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## Classification of Elements and Periodicity in Properties

### Classification of Elements

With the discovery of a large number of elements, it became difficult to study the elements individually, so classification of elements was done to make the study easier.

### Earlier Attempts to Classify Elements

Many attempts were made to classify the known elements from time to time. The earlier attempts are as follows:

#### Prout's Hypothesis (1815)

According to this theory, hydrogen atom was considered as the fundamental unit from which all other atoms were made. It is also known as unitary theory.

#### Dobereiner's Triads (1829)

Dobereiner classified the elements into groups of three elements with similar properties in such a manner so that the atomic weight of the middle element was the arithmetic mean of the other two, e.g.

Element	Li	Na	K
Atomic weight	7	23	39

$$\text{Mean of atomic masses} = \frac{7 + 39}{2} = 23$$

Similarly Cl, Br, I; Ca, Sr, Ba are two more examples of such triads.

### Limitations

Dobereiner could not arrange all the elements known at that time into triads. He could identify only three such triads that have been mentioned.

### Newland's Octaves (1864) (Law of Octaves)

Newland states that when elements are arranged in order of increasing atomic masses, every eighth element has properties similar to the first just like in the musical note [Every eighth musical note is the same as the first mentioned note]. This can be illustrated as given below

sa	re	ga	ma	pa	dha	ni
Li	Be	B	C	N	O	F
Na	Mg	Al	Si	P	S	Cl

### Limitations

1. This classification was successful up to the element calcium.
2. When noble gas elements were discovered at a later stage, their inclusion in these octaves disturbed the entire arrangement.

### Lothar Meyer's Atomic Volume Curve (1869)

Meyer presented the classification of elements in the form of a curve between atomic volume and atomic masses and stated that the properties of the elements are the periodic functions of their atomic volumes.

$$\left[ \text{Here, atomic volume} = \frac{\text{Molecular mass}}{\text{Density}} \right]$$

He concluded that the elements with similar properties occupy similar position in the curve.

### Mendeleev's Periodic Table

Mendeleev's periodic table is based upon Mendeleev's periodic law which states "The physical and chemical properties of the elements are a periodic function of their atomic masses."

At the time of Mendeleev, only 63 elements were known.

This periodic table is divided into seven horizontal rows (**periods**) and eight vertical columns (**groups**). Zero group was added later on in the modified Mendeleev's periodic table.

## Importance of Mendeleev's Periodic Table

Few important achievements of periodic table are

- Systematic study of the elements.
- Prediction of new elements and their properties, he left space for the elements yet to be discovered, e.g. he left spaces for Ga and Ge and named these elements as **EK<sub>a</sub>-aluminium** (Ga) and **EK<sub>a</sub>-silicon** (Ge) respectively.
- Atomic mass correction of doubtful elements on the basis of their expected positions and properties.

### Modified Form of Mendeleev's Periodic Table

Group →	I		II		III		IV		V		VI		VII		VIII			0
Period ↓	A	B	A	B	A	B	A	B	A	B	A	B	A	B				Zero
1	H 1.008																	He 4.003
2	Li 6.94		Be 9.01		B 10.82		C 12.01		N 14.00 8		O 16		F 19					Ne 20.183
3	Na 22.99		Mg 24.32		Al 26.98		Si 28.09		P 30.975		S 32.06		Cl 35.46					Ar 39.944
4	K 39.10  Cu 63.54		Ca 40.08  Zn 65.38		Sc 44.96  Ga 69.72		Ti 47.90  Ge 72.60		V 50.95  As 74.91		Cr 52.01  Se 78.96		Mn 54.94  Br 79.91		Fe 55.85		Co 58.94  Ni 58.69	Kr 83.80
5	Rb 85.48  Ag 107.88		Sr 87.63  Cd 112.41		Y 88.92  In 114.76		Zr 91.22  Sn 118.70		Nb 92.91  Sb 121.76		Mo 95.95  Te 127.61		Tc 99  I 126.9		Ru 101.1		Rh 102.91  Pd 106.7	Xe 131.3
6	Cs 132.91  Au 197.0		Ba 137.36  Hg 200.61		La 138.92  Tl 204.39		Hf 178.6  Pb 207.21		Ta 180.92  Bi 209		W 183.92  Po 210		Re 186.31  At [210]		Os 190.2		Ir 192.2  Pt 195.23	Rn 222
7	Fr 223		Ra 226.05		Ac 227													

### Defects in the Mendeleev's Periodic Table

- Position of hydrogen** Hydrogen has been placed in group IA (alkali metals), but it also resembles with halogens of group VIIA. Thus, its position in the Mendeleev's periodic table is controversial.
- Position of isotopes** As Mendeleev's classification is based on atomic weight, isotopes would have to be placed in different

positions due to their different atomic weights, e.g.  ${}^1_1\text{H}$ ,  ${}^2_1\text{H}$ ,  ${}^3_1\text{H}$  would occupy different positions.

