

Classification of Elements & Periodicity in Properties

EARLIER ATTEMPTS OF PERIODIC CLASSIFICATION OF ELEMENTS

Section - 1

Certain groups of elements have similar chemical properties; we classify elements as members of the same chemical family. Such similarity in the properties of elements has led scientists to classify them in such a form where one can study them in an organized manner. Such an arrangement is called as **Periodic Table**. Some of significant earlier attempts are discussed below.

Dobereiner's Triads

In 1829, J. Dobereiner made an important first step towards a systematic classification by arranging elements into groups of three (triads). He observed that the atomic weight of the middle element of the group was midway between the atomic weights of the other two. He also concluded that the same midpoint relation held true for the physical properties of these elements.

Some of his triads were :

Li, Na, K

Cl, Br, I

Ca, Sr, Ba

Newland's law of Octaves

In 1865, Newland proposed that if the elements are arranged according to the increasing atomic weights (beginning with lightest element, excluding Hydrogen), the chemical and physical properties of a particular element would be similar to those of the elements seven places before and seven places after it (like the eight note in an octave of music). This led to the idea of periodicity for the first time in true sense.

For example, Li, the second element in Newland's list, had properties similar to Na, the ninth element in the list and K, the sixteenth element. Thus these were similar elements represented by numbers 2, 9, 16 that show interval of seven.

Mendeleev's Periodic law and Classification

In 1869, the Russian Chemist Mendeleev was successful in arranging the elements in the form a *periodic table*, in such a way that the elements having similar properties were placed in same vertical columns, called groups.

Mendeleev organized the elements according to a regular increase in the atomic weight. He thus obtained a pattern where similar chemical properties for element recurred periodically. In fact his observations were based on a periodic law stating :

“ The physical and chemical properties of the elements are periodic functions of their respective Atomic weights.”

His proposal was even backed by the predictions for the undiscovered elements. He took a bold step to leave the blank places for such elements. He in fact predicted the properties of these elements and called some of them as *eka-silicon* (Germanium), *eka-aluminum* (Gallium) and *eka-boron* (Scandium). Later on when these elements were discovered, Mendeleev's predictions were found to be amazingly accurate.

Modern Periodic Table

With the establishment of atomic theory in the first quarter of 20th century and work of physicist Henry Moseley, the chemical behavior of an atom is known to be dependent on its electrical characteristic signified by its *Atomic number (Z)*. So Mendeleev's periodic table was modified to include the later developments in so called *Long-form of periodic table*. It is based on modern Periodic Law stated as :

"The physical and chemical properties of the elements are periodic functions of their respective Atomic numbers"

In the long form of periodic, the elements having the same electronic configuration in their outer shell were grouped together. The electrons in the outer shell are termed as valence electrons. Valence electrons determine the properties and chemical reactivity of the elements and participate in chemical bonding (discussed later in the chapter).

Hence a major modification in the long form of periodic table, is the arrangement of elements in order of increasing Atomic numbers rather than increasing Atomic weights.

MODERN PERIODIC TABLE

Section - 2

In modern periodic table, elements are arranged in horizontal rows (*periods*) and vertical columns (*groups*). In all there are seven periods and eighteen groups. The groups were divided into two categories according to old convention. Now the groups are numbered from 1 to 18. In old convention group nos. were IA, IIA, VIIA, IB, IIB VIIB.

IA, IIA, IIIA, VIIA ; now written as 1, 2, 13, 14, 15, 16, 17, 18

IIIB, VIIB ; now written as 3, 4, 5, 6, 7

VIIB corresponds to 8, 9, 10 and IB, IIB correspond to 11, 12 respectively.

Periods :

Ist Period contains only two elements namely Hydrogen (H), Helium(He). It is called as *shortest period*.

IInd period starts with Lithium (Li) and contains eight elements.

Li, Be, B, C, N, O, F, Ne.

IIIrd period starts with Sodium (Na) and contains eight elements.

Na, Mg, Al, Si, P, S, Cl, Ar.

Note: II and III periods are called as *short-periods*.

IVth period contains eighteen elements starting with Potassium (K).

K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Br, Kr.

Vth period contains eighteen elements starting from Rubidium (Rb).

Rb, , Xe (Xenon).

Note: IVth and Vth periods are called as *long-periods*.

Extended or long of the Periodic Table

s-Block Elements (Main-Group elements)		d-Block Elements (Transition elements)										p-Block Elements (Main-Group elements)									
(1)		(2)–(10)										(11)–(18)									
I A		II B – VIII(B)										III A – VII A									
Groups		(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)	(14)	(15)	(16)	(17)	(18)				
Periods		II B	IV B	V B	VI B	VII B	VIII(B)			I B	II B	III A	IV A	V A	VI A	VII A	VIII A				
1	1	2										5	6	7	8	9	10				
	H	He										B	C	N	O	F	Ne				
	1.008	4.003										10.81	12.01	14.01	16.00	19.00	20.18				
2	3	4										13	14	15	16	17	18				
	Li	Be										Al	Si	P	S	Cl	Ar				
	6.941	9.012										26.98	28.09	30.97	32.07	35.45	39.95				
3	11	12										31	32	33	34	35	36				
	Na	Mg										Ga	Ge	As	Se	Br	Kr				
	22.99	24.31										69.72	72.64	74.92	78.96	79.90	83.80				
4	19	20										49	50	51	52	53	54				
	K	Ca										In	Sn	Sb	Te	I	Xe				
	39.10	40.08										114.8	118.7	121.8	127.6	126.9	131.3				
5	37	38										81	82	83	84	85	86				
	Rb	Sr										Tl	Pb	Bi	Po	At	Rn				
	85.47	87.62										204.4	207.2	209.0	(209)	(210)	(222)				
6	55	56										112	113	114	115	116	117				
	Cs	Ba										Uub	Uuh	Uuq	Uur	Uus	Uut				
	132.9	137.3										112	113	114	115	116	117				
7	87	88										112	113	114	115	116	117				
	Fr	Ra										Uub	Uuh	Uuq	Uur	Uus	Uut				
	(223)	(226)										112	113	114	115	116	117				
* Lanthanides series																					
6												66	67	68	69	70	71				
												Dy	Ho	Er	Tm	Yb	Lu				
												162.5	164.9	167.3	168.9	173.0	175.0				
† Actinides series																					
7												98	99	100	101	102	103				
												Cf	Es	Fm	Md	No	Lr				
												(251)	(252)	(257)	(258)	(259)	(260)				

VI period consists of 32 elements, starting from Cesium (Cs) and ending with Radon (Rn). It is called as *longest period*. Apart from the *representative* and *transition* elements this period also contains *Inner transition* elements called as *Lanthanides* (Ce,....., Lu).

