3. CLASSIFICATION OF ELEMENTS AND PERIODICITY IN PROPERTIES

Earlier classifications

1) **Dobereiner's classification**:

Johann Dobereiner classified elements into small groups each containing three elements. These small groups were called *triads*.

E.g. for triads are: i) ^{7}Li ^{23}Na ^{39}K
ii) ^{40}Ca ^{88}Sr ^{137}Ba

In triads, the atomic mass of the middle element is approximately the average of the other two elements. This is known as ***Law of Triads***. This classification was rejected, since the law of triad is applicable only to a very few elements.

2) **Newlands classification:**

Newland arranged elements in the increasing order of their atomic masses. He noted that the properties of every eighth element, starting from a given element, are similar to that of the first element. The relationship is just like the resemblance of first and eighth musical notes. He named this **as law of octaves**.

But his classification was rejected since the law of octaves was applicable to elements upto calcium.

A.E.B. de Chancourtois arranged elements in increasing order of atomic weights and made *a cylindrical table of elements* to display the regular repetition of properties.

3) **Lothar Meyer's classification:** Lothar Meyer plotted the physical properties of elements like *atomic volume, melting point and boiling point* against *atomic weight* and obtained a periodically repeated pattern. Based on this, he developed a periodic table similar to that of Mendeleev's.

4) **Mendeleev's classification:**

Dmitri Mendeleev (a Russian chemist) classified the elements in the increasing order of their atomic weights. He found that the properties of elements repeat after a regular interval. Based on this observation, he proposed a **periodic law** which states that "The properties of elements are the periodic functions of their atomic weights." That is, when elements are arranged in the increasing order of their atomic weights, their properties repeat after a regular interval.

Mendeleev's periodic table contains horizontal rows called series (periods) and vertical columns called groups. Elements with similar properties are placed in the same group. He mainly depends on the similarities in the empirical formulae and the properties of the compounds formed by the elements. So he did not strictly obey the increasing order of atomic weights. Also he corrected the wrong atomic masses of some elements.

When Mendeleev proposed his periodic table, some of the elements were not discovered. He left some vacant places (gaps) for them in the periodic table and predicted some of their properties. For e.g. both ***Gallium and Germanium*** were not discovered at that time. He named these elements as ***Eka-Aluminium and Eka-Silicon*** respectively and predicted their properties. These elements were discovered later and found that Mendeleev's predictions were correct.

Merits of Mendeleev's periodic table

1) It was the first comprehensive classification of elements.
2) He corrected the wrong atomic weights of some elements and placed them in correct position in the periodic table.
3) He left vacant places for undiscovered elements and predicted some of their properties.
4) Elements with similar properties are placed in the same group.

Demerits of Mendeleev’s periodic table

1) Elements with dissimilar properties are found in same group.
2) He could not give an exact position for hydrogen.
3) He could not give exact position for Lanthanoids and Actinoids and also for isotopes.
4) Mendeleev’s periodic table did not strictly obey the increasing order of atomic weights.

Modern Periodic table

Henry Moseley’s work on the X-ray spectra of elements proved that atomic number is a more fundamental property than atomic mass. Based on this observation, he modified the Mendeleev’s periodic law as “*the physical and chemical properties of elements are the periodic functions of their atomic numbers*”. This is known as **Modern Periodic law**.

Based on the modern periodic law, numerous forms of periodic tables have been proposed. The most commonly used is ***the long form of periodic table***.

In this periodic table, the elements are arranged in the increasing order of their atomic number. It contains **7** horizontal rows called **periods** and **18** vertical columns called **groups** or **families**.
In the long form of modern periodic table, hydrogen has given a particular position at the top centre.

PERIODS

There are 7 periods in Modern periodic table. The period number corresponds to the highest principal quantum number of the elements.