- (iii) **Anomalous positions of some elements** Without any proper justification, in some cases the element with higher atomic mass precedes the element with lower atomic mass.

For example, Ar (atomic weight = 39.9) precedes K (atomic weight = 39.1) and similarly Co (atomic weight = 58.9) has been placed ahead of Ni (atomic weight = 58.7).

- (iv) **Position of lanthanoids and actinoids** Lanthanoids and actinoids were not placed in the main periodic table.

## Modern Periodic Table (1913)

Moseley modified Mendeleev's periodic law. He stated "Physical and chemical properties of elements are the periodic function of their atomic numbers." It is known as modern periodic law and considered as the basis of Modern Periodic Table.

When the elements were arranged in increasing order of atomic numbers, it was observed that the properties of elements were repeated after certain regular intervals of **2, 8, 8, 18, 18** and **32**. These numbers are called **magic numbers** and cause of periodicity in properties due to repetition of similar electronic configuration.

## Structural Features of Long Form of Periodic Table

- (i) Long form of periodic table is called **Bohr's periodic table**. There are 18 groups and seven periods in this periodic table.

- (ii) The horizontal rows are called **periods**.

**First period** ( ${}^1_1\text{H}$  —  ${}^2_2\text{He}$ ) contains 2 elements. It is the shortest period.

**Second period** ( ${}^3_3\text{Li}$  —  ${}^{10}_{10}\text{Ne}$ ) and **third period** ( ${}^{11}_{11}\text{Na}$  —  ${}^{18}_{18}\text{Ar}$ ) contain 8 elements each. These are short periods.

**Fourth period** ( ${}^{19}_{19}\text{K}$  —  ${}^{36}_{36}\text{Kr}$ ) and **fifth period** ( ${}^{37}_{37}\text{Rb}$  —  ${}^{54}_{54}\text{Xe}$ ) contain 18 elements each. These are long periods.

**Sixth period** ( ${}^{55}_{55}\text{Cs}$  —  ${}^{86}_{86}\text{Rn}$ ) consists of 32 elements and is the longest period.

**Seventh period** starting with  ${}^{87}_{87}\text{Fr}$  is incomplete and consists of 19 elements.

- (iii) The 18 vertical columns are known as **groups**.

Elements of group 1 are called **alkali metals**.

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

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Elements of group 16 are called **chalcogens** [ore forming elements].

Elements of group 17 are called **halogens**. [sea salt forming elements]

Elements of group 18 are called **noble gases**.

**Anomalous behaviour of the first element of a group.** The first element of a group differs considerably from its congeners (i.e. the rest of the elements of its group).

This is due to (i) small size (ii) high electronegativity and (iii) non availability of *d*-orbitals for bonding. Anomalous behaviour is observed among the second row elements (i.e. Li to F).

- (iv) The periodic table is divided into four main blocks (*s*, *p*, *d* and *f*) depending upon the subshell to which the valence electron enters into.

- (a) **s-block elements** 1st and 2nd group elements belong to this block and the last electron enters in *s*-subshell.

General electronic configuration =  $ns^{1-2}$ .

- (b) **p-block elements** Group 13th to 18th belong to this block in which last electron enters in *p*-orbital.

Their general electronic configuration is  $ns^2np^{1-6}$ .

This is the only block which contains metal, non-metal and metalloids. Examples of metalloids are B, Si, Ge, As, Sb, Te and At.

The elements of *s*- and *p*-block elements are collectively called representative elements.

- (c) **d-block elements** Group 3rd to 10th belong to this block, in which last electron enters in *d*-orbital.

They have inner incomplete shell, so known as transition elements.