VII period is incomplete period and at present contains 19 elements starting from Fr (Francium). Upto Uranium (U) all the elements are naturally occurring but rest are radioactive with very short half-lives. These also include a part of *inner transition* elements, called as *actinides* (Th,...Lr).

Groups :

Group 1 consists of H ($1s^1$), Li ($2s^1$), Na ($3s^1$),... The common outermost electronic configuration is ns^1 . Elements belonging to this group are called as *Alkali Metals*.

Group 2 consists of Be ($2s^2$), Mg ($3s^2$), Ca ($4s^2$),... The common electronic configuration is ns^2 . Elements of this group are called as *Alkaline Earth Metals*.

Group 13 consists of B ($2s^2 2p^1$), Al ($3s^2 3p^1$),... The common electronic configuration is $ns^2 np^1$. Elements of this group are called as *Boron Family*.

Group 14 contains C ($2s^2 2p^2$), Si ($3s^2 3p^2$),... The common electronic configuration is $ns^2 np^2$. This group is known as *Carbon Family*.

Group 15 contains N ($2s^2 2p^3$), P ($3s^2 3p^3$),... The common electronic configuration is $ns^2 np^3$. This group is known as *Nitrogen Family*. The elements of this group are also called as *PNICTOGENS* (*poisonous compounds forming elements*).

Group 16 contains O ($2s^2 2p^4$), S ($3s^2 3p^4$),... The common electronic configuration is $ns^2 np^4$. This group is known as *Oxygen Family*. The elements of this group are also famous as *CHALCOGENS* (*ore-forming elements*).

Group 17 contains F ($2s^2 2p^5$), Cl ($3s^2 3p^5$),... The common electronic configuration is $ns^2 np^5$. Elements of this group are called as *HALOGENS* (*salt forming elements*).

Group 18 (or Zero group) contains He ($1s^2$), Ne ($2s^2 2p^6$), Ar ($3s^2 3p^6$),... The common electronic configuration is $ns^2 np^6$. Elements of this group are called as *Inert Gases* or *Noble Gases*.

PERIODIC TABLE

s-block	p-block	d-block	f-block
<ul style="list-style-type: none"> Elements have last electron in s-orbital i.e. Group 1 and Group 2. Group No. of any element = no. of electrons in valence shell. 	<ul style="list-style-type: none"> Elements have last electron in p-orbital i.e. Group 13 - 18. Group No. of any element = no. of electrons in valence shell + 10. 	<ul style="list-style-type: none"> Elements have last electron in d-orbital i.e. Group 3 - 12. Group No. of any element = no. of elements in penultimate d-shell and valence shell. 	<ul style="list-style-type: none"> Elements have last electron in f-orbital.

H	p-Block																18	
1s	1	2	d-Block										13	14	15	16	17	18
2s	Li	Be											B	C	N	O	F	Ne
3s	Na	Mg											Al	Si	P	S	Cl	Ar
4s	K	Ca											Ga	Ge	As	Se	Br	Kr
5s	Rb	Sr											In	Sn	Sb	Te	I	Xe
6s	Cs	Ba											Tl	Pb	Bi	Po	At	Rn
7s	Fr	Ra											-	Uuq	-	-	-	-
			f-Block															
Lanthanids 4f			Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu		
Actinides 4f			Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr		

Features of Groups 1, 2, 13 – 18

- Elements belonging to these groups are in general called as *Representative Elements*
- General Electronic Configuration for group 1, 2 can be written as: ns^{1-2} and $ns^2 nd^{1-6}$, for group 13- 18.

n : here represents the *number of period* to which a particular elements belongs (principal quantum number).

The total number of electrons i.e., number of electrons in s & p sub-shells gives the *number of group* to which a particular elements belongs.

- Elements of 1 and 2 groups are also called as s -block elements, as final electron in these elements (also called as differentiating electron) enters s sub-shell. Elements of 13 to 18 groups are called as p -block elements, as differentiating electron in these elements enters p sub-shell.

Features of Groups 3 – 12

- Groups 3 to 12 are known as *transition elements* or d -block elements, as the differentiating electron (last electron) in these elements enters d -sub-shell. General electronic configuration of these elements can be written as $(n-1)d^{1-10} ns^{0-2}$.
- Group 3 has a special feature in sense that, it contains elements in which the differentiating electron enters the f sub-shell, hence these elements are also called as f -block elements apart from being called as *Inner transition elements*. These are placed in two horizontal rows below the table and are called as *Lanthanides* (also called as *Lanthanoides*) and *Actinides* (also called as *Actinoids*).

General electronic configuration of these elements is :

Lanthanoides : $4f^n 5d^{0-1} 6s^2$

Actinoids : $5f^n 6d^{0-2} 7s^2$.

Some other features of the periodic table are as follows :

Typical Elements

Elements of third period are also called as *Typical Elements*. These include Na, Mg, Al, Si, P, S, Cl. The properties of all the elements belonging to a particular group resemble the properties of the corresponding typical element of that group. For example, the general properties of Alkali Metal can be predicted from the behaviour of Na, not Li, the first member of the family.