Period No.	Elements	No. of Elements	Subshells filled	Description
I	${}_{1}$H & ${}_{2}$He	2	1s	Very short period
II	${}_{3}$Li to ${}_{10}$Ne	8	2s & 2p	Short periods
III	${}_{11}$Na to ${}_{18}$Ar	8	3s & 3p	
IV	${}_{19}$K to ${}_{36}$Kr	18	4s, 3d & 4p	Long periods
V	${}_{37}$Rb to ${}_{54}$Xe	18	5s, 4d & 5p	
VI	${}_{55}$Cs to ${}_{86}$Rn	32	6s, 4f, 5d & 6p	Longest periods
VII	${}_{87}$Fr to ${}_{118}$Og	32	7s, 5f, 6d & 7p	

The 14 elements each of sixth and seventh periods are placed in separate rows below the main body of the periodic table. These are together called **inner transition elements**. The 14 elements of sixth period [from ${}_{57}$Ce (cerium) to ${}_{71}$Lu (lutetium)] are called *Lanthanides or Lanthanones or Lanthanoids or rare earths*. The 14 elements of seventh period [from ${}_{90}$Th (thorium) to ${}_{103}$Lr (lawrencium)] are called *Actinides or Actinones or Actinoids.*

GROUPS

Vertical columns in Long form of Modern periodic table are called groups or families. There are 18 groups and these are numbered from 1 to 18. Due to the similar outer electronic configuration and same valency, the elements present in the same group have similar properties.

Group No.	**Elements**	**General outer Electronic configuration**	**Family name**
1	Li, Na, K, Rb, Cs & Fr	ns^1	Alkali metals
2	Be, Mg, Ca, Sr , Ba & Ra	ns^2	Alkaline earth metals
3 to 12	4 rows of elements	$(n-1)d^{1\text{ to }10}\ ns^{\ 0\text{ to }2}$	Transition elements
13	B, Al, Ga, In, Tl & Nh	$ns^2\ np^1$	Boron Family
14	C, Si, Ge, Sn, Pb & Fl	$ns^2\ np^2$	Carbon Family
15	N, P, As, Sb, Bi & Mc	$ns^2\ np^3$	Nitrogen Family
16	O, S, Se, Te, Po & Lv	$ns^2\ np^4$	Oxygen Family
17	F, Cl, Br, I, At, Ts	$ns^2\ np^5$	Halogen Family
18	He, Ne, Ar, Kr, Xe, Rn, Og	$ns^2\ np^6$	Noble gases

The Blocks in the Modern periodic table

The Modern periodic table is divided into 4 blocks based on the subshell in which the last electron enters. They are s block, p block, d block and f block.

1. The s-block elements

These are elements in which the last electron enters in the outer most s sub shell. They include elements of the groups 1 and 2. Their general outer electronic configuration is ns^1 or ns^2. They are all reactive metals with low ionization enthalpies. They lose their outer most electrons readily to form +1 and +2 ions. Their metallic character and reactivity increases down the group. They mainly form ionic compounds (except Li and Be).

2. The p-block elements

These are elements in which the last electron enters in the outer most p sub shell. They include elements of the groups 13 to 18. Their general outer electronic configuration is $ns^2\ np^{1\text{ to }6}$. Their non-metallic character increases from left to right in a period and metallic character increases from top to bottom in a group.

The 18th group elements are called Noble gases or inert gases. They have completely filled orbitals and so they do not undergo chemical reactions at ordinary conditions.

s and p block elements are together called ***Representative elements,*** *because these are the only elements which show the general trends in the periodic table and also they contain metals, non-metals and metalloids.*

3. The d-block elements

These are elements in which the last electron enters in the penultimate d sub shell. They include elements of the groups 3 to 12. They are also called **Transition elements (Transition metals)**, since they show a regular transition (change) from the most electropositive s block elements to the least electropositive p block elements. Their general outer electronic configuration is $(n-1)d^{1\text{ to }10}\ ns^{0\text{ to }2}$.

Some properties of transition elements are:

a) *They are all metals.*
b) *They form coloured compounds or ions in aqueous solution.*
c) *They show variable oxidation states and valencies.*
d) *They are generally paramagnetic.*
e) *They show catalytic properties.*

4. The f-block elements

These are elements in which the last electron enters in the anti-penultimate f sub shell. They include *lanthanides of 6th period and actinides of 7th period*. They are also called **Inner transition elements**. Their general outer electronic configuration is $(n-2)f^{1\text{ to }14}(n-1)d^{0\text{ to }1}\ ns^2$. They are all metals. Within each series the properties of these elements are similar. Actinoid elements are radioactive. Elements after Uranium (z=92) in the actinide series are called **trans-uranium elements or trans-uranic elements or artificial elements**. [Neptunium ($_{93}Np$) and Plutonium ($_{94}Pu$) are also found naturally in Pitch blende, an ore of Uranium].

Electronic configuration of an element and its position in the periodic table

From the electronic configuration of an element, we can assign its period, group and block in the periodic table.

