

Periodic Classification of Elements and General Inorganic Chemistry

OVERVIEW

1. Periodic table: It classifies all the known elements in accordance with their properties in such a manner that elements with similar properties are grouped together in the same vertical column and elements with dissimilar properties are separated from one another.

2. Döbereiner's triads or law of triads: Döbereiner arranged similar elements in groups of three elements and showed that their atomic weights are either nearly the same or the atomic weight of the middle element is approximately the arithmetic mean of the other two. For example,

| Triad: | Li | Na | K | Mean of first and third elements |
|----------|----|----|----|----------------------------------|
| At. wt.: | 7 | 23 | 39 | $\frac{7+39}{2} = 23$ |

The law of triads seemed to work only for a few elements. It was dismissed as coincidence.

3. de Chancourtois classification or telluric screw (or helix) classification: de Chancourtois arranged the then known elements in order of increasing atomic weights and made a cylindrical table of elements to display the periodic recurrence of properties.

4. Newlands law of octaves: Newlands arranged lighter elements in the increasing order of their atomic weights and noted that every eighth element had properties similar to the first element. This law seemed to be true only for elements up to calcium (Ca).

5. Lothar Meyer classification: Lothar Meyer plotted a graph between atomic volumes and atomic weights of the elements and observed that elements with similar properties occupied similar position on the curve.

6. Mendeleev's periodic table: It was based on atomic weights. The physical and chemical properties of elements are periodic functions of their atomic weights.

Mendeleev proposed that some of the elements are still undiscovered and therefore left several gaps in the table. Both gallium (Ga) and germanium (Ge) were unknown at that time. He left the gap under aluminium (Al) and a gap under silicon (Si) and called these elements **EKa-aluminium and EKa-silicon**.

Glenn T. Seaborg, the discoverer of element with atomic number 101, named this element as Mendelevium (Md) in his honour. Similarly, element 106 has been named Seaborgium (Sg) in Seaborg's honour.

7. Modern periodic law: The physical and chemical properties of the elements are periodic functions of their atomic numbers. This conclusion was obtained by Moseley's experiment. He observed regularities in the characteristic X-ray spectra of the element. Thus, a plot

of $\sqrt{\nu}$ versus Z gave a straight line (where ν is the frequency of X-rays emitted and Z is the atomic number).

Modern periodic table arranges the elements in order of their atomic numbers in 7 horizontal rows (periods) and 18 vertical columns (groups or families). Atomic numbers in a period are consecutive, whereas in a group they increase in a pattern.

Elements of the same group have similar **valence shell** electronic configuration and, therefore, exhibit similar chemical properties. However, elements of the same period have incrementally increasing number of electrons from left to right and, therefore, have different valencies.

8. IUPAC nomenclature of elements with $Z > 100$: Both the American and Soviet scientists claimed credit for discovering element 104. The Americans named it Rutherfordium (Rf) whereas the Soviets named it Kurchatovium. To avoid such problems, the IUPAC has made recommendation that until a new element's discovery is proved and its name is officially recognised, a systematic nomenclature be derived directly from the atomic number of the element using the numerical root for 0 and numbers 1–9. The roots are put together in order of digits which make up the atomic number and 'ium' is added at the end. For example, IUPAC name and symbol for the element with atomic number 121 is unbiunium (Ubu).

As of now, elements with atomic numbers up to 112, 114 and 116 have been discovered. Elements with atomic numbers 113, 115, 117 and 118 are not yet known.

9. Classification of elements: Four types of elements can be recognised in the periodic table on the basis of their electronic configurations. These are **s-block, p-block, d-block, and f-block elements**.

Hydrogen with one electron in the $1s$ orbital occupies a unique position in the periodic table.

10. s-Block elements: The elements of groups 1 and 2, including hydrogen and helium, in which the s -orbitals are being progressively filled in are called **s-block elements**. The total number of elements in **s-block** are 14. General outer shell electronic configuration of **s-block** elements is ns^{1-2} , where n is 2–7.

11. p-Block elements: The elements of groups 13 to 18 (excluding helium) in which p -orbitals are being progressively filled in are called **p-block elements**. The total number of elements in **p-block** are 30 in the periodic table.

General outer shell electronic configuration of **p-block** elements is $ns^2 np^{1-6}$, where n is 2–6.

12. *d*-Block elements: Elements in which the last electron (differentiating electron) enters into penultimate shell, i.e., $(n-1)d$ orbitals are called ***d*-block elements**.

General outer shell electronic configuration of *d*-block elements is $(n-1)d^{1-10} ns^{0-2}$, where n is 4–7.

13. *f*-Block elements: Elements in which the last electron (differentiating electron) enters into the antepenultimate shell, i.e. $(n-2)f$ orbitals are called ***f*-block elements**.

General outer shell electronic configuration of *f*-block elements is $(n-2)f^{0-14} (n-1)d^{0-1} ns^2$, where n is 6–7.

14. Metals, non-metals and metalloids

a. **Metals:** They comprise 78% of all the known elements. They are usually solid at room temperature with high melting and boiling points. But mercury (Hg) is liquid at room temperature. However, Ga (303 K), Cs (302 K) and Fr (300 K) have low melting points.

They are good conductor of heat and electricity, malleable and ductile.

Ga (gallium), a liquid metal, is used in making high-temperature thermometer. Similarly, Ge (germanium), a liquid metal, is transparent in the infrared (IR) region and, therefore, is used in the making of infrared windows, prisms and lenses.

b. **Non-metals:** They are located at the top right-hand side of the periodic table and are less than 20 in number (i.e. 18). They are either solid or gas (except bromine which is a liquid) at room temperature with low melting and boiling points, poor conductor of heat and electricity, brittle, neither malleable nor ductile.

Boron and carbon have high melting and boiling points.

c. **Metalloids or semi-metals:** Elements which lie at the border line between metals and non-metals (e.g., Si, Ge, As, Sb and Te) are called **metalloids or semi-metals**.

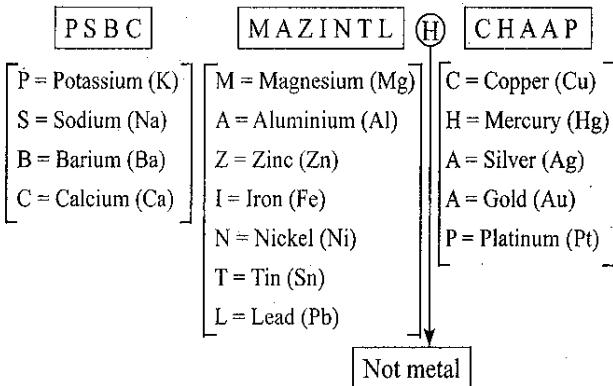
d. **Trends in metallic and non-metallic character:** Metallic character increases down the group (\downarrow) whereas decreases from left to right in a period (\rightarrow). The trend is reverse for non-metallic character. The physical and chemical properties of elements vary periodically with their atomic number.

e. **The useful mnemonic of remembering the metallic character series**

Decreasing order of metallic character is given below:

K > Na > Ba > Ca > Mg > Al > Zn > Fe > Ni > Sn > Pb
[H] > Cu > Hg > Ag > Au > Pt

The useful mnemonic to remember the metallic series is:



Note: That hydrogen is not a metal and comes between MAZINTL and CHAAP

15. Advantages and defects of the modern or long form of the periodic table

a. Advantages:

- It correlates the position of elements to the electronic configuration of their atoms, and thus, elements have been grouped into *s*-, *p*-, *d*- and *f*-blocks. This has helped to understand their properties more easily.
- The transition elements of $3d$, $4d$, $5d$ and $6d$ are assigned proper positions in this periodic table.
- Elements of groups 8–10 consisting of nine elements in three triads (group VIII of the Mendeleev's periodic table) are assigned proper positions in this periodic table.

b. Defects:

- Although hydrogen has been placed along with alkali metals in group I and halogens in group 17, yet its position is not settled. Hydrogen shows many properties similar to both group 1 and 17 elements.
- Lanthanides and actinides have not been included in the main part of the periodic table.

16. Periodic properties: The properties which are related to electronic configuration and which show a regular gradation down the group (\downarrow) and along the period (\rightarrow) are called periodic properties.

17. Atomic radius: Considering an atom to be spherical, the atomic size is the radius of the sphere and known as atomic radius.

It is defined as the distance from the centre of the nucleus to the outermost shell containing electrons.

OR

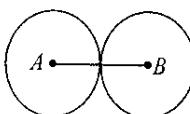
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The distance from the centre of the nucleus to the point up to which the density of electron cloud (i.e., probability of finding the electron) is maximum.

Depending upon whether an element is a metal or a non-metal, there are four different types of atomic radii:

- a. **Metallic radius:** It is half the internuclear distance separating the metal cores in the metallic crystal.

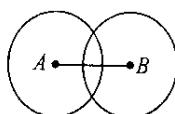
$$\therefore r = \frac{1}{2} AB$$



(No overlapping of atomic orbitals)

- b. **Covalent radius:** It is one-half of the distance between the nuclei of two covalently bonded atoms of the same element in a molecule.

$$\therefore r = \frac{1}{2} AB$$

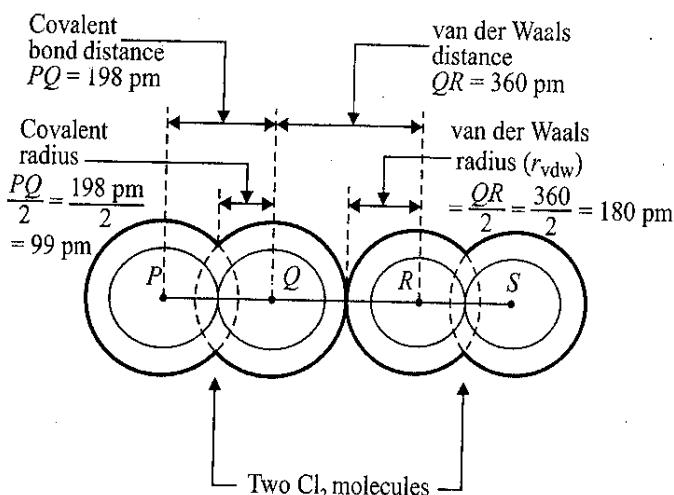


(Overlapping of atomic orbitals to form a covalent bond)

\therefore Metallic radius > Covalent radius

- c. **van der Waals radius:** It is one-half of the distance between the nuclei of two identical non-bonded isolated atoms. Thus,

van der Waals radius > Metallic radius > Covalent radius.



(Comparison of van der Waals and covalent radii in two Cl_2 molecules)

van der Waals radii (r_{vdw}) \propto Number of energy shells and

$$r_{\text{vdw}} \propto \frac{1}{\text{Nuclear charge}}$$

Thus, r_{vdw} of Br > r_{vdw} of Cl > r_{vdw} of F.

Similarly,

r_{vdw} of N > r_{vdw} of O > r_{vdw} of F,
and r_{vdw} of P > r_{vdw} of S.

- d. **Ionic radii:** Ionic radii in an ionic crystal is calculated from the internuclear distance between the two ions (i.e. cation and anion).

- i. **Radius of cation:** It is smaller than that of the corresponding neutral atom.

- ii. **Radius of anion:** It is larger than that of the corresponding neutral atom.

18. Variation of atomic and ionic radii in the periodic table:

Generally, the covalent or van der Waals radii increases down the group (\downarrow) and decreases along the period (\rightarrow). Both cationic and anionic radii increase down the group (\downarrow) due to increase in the number of shells.

Exceptions: Elements of 2nd and 3rd transition series belonging to same vertical columns are similar in size and properties because of the intervention of lanthanides.

- 19. **Isoelectronic species:** They are ions of different elements having same number of electrons but different nuclear charge (Z).

Ionic radii of isoelectronic species decrease with the increase in the magnitude of nuclear charge (Z), e.g. ionic radii, decreases in the order (all have 10 electrons but with $Z = +7, +8, +9, +11, +12$ and $+13$) as:

$$\text{N}^3- > \text{O}^2- > \text{F}^- > \text{Na}^+ > \text{Mg}^{2+} > \text{Al}^{3+}$$

- 20. **Ionisation enthalpy (IE):** It is the minimum amount of energy required to remove the outermost shell electron from an isolated gaseous atom to form a gaseous ion (represented as IE or $\Delta_i H^\ominus$).

It is measured in eV atom^{-1} or kcal mol^{-1} or kJ mol^{-1} .

$$1 \text{ eV atom}^{-1} = 23.06 \text{ kcal mol}^{-1} = 96.49 \text{ kJ mol}^{-1}$$

- 21. **Successive ionisation enthalpies:** The ionisation enthalpies to remove first, second, and third electrons, etc., from an isolated gaseous atom are called successive ionisation enthalpies.

$$\text{IE}_3 > \text{IE}_2 > \text{IE}_1 > \text{or } \Delta_i H_3^\ominus > \Delta_i H_2^\ominus > \Delta_i H_1^\ominus$$

- 22. **Factors affecting the magnitude of ionisation enthalpies**

- a. Size of an atom
- b. Z_{eff} (effective nuclear charge)
- c. Screening effect
- d. Penetration effect
- e. Electronic configuration

- 23. **Variation of IE in the periodic table:** IE_1 generally decreases down the group (\downarrow) and increases along the period (\rightarrow).

Exception:

a. IE_1 of Be > IE_1 of B

IE_1 of Mg > IE_1 of Al

IE_1 of N > IE_1 of O

IE_1 of P > IE_1 of S

b. Exception of IE in group 13 elements.

Elements: B > Al < Ga > In < Tl

$\text{IE}_1(\text{kJ mol}^{-1})$: 801 577 579 558 589

Exception in IE_1 : Ga > Al (imperfect shielding of 3d orbitals in Ga).

c. General trend in IE_1 from $3d \rightarrow 4d$ series is observed but not in $4d \rightarrow 5d$ series because of the incorporation of the 14 lanthanide elements between La and Hf. $5d$ series have the highest IE_1 . The increase in radius due to the addition of extra shell is compensated by the decrease in radius due to lanthanide contraction.

Hence, the radii of $4d$ and $5d$ elements more or less remain the same, due to which Z_{eff} increases to more extent, which results in high IE_1 of the $5d$ elements of transition series.

24. Electron gain enthalpy ($\Delta_{\text{eg}}H^\ominus$): It is the energy released when a neutral isolated gaseous atom accepts an extra electron to form the gaseous ion, i.e., anion.

$\Delta_{\text{eg}}H^\ominus$ for halogens (group 17) is highly negative, because they attain stable noble gas configuration by accepting an extra electron. Whereas noble gases have large positive $\Delta_{\text{eg}}H^\ominus$ value because the extra electron has to be added in the next higher principal quantum energy level thereby producing highly unstable electronic configuration.

Like ionisation energy, $\Delta_{\text{eg}}H^\ominus$ is measured either in eV atom $^{-1}$ or kJ mol $^{-1}$ or kcal mol $^{-1}$.

25. Successive electron gain enthalpies: The energy released to add first, second, third electrons and so on to an isolated gaseous atom is called successive electron gain enthalpy. The addition of second electron is opposed by the electrostatic repulsion and hence energy is required for the addition of second electron. Thus, the second electron gain enthalpy of an element is positive.

For example, $\Delta_{\text{eg}}H_1^\ominus$ of oxygen = -141 kJ mol $^{-1}$

but $\Delta_{\text{eg}}H_2^\ominus$ of O $^\ominus$ = +780 kJ mol $^{-1}$

26. Variation of $\Delta_{\text{eg}}H^\ominus$ in the periodic table: Generally $\Delta_{\text{eg}}H_1^\ominus$ decreases (less negative) down the group (\downarrow) but increases (more negative) along the period (\rightarrow).

27. Factors affecting the magnitude of $\Delta_{\text{eg}}H^\ominus$

a. Size of an atom

b. Z_{eff} (Effective nuclear charge)

c. Electronic configuration

Some exceptions:

i. $\Delta_{\text{eg}}H_1^\ominus$ of Cl > F > Br > I

ii. $\Delta_{\text{eg}}H_1^\ominus$ of Al > B

iii. $\Delta_{\text{eg}}H_1^\ominus$ of P > N

iv. $\Delta_{\text{eg}}H_1^\ominus$ of S > O

28. Electronegativity (EN): It is the tendency of an atom to attract shared pair of electrons towards itself in a covalently bonded molecule. It is represented as χ (chi) or EN.

It is not a measurable quantity. However, various numerical scales of EN have been developed.

The EN of any element is not constant and varies depending upon the element to which it is bonded.

29. Variation of EN in the periodic table: Generally, it increases along the period (\rightarrow) and decreases down the group (\downarrow).

F is the most EN element with a value of 4.0 and C is the least EN element.

Exceptions:

a. EN of Ga and Ge > EN of Al and Si
(due to the d -block contraction)

b. EN of Pb > EN of Tl and Bi

30. Factors affecting the magnitude of EN:

a. Atomic radius $\left(\text{EN} \propto \frac{1}{\text{atomic radius}} \right)$

b. Z_{eff} (Effective nuclear charge) $(\text{EN} \propto Z_{\text{eff}})$

c. Number of inner shells

$\left(\text{EN} \propto \frac{1}{\text{number of inner shells}} \right)$

d. Charge on the ion or oxidation state of the atom
($\text{EN} \propto \text{Number of positive charge}$)

$\left(\text{EN} \propto \frac{1}{\text{number of negative charge}} \right)$

e. Nature and number of substituent atoms attached to the atom

f. State of hybridisation ($\text{EN} \propto s$ -character in the hybrid orbital)

EN decreases from $sp > sp^2 > sp^3$ hybrid orbital.

g. IE and $\Delta_{\text{eg}}H^\ominus$: ($\text{EN} \propto$ higher IE or higher or more negative $\Delta_{\text{eg}}H^\ominus$)

h. EN \propto non-metallic character of elements

i. $\left(\text{EN} \propto \frac{1}{\text{metallic character of elements}} \right)$

Thus, along the period (\rightarrow) non-metallic character increases and down the group (\downarrow) metallic character increases.

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31. Scales of EN

a. Pauling scale:

$$(\chi_A - \chi_B) = 0.208 \left[E_{A-B} - \sqrt{E_{A-A} \times E_{B-B}} \right]^{\frac{1}{2}}$$

kcal mol⁻¹.

where χ_A and χ_B are the EN's of two atoms A and B and E_{A-B} , E_{A-A} and E_{B-B} are bond energies of molecules A-B, A₂ and B₂, respectively, in kcal mol⁻¹.

In SI units,

$$(\chi_A - \chi_B) = 0.1017 \sqrt{\Delta_{A-B}}, \text{ where } \Delta \text{ is in kJ mol}^{-1}$$

$$\text{and } \Delta_{A-B} = [E_{A-B} - \sqrt{E_{A-A} \times E_{B-B}}]$$

Another form of the equation can be written as:

$$\begin{aligned} (\chi_A - \chi_B) &= (eV)^{-1/2} \sqrt{E_{A-B} - \frac{1}{2}[E_{A-A} + E_{B-B}]} \\ &= 0.208 \sqrt{E_{A-B} - \frac{1}{2}[E_{A-A} + E_{B-B}]} \text{ (kcal mol}^{-1}\text{)} \\ &= 0.1017 \sqrt{E_{A-B} - \frac{1}{2}[E_{A-A} + E_{B-B}]} \text{ (kJ mol}^{-1}\text{)} \end{aligned}$$

b. Mulliken's scale:

$$\text{i. EN or } \chi_A = \left[\frac{(IP)_A + (EA)_A}{2} \right], \text{ where IP = Ionisation potential and EA = Electron affinity in eV.}$$

ii. If IP and EA are in kcal mol⁻¹, then

$$\text{EN (or } \chi_A \text{)} = \frac{(IP)_A + (EA)_A}{2 \times 62.5}$$

iii. If IP and EA are in kJ mol⁻¹, then

$$\text{EN (or } \chi_A \text{)} = \frac{(IP)_A + (EA)_A}{540}$$

iv. Mulliken's values of EN are about 2.8 times more than the Pauling scale, i.e.,

$$\text{EN Pauling (or } \chi \text{ Pauling)} = \chi \text{ Mulliken}/2.8.$$

$$= \frac{(IP)_A + (EA)_A}{2 \times 2.8}$$

The constant $\frac{1}{2 \times 2.8} = \frac{1}{5.6}$ is called scale adjustment factor. This factor is used when IP and EA are in eV.

v. Pauling scale in terms of $\Delta_{eg} H^\ominus$:

$$\chi_{\text{Pauling}} = [1E - \Delta_{eg} H^\ominus]/2$$

The Mulliken EN values are scaled down to match the Pauling value by dividing $\left(\frac{IP + EA}{2} \right)$ in eV by 3.17.

c. Allred-Rochow's scale:

$$\text{EN (or } \chi_A \text{)} = 0.359 \times \frac{Z_{\text{eff}}}{r^2} + 0.744$$

where r is the radius of an atom in Å. The value of Z_{eff} is calculated from Slater's rule taking all the electrons.

32. Non-polar and polar bonds:

- a. A bond between two similar atoms is non-polar.
- b. If the EN's of the two atoms forming a bond are different and the bonded atoms acquire $\alpha + \delta$ and $-\delta$ charges is called a polar covalent bond.
- c. Higher the difference in EN of two bonded atoms, the molecule is more polar and have higher dipole moment (μ).
- i. When $(\chi_A - \chi_B) = 1.7$, the bond is 50% ionic and 50% covalent.
- ii. When $(\chi_A - \chi_B) < 1.7$, the covalent character is more than 50%.
- iii. When $(\chi_A - \chi_B) > 1.7$, the ionic character is more than 50%.

d. Percentage of ionic character:

$$\% \text{ of ionic character} = [16(\chi_A - \chi_B) + 3.5(\chi_A - \chi_B)^2]$$

when $(\chi_A - \chi_B) = 2.1$, the compound is 50% ionic

$$\text{e. } (\chi_A - \chi_B) \propto \text{bond strength}$$

33. Acidic and basic nature of oxides of normal elements :

The acidic nature of oxides of normal elements increases whereas the basic nature decreases along the period (\rightarrow) due to increase of EN from left to right in a period.

34. Bond length:

- a. Generally, in case of heteroatomic molecule of AB type, bond length (d_{A-B}) is equal to the sum of covalent radii of A and B atoms.

$$d_{A-B} = \chi_A + \chi_B$$

$$\text{b. } d_{A-B} \propto \frac{1}{\% \text{ of ionic character}}$$

$$\text{c. } d_{A-B} \propto \frac{1}{(\chi_A - \chi_B)} \propto \text{stability of AB molecule}$$

- 35. Bond angle: For AB_x -type molecule (where A is the central atom, B is the atom attached with atom A and x is the number of B atoms), then B-A-B bond angle changes as given.