The typical elements (all having $n = 3$) can take up 18 electrons. Note that, for these elements $3d$ sub-shell is available, but it is not filled i.e., these have vacant d sub-shell. This is not the case with second period elements, hence they have somewhat different properties than the rest of the group or we can say that it is the typical element, which in true sense represents a group.

Bridge Elements

Elements of second period are also called as *Bridge Elements*. The properties of these elements resemble with the properties of elements belonging to third period placed diagonally. This is illustrated as follows.

2 Period	Li	Be	B	C	N	O	F
3 Period	Na	Mg	Al	Si	P	S	Cl

Noble or Inert Gases

Elements of group 18 or zero group are called *Inert* or *Noble Gases*. They have completely filled (2 or 8 electrons in outermost shell) outermost shells, called as stable configuration. Their valency is zero. They are almost inert in their chemical behaviour. They have weak intermolecular forces in them and hence are gases and exist in monatomic states.

Classification of Elements based on their position in the periodic table

1. Metals

This is the largest class of the elements. This includes elements belonging to 1, 2, 3 to 12 (i.e. all transition and inner-transition elements) and some elements of groups 13 to 15 lying near the bottom of the table. The metals are characterized by their nature of readily giving up the electron apart from shining luster. The oxides of metals are basic in nature.

2. Non-metals

These do not give up electron, in fact like to take up the electron to form negative ion. These include 10 elements lying to the right side of the table. They are C, N, O, F (2nd period), P, S, Cl (3rd period), Se, Br (4th period) and I (5th period). The oxides of non-metals are acidic in nature.

3. Metalloid

You can have very easily observed that metallic character has decreased when one moves to the right of the table across a row. It is observed that some elements lying at the border of metallic and non-metallic behaviour, exhibit both the metallic and non-metallic character, these are called as *metalloids*. These include 8 elements namely ; B, Si, Ge, As, Sb, Te, Po and At. The oxides of metalloids are generally amphoteric in nature.

Note: The elements in group 18 do not behave like metals, nor do they behave like non-metals. So they are classified separately as Noble Gases. Also the element Hydrogen (H) is different from any other element and cannot be easily classified into a particular group (*however it is placed along with the Alkali Metals, though it does not exhibit metallic character*).

Properties of Elements like valency, atomic and ionic radii, ionization enthalpy, electron gain enthalpy, electronegativity etc. follow some regular trends as we move down a group or along a period. This is because all these properties depend on the electronic configuration of the atoms.

Besides there are some properties like melting point, boiling point, density, atomic volume etc. which are not defined for individual atoms but for a bulk (collection) of atoms. These properties are also indirectly related to electronic configuration of atoms and follow a regular trend along periods and groups.

- As we proceed down a column (group), outer-shell electronic configuration remains the same. The only difference in the atoms as we go down the table is that the nuclear charge and the number of inner shells increase. This thing happens in a regular manner.
- As we proceed across the periods (from left to right), electronic configuration of each element differs from that of one before in terms of an additional electron and some nuclear charge being added successively. Note that the number of shells in a period remains constant.

Let us discuss some of the important periodic properties.

1. Valency

It is defined as combining capacity of an element. It can also be defined in terms of valence electrons (*electrons in the outer most shells*). The valency is equal to number of valence electrons (*or equal to 8 minus the number of valence electrons*).

For *representative elements*, in general, valency of elements belonging to a chemical family i.e., in a group is constant. It is known from its general electronic configuration. To illustrate, for group 1 (Alkali metals), valency is 1 (ns^1), for group 2 (Alkaline earth metals), it is 2 (ns^2) and for group 3, it is 3 ($ns^2 np^1$).

For *transition elements*, no general trend is observed in the valency of elements. The reason is that those elements have variable valencies due to availability of vacant d-subshells in them.

Similar is the case with inner-transition elements (f-block elements) i.e., no general trend is observed due to variable valency.

2. Types of atomic radii :

It is impossible to define the size of atoms, as we know that atoms have no sharp boundaries due to delocalized picture of electron cloud. This is necessary in order to explain a number of chemical properties of different elements in terms of the size of their atoms or ions. There are four operational concepts which have been widely used. These are :

- (i) Covalent radii (ii) Ionic radii (iii) van der Waals' radii (iv) Metallic radii

(i) Covalent Radii

One of the techniques to define size is to study molecules that are made up of two atoms (for example, H_2 , Cl_2 , O_2 etc). These are held together by covalent bonds. In a molecule, two nuclei remain at a fixed average distance (d) from each other.

Atomic Radius is now defined as the average distance between the centres of two nuclei forming the covalent bond divided by 2. In this case atomic radius is called as *covalent radius* given by $d/2$.

Thus, for a homonuclear diatomic molecule, $r_{\text{covalent}} = \frac{1}{2}$ [Internuclear distance between two bonded atoms]

Since the internuclear distance between two bonded atoms is called the bond length. Therefore,

$$r_{\text{covalent}} = \frac{1}{2} [\text{bond length}]$$

For atoms which do not form such molecules 3s, same technique can be applied to their molecules with other atoms For example. C-Cl bond in CCl_4 etc.

Down the group : The sizes of atoms increases as we go down a column (group) of a periodic table. Each time we go down one step, the outer shell configuration is same, but there is an additional inner shell being added continuously. Consequently, the atomic size increases.

Increasing order of sizes in some families is shown below.

Li (1.33)	Be (0.90)	O (0.74)	F (0.71)
Na (1.54)	Mg (1.36)	S (1.02)	Cl (0.99)
K (1.96)	Ca (1.74)	Se (1.16)	Br (1.14)
Rb (2.16)	Sr (1.92)	Te (1.35)	I (1.33)

(Sizes given in brackets are in Å)

Along the period : In general, the sizes of the atoms decrease as we go down from left to right along the horizontal rows (periods) except group 18 (Noble Gases). All the electrons in an atom are under two influences. One is attraction of the electrons for the positive nucleus and other is mutual repulsion of the electrons for each other. It is important to note that both the forces are inversely proportional to the square of the distance between the electrons and the protons. Now as we go across the period, number of shells remains the same and electrons and protons are continuously added. This leads to considerable force of attraction between electrons and protons and consequently atoms become smaller. You can observe in above illustration that $r_{\text{Li}} > r_{\text{Be}} > r_{\text{O}} > r_{\text{F}}$, where r denotes atomic radii. Some Exceptions occur in case of *d*-block elements i.e. $\text{Ni} < \text{Cu} < \text{Zn}$, $\text{Pd} < \text{Ag} < \text{Cd}$.