Block: The subshell in which the last electron enters.
Period number = the highest principal quantum number in its electronic configuration.
Group number: For s-block elements = no. of valence s electrons
For p-block elements = no. of valence s electrons + valence p electrons + 10
For d-block elements = no. of valence s electrons + no. of penultimate d electrons.

Nomenclature of elements with atomic numbers > 100

For naming elements with atomic number > 100, IUPAC has made some recommendations. A systematic nomenclature be derived directly from the atomic number of the element using the numerical roots for 0 and numbers 1-9.

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

The roots are put together in order of digits which make up the atomic number and "ium" is added at the end.

Atomic Number	Name according to IUPAC nomenclature	Symbol	IUPAC Official Name and Symbol
101	Unnilunium	Unu	Mendelevium (Md)
102	Unnilbium	Unb	Nobelium (No)
103	Unniltrium	Unt	Lawrencium (Lr)
104	Unnilquadium	Unq	Rutherfordium (Rf)
105	Unnilpentium	Unp	Dubnium (Db)
106	Unnilhexium	Unh	Seaborgium (Sg)
107	Unnilseptium	Uns	Bohrium (Bh)
108	Unniloctium	Uno	Hassium (Hs)
109	Unnilennium	Une	Meitnerium (Mt)
110	Ununnilium	Uun	Darmstadtium (Ds)
111	Unununium	Uuu	Rontgenium (Rg)
112	Ununbium	Uub	Copernicium (Cp)
113	Ununtrium	Uut	Nihonium (Nh)
114	Ununquadium	Uuq	Flerovium (Fl)
115	Ununpentium	Uup	Moscovium (Mc)
116	Ununhexium	Uuh	Livermorium (Lv)
117	Ununseptium	Uus	Tennessine (Ts)
118	Ununoctium	Uuo	Oganesson (Og)
119	Ununennium	Uue	
120	Unbinilium	Ubn	

Periodic properties of Elements

The properties which repeat after a regular interval are called periodic properties. Some of the important periodic properties of elements are atomic and ionic radii, ionization enthalpy, electron gain enthalpy, electropositivity, electronegativity etc.

1. Atomic Radius

It is defined as the distance from the centre of the nucleus to the outermost shell having electrons. Atomic radius of individual atoms cannot be determined. So it is expressed in any of the following methods:

a) *Covalent radius*: It is half of the inter nuclear distance between two covalently bonded (single bonded) atoms. It is used to express the atomic radius of non-metal atoms. For e.g. the bond distance of Cl_2 molecule is 198 pm. So the covalent radius is 99 pm.

b) *Metallic radius*: It is the half of the inter nuclear distance between two metallic ions in a metal crystal.

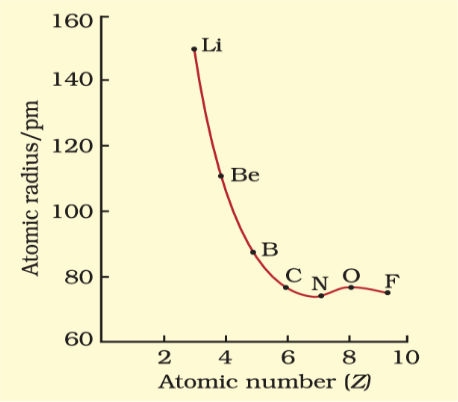
c) *van der Waal's radius:* It is defined as the half of the inter nuclear distance between two non-bonded atoms of separate molecules in the solid state.

Atomic radius is commonly expressed in picometre (pm) or angstrom (A^0) unit. [1 pm = 10^{-12}m and 1 A^0 = 10^{-10} m]. It is measured by x-ray diffraction method or by spectroscopic method.

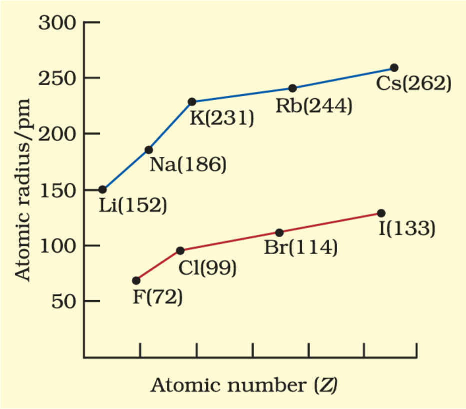
Variation of atomic radius along a group and a period

The atomic size decreases from left to right in a period. This is because in a period, the electrons are added to the same valence shell. Thus the number of shells remains the same, but the effective nuclear charge increases. So the atomic radius decreases. In a given period, alkali metals (group 1) have the maximum size and halogens (group 17) have the minimum size.

