# UNIT - 3

# CLASSIFICATION OF ELEMENTS AND PERIODICITY IN PROPERTIES

## Modern Periodic Law

Physical & chemical properties of the elements are periodic function of their atomic numbers.

- Present Form of the Periodic Table, The long form of periodic table, also called Modern Periodic Table, is based on Modern Periodic Law. In this table, the elements have been arranged in order of increasing atomic numbers.

## Structural Features of the Periodic Table

### Groups

The long form of periodic table ~~also~~ consist of the vertical rows called groups. There are in all 18 groups in the periodic table. Unlike Mendeleev periodic table, each group is an independent group.

### Characteristics of groups:

(i) All the elements present in a group ~~have same~~ have same general electronic configuration of the atoms.

(ii) The elements in a group are separated by definite gaps of atomic numbers (2, 8, 8, 18, 18, 32).

(iii) The atomic sizes of the elements in group increase down the group due to increase in the no. of shells.

(iv) The physical properties of the elements such as m.p., b.p., density, solubility, etc, follow a systematic pattern.

(v) The elements in each group have generally similar chemical properties.

(vi) Metallic character increases as we go down the group.

Periods

Horizontal rows in a periodic table are known as periods.

There are in all seven periods in the long form of periodic table.

Characteristics of periods:

(i) In all the elements present in a period, the electrons are filled in the same valence shell.

(ii) The atomic sizes generally decreases from left to right.

(iii) In moving from left to right in a period, the non-metallic character of the elements increases.

(v) At the end of each period is a noble gas element with a closed valence $ns^2np^6$ configuration.

## Characteristics of S-Block Elements :

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

(i)- All the elements are soft metals.

(ii)- They have low melting & boiling points.

(iii)- They are highly reactive.

(iv)- Most of them impart colours to the flame.

(v)- The generally form ionic compounds.

(vi)- They are good conductors of heat & electricity.

## Characteristics of p-block elements:

General electronic configuration: $ns^2np^{1-6}$

(i)- The compounds of these elements are mostly covalent in nature.

~~(ii)- They show variable oxidation states.~~

~~(iii)- In moving from left to right in a period, the~~

## Characteristics of d-Block elements

General electron configuration: $(n-1)d^{1-10}ns^{0-2}$

(i)- The d-block elements are known as transition elements because they have incompletely filled d-orbitals in their ground state or in any of the oxidation states.

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# Characteristics of f-block Elements

General electronic configuration: $(n-2)f^{1-14}(n-1)d^{0-1}ns^2$

They are known as inner transition elements because in the transition elements of d-block, the electrons are filled in $(n-1)d$ subshell while in the inner transition elements of f-block the filling of electrons takes place in $(n-2)f$ subshell, which happen to be one inner subshell.

(i) The two rows of elements at the bottom of the Periodic Table, called Lanthanoids Ce(Z=58) - Lu(Z=71) & Actinoids Th(Z=90) - Lr(Z=103).

(ii) These two series of elements are called Inner Transition Elements (f-block elements).

(iii) They are all metals. Within each series, the properties of the elements are quite similar.

(iv) Most of the elements of the actinoid series are radio-active in nature.

## Metals

(i) Metals comprise more than 78% of all known elements & appear on the left side of the Periodic Table.

(ii) Metals are solids at room temp.

(iii)- Metals usually have high melting & boiling points.

(iv)- They are good conductors of heat & electricity.

(v)- They are malleable & ductile.

## Non-Metals

(i)- Non-metals are located at the top right hand side of the Periodic Table.

(ii)- Non-metals are usually solids or gases at low temp. with low melting & boiling points.

(iii)- They are poor conductors of heat & electricity.

(iv)- The non-metallic character increases as one goes from left to right across the Periodic Table.

(v)- Most non-metallic solids are brittle & are neither malleable nor ductile.

## Metalloids

The elements (eg., silicon, germanium, arsenic, antimony & tellurium) show the characteristic of both metals & non-metals. These elements are called called semimetal.

## Noble Gases

(i) These are the elements present in group 18.

(ii) Each period ends with noble gas element.

(iii) All the members are of gaseous nature & because of the presence of all the occupied filled orbitals, they have very little tendency to take part in chemical combination.

(iv) These are also called inert gases.

## Representative Elements

The elements of group 1 (alkali metals), group 2 (alkaline earth metals) & group 13 to 17 constitute the representative elements. They are elements of s-block & p-block.