- a. If the EN of central atom decreases and/or the size increases the bond angle decreases, i.e. the bond angle decreases down the group, e.g. bond angle of $\text{NH}_3 > \text{PH}_3 > \text{AsH}_3 > \text{SbH}_3$ and $\text{H}_2\text{O} > \text{H}_2\text{S} > \text{H}_2\text{Se} > \text{H}_2\text{Te}$.

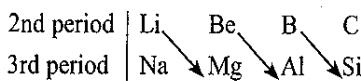
- b. If the EN of atom B decreases, the bond angle (B-A-B) increases, e.g. bond angle of $\text{PI}_3 > \text{PBr}_3 > \text{PCl}_3$ and $\text{NH}_3 > \text{NF}_3$ and $\text{OH}_2 > \text{OF}_2$.
- c. Molecules or ions without nonbonding electrons (i.e. lone pair of e^- 's) on central atom and having regular geometry, the change in the EN of central atom or surrounding atom has no effect on the bond angle. For example, bond angle of $\text{BF}_3 = \text{BCl}_3 = \text{BBr}_3 = \text{AlCl}_3 = 120^\circ$ and similarly $\text{CH}_4 = \text{CBr}_4 = \text{CCl}_4 = \overset{\oplus}{\text{NH}}_4 = 109^\circ 28'$.
- d. For the molecule with same central atom with vacant d -orbitals and with different B atom, bond angle increases with the increase of EN of B atom having lone pair of electrons. For example, bond angle of $\text{PF}_3 > \text{PH}_3$ (opposite to NH_3 and NF_3) (i.e., opposite of point (b)).
- e. Bond angle of $sp > sp^2 > sp^3$ hybrid orbitals ($180^\circ > 120^\circ > 109^\circ 28'$) For example,
 Bond angle of $\text{NO}_2^\oplus > \text{NO}_2 > \text{NO}_3^\ominus > \text{NO}_2^\ominus$
 Bond angle: $180^\circ > 134^\circ > 120^\circ > 115^\circ$

36. **Variation of valence in the periodic table:** Along the period (\rightarrow), the number of valence electrons increases from 1 to 8. But the valence of element w.r.t. H or O, first increases from 1 to 4 and then decreases to zero.

Down the group (\downarrow) elements exhibit same valence.

37. **Typical elements:** They are elements of 3rd period. These include Na, Mg, Al, Si, P, S and Cl. The properties of all elements belonging to a particular group resemble the properties of the corresponding typical elements of that group. For example, the general properties of group 1 can be predicted from the behavior of Na not Li, the first member of the family.

38. **Bridge elements:** They are elements of 2nd period and their properties resemble the properties of elements of 3rd period placed diagonally as shown:



This anomalous behaviour is due to the

- a. Small size
- b. High charge density
- c. High polarising power
- d. High EN of the element

39. Periodic trends and chemical reactivity:

- a. Chemical reactivity of an element is shown by its reactions with oxygen and halogens.

The normal oxide formed by the elements on extreme left is the **most basic** (e.g. Cs_2O), whereas that formed

by the element on extreme right is the **most acidic** (e.g. OF_2 and Cl_2O_7).

Oxides of elements in the centre are **amphoteric** (e.g. Al_2O_3 , As_2O_3) or **neutral** (e.g. CO, NO, N_2O).

40. Magnetic properties:

- a. Diamagnetic substances are weakly repelled by the applied magnetic field and have all the electrons paired in their atoms, e.g. NaCl and H_2O .
- b. Paramagnetic substances are attracted by the applied magnetic field and has one or more unpaired electrons in their atom, e.g., Fe^{3+} and Cr^{3+} .
- c. Ferromagnetic substances keep their magnetism even after the magnetic field is removed, e.g., Fe, Co and Ni.

Using 'spin only' formula, the magnetic moment is given as

$$\mu_s = \sqrt{n(n+2)} \text{ BM}$$

where n is the number of unpaired electrons and it is measured in Bohr Magneton (BM).

$$1 \text{ BM} = \frac{e\hbar}{4\pi mc} = 9.27 \times 10^{-21} \text{ ergs gauss}^{-1}$$

OR

$$= 9.27 \times 10^{-24} \text{ J Tesla}$$

OR

$$= 9.27 \times 10^{-24} \text{ Am}^2$$

41. **Fajans' rule:** It tells about the covalent character or polarisability of a compound. The compound is more covalent when it has the following conditions:

- a. Higher charge on the ions (cation or anion)
- b. Small cation
- c. Large anion
- d. Presence of d electrons

42. **Inert pair effect:** In groups 13–16, down the group (\downarrow), the stability of lower oxidation state increases. This is due to ineffective shielding of ns^2 electrons of valence shell by the intervening d - and f -electrons. So, ns^2 electrons do not participate in bond formation and behave as inert pair. For example, in group 13 Tl exists as Tl^\oplus , in group 14, Pb exists as Pb^{2+} , and in group 15 Bi exists as Bi^{3+} , oxidation states.

43. **Factors that determine the stability of compounds:** The stability of a compound is due to the following conditions:

- a. The compound must have high EN of the element to excite electrons from central atom to vacant orbitals
- b. The central atom must have vacant orbitals
- c. Inert pair effect

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- d. Appropriate sizes of cations and anions, for example,
- NH_3 and NCl_3 exist, but NH_5 and NCl_5 do not exist.
 - PCl_5 exists, but PBr_5 and PI_5 do not exist.
 - PH_3 exists, but PH_5 does not exist.
 - TiCl_3 , PbCl_2 and BiCl_3 are more stable than TiCl_3 , PbCl_4 and BiCl_5 .
 - IF_7 exists, but ICl_7 does not exist.
 - AlCl_3 exists as dimer (Al_2Cl_6), but BCl_3 does not exist.
44. **Lattice enthalpy ($\Delta_U H^\ominus$):** It is the amount of energy released when crystal lattice of one mole of solid ionic compound is formed from their gaseous constituent ions. For example,
- $$\text{Na}^\oplus_{(g)} + \text{Cl}^\ominus_{(g)} \rightarrow \text{Na Cl}_{(s)}, \Delta_U H^\ominus = -788 \text{ kJ mol}^{-1}$$
- It depends on the following factors:
- Size of the ions
 - Magnitude of charges on the ions
- Thus, $\Delta_U H^\ominus \propto \frac{|Z^\oplus| |Z^\ominus|}{r_0}$, where $|Z^\oplus| |Z^\ominus|$ are charges of cation and anion respectively and r_0 is the interionic distance.
- Down the groups (\downarrow) generally, it decreases and increases along the period (\rightarrow).
- It is determined by the use of Born–Haber cycle, which is based upon Hess's law of heat summation.
- Application of lattice energy:** It explains the formation of oxides, peroxides and superoxides of group 1 and group 2 elements.
45. a. **Hydration energy:** It is the amount of energy released when one mole of gaseous ions is dissolved in excess of water to give its constituent aqueous ions, e.g.,
- $$\text{Na}^\oplus(g) + \text{Cl}^\ominus(g) + \text{aq} \rightarrow \text{Na}^\oplus(\text{aq}) + \text{Cl}^\ominus(\text{aq})$$
- $$\Delta_{\text{hyd}} H^\ominus = -\text{ve}$$
- b. **Trend in the periodic table:** Generally, hydration energy decreases down the group (\downarrow) and increases along the period (\rightarrow).
- $$\Delta_{\text{hyd}} H^\ominus \propto \text{charge density} \left(\text{i.e. } \frac{\text{charge}}{\text{size}} \text{ ratio} \right)$$
- c. **Application:**
- Solubility is water:
If $\Delta_{\text{hyd}} H^\ominus > \Delta_U H^\ominus$, the compound is soluble in water.
If $\Delta_{\text{hyd}} H^\ominus < \Delta_U H^\ominus$, the compound is not soluble in water.
 - Lithium is the strongest reducing agent in aqueous solution.
- iii. Ionic mobilities in electric field of *s*-block ions.
Order of decreasing mobilities:
 $\text{Cs}^\oplus > \text{Rb}^\oplus > \text{K}^\oplus > \text{Na}^\oplus > \text{Li}^\oplus$
 $\text{Ba}^{2+} > \text{Sr}^{2+} > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{Be}^{2+}$
- iv. Ionic radii in aqueous solution of ions of *s*-block elements.
Order of decreasing radii of hydrated ions:
 $\text{Li}^\oplus > \text{Na}^\oplus > \text{K}^\oplus > \text{Rb}^\oplus > \text{Cs}^\oplus$
 $\text{Be}^{2+} > \text{Mg}^{2+} > \text{Ca}^{2+} > \text{Sr}^{2+} > \text{Ba}^{2+}$
- v. Compounds of group 2 elements exist as hydrated salts, e.g. $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, whereas NaCl and KCl do not form such hydrates but LiCl exists as $\text{LiCl} \cdot 2\text{H}_2\text{O}$.
- vi. Lanthanides and actinides show, in general, +3 oxidation state.
- vii. Cu^\oplus compounds are unstable in aqueous solution and undergo disproportionation.
- $$2 \text{Cu}^\oplus \rightarrow 2\text{Cu}^{2+} + \text{Cu}$$
- viii. Solubilities in water of hydroxides and fluorides of group 2 elements increase down the group (\downarrow). For example, increasing order of solubilities is as follows:
 $\text{Be F}_2 < \text{Mg F}_2 < \text{Ca F}_2 < \text{Sr F}_2 < \text{Ba F}_2$
 $\text{Be(OH)}_2 < \text{Mg(OH)}_2 < \text{Ca(OH)}_2 < \text{Sr(OH)}_2 < \text{Ba(OH)}_2$
- ix. Solubilities in water of carbonates, bicarbonates and sulphates of group 2 elements decrease down the group (\downarrow). For example, the decreasing order of solubility is as follows:
 $\text{BeCO}_3 > \text{MgCO}_3 > \text{CaCO}_3 > \text{SrCO}_3 > \text{BaCO}_3$
 $\text{Be(HCO}_3)_2 > \text{Mg(HCO}_3)_2 > \text{Ca(HCO}_3)_2 > \text{Sr(HCO}_3)_2 > \text{Ba(HCO}_3)_2$
 $\text{BeSO}_4 > \text{MgSO}_4 > \text{CaSO}_4 > \text{SrSO}_4 > \text{BaSO}_4$
46. **Flame colouration:** When the elements or their salts are heated in a bunsen flame, they impart characteristic colour to the flame.
- Principle:** Same excitation energy of bunsen flame excites electrons in different element to different level due to difference in their IE's.
- | Flame colouration | Li | Na | K | Rb | Cs |
|-------------------|-------------------|---------------|-----------|------------|---------------------|
| Group 1 | Crimson | Golden yellow | violet | Red violet | Blue |
| Group 2 | Be | Mg | Ca | Sr | Ba Ra |
| | | | Brick red | Crimson | Apple green Crimson |
| Cu | Deep bluish green | | | | |
| Pb | Pale blue grey | | | | |

Be and Mg do not impart flame colourations, since the excitation energy of the flame is not sufficient to excite electrons to higher energy level, due to very high IE of Be and Mg.

- 47. Colour of substance in visible light:** When molecules absorb light of specific wavelengths in the visible region of electromagnetic spectrum, the outer (valence) electrons are excited to higher energy levels. When these excited electrons return to their original (ground) energy level, they emit radiation in the visible region corresponding to the energy absorbed and give complementary colours.

Application:

- a. Halogens are coloured, e.g.

| Halogens | Observed (complimentary colour) |
|---------------------|------------------------------------|
| F ₂ (g) | Yellow |
| Cl ₂ (g) | Greenish yellow |
| Br ₂ (l) | Red or brown or orange |
| I ₂ (s) | Violet |

- b. When group 1 elements are dissolved in liquid NH₃, they give blue colour whereas group 2 elements give deep blue black colour.

c. **The colour in the coordination compounds:**

- i. It is explained in terms of CFT (crystal field theory). It is due to *d-d* transition or more specifically ($t_{2g} \rightarrow e_g$) transition in case of octahedral complexes and ($e \rightarrow t_2$) transition in case of tetrahedral complexes.
- ii. The colour in lanthanides and actinides is due to *f-f* transitions.
- iii. Colour of compounds having d^0 configuration i.e., when *d*-orbitals are empty, colour is due to charge transfer theory, e.g., purple colour of KMnO₄ and orange colour of K₂Cr₂O₇.
- iv. Some solid compounds change their colour on heating due to non-stoichiometric defects, i.e., metal excess defects and these are of two types (i) Anion vacancies or F-centre and (ii) the presence of extra cations in interstitial sites.

For example, when alkali metal halides are heated in alkali metal vapours, the colour is observed (due to F-centre). Excess of Li in LiCl gives a pink colour and excess of K in KCl makes it violet.

On heating ZnO turns yellow and on cooling it turns white due to the presence of extra cations in interstitial sites.

- 48. $p\pi-p\pi$ bond:** C, N and O have unique ability to form $p\pi-p\pi$ multiple bond with itself and with other elements

having (i) small size (ii) high EN, (iii) high IE and (iv) non-availability of *d*-orbitals.

- 49. ($p\pi-d\pi$) multiple bonding:** Heavier members of groups 14, 15 and 16 form $p\pi-d\pi$ bonds by the overlap of *p*-orbital of one atom and *d*-orbital of another atom. This tendency is found particularly in case of Si linked to O and N.

Examples:

- a. Trimethyl amine, N(CH₃)₃, is pyramidal and more basic whereas trisilyl amine, N(SiH₃)₃, is planar and is less basic.
- b. CCl₄ and SiCl₄, both are covalent compounds, but CCl₄ is not hydrolysed with water while SiCl₄ is hydrolysed (due to $p\pi-d\pi$ multiple bonding).
- c. MnF₇ does not exist, although Mn₂O₇ exists, due to the ability of oxygen to form $p\pi-d\pi$ multiple bonds.

50. Hydrogen bonding (Refer Chapter 2, Section 2.23.6)

51. Geometry, shape and hybridisation of compounds and their ions (Refer Chapter 2, Section 2.21)

52. Dipole moment (Refer Chapter 2, Section 2.17)

53. Summary of trends of periodic properties:

- a. Increases along the period

- The following properties decrease down the group (\downarrow) but increase along the period (\rightarrow).
- Decreases down the groups
1. IE, EA, Δ_{eg} H[⊖] and EN.
 2. Lattice enthalpy (Δ_U H[⊖]), hydration enthalpy (Δ_{hyd} H[⊖])
 3. Charge density ($\frac{\text{charge}}{\text{size}}$ ratio)
 4. Metallic bonding
 5. Non-metallic character
 6. Acidic character of oxides

- b. The following properties increase down the group (\downarrow) and decrease along the period (\rightarrow)

- Increases down the group (\downarrow)
- Decreases along the period
1. Atomic radii
 2. Metallic character
 3. Basic character of oxides
 4. Electropositivity or metallic character

54. Some important facts:

- Metals have low IE and low EN whereas non-metals have high IE and high EN.
- I₂ sublimes on heating and is a non-metal with metallic lusture.
- Br₂ is a liquid non-metal at room temperature.

1.10 Inorganic Chemistry

- Hg is the lowest melting point liquid metal.
- Gallium (Ga) (m. pt. 29.8°C), caesium (Cs) (m. pt. 28.5°C) and francium (Fr) (m. pt. 27.0°C) are metals having low melting points.
Ga is used in making high temperature thermometer because of its low melting and high boiling points.
- Germanium (Ge) is transparent in the infrared (IR) region and therefore it is used in the making of infrared windows, prisms and lenses.
- Selenium (Se) is used as a photo conductor in photo copying (Xerox) machines and also for decolouriser of glass.
- Tellurium (Te) and polonium (Po) are highly toxic, the latter more so because of intense radioactivity.
- Among metals, tungsten (W) has highest melting and boiling points.
- Na, K, Rb and Cs are kept in kerosene oil.
- Phosphorous (P_4) (white or yellow) is kept in water.
- Fluorine (F) is the most EN element and caesium (Cs) is the most EP (electropositive) element.
- H^\ominus and I^\ominus ions are the smallest and largest anions, respectively.
- H^\oplus and Cs^\oplus are the smallest and largest cations, respectively.

- Helium (He) has the maximum ionisation potential.
- Oxygen is the most abundant element on the earth.
- Aluminium (Al) is the most abundant metal.
- Iron (Fe) is the most abundant transition metal.
- Nitrogen (N_2) is the most abundant gas in atmosphere.
- Among metals silver (Ag) is the best conductor of electricity and lead (Pb) is the poorest conductor of electricity.
- Among non-metals, carbon (C) has the highest melting point (4100°C).
- Diamond (carbon) is the hardest natural substance.
- Chlorine (Cl) has maximum EA or $\Delta_{eg} H^\ominus$.
- Uranium (U) is the heaviest naturally occurring element.
- Plutonium (Pu) is the most poisonous element.
- Caesium (Cs) has the lowest EN and lightest liquid metal.
- Tellurium (Te) is the most stable element.
- Boron (B) is the lightest solid non-metal with highest tensile strength.
- Among non-metals sulphur (S_8) is the most poorest conductor of current.
- Osmium (Os) is the heaviest solid metal with density (22.57 g mL⁻¹).

1.1 INTRODUCTION

'The periodic table of elements is one of the most powerful icons in science—a single document that consolidates much of our knowledge of chemistry.' The periodic table is considered as one of the greatest scientific achievements as it provides the vast amount of information available on the chemical behaviour of the elements into a few single and logical patterns. It is a remarkable demonstration of the fact that the chemical elements are not a random cluster of entities but instead display trends and lie together in families.

The elements are arranged in rows and columns. Knowing the position of an element in the periodic table, it is possible to predict its chemistry.

In this chapter, we will study the historical development of the periodic table and the modern periodic law. Moreover, we will also understand how the periodic classification follows as a logical consequence of the electronic configuration of atoms. *Nonetheless*, we will also learn some of the periodic trends in the physical and chemical properties of the elements.

1.2 NEED TO CLASSIFY ELEMENTS

It is well known by now that the elements are the basic units of all types of matter. In 1800, only 31 elements were known but by 1865, the number of elements discovered were 63 and at present 114 elements are known. Out of them, the recently discovered elements are synthetic. With such a large number of elements, it is very difficult to study individually the chemistry of all these elements and millions of their compounds. So, scientists searched for a systematic and simple method to study the properties of various elements and their compounds by classifying the elements. Ultimately scientists were successful in arranging the various elements into groups in such a way that similar elements were grouped together. This arrangement of elements is called classification of elements which led to the formation of a periodic table.

Thus, a periodic table is defined as the table which classifies all the elements in such a way that elements with similar properties are grouped together in the same vertical column and elements with dissimilar properties are separated from one another.

1.3 GENESIS OF PERIODIC CLASSIFICATION: FROM DÖBEREINER TO MENDELEEV

Several chemists tried to classify the elements and to find patterns in their properties. The German chemist, Johann Döbereiner, in 1817, suggested that there were sets of three elements (triads) which showed similar chemical properties. In each case, he observed that the atomic weight of the central element of the triads was approximately the mean of the atomic weights of other two elements (Table 1.1) and the properties of the middle

elements were in between those of the other two members. This relationship referred to as the *law of triads*. However, it was dismissed later on since it worked only for a few elements.

Table 1.1 Döbereiner's triads

| | Elements | Atomic weight | Mean of 1st and 3rd | Elements | Atomic weight | Mean of Ist and 3rd | Elements | Atomic weight | Mean of Ist and 3rd |
|----|----------|---------------|-----------------------|----------|---------------|---------------------------|----------|---------------|------------------------------|
| 1. | Li | 7 | $\frac{7+39}{2} = 23$ | Ca | 40 | $\frac{40+137}{2} = 88.5$ | Cl | 35.5 | $\frac{35.5+127}{2} = 81.25$ |
| 2. | Na | 23 | | Sr | 88 | | Br | 80 | |
| 3. | K | 39 | | Ba | 137 | | I | 127 | |

In 1862, a French geologist, A.E.B. de Chancourtois, arranged the then known elements in order of *increasing atomic weights* and made a cylindrical table of elements to show the periodic recurrence of properties. This also was dismissed later on.

1.3.1 Newlands' Octaves Law (1865)

However in 1865, the English chemist, John Alexander Newlands developed the *law of octaves*. He arranged the elements in increasing order of their *atomic weights* and found that every eighth element had properties similar to that of the first element (Table 1.2).

Table 1.2 Newlands' octaves

| Elements | Li | Be | B | C | N | O | F |
|---------------|----|----|----|----|----|----|------|
| Atomic weight | 7 | 9 | 11 | 12 | 14 | 16 | 19 |
| Elements | Na | Mg | Al | Si | P | S | Cl |
| Atomic weight | 23 | 24 | 27 | 29 | 31 | 32 | 35.5 |
| Elements | K | Ca | | | | | |
| Atomic weight | 39 | 40 | | | | | |

The relationship was just like every eighth note resembles the first octaves of music (Table 1.3).

Table 1.3

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

Note: i. Inert gases were not discovered till that time.
ii. All elements could not be classified on this basis.

Law of octaves was found to be true up to calcium but this law was not widely accepted. However, this law was recognised much later by the Royal Society, London, by awarding Newlands the Davy Medal in 1887.

A breakthrough in the development of the periodic table owes its development to the Russian chemist Dmitri Mendeleev (1834–1907) and the German chemist Lothar Meyer (1830–1895).

1.12 Inorganic Chemistry

Working independently, both the scientists in 1869 proposed that on arranging elements in the increasing order of their atomic weights, similarities appear in physical and chemical properties at regular intervals.

1.3.2 Lothar Meyer's Atomic Volume Curve (1869)

1. Lothar Meyer plotted the physical properties such as atomic volume (i.e. atomic weight in solid state/density), melting points and boiling points against atomic weights (Fig. 1.1).
2. He observed elements with similar properties occupied the

similar positions on the graph, i.e. a periodically repeated pattern.

3. Elements of the 1st group (strong electropositive elements) such as Li, Na, K, Rb, Cs etc., occupied the top position.
4. Elements of the 2nd group such as Be, Mg, Ca, Sr, Ba etc., occupied the positions on the ascending part of the graph.
5. Halogens occupied the positions on the descending part of the graph.
6. Inert gases except helium (He) also occupied the positions on the descending part of the graph.