General electronic configuration is  $ns^{1-2}(n-1)d^{1-10}$ .

*d*-block elements are generally coloured, paramagnetic and exhibit variable valency.

- (d) **f-block elements** They constitute two series 4f (lanthanoids) and 5f (actinoids) in which last electron is in 4f and 5f subshell respectively.

General electronic configuration

$$(n-2)f^{1-14}(n-1)d^{0-1}ns^2$$

The *f*-block elements are also called as **inner-transition elements**.

Elements with atomic number greater than 92 ( $U_{92}$ ) are called the **transuranic** or **transuranium elements**. All these elements are man-made through artificial nuclear reactions.

Very recently, on August 16, 2003, IUPAC approved the name for the element of atomic number 110, as **Darmstadtium**, with symbol Ds.

### Limitations of Long Form of Periodic Table

In the long form of the periodic table:

- (i) The position of hydrogen still remains uncertain.
- (ii) The inner-transition elements do not find a place in the main body of the table. They are placed separately.

### Predicting the Position of an Element in the Periodic Table

First of all write the complete electronic configuration. The principle quantum number of the valence shell represents the period of the element.

The subshell in which the last electron is filled corresponds to the block of the element.

Group of the element is predicted from the electrons present in the outermost ( $n$ ) or penultimate ( $n-1$ ) shell as follows :

For *s*-block elements,

group number = number of *ns*-electrons

(Number of valence electrons)

For *p*-block elements,

group number = 10 + number of *ns* and *np* electrons

For *d*-block elements,

group number = the sum of the number of ( $n-1$ ) *d* and *ns* electrons.

For *f*-block elements, group number is always 3.

[illegible]

**Note** The International Union of Pure and Applied Chemistry has approved the name and symbols of four newly discovered elements :  
Nihonium (Nh), Moscovium (Mc), Tennessine (Ts) and Oganesson (Og) respectively for element 113, 115, 117 and 118.

## IUPAC Nomenclature of Elements With $Z > 100$

The names are derived directly from the atomic numbers using numerical roots for 0 and numbers from 1-9 and adding the suffix *ium*.

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

The IUPAC names and symbols of elements with  $Z > 100$  are

Z	101	102	103	104	105	106	107	108	109	110
IUPAC name	Unnilunium	Unnilbium	Unniltrium	Unnilquadium	Unnilpentium	Unnilhexium	Unnilseptium	Unniloctium	Unnilennium	Unnililium
Symbol	Unu	Unb	Unt	Unq	Unp	Unh	Uns	Uno	Une	Uun

## Metals, Non-metals and Metalloids

- **Metals** comprise more than 78% of all known elements and appears on the left side of the periodic table.
- In contrast, **non-metals** are located at the top right handside of the periodic table.
- Within the non-metals, some elements show the properties of both metals and non-metals, i.e. metalloids. These elements border the *zig-zag* line beginning from boron and running diagonally across the *p*-block.

## Periodic Properties

The properties which are directly or indirectly related to their electronic configuration and show gradual change when we move from left to right in a period or from top to bottom in a group are called periodic properties.

### Atomic Radius

It is the distance from the centre of the nucleus to the outermost shell containing of electrons. It is an hypothetical definition because in a single atom, it is almost impossible to measure this distance. Hence, practically, atomic radius is defined in the following four ways :



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### Covalent radius

If the combining atoms are non-metals (except noble gases) and the bond between them is the single covalent bond then their radius is called the covalent radius. It is measured as the half of their internuclear distance, i.e. For an atom  $A$  in a molecule  $A_2$ .

$$r_A = \frac{r_A + r_A}{2} = \frac{d_{A-A}}{2}$$

[Distance $_{A-A}$  = Radius of  $A$  + Radius of  $A$ ]

For heterodiatomic molecule  $AB$ ,

$$d_{A-B} = r_A + r_B + 0.09(X_A - X_B)$$

Where,  $X_A$  and  $X_B$  are electronegativities of  $A$  and  $B$ .

### van der Waals' Radius

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

### Metallic Radius

It is defined as one-half of the internuclear distance between the centres of nuclei of the two adjacent atoms in the metallic crystal.