## Transition Elements

The transition elements include, all the d-block elements & they are present in the centre of the periodic table between s & p block elements.

## Inner Transition Elements

Lanthanoids (the fourteen elements after Lanthanum) & actinides (the fourteen elements after actinium) are called inner transition elements. They are also called f-block elements.
The elements after uranium are also called transuranic elements.

# Periodic Trends in Properties of Elements

## Trends in Physical Properties:

**Atomic Radii:** It is defined as the distance from the centre of nucleus to the outermost shell containing the electrons.
Depending upon whether an element is a non-metal or a metal, three types of atomic radii are used. These are:

(a) Covalent Radius: It is equal to half of the distance between the centres of the nuclei of two atoms held together by a purely covalent single bond.

(b) Ionic Radius: It may be defined as the effective distance from the nucleus of an ion upto which it has an influence in the ionic bond.

(c) Van der Waals Radius: Atoms of noble gases are held together by weak Van der Walls forces of attraction. The van der Waals radius is half of the distance between the centre of nuclei of atoms of noble gases.

(d) Metallic Radius: It is defined as half of the internuclear distance between the two adjacent metal ions in the metallic lattice.

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## Variation of Atomic Radius in the Periodic Table

### Variation in a Period:

Along a period, the atomic radii of the elements generally decreases from left to right.

### Variation in a Group:

The atomic radii of the elements in every group of the periodic table increases as we move downwards.

### Ionic Radius

The ionic radii can be estimated by measuring the distance between cations & anions in ionic crystals. In general, the ionic radii of elements exhibit the same trends as the atomic radii.

**Cation:** The removal of an $e^-$ from an atom results in the formation of a cation. The radius of cation is always smaller than that of the atom.

**Anion:** Gain of an $e^-$ leads to an anion. The radius of the anion is always larger than that of the atom.

**Isoelectronic Species:** Some atoms & ions which contain the same no. of electrons, we call them isoelectronic species.
For example, $O^{2-}$, $F^-$, $Na^+$ & $Mg^{2+}$ have the same no. of electrons (10). Their radii would be different because of their different nuclear charges.

## Ionisation Enthalpy

It is the energy required to remove an $e^-$ from an isolated gaseous atom in its ground state.

$M(g) + I.E \dashrightarrow M^+(g) + e^-$

The unit of ionisation enthalpy is $KJmol^{-1}$ & the unit of ionisation potential is electron volt per atom.

Succesive Ionisation Enthalpies

If a gaseous atom is to lose more than $1e^-$, they can be removed one after the other i.e., in succession & not simultaneously. This is known as successive ionisation enthalpy (or potential).

The ionisation enthalpies required to remove first, second & third $e^-$ from a gaseous atom are known as first ($\Delta_i H_1$), second ($\Delta_i H_2$) & third ($\Delta_i H_3$) ionisation enthalpies respectively. The successive ionisation enthalpies for $Al(g)$ atom are as follows:

| | |
|---|---|
| $Al(g) \rightarrow Al^+(g) + e^-$ | $\Delta_i H_1 = 577\ kJmol^{-1}$ |
| $Al^+(g) \rightarrow Al^{2+}(g) + e^-$ | $\Delta_i H_2 = 1816\ kJmol^{-1}$ |
| $Al^{2+}(g) \rightarrow Al^{3+}(g) + e^-$ | $\Delta_i H_3 = 2744\ kJmol^{-1}$ |

Thus $\Delta_i H_3 > \Delta_i H_2 > \Delta_i H_1$

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# Variation of Ionisation Enthalpies in the Periodic Table:

## Along a Period

Along a period ionisation enthalpies are expected to increase in moving across from left to right, because the nuclar charge increases & the atomic size decreases.

## In a Group

The ionisation enthalpies of the elements decrease on moving from top to the bottom in any group. The decrease in ionisation enthalpies down any group is because of following factors:

(i) There is an increase in the no. of main energy shells (n) in moving from one element to other.

(ii) There is also an increase in the magnitude of the screening effect due to gradual increase in the no. of inner electrons.

