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Subject:Engineering Chemistry

Unit: VII

Topic: Periodic properties

CLASSIFICATION OF ELEMENTS AND PERIODICITY IN PROPERTIES

Need for classification:

It is very difficult to study individually the chemistry of all the elements and millions of their compounds,

Hence to simplify and systematize the study of chemistry of the elements and their compounds, they are classified into groups and periods. Early attempt to classify the elements:

Classification of Lavoiser

Elements had been classified into two major groups by Lavoiser

1. Metals 2. Non–metals

This classification was based on the differences in their properties.

Dobereiner's law of traids:

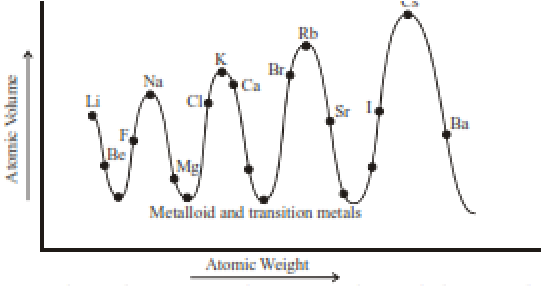
It was first attempt towards classification. He arranged similar elements in a group of three elements called triad and the atomic mass of the middle elements of the traid is approximately the arithmetic mean of the other two.

Triad of atoms			Mean of first and last element
Li	Na	K	$\frac{7+39}{2}=23$
7	23	39	
Be	Mg	Ca	$\frac{8+40}{2}=24$
8	24	40	

Newland's law of octaves:

When the lighter elements are arranged in order of their increasing atomic weights, then every eighth element is similar to the first element in its properties, similarly as the eighth node of a musical scale is similar to first one. E.g. Na 8thelement resembles in their properties with Li. Similarly, K the 8th element with Na and so on.

Lother Meyer arrangement:



The graphs plotting the atomic volumes against atomic weights are known as Lothar Mayer volume curves. The alkali metals have highest atomic volumes. Alkaline earth metals (Be, Mg Ca, Sr, Ba, etc.) which are relatively a little less electropositive. Occupy positions on the descending part of the curve. Halogens and the noble gases (except helium) occupy positions on the ascending part of the curve. Transition elements have very small volumes and therefore these are present at the bottoms of the curve.

MENDELEEV'S PERIODIC LAW

Mendeleev's Periodic Law - The physical and chemical properties of elements are the periodic function of their atomic weight

ii. Characteristic of Mendeleev's Periodic Table

(a)It is based on atomic weight

(b) 63 elements were known, noble gases were not discovered.

(c) 12 Horizontal rows are called periods.

(d) Vertical columns are called groups and there were 8 groups in Mendeleev's Periodic table. (e) Each group up to VIIth is divided into A & B subgroups. 'A'sub groups element are called normal elements and 'B'sub group's elements are called transition elements.

(f) The VIIIth group was consists of 9 elements in three rows (Transition metals group).

(g) The elements belonging to same group exhibit similar properties.

Merits or advantages of Mendeleev's periodic table

(a)Study of elements - First time all known elements were classified in groups according to theirsimilar properties. So study of the properties becomes easier of elements.

(b) Prediction of new elements - It gave encouragement to the discovery of new elements as some gaps were left init. Sc(Scandium), Ga (Gallium), Ge (Germanium), Tc(Technetium) were the elements for whom position and properties were defined by Mendeleev even before their discoveries and he left the blank spaces for them . e.g.- Blank space at atomic weight 72 in silicon group was called Eka silicon (means properties like silicon) and element discovered later was named Germanium. Similarly, other elements discovered after Mendeleev periodic table were.

Eka aluminium- Gallium(Ga) Eka Boron - Scandium (Sc)

Eka Silicon - Germanium(Ge) Eka Manganese - Technetium(Tc)

(c) Correction of doubtful atomic weights - Correction was done in atomic weight of some elements.

Atomic Weight =Valency × Equivalent weight.

Initially, it was found that equivalent weight of Be is 4.5and it is trivalent (V=3), so the weight of Be was 13.5 and there is no space in Mendeleev’s table for this element. So, after correction, it was found that Be is actually divalent (V= 2). So, the weight of Be became 2 × 4.5 = 9 and there was a space between Li and Bfor this element in Mendeleev’s table. – Corrections were done in atomic weight of elements are – U, Be, In, Au, Pt.

Demerits of Mendeleev’s periodic table –

(a) Position of hydrogen - Hydrogen resembles both, the alkali metals (IA) and the halogens (VIIA) in properties so Mendeleev could not decide where to place it.

(b) Position of isotopes - As atomic weight of isotopes differs, they should have placed in different position in Mendeleev’s periodic table. But there were no such places for isotopes in Mendeleev’s table.

(c) Anomalous pairs of elements - There were some pair of elements which did not follow the increasing order of atomic wts.**eg.** Ar and Co were placed before K and Ni respectively in the periodic table, but having higher atomic weights.

(d) Like elements were placed in different groups.

There were some elements like Platinum (Pt) and Gold (Au) which have similar properties but were placed in different groups in Mendeleev’s table.

Pt – VIII Au – IB

(e) Unlike elements were placed in same group. Like cu and Ag placed together. Ist group with Na.

MODERN PERIODIC LAW

Mosley proved that the square root of frequency of the rays, which are obtained from metal on showering high velocity electrons is proportional to the nuclear charge of the atom. This can be represented by the following expression.

= a (Z–b) where Z is nuclear charge on the atom and a and b are constants.

The nuclear charge on an atom is equal to the atomic number.

According, to modern periodic law:”The properties of elements are the periodic functions of their atomic numbers”.

Cause of periodicity: It is due to the repetition of similar outer shell electronic configuration at a certain regular intervals.

Structural features of the long form of the periodic table:

On the basic of the modern periodic law, a scientist named **Bohr** proposed a long form of periodic table that was prepared by Rang and Warner.

(i) It consists of 18 vertical columns called **groups** and 7 horizontal rows called periods.

