Classification of elements and periodicity in Properties

In 1800 only 31 elements were known. By 1865 the number of elements identified more than 63. At present 118 elements are known. With such a large number of elements it is very difficult to study each element individually. To make it easy scientist proposed a systematic way to organise the elements.

Genesis of periodic table

- ➢ **Law of triads** Johann Dobereiner first gave the idea of trends among properties of elements. In 1829 he propounded that several groups of three elements having similar physical and chemical properties which were later known as triads.
- ➢ According to him in each triad middle element's atomic weight is average of other two element's atomic weight.

Table: Dobereriner's Triads

➢ **Law of Octaves-** In 1865 John Alexander Newlands propounded the law of octaves. He arranged elements in increasing order of their atomic weights and found that every eight-element had similar properties to first element.

Table: Newlands' Octaves

- ➢ **Periodic law –** Dmitri Mendeleev and Lother Meyer both chemists propounded that on arranging the elements in increasing order of atomic weight similarity appear in chemical and physical properties.
- \triangleright Lother Meyer plotted the physical properties such as atomic volume, melting point and **boiling** point against atomic weight and obtained a periodically repeated pattern.
- \triangleright Mendeleev published the periodic law first time. It states "the properties of the elements are a periodic function of their atomic weights."
- ➢ Mendeleev arranged elements in horizontal rows and vertical column of a table in order of their increasing atomic weights in such a manner that elements with similar properties occupied same vertical column.
- \triangleright Mendeleev left the gap under aluminium and silicon, called these elements ka- Aluminium and Eka- Silicon. He predicted the existence of gallium, germanium and described their physical properties. These elements were discovered later.

Table: Mendeleev's Prediction for the elements Eka-aluminium (Gallium) and Eka-silicon (Germanium)

Figure: Mendeleev's periodic table earlier

Modern periodic law

- \triangleright According to this law "the physical and chemical properties of the elements are periodic functions of their atomic numbers".
- \triangleright A modern version or long form of the periodic table of the element is the most convenient and used.
- \triangleright Horizontal rows are called periods and vertical column are groups.
- ➢ Elements having same outer electronic configuration in their atoms are arranged in vertical column and referred as families.
- \triangleright The groups are numbered from 1 to 18 replacing the older notation of groups IA… VIIA, VIII, IB and 0.
- \triangleright The first period contains 2 elements. The subsequent periods consist of 8, 8, 18, 18 and 32 elements respectively.
- \triangleright Seventh period is incomplete.
- ≥ 14 elements of both sixth and seventh periods are placed in separate panels at the bottom.

f - luner transition elements

Figure: Long form of the periodic table

Nomenclature of elements with atomic numbers> 100

- \triangleright Traditionally the new elements named after the name of discoverer. IUPAC (International Union of Pure and Applied Chemistry) ratified it.
- ➢ In case of element 104 both Americans and Soviet scientists claimed credit for discovering it. The Americans named it Rutherfordium and Soviets named it Kurchatovium. To avoid such problems IUPAC established.
- \triangleright A systematic nomenclature derived from the numerical roots for 0-9 numbers.
- \triangleright The new element first gets a temporary name with a symbol of three letters. Later permanent name and symbol are given by IUPAC representatives from each country.
- ➢ Today 118 elements with atomic numbers and official names by IUPAC are discovered.

Table: Notation for IUPAC Nomenclature of Element

Table: Nomenclature of Elements with atomic number above 100

Electronic configuration of elements and the periodic table

- \triangleright The characteristics of an electron in an atom are denoted by four quantum numbers n, l, s, m. The principal quantum (n) defines the main energy level known as shell. Filling of electrons in to subshell i.e., orbitals s, p, d, f in atom take place.
- \triangleright The distribution of electrons into orbitals of an atom is called its electronic configuration.
- \triangleright There is a direct connection between electronic configuration of an element and its position in periodic table.