## Electron Gain Enthalpy

Electron Gain Enthalpy is the energy released when an $e^-$ is added to an isolated gaseous atom so as to convert it into a negative ion. The process is represented as:

$$\underbrace{X(g)}_{\text{neutral gaseous atom}} + e^- \longrightarrow \underbrace{X^-(g)}_{\text{anion}}$$

$$\Delta H = \Delta_{eg} H$$

For majority of the elements the $e^-$ gain enthalpy is negative.
For example, the electron gain enthalpy for halogens is highly negative because they can acquire the nearest noble gas configuration by accepting an extra electron.
In contrast, noble gases have large positive electron gain enthalpies because the extra electron has to be placed in the next higher principal quantum energy level thereby producing highly unstable electronic configuration.

Successive Electron Gain Enthalpies
We have studied that electrons from a gaseous atoms are lost in succession (i.e., one after the other). Similarly, these are also accepted one after the other, i.e., in succession. After the addition of one $e^-$, the atoms become -vely charged & the IInd $e^-$ is to be added to a -vely charged ion. But the addition of second $e^-$ is opposed by electrostatic repulsion. & hence the energy has to be supplied for the addition of IInd $e^-$. Thus the IInd $e^-$ gain enthalpy of an element is +ve.
For example, when an $e^-$ is added to oxygen to form $O^-$ ion, energy is released. But when another $e^-$ is added to $O^-$ ion to form $O^{2-}$ ion, energy is absorbed to overcome the strong

electrostatic repulsion between the -vely charged $O^-$ ion & the IInd $e^-$ being added. Thus, first electron gain enthalpy:

$$O(g) + e^-(g) \longrightarrow O^-(g)$$

$$\Delta_{eg}H = -141 \text{ KJ mol}^{-1}$$

(Energy is released)

Second electron gain enthalpy:

$$O^-(g) + e^-(g) \longrightarrow O^{2-}(g)$$

$$\Delta_{eg}H = +780 \text{ kJ mol}^{-1}$$

(Energy is absorbed)

Factors on which Electron Gain Enthalpy depends:

(i)- Atomic size: As the size of an atom increases, the distance b/w its nucleus & the incoming $e^-$ also increases and $e^-$ gain enthalpy becomes less -ve.

(ii)- Nuclear charge: With the increase in nuclear charge, force of attraction b/w the nucleus & the incoming electron increases & thus $e^-$ gain enthalpy becomes more -ve.

(iii)- Symmetry of the Electronic Configuration: The atoms with symmetrical configuration (having full filled or half-filled orbitals in the same sub shell) do not have any urge to take up extra $e^-$ because this configuration will become unstable.

In that case, the energy will be needed & $e^-$ gain enthalpy ($\Delta_{eg}H$) will be positive. For example, noble gas elements have +ve $e^-$ gain enthalpies.

## Variation of Electron Gain Enthalpy Across Period

Electron gain enthalpy becomes more -ve with increase in the atomic no. across a period.

## Variation of Electron Gain Enthalpy in a Group

Electron gain enthalpy becomes less negative as we go down a group.

## Electronegativity

A qualitative measure of the ability of an atom in a chemical compound to attract shared electrons to itself is called electronegativity.
Unlike ionisation enthalpy & electron gain enthalpy, it is not a measurable quantity.
However, a no. of numerical scales of elements viz, Pauling scale, Milliken-Jaffe scale, Allred Kochow scale have been developed. The electronegativity of an element is not constant, it varies depending on the element to which it is bound.

## Across a Period

Electronegativity generally increases across a period from left to right.

In a Group
It decreases down a group.

## Periodic Trends in Chemical Properties

Along a Period

(i) Metallic character: Decrease across a period.
max. on the extreme left (alkali metals).

(ii)- Non-metallic character: Increases along a period.
(From left to right).

(iii)- Basic nature of oxides: Decreases from left to right in a period.

(iv)- Acidic nature of oxides: Increases from left to right in a period.

Moving down a Group.

(i) Metallic character: Generally increase because increase in atomic size & hence decrease in the ionization energy of the elements in a group from top to bottom.

(ii)- Non-metallic character: Generally decreases down a group. As electronegativity of elements decreases from top to bottom in a group (iii)- Basic nature of oxides: Since metallic character as electropositivity of elements increases in going from top to bottom in a group, basic nature of oxidise naturally increases.

(iv)- Acidic character of oxides: Generally decreases as non-metallic character of elements decreases in going from top to bottom in a group.

(v)- Reactivity of metals: Generally increases down a group. Since tendency to lose $e^-$ increases.

(vi)- Reactivity of non-metals: Generally decreases down the group, higher the electro-negativity of non-metals, greater is their reactivity. Since electronegativity of metals in a group decreases from top to bottom, their reactivity also decreases.