(ii) Ionic Radii

It is defined as the distance between the nucleus and outermost shell of an ion. Losing an electron or two from the neutral atom forms a cation.

A positive ion is formed when the electrons are lost from the outer most shell. This ion is always smaller than the corresponding neutral atom. because it contains smaller number of electrons compared to neutral atom, while both contain same number of protons. The electrons in positive ions therefore experience a stronger pull towards nucleus as compared to neutral atoms and hence ion becomes smaller.

A negative ion is formed when an extra electron is added to a neutral atom. This ion is always larger than the corresponding neutral atom. because it has more electrons than neutral atom. Additional electron in negative ion creates more repulsion in the outer most shell and thus outer shell expands.

Periodic Properties of Elements

- The sizes of ions increase as we go down a group provided that we are comparing ions of same charge. For example
 $\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Rb}^+$
 $\text{Be}^{2+} < \text{Mg}^{2+} < \text{Ca}^{2+} < \text{Sr}^{2+}$
 $\text{F}^- < \text{Cl}^- < \text{Br}^- < \text{I}^-$
- Atoms or ions with the same electronic configuration are called as *isoelectronic*. If we consider a series of iso-electronic species (atoms or ions), the size decreases with the increasing atomic number. This is because the number of electrons and shell remain constant while positive charge of nucleus increase which pull the electrons more strongly. To illustrate the concept, Consider the following iso-electronic species all having 10 electrons.

Iso-electronic species	O^{2-} (1.40 ¹)	F^- (1.36)	Ne (1.31)	Na^+ (0.95)	Mg^{2+} (0.65)
Atomic number (Z)	8	9	10	11	12

(sizes given in the bracket are in Å)

- The size of cations of same element decreases with the increase in the magnitude of positive charge. For example, Cu^{2+} is smaller than Cu^+ , Fe^{3+} is smaller than Fe^{2+} , Sn^{4+} is smaller than Sn^{2+} .

(iii) Van der Waals' radius

It is defined as one-half the distance between the nuclei of two identical non-bonded isolated atoms or two adjacent identical atoms belonging to two neighbouring molecules of an element in the solid state.

The magnitude of the van der Waals' radii depends upon the packing of the atoms when the element is in the solid state.

(iv) Metallic radius

It is defined as one-half the inter-nuclear distance between the two adjacent metal ions in the metallic lattice.

According to Electron-sea model, a metal lattice or crystal consists of positive kernels or metal ions (left after the removal of valence electrons) arranged in a definite pattern in a sea of mobile valence electrons. Thus, each kernel (i.e., metal ion) is simultaneously attracted by a number of mobile electrons and each mobile electron is attracted by a number of metal ions. This simultaneous force of attraction between the mobile electrons and the positive kernels is called the *metallic bond*.

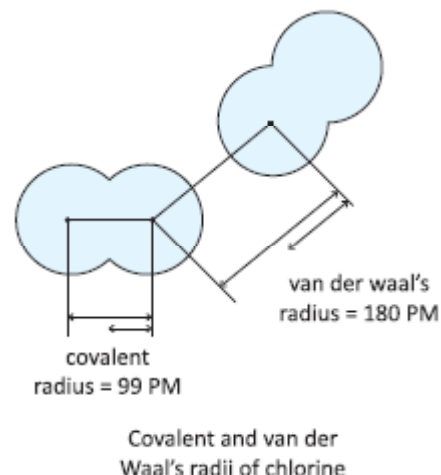
The inter-nuclear distance is determined by X-ray studies and the metallic radius is usually expressed in angstrom units or picometers.

Since in a metallic lattice, the valence electrons are mobile, therefore, they are only weakly attracted by the metal ions or kernels. In contrast to covalent bond, a pair of electrons is strongly attracted by the nuclei of two atoms. Thus, a metallic radius is always longer than its covalent radius.

Comparison of covalent radius and van der Waal's radius

Van der Waal's radius of an element is always larger than its covalent radius because of the following two reasons :

- (i) Since the van der Waal's forces of attraction are weak, therefore the inter-nuclear distances in case of atoms held by van der Waal's forces are much larger than those between covalently bonded atoms. *Therefore, van der Waal's radii are always larger than covalent radii.*

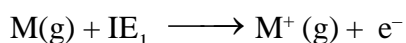


- (ii) Since a covalent bond is formed by overlap of two half-filled atomic orbitals, a part of the electron cloud becomes common. *Therefore, covalent radii are always smaller than the van der Waals' radii.*

A comparison of three types of atomic radii discussed above reveals that van der Waal's radius is the longest while covalent radius of an atom is the shortest, i.e., *vander Waal's radius > metallic radius > covalent radius.*

3. Ionisation energy

First ionization energy is defined as the energy required to remove a single electron from the outer shell of a neutral gaseous atom. Consequently the atom changes to a mono-valent cation



Down the Group: First ionization energy decreases as we go down a group in the table. It measures the ease of removing an electron from the outer shell. As we go down a group, this shell is farther away from the nucleus. It is true that the positive charge of nucleus increases, but its effect is weakened due to the shielding supplied by the inner shells to the outer most shell. As a result nuclear attraction decreases. Some exception occurs in group 13 where the ionisation energy of Ga is more than that of Al. It is due to the fact that Ga has electrons filled in d-shell and shielding of d shell to nucleus is comparatively small. So increased nuclear charge effect dominates here.