### Ionic Radius

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

In case of iso-electronic ions, the higher the nuclear charge, smaller is the size, e.g.  $Al^{3+} < Mg^{2+} < Na^+ < F^- < O^{2-} < N^{3-}$

The order of radii is :

covalent radius < metallic radius < van der Waals' radius

In general, the atomic size decreases on moving from left to right in a period due to increase in effective nuclear charge and increases on moving from top to bottom in a group due to addition of new shells.

The concept of effective nuclear charge is discussed below :

### Effective Nuclear Charge

In a multielectron atom, the electron of the inner-shell decrease the force of attraction exerted by the nucleus on the valence electrons. This is called shielding effect. Due to this, the nuclear charge ( $Z$ ) actually present on the nucleus, reduces and is called effective nuclear charge ( $Z_{\text{eff}}$ ).

It is calculated by using the formula

$$Z_{\text{eff}} = Z - \sigma$$

where,  $\sigma$  = screening constant

The magnitude of  $\sigma$  is determined by Slater's rules.

### Slater Rules

- (i) Write the electronic configuration in the following order and groups.  
(1s) (2s, 2p) (3s, 3p) (3d), (4s, 4p) (4d) (4f) (5s, 5p) etc.
- (ii) Electrons of  $(n + 1)$  shell (shell higher than considering electrons) do not contribute in shielding, i.e.  $\sigma = 0$
- (iii) All other electrons in  $(ns, np)$  group contribute  $\sigma = 0.35$  each.
- (iv) All electrons of  $(n - 1)s$  and  $p$  shell contribute  $\sigma = 0.85$  each.
- (v) All electrons of  $(n - 2)s$  and  $p$  shell or lower shell contribute  $\sigma = 1.00$  each
- (vi) All electrons of  $nd$  and  $nf$  orbital contribute  $\sigma = 0.35$  and those of  $(n - 1)$  and  $f$  or lower orbital contribute  $\sigma = 1.00$  each.

e.g.

$$\text{Be (4)} = 1s^2, 2s^2$$

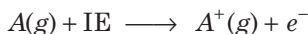
$$\text{(for 2s)} \quad \text{for 1s}$$

$$\sigma = 0.35 + 2 \times 0.85 = 2.05$$

$$Z_{\text{eff}} = Z - \sigma = 4 - 2.05 = 1.95$$

### Ionisation Enthalpy (IE)

It is the amount of energy required to remove the loosely bound electron from the isolated gaseous atom.



Various factors with which IE varies are :

- (i) Atomic size : varies inversely
- (ii) Screening effect : varies inversely
- (iii) Nuclear charge : varies directly

Generally left to right in periods, ionisation enthalpy increases; down the group, it decreases.

IE values of inert gases are exceptionally higher due to their stable configurations. Successive ionisation enthalpies

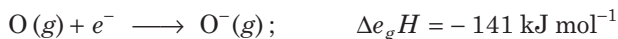
$$\text{IE}_3 > \text{IE}_2 > \text{IE}_1$$

$\text{IE}_1$  of N is exceptionally greater than that of oxygen due to stable half-filled  $2p$ -orbitals.

Among transition elements of  $3d$ -series,  ${}_{24}\text{Cr}$  and  ${}_{29}\text{Cu}$  have higher  $\text{IE}_2$  due to half-filled and fully-filled stable  $d$ -orbitals.

**Electron Gain Enthalpy ( $\Delta_e H$ )**

It is the amount of energy released when an electron is added in an isolated gaseous atom. First electron gain enthalpy is negative while the other successive electron gain enthalpy will be positive due to repulsion between the electrons already present in the anion and the electron being added.



Various factors with which electron gain enthalpy varies are :

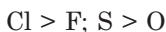
- (i) Atomic size : varies directly
- (ii) Nuclear charge : varies directly

Along a period, electron gain enthalpy becomes more and more negative while on moving down the group, it becomes less negative.

Noble gases have positive electron gain enthalpies.

Halogens have maximum value of  $\Delta_e H$  within a period due to smallest atomic size.

F and O atom have small size and high charge density, therefore they have lower values of electron gain enthalpy, than Cl and S respectively.



Elements having half-filled and fully-filled orbitals exhibit more stability, therefore, electron gain enthalpy will be low for such elements.

Electron gain enthalpy can be measured by Born-Haber cycle and elements with high  $\Delta_e H$ , are good oxidising agent.