Anomalous Properties of Second Period Elements: The first element of each of the group 1 (lithium) & 2 (beryllium) & group 13-17 (boron to fluorine) differs in many respect from the other members of their respective groups. For example, lithium unlike. For example, lithium unlike other alkalic metals, & beryllium unlike other alkaline earth metals form compounds which have significant covalent character; the other

members of these groups pre-dominantly form ionic compounds.
It has been observed that some elements of the second period show similarities with the elements of the third period placed diagonally to each other, though belonging to different groups:

| Group 1 | Group 2 | Group 13 | Group 14 |
|---|---|---|---|
| Li | Be | B | C |
| Na | Mg | Al | Si |

This similarity in properties of elements placed diagonally to each other is called diagonal relationship.

## Oxidation Numbers

Oxidation numbers are simply +ve or −ve numbers assigned on the basis of a set of arbitrary rules. It is imp. for you to realize that these are not electric charges. For this reason, we write an oxidation with the sign preceding the no., as in +2 or "posive two." This differs from an ion charge of 2+ or "two positive" units of electric charge.

## Common Oxidation Numbers

| | | |
|---|---|---|
| Rule 1 | All elements in uncombined state | 0 |
| Rule 2 | All monoatomic ions | Same as their charge |
| Rule 3 | Hydrogen in all compounds | +1 |
| Rule 4 | Hydrogen in hydrides ($NaH$, $MgH_2$) | -1 |
| Rule 5 | Oxygen in all compounds | -2 |
| Rule 6 | Oxygen in peroxides ($H_2O_2$) | -1 |
| Rule 7 | All group 1 elements in compounds | +1 |
| Rule 8 | All group 2 elements in compounds | +2 |
| Rule 9 | All halogens in group 1 & 2 compounds | -1 |
| Rule 10 | The sum of oxidation no. in a compound | 0 |
| Rule 11 | The sum of oxidation no. in a polyatomic ion | Same as its charge |

Oxidation no. of carbon in methane, $CH_4$

Assign oxidation no. to hydrogen.

$$\overset{x}{C}\overset{+1}{H_4}$$

$x + 4(+1) = 0$ [Hint: Total of oxidation no. for a compound must be equal to 0)

$x + 4 = 0$

$x = -4$

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Oxidation no. of sulphur in sodium sulphate, $Na_2SO_4$

Sodium oxidation no. $= +1$

Sulphur oxidation no. $= x$

Oxygen oxidation no. $= -2$

$$2(+1) + x + 4(-2) = 0$$
$$2 + x - 8 = 0$$
$$x - 6 = 0$$
$$x = +6$$

Oxidation no. of manganese in a permanganate ion, $MnO_4^-$

Manganese oxidation no. $= x$

Oxygen oxidation no. $= -2$

$x + 4(-2) = -1$ [Hint: Total no. of oxidation no. is equal to the charge of the ion

$$x + (-8) = -1$$
$$x = +7$$

Oxidation no. of S in $SO_2$

$$x + 2(-2) = 0$$
$$x - 4 = 0$$
$$x = 4$$

Oxidation no. of Cl in $HClO_4$

$$1 + x + 4(-2) = 0$$
$$1 + x - 8 = 0$$
$$x = +7$$

Determine the oxidation no. of S in $SO_4^{2-}$

$$x + 4(-2) = -2$$
$$x - 8 = -2$$
$$x = +6$$

Oxidation no. of Cr in $Cr_2O_7^{2-}$

$$2x + 7(-2) = -2$$
$$2x - 14 = -2$$
$$2x = +12$$
$$x = +6$$

Oxidation no. of nitrogen in $NO_2$

$$x + 2(-2) = 0$$
$$x - 4 = 0$$
$$x = +4$$

Oxidation no. of nitrogen in $NH_3$

$$x + 3(+1) = 0$$
$$x = -3$$

Oxidation no. of nitrogen in $NaNO_3$

$$1 + x + 3(-2) = 0$$
$$1 + x - 6 = 0$$
$$x - 5 = 0$$
$$x = +5$$

Oxidation no. of nitrogen in $N_2$

0 [Hint: All elements have a oxidation no. of 0]

Oxidation no. of nitrogen in $NH_4Cl$

$$x + 4(+1) + 1(-1) = 0$$
$$x + 4 - 1 = 0$$
$$x + 3 = 0$$
$$x = -3$$