Along the period: As we go from left to right across a period, the atomic size decreases. As the number of shells in a particular period remains same and new electrons are being continuously introduced in the outer shell, the outer electrons are greatly attracted to the nucleus. Hence it becomes difficult to remove them and consequently first ionization energy increases.

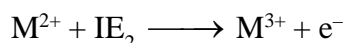
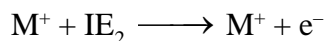
In the following table, I ionization energies (in eV) of II period are shown :

Li	Be	B	C	N	O	F	Ne
5.39	9.32	8.3	11.26	14.53	13.62	17.42	21.56

You should have clearly noted two irregularities as we move from left to right in the above table.

- I.E. of B < I.E. of Be. When Be loses an electron, it is removed from a fully filled $2s$ sub-shell, whereas B gives its lone $2p$ electron. Hence *extra-stability of fully filled sub-shell* is the cause of this irregularity.
- I.E. of O < I.E. of N. Here half filled ($2p^3$) outer most sub-shell of N is highly stable and hence it becomes difficult to remove the electron. Thus *extra-stability of half filled sub-shells* is the cause of irregularity.

Second ionization energy is defined as the amount of energy required to remove the second electron from an atom that has already lost an electron, i.e. to remove an electron from a mono-valent cation. Third and higher I.E.(s) are analogously defined.



In general : $IE_1 < IE_2 < IE_3 < \dots\dots\dots$

This happens because, as the number of electrons decreases regularly, the attraction of the nucleus for the remaining electrons increases considerably (which are now less in number), and hence subsequent I.E.(s) increase.

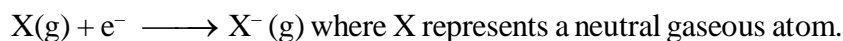
- Whenever all the outer-shell electrons are removed, the next I.E. is much greater than the previous value of I.E. for the same element. Note that first I.E. of Li is 5.39 eV and the second I.E. for the same is 75.64 eV.
- If we compare first I.E.s of the elements in a period (e.g., Li.....Ne), the noble gas (Ne in present case) had the highest I.E. A noble gas configuration ($ns^2 np^6$) is completely filled and hence highly stable.
- The electrons in different orbitals (s, p, d or f) belonging to the same energy level (i.e., same value of n) experience different pull of the nucleus. The I.E. for pulling out an s -electron is maximum and it decreases in pulling out p -electron, a d -electron or a f -electron of the same principal energy shell in the order of their mention. Hence we can say that I.E. for pulling out an electron from a given energy level decreases in the order $s > p > d > f$ orbitals. For example first I.E. of Al is lower than that of Mg. Here two factors govern the first I.E. the extra stability of fully filled sub-shells apart from the above mentioned factor.

Factors affecting the ionisation energy

- | | |
|---|--|
| 1. The charge on the nucleus | 2. The size of the atom |
| 3. Presence of half filled or fully filled orbitals | 4. Shielding of s, p, d or f orbitals. |

4. Electron Affinity

It is defined as the energy given out when a neutral gaseous atom takes up an extra electron.



Electron affinity of an atom measures the tightness with an atom bonds an extra electron to it. The value of electron affinity shows the same trend as atomic size and ionization energy. It is also known as *Electron Gain Enthalpy*.

- It decreases down a group, because as the atom gets larger (due to increasing atomic size), the attraction of positive nucleus for an outside electron decreases. Exception: in halogens, Fluorine (F) has lower electron affinity than Chlorine (Cl). It is mainly due to extremely small size of F atom as compared to that of Cl. The addition of an extra electron creates a high electron density and hence strong electron-electron repulsion is not highly favoured. Due to the same reason oxygen has smaller affinity than sulphur.
- It in general increases when one moves from left to right across a period. It is due to decreasing atomic size (across a period) that the nuclear attraction for an additional electron increases. Hence the electron affinity and I.E. of metals is low while that of non-metals is high.
- The electronic configuration of elements also affects their electron affinities. Electron affinities of Noble gases are zero. It is attributed to their fully filled stable configuration ($ns^2 np^6$). Also the electron affinity of N and Be atoms are quite low due to extra stability of half filled orbitals and fully-filled orbitals (p^3 in N and s^2 in Be).
- The concept of higher electron affinities is rather interesting. After taking up an extra electron an atom becomes negatively charged (*anion*) and now a second electron is to be added to it. The anion will repel the incoming of an electron and an additional energy will be required to add it to the anion. This means first E.A is the energy released while the second E.A. is the energy required. If one considers the energy released as *negative* and that required as *positive* then first E.A of O is -141 KJ/mol and second E.A. is $+770 \text{ KJ/mol}$.

Factors on which the Electron Gain Enthalpy depends

Some important factors on which electron affinity depend are discussed below:

- (i) **Atomic size** : As the size of the atom increases, the distance between the nucleus and the last shell which receives the incoming electron, increases. As a result, the force of attraction between the nucleus and the incoming electron decreases and hence the electron gain enthalpy becomes less negative.
- (ii) **Nuclear charge** : As the nuclear charge increases, the force of attraction between the nucleus and the incoming electron increases and hence the electron gain enthalpy becomes more negative.
- (iii) **Electronic configuration** : Elements having exactly half-filled or completely filled orbitals are very stable. As a result, energy has to be supplied to add an electron. Hence their electron gain enthalpies have large positive values the additional electron so easily and easily and hence their electron affinities are either very low or are almost zero.

5. Electronegativity

It is the measure of the ability of an atom in a combined state (i.e. in a molecule) to attract to itself the electrons within a chemical bond. In general in the covalent bond both the atoms don't share the electron pair equally. It depends upon the pulling power (electronegativity) of the atom for electrons that which atom will share the electron pair dominantly. More the electronegativity of the atom, more dominantly it will share the electron pair. Electron pair will get slightly shifted towards the more electronegative atom and this atom will acquire a δ^- charge resulting in δ^+ charge on the other atom.

In general, non-metals have high value of electronegativity while the metals have a quite low value. For example F, O, N and Cl (non-metals) are highly electronegative whereas K, Rb and Cs (metals) are non-electronegative, *in fact they are electropositive*.

