CHEMISTRY

Inorganic Chemistry

Main Group Elements
## MAIN GROUP ELEMENTS

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PERIODICITY

Periodic Table: It is the arrangement of chemical elements in increasing atomic number such that elements with similar properties are arranged in the same column (called group) and elements with same number of electron shells are arranged in same row (called period).

Periodicity: It is the repetition of elements with similar properties after certain regular intervals when the elements are arranged in the order of increasing atomic number.

- Repetition of properties occur after 2, 8, 18 and 32 elements in 1st, 2nd, 3rd and 4th period respectively hence these numbers 2, 8, 18, 32 are termed as magic numbers.

Mendeleev’s Periodic table Law:- The physical and chemical properties of the elements are a periodic function of their atomic weight.

Moseley’s law: Long form (modern) periodic table:- The physical and chemical properties of elements are a periodic function of their atomic number or electronic configuration. It was proposed by Moseley on basis of X-ray diffraction.

\[ \nu \propto z^2 \]

- Frequencies of certain characteristic X-rays emitted from chemical elements are proportional to the square of element’s atomic number.

Characteristic features of Long form of periodic table:-

- Modern periodic table is divided into :-
  - 18 vertical columns (called groups) − same valence shell electronic configuration
  - 7 horizontal rows (called periods) − same electronic shell.
  - Elements of group 1A to VII A (1, 2, 13, 14, 15, 16, 17) are known as main group elements (representative elements) and group 1B to VIII B (3 to 12) are known as transition elements.
  - Elements of group-18 are called noble gases or zero group elements.
GENERAL CHARACTERISTICS

PERIODIC PROPERTIES

1) SIZE :-

Atomic radii :- It is defined as the distance from atomic nucleus to the outermost electron orbital. It depend on following factors :-

1) Principal Quantum Number (n)
2) Effective nuclear charge

Principal Quantum number (n) :- It is one of four quantum numbers which are assigned to each electron in an atom to describe that electron's state. It is denoted by symbol n and always having an integer value. As n increases, the number of electronic shells increases and atomic size increases.

Atomic size $\propto n$

Effective nuclear charge :- It is defined as the net positive charge experienced by the valence electrons from the atomic nucleus.

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

Where $Z =$ atomic number $Z_{\text{eff}} =$ effective nuclear charge $\sigma =$ screening constant

Note :- Valence electron experience attractive force from nucleus and this attractive force is reduced by innerlying electrons which acts as shield or screening to outermost valence electron.

**Gate tips :-** Magnitude of shielding $\propto$ Energy $\propto 1/$penetration effect

So the order of energy of various orbital is

$2s < 2p$

$3s < 3p < 3d$

$4s < 4p < 4d$

Screening effect :- The decrease in force of attraction on the outermost electron due to repulsive force of inner electrons is called screening effect.

As a result the outermost electron do not experience the complete nuclear charge

Slater rules for calculation of effective nuclear charge :- Value of $\sigma$ can be evaluated as follows

1) Write the electronic configuration of atom in following order and groupings

$(1s), (2s, 2p), (3s, 3p), (3d), (4s, 4p), (4d)(4f), (5s, 5p)$

2) Electron in any group higher in this sequence than the electron under consideration contributes zero to value of shielding constant.
3) For an electron in ns and np orbital

- All other electron in (ns, np) group contribute = 0.35 each
- All electron in (n−1) shell contribute = 0.85 each
- All electron in (n−2) shell or lower shell contribute =1 each

4) For an electron in nd and nf orbital

- All electron in same group contribute = 0.35 each
- Those in lower shell than nd and nf contribute =1 each.

Ques 1. Calculate the effective nuclear charge for potassium K?

Ans = Step 1:- Write electronic configuration

1s²2s²2p⁶3s²3p⁶4s¹

Step 2:- Arrange in group

(1s²) (2s² 2p⁶) (3s² 3p⁶) (4s¹)

Step 3:- Calculated $\sigma$

$\sigma = (0.85 \times 8) + (1 \times 10) = 16.80$

Step 4 :- $Z_{\text{eff}} = Z - \sigma$ and Z = 19 so $Z_{\text{eff}} = 19 - 16.80 = 2.20$

Penetration effect:- Electron in s-orbital is closer to nucleus than electron in p-orbital and electron in p-orbital is closer to nucleus than electron in d orbital and so on. So more energy is required to remove an electron from s-orbital than p-orbital inspite of having same principal quantum number. In the same way p-orbital require more energy than d-orbital. This is called penetration effect.

It decreases in the order s > p > d > f for same value of n.

Gate tips :- General trend :-1s > 2s > 2p > 3s > 3p > 3d > 4p > 5s > 4d > 5p > 6s > 4f……

Trend :- Atomic size increase from top to down in a group.