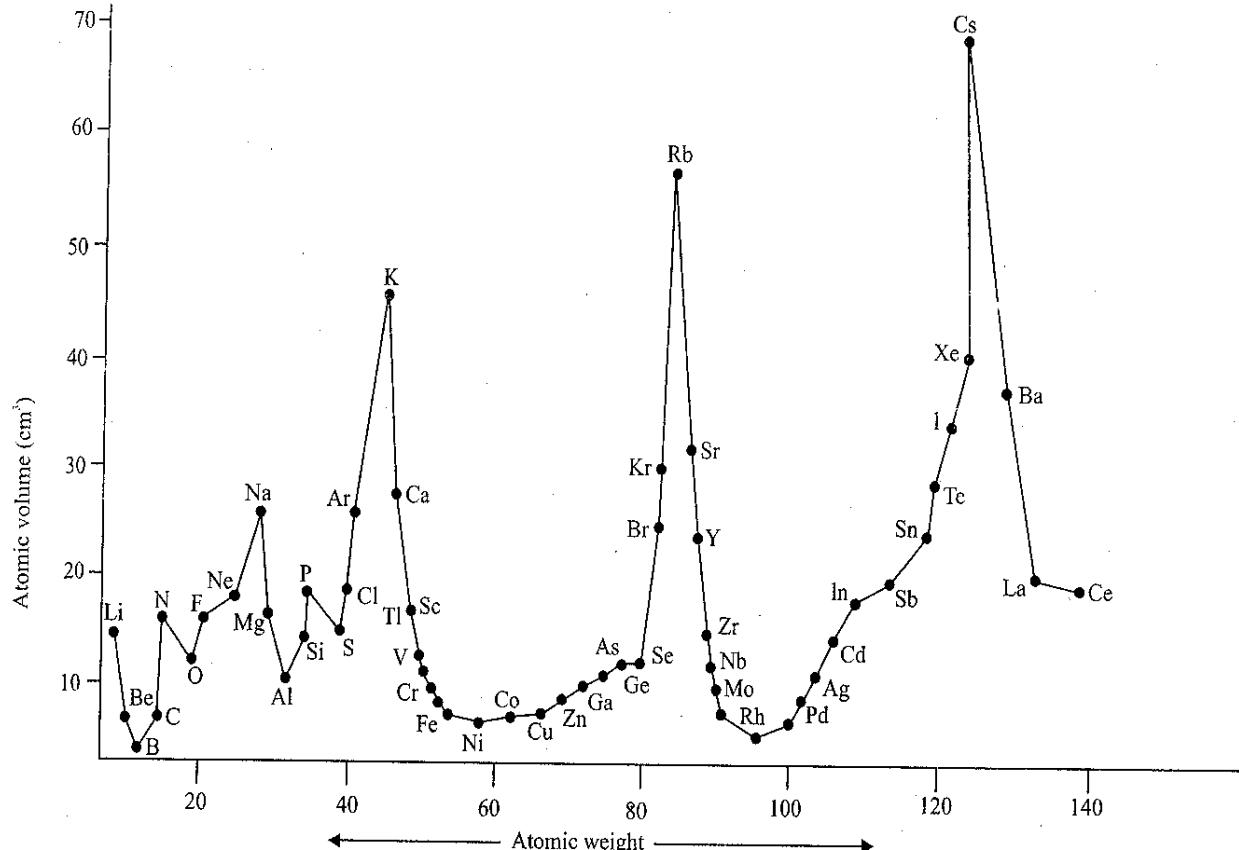


Fig. 1.1 Lothar Meyer's curve

1.3.3 Mendeleev's Periodic Law

By 1868, Lothar Meyer had developed a table that closely resembles the modern periodic table. However, his work was not published until the work of Mendeleev.

Döbereiner initiated the study of periodic relationship but Mendeleev published the periodic law for the first time. It states as follows:

- The physical and chemical properties of elements are periodic functions of their atomic weights.
- If the elements are arranged in the order of their increasing atomic weights, after a regular interval similar properties of elements are repeated.

Mendeleev's system of classifying elements was more elaborate than that of Lothar Meyer's. Mendeleev relied on the similarities in the empirical formulas and properties of the compounds formed by the elements. He found that some of the elements did not fit in with his scheme of classification if the order of atomic weight was strictly followed. So, he ignored the order of atomic weights and placed the elements with similar properties together.

For example, iodine with lower atomic weight (126.90) than that of tellurium (127.60, group VI) was placed in group VII along with F, Cl, Br because of similarities in properties (Fig. 1.2).

PERIODIC SYSTEM OF THE ELEMENTS IN GROUPS AND SERIES

| Series | Groups of elements | | | | | | | | |
|--------|-----------------------|------------------------|-------------------------|-------------------------------|------------------------------------|--|------------------------------------|-------------------------------------|--|
| | O | I | II | III | IV | V | VI | VII | VIII |
| 1 | | Hydrogen H | | | | | | | |
| 2 | Helium He 4.0 | Lithium Li 7.03 | Beryllium Be 9.1 | Boron B 11.0 | Carbon C 12.0 | Nitrogen N 14.04 | Oxygen O 16.00 | Fluorine F 19.0 | |
| 3 | Neon Ne 19.9 | Sodium Na 23.5 | Magnesium Mg 24.3 | Alumin- ium Al 27.0 | Silicon Si 28.4 | Phosphorus P 31.0 | Sulphur S 32.06 | Chlorine Cl 35.45 | |
| 4 | Argon Ar 38 | Potassium K 39.1 | Calcium Ca 40.1 | Scan- dium Sc 44 | Titanium Ti 48.1 | Vanadium V 51.4 | Chromium Cr 52.1 | Manga- nese Mn 55.0 | Iron Cobalt Nickel Fe Co Ni (Cu) |
| 5 | | Copper Cu 63.6 | Zinc Zn 65.4 | Gallium Ga 70.0 | German- ium Ge 72.3 | Arsenic As 75 | Selenium Se 79 | Bromine Br 79.95 | |
| 6 | Krypton Kr 81.8 | Rubidium Rb 85.4 | Strontium Sr 87.6 | Yttrium Y 89.0 | Zirconium Zr 90.6 | Niobium Nb 94.0 | Molybde- num Mo 96.0 | | Ruthenium Rhodium Pal- ladium Ru Rh Pd(Ag) |
| 7 | | Silver Ag 107.9 | Cadmium Cd 112.4 | Indium In 114.0 | Tin Sn 119.0 | Antimony Sb 120.0 | Tellurium Te 127.6 | Iodine I 126.9 | 101.7 103.0 106.5 |
| 8 | Xenon Xe 128 | Caesium Cs 132.9 | Barium Ba 137.4 | Lantha- num La 139 | Cerium Ce 140 | — | — | — | |
| 9 | | | | | | | | | |
| 10 | — | | | Ytter- bium Yb 173 | | Tantalum Ta 183 | Tungsten W 184 | — | Osmium Iridium Platinum Os Ir Pt (Au) |
| 11 | | Gold Au 197.2 | Mercury Hg 200.0 | Thallium Tl 204.1 | Lead Pb 206.9 | Bismuth Bi 208 | | 191 193 194.9 | |
| 12 | — | — | Radium Ra 224 | — | Thorium Th 232 | — | Uranium U 239 | — | |
| | R | R ₂ O | RO | R ₂ O ₃ | RO ₂ RH ₄ | Higher saline oxides R ₂ O ₅ RH ₃ | RO ₃ RH ₂ | R ₂ O ₇ RH | RO ₄ |
| | | | | | | Higher gaseous hydrogen compounds | | | |

Fig. 1.2 Mendeleev's periodic table

While arranging the elements of similar properties in the same group, Mendeleev noticed that some of the elements were still undiscovered and, therefore, left several gaps in the table.

For example, both gallium (Ga) and germanium (Ge) were unknown at that time. He left the gap under aluminium and a gap under silicon and called these element *Eka-aluminium* and *Eka-*

silicon. Besides predicting the existence of these elements he also predicted some of their physical properties. These elements were discovered later on. Some of the properties predicted by Mendeleev for these elements and those found experimentally are given in Table 1.4. Mendeleev's periodic table was published in 1905 (Fig. 1.2).

1.14 Inorganic Chemistry

Mendeleev's name has been immortalised by naming the element with atomic number 101, as Mendelevium (Md) (see Fig. 1.3). This name was proposed by the American scientist Glenn T. Seaborg, the discoverer of this element, "in recognition of the pioneering role of Mendeleev, a great Russian chemist who was the first to use the periodic system of elements to predict the chemical properties of undiscovered elements, a principle which led to the discovery of nearly all transuranium elements". Mendeleev was a versatile genius. He invented an accurate barometer. He worked on many problems connected with Russia's natural resources.

Table 1.4 Mendeleev's predictions for the elements Eka-aluminium (Gallium) and Eka-silicon (Germanium)

| Property | Eka-aluminium (predicted) | Gallium (found) | Eka-silicon (predicted) | Germanium (found) |
|-------------------------------|-------------------------------|--------------------------------|-------------------------|-------------------|
| Atomic weight | 68 | 70 | 72 | 72.6 |
| Density/(g cm ⁻³) | 5.9 | 5.94 | 5.5 | 5.36 |
| Melting point/K | Low | 29.78 | High | 1231 |
| Formula of oxide | E ₂ O ₃ | Ga ₂ O ₃ | EO ₂ | GeO ₂ |
| Formula of chloride | ECI ₃ | GaCl ₃ | ECI ₄ | GeCl ₄ |

1.3.4 Mendeleev's Periodic Table

Mendeleev arranged the 63 discovered elements in the periodic table into 7 horizontal rows known as periods and 8 vertical columns known as groups numbered 1 to 8.

1.3.4.1 Uses of Mendeleev's Periodic Table

1. Atomic weights of elements were determined with the help of periodic table. Atomic weight = valency × equivalent weight.
2. Atomic weights of elements were corrected. Atomic weight of Be was calculated to be $3 \times 4.5 = 13.5$ by considering valency 3, but Mendeleev calculated it to be $2 \times 4.5 = 9$.
3. Discovery of new elements: In Mendeleev's periodic table two consecutive members differ by two or three units in the atomic weight. Where this gap was more, the gaps were left in the periodic table.
4. The discovery of the first two noble gases helium (He) and argon (Ar) in 1890 suggested the possibilities that there must be other similar elements to fill an entire family. This idea led Ramsay to his successful search for krypton (Kr) and xenon (Xe).
5. Work on the radioactive decay series for uranium (U) and thorium (Th) was also guided by the periodic table.

1.3.4.2 Defects of Mendeleev's Periodic Table

The following is a list of defects:

1. Position of hydrogen is uncertain. It has been placed in IA and VIIA groups because of its resemblance with both the groups.
2. No separate positions given for isotopes.
3. No separate group for lanthanides and actinides.
4. Although there is no resemblance expect valency of subgroups A and B, they have been put in the same group.
5. The order of increasing atomic weights is not strictly followed in the arrangement of elements in the periodic table. For example, Co (At.wt. 58.9) is placed before iodine (At.wt. 127) and Ar (At.wt. 39.9) before K (At.wt. 39).

1.4 MODERN PERIODIC LAW AND THE PRESENT LONG FORM OF THE PERIODIC TABLE OR MOSELEY'S PERIODIC TABLE

In 1913, the English physicist, Henry Moseley observed regularities in the characteristics X-ray spectra of the elements. Moseley studied the frequency (ν) of X-rays produced by the bombardment of a strong beam of electrons on a metal target. He found that a plot of $\sqrt{\nu}$ (where ν is the frequency of X-rays emitted) against the atomic number or nuclear charge (Z) gave a straight line and not the plot of $\sqrt{\nu}$ versus atomic mass, and gave the following relation:

$$\sqrt{\nu} = a(Z - b)$$

where a and b are constants. So, Moseley related the properties of elements with their atomic numbers and gave the new periodic law, known as the *modern periodic Law*, and is defined as:

The physical and chemical properties of elements are periodic functions of their atomic numbers.

If the elements are arranged in order of their increasing atomic numbers, after a regular interval, elements with similar properties are repeated.

The periodic law has stimulated renewed interest in inorganic chemistry and has carried till date with the creation of artificially produced short half-life elements.

The periodic law has also revealed important similarities among the 94 naturally occurring elements. For example, neptunium (Np) and plutonium (Pu) like actinium (Ac) and protoactinium (Pa) are also found in pitch blende—an ore of uranium (U).

It is now recognised that the periodic law is the consequence of the periodic variation in electronic configurations which determine the physical and chemical properties of elements and their compounds.

Although numerous forms of periodic table have been made. Out of which some forms emphasise chemical reactions and valence, whereas others emphasise the electronic configurations of elements. But the '*long form*' of the *periodic table* of the elements (Fig. 1.3) (or modern periodic table) is the most easy and widely used.

The horizontal rows (which Mendeleev called **series**) are called **periods** and the vertical columns, **groups**. Elements having similar outer electronic configurations in their atoms are arranged in vertical columns, referred to as **groups or families**. According to the recommendation of International Union of Pure and Applied Chemistry (IUPAC), the groups are numbered from 1 to 18 replacing the older notation of groups IA... VIIA, VIII, IB ... VIIB and O.

There are altogether seven periods. The period number corresponds to the highest principal quantum number (n) of the elements in the period. The first period contains 2 elements. The subsequent periods consist of 8, 8, 18, 18 and 32 elements, respectively. The seventh period is incomplete and like the sixth period would have a theoretical maximum (on the basis of quantum numbers) of 32 elements. In this form of the periodic table, 14 elements of both the sixth and seventh periods (lanthanoids and actinoids, respectively) are placed in separate panels at the bottom.

1.4.1 Magic Numbers

The examination of the properties of elements shows that the atomic number intervals at which the elements with similar properties reappear are 2, 8, 8, 18, 32 and 32, i.e. we have to pass 2, 8, 8, 18, 18 and 32 elements before we come across an element with similar properties. The repetition of the elements with similar properties in the order of increasing atomic number as in the periodic table is called periodicity of properties and the numbers 2, 8, 18 and 32 are called magic numbers.

Note: Glenn T. Seaborg's work starting with the discovery of plutonium in 1940 followed by those of all the transuranium elements from 94 to 102 led to reconfiguration of the periodic table placing the actinoids below the lanthanoids. In 1951, Seaborg was awarded the Nobel Prize in Chemistry for his work. Element 106 has been named Seaborgium (Sg) in his honour.

1.4.2 Electronic Configuration in Periodic Table

The following is a list of electronic configuration:

- Each period starts with an alkali metal whose outermost electronic configuration is ns^1 .
- Each period ends with a noble gas of outermost electronic configuration ns^2np^6 except He. The electronic configuration of He is $1s^2$.
- The number of elements in a period is equal to the number of necessary electrons to acquire ns^2np^6 configuration in

the outermost shell of the first element (alkali metal) of the period. First period contains two elements.

- The number of elements in each period may be determined by the number of electrons in a stable configuration as under.

| Periods | Stable electronic configuration | Number of electrons |
|---------|---------------------------------|---------------------|
| First | $1s^2$ | 2 |
| Second | $2s^22p^6$ | 8 |
| Third | $3s^23p^6$ | 8 |
| Fourth | $4s^23d^104p^6$ | 18 |
| Fifth | $5s^24d^105p^6$ | 18 |
| Sixth | $6s^24f^{14}5d^106p^6$ | 32 |
| Seventh | | Remaining elements |

1.5 NOMENCLATURE OF ELEMENTS WITH ATOMIC NUMBERS >100

The naming of the new elements was given traditionally on the name of its discoverer (or discoverers) and the suggested name was ratified by the IUPAC. In recent years this has led to some controversies. For example, both the American and Soviet scientists claimed credit for discovering element 104. The Americans named it *Rutherfordium* whereas the Soviets named it *Kurchatovium*.

To avoid such controversies, the IUPAC has made recommendation that until a new element's discovery is proved, and its name is officially recognised, a systematic nomenclature be derived directly from the atomic number using the numerical roots for 0 and numbers 1–9. These are shown in Table 1.5.

The roots are strung together in the order of digits which makes up the atomic numbers and 'ium' is added at the end. The IUPAC names for elements with Z above 103 are shown in Tables 1.5 and 1.6. As of now, elements with atomic numbers up to 112, 114 and 116 have been discovered. Elements with Z = 113, 115 117 and 118 and beyond are not yet known.

Table 1.5 Notation for IUPAC nomenclature of elements

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

long form of the periodic table of the elements with their atomic numbers and ground state outer electronic configurations. The groups are numbered 1–18 in accordance with the 1984 IUPAC recommendations. This notation replaces the old numbering scheme of IA–VIIA, VIIIB–VIIIB and 0 for the elements.

Table 1.6 Nomenclature of elements with atomic number above 100

| At. no. | Name | Symbol | IUPAC official name | IUPAC symbol |
|---------|--------------|--------|---------------------|--------------|
| 101 | Unnilunium | Unu | Mendelevium | Md |
| 102 | Unnilbium | Unb | Nobelium | No |
| 103 | Unniltrium | Unt | Lawrencium | Lr |
| 104 | Unnilquadium | Unq | Rutherfordium | Rf |
| 105 | Unnilpentium | Unp | Dubnium | Db |
| 106 | Unnilhexium | Unh | Seaborgium | Sg |
| 107 | Unnilseptium | Uns | Bohrium | Bh |
| 108 | Unniloctium | Uno | Hassium | Hs |
| 109 | Unnilennium | Une | Meitnerium | Mt |
| 110 | Ununnium | Uun | Darmstadtium | Ds |
| 111 | Unununium | Uuu | Rontgenium* | Rg* |
| 112 | Ununbium | Uub | * | * |
| 113 | Ununtrium | Uut | + | |
| 114 | Ununquadium | Uuq | * | * |
| 115 | Ununpentium | Uup | + | |
| 116 | Ununhexium | Uuh | * | * |
| 117 | Ununseptium | Uus | + | |
| 118 | Ununoctium | Uuo | + | |

*Official IUPAC name yet to be announced.

+ Elements yet to be discovered.

Thus, the new element first gets a temporary name, with symbol consisting of three letters. Later on a permanent name and a symbol are given by a process of voting of the IUPAC representatives from each country. The permanent name might reflect the country (or the state of the country) in which the element was discovered, or pay tribute to a notable scientist.

Illustration 1.1 What would be the IUPAC name and symbol for the element with atomic number 120?

(NCERT Example 3.1)

Sol. From Table 1.5, the roots for 1, 2 and 0 are Un, bi and nil, respectively. Hence, the symbol and the name respectively are Ubn and unbinilium.

Illustration 1.2 There are 2, 8 and 8 elements in the first, second and third periods of periodic table respectively. Explain.

Sol. The first period ($1s$) is completed with two electrons. The second period ($2s, 2p$) is completed with 2 and 6 electrons respectively in $2s$ and $2p$.

Likewise the third period ($3s, 3p$) is completed with 2 and 6 electrons. Thus, 2, 8 and 8 elements are present in the first, second and third periods respectively.

Illustration 1.3 Which of the following is correct:

- The element Mendelevium (Md) has been named in the honour of Mendeleev. What is the atomic number of that element?
i. 100 ii. 101 iii. 102 iv. 103
- The element Seaborgium (Sg) has been named in the honour of Glenn T. Seaborg. What is the atomic number of that element?
i. 104 ii. 105 iii. 106 iv. 107
- Glenn T. Seaborg was awarded Nobel Prize in 1951 for the discovery of which element/elements?
i. Uranium (U)
ii. Elements from 90 to 93
iii. Elements from 94 to 102
iv. Elements from 103 to 106

Sol. a. ii b. iii c. iii

Illustration 1.4

- What is the atomic numbers and the IUPAC name and symbol for the elements Mendelevium (Md) and Seaborgium (Sg)?
- What is the atomic number of the element for which both the American and Soviet scientists claimed credit for the discovery?
- Refer to the problem (b) above, what name is given to the above element by the American and Soviet scientists?
- Which other elements are found in pitch blende—an ore of uranium?
- Which other elements are found in the naturally occurring element with atomic number 94?

Sol.

- i. Atomic number for Mendelevium is 101. Its IUPAC name and symbol is Unnilunium (Unu).
- ii. Atomic number for Seaborgium is 106. Its IUPAC name and symbol is Unnilhexium (Unh).
- b. Atomic number of that element is 104.
- c. The American scientist called it Rutherfordium (Rf) and the Soviet scientist called it Kurchatovium.
- d. Actinium (Ac) and Protoactinium (Pa).
- e. Neptunium (atomic number 93) and plutonium (atomic number 94).

1.6 ELECTRONIC CONFIGURATIONS OF ELEMENTS AND THE PERIODIC TABLE

An electron in an atom is characterised by a set of four quantum numbers, and the principal quantum number (n) defines the main energy level known as shell. The filling of electrons into different subshells, also referred to as orbitals (s, p, d, f) in an atom, is called its electronic configuration.

1.6.1 Electronic Configurations in Periods

The period indicates the value of n for the outermost or valence shell. In other words, successive period in the periodic table is associated with the filling of the next higher principal energy level ($n = 1, n = 2$ etc.). We know that the number of elements in each period is twice the number of atomic orbitals available in the energy level that is being filled.

The first period ($n = 1$) starts with the filling of the lowest level ($1s$) and therefore has two elements—hydrogen ($1s^1$) and helium ($1s^2$) when the first shell (K) is completed.

The second period ($n = 2$) starts with lithium and the third electron enters the $2s$ orbital.

The next element, beryllium, has four electrons and has the electronic configuration $1s^2 2s^2$.

In the next element, boron, the $2p$ orbitals are filled with electrons when the L shell is completed at neon ($2s^2 p^6$). Thus, there are 8 elements in the second period.

The third period ($n = 3$) begins at sodium, and the added electron enters a $3s$ orbital. Successive filling of $3s$ and $3p$ orbitals gives rise to the third period of 8 elements from sodium to argon.

The fourth period ($n = 4$) starts at potassium, and the added electrons fill up the $4s$ orbital. Now before the $4p$ orbital is filled, filling up of $3d$ orbitals becomes energetically favourable and $3d$ transition series of elements begins. This starts from scandium ($Z = 21$) which has the electronic configuration $3d^1 4s^2$. 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. Altogether there are 18 elements in this fourth period.

The fifth period ($n = 5$) begins with rubidium is similar to the fourth period and contains the $4d$ transition series starting at yttrium ($Z = 39$). This period ends at xenon with the filling up of the $5p$ orbitals.

The sixth period ($n = 6$) contains 32 elements and successive electrons enter $6s$, $4f$, $5d$ and $6p$ orbitals, in the order of filling up of the $4f$ orbitals begins with cerium ($Z = 58$) and ends at lutetium ($Z = 71$) to give the $4f$ inner transition series which is called the **lanthanoid series**.

The seventh period ($n = 7$) is similar to the sixth period with the successive filling up of the $7s$, $5f$, $6d$ and $7p$ orbitals and includes most of the man-made radioactive elements. This period will end at the element with atomic number 118 which would belong to the noble gas family.

Filling up of the $5f$ orbitals after actinium ($Z = 89$) gives the $5f$ inner transition series known as the **actinoid series**. The $4f$ and $5f$ inner transition series of elements are placed separately

in the periodic table to maintain its structure and to preserve the principle of classification by keeping elements with similar properties in a single column.

The number of elements in a period and the type of orbitals being filled up is given in Table 1.7.