- It follows the same trends as shown by electron affinity or ionization energy. This means that *higher I.E. and greater E.A., both results in high electronegativity*.
- Across a period from left to right the electronegativity increases due to increase in the nuclear charge and decrease in atomic size. Down the group electronegativity decreases due to the increase in effective nuclear attraction force. Fluorine has the highest electronegativity of any element.
- The difference in electronegative values of two atoms in a compound predicts the nature of chemical bond formed between two atoms. More the difference between the electronegativity of two atoms involved in a bond more will be the ionic character. There is no direct method to measure the value of electronegativity, however there are some scales to measure its value.

Pauling scale

According to Pauling, electronegativity difference ($X_A - X_B$) in between two atoms A & B is given by :

$X_A - X_B = 0.208 \sqrt{\Delta}$ where $\Delta = E_{A-B} - \sqrt{E_{A-A} \times E_{B-B}}$ where E_{A-B} , E_{A-A} and E_{B-B} are bond energy of molecules AB, A_2 and B_2 respectively in kcal/mole. This scale is the most popular scale.

Mulliken scale

According to Mulliken, the electronegativity of an atom is the average of the two values i.e.. electron affinity and ionization energy.

$$\text{Electronegativity} = \frac{IE + EA}{2} \text{ where I.E. and E.A. are in kJ/mol.}$$

$$\text{Note : } X_{\text{Mulliken}} = X_{\text{Pauling}} \times 2.8$$

Allred - Rechow scale

According to this concept, electronegativity of an atom is simple electrostatic force of attraction between atoms and an electron separated from the nucleus by the covalent radius. i.e. electronegativity

$$= \frac{0.359 Z_{\text{eff}}}{r^2} + 0.744, \text{ where } Z_{\text{eff}} \text{ is the effective nuclear charge and } r \text{ is covalent radius of atom in } \text{\AA}.$$

6. Atomic Volume

Atomic volume of an element is the ratio of its gram-atomic weight to its density. In a group, atomic volume generally increases from top to the bottom. Actually it is not a very good periodic property as different elements have different packing arrangements in solid states, so a general trend is not observed. This is particularly true in right side of the periodic table where in halogens and Fe-Pt sub-groups it becomes nearly constant. Note that atomic volume is a bulk property. It depends on the packing of atoms as well.

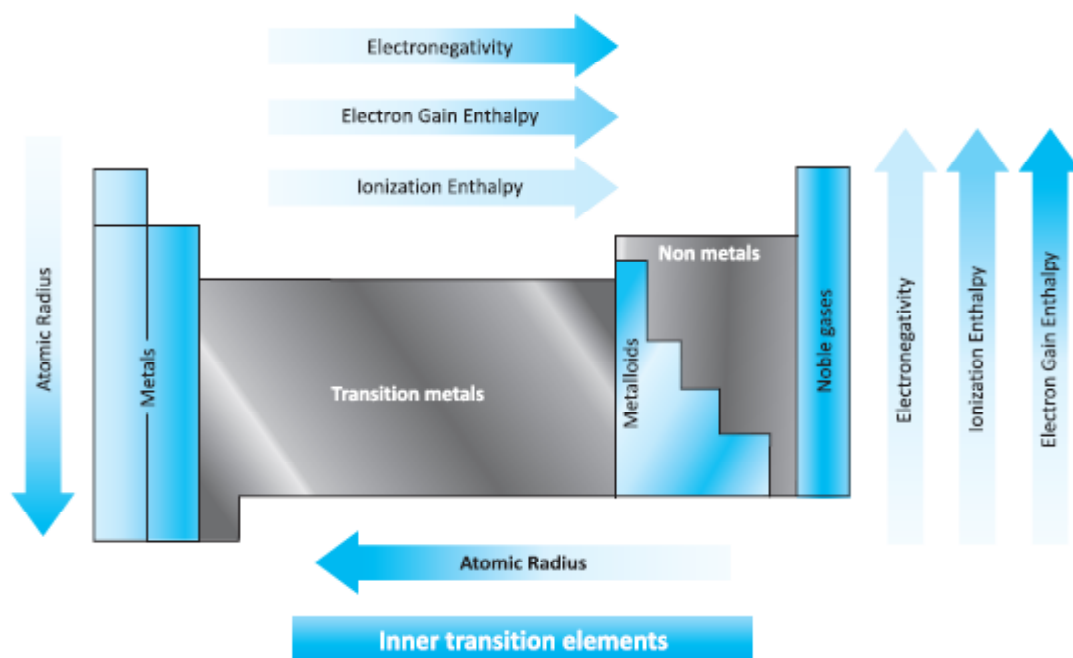
7. Metallic Character

Metallic character or the electropositive character of an element is defined as its tendency to lose electrons and form positive ions. Metallic character increases down the group and decreases along the period (from left to right). There is a series of metallic (electropositive) character that is good to remember.



The trick to remember this series is to remember the name PSBC MAZINTL CHAAP

In PSBC P = Potassium, S = Sodium, B = Barium, C = Caesium. In MAZINTL, M = Mg, A = Al, Z = Zn, I = Iron, N = Nickel, T = Tin, L = Lead. In chaap C = Cu, A = Ag, A = Au, P = Pt. Also note that Hydrogen (not a metal) comes between Mazintl and Chaap.



Summary of the trends in the Periodic Properties of Elements in the Periodic Table

Note : Direction of arrow represents the increase in property.

Note that Electronegativity, Ionisation Enthalpy, electron gain Enthalpy follow the same trends because they all represent the same character - attraction of nucleus for the outermost shell electron. While Atomic radius follows trends opposite the three.

There are some effects which sometimes affect the periodic properties.