Explanation :- Electronic configuration of elements indicates that addition of electron in same group means addition of new shell and repulsion between electron increases as we move down the group result in increase in size. Secondly number of protons are also increasing which results in increase in force of attraction between electron and nucleus and effective nuclear charge increases which tries to decrease size.

But the repulsion between electrons due to addition of new shell is dominating factor and hence atomic size increases.

Trend :- Atomic size decrease from left to right in a period.

Explanation :- Addition of electron takes place in the same shell and number of protons increase from left to right with increase in atomic number resulting in increase in nuclear charge which results in increasing attractive force on outermost electron and hence size decrease.
where \( F = \) electrostatic force and \( r = \) radius and \( q_1 \) and \( q_2 \) are charge particles electrons and protons.

Note: Along period \( r = \) nearly same so \( q_1 \) and \( q_2 \) increase and electrostatic force increases and radius decrease.

Along group \( r \) increases and force of attraction decreases.

**General Diagram showing trend of various periodic properties:**

- An atom does not have a sharp boundary so atomic radii cannot be estimated by direct method instead by indirect methods in the combined state of atoms.

Chemical compounds can be classified into four major types on the basis of nature of chemical bonds:

1) Covalent molecules
2) Ionic molecules
3) Metals
4) Atomic crystals

The atomic radii of atoms of these compounds are classified as follows:

1) **Covalent radius** (in covalent molecules) – non metals
2) **Ionic radii** (in ionic crystals) – for ions, cation and anion
3) **Vander waal radius (in atomic crystals)** – for atoms

4) **Metallic radius (in metals)** – for metals

**Gate tips**: For covalent and vander waal radius \( F \propto r \)

**Covalent radii**: It is defined as one half of the bond length when two atoms of the same kind are bonded through a single bond in neutral molecules.

**Covalent bond length** = \( R_a + R_a \)

**Covalent radius** = Covalent bond length /2

**Covalent radii in heteroatomic molecules**:

Eg: In H-Cl distance between H-Cl is 1.31\( \text{Å} \) and \( r_{\text{Cl}} = 0.99 \text{ Å} \) and \( r_{\text{H}} = 1.31 - 0.99 = 0.32 \text{ Å} \) i.e it will not be same.

2) **Ionic radii**: It is the distance between the nucleus and outermost shell of an ion (cation or anion).

**Internuclear distance** = \( r_{\text{Na}^+} + r_{\text{Cl}^-} = 95 + 181 = 276 \text{ pm} \)

Ionic radius of \( \text{Na}^+ = 95 \text{ pm} \)

Ionic radius of \( \text{Cl}^- = 181\text{pm} \)

3) **Metallic radius**: It is defined as one half the distance between two lattice point of metals.
4) Van der Waal's radius: It is defined as half of the internuclear separation of two non-bonded atoms of the same element on their closest possible approach and is denoted $r_v$.

Size of isoelectronic ions: The word iso means same so they have same number of electrons.

Eg: Na$^+$, F$^-$, Mg$^{2+}$ all have same number of 10 electrons so they are isoelectronic.

Gate tip: A cation is smaller than its parent atom because cation has less electron than parent atom while nuclear charge remains same resulting in more nuclear attraction between nucleus and outermost electron.

Eg: Atomic size of Na = 186pm

Ionic radius of Na$^+$ = 95pm

Gate tip: An anion will always be larger than its parent atom because of addition of few extra electrons while nuclear charge remains same which reduces the nuclear pull on the outermost electron because of more number of electron.

Eg: atomic radius of fluorine is F = 64pm while ionic radius of F$^-$ = 136pm

Ques 2. Predict the order of ionic radius of Cl$^+$, Cl, Cl$^-$.

Ans = First calculate number of protons, electrons and then ratio of p/e where p=proton e=electron

For Cl$^+$ p = 17 e = 16 and ratio is 17/16

For Cl p = 17 e = 17 ratio is 17/17

For Cl$^-$ p = 17 e = 18 and ratio is 17/18.

As ratio of p/e increases force of attraction or effective nuclear charge on outermost electron increase and size decreases.

So order of size is Cl$^-$ > Cl > Cl$^+$. 
Ques 3. Predict order of ionic radius of Na\(^+\), Mg\(^{2+}\), Al\(^{3+}\), Si\(^{4+}\), P, P\(^-\), P\(^{-2}\), P\(^{-3}\).

Ans = Step 1: Calculate number of protons and electrons and then p/e

For Na\(^+\) = p = 11 e = 10 & p/e = 11/10
Mg\(^{2+}\) = p = 12 e = 10 & p/e = 12/10
Al\(^{3+}\) = p = 13 e = 10 & p/e = 13/10
Si\(^{4+}\) = p = 14 e = 10 & p/e = 14/10
P = p = 15 e = 15 & p/e = 15/15
P\(^-\) = p = 15 e = 16 & p/e = 15/16
P\(^{-2}\) = p = 15 e = 17 & p/e = 15/17
P\(^{-3}\) = p = 15 e = 18 & p/e = 15/18.