Table 1.7 Number of elements in different periods

| Period | Number of energy level being filled | Orbitals being filled | Number of orbitals | Number of electrons or elements in the period |
|--------|-------------------------------------|-----------------------|---|--|
| 1 | $n = 1$ | $1s$ | one s | 2 |
| 2 | $n = 2$ | $2s, 2p$ | one s + three $p = 4$ | $2 + 6 = 8$ |
| 3 | $n = 3$ | $3s, 3p$ | one s + three $p = 4$ | $2 + 6 = 8$ |
| 4 | $n = 4$ | $4s, 3d, 4p$ | one s + five d + three $p = 9$ | $2 + 10 + 6 = 18$ |
| 5 | $n = 5$ | $5s, 4d, 5p$ | one s + five d + three $p = 9$ | $2 + 10 + 6 = 18$ |
| 6 | $n = 6$ | $6s, 4f, 5d, 6p$ | one s + seven f + five d + three $p = 16$ | $2 + 14 + 10 + 6 = 32$ |
| 7 | $n = 7$ | $7s, 5f, 6d, 7p$ | one s + seven f + five d + three $p = 16$ | $2 + 14 + 10 + 6 = 32$. In this period only 29 elements are known so far. |

The first three periods (1st, 2nd and 3rd) containing 2, 8 and 8 elements, respectively, are known as **short periods** while the next three periods (4th, 5th and 6th) containing 18, 18 and 32 elements, respectively, are called **long periods**.

Illustration 1.5 How would you justify the presence of 18 elements in the 5th period of the periodic table?

(NCERT Example 3.2)

Sol. When $n = 5$, $l = 0, 1, 2, 3$ and 4. The order in which the energy of the available orbitals $4d$, $5s$ and $5p$ increases is $5s < 4d < 5p$. The total number of orbitals available is 9. The maximum number of electrons that can be accommodated is 18; and therefore 18 elements are there in the 5th period.

1.6.2 Groupwise Electronic Configurations

Elements in the same vertical column or group have similar valence shell electronic configurations, the same number of electrons in the outer orbitals, and similar properties. For example, the Group 1 elements (alkali metals) have ns^1 valence shell electronic configuration as shown in Table 1.8.

Table 1.8 Electronic configuration of group 1 elements

| Atomic number | Symbol | Electronic configuration |
|----------------|--------|---|
| 3 | Li | $1s^2 2s^1$ (or) $[He]2s^1$ |
| $3 + 8 = 11$ | Na | $1s^2 2s^2 2p^6 3s^1$ (or) $[Ne]3s^1$ |
| $11 + 8 = 19$ | K | $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$ (or) $[Ar]4s^1$ |
| $19 + 18 = 37$ | Rb | $1s^2 2s^2 2p^6 3s^2 3p^6 3d^1 4s^2 4p^6 5s^1$ (or) $[Kr]5s^1$ |
| $37 + 18 = 55$ | Cs | $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 5s^1$ $4s^2 4p^6 4d^{10} 5s^2 5p^6 6s^1$ (or) $[Xe]6s^1$ |
| $55 + 32 = 87$ | Fr | $[Rn] 7s^1$ |

Thus, it can be seen that the properties of an element have periodic dependence upon its atomic number and not on relative atomic mass.

1.7 ELECTRONIC CONFIGURATIONS AND TYPE OF ELEMENTS: *s*-, *p*-, *d*-, and *f*-BLOCKS

The *aufbau* (build up) principle and the electronic configuration

of atoms provide a theoretical foundation for the periodic classification. The elements in a vertical column of the periodic table constitute a group or family and exhibit similar chemical behaviour. This similarity arises because these elements have the same number and same distribution of electrons in their outermost orbitals. The elements are classified into four blocks viz. **s-block**, **p-block**, **d-block** and **f-block** depending on the type of atomic orbitals that are being filled with electrons (Fig. 1.4).

There are two exceptions to this categorisation. Helium belongs to the *s-block* but its positioning in the *p-block* along with other group 18 elements is justified because it has a completely filled valence shell ($1s^2$) and as a result, exhibits properties characteristic of other noble gases.

The other exception is hydrogen. It has a lone *s*-electron and hence can be placed in group 1 (alkali metals). It can also gain an electron to achieve a noble gas arrangement and hence it can behave similar to a group 17 (halogen family) elements. But Mendeleev placed it at the top of the periodic table as shown in Fig. 1.3 and hydrogen separately.

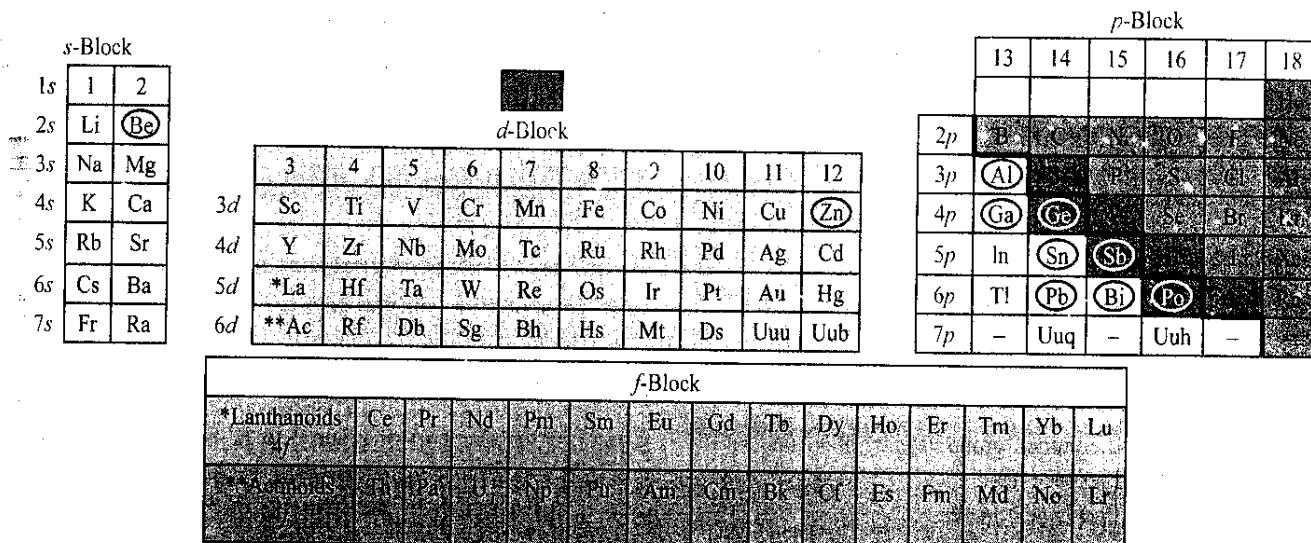


Fig. 1.4 The types of elements in the periodic table based on the orbitals that are being filled. Also shown is the broad division of elements into metals (■■■■■), non-metals (■■■■) and metalloids (■■■). Elements in circle show their compounds are amphoteric in nature.

1.7.1 Merits of Long Form of Periodic Table Over Mendeleev's Periodic Table

The merits of the long form of periodic table are as follows:

1. The classification of the elements is based on more fundamental property i.e. atomic number.
2. It relates the position of an element to its electronic configuration. Thus, each group contains elements with similar electronic configuration and hence similar properties. For example, all the alkali metals have similar valence shell electronic configuration i.e. ns^1 configuration and hence have similar properties.
3. The inert gases having completely filled electron shells have been placed at the end of each period, which represents a logical completion of each period.

4. The elements of the two subgroups have been placed separately and thus dissimilar elements do not fall together.
 5. It provides a clear demarcation of different types of the elements such as active metals, transition elements, non-metals, metalloids, inert gases, lanthanides and actinides.
 - a. Active metals (groups 1 and 2) are located at the extreme left of the periodic table.
 - b. Transition metals are placed in the middle of the table.
 - c. The elements lying to the right of the dark line, shown in Fig 1.4, in the form of a ladder (i.e. steps) are noble gases and non-metals while those lying to the left of the dark line are metals (active metals and transition metals).
- The elements shown in the circle are metalloids and their oxides are amphoteric, in the decreasing order as shown.

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Pb is the least amphoteric and its oxides are almost acidic.

6. It is easier to remember, understand and reproduce.

1.7.2 Defects of Long Form of Periodic Table

Although the long form of the periodic table is superior to Mendeleev's periodic table in many respects, yet it has some defects:

1. Like Mendeleev's table, it fails to accommodate the lanthanides and actinides in the main body of the table.
2. Position of hydrogen is not solved though it can be placed along with alkali metals in group 1 and halogens in group 17, since it shows many properties similar to both alkali metals and halogens.
3. The arrangement is unable to reflect the electronic configuration of many elements.

1.7.3 The s-Block Elements

The elements of group 1 (alkali metals) and group 2 (alkaline earth metals) which have ns^1 and ns^2 outermost electronic configuration belong to the *s-block elements*. They are all reactive metals with low ionisation enthalpies. They lose the outermost electron(s) readily to form +1 (in the case of alkali metals) or +2 ions (in the case of alkaline earth metals). The metallic character and the reactivity increase as we go down the group. The compounds of the *s*-block elements, with the exception of those of beryllium are predominantly ionic.

1.7.3.1 Characteristics of s-Block Elements

1. They have the common group valency of +1 and +2 for group 1 and 2 respectively.
2. They are malleable and ductile.
3. They are good conductors of heat and electricity.
4. They are prepared by the electrolysis of their fused compounds.
5. Chemically they are very reactive as their last shell contains only 1 or 2 electrons which can be given out easily.
6. They have low ionisation potential.
7. They form ionic compounds (except lithium and beryllium).
8. They are diamagnetic and form colourless compounds except chromates, permanganates and dichromates.
9. They are good reducing agents.

Note: The above properties are not applicable to hydrogen.

1.7.4 The p-Block Elements

The *p-block elements* comprise those belonging to groups 13 to 18 and together with the *s-block elements* are called the representative elements or normal or main group elements. The

outermost electronic configuration varies from ns^2np^1 to ns^2np^6 in each period. Each period ends in a noble gas with a closed shell ns^2np^6 configuration. All the orbitals in the valence shell of the *noble gases* are completely filled by electrons and it is very 'difficult to alter this stable arrangement by the addition or removal of electrons. The noble gases thus exhibit very low chemical reactivity. Preceeding the noble gas family are two chemically important groups of non-metals. They are the *halogens* (group 17) and the *chalcogens* (group 16). These two groups of elements have high negative electron gain enthalpies and readily add one or two electrons, respectively, to attain the stable noble gas configuration. The non-metallic character increases as we move from left to right across a period (\rightarrow) and metallic character increases as we go down the group (\downarrow).

1.7.4.1 Characteristics of p-Block Elements

1. They have variable valencies and oxidation states, e.g. +3 and +5.
2. Most of them are electronegative.
3. Most of them are non-metals.
4. They are bad conductors of heat and electricity (except metals).
5. They form both covalent and ionic bonds.
6. The non-metallic oxides are acidic in character, e.g. NO_2 , P_2O_5 , SO_3 etc.
7. They form both coloured and colourless compounds.
8. Most of the non-metals have polyatomic molecules.

1.7.5 The d-Block Elements (Transition Elements)

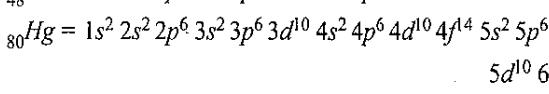
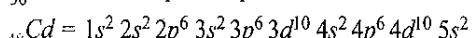
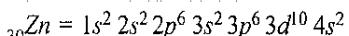
These are the elements of group 3 to 12 in the centre of the periodic table. These elements are characterised by the filling of the inner *d* orbitals by electrons and are therefore referred to as *d-block elements*. These elements have the outer electronic configuration $(n-1)d^{1-10}ns^{1-2}$. They are all metals. They mostly form coloured ions and Hg which have the $(n-1)d^{10}ns^2$ electronic configuration do not show most of the properties of transition elements. In a way, transition metals form a bridge between the chemically active metals of *s-block elements* and the less active metals of groups 13 and 14 and thus take their familiar name 'transition elements'.

1.7.5.1 Characteristics of d-Block Elements

1. They have variable valencies and oxidation states, e.g. Fe(II), Fe(III), Cu(I), Cu(II), Mn(II), Mn(IV), Mn(VI) and Mn(VII).
2. They are malleable and ductile.
3. They are hard and have high density and melting point.
4. They are good conductors of heat and electricity.
5. They form ionic compounds as well as giant molecules and complexes in which they are covalent.

6. They are paramagnetic since they contain unpaired electrons (each electron acts as a small magnet).
7. They form coloured compounds and coloured complexes. They have vacant orbitals. Electrons take up energy and move to higher energy levels and thus appear coloured.
8. They have higher ionisation potential than *s*-block elements.

Note: Those *d*-block elements which have partially filled *d*-orbitals or form ions in which the *d*-orbitals are only partially filled, have some special characteristics and are defined as transition elements or metals. Exceptions are Zn, Cd and Hg. Zn has all the *d*-orbitals completed both in the metal atoms and in Zn^{2+} ions.



II B group metals cannot be included in transition metals.

Other exceptions are Sc and Cu, where Cu shows intermediate behaviour since it forms compounds in two oxidation states Cu^\oplus and Cu^{2+} . The latter ion is transition metal ion.

1.7.6 The *f*-Block Elements (Inner-Transition Elements)

The two rows of elements at the bottom of the periodic table, called the *lanthanoids* $_{58}Ce - _{71}Lu$ and *actinoids* $_{90}Th - _{103}Lr$ are characterised by the outer electronic configuration $(n-2)f^{1-14}(n-1)d^{0-1}ns^2$. The last electron added to each elements is an *f*-electron. These two series of elements are hence called the inner transition elements (*f-block elements*). They are all metals. Within each series, the properties of the elements are quite similar. The chemistry of the early actinoids is more complicated than the corresponding lanthanoids, due to the large number of oxidation states possible for these actinoid elements.

1.7.6.1 Characteristics of *f*-Block Elements

1. All are metals.
2. They show variable valency. The +3 is the most important oxidation state. Few elements show +2 and +4 oxidation states.
3. They are paramagnetic in nature.
4. They form coloured compounds.
5. They have tendency to form complexes.
6. Chemically, lanthanides are very similar. It is difficult to separate them from a mixture by application of a chemical property. Similarly, actinides have similar chemical properties. The members of actinides show the phenomenon of radioactivity. Elements above atomic number 92 are called transuranium elements (Z = 94 to

102) and are not found in nature. These are man-made. They are obtained in nanogram or even less by nuclear reactions.

For names and shapes of *f*-orbitals, refer to the table and figure given in Example 1.34.

1.7.7 Inert Gases

The elements which belong to the 0 (zero) group of the periodic table are known as inert gases. They have 8 electrons (except helium) in their outermost shell. Therefore, their combining capacity (valency) is zero. Hence, they are inert in nature. However, it was discovered recently that they form a number of compounds with the most electronegative element, fluorine. In inert gases, atomic radii are very large. Interatomic forces are weak since electrons are paired. They exist in monoatomic state.

Elements in the long form of the periodic table have been divided into four blocks i.e. *s*, *p*, *d* and *f*, based upon the name of orbitals in which the last electron enters. These are shown in Table 1.9.

Table 1.9 Division of periodic table into *s*, *p*, *d* and *f*-blocks

| <i>s</i> -Block elements | <i>p</i> -Block elements |
|---|-----------------------------------|
| ns^{1-2} (two groups) | $n_s^2 n_p^{1-6}$ (six groups) |
| Transition elements (<i>d</i> -Block elements) $(n-1)d^{1-10}ns^{0-2}$ (ten groups) | |

Transition and inner transition elements: lanthanides and actinides.
f-Block elements: $(n-2)f^{0-14}(n-1)d^{0-1}ns^2$.

1.8 METALS, NON-METALS AND METALLOIDS

The elements can be further divided into metals, non-metals and metalloids (see Fig. 1.4).

1.8.1 Metals

1. The constituent particles of metals are atoms held together by the bonds called metallic bonds.
2. They comprise more than 78% of all known elements.
3. They appear on the left side of the *periodic table*.
4. They usually have high melting and boiling points.
5. They are usually solids at room temperature (except mercury (Hg)). Gallium (Ga) and cesium (Cs) have low melting points (303 K and 302 K).

Note: Due to low melting point and high boiling point of Ga, it is used in making high temperature thermometer.

6. They are good conductors of heat and electricity.
7. They are malleable (can be flattened into thin sheet by hammering) and ductile (can be drawn into wires).

1.8.2 Non-metals

1. They are located at the right side of the *periodic table*.
2. In a horizontal row, the property of elements changes from metallic on the left to non-metallic on the right.

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3. They are poor conductors of heat and electricity.
4. Mostly they are brittle and are neither malleable nor ductile.
5. Down the group, the metallic character increases and non-metallic character increases along the period (i.e., as one goes from the left to the right).
6. They are usually solids or gases at room temperature with low melting and boiling points [except boron (B) and carbon (C)].

Note: Boron has the highest melting point in its group because boron exist as B_{12} (icosahedron structure).

1.8.3 Metalloids or Semi-metals

They show properties that are characteristics of both metals and non-metals. The change from metallic to non-metallic character is not abrupt as shown by the thick zig-zag line in Fig. 1.4.

For example, the elements, i.e. silicon (Si), germanium (Ge), arsenic (As), antimony (Sb) and tellurium (Te) bordering this line and running diagonally across the periodic table are metalloids.

Note: Ge is transparent in the infrared region and therefore is used in the making of infrared windows, prisms and lenses. Si is a very important component of ceramics, glass and cement. Si and Ge (though to lesser extent) are used in the production of semiconductors and integrated circuit.

1.8.4 Nature of Bonding in Metals

The bonding among metal atoms cannot be ionic, covalent or van der Waals types as explained below:

1. Taking the example of lithium, it is known that each lithium atom has eight nearest neighbours. Electronic configuration of Li is $1s^2 2s^1$ i.e. it has only one valence electron. Hence, the possibility of its forming electron pair covalent bonds with eight other atoms is ruled out.
2. Presence of only one kind of atoms in a metal without any electronegativity difference rules out the possibility of ionic bonding.
3. The fact that the metals are quite strong rules out the possibility of their being held together by the weak van der Waals forces.

1.8.5 Electron Sea Model or Electron Gas Model

To explain the various characteristics of metals such as conductivity, lustre, malleability, ductility etc., a model called electron sea model or electron gas model has been put forward. According to this model, as metals have low ionisation energy, their valence electrons are held very loosely, i.e. they are almost like free electrons (Fig. 1.5).

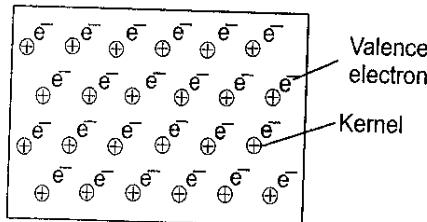


Fig. 1.5 Structure of metals (electron sea model)

All atoms contribute to form a pool of electrons which is mobile. Leaving the valence electrons, the remainder portion of the metal atom is a positive ion called 'kernel'. For example, in lithium, each atom contributes one valence electron to the pool leaving behind Li^{+} ions; in case of Mg, each atom contributes two valence electrons to the pool leaving behind Mg^{2+} ion. These positive ions or kernels are held in the three-dimensional space in a definite pattern in the sea of mobile electrons. This model is called electron gas model because the electrons are free to move in all directions like the molecules of a gas.

The simultaneous attraction between the kernels and the mobile electrons which holds the kernels together is called the metallic bond.

1.8.6 Comparison of Covalent Bond and Metallic Bond

A few important points of differences are as follows.

Covalent bond:

1. In a covalent bond, the valence electrons are localised between the atoms and hence it has a directional character.
2. Covalent bonds are quite stronger as the valence electrons in them are strongly attracted by the nuclei of the atoms.

Metallic bond:

1. In the metallic bond, the valence electrons are spread all over the crystal more or less uniformly. Hence, it is *non-directional in character*.
2. In this case, the valence electrons are mobile and are weakly attracted by the nuclei (kernels) and hence it is weaker.

1.8.7 Characteristics of Metals and Their Explanation by Electron Sea Model

The characteristic properties of metals and their explanation on the basis of electron gas model of the metallic bond are given below:

1. **Electrical conductivity:** Electrical conductivity of the metals is due to mobile electrons. In a metal crystal, the electrons are flowing equally in all directions. But when a potential difference is applied across a metal, there will be a directed flow of electrons towards the positive electrode.

The directed flow of electrons carries the electric current from one point to another and, therefore, the metals are known to be good conductors.

- 2. Effect of temperature on conductivity:** The conductivity of the metal decreases with the rise in temperature. This is because with the rise in temperature the positively charged kernels also start vibrating which interfere with the movement of electrons. As a result conductivity decreases.

In metals, the electrons are the charge carriers while in ionic liquids the charge is carried by the ions. Further, the electrons are lighter than ions and hence are more mobile. It is because of this reason that the electrical conductivity of metals is much higher than the electrical conductivity of ions in liquids.

- 3. Thermal conductivity:** Thermal conductivity of the metals is also due to mobile electrons. On heating a part of the metal, the kinetic energy of the electrons in that region increases. The energised electrons move rapidly to the cooler parts and give their excess kinetic energy to other electrons in the cooler part of the metal. Thus, the heat is conducted throughout the metal.

- 4. Metallic lustre:** The bright metallic lustre is due to the delocalised mobile electrons. When light falls on the surface of a metal, the most loosely bound electrons absorb photon of a radiant energy of visible light. Consequently, the electrons start vibrating at a frequency equal to that of the incident light. The vibrating electrons emit electromagnetic radiations in the form of light. As such it appears as if light is being reflected from metal surface and the surface gains a shining appearance which is known as metallic lustre.

- 5. Malleability and ductility:** Since the metallic bond is non-directional; metals can be twisted, drawn into wires or beaten into sheets. This is because the kernels can slip over each other when a deforming force is applied.

1.8.8 Electropositive or Metallic Character

The alkaline earth metals are highly electropositive and hence metallic and their electropositive or metallic character increases down the group. However, they are less electropositive or metallic than the alkali metals.

Explanation: On account of their relatively low ionisation energies, the alkaline earth metals have a strong tendency to lose both the valency electrons to form dipositive cations. Thus, these elements show strong electropositive or metallic character.

Down the group (\downarrow), the atomic radii increase and ionisation energies decrease. Consequently, the electropositive or metallic character increases.

Further, since the atoms of the alkaline earth metals have

smaller size and higher ionisation energies as compared to the corresponding alkali metals, their tendency to lose valence electrons is lesser than those of alkali metals. Consequently, alkaline earth metals have less electropositive or metallic character as compared to alkali metals.

Due to the smaller size of the kernel and greater number of valence electrons, the metallic bonding in alkaline earth metals is stronger as compared to alkali metals. Because of this reason, these metals are less soft (harder) than alkali metals.