**Electronegativity (EN)**

It is defined as the tendency of an atom to attract the shared electron pair towards itself in a polar covalent bond. Various factors with which electronegativity varies are :

- (i) Atomic size : varies inversely
- (ii) Charge on the ion : varies directly, e.g.  $\text{Li} < \text{Li}^+$ ,  $\text{Fe}^{2+} < \text{Fe}^{3+}$
- (iii) Hybridisation : (Electronegativity  $\propto$  % age s-character in the hybrid orbital)

Electronegativity of carbon atom =  $\text{C}_2\text{H}_6 < \text{C}_2\text{H}_4 < \text{C}_2\text{H}_2$

In periods as we move from left to right electronegativity increases, while in the groups electronegativity decreases down the group.

For noble gases, its value is taken as zero.

Electronegativity helps to predict the polarity of bonds and dipole moment of molecules.

Electronegativity order of some elements (on Pauling scale) is

$$\begin{array}{ccccccc} \text{F} & > & \text{O} & > & \text{N} & \approx & \text{Cl} > \text{Br} \\ (4.0) & & (3.5) & & (3.0) & & (3.0) & (2.8) \end{array}$$

(i) **Mulliken scale**

$$\text{Electronegativity } (x) = \frac{\text{IE} + \Delta e_g H}{2}$$

- (ii) **Pauling scale** The difference in electronegativity of two atoms  $A$  and  $B$  is given by the relationship

$$x_B - x_A = 0.208 \sqrt{\Delta}$$

$$\text{where, } \Delta = E_{A-B} - \sqrt{E_{A-A} \times E_{B-B}}$$

( $\Delta$  is known as resonance energy.)

$E_{A-B}$ ,  $E_{A-A}$  and  $E_{B-B}$  represent bond dissociation energies of the bonds  $A-B$ ,  $A-A$  and  $B-B$  respectively.

(iii) **Allred and Rochow's scale**

$$\text{Electronegativity} = 0.744 + \frac{0.359 Z_{\text{eff}}}{r^2}$$

Where,  $Z_{\text{eff}}$  is the effective nuclear charge  $= Z - \sigma$

Where,  $\sigma$  is screening constant. It's value can be determined by Slater's rule.

## Valency

It is defined as the combining capacity of the element. The valency of an element is related to the electronic configuration of its atom and usually determined by electrons present in the valence shell.

On moving along a period from left to right, valency increases from 1 to 4 and then decreases to zero (for noble gases) while on moving down a group the valency remains the same.

Transition metals exhibit variable valency because they can use electron from outer as well as penultimate shell.

## Chemical Reactivity

Reactivity of metal increases with decrease in IE, electronegativity and increase in atomic size as well as electropositive character.

Reactivity of non-metals increases with increase in electronegativity as well as electron gain enthalpy and decrease in atomic radii.

## Melting and Boiling Points

On moving down the group, the melting point and boiling point for metallic elements go on decreasing due to the decreasing forces of attraction. However, for non-metals, melting point and boiling point generally increase down the group.

Along a period from left to right, melting point and boiling point increases and reaches a maximum value in the middle of the period and then start decreasing.

Tungsten (W) has highest melting point (3683 K) among metals, carbon (diamond) has the highest melting point among non-metals. Helium has lowest melting point ( $-270^{\circ}\text{C}$ ) among all elements,

## Electropositivity or Metallic Character

The tendency of an atom of the element to lose valence electrons and form positive ion is called electropositivity.

Greater the electropositive character, greater is the metallic character.

Electropositive character decreases on moving across the period and increases on moving down the group.

Alkali metals are the most electropositive and halogens are the least electropositive element in their respective period.

Basic nature of oxides  $\propto$  metallic character, i.e. it also decreases along a period and increases down the group.

## Density

Li metal has minimum density while osmium (Os) metal has maximum density.

## Diagonal Relationship

Certain elements of 2nd period show similarity in properties with their diagonal elements in the 3rd period as shown below :

	Group 1	Group 2	Group 13	Group 14
2nd period	Li	Be	B	C
3rd period	Na	Mg	Al	Si

Thus, Li resembles Mg, Be resembles Al and B resembles Si. This is called diagonal relationship and this is due to the reason that these pairs of elements have almost identical ionic radii and polarizing power (i.e. charge/size ratio). Elements of third period, i.e. Mg, Al and Si are known as **bridge elements**.