As value of p/e increases, effective nuclear charge increases and size decreases.

So order of size is Si\(^{4+}\) < Al\(^{3+}\) < Mg\(^{2+}\) < Na\(^+\) < P < P\(^-\) < P\(^{-2}\) < P\(^{-3}\).

Gate tips :- Oxidation state is inversely proportional to radius r.

Ionization energy/Ionization potential :- It is defined as the minimum amount of energy required to remove the most loosely bound electron in its ground state from isolated gaseous atom.

Ionisation energy is also called as ionization potential (IP).

\[ M(g) + IE \rightarrow M^+(g) + e^- \]

For ionisation (I.E) \( \geq E_{valence} \)

I.E min = \( E_{valence} \)

Ionisation energy is also expressed in unit of energy i.e eV.

Ionisation energy (eV) = Ionisation energy in joules/charge of electron.

Key point: Ionization energy increases across a period and decreases down a group and it is having positive value i.e endothermic process.

Down the group radius increase, electrostatic force of attraction decrease and energy of valence electron decrease and hence ionisation energy decrease.

\[ M^+(g) + IE_2 \rightarrow M^{2+}(g) + e^- \]
\[ M^+(g) + IE_3 \rightarrow M^{3+}(g) + e^- \]

IE, IE\(_2\), IE\(_3\) are respectively called first, second, third ionisation energy required to remove 1\(^{st}\), 2\(^{nd}\), 3\(^{rd}\) electron from the isolated gaseous atoms.
Magnitude of IE increases after successive removal of electron as the atom becomes positively charged and hence effective nuclear charge increases and hence p/e ratio increases and remaining electrons are held more tightly by nucleus and it becomes difficult to remove successive electron.

**Gate tips:** (IE) < (IE)$_2$ < (IE)$_3$

**Factors affecting ionisation energy:**

1) **Atomic size** :- Ionisation energy decreases as atomic size increases because of decrease in nuclear force.

\[ \text{IE} \propto \frac{1}{\text{size}} \]

2) **Nuclear charge** :- Ionisation energy increase with increase in nuclear charge.

\[ \text{IE} \propto \text{nuclear charge} \]

3) **Screening or shielding effect** :- Larger the number of electrons in the inner shells, greater will be value of screening constant and smaller the value of effective nuclear charge resulting in lower ionisation energy.

4) **Penetration effect** :- Smaller size orbitals have more tendency for penetration to nucleus and thus s orbitals are held more tightly followed by p, d, f orbital and hence experience greater pull from nucleus and value of ionisation energy increases.

Penetration effect & ionisation energy

**Order of penetrating power** s > p > d > f and order of IE = s > p > d > f.

5) **Electronic configuration** :- If an atom has fully filled or exactly half filled orbital in the valence shell, its ionisation energy is higher than expected normally from its position.

Eg :- Ionisation energy of noble gas are highest in their respective period and I.E of N > O due to half-filled p-orbital configuration in nitrogen.
In case of transition element (IE) for 5d series is more than 4d and 3d series because of smaller size of atoms and (IE) for 3d and 4d is nearly same.

**Ques 4 :-** Predict the order of (IE) for following elements C, N, O, F ?

Ans = $C = 1s^2 \ 2s^2 \ 2p^2 \ N = 1s^2 \ 2s^2 \ 2p^3 \ O = 1s^2 \ 2s^2 \ 2p^4 \ F = 1s^2 \ 2s^2 \ 2p^5$

Order of (IE) is $N > F > O > C$. This can be explained as follows. All these element belong to same period and ionisation energy increases along a period and secondly half-filled configuration is more stable than partially filled so nitrogen is having highest IE because half-filled followed by fluorine having smallest size.

Order of (IE) is $O > F > N > C$. This can be explained as follows after removal of first electron oxygen attain stable half-filled configuration of nitrogen and require high (IE) for removal of second electron

$O (g) + I.E \rightarrow O^+ (g) + e^-$

$1s^2 \ 2s^2 \ 2p^4 \ 1s^2 \ 2s^2 \ 2p^3$ (stable half-filled configuration)

$O^+ (g) + I.E_2 \rightarrow O^{2+}(g) + e^-$

**Ques 5 :-** Arrange the following elements S, Se, Cl, P in increasing order of their ionisation energy?

Ans = $Se < S < Cl < P$

Selenium (Se) belong to sulphur family and down the group ionisation energy decreases whereas S,Cl belong to same period and along period ionisation energy increases so Cl having high IE whereas P having highest value because of stable half-filled electronic configuration.