In a group, the atomic radius increases from top to bottom. This is because of the increase in no. of shells and shielding effect. (In atoms with higher atomic number, the inner electrons partially shield the attractive force of the nucleus. So the outer electrons do not experience the full attraction of the nucleus and this is known as shielding effect or screening effect).



Variation of atomic radii along 2nd period



Variation of atomic radii along 1st and 17th groups.

Atomic radius of noble gases is larger than that of halogens. This is because noble gases are monoatomic. So van der Waal's radius is used to express their atomic radius which is greater than covalent radius or metallic radius.

2. Ionic radius

It is defined as the half of the inter nuclear distance between cations and anions of an ionic crystal. The variation of ionic radius is same as that of atomic radius.

Generally a cation is smaller than its parent atom (e.g. Na^+ is smaller than Na atom). This is because a cation has fewer electrons, but its nuclear charge remains the same as that of the parent atom.

An anion is larger than its parent atom (e.g. Cl^- is larger than Cl atom). This is because the addition of one or more electrons would result in an increased electronic repulsion and a decrease in effective nuclear charge.

Isoelectronic species:

Species (atoms and ions) having the same number of electrons are called isoelectronic species. E.g. N^{3-}, O^{2-}, F^-, Ne, Na^+, Mg^{2+}, Al^{3+} etc. (All these contain 10 electrons).

Among isoelectronic species, *the cation with greater positive charge will have the smaller radius*. This is because of the greater attraction of electrons to the nucleus. *The anion with greater negative charge will have the larger radius*. Here the repulsion between electrons is greater than the attraction of the nucleus. So the ion will expand in size.

Thus among the isoelectronic species N^{3-}, O^{2-}, F^-, Ne, Na^+, $Mg^{2+}$and Al^{3+}, the largest ion is N^{3-} and the smallest ion is Al^{3+}.

3. Ionisation enthalpy (Δ_iH)

It is defined as the energy required to remove an electron from the outer most shell of an isolated gaseous atom in its ground state. Or, it is the energy required to convert a gaseous neutral atom to a gaseous unipositive ion. It may be represented as:

$$X_{(g)} + \Delta_iH \rightarrow X^+_{(g)} + e^-$$

Its unit is kJ/mol or J/mol.

The energy required to remove the first electron from the outer most shell of a neutral atom is called *first ionisation enthalpy* (Δ_iH_1).

$$X_{(g)} + \Delta_iH_1 \rightarrow X^+_{(g)} + e^-$$

Second Ionisation enthalpy (Δ_iH_2) is the amount of energy required to remove an electron from a unipositive ion.

$$X^+_{(g)} + \Delta_iH_2 \rightarrow X^{2+}_{(g)} + e^-$$

Energy is always required to remove an electron from an atom or ion. So *Δ_iH is always positive*.

The *second ionisation enthalpy is always higher than first ionization enthalpy*. This is because it is more difficult to remove an electron from a positively charged ion than from a neutral atom.

Similarly third ionisation enthalpy is higher than second ionisation enthalpy and so on.

i.e. $\Delta_iH_1 < \Delta_iH_2 < \Delta_iH_3$…………

As the ease of removal of electron increases, the ionisation enthalpy decreases.

Factors affecting ionisation enthalpy

The important factors which affect ionisation enthalpy are:

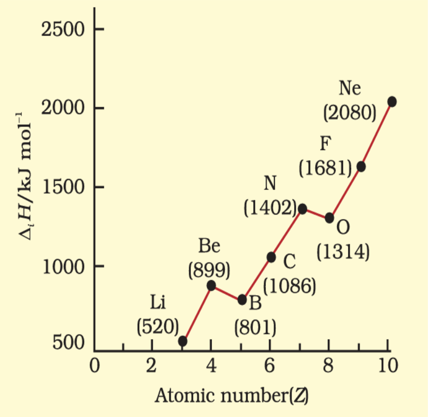
a) *Atomic size*: Greater the atomic size (atomic radius), smaller will be the ionisation enthalpy.
b) *Nuclear charge*: The value of ionisation enthalpy increases with nuclear charge.
c) *Shielding effect*: As the shielding effect increases, the electrons can easily be removed and so the ionisation enthalpy decreases.
d) *Presence of half-filled or completely filled orbitals* increases ionisation enthalpy.