1.8.9 Metallic Character of Transition Elements

All the transition elements are metals having *hcp*, *ccp* or *bcc* lattices. They exhibit all the characteristic of metals, e.g. they are hard, lustrous, malleable and ductile, have high melting and boiling points, high thermal and electrical conductivity and high tensile strength.

Explanation: Transition elements have relatively low ionisation energies and have one or two electrons in their outermost energy level (ns^1 or ns^2). As a result, metallic bonds are formed. Hence they behave as metals. The unpaired *d*-electrons also result in the formation of metallic bonds. Greater the number of unpaired *d*-electrons, stronger is the bonding due to the overlapping of unpaired electrons between different metal atoms. Cr, Mo and W have maximum number of unpaired *d*-electrons and are therefore hard metals whereas Zn, Cd and Hg are not very hard metals due to the absence of unpaired electrons.

1.8.10 Melting and Boiling Points

Transition metals have very high melting and boiling points. The melting points of the transition elements rise to a maximum and then fall as the atomic number increases. Manganese and technetium have abnormally low melting points.

Explanation: Strong metallic bonds between the atoms of these elements are responsible for the high melting and boiling points. This is clear from their high enthalpies of atomisation (i.e. heat required to break the metal lattice to get free atoms).

The strength of the metallic bond depends upon the number of unpaired *d*-electrons (half-filled *d*-orbitals). Greater is the number of unpaired electrons (half-filled orbitals) stronger is the metallic bonding. Because of the stronger metallic bonding, these elements have high melting and boiling points.

In a particular series, the metallic strength increases up to the middle with the increasing number of unpaired electrons, i.e. up to d^5 configuration (e.g. Sc has 1, Ti has 2, V has 3 and Cr has 5 unpaired electrons). After Cr the number of unpaired electrons goes on decreasing (e.g. Fe has 4, Co has 3 unpaired electrons and so on). Accordingly the melting points decrease after the middle of the increasing pairing of electrons.

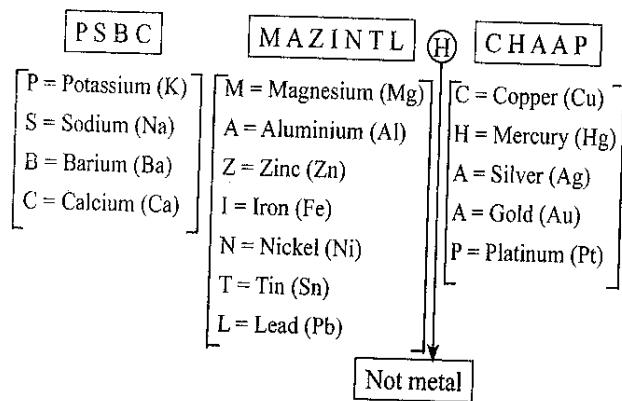
1.24 Inorganic Chemistry

As there are no unpaired electrons in Zn, Cd and Hg, they are soft and have low melting points. Hg is liquid at ordinary temperature with melting point of 234 K.

Decreasing order of metallic character is given below:

K > Na > Ba > Ca > Mg > Al > Zn > Fe > Ni > Sn > Pb
H > Cu > Hg > Ag > Au > Pt

The useful mnemonic to remember the metallic series is:



Note: That hydrogen is not a metal and comes between MAZINTL and CHAAP

Illustration 1.6 Considering the atomic number position in the periodic table, arrange the following elements in the increasing order of metallic character: Si, Be, Mg, Na, P.

(NCERT Example 3.3)

Sol. Metallic character increases down a group and decreases along a period as we move from the left to the right. Hence, the order of increasing metallic character is P < Si < Be < Mg < Na.

1.9 PREDICTION OF GROUP, PERIOD AND BLOCK OF A GIVEN ELEMENT

The group, period and block of any element can be predicted from its electronic configuration by the following ways:

1. Principal quantum number of the valence shell corresponds to the period of an element.
2. The orbital containing the last electron indicates the block of an element.
3. The group of an element is predicted from the number of electrons in the valence shell or a penultimate shell ($n-1$) as follows.
 - a. For s-block elements, the group number is equal to the number of valence electrons.
 - b. For p-block elements, the group number is equal to $10 + \text{number of electrons in the valence shell}$.
 - c. For d-block elements, the group number is equal to the number of electrons in $(n-1)d$ -subshell + number of electrons in valence shell (n th shell) Alternately one

can calculate group number = number of electrons in (penultimate shell + valence shell) - 8.

- d. For f-block elements, the group number is always 3 or III B.

Note: The element with atomic number 103 is present in the 3rd group (or III B) and 7th period. Similarly, the element with atomic number 104 is present in the 4th group (or IV B) and 7th period. Likewise elements with atomic numbers from 105 to 118 are present in the 5th, 6th, 7th, 8th, 9th, 10th, 11th, 12th, and so on up to 18th group and all of them are present in the 7th period. Element with atomic number 119 again is present in the 1st or IA group and in 8th period and so on.

Illustration 1.7 Predict the period, group number and block of the following elements. A (at. no. = 8), B (at. no. = 11), C (at. no. = 28) and D (at. no. = 54).

Sol. Electronic configurations of different elements are

$$A \rightarrow 1s^2 2s^2 2p^4$$

$$B \rightarrow 1s^2 2s^2 2p^6 3s^1$$

$$C \rightarrow 1s^2 2s^2 2p^6 3s^2 3p^6 3d^8 4s^2$$

$$D \rightarrow 1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6$$

Element A: p-block element

Group number = 10 + number of electron in the valence shell = $10 + 6 = 16$

Period of the element = Principal quantum number of the valence shell = 2nd.

Elements B: s-block element

Group number = Number of electrons in valence shell = 1

Period number = 3rd

Element C: d-block element

Group number = Number of electrons in penultimate shell and valence shell = $8 + 2 = 10$

Period of the = Principal quantum number of the valence shell = 4th

Element D: p-block element

Group number = 10 + number of electron in the valence shell = $10 + 8 = 18$

Period number = 5

Illustration 1.8 What is the atomic number of the element having maximum number of unpaired 2p electrons? To which group it belongs?

Sol. γ N. It belongs to 15 (or VA gp) group

Illustration 1.9 The elements Z = 117 and 120 have not yet been discovered. In which family/group would you place these elements and also give the electronic configuration in each case.

(NCERT Example 3.4)

Sol. The elements with $Z = 117$ belong to the halogen family (group 17) and the electronic configuration is $[Rn]5f^{14}6d^{10}7p^5$. The elements with $Z = 120$ will be placed in group 2 (alkaline earth metals) and will have the electronic configuration $[Uuo]8s^2$.

Illustration 1.10 Write the electronic configuration of the elements given below and also predict the block, group number and period to which they belong. (Z = Atomic number)

- I. A ($Z = 5$), B ($Z = 11$), C ($Z = 28$),
D ($Z = 54$), E ($Z = 59$), F ($Z = 90$).

II. Classify them as representative elements, transition, inner transition elements and noble gases.

Sol. I. **Element A** ($Z = 5$): Name of element = Boron, (*B*)
Electronic conjugation of A = $1s^2 2s^2 2p^1$

The last electron enters in $2p$ orbital, therefore it belongs to *p-block elements*

Group number = 10 + Number of electrons in the valence shell

$$= 10 + 3 = 13$$

Period of the element = Number of the principal quantum number of the valence shell = 2nd.

Element B ($Z = 11$): Name of element = sodium (Na)

Electronic configuration of B = $1s^2 2s^2 2p^6 3s^1$

The last electron is present in $3s$ -orbital, therefore it belongs to *s-block elements*.

Group number = Number of electrons in the valence shell = 1

Period of the element = Number of the principal quantum number of shell = 3rd

Element C ($Z = 28$): (Name of element = Nickel) (Ni)

Electronic configuration of C: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^8 4s^2$.

The last electron enters into $3d$ -orbital, therefore it belongs to *d-block elements*.

Group Number = Number of electrons in the penultimate shell + number of electrons in the valence shell = $8 + 2 = 10$.

Period of the element: Number of principal quantum number of the valence shell = 4th.

Element D ($Z = 54$): of D Name of element = Xenon (Xe)

Electronic configuration: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6$

The last electron is present in $5p$ -orbital, therefore it belongs to the *p-block elements*.

Group number = 10 + Number of electrons in the valence shell = $10 + 8 = 18$.

Period of the element = Number of principal quantum number of the valence shell = 5th.

Element E ($Z = 59$): Name of element

= Praseodymium (Pr)

Electronic configuration of E: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 6s^2 5d^1 4f^2$.

But its actual electronic configuration is $6s^2, 4f^3$.

The last electron enters into the $4f$ -orbital, therefore it belongs to *f-block elements*.

Group Number: Since it belongs to the lanthanide series, therefore as such it does not have any group number of its own but it is considered to lie in group 3.

Period of elements: Number of principal quantum number of the valence shell = 6th.

Element F ($Z = 90$): Name of the element = Thorium (Th)

Electronic configuration of F: $[Rn] 6d^1 7s^2 5f^1$

But its actual electronic configuration is $[Rn] 6d^2 7s^2$.

The last electron enters into the $5f$ -orbital, therefore it belongs to *f-block elements*.

Group number: Since it belongs to actinide series, therefore as such it does not have any group number of its own but it is considered to lie in group 3.

Period of the elements = Number of principal quantum number of the valence shell = 7th.

II. **Elements A and B are representative elements** since their last electron enters in *s*- and *p*-orbitals respectively.

Element C is a transition element since its last electron enters in the *d*-orbital.

Element D is a p-block element with completely filled *s*- and *p*-orbitals of the valence shell and is called a noble gas.

Elements E and F are an inner transition elements since their last electron enters in the *f*-orbital.

QUESTION Write the names and the atomic numbers (Z) of the following elements:

- The fourth alkaline earth metal
- The fifth alkali metal
- The sixth element of the first transition series
- The second inner transition elements and
- The third noble gas

Sol. a. Sr ($Z = 38$)

b. Cs ($Z = 55$)

c. Fe ($Z = 26$)

d. Pr ($Z = 59$)

e. Ar ($Z = 18$)

QUESTION How do the electronic configuration of the elements with $Z = 106$ – 108 differ from one another?

Sol. Electronic configuration of $Z = 106 = 6d^4 7s^2$

$$Z = 107 = 6d^5 7s^2$$

$$Z = 108 = 6d^6 7s^2$$

Elements with $Z = 106$, has four, $Z = 107$, has five, while $Z = 108$ has six d -electrons.

Illustration 1.13 Predict the name and position of the element in the periodic table with the electronic configuration $(n - 1)d^8 ns^2$ for $n = 5$.

Sol. For $n = 5$, the electronic configuration $= (5 - 1)d^8$
 $5s^2 = 4d^8 5s^2$. The element corresponding to this configuration is palladium (Pd) ($Z = 46$), which is a d -block element.

$$\begin{aligned}\text{Group number} &= \text{Number of electrons in } (n - 1) \text{ subshell} \\ &\quad + \text{number of electrons in } n \text{th shell} \\ &= 8 + 2 = 10\end{aligned}$$

Period of the elements: Number of principal quantum number of the valence shell = 5th.

Illustration 1.14 Elements A to E have the following electronic configuration:

- A: [He]2s²2p², B: [Ne]3s²3p², C: [Ne]3s²3p³,
D: [Ne]3s²3p⁴, E: [Ar]4s².

Which of the above will belong to the same group in the periodic table?

Sol. Elements having similar valence electronic configuration belong to the same group of the periodic table.

Therefore, elements A and B having four electrons in the valence shell, i.e. 2s², 2p² and 3s² 3p² respectively belong to the same group, i.e. group 14 of the periodic table.

1.10. GENERAL INORGANIC CHEMISTRY OR PERIODIC TRENDS IN PROPERTIES OF ELEMENTS

The periodic law states that properties of the elements vary periodically with their atomic numbers. The basis of this periodicity lies in the periodic repetition of the electronic configuration of the elements as the atomic number increases. Regular variations in physical and chemical properties are observed down the group (\downarrow) or along the period (\rightarrow) in the periodic table. This regular gradation in properties is called periodicity.

For example, along the period (\rightarrow), chemical reactivity tends to be high in group 1 metals, lower in elements towards the middle of the table, and increases to a maximum in the group 17 non-metals.

Similarly, down the group (\downarrow) of representative metals (alkali and alkaline earth metals) reactivity increases whereas down the group (\downarrow) of non-metals (e.g. halogens) reactivity decreases.

1.10.1 Explanation of Periodicity

- In a period from the left to the right there is a regular change in electronic configuration of elements.
- In a group from the top to the bottom the outermost shell electronic configuration is similar.
- The chemical properties of the element depend upon their electronic configuration. So, there is a regular change in chemical properties in a period and in a group, elements have similar chemical properties.

1.10.2 Trends in Physical Properties

There are various physical properties of elements which show periodic variation such as

- Atomic and ionic radii
- Screening or shielding effect
- Penetration effect
- Ionisation energy (IE or $\Delta_i H^\ominus$)
- Electron gain enthalpy ($\Delta_{eg} H^\ominus$) and electron affinity (EA)
- Electronegativity (EN) and its scales
- Metallic and non-metallic properties
- Polarity of covalent bond and percentage of ionic character
- Bond strength
- Acidic, basic and amphoteric character
- Bond length
- Bond angles
- Periodicity of valence or oxidation states
- Typical elements
- Bridge elements
- Periodic trends and chemical reactivity
- Magnetic properties
- Fajans' rule (or change of ionic character to covalent character) or polarisability or polarisation
- Inert pair effect
- Factors which determine the formation (or stability) of the compounds
- Lattice enthalpy ($\Delta_U H^\ominus$)
- Hydration enthalpy ($\Delta_{hyd} H^\ominus$)
- Flame colouration
- Colour of substance in visible light
- p π -p π multiple bond
- p π -d π multiple bond
- Hydrogen bonding
- Geometry, shape and hybridisation of compounds and ions
- Lanthanide and actinide contraction
- Dipole moment

1.11 ATOMIC RADIUS

Determination of the size of an atom is very complicated and cannot be precise due to:

1. The size of an atom ($\sim 1.2 \text{ \AA}$ or $1.2 \times 10^{-10} \text{ m}$ in radius) is very small.
2. The electron cloud surrounding the atom does not have a sharp boundary.

There is no practical way by which the size of an individual atom can be measured. However, atomic size can be made by knowing the distance between the atoms in the combined state.

The distance from the centre of the nucleus to the outermost shell containing the electrons is called atomic radius. It is a very important property of an atom since different physical and chemical properties of atoms are related to it. It refers to both the covalent or metallic radii depending on whether the element is a non-metal or a metal. Atomic radii can be measured by spectroscopic methods (e.g. UV (ultraviolet) and IR (infrared) and by X-ray diffraction and electron diffraction techniques. Atomic radii of few elements are listed in Table 1.10 (a) and Figs. 1.6 (a) and 1.6 (b).

Table 1.10 (a) Atomic radii/pm across the periods

| Atom (periods II) | Atomic radius | Atom (periods III) | Atomic radius |
|----------------------|------------------|-----------------------|------------------|
| Li | 152 | Na | 186 |
| Be | 111 | Mg | 160 |
| B | 88 | Al | 143 |
| C | 77 | Si | 117 |
| N | 70 | P | 110 |
| O | 74 | S | 104 |
| F | 72 | Cl | 99 |

Table 1.10 (b) Atomic radii/pm down the group across a family

| Atom (group I) | Atomic radius | Atom (group 17) | Atomic radius |
|-------------------|------------------|--------------------|------------------|
| Li | 152 | F | 72 |
| Na | 186 | Cl | 99 |
| K | 231 | Br | 114 |
| Rb | 244 | I | 133 |
| Cs | 262 | At | 140 |

Note: Atomic radius of O > F > N.

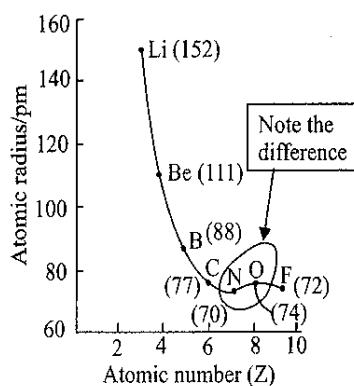


Fig. 1.6 (a) Variation of atomic radius with atomic number across the second period

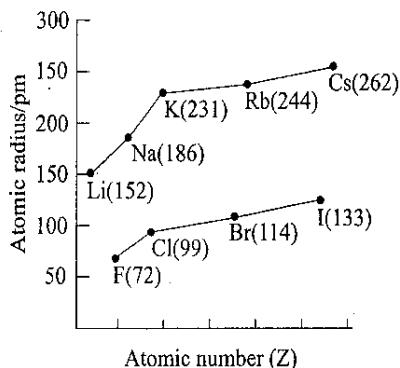


Fig. 1.6 (b) Variation of atomic radius with atomic number for alkali metals and halogens

Exceptions: Elements of 2nd and 3rd transition series (i.e. 4d and 5d series) belonging to the same vertical columns are similar in size and properties because of the intervention of lanthanides as shown in Fig. 1.6(c).

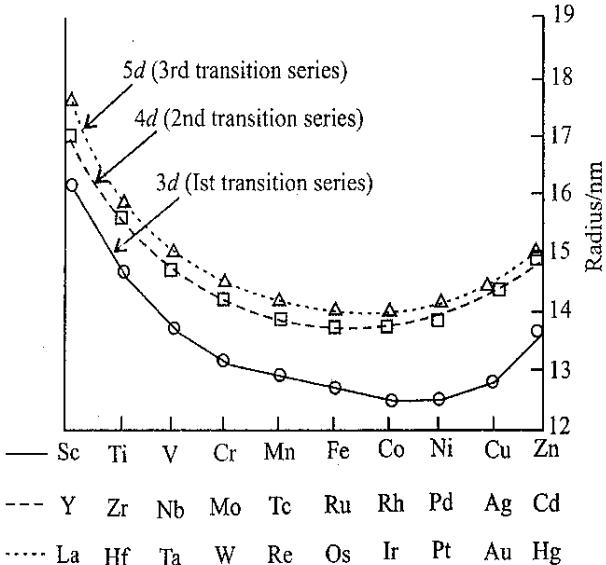


Fig. 1.6 (c) Trends in atomic radii of transition elements

1.11.1 Types of Atomic Radii

These are of four types:

- 1. Covalent radius:** It is one-half of the distance between the nuclei (internuclear distance) of two covalently bonded like atoms in a homo-diatom molecule which is called the covalent radius of that atom.

$$r_{\text{covalent}} \text{ or } r_c = \frac{1}{2} [\text{bond length}]$$

For example, bond distance in Cl_2 molecule = 198 pm.

$$r_{\text{Cl}} (\text{covalent}) = 198/2 = 99 \text{ pm.}$$

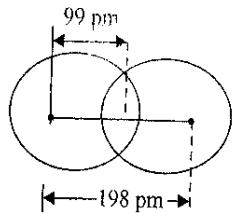


Fig 1.7 Overlapping of atomic orbitals to form a covalent bond

The covalent radius is measured approximately as the radius of an atom's core which is in contact with the core of an adjacent atom in a bonded situation.

- 2. Metallic radius:** Metal atoms are assumed to be closely packed spheres, which are considered to touch one another in metallic crystal.

Metallic radius is half the internuclear distance separating the metal cores in the metallic crystal. For example, the distance between the two adjacent copper atoms in solid copper is 256 pm; hence, the metallic radius of copper is $256/2 = 128 \text{ pm}$.

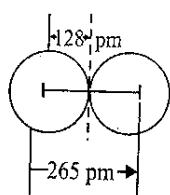


Fig. 1.8 No overlapping of atomic orbitals

Thus, metallic radius > covalent radius.

- 3. van der Waals radius:** It represents the overall size of the atom which includes its valence shell in a non-bonded situation. It is half of the distance between two similar atoms in separate molecules in a solid.

Thus, van der Waals radius > metallic radius > covalent radius.

Covalent radius of two Cl atoms in Cl_2 molecule [Fig. 1.9 (a)], van der Waals radius of Cl atoms in two non-bonded isolated Cl atoms [Fig. 1.9 (b)] and covalent and van der Waals radii in two Cl_2 molecules [Fig. 1.9(c)] are shown below.

Covalent radii of some common elements are listed in Table 1.11.

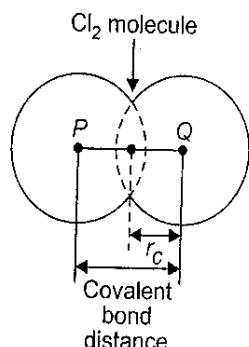


Fig. 1.9(a)

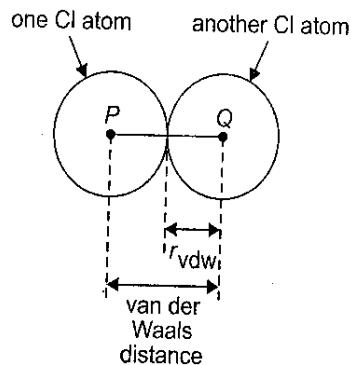


Fig. 1.9(b)

In Fig. 1.9 (a), electron clouds of two Cl atoms merge with each other and $r_c = PQ/2$, while in Fig. 1.9 (b), two Cl atoms are just in contact with each other (no bond formation). Therefore $r_{\text{vdw}} = PQ/2$.

When two Cl_2 molecules formed by overlapping of electron clouds of two Cl atoms that are brought in close contact with each other (no bond formation) (Fig. 1.9(c)). Then r_{vdw} of two Cl_2 molecules = $PS/2 = 180 \text{ pm}$; and r_c of two Cl_2 molecules = $RS/2 = 99 \text{ pm}$.

It may be noted that r_{vdw} of two atoms or of two Cl_2 molecules is greater than r_c of two atoms or molecules. This is because in the formation of covalent bond, atoms have to overlap each other while in the formation of bonds, atoms/molecules simply come closer to each other and do not enter overlapping (no bond formation).

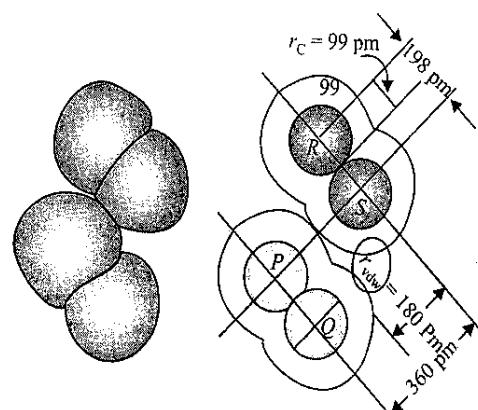


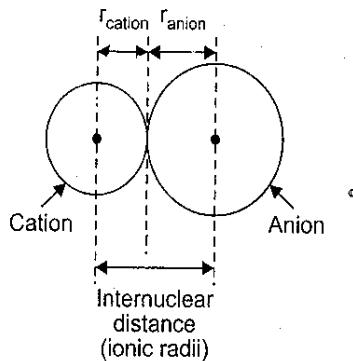
Fig. 1.9 (c) Covalent and van der Walls radii in a chlorine molecule. The inner circles correspond to the size of the chlorine atom (r_{vdw} and r_c are van der Waals and covalent radii respectively).