(ii) Elements of groups, 1, 2, 13 – 17 are called **normal** or **representative elements.**

(iii) Elements of groups 3 – 11 are called **transition elements.**

(iv) The 14 elements with atomic numbers (Z) = 58 – 71 (occurring after lanthanum La in the periodic table) are called **lanthanides** or **rare earth elements and** are placed at the bottom of the periodic table. The 14 elements with atomic numbers (Z) = 90 – 103 (Occurring after actinium Ac in the periodic table) are called **actinides** and are placed at the bottom of the periodic table.

(v) The Eleven elements with Z = 93 – 103 (93Np –Lr103) which occur in the periodic table after uranium and have been prepared from it by artificial means are called **transuranics.** These are all radioactive elements.

(vi)The elements belonging to a particular group are said to constitute a chemical family which is usually named after the name of the first element. For example, Boron family (group 13), carbon family (group 14), nitrogen family (group 15), and oxygen family (group 16). In addition to this, some groups have typical names. For example, Elements of group 1 are called **alkali metals**

Elements of group 2 are called **alkaline earth metals**

Elements of group 16 are called **chalcogens**

Elements of group 17 are called **halogens**

MODERN PERIODIC TABLE (Extended Form)

s-Block Elements ($n\,s^{1-2}$)

d-Block Elements $(n-1)\,d^{1-10}\,n\,s^{0-2}$ (Transition Metals)

p-Block Elements ($n\,s^2p^{1-6}$)

→ Groups	1 or IA	2 or IIA	3 or IIIB	4 or IVB	5 or VB	6 or VIB	7 or VIIB	Group 8–10 VIII			11 or IB	12 or IIB	13 or IIIA	14 or IVA	15 or VA	16 or VIA	17 or VIIA	18 or 0
	s^1	s^2	d^1s^2	d^2s^2	d^3s^2	d^5s^1	d^5s^2	d^6s^2	d^7s^2	d^8s^2	$d^{10}s^1$	$d^{10}s^2$	s^2p^1	s^2p^2	s^2p^3	s^2p^4	s^2p^5	s^2p^6
Periods ↓ 1 (1s)	H 1												Metalloids and Non-metals					He 2
	Active Metals																	
2 (2s 2p)	Li 3	Be 4											B 5	C 6	N 7	O 8	F 9	Ne 10
3 (3s 3p)	Na 11	Mg 12											Al 13	Si 14	P 15	S 16	Cl 17	Ar 18
4 (4s 3d 4p)	K 19	Ca 20	Sc 21	Ti 22	V 23	Cr 24	Mn 25	Fe 26	Co 27	Ni 28	Cu 29	Zn 30	Ga 31	Ge 32	As 33	Se 34	Br 35	Kr 36
5 (5s 4d 5p)	Rb 37	Sr 38	Y 39	Zr 40	Nb 41	Mo 42	Tc 43	Ru 44	Rh 45	Pd 46	Ag 47	Cd 48	In 49	Sn 50	Sb 51	Te 52	I 53	Xe 54
6 6s(4f)5d6p	Cs 55	Ba 56	La* 57	Hf 72	Ta 73	W 74	Re 75	Os 76	Ir 77	Pt 78	Au 79	Hg 80	Tl 81	Pb 82	Bi 83	Po 84	At 85	Rn 86
7 7s (5f) 6d	Fr 87	Ra 88	Ac** 89	Unq 104	Unp 105	Unh 106	Uns 107	Uno 108	Une 109	Unn 110		Eka-mercury 112						

f-Block Elements (Inner Transition Elements) $(n-2)\,f^{1-14}\,(n-1)\,d^{0-1}\,n\,s^2$

* Lanthanides 4f	Ce 58	Pr 59	Nd 60	Pm 61	Sm 62	Eu 63	Gd 64	Tb 65	Dy 66	Ho 67	Er 68	Tm 69	Yb 70	Lu 71
** Actinides 5f	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Elements of group 18 are called zero group or noble gases.

The long form of the periodic table contains seven periods.

These are :

1st period (1H –He) contains only two elements. This is the shortest period.

2nd period (3 Li –10Ne) and third period (11Na –Ar) contain 8 elements each and are called short periods.

4th period (19K –36Kr) and 5th period (37Rb –54Xe) contain 18 elements each and are called long periods.

6th period (55Cs –86Rn) contains 32 elements and is the longest period.

7th period (87Li –) is, however, incomplete and contains at present only 24 elements.

In yet another classification, the long form of the periodic table has been divided into four blocks (i.e. s, p, d and f), depending upon the subshell to which the last electron enters.

CLASSIFICATION IN BLOCKS

s-block elements.

Elements of groups 1 and 2 including He in which the last electron enters the s-orbital of the valence shell are called s-block elements. There are only **14 s-block elements** in the periodic table.

p-block elements.

Elements of groups 13–18 in which the last electron enters the p-orbitals of the valence shell are called p-block elements.

d-block elements.

There are three complete series and one incomplete series of d-block elements. These are: 1st or 3dtransition series which contains ten elements which atomic numbers 21–30 (Sc- Zn).

2nd or 4d transition series contains ten elements with atomic numbers 39 – 48 (Y-Cd).

3rd or 5d transition series also contains ten elements which atomic numbers 57 and 72 –80 (57La, 72Hf –80Hg).

4th or 6d transition series is incomplete at present and contains only nine elements.

Z = 111 has not been discovered so far. Thus, in all there are 39 d-block elements.

f-Block elements are called inner-transition elements. In these elements, the f-subshell of the anti-penultimate is being progressively filled up. There are two series of f-block elements each containing 14 elements. The fourteen elements from 58 Ce –Lu in which 4 f-subshell is being progressively filled up are called lanthanides or rare elements. Similarly, the fourteen elements from 90Th –103Lr in which 5 f-subshell is being progressively filled up are called **actinides.**

EFFECTIVE NUCLEAR CHARGE

- In a poly-electronic atom, the internal electrons repel the electrons of the outermost orbit. This results in decrease the nuclear attraction on the electrons of the outermost orbit.
- Therefore, only a part of the nuclear charge is effective on the electrons of the outermost orbit. Thus, the inner electrons protect or shield the nucleus and thereby decrease the effect of nuclear charge towards the electrons of the outermost orbit.
- Thus the part of the nuclear charge works against outer electrons, is known as **effective nuclear charge**

$Z * Z= - \sigma$

Z* = effective nuclear charge

s = shielding constant and Z= nuclear charge

A scientist named **slater**, determined the value of shielding constant and put forward some rules as following.