4) **Electron affinity (EA) or electron gain enthalpy ($\Delta_{eg} H$)** :- It is defined as the amount of energy released when an electron is added to isolated gaseous atom or ion.

$X (g) + e^- \rightarrow X^-(g) + \text{Energy (EA)}$

As the incoming electron is added it feels nuclear attraction so energy is released.

$EA \propto F_{\text{electr}} \propto 1/r$

**Note :-** We generally talk about electron affinity of non-metals i.e p block elements as addition of electron to s block is very difficult.

**Value of electron affinity depends on**

1) Effective nuclear charge

2) Stability of valence shell electronic configuration

3) Size of the atom.

**Gate tip :-** If EA is high, it means electron is strongly bounded to nucleus and more stable anion than parent atom.

If EA is low, it means electron is weakly bounded to nucleus and less stable anion than parent atom.

**Note :-** E.A of fully filled or exactly half-filled configuration is zero.
EA of noble gases are zero because they have stable electronic configuration and no chance of extra addition of electron.

Addition of 2nd electron is endothermic process as second electron is added against electrostatic repulsion and requires energy for addition to overcome that repulsion.

**Trend**: Electron affinity increases across a period and decreases down a group and generally it is having negative value i.e. exothermic process except some exceptions.

Electron affinity decrease along group because on moving down the group the size of atom increases and as size decrease force of attraction on incoming electron decreases as force is inversely related to radius.

**Exceptions**: Generally electron affinity increases along period but carbon has high EA than nitrogen.

**Explanation**: Electronic configuration of carbon = 1s^22s^22p^2

Electronic configuration of N = 1s^22s^22p^3

So Carbon needs one more electron to form stable half-filled configuration of 2p orbital so has high electron affinity whereas nitrogen is already half filled and stable and destabilized by addition of extra electron.

**Exception**: Generally in group value of E.A affinity decrease from top to bottom but E.A of Cl is higher than F and E.A of S is higher than oxygen.

**Explanation**: When an electron is added to oxygen and fluorine, it goes to smaller 2p orbital i.e \( n = 2 \) quantum level and it results in significant repulsion from the other electron present in the shell so addition of electron is not that much favourable and it has low E.A whereas for S or Cl addition of electron takes place to \( n = 3 \) quantum level i.e 3p and added electron occupies large region and electron electron repulsion minimized.

**Trend of E.A in decreasing order**: Cl > F > Br > I S > Se > Te > Po > O

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<th>Table 12-4</th>
<th>Electron Affinities (in kilojoules per mole)</th>
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<tr>
<td></td>
<td>He</td>
</tr>
<tr>
<td></td>
<td>72.8</td>
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<tr>
<td>Li</td>
<td>59.8</td>
</tr>
<tr>
<td>Be</td>
<td></td>
</tr>
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<td>B</td>
<td></td>
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<tr>
<td>C</td>
<td></td>
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<tr>
<td>N</td>
<td></td>
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<tr>
<td>O</td>
<td>141</td>
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<tr>
<td>F</td>
<td></td>
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<tr>
<td>Cl</td>
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<tr>
<td>Br</td>
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<td>I</td>
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<tr>
<td>S</td>
<td>52.9</td>
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<tr>
<td>Se</td>
<td></td>
</tr>
<tr>
<td>Te</td>
<td></td>
</tr>
<tr>
<td>Po</td>
<td></td>
</tr>
<tr>
<td>Ar</td>
<td>49.0</td>
</tr>
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</table>

**Note**: From this table it can be concluded that E.A of third period elements is higher than second period elements.

**Ques 6**: Which has higher value of electron affinity O or O^−?
Ans = Clearly O\(^-\) has higher value of E.A as O\(^-\) has 9 electron and has similar electronic configuration of fluorine [He] 2s\(^2\)2p\(^5\) and addition of one more electron makes its fully filled configuration and has high E.A.

Successive Electron affinities:-

\[
\begin{align*}
\text{Cl}(g) + e^- &\rightarrow \text{Cl}^-(g) & 1\text{st EA} = -142 \text{ kJ mol}^{-1} \\
\text{Cl}^-(g) + e^- &\rightarrow \text{Cl}^{2-}(g) & 2\text{nd EA} = +844 \text{ kJ mol}^{-1}
\end{align*}
\]

**Gate tip**: Chlorine is the element with highest E.A while F has highest Ionisation energy. Both ionisation energy and electron affinity are energies with opposite sign.

Ionisation energy is energy absorbed to remove an electron from isolated gaseous atom while E.A is energy released on addition of an electron.

5) **Electronegativity**: It is defined as the tendency to attract the shared pair of electrons to itself. It is not the property of an isolated atom. It depends on the element to which the atom is bonded. It is denoted by symbol \(\chi\).