Table 1.11 Covalent radii, r_{cov} /(pm)

| | | | | | | | |
|---|-------|----|-------|----|--------|----|-----|
| H | 37 | | | | | | |
| C | 77(1) | N | 74(1) | O | 66(1) | F | 64 |
| | 67(2) | | 65(2) | | 57(2) | Cl | 99 |
| | 60(3) | | 55(3) | | | | |
| | | P | 110 | S | 104(1) | Br | 114 |
| | | | | | 95(2) | | |
| | | As | 121 | Se | 104 | I | 133 |
| | | Sb | 141 | Te | 137 | | |

* The values cited are for single bonds, double bonds and triple bonds as indicated by 1, 2 and 3 in parenthesis respectively.

4. Ionic radii: A neutral atom changes to a cation by the loss of one or more electrons and to an anion by the gain of one or more electrons. The number of charge on cation and anion is equal to the number of electrons lost or gained respectively. The ionic radii of the ions present in an ionic crystal may be calculated from the internuclear distance between the two ions.



The ionic radius is the distance between the nucleus of an ion and the point where the nucleus exerts its influence on the electron cloud.

The characteristics of ionic radii are as follows:

- The ionic radius of a particular ion is of constant magnitude.
- Ionic radii have an additive character, i.e. the inter nuclear distance between two ions is equal to the sum of the radii of the ions of which the ionic crystal is composed. Thus,

$$r_{\text{cation}} + r_{\text{anion}} = r_{\text{ionic radii}}$$

For example, $r_{\text{Na}^+} = 95 \text{ pm}$ and the internuclear distance between the ion pairs in NaCl ionic crystal is 276 pm.

$$\therefore r_{\text{Cl}^-} + r_{\text{Na}^+} = r_{\text{ionic radii}}$$

$$\therefore r_{\text{Cl}^-} = r_{\text{ionic radii}} - r_{\text{Na}^+}$$

$$= 276 - 95 = 181 \text{ pm}$$

- Radius of cation:** Radius of a cation is invariably smaller than that of the corresponding neutral atom

| Na | Na ⁺ |
|--------------------------------|-------------------------|
| Number of electrons = | 11 |
| Number of protons (p^-s) = | 11 |
| | $1s^2, 2s^2 2p^6, 3s^1$ |
| | $1s^2, 2s^2 2p^6$ |

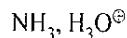
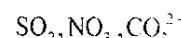
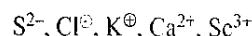
- Radius of an anion:** Radius of an anion is invariably bigger than that of corresponding atom
- | Cl | Cl ⁶⁻ |
|--------------------|------------------|
| Number of e^- = | 17 |
| Number of p^-s = | 17 |

- Isoelectronic species:** A series of atom, ions and molecules in which each species contains same number of electrons but different nuclear charge is called isoelectronic species.

| | | | | | | | |
|------------------------------------|-----------------|-----------------|----------------|-----|------------------|------------------|------------------|
| Number of electrons | N ³⁻ | O ²⁻ | F ⁻ | Ne | Na ⁶⁻ | Mg ²⁺ | Al ³⁺ |
| Number of protons | 10 | 10 | 10 | 10 | 10 | 10 | 10 |
| Ratio $\left(\frac{Z}{e^-}\right)$ | 7 | 8 | 9 | 10 | 11 | 12 | 13 |
| Ionic radius(pm) | 0.7 | 0.8 | 0.9 | 1.0 | 1.1 | 1.2 | 1.3 |
| | 171 | 140 | 136 | 112 | 95 | 65 | 50 |

Note: Smaller the value of $\left(\frac{Z}{e^-}\right)$, larger the size of that species.

- Number of electrons is same.
- Number of protons is increasing.
- So, the effective nuclear charge is increasing and atomic size is decreasing. In an isoelectronic series, atomic size decreases with the increase of charge. Some of the examples of isoelectronic series are as under.



1.11.2 Periodicity in Atomic Radius and Ionic Radius

1. For normal elements:

- In a period from the left to the right the effective nuclear charge (Z_{eff}) increases because the next electron fills in the same shell. So, the atomic size decreases. For example, the covalent radii of the second period elements in Å are as follows:

| | | | | | | |
|------|------|------|------|------|------|------|
| Li | Be | B | C | N | O | F |
| 1.23 | 0.89 | 0.80 | 0.77 | 0.74 | 0.74 | 0.72 |

- In a group moving from the top to the bottom the number of shells increases. So, the atomic size increases. Although the effective nuclear charge

increases its effect is negligible in comparison to the effect of increasing number of shells. For example, the covalent radii of IA group elements in Å are as follows:

| Li | Na | K | Rb | Cs |
|------|------|------|------|------|
| 1.23 | 1.57 | 2.03 | 2.16 | 2.35 |

2. The atomic radius of the inert gas (zero group) is shown the largest in a period because of its van der Waals radius which is generally larger than the covalent radius. The van der Waals radius of inert gases also increases in moving from the top to the bottom in a group.

Illustration 1.15 Which of the following species will have the largest and the smallest size Mg , Mg^{2+} , Al , Al^{3+} ?

(NCERT Example 3.5)

Sol. Atomic radii decrease along the period. Cations are smaller than their parent atoms. Among isoelectronic species the one with the larger positive nuclear charge will have a smaller radius.

The largest species is Mg ; the smallest one is Al^{3+} .

Illustration 1.16 a. Compare the size of Cl , Cl^{\ominus} and Fe^{2+} ion.

b. The radii of Ar is greater than the radii of chlorine. Explain.

$$\text{Sol. a. } \frac{Z}{e^-} \text{ ratio for } Cl = \frac{17}{17} = 1.00$$

$$Cl^{\ominus} = \frac{17}{18} = 0.944$$

$$Fe^{2+} = \frac{26}{24} = 1.08$$

$$Cl^{\ominus} > Cl > Fe^{2+}$$

- b. **Explanation:** In chlorine, the radii mean the atomic or covalent radii which is actually half the intermolecular distance between two atoms, whereas in argon the radii mean the van der Waals radii as argon is not a diatomic molecule. van der Waals radii is actually half the distance between adjacent molecule. So, van der Waals radii being larger than the atomic radii. Hence, argon has a larger radii than chlorine.

Illustration 1.17

- a. Give and explain the decreasing order of atomic radius of fluorine (F), nitrogen (N) and oxygen (O).
 b. Give the decreasing order of van der Waals radii: N , O , H , Cl , Br .

Sol. a. Decreasing order of atomic radius is $O > F > N$.

Explanation: The atomic size generally decreases across a period as shown Fig. 1.5 (a) for the elements of the second period. Because within 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 of electrons to the nucleus.

So, the decreasing order of atomic radius should be $N > O > F$.

But it is not observed, since from N to O , Z_{eff} increases, so the size should decrease from N to O . But in oxygen pairing of electrons takes place, so due to the repulsion between paired electrons, size of $O > N$. [$N = 2s^2 2p^3$, $O = 2s^2 2p^4$]

Similarly, due to the repulsion between two lone pairs of electrons in F ($2s^2 2p^5$), the size should increase from O to F . But high nuclear charge of F than that of O , compensates the repulsion between two pairs of electrons. Hence, size of $O > F$.

Thus decreasing order of atomic radius is $O > F > N$.

- b. $r_{vdw} \propto$ Numbers of energy shells and

$$r_{vdw} \propto \frac{1}{\text{Nuclear charge}}$$

- i. H has only one energy shell ($n = 1$), Cl has three ($n = 3$) and Br has four ($n = 4$). Therefore,

$$r_{vdw} \text{ of } Br > r_{vdw} \text{ of } Cl > r_{vdw} \text{ of } H$$

- ii. Both N and O have two energy shells ($n = 2$), but Z on oxygen (+8) is greater than on N (+7). Therefore,

$$r_{vdw} \text{ of } N > r_{vdw} \text{ of } O$$

Hence, the decreasing order of r_{vdw} is

$$Br > Cl > N > O > H$$

Illustration 1.18

- a. In the sixth period, after filling of $6p$ orbitals, the next electron (i.e. 57th) enters the $5d$ -orbital against *aufbau principle* and there after the filling of seven $4f$ -orbitals starts with cerium ($Z = 58$) and ends up with lutetium ($Z = 71$). Explain this anomalous behaviour.
 b. In the seventh period, after the filling of $7s$ -orbital, the next two electrons (i.e. 89th and 90th) enter the $6d$ -orbital against *Aufbau principle* and there after the filling of seven $5f$ -orbitals begins with proactinium (Pr , $Z = 91$) and ends up with lawrencium (Lr , $Z = 103$). Explain this anomalous behaviour.

- Sol. a.** This can be explained on the basis of greater stability of the xenon (inert gas) core. After barium (Ba , $Z = 56$), the addition of the next electron (i.e. 57th), should occur in $4f$ -orbitals in accordance with *aufbau principle*. Since the $4f$ -orbitals lie inside the core, and will tend to destabilise the xenon core.

$$Z = 54, \Rightarrow [Kr]4d^04f^05s^25p^65d^0$$

Therefore, the 57th electron prefers to enter $5d$ -orbitals which lies outside the xenon core and whose energy is only slightly greater than that of $4f$ -orbitals.

Thus, stability of the atom due to xenon core compensates more than the slight instability caused by the addition of one electron to the higher energy $5d$ -orbital instead of the lower energy $4f$ -orbital.

Thus, the outer electronic configuration of La ($Z = 57$) is $5d^16s^2$ rather than the expected $4f^16s^2$. Once $5d$ -orbital has one electron, the next electron (i.e. 58th) instead of entering the outer $5d$ -orbital, enters the inner $4f$ -orbital. This is due to greater nuclear charge and thereafter the continuous filling of the $4f$ -sub shell occurs till it is complete at lutetium (Lu, $Z = 71$, $4f^{14}5d^16s^2$)

b. The anomalous behaviour is due to:

- i. The smaller energy difference between $5f$ - and $6d$ -orbitals than between $4f$ - and $5d$ -orbitals.
- ii. Due to the greater stability of radon (Rn, $Z = 86$), the next two electrons (i.e. 89th and 90th) after filling the $7s$ -orbital prefer to enter $6d$ -orbitals before filling of $5f$ -orbitals begin with protactinium (Pa, $Z = 91$) and continues till it is complete with lawrencium (Lr, $Z = 103$).

Illustration 1.19 Which of the following species are isoelectronic?

- i. Ne ii. O^{2-} iii. Mg^{2+} iv. F
- v. Al^{3+} vi. Cl^{\ominus} vii. K viii. Na

Arrange them in decreasing order of their size.

Sol. The number of electrons in these species are:

- | | |
|------------------------------|----------------------------------|
| i. Ne = 10 | ii. $O^{2-} = 8 + 2 = 10$ |
| iii. $Mg^{2+} = 12 - 2 = 10$ | iv. F = 9 |
| v. $Al^{3+} = 13 - 3 = 10$ | vi. $Cl^{\ominus} = 17 + 1 = 18$ |
| vii. K = 19 | viii. Na = 11 |

Thus Ne, O^{2-} , Mg^{2+} , Al^{3+} are isoelectronic species (each one of which has 10 electrons).

Nuclear charge on these isoelectronic species are as:

$$\begin{array}{ll} \text{Ne} = +10 & \text{O}^{2-} = +8 \\ \text{Mg}^{2+} = 12 & \text{Al}^{3+} = 13. \end{array}$$

Size of the species decreases as the nuclear charge increases, therefore the size of isoelectronic species decreases in the order.

$$O^{2-} > \text{Ne} > \text{Mg}^{2+} > \text{Al}^{3+}.$$

Illustration 1.20 Which of the following species has the smallest size?

- a. K^{\oplus} , Sr^{2+} , Ar
- b. Si, P, Cl
- c. O, O^{\ominus} , O^{2-}

Sol. Z for Sr^{2+} , K^{\oplus} and Ar = 38, 19 and 18 respectively.

Electronic configuration of Sr = [Kr] $5s^2$

Electronic configuration of Sr^{2+} = [Kr] (it has four shells)

Electronic configuration of K = [Ar] $4s^1$

Electronic configuration of K^{\oplus} = [Ar] (it has three shells)

Ionic size of Sr^{2+} is smaller than that of K^{\oplus} , due to higher nuclear charge which compensates the effect of additional shell.

Since K^{\oplus} and Ar are isoelectronic species with 18 electron each. So, $\frac{Z}{e^-}$ for K^{\oplus} = $\frac{19}{18} = 1.05$ and $\frac{Z}{e^-}$ for Ar =

$\frac{18}{18} = 1.0$. Smaller is the value of $\frac{Z}{e^-}$, larger the size of that species.

So decreasing order of size is

$$Ar > K^{\oplus} > Sr^{2+}$$

- b. Z for Si, P and Cl = 14, 15, 17

Decreasing order of size is

$$Si > P > Cl$$

Thus, Cl is of the smallest size.

Moreover, along the period, size decreases from the left to the right. All of them belong to the 3rd period.

- c. Species with more negative charge is larger than its parent atom.

Thus, the decreasing order of size is

$$O^{2-} > O^{\ominus} > O$$

Thus, O is the smallest in size.

Illustration 1.21 Arrange the following in order of decreasing radii?

- a. F^{\ominus} , O^{2-} , N^{3-} , S^{2-}
- b. P, Si, N, C
- c. I^{\ominus} , I^{\oplus} , I

Sol. a. Since F^{\ominus} , N^{3-} , O^{2-} are isoelectronic species (with 10 electrons). So, size of anions decreases as nuclear charge increases (Z for F^{\ominus} , O^{2-} , N^{3-} = 9, 8 and 7 respectively) So, decreasing order of size among isoelectronic anions are as:

$$N^{3-} > O^{2-} > F^{\ominus}$$

Since S belongs to the 3rd period while F, O, N all belong to the 2nd period. Therefore, size of S^{2-} is largest.

Thus overall order of decreasing size is

$$S^{2-} > N^{3-} > O^{2-} > F^{\ominus}$$

- b. C and N belong to the 2nd period whereas Si and P belong to the 3rd period. Elements in the 3rd period have higher atomic sizes than those of the 2nd period due to increase in shells. Thus, size of Si and P are higher than those of C and N respectively.

Moreover, along the period atomic sizes decrease from the left to the right due to the increased nuclear charge. Thus, size of C > N and Si > P. Thus, overall decreasing order of atomic sizes is

$$Si > P > C > N$$

1.32 Inorganic Chemistry

- c. Decreasing order of radii is

$$I^- > I > I^+$$

because the size of anion is always greater while that of an cation is always smaller than the parent atom.

1.12 SCREENING OR SHIELDING EFFECT OF INNER SHELL ELECTRONS ON THE VALENCE SHELL ELECTRON

In multi-electron atoms, the valence shell electrons are attracted by the nucleus and repelled by the electrons in the inner shell. The combined effect of these two opposing forces is that the attractive force exerted by the nucleus on the valence shell electrons is partially decreased or weakened by the repulsive force exerted by the electrons present in the inner shell. Thus, the valence shell electrons experience less charge of the nucleus.

The actual charge experienced by the valence shell electrons is called *effective nuclear charge* and the repulsive force experienced by the valence shell electrons from the electrons present in the inner shells is called the *shielding or screening effect*. Thus, the effective nuclear charge (Z_{eff}) is

$$Z_{\text{eff}} = \text{Total nuclear charge } (Z) - \text{Screening constant } (\sigma)$$

1.12.1 Factors Affecting the Magnitude of Screening Effect

Number of inner shells: σ depends on the numbers of electrons in the inner shells. The greater the number of inner electrons, large is the screening effect and hence larger is the magnitude of σ and hence the magnitude of Z_{eff} will decrease.

As the screening effect increases, Z_{eff} decreases. Consequently the force of attraction by the nucleus for the valence shell electrons decreases and hence the ionisation enthalpy decreases down the group (\downarrow).

1.12.2 Calculation of σ and Z_{eff} by Slater's Rule

The magnitude of ' σ ' and hence that of ' Z_{eff} ' can be calculated by using Slater's rule, as follows.

1. For ns - or np -orbital electrons:

- Write the electronic configuration of the element in the following order and group them as
(1s), (2s, 2p), (3s, 3p), (3d), (4s, 4p), (4d, 4f), (5s, 5p), (5d, 5f), (6s, 6p), etc.
- Electrons to the right of the (ns , np) group are not effective in shielding the ns or np electrons and contribute nothing to σ .
- All other electrons in the (ns , np) group contribute to the extent of 0.35 each to the screening constant (except for 1s for which the value is 0.30).
- All the electrons in the ($n-1$)th shell contribute 0.85 each to the screening constant.

- e. All the electrons in the ($n-2$)th shell or lower contribute 1.0 each to the screening constant.

2. For d -or f -electrons: Rules (a) to (c) remain the same but rules (d) and (e) get replaced by the rule (f).

- f. All the electrons in the groups lying left to (nd , nf) group contribute 1.0 each to the screening effect.

Calculate the effective nuclear charge experienced by the $4s$ -electron in potassium atom ($Z = 19$).

Sol: The electronic configuration of K is $1s^2, 2s^2 2p^6, 3s^2 3p^6, 4s^1$, and this atom has 4 shells in it. Therefore,

$$(Z_{\text{eff}})_{4s} = Z - \sigma$$

$$\sigma = \left[\begin{array}{l} 0.85 \times \text{number of electrons in } (n-1)\text{th} \\ \text{shell} + 1.00 \times \text{total number of electrons} \\ \text{in the inner shell} \end{array} \right]$$

$$= 0.85 \times 8 + 1.00 \times 10$$

$$= 16.80$$

$$\text{Hence, } Z_{\text{eff}} = Z - \sigma = 19 - 16.80$$

$$= 2.20$$

Calculate the effective nuclear charge of the last electron in an atom. The electronic configuration is $1s^2, 2s^2 2p^6, 3s^2 3p^5$.

Sol. $Z = 2 + 2 + 6 + 2 + 5 = 17$, and this atom has 3 shells in all.

$$\sigma = \left[\begin{array}{l} 0.35 \times \text{number of electrons left} \\ \text{in } n\text{th shell} + (0.85 \times \text{number of} \\ \text{electrons in } (n-1)\text{th shell} + (1.00 \times \\ \text{total number of electrons in the} \\ \text{inner shells})) \end{array} \right]$$

$$= (0.35 \times 6) + (0.85 \times 8) + (1 \times 2)$$

$$= 10.9$$

$$\text{Thus, } Z_{\text{eff}} = (Z - \sigma)$$

$$= 17 - 10.9 = 6.1$$

Calculate the screening constant in Zn.

- a. For a 4 s -electron b. For a 3 d -electron

Sol. The electronic configuration of Zn ($Z = 30$) is

$$1s^2, 2s^2 2p^6, 3s^2 3p^6, 3d^{10}, 4s^2$$

Since σ is calculated for one electron in $4s$ shell, so one electron is left in $4s$ shell.

$$\text{a. } \sigma = \left[\begin{array}{l} (0.35 \times \text{number of electrons left in } 4s \text{ or} \\ n\text{th shell}) + (0.85 \times \text{number of electrons in} \\ (n-1)\text{th shell}) + (1.00 \times \text{total number of} \\ \text{electrons in the inner shell}) \end{array} \right]$$

$$= (0.35 \times 1) + (0.85 \times 18) + (1.00 \times 10)$$

$$= 25.65$$

- b. i. σ for $4s = 0$, [Rule (b)]. (σ for right of (ns , np) is zero).

- ii. Since σ is calculated for one electron in $3d$ -orbital, so, 9 electrons are left in $3d$ -orbital.

$$\therefore \sigma = \left[\begin{array}{l} (0.35 \times \text{number of electrons left in} \\ \text{ } 3d \text{ shell or } n\text{th shell} \end{array} \right] \\ + \left[\begin{array}{l} (1.00 \times \text{number of electrons in the} \\ \text{ } \text{inner shell} \end{array} \right] \\ = (0.35 \times 9) + (1.0 \times 18) \\ = 21.15 \end{math>$$

3. Type of orbitals occupied by the electrons:

- a. Due to different shapes and orientation of different orbitals, the screening power decreases as follows:

$$\xrightarrow{\text{Screening power decreases}} ns > np > nd > nf$$

From the shapes of electron charge clouds of orbitals, it is clear that the ns -orbitals are spherical symmetrical in shape. Therefore, it screens the nuclear charge more effectively than np -orbitals which are dumbbell in shape. Similarly, np -orbitals screen the nuclear charge more effectively than nd -orbitals which are double dumbbell in shape which in turn screens the nuclear charge much more effectively than nf -orbitals which are diffused and complex in shape and orientation.

This order also means that the electrons present in d - and f -orbitals are much more shielded than those in s - or p -orbitals by the inner shell electrons. Thus an electron in np -orbital is more effectively shielded than the ns -electron by the inner shell electrons.

For example, consider Be ($1s^2 2s^2$) and B ($1s^2 2s^2 2p^1$) atoms, $2p$ electrons of B atom are more effectively shielded by $1s$ and $2s$ electrons while the $2s$ electrons of Be atom are not effectively shielded by the $1s$ electrons and second $2s$ electron.

- b. An electron present in the n th orbital is more effectively shielded by the electrons in the $(n-1)$ th orbital while the same electron is not effectively shielded by the other electron present in the same orbital.

For example, in Li atom ($1s^2 2s^1$); $2s^1$ electron is more effectively shielded by two electrons present in $1s$ -orbital while in He atom ($1s^2$) one of the two electrons in $1s$ -orbital is not effectively screened by the other electron present in the same orbital i.e., $1s$ -orbital.

c. Application of shielding effect:

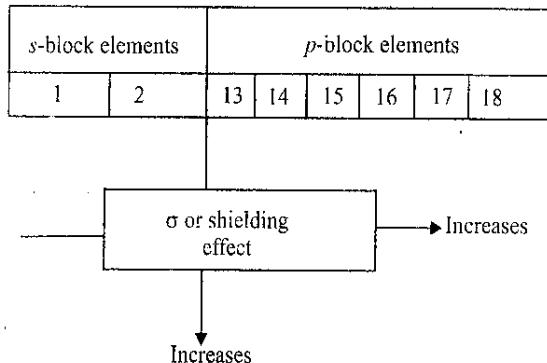
- This concept has been used to explain why the ionisation potential values of the elements of a given group decreases down the group (\downarrow).
- It has been used to explain why a large decrease in

the value of ionisation potential is observed when we proceed from an inert gas to alkali metals.

- It has been used in explaining the inert pair effect.
- It has been used to explain the lanthanide and actinide contraction.