(1) The shielding effect or screening effect of each electron of 1s orbital is 0.30.

(2) The shielding effect of each electrons of ns and np i.e. electron of the outermost orbit, is 0.35.

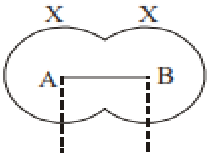
(3) The shielding effect of each electron of s or p orbitals of the penultimate orbit (n – 1) is 0.85.

(4) The shielding effect of each electron of s or p orbital of the pre penultimate orbit (n– 2) and below this is1.0.

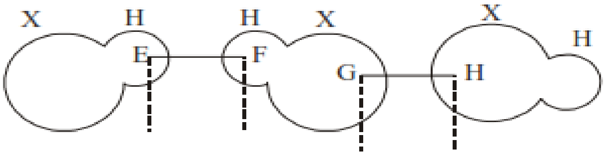
Periodic Properties:

Properties which are directly or indirectly related to their electronic configuration and show a regular gradation when we move from left to right in a period or from top to bottom in a group are called **periodic properties.** Some important periodic properties are atomic size, ionization energy electron affinity, electronegativity, valency, density, atomic volume, **melting and boiling** points etc.

(a) Atomic size: It refers to the distance between the centre of the nucleus of the atom to the outermost shell containing electrons. Since absolute value of the atomic size cannot be determined, it is usually expressed in terms of the following operational definitions.



$1/2\ AB = r_{covalent}$
(of element X)



$1/2\ EF = r_{van\ der\ Waals}$ of hydrogen in HX molecule
$1/2\ GH = r_{van\ der\ Waals}$ of X in HX molecule

$$r_n = \frac{n^2 a_0}{Z^*}$$

(i) **Covalent radius.** It is defined as one-half of the distance between the nuclei of two covalently bonded atoms of the same element in a molecule.

Single Bond Covalent Radius, SBCR- (a) For Homo-atomic molecules

d_{A-A}== $r_A + r_A$or $2r_A$

(b) For hetro-diatomic molecules while electronegativity is approx.Same.

$d_{A-B} = r_A + r_B$,,

For heteronuclear diatomic molecule A–B, while difference between the electronegativity values of atom A and atom B is relatively larger, (X_A and Xb) are the electron negativity in Pauling Scale.

$dA-B = rA + rB - 0.09\ |(XA-XB)|$ [Bond length or radius expressed in Å]

Where, XA and X Bare electronegativity values of high electronegative element A and less electronegative element B, respectively. This formula was given by **Stevenson &Schomaker**.

Note:*Covalent radius is slightly smaller than actual radius.*

(ii)**Van der Waals' radius.**It is defined as one-half of the distance between the nuclei of two non-bonded isolated atoms or two adjacent atoms belonging to two neighbouring molecules of an element in the solid state.

By definition, van der Waals' radius of an element is always larger than its covalent radius.

Variation of atomic radii :

(i) Across the period atomic radii decreases

(ii) Where we move from 17 th g group to 18th atomic radii increases the period decreases

Ionic size: An atom can be changed to a cation by loss of electrons and to an anion by gain ofelectrons. A cation is always smaller than the parent atom because during its formation effectivenuclear charge increases and sometimes a shell may also decrease. On the other hand, the size of

An**anion** is always larger than the parent atom because during its formation effective nuclear charge decreases e.g.$Mg2+ < Mg$, $Cl– > Cl$

The size of a cation is smaller in comparison to the size of its corresponding atom. This is because of the fact that an atom on losing electrons/s forma cation, which has lesser number of electrons/s than the number of proton/s. This results in increase in the effective nuclear charge.

The size of an anion is greater than the size of its corresponding atom, because the number of electrons present in the anion gets larger than the number of protons due to gain of electron/s. This results in decrease in the effective nuclear charge.

Size of anion ∝ Amount of negative charge

$O_0 < O_{-1} < O_{-2}$

Size of Isoelectronic Series

Isoelectronic ions or species are the neutral atoms, cations or anions of different elements which have the same number of electrons but different nuclear charge e.g..

The size of the isoelectronic species depends upon their nuclear charge Greater the nuclear charge, lesser the radii.

The ionic radii decrease moving from left to right across any period in the periodic table

Size in an isoelectronic series ∝ Nuclear charge

Na_{+}, Mg_{2+} is 102pm , 72 pm.

IONISATION POTENTIAL

The energy required to remove the most loosely bound electron from the outermost orbit of one mole of isolated gaseous atoms of an element, is called **ionisation potential (IP)**. This ionisation is an endergonic or energy-absorbing process.

An electron cannot be removed directly from an atom in solid state. For this purpose, the solid state is converted to gaseous state and the energy required for this is called **sublimation energy**.

The energy required to remove one electron from a neutral gaseous atom to convert it to mono-positive cation, is called first ionisation potential (I Ist IP). The energy required to convert a mono positive cation to a dipositive cation is called second ionisation potential (I

IstIP<IIndIP<IIIrdIP) of an atom IP because as the electrons go out of the atom, the ionic size goes on decreasing and the amount of positive charge goes on increasing.

Factors Affecting Ionisation Potential

(i) Atomic size: When the size of an atom is very large the electron of the outermost orbit bound to the nucleus by weaker attractive forces. Such an electron will be readily removed from the atom. Therefore.the value of ionisation potential will be low.

(ii) Effective Nuclear Charge: Atomic size decreases with increase in effective nuclear charge because, higher the effective nuclear charge stronger will be the attraction of the nucleus towards the electron of the outermost orbit and higher will be the ionisation potential

(iii) Shielding Effect: The electrons of internal orbits repel the electrons of the electron of the outermost orbit due to which the attraction of the nucleus towards the electron of the outermost orbit decreases and thus atomic size increases and the value of ionisation potential decreases.