Eg:-

Cl is having delta negative charge because it is more electronegative.

**Factors influencing Electronegativity:-**

1) **Charge on atom** :- An atom which acquires a positive charge either partial or integral would attract electron more strongly than neutral atom.

Eg :- Order of electronegativity O\(^+\) > O > O\(^-\)

2) **Hybridisation**: Electronegativity of the atom would increase with increase in the s character of hybrid orbital.

**Order of electronegativity** C\(_2\)H\(_6\) < C\(_2\)H\(_4\) < C\(_2\)H\(_2\)

Hybridisation sp\(^3\) sp\(^2\) sp

% s character  50 33.3 25

3) **Effect of substituents**: Electronegativity of central atom is enhanced by the electronegative substituents.
Eg.: CF₃I > CH₃I carbon atom in CF₃I acquires more positive charge than in CH₃I and hence carbon atom in CF₃I is more electronegative.

**Trend of Electronegativity in periodic table:** Electronegativity decreases down the group and as we move from left to right across a period it increases.

**Explanation:** As we move down the group atomic radii increases, due to which the tendency to pull electron towards itself decreases. On moving from left to right across a period atomic radii decreases as the force of attraction on the outer valence electron by nucleus increases and hence electronegativity increases.

**Note:** Fluorine is the highest electronegative element (value = 4). EN of F > O > N.

**Note:** Non-metals has the tendency to gain electrons so non-metallic properties is directly related to electronegativity.

**Measurement of Electronegativity:**

1) **Pauling’s scale:** For a reaction of type $A_2 + B_2 \rightarrow 2AB$

The electronegativity difference between two atoms ($X_A - X_B$) can be determined by the expression

$$X_A - X_B = 0.208 \left[ \frac{E_{A,B} - (E_{A,A} \times E_{B,B})^{1/2}}{2} \right]$$

Where $X_A =$ electronegativity of A $X_B =$ electronegativity of B $E_{A,A} =$ bond energy of A-A molecule

$E_{B,B} =$ bond energy of B-B molecule $E_{A,B} =$ bond energy of A-B molecule

**Gate tip:** Bond energy of A-B compound is always greater than A-A and B-B and if we know the electronegativity of one atom and all bond energies, electronegativity of other atom can be calculated.

$$E_{A,B} - \left( E_{A,A} \times E_{B,B} \right)^{1/2} = \text{Ionic resonance energy and a measure of partial ionic character.}$$

2) **Mulliken Scale:** Electronegativity of an atom can be regarded as average of ionisation potential and electron affinity.

$$\text{E.N.} = \frac{\text{I.E.} + \text{E.A}}{2}$$

where the ionisation energy and electron affinity value are in eV.

Similar calculation for pauling scale:-

$$\text{E.N.} = \frac{(\text{I.E.} + \text{E.A})}{5.6}$$

**Application of Electronegativity:**

1) **Nature of the bond of a molecule:**

If $X_A$-$X_B$ i.e $\Delta$E.N > 1.7 then bond has more ionic character. Eg.: NaCl where $X_A$-$X_B = 2.1$ so ionic

If $X_A$-$X_B$ i.e $\Delta$E.N < 1.7 then bond has more covalent character. Eg.: H-Cl where $X_A$-$X_B = 0.9$ so covalent

If $X_A$-$X_B$ i.e $\Delta$E.N = 0 then non polar bond. Eg.: H-H where $X_A$-$X_B = 0$.

**Note:** Hanny-Smith formula for calculating ionic character of a bond = $6 [X_A$-$X_B] + 3.5 [X_A$-$X_B]^2$
2) **Polarity of a molecule:**- As $X_A-X_B$ increases the polarity between two bonded atoms increases and dipole moment also increases.

Eg:- $\text{H}_2\text{O} > \text{NH}_3$ $\text{H}_2\text{O} > \text{H}_2\text{S}$

The direction of dipole is always from less electronegative to more electronegative atom $A\rightarrow B$ which is determined by $X_A-X_B$.

3) **Bond Strength Determination:**- As $\Delta E.N = X_A-X_B$ increases bond strength increases.

**Order of bond strength** $\text{H-F} > \text{H-Cl} > \text{H-Br} > \text{H-I}$

$X_A-X_B$  
1.9 0.9 0.7 0.4

**Inert Pair Effect** :- It is defined as the reluctance(unwillingness) of two electrons of s-orbital of the valence shell to participate in chemical bond formation as we move down the group. As a result elements of these groups shows oxidation state two unit lower than group oxidation state.