A). **Electronic configuration in Periods**

- \triangleright The period indicates the value of n for the outermost or valence shell.
- \triangleright The first period (n=1) starts with the filling of the lowest level (1s). It has two elements hydrogen (1s¹) and helium (1s²), the first shell (K) completed.
- \triangleright The second period (n=2) starts with lithium and third electron enters the 2s orbital. The next element Be has four electrons. It's electronic configuration is 1s²1s².
- \triangleright The next element Boron (B), 2p orbital is filled by one electron. 2p orbital is filled till the L shell is completely filled at Neon ($2s^22p^6$). Thus, there are eight elements in second period.
- \triangleright The third period begins from sodium (Na) and end at argon. The electron enters 3s orbital in case of sodium and completely filled 3p orbital in argon. Third period have eight elements from sodium to argon.
- \triangleright The fourth period (n=4) starts from potassium and electron enter 4s orbital. Now 3d orbital is filled before 4s orbital because 3d is energetically more favourable. We enter 3d transition series of elements which starts from scandium (Sc) ($Z=21$). Sc has electronic configuration $3d¹4s²$.
- \triangleright The 3d orbitals are filled at Zinc (Z=30) with electronic configuration $3d^{10}4s^2$. The fourth period ends at krypton with the filling up of the 4p orbitals. There are 18 elements in the fourth period.
- \triangleright The fifth period (n=5) beginning with Rubidium. The fifth period contains 4d transition series. It starts from Yttrium and end at Xenon.
- \triangleright The sixth period (n=6) contains 32 elements. Successive electrons enter 6s, 4f, 5d and 6p orbitals. The filling of 4f orbitals starts from Cerium (Z=58) and ends at Lutetium (Z=71) to give the 4f inner transition series which is known as Lanthanoid series.
- \triangleright In seventh period (n=7) successive filling of 7s, 5f, 6d and 7p orbitals take place. Most of the elements of this series are man-made radioactive elements.
- \triangleright The 5f inner transition starts from actinium (Z=89) by filling up 5f orbitals. This series is also known as actinoid series.
- ➢ The 4f and 5f inner transition series of elements are placed separately in the periodic table.

B) **Group wise electronic configurations**

➢ Elements which have same vertical column or group have similar valence shell electronic configuration; same number of electrons in the outer orbitals. For example group-I elements have $ns¹$ valence shell electronic configuration.

Table: electronic configuration of group-I

Electronic configurations and types of elements in s, p, d, f blocks

- \triangleright The elements in a vertical column of the periodic table have similar chemical behaviour. This similar behaviour arises because these elements have same number of electrons in their outermost orbitals.
- \triangleright We can classify the elements of periodic table into four blocks i.e. sblock, p-block, d-block and f-block.
- \triangleright There are two exceptions to this categorisation- first one is hydrogen, it has only one s-electron and hence can be group-I. It can also gain an electron to achieve a noble gas arrangement hence it can be placed in group- 17. It is a special case so hydrogen separately place at the top of periodic table.

Second exception is helium belongs to the s-block but it is positioned in the p-block along with other group 18 elements because it has a completely filled valence shell i.e. 1s². It shows properties similar to noble gases.

The s-block elements

- ➢ The elements of group-1 (alkali metals) and group -2 (alkaline earth meals) which have $ns¹$ and $ns²$ electronic configuration of outermost valence shell.
- \triangleright S-block elements are reactive metals with low ionization enthalpies. They tend to lose one or two outer most electrons to form +1 ion or +2 ions.
- \triangleright The metallic character and reactivity increase as we go down the group.

The p-block elements

- ➢ Elements of group 13 to 18 forms p-block. s-block and p-block collectively known as Representative elements or Main group elements.
- **►** Outermost electronic configuration varies from ns²np¹ to ns²np⁶ in each period.
- \triangleright The valence shell of the noble gases is completely filled. It is very stable electronic configuration. The noble gases show very low chemical reactivity. Halogens and chalcogens are the important groups of nonmetal elements.
- ➢ Halogens and chalcogens have highly negative electron gain enthalpies. They are readily accept or gain electron to attain noble gas configuration.
- ➢ As we move from left to right across a period non-metallic character increases.
- \triangleright As we move down the group metallic character increases.