(iv)Stability of half filled and fully filled orbitals: The atoms whose orbitals are half-filled (p) or fully-filled (s2, p6) have greater stability than the others. Therefore, they required greaterenergy to for removing out electron. However stability of fully filled orbitals is greater than that of the half- filled orbitalsI .P .of fully filled orbitals I.P. of half- filled orbitals□

(v) Penetration power: In any atom the *s* orbital is nearer to the nucleus in comparison to *p*, *d* and *f* orbitals. Therefore, greater energy is required to remove out electron forms orbital than from *p*, *d* and *f* orbitals. Thus the decreasing order of ionisation potential of *s*, *p*, *d* and *f* orbitals is as follows

$s > p > d > f$

Periodic Table &Ionisation Potential

(a) In a Period : The value of Ionisation potential normally increase on going from left to right in a period, because effective nuclear charge increases and atomic size decreases.

Exceptions:

In second period ionisation potential of Be is greater than that of B, and in the third period ionisation potential of Mg is greater than that of Al due to high stability of fully filled orbitals.

In second period ionisation potential of Nis greater than Oand in the third period ionisation potential of

P is greater than that of S, due to stability of half- filled orbitals.

The increasing order of the values of ionisation potential of the second period elements is

Li < B < Be < C < O < N < F < Ne

The increasing order of the values of ionisation potential of the third period elements is

Na < Al < Mg < Si < S < P < Cl <Ar

InnerTransitionElements: The size of inner transition elements is greater than that of d block elements. Therefore the value of ionisation potential of f -block elements is smallerthan that of d block elements and due to almost constant atomic size of f block elements in a period the value of their ionisation potential remains more constant than that of d block elements.

In a Group

The value of ionisation potential normally decreases on going from top to bottom in a group because both atomic size and shielding effect increase.

Exception:

- The value of ionisation potential remains almost constant from Al to Ga in the IIIA group.(B>Al , Ga > In)
- In the periodic table the element having highest value of ionisation potential is He.
- The values of ionisation potential of noble gases are extremely high, because the orbitals of outermost orbit are fully-filled (ns2, np6) and provide great stability.
- In a period, the element having least value of ionisation potential is an alkali metal (group IA) and that having highest value is inert gas (Group 0)

Applications of Ionisation Potential

- The elements having high values of ionisation potential have low reactivity, e.g. inert gases.
- The value of ionisation potential decreases more on going from top to bottom in a group in comparison to a period. Therefore, reactivity of metal increases and the atom forms a cation by loss of electron.
- The elements having low value of ionisation potential readily lose electron and thus behave as strong
- The elements having low value of ionization potential readily lose electron and thus exhibit greater
- The elements having low value of ionisation potential readily lose electron and thus have basic property.

ELECTRON AFFINITY (EA)

- The energy released on adding up one mole of electron to one mole of neutral atom(A) in its gaseous state to form an anion (A–) is called **electron affinity** of that atom. In general, **electron affinity** is associated with an exothermic process.

$A(g) + e^{-} \longrightarrow A^{-}(g)$, $\Delta H_{eg} = -E_{n}$

- When one electron adds up to a neutral atom, it gets converted to a unit negative ion and energy is released. On adding one more electron to the mono-negative anion, there is a repulsion between the negatively charged electron and anion. In order to counteract the repulsive forces, energy has to be provided to the system. Therefore, the value of the second electron affinity is positive.

$A^{-}(g) + e^{-} \longrightarrow A^{-2}(g)$,$\Delta H_{eg} = + E_{n}$$\Delta H_{eg}$: Electron gain enthalpy

Factors Affecting Electron Affinity

Effective Nuclear charge: When effective nuclear charge is more, then the atomic size less. Hence EA increases.

Atomic Size or Atomic Radius: When the size or radius of an atom increases, the electron entering the outermost orbit is more weakly attracted by the nucleus and the value of electron affinity is lower.

Shielding Effect: Shielding effect is directly proportional to atomic size and atomic size is inversely proportional to electron affinity.

Stability of Fully-Filled and Half-Filled Orbitals:

The stability of the configuration having fully-filled orbitals (p6, d10) andhalf-filled orbital (p) is relatively higher than that of other configurations.

Periodic Table and Electron Affinity:

In a period, atomic size decreases with increase in effective nuclear charge and hence increase in electron affinity.

POLARIZABILITY

The basics of trends across and down the Periodic Table, we can use the concepts of Effective Nuclear Charge and Electronegativity to discuss the factors that contribute to the types of bonds formed between elements.

Fajans' Rules

Rules formulated by Kazimierz Fajans in 1923, can be used to predict whether a chemical bond is expected to be predominantly ionic or covalent, and depend on the relative charges and sizes of the cation and anion. *If two oppositely charged ions are brought together, the nature of the bond between them depends upon the effect of one ion on the other*.

Although the bond in a compound like $\mathbf{X^+Y^-}$ may be considered to be 100% ionic, it will always have some degree of covalent character. When two oppositely charged ions(X+ and Y-) approach each other, the cation **attracts** electrons in the outermost shell of the anion but **repels** the positively charged nucleus. This results in a distortion, deformation or polarization of the anion. If the degree of polarization is quite small, an ionic bond is formed, while if the degree of polarization is large, a covalent bond results.

The ability of a cation to distort an anion is known as its **polarization power** and the tendency of the anion to become polarized by the cation is known as its **polarizability**.

The polarizing power and polarizability that enhances the formation of covalent bonds is favoured by the following factors:

Small cation: the high polarizing power stems from the greater concentration of positive charge on a small area. This explains why LiBr is more covalent than KBr (Li^+ 90 pm cf. K^+ 152 pm).

Large anion: the high polarizability stems from the larger size where the outer electrons are more loosely held and can be more easily distorted by the cation. This explains why for the common halides, iodides, are the most covalent in nature (I^-206 pm).

Large charges: as the charge on an ion increases, the electrostatic attractions of the cation for the outer electrons of the anion increase, resulting in the degree of covalent bond formation increasing.

Large cations are to be found on the bottom left of the periodic table and small anions on the top right. The greater the positive charge, the smaller the cation becomes and the *ionic potential* is a measure of the charge to radius ratio.