**Note:-** It is generally observed in heavier members of group 13,14 and 15.

**Reason :-** The outer electronic configuration of group 13$^{\text{th}}$, 14$^{\text{th}},15^{\text{th}}$ is $\text{ns}^2\text{np}^1$, $\text{ns}^2\text{np}^2$ and $\text{ns}^2\text{np}^3$. Since valence p electrons has less probability of being near to nucleus than valence s electrons. So valence p orbitals are easily removed or excited at time of bond formation than s orbitals and they are thought to be inert.

Eg:- For Boron family group oxidation state is +3 and +1. As we move down the group +1 oxidation state becomes more and more stable.

**Major Oxidation state of group 13**

$\text{Al} = +3$  
$\text{Ga} = +3$  
$\text{In} = +1 \& +3$  
$\text{Tl} = +1$ stable oxidation state.

**Similarly for carbon family +2 state become more and more stable for tin and lead.**

**Ques 7:-** Which of the following halide is least stable and has doubtful existence?

(a) $\text{CCl}_4$  
(b) $\text{GeI}_4$  
(c) $\text{SnI}_4$  
(d) $\text{PbI}_4$

Ans = (d) $\text{PbI}_4$ is least stable due to inert pair effect. It forms compound in +2 oxidation state.

**Melting and Boiling Point:**-

**Variation in group:**- As we move down the group melting and boiling point show a regular gradation with different variation in different groups. Eg:- For alkali metal the melting and boiling point decrease regularly as we move down the group.

**Explanation:** Melting and boiling point depend on force of attraction between constituent atoms. On moving down the group size increases and force of attraction decrease as $F_{\text{attr}}$ is inversely related to $1/r^2$.resulting in increase in metallic character and melting point decrease.
Gate tip :- Upto group 14 as we move down the group melting and boiling point decreases but after group 14 the melting and boiling point increases as we move down the group as the major predomination force is vander waal force of attraction($F_{\text{van}} \propto r$) which increase with size resulting in high melting and boiling point.

Eg:- Melting point of $I > Br > Cl > F$ $C > Si > Ge > Sn < Pb$

Variation in period:- On moving across a period the melting and boiling point first increases and reach maximum value for group 14 and after that it start decreasing. Noble gas has minimum melting and boiling point across a period.

Eg:- Melting and boiling point of Li < Be < B < C $C > N > O > F > Ne$

Explanation:- Across period first it increases upto group 14 where the major force of interaction is attractive which increase as size decrease and afterwards it is vander waal force of interaction which decreases as size decreases.

Ques8: Arrange the following in increasing order of melting point He, Ne, Ar, Kr?
Ans: Kr > Ar > Ne > He (major force is van der waal which increases as size increases)

Hydration energy:- It is the enthalpy change accompanying the dissolution of one mole of gaseous ions in water.

$$\text{Li}^+(g) + H_2O \rightarrow [\text{Li}(H_2O)]^+ \quad \Delta H = -806 \text{KJ/mol}$$

During this process some new bonds with water are formed and bond formation is exothermic process so it is having negative value. As $\Delta H$ of hydration increases, solubility increases

Gate tips :- $\Delta H_{\text{hydr}} \propto 1/r \propto \text{solubility}$

Extent of hydration depend on charge density i.e Charge density = Charge/Size of ion

Note:- Greater the charge and smaller the size of ion i.e greater the charge density, greater the attraction of ion pair with water and hence large amount of hydration energy is released.

Small size ions have high charge density and more affinity for hydration and after hydration their size become larger. Larger size ions moves slowly and have low value of ionic mobility.

Eg:- Li$^+ < Na^+ < K^+ < Cs^+$ order of size before hydration

Li$^+ > Na^+ > K^+ > Cs^+$ order of size after hydration

Li$^+ < Na^+ < K^+ < Cs^+$ order of ionic mobility after hydration

Acidic-Basic Character of oxides: A substance having less electron density is an lewis acid so acidic character of oxide is directly related to oxidation state.

Trend in periodic table:- On moving across a periodic table the acid character of oxide increases and basic character decreases as oxidation state of oxide increases on moving across period.

Note :- On moving down the group acidic character decreases while basic character increases.

Gate tips :- Oxidation state $\propto 1/r \propto 1/$basic character $\propto$ acidic character

Li$_2$O < MgO < Al$_2$O$_3$ < SiO$_2$ < SO$_3$ < Cl$_2$O$_7$ increasing acidic character order
Li_2O < Na_2O < K_2O < Rb_2O < Cs_2O  

increasing basic character

**Note:** Stability of oxide decreases along a period, while its reactivity increases.

**General Reaction of Acidic oxide with water:**

M–OH + H_2O → MO^+ + H_3O^+

**General Reaction of basic oxide with water:**

M–OH + H_2O → (M–OH)_2^+ + OH^–

**Amphoteric oxide:** Those oxide which reacts with both acid and base to form salt are called amphoteric oxide.

Eg:– Al_2O_3 + 6HCl → 2AlCl_3 + H_2O  

Al_2O_3 + 2NaOH + 3H_2O → 2Na[Al(OH)_4]

**Gate tips:** Oxide of following elements are amphoteric H, Be, Al, Ga, In, Tl, Sn, Pb, Sb, Bi, Po

H_2O is amphoteric, also called as amphioprotic.

