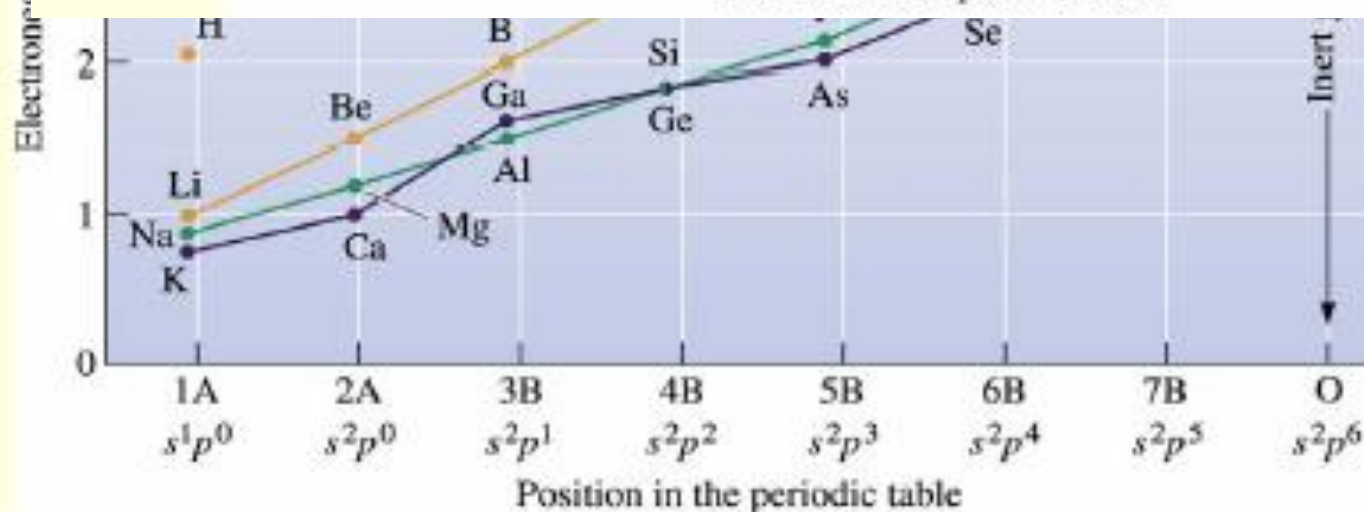
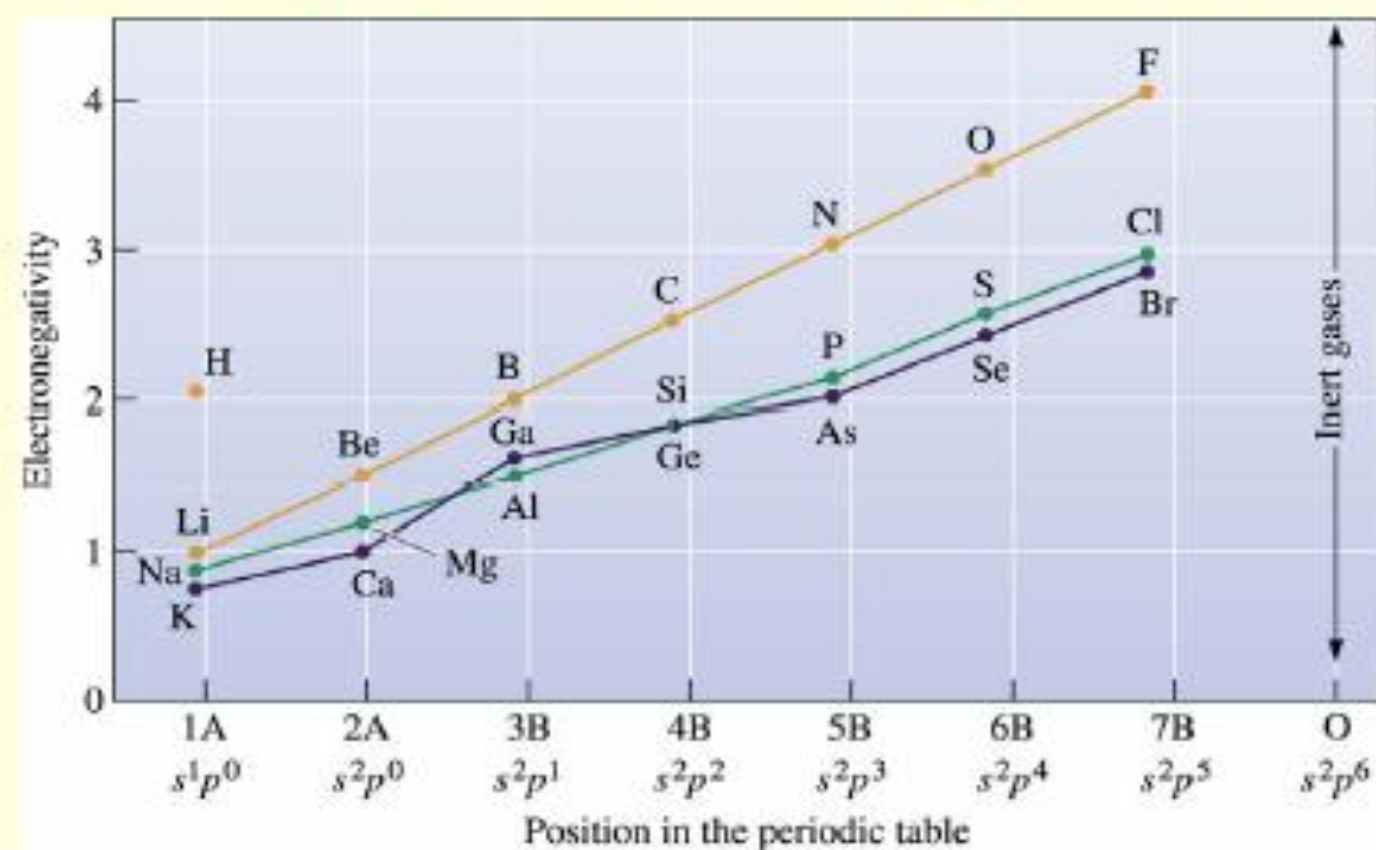
In **grp.**----- **decrease** electronegativity from top to bottom. **Except VIIIA(inert gas).**

The most electronegative element is F and the least electronegative element is Francium (Fr)(IA).

Table : Pauling electronegative scale

Electronegativity

➤ Tendency of an atom to gain an electron



Nuclear charge increases
Shielding increases
Atomic radius increases
Ionic size increases
Ionization energy decreases
Electronegativity decreases

Shielding is constant
Atomic Radius decreases
Ionization energy increases
Electronegativity increases
Nuclear charge increases