ELECTRONEGATIVITY

Electronegativity is a measure of the tendency of an atom to attract a bonding pair of electrons.

The Pauling scale is the most commonly used. Fluorine (the most electronegative element) is assigned a value of 4.0, and values range down to caesium and francium which are the least electronegative at 0.7.

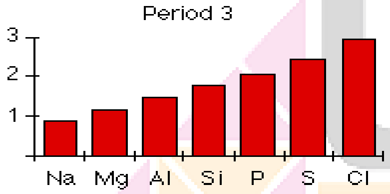
Consider a bond between two atoms, A and B. Each atom may be forming other bonds as well as the one shown - but these are irrelevant to the argument.

If the atoms are equally electronegative, both have the same tendency to attract the bonding pair of electrons, and so it will be found on average half way between the two atoms. To get a bond like this, A and B would usually have to be the same atom. You will find this sort of bond in, for example, H_2 or Cl_2 molecules.

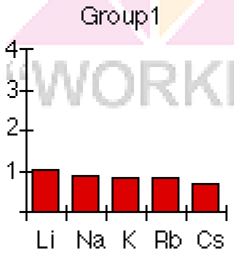
Polar bond:

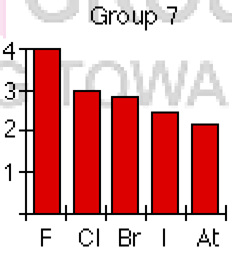
A polar bond is a covalent bond in which there is a separation of charge between one end and the other - in other words in which one end is slightly positive and the other slightly negative. Examples include most covalent bonds. The hydrogen-chlorine bond in HCl or the hydrogen-oxygen bonds in water are typical.

Across a period the electronegativity increases. The chart shows electronegativity’s from sodium to chlorine - you have to ignore argon. It doesn't have electronegativity, because it doesn't form bonds.



Electronegativity decreases. (If it increases up to fluorine, it must decrease as you go down.)





The chart shows the patterns of electronegativity in Groups 1 and 7.

QUANTUM NUMBERS:

Quantum numbers work like addresses for electrons in an atom.. Quantum numbers work the same way: energy level type of orbital orientation of orbital orientation of electron. Every electron in an atom will have a unique set of quantum numbers in the form [n, l, ml ,ms].

Principal Quantum Number (n = 1, 2, 3, 4, …) The principal quantum number, n, defines the energy level or shell of the electron. It is the first quantum number that must be determined, as it defines the available values for all other quantum numbers. Think of Bohr’s model for the atom; n defines the ring on which the electron resides. The value of n tells you how many levels away from the nucleus the electron is. The valence shell of an atom is the highest occupied shell and is mathematically equivalent to the period of the element (i.e., H is in period 1, so the valence shell for H is n = 1).

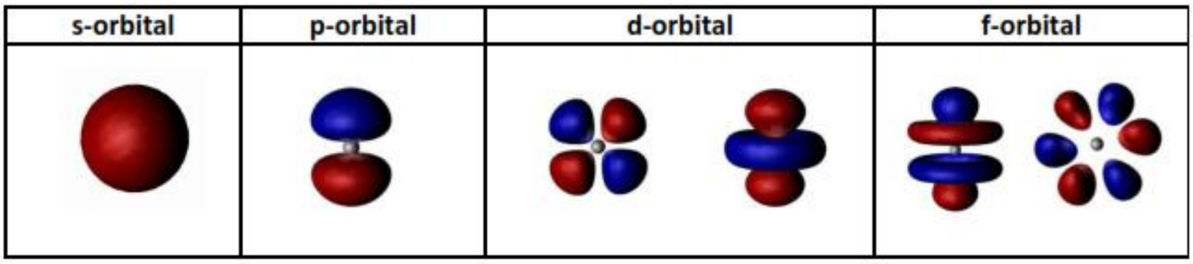
Azimuthal (Angular Momentum) Quantum Number (l = 0, 1, 2, …(n-1)) The azimuthal, or angular momentum, quantum number, l, defines the type or shape of the orbital where the electron most probably resides. It is the second quantum number to be determined as its value relies only on n (i.e., if n = 2, then l = 0 or 1 since n – 1 = 1). Each type of orbital has a unique number of nodes (e.g., where the wave changes phases) which is mathematically equivalent to l.

If l = 0, the electron is in an s-orbital that has 0 nodes.

If l = 1, the electron is in a p-orbital that has 1 node.

If l = 2, the electron is in a d-orbital that has 2 nodes.

If l = 3, the electron is in an f-orbital that has 3 nodes.



Magnetic Quantum Number (ml = -l…0…+l) The magnetic quantum number, ml , defines the orientation of the orbital in which the electron inhabits. The number of ml values is called the degeneracy, or the number of orbitals in the atom that are at the same energy level. Note that to have the same energy, the orbitals must be on the same energy level as well as be the same type of orbital (n and l values are equal).

A 2s orbital is not degenerate (e.g., the same energy) with a 2p or a 1s orbital. The ml values are entirely dependent on the l values; each type of orbital has a set degeneracy.

For an s-orbital, ml = 0, and degeneracy = 1.

For a p-orbital, ml = -1, 0, +1, and degeneracy = 3.

For a d-orbital, ml = -2, -1, 0, +1, +2, and degeneracy = 5.

For an f-orbital, ml = -3, -2, -1, 0, +1, +2, +3, and degeneracy = 7.

NOTE: A set of 2p orbitals and 3p orbitals may have the same degeneracy value, but they are NOT degenerate with each other. They both include three total orbitals, but they are not at the same energy: they have different n values.

Spin Quantum Number (ms = - ½, + ½) The spin quantum number, ms, is completely independent of the values of n, l, and ml . It is always + ½ for an electron who has its spin oriented up, and – ½ for an electron who has its spin oriented down. This means that there are only two electrons allowed per orbital, no matter the energy level, shape, or orientation (i.e., a 1s orbital holds 2 electrons, as does 4d orbital). As of yet, we cannot determine whether an electron is pointed up or down, so it can be assumed always that ms = ± ½..