[As the ease of removal of electron increases, ionisation enthalpy decresaes].

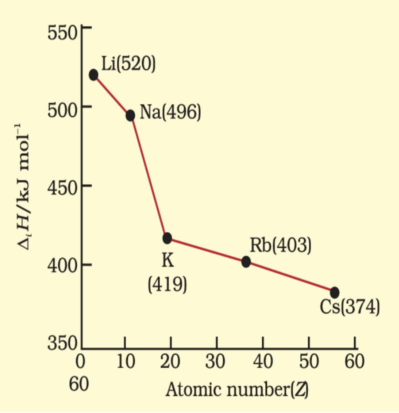
Variation of Δ_iH along a period and a group

Along a *period*, ionisation enthalpy *increases* from left to right. This is because of the *decrease in atomic radius and increase in nuclear charge*. Thus alkali metals have the least Δ_iH and noble gases have the most.

Down a *group*, $\Delta_i H$ *decreases due to increase in atomic radius and shielding effect*. Thus among alkali metals, lithium has the highest $\Delta_i H$ and francium has the lowest.



Variation of ionisation enthalpy along 2nd period



Variation of ionisation enthalpy along 1st group

In the second period of modern periodic table, *the first ionisation enthalpy of Boron is slightly less than that of Beryllium*. This is because after the removal of one electron from boron, it gets the stable configuration ($1s^22s^2$). So B loses one electron faster.

Similarly *the first ionisation enthalpy of nitrogen is greater than that of oxygen*. This is because N has half filled electronic configuration ($1s^22s^22p^3$), which is more stable and so more energy is required to remove an electron.

4. Electron gain enthalpy ($\Delta_{eg}H$)

It is the heat change (enthalpy change) when an electron is added to the outer most shell of an isolated gaseous atom. It can be represented as $X_{(g)} + e^- \rightarrow X^-_{(g)}$

Its unit is kJ/mol. It may be positive or negative depending on the nature of the element. For most of the elements, energy is released when electron is added to their atoms. So $\Delta_{eg}H$ is negative.

Noble gases have large positive electron gain enthalpy because of their stable completely filled electronic configuration.

Electron gain enthalpy also depends on atomic size, nuclear charge, shielding effect etc. As the atomic size increases, $\Delta_{eg}H$ becomes less negative. When nuclear charge increases, electron gain enthalpy becomes more negative. As shielding effect increases, $\Delta_{eg}H$ becomes less negative. Presence of half-filled or completely filled orbitals make $\Delta_{eg}H$ less negative.
[As the ease of addition of electron increases, electron gain enthalpy becomes more negative].

Periodic variation of $\Delta_{eg}H$

From left to right across a *period*, $\Delta_{eg}H$ become *more negative*. This is *because of decrease in atomic radius and increase in nuclear charge*. So the ease of addition of electron increases.
Down a *group*, $\Delta_{eg}H$ becomes less negative. This is *due to increase in atomic radius and shielding effect*.

Electron gain enthalpy of fluorine is less negative than chlorine. This is because, when an electron is added to F, it enters into the smaller 2nd shell. Due to the smaller size, the electron suffers more repulsion from the other electrons. But for Cl, the incoming electron goes to the larger 3rd shell. So the electronic repulsion is low and hence Cl adds electron more easily than F. *[OR, Due to the compactness of the 2p subshell of F, electronic repulsion is greater in F and hence it does not easily add electron]. Due to the same reason $\Delta_{eg}H$ of oxygen is less negative than sulphur.*

Thus in modern periodic table, alkali metals have the least negative $\Delta_{eg}H$ and halogens have the most negative $\Delta_{eg}H$. Among halogens, $\Delta_{eg}H$ becomes less negative in the order: Cl> F > Br > I
[The negative electron gain enthalpy is also called electron affinity].

5. Electronegativity

Electronegativity of an atom in a compound is the ability of the atom to attract shared pair of electron of electrons. It is not a measurable quantity and so it has *no* unit. There are different scales for measuring the Electronegativity of elements. The most commonly used one is the **Pauling Electronegativity scale** developed by Linus Pauling. The other electronegativity scales are Mulliken-Jaffe scale, Allred-Rochow scale etc.

Electronegativity depends on atomic size and nuclear charge. As the atomic radius increases, electronegativity decreases. Greater the nuclear charge, greater will be the electronegativity.