The d-block elements (Transition elements)

- \triangleright These are the elements of group 3 to 12 situated in the centre of the periodic table.
- \triangleright It is known as d-block elements because electrons are filled in d orbitals.
- Fine general outer electronic configuration is $(n-1)d^{1-10}ns^{0-2}$.
- \triangleright They are metals and mostly form coloured ions, exhibit variable oxidation states, para-magnetism and used as catalysts.

 \triangleright The transition metals form a bridge between the chemically active metals of s-block elements and less active elements of group 13 and 14 and thus take their familiar name Transition elements.

The f-block elements (Inner transition elements)

- \triangleright The two rows of elements at bottom of the periodic table called Lanthanoids $[Ce (Z=58)$ to Lu $(Z=71)$], Actinoids $[Th (Z=90)$ to Lr $(Z=103)]$
- \triangleright The general outer electronic configuration is (n-2)f¹⁻14(n-1)d⁰⁻¹ns²
- \triangleright Lanthanoids and actinoids elements are known as inner transition elements (f-block elements).
- ➢ All elements show metallic characteristics. Actinoids elements are radioactive.
- \triangleright The elements after uranium are called Trans uranium elements.

Metals, non-metals and metalloids

- ➢ The elements can be divided into metals and non-metals. 78% of elements of **periodic table** are in metallic nature.
- \triangleright Metals are solid at room temperature. Mercury is an exception.
- \triangleright They are situated on the left side of periodic table. Metals usually have melting point. They are good conductor of electricity and heat. They are malleable and ductile.
- \triangleright Non-metals are situated at top right-hand side of the periodic table.
- ➢ Non-metals are solid or gases at room temperature. They are poor conductor of heat and electricity.
- \triangleright Most non-metal solids are brittle. They are neither ductile nor malleable.
- ➢ Metallic characters increase as we move down a group. Non-metallic characters increases as we move left to right across the periodic table.
- \triangleright The elements bordering this line and running diagonally across the periodic table show properties similar to both metals and non-metals. These elements are known as semi-metals or metalloids.

Periodic trends in properties

There are many observable unique patterns in the chemical and physical properties of elements as we move across a period or down in a group in the periodic table. There are some trends in chemical and physical properties of atoms which are discussed below:

Trends in physical properties

- \triangleright There are various physical properties of elements such as boiling point, melting point, heats of fusion and vaporization, energy of atomization, etc.
- \triangleright Periodic trends with respect to ionic and atomic radii, ionization enthalpy, electron gain enthalpy and electronegativity discussed one by one below-
- **1. Atomic radius**
	- \triangleright The size of an atom is \sim 1.2 Å, which is very small. There is not any practical way to measure the size of an individual atom.
	- \triangleright There is a practical approach to measure radius is first measure the distance between two atoms when they are bound together by a single bond in a covalent molecule and from this value the covalent radius of element can be calculated.
	- \triangleright For example in Cl₂, the bond distance between two chlorine molecule is 198pm and half of this distance i.e. 99pm ids atomic radius of chlorine.
	- \triangleright In case of metals we called it metallic radius. Metallic radius is half of the internuclear distance separating the metal cores in the metallic crystal. For example the internuclear distance between two copper atoms in solid copper is 265pm. The metallic radius of copper will be 265/2 i.e., 128pm.
	- \triangleright We can refer atomic radius for both metallic and covalent radius.
	- \triangleright Generally, the atomic size decreases across a period because with in a period the outer electrons are in the same valence shell and the effective nuclear charge (Z_{eff}) increases as the atomic number increases, resulting in the increased attraction between nucleus and electrons.
	- \triangleright In case of family or vertical column of a periodic table, atomic radius increases regularly with atomic number