If n is:	then *l* can be:	so m_l is:	with a degeneracy of:	and m_s as:
1	0	0	1	- ½ , + ½
2	0	0	1	- ½ , + ½
	1	-1, 0, 1	3	- ½, + ½
3	0	0	1	- ½ , + ½
	1	-1, 0, 1	3	- ½ , + ½
	2	-2, -1, 0, 1, 2	5	- ½ , + ½
4	0	0	1	- ½ , + ½
	1	-1, 0, 1	3	- ½ , + ½
	2	-2, -1, 0, 1, 2	5	- ½ , + ½
	3	-3, -2, -1, 0, 1, 2, 3	7	- ½ , + ½

AUFBAU PRINCIPLE:

The Aufbau principle dictates the manner in which electrons are filled in the atomic orbitals of an atom in its ground state. It states that electrons are filled into atomic orbitals in the increasing order of orbital energy level. According to the Aufbau principle, the available atomic orbitals with the lowest energy levels are occupied before those with higher energy levels.

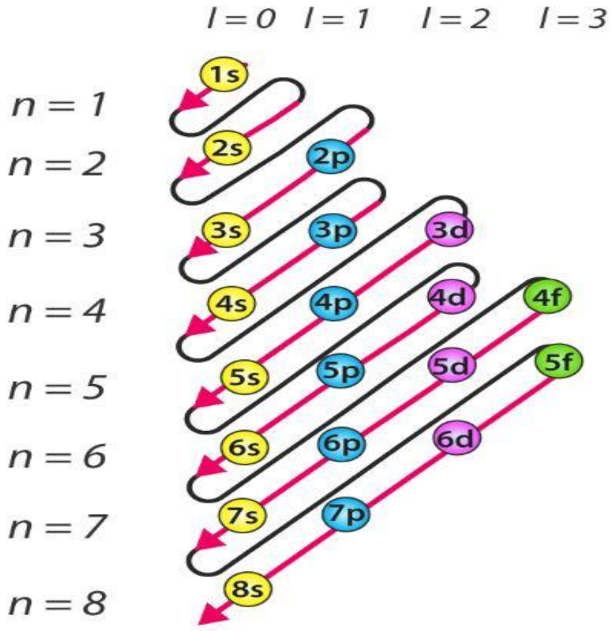
The word 'Aufbau' has German roots and can be roughly translated as 'construct' or 'build up'. A diagram illustrating the order in which atomic orbitals are filled is provided below. Here, 'n' refers to the principal quantum number and 'l' is the azimuthal quantum number.

The Aufbau principle can be used to understand the location of electrons in an atom and their corresponding energy levels. For example, carbon has 6 electrons and its electronic configuration is $1s^2 2s^2 2p^2$.

It is important to note that each orbital can hold a maximum of two electrons. Also, the manner in which electrons are filled into orbitals in a single subshell must follow , i.e. every orbital in a given subshell must be singly occupied by electrons before any two electrons pair up in an orbital.

Salient Features of the Aufbau Principle

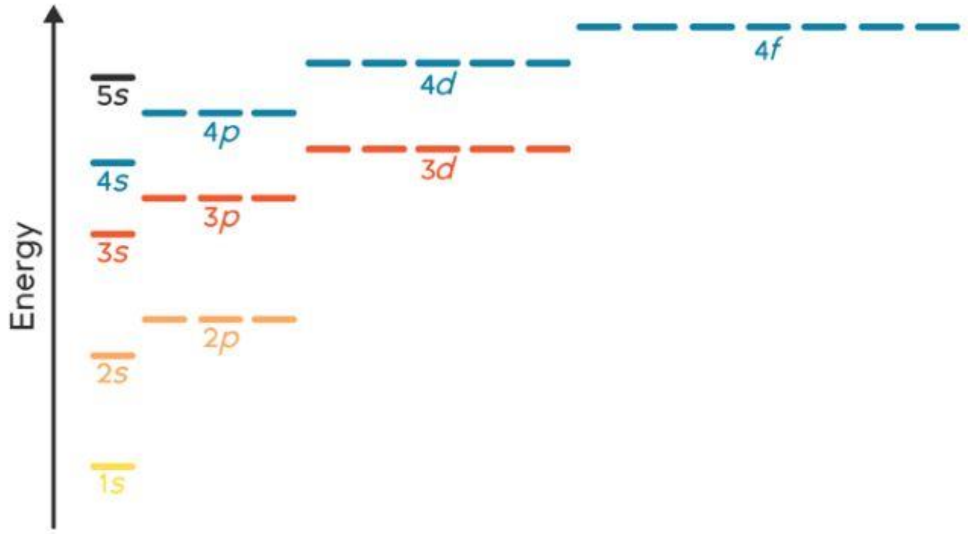
- According to the Aufbau principle, electrons first occupy those orbitals whose energy is the lowest. This implies that the electrons enter the orbitals having higher energies only when orbitals with lower energies have been completely filled.
- The order in which the energy of orbitals increases can be determined with the help of the (n+l) rule, where the sum of the principal and azimuthal quantum numbers determines the energy level of the orbital.
- Lower (n+l) values correspond to lower orbital energies. If two orbitals share equal (n+l) values, the orbital with the lower n value is said to have lower energy associated with it.
- The order in which the orbitals are filled with electrons is: 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f, 6d, 7p, and so on.



Exceptions

The electronic configuration of chromium is [Ar]$3d^5 4s^1$ and not [Ar]$3d^4 4s^2$ (as suggested by the Aufbau principle). This exception is attributed to several factors such as the increased stability provided by half-filled subshells and the relatively low energy gap between the 3d and the 4s subshells.

The energy gap between the different subshells is illustrated below.



Half filled subshells feature lower electron-electron repulsions in the orbitals, thereby increasing the stability. Similarly, completely filled subshells also increase the stability of the atom. Therefore, the electron configurations of some atoms disobey the Aufbau principle (depending on the energy gap between the orbitals).

For example, copper is another exception to this principle with an electronic configuration corresponding to [Ar]$3d^{10}4s^1$. This can be explained by the stability provided by a completely filled 3d subshell.