- Variation of screening effect or σ in the periodic table:** Greater is the magnitude of σ , greater is the amount of shielding effect caused by the intervening electrons on the valence shell electrons.

Since σ increases both down the group (\downarrow) and along the period (\rightarrow), so the magnitude of screening effect also increases in the same direction.



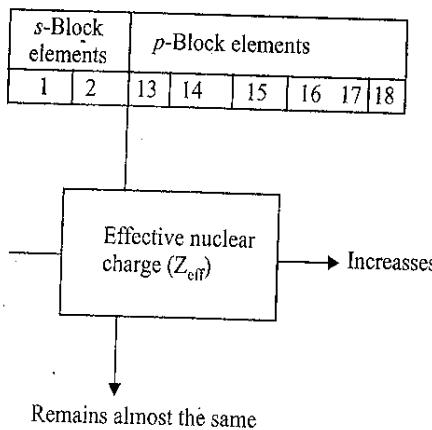
5. Variation of effective nuclear charge in the periodic table:

- It is observed that the magnitude of effective nuclear charge or effective atomic number increases in a period when we move from the left to the right.

| IInd period | Li | Be | B | C | N | O | F | Ne |
|---------------------------------|-----|------|------|------|------|------|------|------|
| Z | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
| σ | 1.7 | 2.05 | 2.40 | 2.75 | 3.10 | 3.45 | 3.80 | 4.15 |
| $Z_{\text{eff}} = (Z - \sigma)$ | 1.3 | 1.95 | 2.60 | 3.25 | 3.90 | 4.55 | 5.20 | 5.85 |

- In the subgroup of normal elements the magnitude of effective atomic number remains almost the same, as shown below:

| Ist group | Li | Na | K | Rb | Cs |
|---------------------------------|------|------|-------|-------|-------|
| Z | 3 | 11 | 19 | 37 | 55 |
| σ | 1.7 | 8.8 | 16.8 | 34.8 | 52.8 |
| $Z_{\text{eff}} = (Z - \sigma)$ | 1.3 | 2.2 | 2.2 | 2.2 | 2.2 |
| 2nd group | Be | Mg | Ca | Sr | Ba |
| Z | 4 | 12 | 20 | 38 | 56 |
| σ | 2.05 | 9.15 | 17.15 | 35.15 | 53.15 |
| $Z_{\text{eff}} = (Z - \sigma)$ | 1.95 | 2.85 | 2.85 | 2.85 | 2.85 |



6. Application of effective nuclear charge: On the basis of Z_{eff} , the following facts can be explained:

- A cation is smaller in size than its parent atom.
- An anion is larger in size than its parent atom.
- The order of successive ionisation potential $\text{IP}_1, \text{IP}_2, \text{IP}_3 \dots$ etc. of an atom is in the following order:
 $\text{IP}_1 < \text{IP}_2 < \text{IP}_3$
- Why 4s-orbital is filled before 3d-orbitals:* The lower the values of Z_{eff} acting on the 3d-electron as compared to on 4s-electrons, shows that 3d-electron is less tightly bound to the nucleus than the 4s-electron.

Consequently, the additional electron in atom prefers to enter 4s-orbital than 3d-orbital.

For example, let the two electronic configurations of potassium (K, Z = 19), are as shown below:

- $1s^2, 2s^2 2p^6; 3s^2 3p^6 3d^0; 4s^1$ (4s-orbital is filled before 3d orbitals)
- $1s^2, 2s^2 2p^6; 3s^2 3p^6 3d^1; 4s^0$ (3d-orbital is filled before 4s-orbital)

Therefore, σ on 4s-electron as calculated by Slater rule is

$$(\sigma)_{4s^1} = [(0.85 \times \text{No. of electrons in } (n-1)\text{th shell}) + 1.00 \times \text{No. of electrons in the inner shell}] \\ = (0.85 \times 8) + (1.00 \times 10) = 16.8$$

$$\therefore Z_{\text{eff}} = Z - \sigma = 19 - 16.8 = 2.20$$

Similarly, σ on 3d-electron is

$$(\sigma)_{3d^1} = [1.00 \times \text{Total no. of inner electrons}] \\ = (1.00 \times 18) = 18$$

$$\therefore Z_{\text{eff}} = Z - \sigma = 19 - 18 = 1$$

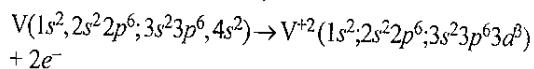
Hence, Z_{eff} of 3d-electron is less than that of 4s-electron. So, additional electron in potassium (K) atom prefers to enter 4s-orbital than 3d-orbital.

- Why 4s-electrons are removed before 3d-electrons in the conversion of 3d-transition elements into cations:*

The greater the value of Z_{eff} on one of the 3d-electrons

than 4s-electrons in an atom shows that 3d-electrons are more tightly held to the nucleus than the 4s-electrons. Consequently, in the conversion of atom into cations the electrons to be removed are 4s-electrons and not 3d-electrons.

For example, consider the conversion of vanadium atom ($V; Z = 23$) into V^{+2} cation and V^{+2} is formed by the removal of two electrons from 4s-orbitals and not from 3d-orbital. Thus,



Calculation Z_{eff} on of the 4s-electron is given by:

$$(\sigma)_{4s^1} = [(0.35 \times \text{No. of electrons left in the } n\text{th shell}) + (0.85 \times \text{No. of electrons in } (n-1)\text{th shell}) + (1.00 \times \text{No. of electrons in the inner shell})] \\ = (0.35 \times 1) + (0.85 \times 11) + (1.00 \times 10) = 19.70$$

$$Z_{\text{eff}} = Z - \sigma = 23 - 19.70 = 3.30$$

Calculation of Z_{eff} on one of the 3d-electron is given by:

$$(\sigma)_{3d^1} = [(0.35 \times \text{No. of electrons left in the } 3d\text{-orbitals}) + (1.00 \times \text{Total no. of electrons in the inner orbitals})] \\ = (0.35 \times 2) + (1 \times 18) = 18.70$$

$$Z_{\text{eff}} = Z - \sigma = 23 - 18.70 = 4.30$$

Hence, Z_{eff} of one of the 3d-electrons is greater than 4s-electrons in vanadium atom shows that 3d-electrons are more strongly held to the nucleus than the 4s-electrons. Consequently in the conversion of $V \rightarrow V^{+2}$, 4s-electrons are removed and not 3d-electrons.

CONCEPT APPLICATION EXERCISE 1.1

Solutions on page 1.144

- 3d-, 4d- and 5d-series consists of 10 elements each? Explain.
- Why the f-block elements are called inner transition elements?
- Transition elements show horizontal as well as vertical relationship. Explain.
- Be and Al are placed in different periods and groups but they show the similar properties. Explain.
- The outer electronic configuration of some elements are given below:
 - $6d^1 7s^2$
 - $4f^1 5d^1 6s^1$
 - $2s^2 2p^6 3s^2$
 - $3d^5 4s^1$
 - $4s^2 4p^3$
 State to which of the periodic table each of these elements belongs.
- Arrange the following elements in decreasing order of metallic character:
 K, Mg, B, Al.

7. Name the species that will be isoelectronic with the following atoms or ions.
- Ca^{2+}
 - Ne
 - Cl^-
 - Rb^+
8. Which one of the following pairs would have a smaller size. Explain.
- Na^+ or Mg^{2+}
 - O^{2-} or F^-
 - P or As
9. Arrange the following ions in order of their decreasing ionic radii.
- $$\text{Li}^+, \text{K}^+, \text{Mg}^{2+}, \text{Al}^{3+}$$
10. What property did Mendeleev use to classify the elements in his periodic table.
11. Elements with $Z = 107, 108$ and 109 have been made recently. Indicate the groups to which they belong.
12. Why Zn, Cd and Hg are not considered as typical transition elements?
13. Why Cu, Ag and Au are transition elements, although they have completely filled d -orbitals?
14. Half-filled and full-filled orbitals are stable. Why?

Very Short Answer Type

- What are super heavy elements?
- How many anomalous pairs were present in original Mendeleev periodic table?
- How many s -block elements are known?
- Which block of elements consists of metals, non metals and metalloids?
- Which is the hardest elements?
- Which elements is lowest melting point liquid metal?
- Which element is heaviest melting and boiling point metal?
- Name the liquid non-metal.
- Name the best and the poorest conductor of current among metals.
- Name the heaviest solid metal.
- Name the most poisonous element.
- Name the heaviest naturally occurring element.
- Among the radioactive elements, which is a liquid element?
- Name the element having the lowest electronegative, lightest and liquid metal.
- Name the lightest solid non-metal having the highest tensile strength.
- Which element has highest catenation property?
- Which non-metal sublime on heating and have metallic lusture.
- Which is the most stable element?
- Name the element which is the poorest conductor of current among non-metals.

34. Name the elements with highest EN and with highest EA or $\Delta_{eg} \text{H}^\ominus$.

35. Which element is used in the making of high temperature thermometer?

36. Which element is used in the making of infrared (IR) windows, prisms and lenses?

Objective Type

37. Which of the following statement is wrong?

- Among the following elements:

K, Mn, Ca, Cs, Fe, Cu, Pb, Os, Y

The number of transition element is 4.

- All the lanthanides and actinides belong to III B or the 3rd group in the periodic table.

- The inner transition elements belong to the f -block of the periodic table and are shown separately at the bottom of the periodic table.

- The d -block elements have variable valency.

38. Which of the following statement is wrong?

- In the lanthanide series the electrons occupy $4f$ -orbitals in preference to $5d$ the and $6p$ -orbitals.

- Zero group was not present in the periodic table when Mendeleev presented it.

- Law of octave was presented by Newland.

- Cuprous compounds are coloured while cupric compounds are colourless.

39. Which of the following triads have approximately equal size?

- $\text{Na}^+, \text{Mg}^{2+}, \text{Al}^{3+}$ (isoelectronic)

- $\text{F}^-, \text{Ne}, \text{O}^{2-}$ (isoelectronic)

- Fe, Co, Ni

- $\text{Mn}^{1+}, \text{Fe}^{2+}, \text{Cr}$ (isoelectronic)

40. Which is the correct order of size?

- ($\text{O}^\ominus, \text{O}^{2-}, \text{F}^\ominus$ and F ?)

- $\text{O}^{2-} > \text{O}^\ominus > \text{F}^\ominus > \text{F}$

- $\text{O}^\ominus > \text{O}^{2-} > \text{F}^\ominus > \text{F}$

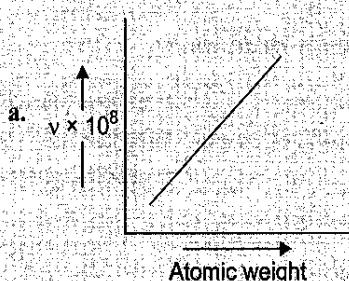
- $\text{O}^{2-} > \text{F}^\ominus > \text{F} > \text{O}^\ominus$

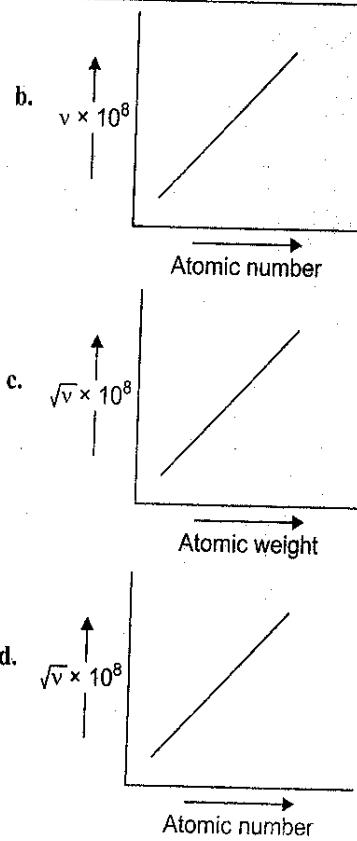
- $\text{O}^{2-} > \text{F}^\ominus > \text{O}^\ominus > \text{F}$

41. Select the correct statement:

Which of the following graph represents Moseley's experiment.

($v =$ frequency of X-rays)





42. Calculate the screening constants of alkali metals for valency electrons.
43. Calculate the screening constants of members of the 2nd period for valency electrons.
44. **Answer the following:**
 - a. Name the element not known at the time of Mendeleev.
 - b. Name any two typical elements.
 - c. Name any two bridge elements.
 - d. Name two pairs showing diagonal relationship.
 - e. Name two transition elements.
 - f. Name two rare earth elements.
 - g. Name two transuranic elements.
 - h. In which case compounds of Cr show maximum radius.
- i. K_2CrO_7 ii. CrO_2Cl_2 iii. $Cr_2(SO_4)_3$
iv. $CrCl_2$
45. In s- and p-block elements the OS. changes by 2 units, but in transition elements it changes in units of one. Explain?
46. Mn_2O_7 is an acidic oxide, why?
47. Why Ar (argon) (at. wt. = 39.94) has been placed before K (at. wt. = 39.10) in the periodic table?
48. Why Ag is a noble metal and K is a highly reactive metal?

ANSWER KEYS

8. a. Mg^{2+} b. F^- c. P
9. $K^+ > Mg^{2+} > Al^{3+} > Li^+$
10. Atomic masses
11. 7, 8 and 9 groups respectively
15. $Z > 100$
16. Four (Ar, K), (Co, Ni), (Te, I) and (Th, Pa)
17. Thirteen 18. p-block
19. Carbon (diamond) 20. Hg
21. Tungsten (W) 22. Br
23. Ag and Pb 24. Os
25. Pu
26. U 27. Fr 28. Cs 29. B
30. C 31. I 32. Te 33. S
34. F and Cl respectively 35. Ga 36. Ge

Objective Type

37. a 38. d 39. c
40. a 41. d
42. Li = 1.7, Na = 8.8; K = 16.8, Rb = 34.8, Cs = 52.8
43. Li = 1.7, Be = 2.05, B = 2.40, C = 2.75, N = 3.10, O = 3.45, F = 3.80, Ne = 4.15
44. a. Zero group b. Li and Be
c. Na and Mg d. Li and Mg; Be and Al
e. Fe and Co f. La and Ce
g. Np and Pu h. iv
- 45.-48. Refer to Hints and Solutions section.

1.13 PENETRATION EFFECT OF THE ELECTRONS IN DIFFERENT ORBITALS

Due to different shapes and orientation of different orbitals, the penetration effect decreases as follows:

$$\xrightarrow{\text{penetration effect decreases}} ns > np > nd > nf$$

From the shapes of electron charge clouds of orbitals, it is clear that ns -orbitals are spherical symmetrical, therefore the electrons of ns -orbital has the maximum probability of being found near the nucleus and this probability goes on decreasing in case of p -, d -, and f -orbitals of the same shell.

In other words, ns -orbitals are spherical symmetrical in shape, therefore they are much more penetrated or attracted towards the nucleus than np -orbitals which are dumbbell in shape. Similarly, np -orbitals are much more penetrated towards the nucleus than nd -orbitals which are double dumbbell in shape, which in turn are more effectively penetrated towards the nucleus than nf -orbitals which are diffused and complex in shape and orientation.

1.13.1 Application of Penetration Effect

- If penetration effect of the electron is more, it will be closer to the nucleus and hence will be held more strongly by the nucleus. Consequently, the ionisation potential/energy will be high.

Ionisation energy increases with the increase in the penetration effect of electrons in different orbitals.

- Thus, the ionisation energy will be more to remove an electron from ns -orbital than an electron from np -orbital, which in turn, will be more than that required to remove an electron from nd -orbitals and so on.
- For example, the first ionisation enthalpy of B < Be and Al < Mg.

According to the general trend ionisation enthalpy increases along the period (\rightarrow). But the observed order is found to be reverse, which can be explained by the penetration effect as below:

Boron (B; Z = 5); $1s^2 2s^2 2p^1$

Beryllium (Be, Z = 4); $1s^2 2s^2$

In case of boron, an electron has to be removed from $2p$ -orbital to form B^\oplus -ion. Whereas in case of Be, an electron has to be removed from $2s$ -orbital to produce Be^\oplus -ion. Since $2s$ -orbital is much more penetrated towards the nucleus than $2p$ -orbital, hence the $2p$ -electrons of B is more shielded from the nucleus by the inner core of electrons than the $2s$ -electrons of Be. Therefore, it is easier to remove an electron from $2p$ -orbital than $2s$ -orbital of the same shell.

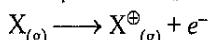
Therefore, the first ionisation enthalpy of B is lower than that of Be.

Similarly, the first ionisation enthalpy

Al (Z = 13) ($1s^2, 2s^2 2p^6; 3s^2 3p^1$) is lower than that of Mg (Z = 12) ($1s^2, 2s^2 2p^6; 3s^2$).

1.14 IONISATION ENERGY/ENTHALPY (IE OR E_0) AND IONISATION POTENTIAL (IP)

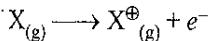
- Ionisation energy/enthalpy of an element is defined as the minimum amount of energy required to remove the outermost shell electron from an isolated gaseous atom (X) to form gaseous ion. It is usually represented as $\Delta_r H^\ominus$, or IE₁. For example,



- Ionisation enthalpy is also known as ionisation potential (IP) since it is the minimum potential difference (in a discharge tube) required to remove the outermost electrons from an isolated gaseous atom to form gaseous ion.

- Difference between ionisation energy (E_0 or $\Delta_r H^\ominus$) and ionisation enthalpy ($\Delta_r H^\ominus$):

Ionisation energy is defined as absolute zero, whereas at any other temperature it is defined as ionisation enthalpy and in that case heat capacities for the reactants and products have to be taken into account. For example, enthalpies of reactions at any temperature (T) is:



$$\Delta_r H^\ominus(T) = \Delta_r H^\ominus(O) + \int_0^T \Delta_r C_p dT$$

The value of C_p for each species in the above equation is

$$\frac{5}{2} R \left(C_V = \frac{3}{2} R \right)$$

$$\text{So, } \Delta_r C_p = \frac{+5}{2} R \text{ (for ionisation).}$$

Therefore,

$$\Delta_r H^\ominus \text{ (ionisation enthalpy)} = E_0 \text{ (ionisation energy)} + \frac{5}{2} \frac{RT}{R}$$

- Units of IE and IP: It is measured in electron volts per atom ($eV \text{ atom}^{-1}$) or kilo calories per mole (kcal mol^{-1}) or kilo joules per mole (kJ mol^{-1}). These quantities are related as:

Note: One electron volt is the energy acquired by an electron while moving under a potential difference of one volt.

$$\begin{aligned} (1 \text{ eV atom}^{-1}) &= 3.83 \times 10^{-20} \text{ cal atom}^{-1} \\ &= 1.602 \times 10^{-19} \text{ J atom}^{-1} (1 \text{ cal} = 4.184 \text{ J}) \\ &= 3.83 \times 10^{-20} \times 6.022 \times 10^{23} \text{ cal mol}^{-1} \\ &= 23.06 \times 10^3 \text{ cal mol}^{-1} \\ &= 23.06 \text{ k cal mol}^{-1} \\ &= 1.602 \times 10^{-19} \times 6.022 \times 10^{23} \text{ J mol}^{-1} \\ &= 96.49 \text{ kJ mol}^{-1} \end{aligned}$$

Energy is required to remove electrons from an atom and hence ionisation enthalpies are always positive.

Ionisation enthalpy of hydrogen atom is $13.58 \text{ eV mol}^{-1}$ or $13.58 \times 96.49 = 1310.334 \text{ kJ mol}^{-1}$.

1.14.1 Successive Ionisation Enthalpies ($\Delta_r H^\ominus$ or IE)

The ionisation enthalpies to remove first, second, third etc. electrons from an isolated gaseous atom are called successive ionisation enthalpies. It is found that $\Delta_r H_2^\ominus > \Delta_r H_1^\ominus$ and $\Delta_r H_3^\ominus > \Delta_r H_2^\ominus$ and so on, i.e. $\Delta_r H_1^\ominus < \Delta_r H_2^\ominus < \Delta_r H_3^\ominus$ or $IE_1 < IE_2 < IE_3$

Explanation: The second ionisation enthalpy will be greater than the first ionisation enthalpy because it is more difficult to remove an electron from a positively charged ion than from a neutral atom.

In the same way the third ionisation enthalpy will be greater than the second and so on.

The term 'ionisation enthalpy', if not mentioned, is taken as the first ionisation enthalpy.

1.14.2 Factors Affecting the Magnitude of the Ionisation enthalpy

It depends on the following factors:

- Size of atom:** The values of ionisation potential of an element decreases (less positive value) as the atomic size increases.

$$\Delta H^\ominus \text{ or } IE \propto \frac{1}{\text{Atomic radius}}$$

In a larger atom, the outer electrons are far away from the nucleus and thus the force of attraction with which they are attracted by the nucleus is less and hence can be easily removed, so less IE.

For example, IE decreases down the group (\downarrow) as shown in Table 1.12

Table 1.12 First IE of alkali metals in kJ mol^{-1}

| Element | Li | Na | K | Rb | Cs |
|-----------------------------|-----|-----|-----|-----|-----|
| IE (kJ mol^{-1}) | 520 | 496 | 419 | 403 | 374 |

- Effective nuclear charge (Z_{eff}):** The greater the Z_{eff} on the nucleus of an atom, the more difficult it would be to remove an electron from the atom.

$$\Delta H^\ominus \text{ (or) } IE \propto Z_{\text{eff}}$$

With the increase in Z_{eff} , the electrons of the outer shell are more strongly held by the nucleus and hence greater energy is required to remove an electron from the atom.

For example, IE increases along the period (\rightarrow) due to the increased Z_{eff} as shown in Table 1.13.

Table 1.13 First IE of second period elements in kJ mol^{-1}

| Element | Li | Be | B | C | N | O | F | Ne |
|-----------------------------|------|------|------|------|------|------|------|------|
| Nuclear charge (Z) | +3 | +4 | +5 | +6 | +7 | +8 | +9 | +10 |
| Z_{eff} | 1.30 | 1.95 | 2.60 | 3.25 | 3.90 | 4.55 | 5.20 | 5.85 |
| IE (kJ mol^{-1}) | 520 | 899 | 801 | 1086 | 1402 | 1314 | 1681 | 2080 |

Note the trends \uparrow \uparrow

- Shielding or screening effect of the inner shell electrons** (refer to Section 1.12): The shielding or screening effect increases if the number of electrons in the inner shells between the nucleus and the outermost electrons increases.

The screening effect reduces the force of attraction between the outermost electrons and the nucleus, hence the outermost electrons can be easily removed. Hence the value of IE decreases with the increase in screening effect.

$$\Delta H^\ominus \text{ (or) } IE \propto \frac{1}{\text{Screening effect}}$$

- Penetration effect of orbitals** (refer to Section 1.13):

Ionisation enthalpy increases as the penetration effect of the electrons in different orbitals increases. The order of energy required to remove electrons from s -, p -, d - and f -orbitals within the same shell is $s > p > d > f$.