Atom (period II)	Li	Be	B		N		
Atomic radius		$152 \mid 111$	88	\vert 77 \vert	74	66	64
Atom (period III)	Na	Mg	Al	Si	P		
Atomic radius	186	160	143	117	110	104	99

Table: Atomic radii (pm) across the periods

Table: Atomic Radii (pm) down a family

Figure: variation of atomic radius with atomic number across the second period

Atomic number (Z)

Figure: Variation of atomic radius with atomic number for alkali metals and halogens

2. Ionic Radius

- \triangleright The removal of an electron from an atom result in the formation of a cation and gain of an electron leads to an anion.
- \triangleright The ionic radii can be measured by calculating the distance between cation and anion in an ionic crystal.
- \triangleright The size of cation is smaller than its parent atom as it has less electrons but nuclear charge remains same.
- \triangleright The size of an anion will be larger than that of parental atom because the addition of one or more electrons increases repulsion among electrons and decrease in Zeff.
- \triangleright Example: Ionic radius of fluoride ion (F) = 136 pm; atomic radius of fluorine = 64 pm

The atomic radius of sodium = 186 pm; ionic radius of $Na⁺ = 95$ pm.

Isoelectronic species: some atoms and ions which contain the same number of electrons are known as isoelectronic species. O^{-2} , F, Na⁺ and Mg+2 have same number of electrons i.e. 10. But the radius would be different due to different nuclear charges.

3. Ionization Enthalpy

- \triangleright The tendency of an element to lose electron is known as ionization enthalpy.
- \triangleright The energy required to remove an electron from an isolated gaseous atom in its ground state is called ionization enthalpy.
- \triangleright The first ionization enthalpy for an element X:

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

- > The ionization enthalpy (Δ_iH) is expressed in unit of kJ mol⁻¹.
- \triangleright The second ionization enthalpy is energy required to remove the second most loosely bound electron.

$$
X^+(g) \rightarrow X^2 + (g) + e^-
$$

➢ It is an endothermic process. Ionization enthalpies are always positive.

$$
\Delta_i \mathbf{H} = (+i \mathbf{ve})
$$

➢ Successive ionization enthalpies are increase.

$$
X(g) + (IE)_1 \rightarrow X^+(g) + 1e^{-}
$$

$$
X^+(g) + (IE)_2 \rightarrow X^{2+}(g) + 1e^{-}
$$

$$
X^{+2}(g) + (IE)_3 \rightarrow X^{3+}(g) + 1e^{-}
$$

Here IE = Ionization enthalpy

 $(IE)_3$ > $(IE)_2$ > $(IE)_1$

Figure: variation of first ionization enthalpies (∆iH) with atomic number of elements with Z=1 to 60

Figure: First Ionization enthalpies (∆iH) of elements of the second period as a function of atomic number (Z)

Figure: ∆iH of alkali metals as a function of Z

- ➢ There are two factors responsible for the various trends of ionization enthalpy in the periodic table $-$ (1) the attraction of electrons towards the nucleus (2) the repulsion of electrons from each other.
- \triangleright The Z_{eff} experienced by a valence electron in an atom will be less than the actual charge on the nucleus because of **shielding** or **screening of valence electron from the nucleus by the superseding** core electrons. In case of 2s electron in Li is shielded from the nucleus by the inner 1s electrons. The valence electron experiences a net positive charge which is less than the actual charge of +3.

4. Electron gain enthalpy

- \triangleright Electron gain enthalpy is the amount of energy that is released when an electron is added in valence shell of an isolated gaseous atom.
- \triangleright It is denoted as (Δ_{ee} H). It can be either exothermic or endothermic process.

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

Table: Electron gain enthalpies (kJ mol⁻¹) of some main group elements

 \triangleright Electron gain enthalpy becomes more negative with increase in the atomic number across a period. The Z_{eff} increases from left to right across a period and consequently it would be easier to add an electron to a smaller atom.