**Note:** Acidic character of oxide is directly proportional to non-metallic character.

**Ques 9:** Arrange the following oxides in increasing order of non-metallic and acidic character Cl_2O_7, SO_3, P_2O_5, PbO_2, CaO.

**Ans:** Acidic character & oxidation state & non-metallic character

So order of acidic character:  
Cl_2O_7 > SO_3 > P_2O_5 > PbO_2 > CaO

Non-metallic character order:  
Cl_2O_7 > SO_3 > P_2O_5 > PbO_2 > CaO

Oxidation number: +7 +6 +5 +4 +2

**Diagonal Relationship:**

On moving diagonally across periodic table, the elements of 3rd period lying at diagonal position w.r.t 2nd period have almost similar properties.

<table>
<thead>
<tr>
<th>Group 1</th>
<th>Group 2</th>
<th>Group 13</th>
<th>Group 14</th>
</tr>
</thead>
<tbody>
<tr>
<td>Period 2</td>
<td>Li</td>
<td>Be</td>
<td>B</td>
</tr>
<tr>
<td>Period 3</td>
<td>Mg</td>
<td>Al</td>
<td>Si</td>
</tr>
</tbody>
</table>

**Reason for showing diagonal Relationship:**

Polarising power = Ionic charge/Ionic size.
On moving from left to right across a period, ionic charge increases and ionic size decreases thus resulting in increasing polarising power. While moving down the group, ionic charge remains same, but ionic size increases resulting in decrease in polarising power. So, on moving diagonally, these two effects cancel each other and hence same polarising power and similar properties of diagonal elements.

**Note:** This reason is valid for explaining diagonal relationship of Li & Mg, Be & Al, B & Si.

For **non metals** exhibiting diagonal relationship it can be explained on the basis of similarity in **electronegativities**. Concept of ionic charge cannot explain because these elements have no metallic character.

![Electronegativity Chart](image)

This diagram shows diagonal relationship on the basis of similarity in electronegativity.

**Oxidising and Reducing Properties:**

**Oxidising agent:** A substance is called an oxidising agent if it can gain electron. It is reverse of oxidation (tendency to lose electrons).

**Note:** An oxidising agent oxidises other substance while reduce itself (gain electron) in a chemical reaction.

**Reducing agent:** A substance which can lose electron. It is reverse of reduction (tendency to gain electrons).

**Note:** A reducing agent can reduce other substance while oxidises itself in a chemical reaction.

**Trend in periodic table:**

**Gate tips:** Size (r) $\propto$ reducing character $\propto 1$/oxidising character.

As size increases along group, tendency to lose electron increases and reducing character increases and oxidising character decreases.

Eg: Na is a weak reducing agent while Cs is a strong reducing agent.

Along period size decreases so reducing character decreases and oxidising character increases along period.

Eg: Sodium(Na) is a reducing agent while Cl is an oxidising agent.

**Ques 10:** Which among the following is a strong oxidising agent PbCl$_4$ or PbCl$_2$?

**Ans:** PbCl$_4$($+4$ O.S) is a strong oxidising agent as it has the tendency to accept electron and convert to PbCl$_2$($+2$ O.S) which is stable due to inert pair effect.
**Hydrides** :- Hydrogen combines with a number of other elements which includes metals and non-metals to form compounds called hydrides.

**Type of hydrides:-**

1) **Ionic hydrides**:- When hydrogen combines with metals which are more electropositive than hydrogen, ionic hydrides are formed.

Eg:- Alkali and alkaline metal hydride like NaH, CaH2, CsH.

**Note**: Thermal stability of hydride decrease as we move along a group but chemical reactivity increases.

**Stability** $\propto \frac{1}{\text{reactivity}}$

**Order of thermal stability** :- LiH > NaH > KH > RbH > CsH.

**Application** :- Ionic hydrides and their complexes (Li[AlH4], Na[BH4]) are used as reducing agent.

2) **Covalent or molecular hydrides**:- These are predominately formed by non – metals on reaction with hydrogen except Be and Mg.

Eg:- BeH2, BH3, AlH3, NH3 etc.

**Stability of hydride** :- In covalent hydrides H-X bond energy decrease with increase in atomic number. So stability of covalent hydrides decreases down the group while it increases along period.