(i) Penetration effect of the electrons

Ionization enthalpy increases as the penetration effect of the electrons increases. It is a well known fact that in case of multi-electron atoms, the electrons of the s-orbital has the maximum probability of being found near

the nucleus and this probability goes on decreasing in case of p , d and f -orbitals of the same shell. In other words, s -electrons of any shell are more penetrating towards the nucleus than p -electrons of the same shell. Thus, within the same shell, the penetration effect decreases in the order : $s > p > d > f$

Obviously, if the penetration effect of the electron is more, it will be closer to the nucleus and hence will be held more firmly by the nucleus. Consequently, the ionization enthalpy will be high. In other words, ionization enthalpy increases with the increase in the penetration effect of electrons. *Thus, the ionization enthalpy will be more to knock out a s -electron of the same shell, which in turn, will be more than that required to remove a d -electron and so on.*

(ii) Screening (shielding) Effect

The electrons in the valence shell experience an attractive force from the nucleus and a repulsive force from the electrons in the inner shells. The overall effect of these two opposing forces is that the attractive force exerted by the nucleus on the valence shell electrons is somewhat reduced by the repulsive force exerted by the electrons present in the inner shells. This affects the nuclear attraction of the positive nucleus for the outer electrons. In d -block elements (transition elements), while writing electronic configuration of elements, it is seen that the new electrons are being added to the inner shell i.e., penultimate shell ($3d$ after $4s$, $4d$ after $5s$ and so on). As the differentiating electron enters the inner shells, they tend to screen or shield the outer shell electrons from the nucleus and hence offset the nuclear attractive force.

The actual charge felt by the valence shell electrons is called effective nuclear charge and the repulsive force felt by the valence shell electrons from the electrons present in the inner shells is called the shielding effect or screening effect. Shielding effect of shells closer to nucleus is higher and it follows the trends $s > p > d > f$. Due to this effect, the atomic size of transition elements (*which should have been decreasing across a period*) remains nearly same or constant. The same is the case with ionisation energy, electron affinity and other periodic properties when one moves across a period.

(iii) Inert Pair Effect

Inert pair effect occurs when electrons are pulled closer to nucleus making them stabler and more difficult to ionise. It is basically the tendency of outermost (or valence) 's' electrons to remain non-ionised (and not participate in bonding). It occurs because of the poor shielding of the nucleus by the inner 'd' -electrons due to which the outer 's' electrons are more tightly bound to the nucleus and become less able to participate in bond formation. This effect is especially seen in group 13 and 14 of the periodic table, in which the heavier elements in the group tend to form compounds with valency two lower than the expected group valency. For e.g. the lighter elements in Group IV tend to have a valency of +4 whereas the heavier elements form $2+$ ions that are more stable than $4+$ ions. For example, PbO is much more stable than PbO_2 which decomposes readily to PbO .

Magnetic Properties

Each element has some kind of magnetic properties associated with it. These magnetic properties are direct consequence of the electronic configuration of the atom. An electron in an atom has two kind of motions. One is its motion about the nucleus and the other is its spin about its own axis. A single electron spinning about its

own axis generates a magnetic field. For two electrons in an orbital the spins are opposite and hence the fields cancel each other. Thus on the basis of magnetic properties substances can be classified broadly into three categories (i) Paramagnetic (ii) Diamagnetic (iii) Ferromagnetic.

- (i) **Paramagnetism:** Some substances have one or more unpaired electrons in their atoms. These substances are called as paramagnetic substances. These substances are weakly attracted by magnetic field. Cu^{2+} , Fe^{3+} , Cr^{3+} and O_2 are some examples of these kind of substances.
- (ii) **Diamagnetism:** Some substances have all the electrons paired in their atoms. These substances are called as diamagnetic substances. Thus substances are weakly repelled by magnetic field. NaCl and H_2O are some examples of diamagnetic substances.
- (iii) **Ferromagnetism:** Beside paramagnetic and diamagnetic substances there are some kind of substances which are strongly attracted by magnetic field. These substances are called Ferromagnetic substances. Ferromagnetism is much stronger than paramagnetism and diamagnetism. Ferromagnetic substances keep their magnetism even after the field is removed while paramagnetic and diamagnetic substances fail to do so. Iron, cobalt and Nickel are some examples of these kind of substances.

Some Additional Information

All the elements with $Z = 101 - 112$ and $Z = 114$ have recently been identified. Although names and symbols to many of these elements have been assigned but these are still not universally accepted. Also some of these elements have been assigned two names/symbols. For example, element with $Z = 104$ is called either Kurchatovium (Ku) or Rutherfordium (Rf) while element with $Z = 107$ is called Neilsbohrium (Ns) or simply Bohrium (Bh). To overcome all these difficulties, IUPAC approved the official names for elements with $Z = 104$ to $Z = 109$ and suggested a systematic nomenclature for naming other elements with $Z > 100$ (also collectively called as super heavy elements) till their names are officially announced.

The main points of this nomenclature are :

- (i) The names are derived directly from the atomic numbers using numerical roots for 0 and numbers from 1 – 9 and adding the suffix ium. A strange mixture of Latin Greek roots has been chosen to ensure that the symbols are all different. The roots for the numbers 0 – 9 are :

Roots for IUPAC Nomenclature of Elements

Digit	0	1	2	3	4	5	6	7	8	9
Root	nil	un	bi	tri	quad	pent	hex	sept	oct	enn
Abbreviation	n	u	b	t	q	p	h	s	o	e

- (ii) In certain cases, the names are shortened. For example, *bi ium* and *tri ium* are shortened to *bium* and *trium* and *enn nil* is shortened to *ennil*.
- (iii) The symbol of the element is then obtained from the first letters of the roots of numbers which make up the atomic number of the element. The recommended and official names of some super heavy element are given in Table.