Generally electronegativity increases across a period and decreases along a group. So in modern periodic table, Fluorine is the most electronegative element and Francium is the least electronegative element. Since francium is radioactive, caesium is the least electronegative stable element. *In Pauling Scale, electronegativity of Fluorine is 4.0 and that of Oxygen is 3.5.*

The electronegativity of an element is *not constant*. It varies depending on the element to which it is bound. It is directly related to the non-metallic character of elements. *An increase in electronegativity across a period indicates an increase in non-metallic character and decrease in metallic character*.

6. Electropositivity

It is the tendency of an atom to lose the most loosely bound electron (valence electron). It is directly related to the metallic character of elements. It depends on atomic size and nuclear charge. As the atomic radius increases, electropositivity increases.

Along a period, electropositivity decreases from left to right. But down a group, it increases. So francium is the most electropositive element and fluorine is the least electropositive element.

7. Valency

It is the combining capacity of an element. Or, it is the number of electrons lost or gained by an atom during a chemical reaction.

Along a period, valency first increases upto the middle and then decreases (for s and p block elements only). In a group, valency remains constant. Transition elements can show variable valency.

Valency is numerically equal to oxidation number of the element. The difference is that oxidation number has a positive or negative sign but the valency doesn't.

Anomalous Properties of Second Period Elements

The first element in groups 1 (lithium) and 2 (beryllium) and groups 13 to 17 (boron to fluorine) differs from the other members of their respective group in their properties. This is known as anomalous properties. *This is due to their small size, large charge to radius ratio, high electronegativity and absence of vacant d-orbitals.*

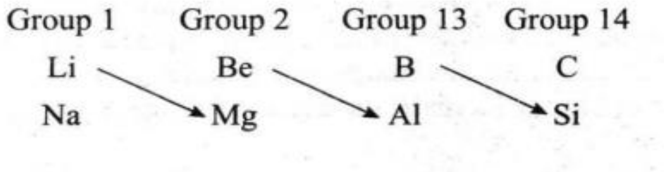
Some of the anomalous properties are:

- *They can form multiple bonds with themselves* (e.g. C = C, N ≡ N etc.) *and with other elements of the second period* (e.g. C = O, C ≡ N etc.).
- *Their maximum co-valency is 4, due to the absence of vacant d-orbitals.* But other elements of the respective groups can expand their covalency beyond 4 (due to the presence of vacant d-orbitals). *For this reason, Aluminium forms $[AlF_6]^{3-}$ whereas boron cannot form $[BF_6]^{3-}$ but forms only $[BF_4]^-$. Similarly, Phosphorus forms PCl_5 while nitrogen cannot form NCl_5.*

Diagonal relationship

The similarities in properties shown by the diagonally placed elements of the 2nd and 3rd periods in the Modern periodic table are called Diagonal relationship. This is due to their similar atomic radii, ionisation enthalpy, electronegativity etc.

E.g. Lithium shows similarities with Mg, Be with Al, B with Si etc.



Periodic Trends and Chemical Reactivity

The periodicity in properties of elements is related to electronic configuration. That is, elements having similar outer electronic configuration show similarities in chemical and physical properties.

The atomic and ionic radii, generally decrease in a period from left to right. As a consequence, the ionization enthalpies generally increase and electron gain enthalpies become more negative across a period. This results into high chemical reactivity at the two extremes and the lowest in the centre. Thus, the maximum chemical reactivity at the extreme left (among alkali metals) is exhibited by the loss of an electron leading to the formation of a cation and at the extreme right (among halogens) shown by the gain of an electron forming an anion. This property can be related with the reducing and oxidizing behaviour of the elements. i.e. Elements at the extreme left (alkali metals) of the periodic table are good reducing agents and those at the extreme right (halogens) are good oxidising agents.

The chemical reactivity of an element can be explained by its reactions with oxygen. Elements on two extremes of a period (1st and 17th groups) easily combine with oxygen to form oxides. The normal oxide formed by the element on extreme left (1st group) is the most basic (e.g. Na_2O), whereas that formed by the element on extreme right (17th group) is the most acidic (e.g. Cl_2O_7). Oxides of elements in the centre are amphoteric (e.g. Al_2O_3, As_2O_3) or neutral (e.g. CO, NO, N_2O). Amphoteric oxides behave both as acidic (with bases) and basic (with acids), while neutral oxides have no acidic or basic properties.

##