**Gate tips** :- Stability of hydride $\propto \frac{1}{\text{size}} \propto \frac{1}{\text{reactivity}}$.

**Boiling point of hydrides** :- The boiling point of covalent hydrides(except first element) increase regularly with increase in atomic number i.e increases along a group.

**Order of Boiling point** :- SbH3 > NH3 > AsH3 > PH3, H2O > H2Te > H2Se > H2S, HF > HI > HBr > HCl

**Note** :- The abnormal high boiling point of first element hydride is due to association of molecules through H-bonding.

**Ques 11**: Predict the order of boiling point of following hydrides CH4, SiH4, GeH4, SnH4 ?

**Ans** = SnH4 > GeH4 > SiH4 > CH4

In this case there is no association of CH4 molecules through H-bonding and boiling point increase with increase in molar mass.

3) **Interstitial hydrides** :- These hydrides are formed by combination of hydrogen with transition and inner transition elements. Hydrogen occupies interstitial position in these hydrides so they are termed as interstitial hydrides.

Eg:- TiH1.7, ZrH1.9, HfH1.9, YbH2, YbH4, YbH2.5

**Note** :- Transition metal hydrides are predominately non stoichiometric while inner transition element hydrides are both stoichiometric & non-stoichiometric.
**Bond Dissociation energy**: It is defined as the amount of energy required to break one mole of a bond to give separated atoms with everything being in gaseous state. It is the term which is frequently used for covalent compounds.

As the bond length increases, it becomes easy to break a bond.

**Bond order**: It is the number of chemical bonds between a pair of atoms. Higher bond order means smaller bond length.

Eg:- \( \text{CH}≡\text{CH} < \text{CH}_2=\text{CH}_2 < \text{CH}_3\text{CH}_3 \) order of bond length

\[
3 \quad 2 \quad 1 \text{ value of bond order}
\]

Value of bond order for molecular ions can be calculated by \( \text{B.O} = (\text{Nb} - \text{Na})/2 \).

**Gate tip**: \( \text{BDE} \propto \text{Stability} \propto \text{B.O} \propto 1/\text{Bond length} \propto 1/\text{reactivity} \)

Where \( \text{BDE} = \text{bond dissociation energy} \) \( \text{B.O} = \text{bond order} \).

**Lattice energy**: It is defined as the amount of energy released when a lattice or ionic solid is formed from its constituent ions. Since energy is released, so it is an **exothermic process**.

\[
\text{Uo} = Kq_1q_2/d \text{ where } q_1 \text{ and } q_2 \text{ are charge on respective ions and } d = \text{distance between cation and anion.}
\]

\( \text{Uo} \propto \text{Lattice energy} \propto 1/r \)

**Gate tips**: \( \text{F}_{\text{elect}} \propto \text{Uo} \propto \text{M.P} \propto \text{B.P} \propto 1/\text{solubility} \propto 1/r \).

**Practice Questions**:

**Ques 1**: Arrange the following in increasing order of lattice energy \( \text{LiF, NaF, KF, RbF, CsF?} \)

**Ans**: \( \text{LiF} > \text{NaF} > \text{KF} > \text{RbF} > \text{CsF} \)

**Ques 2**: Arrange the following molecules in increasing order of bond dissociation energy and decreasing order of reactivity?

\[
\begin{align*}
\text{(i) Cl}_2  \\
\text{(ii) F}_2  \\
\text{(iii) Br}_2  \\
\text{(iv) I}_2
\end{align*}
\]

**Ans** =  

**Order of Bond dissociation energy is** \( \text{Cl}_2 > \text{Br}_2 > \text{F}_2 > \text{I}_2 \)

**Order of Reactivity** \( \text{I}_2 > \text{F}_2 > \text{Br}_2 > \text{Cl}_2 \)

**Ques 3**: Arrange the following molecular ions in increasing order of reactivity?

\[
\begin{align*}
\text{(i) O}_2  \\
\text{(ii) O}_2^+  \\
\text{(iii) O}_2^-  \\
\text{(iv) O}_2^{2-}
\end{align*}
\]

**Ans** = \( \text{O}_2^{2-} > \text{O}_2^- > \text{O}_2 > \text{O}_2^+ \)
**Fill in the blanks questions:-**

**Ques 1:** Ca\(^{2+}\) has a smaller ionic radius than K\(^+\) because it has ……………?

**Ans =** High effective nuclear charge

**Ques 2:** Compounds that formally contain Pb\(^{4+}\) are easily reduced to Pb\(^{2+}\). The stability of lower oxidation state is called …………?

**Ans =** Inert pair effect

**Ques 3:** The energy released when an electron is added to neutral gaseous atom is called …………?

**Ans =** Electron affinity

**Ques 4:** On Mulliken scale the average of ionisation potential and electron affinity is called …………?

**Ans =** Electronegativity