5. Electronegativity

- \triangleright A qualitative measure of the ability of an atom in a chemical compound to attract shared electrons to itself, is called electronegativity.
- \triangleright It is not a measurable quantity. Pauling scale is mostly used to measure the electronegativity.
- \triangleright Electronegativity of any given element is not constant. It varies depending upon the element to which it is bound.
- \triangleright Electronegativity generally increases across a period from left to right in the period.

Figure: The periodic trends of elements in the periodic table

Table: Electronegativity values (on Pauling scale) across the periods

Atom (Period II) Li		Be			
Electronegativity	1.0	1.5		3.0	
Atom (period III) Na		Mg			
Electronegativity 0.9		1.2			3.0

Table: Electronegativity values (on Pauling scale) down a family

➢ Electronegativity is directly related to non-metallic properties of elements. Electronegativity is inversely related to the metallic properties of elements. The increase in electronegativity across a period is accompanied by an increase in non-metallic properties of elements. The decrease in non-metallic properties of elements.

Periodic trends in chemical properties

1. Periodicity of valence or oxidation states

- \triangleright The valence is the most characteristic property of the elements.
- \triangleright Valence of electron = number of electrons in outermost orbital

Oriented States (States States)

Valence of electron = 8- number of outermost electron

 \triangleright The term oxidation state is used valence. For example: In OF₂ and Na₂O. Order of electronegativity is $F > 0 > Na$. Electronic configuration of fluorine is 2s²2p⁵, fluorine shares one electron with oxygen in the OF₂ molecule. Being highest electronegative element, here fluorine's oxidation state is -1. Oxidation state of oxygen is +2 as it shares 2 electrons with fluorine. In Na₂O, oxygen is more electronegative and accepts two electrons; one from each of the two sodium atoms thus shows oxidation state -2. Sodium oxidation state is $+1$.

The oxidation state of an element in a particular compound can be defined as the charge acquired by it's atom on the basis of electronegative consideration from other atoms in the molecule.

Table: Periodic trends in Valence of elements as shown by the formulas of their compounds

2. Anomalous properties of second elements

- \triangleright The first element of each of the group-I (lithium) and group-II (beryllium) and group 13-17 (boron to fluorine) different in many respects from the other members of their respective group.
- \triangleright Behaviour of Li and Be is more similar with the second element of the group *i.e.*, Mg and AI respectively. This type of similarity is known as **diagonal relationship** in the periodic properties.

- \triangleright The anomalous behaviour is attributed to the small size, large charge/ radius ratio and high electronegativity of the element.
- \triangleright In addition to it, the first member of group has only four valence orbitals (2s and 2p) available for bonding while the second member of the groups have nine valence orbitals (3s, 3p, 3d).
- \triangleright The maximum covalency of the first member of each group is 4, [BF₄] whereas the other members can expand their valence shell to accommodate more than four pairs of electrons $[AlF_6]^{3}$.

Periodic trends and Chemical reactivity

- \triangleright The entire chemical and the physical properties are an expression of the electronic configuration of elements.
- \triangleright There is high chemical reactivity at the two extremes (i.e the right and left one in the periodic table). It is exhibited by the loss of an electron and formation of cation take place at the left extreme. At the extreme right exhibited by gain of an electron and formation of an anion take place.
- \triangleright The chemical reactivity of an element is described well by its reaction with $O₂$ gas and halides.
- \triangleright Elements positioned at the extreme gives oxide by reacting with oxygen, elements on extreme left mostly gives basic oxide (example- Na2O) while the elements of extreme right gives acidic oxide (example- $Cl₂O₇$). Elements in the centre of periodic table gives amphoteric oxides like Al_2O_3 , As_2O_3 or neutral oxides like CO, NO, N₂O.
- \triangleright In case of transition elements, the change in atomic radius is much smaller than representative elements across the period. The change in atomic radius is also small in case of inner transition metals i.e. 4f series.