Electronic Configuration using the Aufbau Principle

Writing the Electron Configuration of Sulfur

- The atomic number of sulfur is 16, implying that it holds a total of 16 electrons.
- As per the Aufbau principle, two of these electrons are present in the 1s subshell, eight of them are present in the 2s and 2p subshell, and the remaining are distributed into the 3s and 3p subshells.
- Therefore, the electron configuration of sulfur can be written as $\mathbf{1s^2 2s^2 2p^2 3s^2 3p^4}$.

Writing the Electron Configuration of Nitrogen

- The element nitrogen has 7 electrons (since its atomic number is 7).
- The electrons are filled into the 1s, 2s, and 2p orbitals.
- The electron configuration of nitrogen can be written as $\mathbf{1s^2 2s^2 2p^3}$

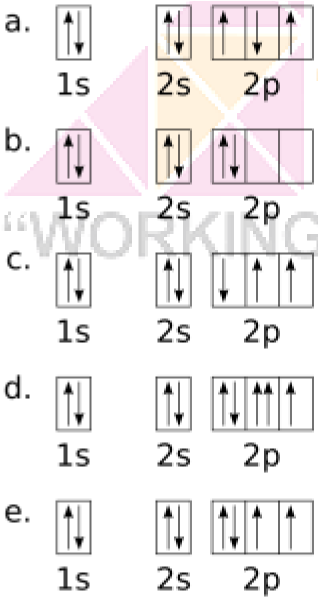
INTRODUCTION TO HUND’S RULE

Aufbau principle tells us that the lowest energy orbitals get filled by electrons first. After the lower energy orbitals are filled, the electrons move on to higher energy orbitals. The problem with this rule is that it does not tell about the three 2p orbitals and the order that they will be filled in. The rule states that, for a stated electron configuration, the greatest value of spin multiplicity has the lowest energy term. It says if two or more than two orbitals having the same amount of energy are unoccupied then the electrons will start occupying them individually before they fill them in pairs. It is a rule which depends on the observation of atomic spectra, which is helpful in predicting the ground state of a molecule or an atom with one or more than one open electronic shells. This rule was discovered in the year 1925 by Friedrich Hund.

According to Hund's rule:

- Before the double occupation of any orbital, every orbital in the sub level is singly occupied.
- For the maximization of total spin, all electrons in a single occupancy orbital have the same spin.

An electron will not pair with another electron in a half-filled orbital as it has the ability to fill all its orbitals with similar energy. A large number of unpaired electrons are present in atoms which are at the ground state. If two electrons come in contact they would show the same behaviour as two magnets do. The electrons first try to get as far away from each other as possible before they have to pair up.



Hund's Rule

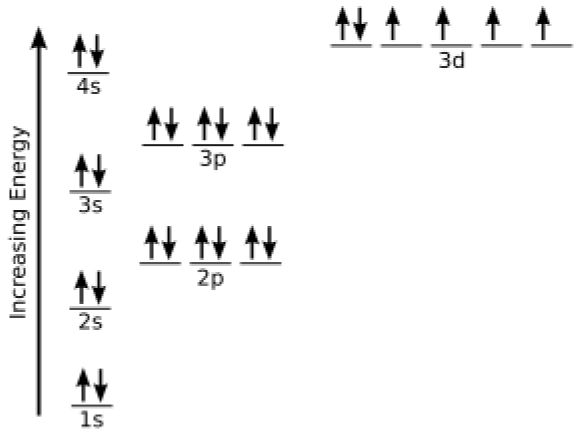
Explanation of Hund's Rule

The electrons enter an empty orbital before pairing up. The electrons repel each other as they are negatively charged. The electrons do not share orbitals to reduce repulsion.

When we consider the second rule, the spins of unpaired electrons in singly occupied orbitals are the same. The initial electrons spin in the sub-level decides what the spin of the other electrons would be. For instance, a carbon atom's electron configuration would be $1s^2 2s^2 2p^2$.

The same orbital will be occupied by the two 2s electrons although different orbitals will be occupied by the two 2p electrons in reference to Hund’s rule.

Electron Configuration and its Purpose



Electron Configuration

The valence shells of two atoms that come in contact with each other will interact first. When valence shells are not full then the atom is least stable. The chemical characteristics of an element are largely dependent on the valence electrons. Similar chemical characteristics can be seen in elements that have similar valence numbers.

The stability can also be predicted by the electron configuration. When all the orbitals of an atom are full it is most stable. The orbitals that have full energy level are the most stable, for example, noble gases. These types of elements do not react with other elements.

Pauli Exclusion

Pauli’s exclusion principle states that in a single atom no two electrons will have an identical set or the same quantum numbers (n, l, m_l, and m_s). To put it in simple terms, every electron should have or be in its own unique state (singlet state). There are two salient rules that the Pauli Exclusion Principle follows:

- Only two electrons can occupy the same orbital.
- The two electrons that are present in the same orbital must have opposite spins or it should be antiparallel.

However, Pauli Exclusion Principle does not only apply to electrons. It applies to other particles of half-integer spin such as fermions. It is not relevant for particles with an integer spin such as bosons which have symmetric wave functions. Moreover, bosons can share or have the same quantum states, unlike fermions. As far as the nomenclature goes, fermions are named after the Fermi–Dirac statistical distribution that they follow. Bosons, on the other hand, get their name from the Bose-Einstein distribution function.

Formulation of the Principle

An Austrian physicist named Wolfgang Pauli formulated the principle in the year 1925. With this principle, he basically described the behaviour of electrons. Later in the year 1940, he expanded on the principle to cover all fermions under his spin-statistics theorem. Meanwhile, fermions that are described by the principle include elementary particles such as quarks, electrons, neutrinos, and baryons.

Wolfgang Pauli was also awarded the Nobel prize in the year 1945 for the discovery of the Pauli exclusion principle and his overall contribution in the field of quantum mechanics. He was even nominated by Albert Einstein for the award.