IUPAC Nomenclature of Elements with Atomic Number above 100

Atomic Number	Name	Symbol
101	Un-nil-unium	Unu
102	Un-nil-bium	Unb
103	Un-nil-trium	Unt
104	Un-nil-quadium	Unq
105	Un-nil-pentium	Unp
106	Un-nil-hexium	Unh
107	Un-nil-septium	Uns
108	Un-nil-octium	Uno
109	Un-nil-ennium	Une

Atomic Number	Name	Symbol
110	Un-un-nillium	Uun
111	Un-un-unium	Uuu
112	Un-un-bium	Unb
113	Un-un-trium	Unt
114	Un-un-quadium	Uuq
115	Un-un-pentium	Uup
116	Un-un-hexium	Uuh
117	Un-un-septium	Uus
118	Un-un-octium	Uuo

Illustration - 1

The formation of $F^{-}(g)$ from $F(g)$ is exothermic whereas that of $O^{2-}(g)$ from $O(g)$ is endothermic. Explain.

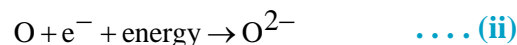
SOLUTION :

The addition of an electron to a neutral atom is an exothermic process.



The addition of second electron to a monovalent anion O^{-} , as to make it O^{2-} is difficult because both have the same charge and experience a lot of repulsion.

Thus, the addition of an electron to O^{-} requires energy to overcome the force of repulsion.



The energy absorbed in (ii) step is more than the energy in the step(i). Hence, the formation of O^{2-} from O is endothermic in nature.

Illustration - 2

(a) Why chlorine has higher negative electron gain enthalpy than F ?

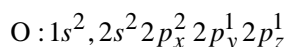
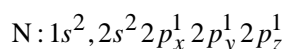
(b) Why N has higher 1^{st} ionization enthalpy than O -atom ?

(c) Why Mg has higher 1^{st} ionization enthalpy than Al -atom ?

SOLUTION :

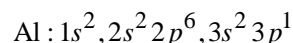
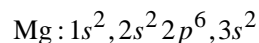
(a) The size of fluorine atom is small and thus electron density is high. This resists the addition of electron, hence electron gain enthalpy of fluorine is less.

(b) The electronic configurations of nitrogen and oxygen are follows:



In, N p -orbitals are half and hence, its structure is stable. It requires more energy to remove an electron. Hence, the IE of nitrogen is higher than oxygen atom which has less stable structure.

(c) The electronic configurations of Mg and Al are as follows:



It is difficult to remove an electron from $3s$ in comparison to $3p$ ($3s$ paired and $3p$ singly occupied).

Hence, IE of Mg is higher than Al .

Periodic Properties of Elements

Illustration - 3 Arrange the following in order of increasing radii :

- (i) I, I^+, I^- (ii) C, N, Si, P (iii) O^{2-}, F^-, Ne, Mg^{2+} (iv) Fe, Fe^{2+}, Fe^{3+}

SOLUTION :

- (i) $I^+ < I < I^-$

z/e values are $\frac{53}{52}, \frac{53}{53}, \frac{53}{54}$ respectively.

Since z/e decreases, hence size increases.

- (ii) $N < C < P < Si$

(a) Effective nuclear charge in nitrogen is higher than in carbon, hence $N < C$.

(b) Effective nuclear charge in phosphorus is higher than in silicon, hence $P < Si$.

(c) C and Si both belong to same group.

C $1s^2, 2s^2 2p^2$ (Two orbits)

Si $1s^2, 2s^2 2p^6, 3s^2 3p^2$ (Three orbits) $C < Si$

- (iii) $Mg^{2+} < Ne < F^- < O^{2-}$

z/e values are $\frac{12}{10}, \frac{10}{10}, \frac{9}{10}, \frac{8}{10}$ respectively.

Since z/e decreases, hence size increases.

- (iv) $Fe^{3+} < Fe^{2+} < Fe$

z/e values are $\frac{26}{23}, \frac{26}{24}, \frac{26}{26}$ respectively.

Since z/e decreases, hence size increases.

Illustration - 4 Give the formula of a species that will be isoelectronic with the following atoms or ions :

- (i) Ar (ii) F^- (iii) K^+ (iv) Sr^{2+}

SOLUTION :

(i) Ar has 18 electrons. Therefore, the species $P^{3-}, S^{2-}, Cl^-, K^+, Ca^{2+}$, etc., are isoelectronic to Ar.

(ii) F^- has 10 electrons. Therefore, the species $N^{3-}, O^{2-}, Ne, Na^+, Mg^{2+}$, etc., are isoelectronic to F^- .

(iii) K^+ has 18 electrons. Therefore, the species $P^{3-}, S^{2-}, Cl^-, Ar, Ca^{2+}$, etc., are isoelectronic to K^+ .

(iv) Sr^{2+} has 36 electrons. Therefore, the species Br, Kr, Rb^+ , etc., are isoelectronic to Sr^{2+} .

Illustration - 5 The ionization enthalpy of lithium is 520 kJ mol^{-1} . Calculate the amount of energy required to convert 140 mg of lithium atoms in gaseous state into Li^+ ion.

SOLUTION :

Mass of lithium = $140 \text{ mg} = 140 \times 10^{-3} \text{ g} = 14 \times 10^{-2} \text{ g}$

No. of moles of lithium = $\frac{14 \times 10^{-2}}{7} = 2 \times 10^{-2} \text{ mole}$

Energy required to convert $2 \times 10^{-2} \text{ mole}$ atoms of lithium into Li^+ ions = $520 \times 2 \times 10^{-2} = 10.4 \text{ kJ}$

Illustration - 6 The first and second ionization enthalpies (kJ mol^{-1}) of three elements I, II and are given below.

	I	II	III
$\Delta_i H_1$	403	549	1142
$\Delta_i H_2$	2640	1060	2080

Identify the element which is likely to be :

- (a) non-metal (b) an alkali metal (c) an alkaline earth metal.

SOLUTIONS :

- (a) Element (III) is a non-metal because its $\Delta_i H_1$ is highest among the three.
- (b) Element (I) is an alkali metal as its first ionization enthalpy is lowest and second ionization enthalpy is very high.
- (c) Element (II) is an alkaline earth metal because its first ionisation enthalpy is near to enthalpy of element (I) and second ionisation enthalpy is not very high.