Pauli Exclusion Principle in Chemistry

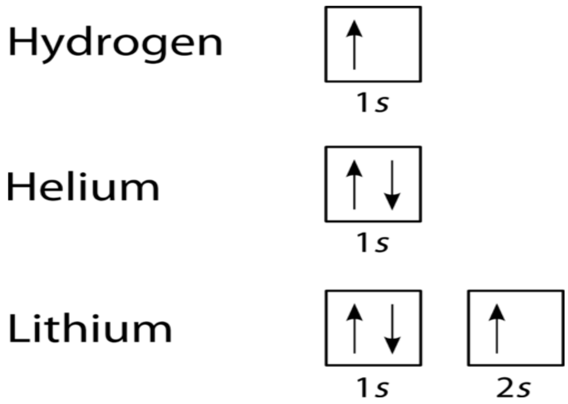
In chemistry, the law is mainly used to explain or determine the electron shell structure of atoms and predict which atoms are likely to donate electrons. An atoms whenever it gains a new electron or electrons it usually moves to the lowest energy state or it shifts to the outermost shell. If the state has one electron then it can either be spin-up or spin down. Now, if we consider the Pauli exclusion principle if there are two electrons in a state, then each of the electrons will have spin-up or spin down-state but not the same.

Pauli Exclusion Principle Example

We can take a neutral helium atom as a common Pauli Exclusion Principle example. The atom has 2 bound electrons and they occupy the outermost shell with opposite spins. Here, we will find that the two electrons are in the 1s subshell where $n = 1$, $l = 0$, and $m_l = 0$.

Their spin moments will also be different. One will be $m_s = -1/2$ and the other will be $+1/2$. If we draw a diagram then the subshell of the helium atom will be represented with 1 “up” electron and 1 “down” electron. In essence, 1s subshell will consist of two electrons, which have opposite spins.

Similarly, if we take Hydrogen it will have 1s subshell with 1 “up” electron ($1s_1$). Lithium will have the helium core (1s2) and then one more “up” electron (2s1). What we are trying to depict here is that the electronic configuration of elements is written in this manner.



Formulation of the Pauli Exclusion Principle

From the above example, we can further deduce that successive larger elements will have shells of successively higher energy. The number of electrons in outermost shell is also directly related to the different chemical properties that elements possess. Elements with the same number of electrons in the outermost shell will have similar properties.

Importance and Applications of Pauli Exclusion Principle

- The Pauli's exclusion principle helps to explain a wide variety of physical phenomena.
- It helps in describing the various chemical elements and how they participate in forming chemical bonds.
- The periodic table can also be defined with the help of this principle.
- Apart from chemistry, the principle is a fundamental principle in quantum mechanics which is mainly studied in physics.
- It is also used in astrophysics.

Electronic Configuration of Elements

An atom of an element has different shells, sub-shells and orbitals and the distribution of electrons in these shells is called the electronic configuration. Electronic configuration of any orbital can also be represented by simple notation nlx,

where,

n = number of main or principle shell or the principal quantum number

l = symbol of sub-shell or orbital

x = no. of electrons present in that orbital

For example, 3p2 means that the p sub-shell in the 3rd main shell contains 2 electrons.

In order to fetch full electronic configuration of an atom, these notations are written one after the other in the increasing order of the orbital's energy. The filling of electrons in orbitals always starts from the orbital having the lowest energy with the electrons occupying the lower energy orbitals first.

Electronic configuration of few elements is given below:

Helium = $1s^2$

Beryllium = $1s^2 2s^1$

Carbon = $1s^2 2s^2 2px^1 2py1$

Element	**General outer electronic configuration**
s–block(alkali metals)	ns^{1-2}, where n = 2 – 7
p–block(metals &non metals)	$ns^2 np^{1-6}$, where n = 2 – 6
d–block(transition elements)	$(n-1)\ d^{1-10}\ ns^{0-2}$, where n = 4 – 7
f–block(inner transition elements)	$(n-2)f^{1-14}(n-1)d^{0-10}ns^2$, where n = 6 – 7

Stability of Completely Filled and Half-filled Orbitals

Almost all the elements follow the same trend for writing electronic configuration. Sometimes when two sub-shells differ in the energies, an electron from the lower energy moves to higher energy.

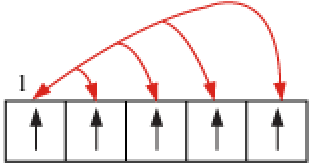
This is because of two reasons:

1. Symmetrical distribution: As everyone knows that symmetry leads to stability. The orbitals in which the sub-shell is exactly half-filled or completely filled are more stable because of the symmetrical distribution of electrons.

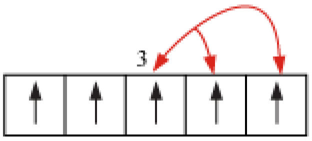
2. Exchange energy: The electrons which are there in degenerate orbitals have a parallel spin and tend to exchange their position. Exchange energy is nothing but the energy released during this process. When the orbitals are half-filled or completely filled then the number of exchanges is maximum. Therefore, its stability is maximum.

The electrons can be exchanged from one orbital to another if both orbitals are degenerate, i.e. they have same energy level.

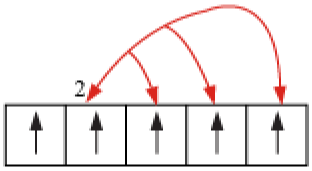
More the options for exchange, more is the electron's stability. The number of exchange pairs is maximum in half filled orbitals, hence it is more stable compared to partially filled



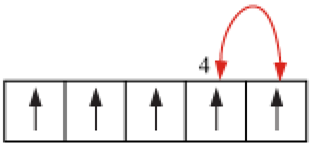
4 exchange by electron 1



2 exchange by electron 3



3 exchange by electron 2



1 exchange by electron 4

In case of copper there are two possibility or electronic arrangement I.e. 9 electrons in 3d subshell and 2 electrons in 4s subshell, another arrangement is 10 electrons in 3d subshell and 1 electron in 4s subshell but 1st type of electronic arrangement is in accordance of Aufbau principle but second type arrangement is not in accordance with Aufbau principle, similarly we have to compare the energy of 3d subshell having 9 electron and 3d subshell having 10 electron system whose energy is low that will be more stable.

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