Since s -orbital is more close to the nucleus and thus is more penetrated (or attracted) towards nucleus than the p -orbital of the same shell. Thus, it is easier to remove an electron from a p -orbital in comparison to s -orbital.

Generally the IE increases along the period (\rightarrow).

↓
Down the group (\downarrow)
↓

(With exception from Be to B and Mg to Al and N to O and P to S.)

Generally the IE decreases down the group (\downarrow) with some exception in transition elements.

Application: First IE of B and Al should be greater than Be and Mg respectively. But the first IE of Be $>$ B and Mg $>$ Al. This is occurred due to the penetration effect of orbitals (refer to Section 1.13).

- Stability of half-filled and fully filled orbitals:** According to Hund's rule the stability of half-filled and completely filled degenerate orbitals has extra stability. Therefore, the removal of an electron from such an atom requires more energy than expected. For example,

a. IE_1 of Be ($Z = 4$) ($1s^2 2s^2$) $>$ B ($Z = 5$) ($1s^2 2s^2 2p^1$), because Be has fully filled orbitals which is a stable electronic configuration.

b. Similarly, IE_1 of Mg ($Z = 12$) ($1s^2 2s^2 2p^6 3s^2$) $>$ Al ($Z = 13$) ($1s^2 2s^2 2p^6 3s^2 3p_x^1$)

c. i. IE_1 of N ($Z = 7$) ($1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$) $>$

O ($Z = 8$) ($1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$)

Because N contains exactly half-filled p -orbitals which imparts greater stability to N, so removal of electron from N is difficult and hence IE_1 is high.

- Electronic configuration of O ($Z = 8$) ($1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$)

Electronic configuration of O[⊕]

(Z = 8) (1s² 2s² 2p_x¹ 2p_y¹ 2p_z¹)

Electronic configuration of N

(Z = 7) (1s² 2s² 2p_x¹ 2p_y¹ 2p_z¹)

Electronic configuration of N[⊕]

(Z = 7) (1s² 2p_x¹ 2p_y¹ 2p_z⁰)

Electronic configuration of O[⊕] (obtained after removal of one e⁻) is exactly half-filled 2p-sub shell while this is not in the case of N[⊕].

Since the removal of an electron from O gives a more stable arrangement than that of N; hence, IE₁ of O < IE₁ of N.

- d. Similarly, IE₁ of P (Z = 15) (1s² 2s² 2p⁶ 3s² 3p_x¹ 3p_y¹ 3p_z¹) is greater than IE₁ of S (Z = 16) (1s² 2s² 2p⁶ 3s² 3p_x² 3p_y¹ 3p_z¹)

- e. Noble gases have the highest IE₁ in their respective period.

For example, IE₁ of Ne is higher than any other elements of the second period.

Similarly, IE₁ of Ar is higher than any other element of the third period. Because they have ns²np⁶ arrangement which is a stable electronic configuration hence the large amount of energy is required to remove an electron from such stable arrangement.

Note: The more stable the electronic configuration, the greater is the IE or ΔH^\ominus .

1.14.3 Variation of IE or ΔH^\ominus in the Periodic Table

The IE₁ of the representative elements and noble gases given in Table 1.14 and IE₁ of elements having Z = 60 are plotted in Fig. 1.10.

Table 1.14 IE₁ of representative and noble gases (kJ mol⁻¹)

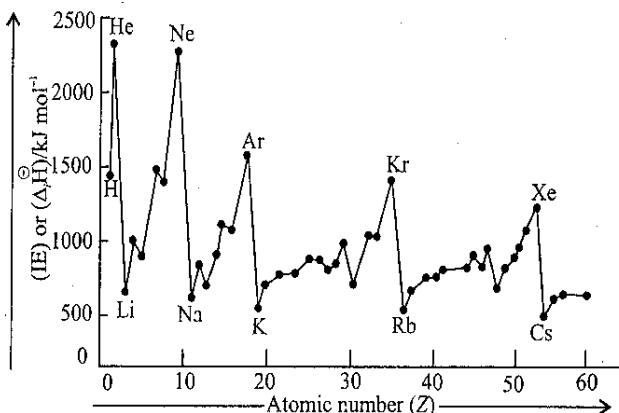
| | 1 | IE ₁ increases along the period | | | | | | 18 |
|---|-----------|--|-----------|-----------|-----------|------------|------------|------------|
| IE ₁ decreases down in group | | | | | | | | |
| H | 1312 | 2 | 13 | 14 | 15 | 16 | 17 | He 2372 |
| Li 520 | Be 899 | B 801 | C 1086 | N 1402 | O 1314 | F 1681 | Ne 2080 | |
| Na 496 | Mg 738 | Al 577 | Si 786 | P 1011 | S 999 | Cl 1255 | Ar 1520 | |
| K 419 | Ca 590 | Ga 579 | Ge 760 | As 946 | Se 941 | Fr 1142 | Kr 1350 | |
| Rb 403 | Sr 549 | In 558 | Sn 708 | Sb 884 | Te 869 | I 1009 | Xe 1170 | |
| Cs 374 | Ba 502 | Tl 589 | Pb 715 | Bi 703 | Po 813 | At 917 | Rn 1037 | |

[Note the trend in the elements circled]

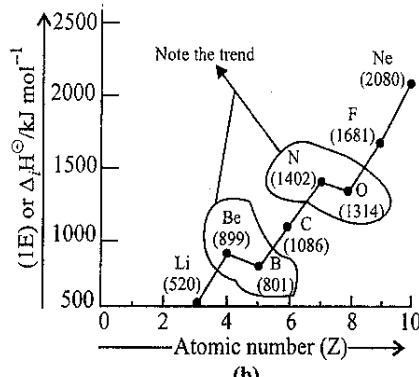
IE of an element mostly depends upon its electronic configuration and thus shown periodicity in the graph (Fig. 1.10). There is a maxima at the noble gases which have closed electron shells and very stable electronic configuration. On the other hand, minima occurs at the alkali metals. Thus, alkali metals have the lowest IE₁ and hence have high activity.

On the contrary, noble gases with stable configuration (ns²np⁶) have highest IE₁ and hence are chemically inert.

Note: Cs have the lowest IE₁ and is the most electropositive elements.



(a)



(b)

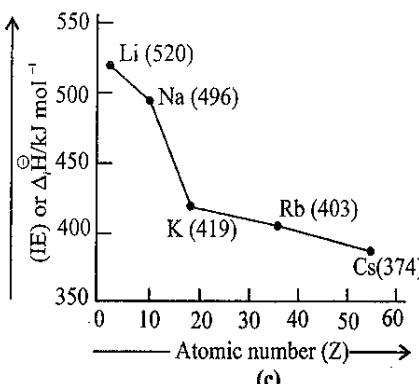


Fig. 1.10 (a) Variation of first ionisation enthalpies ΔH^\ominus with atomic number for elements with Z = 1 to 60.

(b) First ionization enthalpies ΔH^\ominus of the second period as a function of atomic number (Z). (c) First ionisation enthalpies ΔH^\ominus of alkali metals as a function of atomic number (Z).

1.14.4 Variation of IE Along the Period and Down the Group

1. IE_1 generally decreases down the group (\downarrow).
2. IE_1 generally increases along the period (\rightarrow), with exception as marked in Table 1.14 and Figs. 1.10 and 1.11, i.e. from Be to B, Mg to Al, N to O and P to S.

These trends are shown in Figs. 1.11(a) and 1.11(b) for the 2nd period and 1st group of the periodic table.

The observed trends are explained on the basis of three factors:

- a. The attraction of electrons to the nucleus, i.e. on the basis of Z_{eff}
- b. The repulsion of electrons from each other.
- c. Atomic radii (IE and atomic radii are closely related properties).

Explanation: Along the period (\rightarrow), the nuclear charge (Z) increases and atomic radii decrease although shell remains the same. Due to these opposing factors, the outermost electrons are more strongly held by the nucleus, so more energy is required to remove the electrons. Hence IE_1 increases along the period (\rightarrow).

However, some exceptions are observed in this general trend. These are due to:

1. Extra stability of the half-filled and full-filled electronic configuration.
2. Types of electrons to be removed. Considering the IE_1 of the 2nd period elements:
 - a. **Li to Be:** From Li to Be, IE_1 increases due to increase in nuclear charge and smaller atomic radii of Be than that of Li.
 - b. **Be to B (exceptional case):** Although from Be to B nuclear charge increases, yet the IE_1 of Be $>$ B (explained in section 1.13.1-(3)).
 - c. **B to C and to N:** From B to C and to N, IE_1 increases due to the increasing nuclear charge and decreasing atomic radius.
 - d. **N to O (exceptional case):** IE_1 of N should be less than IE_1 of oxygen, but the observed trend is IE_1 of N $>$ IE_1 of O, as explained in Section 1.14.2 (5) (c) (i and ii).
 - e. **O to F and to Ne:** IE_1 increases from O to F and to Ne, because of the increasing nuclear charge. Ne has the highest IE_1 in the 2nd period due to the stable noble gas configuration (ns^2, np^6).

Similar trends in the IE_1 of the 3rd period have been observed.

1.14.5 Variation of IE Down the Group (\downarrow)

IE_1 decreases down the group (\downarrow) [see Fig 1.11(b)] and Table 1.14.

Explanation:

1. **Increase of atomic size:** Down the group (\downarrow), the atomic size increases gradually due to the addition of new shell at each succeeding element. So, distance of the valence electrons from the nucleus increases. Consequently, the force of attraction between nucleus and outermost electron decreases and hence IE should decrease.
2. **Increase of screening effect:** The number of inner electrons increases with the addition of new shells thereby the screening effect increases. Thus, the force of attraction between the nucleus and the outermost electron further decreases and hence *IE should decrease*.
3. **Increase of nuclear charge (Z):** Z increases with the increase in atomic number, which results in the increase of force of attraction between the nucleus and the outermost electron and accordingly *IE should increase*.

The combined effect of the increase in the atomic size and the shielding effect compensate the effect of the increased nuclear charge. Consequently, the outermost electrons are held weakly by the nucleus and hence IE decreases down the group (\downarrow).

| | | |
|---------------|---------------|---------------|
| Ion | Cu^{\oplus} | Na^{\oplus} |
| Size | 0.96 Å | 0.95 Å |
| Compound | $CuCl$ | $NaCl$ |
| Melting point | 442°C | 800°C |

1.14.6 Importance of Ionisation Potential

A number of conclusions can be drawn from the concept of ionisation potential.

1. The elements having low values of ionisation potential readily lose their valency electrons and act as electropositive elements. These elements form cations and ionic compounds.
2. The elements having low values of ionisation potential act as strong reducing agents.
3. Stability of the various oxidation states of an element can be predicted. When the difference in ionisation potential ($\Delta_i H^{\oplus}$) of two successive states is approximately 10 to 15 eV atom $^{-1}$ (or 965–1450 kJ mol $^{-1}$) or less, the lower oxidation state is not stable one. For example, in case of Al, $\Delta_1 H_1^{\oplus} = 6.0$, $\Delta_2 H_2^{\oplus} = 18.8$, $\Delta_3 H_3^{\oplus} = 28.4$ and $\Delta_4 H_4^{\oplus} = 120$ eV atom $^{-1}$ are the values of successive ionisation potential. Al^{4+} state is not possible because the $\Delta_4 H_4^{\oplus}$ is very high. Differences in successive ionisation enthalpies are:

$$(\Delta_2 H_2^{\oplus} - \Delta_1 H_1^{\oplus}) = (18.8 - 6.0) = 12.8 \text{ eV atom}^{-1}$$

$$(\Delta_3 H_3^{\oplus} - \Delta_2 H_2^{\oplus}) = (28.4 - 18.8) = 96 \text{ eV atom}^{-1}$$

$$(\Delta_4 H_4^{\oplus} - \Delta_3 H_3^{\oplus}) = (120.0 - 28.4) = 91.6 \text{ eV atom}^{-1}$$

Since the difference in the successive ionization enthalpies between $(\Delta_i H_2^\ominus - \Delta_i H_1^\ominus)$ and $(\Delta_i H_3^\ominus - \Delta_i H_2^\ominus)$ is less than $10\text{--}15 \text{ eV atom}^{-1}$ and that of $(\Delta_i H_4^\ominus - \Delta_i H_3^\ominus)$ is much more than 15 eV atom^{-1} . So, Al^{3+} is stable while Al^{\oplus} and Al^{2+} are unstable.

4. When the difference in ionisation potential ($\Delta_i H^\ominus$) is about 16 eV atom^{-1} or more, the lower oxidation state is stable one.

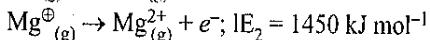
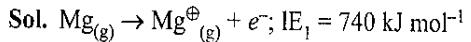
For example, in the case of sodium ($\text{Na}, Z = 11$), $\Delta_i H_1^\ominus = 5.1$ and $\Delta_i H_2^\ominus = 47.3 \text{ eV atom}^{-1}$ are the successive IP, hence Na^\oplus is a stable state and formation of Na^{2+} is not easy because high energy is required.

5. The elements with low values of IP are basic in character.

Illustration 1.25 The first ionisation enthalpy ($\Delta_i H^\ominus$) values of the third period elements, Na , Mg and Si are respectively 496 , 737 and 786 kJ mol^{-1} . Predict whether the first $\Delta_i H^\ominus$ value for Al will be more close to 575 or 760 kJ mol^{-1} ? Justify your answer.

Sol. It will be more close to 575 kJ mol^{-1} . The value for Al should be lower than that of Mg because of the effective shielding of $3p$ electrons from the nucleus by $3s$ -electrons.

Illustration 1.26 Calculate the energy required to convert all atoms of Mg to Mg^{2+} ions present in 48 mg of Mg vapours. IE_1 and IE_2 of Mg are 740 and 1450 kJ mol^{-1} respectively.



\therefore Total energy required to convert 1 mol of $\text{Mg}_{(g)}$ into

$$\begin{aligned} \text{Mg}_{(g)}^{2+} \text{ ion} &= \text{IE}_1 + \text{IE}_2 \\ &= (740 + 1450) \text{ kJ mol}^{-1} \\ &= 2190 \text{ kJ mol}^{-1} \end{aligned}$$

$$\begin{aligned} 48 \text{ mg of Mg} &= \frac{48 \times 10^{-3}}{24} \text{ mol} \\ &= 2 \times 10^{-3} \text{ mol} \end{aligned}$$

$$\begin{aligned} \therefore \text{Energy required to ionise } 20 \times 10^{-3} \text{ mol of Mg}_{(g)} &= 2190 \times 2 \times 10^{-3} \\ &= 4.380 \text{ kJ} \end{aligned}$$

Illustration 1.27 The first (IE_1) and second (IE_2) ionisation energies (k J mol^{-1}) of a new elements designated by roman numerals are shown below:

| | IE_1 | IE_2 |
|-----|---------------|---------------|
| I | 2370 | 5250 |
| II | 520 | 7300 |
| III | 900 | 1800 |
| IV | 1700 | 3400 |

Which of the above elements is likely to be:

- a. A reactive metal

- b. A reactive non-metal

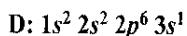
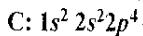
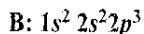
- c. A noble gas

- d. A metal that forms a stable binary halide of the formula AX_2 (X = the halogen).

Sol.

- a. Most reactive metal will be an alkali metal of the 1st group with its $\text{IE}_2 > \text{IE}_1$. Thus, the most reactive metal is II.
- b. Most reactive non-metal will be a halogen of the 17th group. Its IE_1 will be quite high. Thus, most reactive non-metal is IV.
- c. A noble gas will have very high IE_1 . Thus, I is a noble gas.
- d. A metal that forms a stable binary halide will be an alkaline earth metal of the 2nd group. Its IE_2 will not be much higher than IE_1 . Thus, III is such a metal that forms a stable binary halide of formula AX_2 .

Illustration 1.28 The electronic configuration for some neutral atoms are given below.



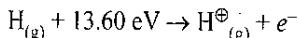
In which of this electronic configuration would you expect to have highest (a) IE_1 and (b) IE_2 .

Sol.

- a. B: Because of exactly half-filled $2p$ subshell its IE_1 will be more than A and C.
- b. D: Because after the removal of one electron, D will acquire a configuration of a noble gas and thus its IE_2 will be the highest.

Illustration 1.29 The ionisation potential of hydrogen is 13.60 eV . Calculate the energy required to produce one mole of H^\oplus ion ($1 \text{ eV} = 96.3 \text{ kJ mol}^{-1}$).

Sol. The ionisation potential may be represented as



We know $1 \text{ eV} = 96.3 \text{ kJ mol}^{-1}$

$$13.60 \text{ eV} = 96.3 \times 13.60 = 1309.68 \text{ kJ}$$

Thus, energy per mol = 1309.68 kJ

Illustration 1.30 Which of the following electronic configurations has the lowest value of ionisation energy? Explain.

- a. $1s^2 2s^2 2p^6$ b. $1s^2 2s^2 2p^5$ c. $1s^2 2s^2 2p^6 3s^1$

Sol. The electronic configuration $1s^2, 2s^2 2p^6, 3s^1$ has the lowest value of ionisation energy because the outermost electron $3s^1$ is far away from the nucleus. As a result atomic radius is the largest of the three and force of attraction between the nucleus and the outermost electron is less. Therefore, electron can be easily removed and has the lowest value of IE.

Illustration 1.31 For each of the following pairs which has greater IE and why?

- a. Li, Li^+ b. K, Br c. Br, I d. Na $^+$, Ne

Sol.

- a. Li^+ . Because the size of Li^+ is smaller and Z_{eff} is greater than the corresponding values of Li.
- b. Br. Because Br has seven electrons in the outermost shell and has tendency to gain an electron rather than losing it. Moreover, the smaller size and high nuclear charge favour high IE for Br.
- c. Br. It is due to the smaller atomic radius of Br than that of I.
- d. Na $^+$. As it has small atomic radius and high value of Z_{eff} than Ne.

Illustration 1.32 Calculate the percentage of $\text{Mg}_{(g)}^+$ and $\text{Mg}_{(g)}^{2+}$ if 2.4 g of Mg absorbs 120 kJ of energy. The IE_1 and IE_2 of $\text{Mg}_{(g)}$ are 740 and 1450 kJ mol^{-1} .

$$\text{Sol. Moles of Mg} = \frac{2.4}{24} = 0.1$$

Energy required in the conversion of 0.1 mol of $\text{Mg}_{(g)}$ to $\text{Mg}_{(g)}^+$

$$= 740 \times 0.1 = 74 \text{ kJ}$$

Energy left unused = $120 - 74 = 46 \text{ kJ}$

So, 46 kJ of energy will be used to ionise $\text{Mg}_{(g)}^+$ to $\text{Mg}_{(g)}^{2+}$

∴ Number of moles of $\text{Mg}_{(g)}^+$ converted into

$$\text{Mg}_{(g)}^{2+} = \frac{46}{1450} = 0.03$$

$$\text{Number of moles of } \text{Mg}_{(g)}^+ \text{ left} = 0.1 - 0.03 = 0.07$$

$$\therefore \% \text{ of } \text{Mg}_{(g)}^+ = \frac{0.07}{0.1} \times 100 = 70\%$$

$$\text{and \% of } \text{Mg}_{(g)}^{2+} = 100 - 70 = 30\%$$

Illustration 1.33 The electronic configuration for the following atoms are given below:

- a. $1s^2 2s^2 2p^5$ b. $1s^2 2s^2 2p^4$ c. $1s^2 2s^2 2p^6 3s^2$
d. $1s^2 2s^2 2p^6$ e. $1s^2 2s^2 2p^6 3s^1$

- From the above configuration, arrange them in decreasing IE.
- Which of the electronic configuration given above will have the lowest IE?
- Which of the electronic configuration given above will be for noble gases?

Sol.

- i. Arrange the electronic configuration of all the atoms in decreasing order of atomic number, in such a manner that atoms containing the same outer energy shell are grouped together, e.g.

$1s^2 2s^2 2p^6 3s^2 (Z = 12) > 1s^2 2s^2 2p^6 3s^1 (Z = 11) \dots \text{M-shell}$

(c)

(e)

$> 1s^2 2s^2 2p^6 (Z = 10) > 1s^2 2s^2 2p^5 (Z = 9) > 1s^2 2s^2 2p^4$

$(Z = 8) \dots \text{L shell}$

(d)

(a)

(b)

ii. Since the M-shell is far away from the nucleus than L-shell, so lesser amount of energy is required to remove an electron from M-shell than from L-shell.

Thus, the IE of atoms (c) and (e) should be lower than that of atoms (a), (b) and (d).

Moreover, in case of atom (c) the electron is to be removed from the more stable completely filled $3s$ -orbitals, whereas in case of atom (e) is not so.

Therefore, the IE of atom (c) should be higher than that of atom (e) [i.e. (c) $>$ (e)].

iii. The nuclear charge on atoms (d), (a) and (b) is +10, +9 and +8 respectively. Since the IE increases with the increase in nuclear charge so the decreasing order of IEs are:

(d) $>$ (a) $>$ (b)

iv. Therefore, decreasing order of IEs of all the atoms is
(d) $>$ (a) $>$ (b) $>$ (c) $>$ (e)

v. From the above discussion it is clear that atom (e) has the lowest IE.

vi. The electronic configuration of atom (d) represents the noble gas $1s^2 2s^2 2p^6$ since the configuration of noble gases is $ns^2 np^6$.

Illustration 1.34 The IE_1 and IE_2 (kJ mol^{-1}) of three elements A, B and C are given below:

| | A | B | C |
|---------------|------|------|------|
| IE_1 | 400 | 550 | 1150 |
| IE_2 | 2650 | 1070 | 2090 |

Identify the elements which represent (a) an alkali metal, (b) an alkaline earth metal or (c) non-metal.

Sol. (a) (A)

Since IE_2 of element (A) is very high as compared to IE_1 , therefore it is an alkali metal.

(b) (B)

Since IE_1 of element (B) is higher than that of element (A) and lower than that of element (C), therefore it is an alkaline earth metal.

(c) (C)

Since IE_1 of element (C) is the highest of the two elements A and B, therefore it is a non-metal.

Illustration 1.35 The sum of IE_1 and IE_2 and those of IE_3 and IE_4 in (kJ mol^{-1}) of Ni and Pt are:

| | $(\text{IE}_1 + \text{IE}_2)$ | $(\text{IE}_3 + \text{IE}_4)$ | Total |
|----|-------------------------------|-------------------------------|--------------------|
| Ni | 2.5×10^3 | 8.8×10^3 | 11.3×10^3 |
| Pt | 2.7×10^3 | 6.7×10^3 | 9.4×10^3 |

- What is the most common oxidation state (O.S.) of Ni and Pt.
- Name the metal (Ni or Pt) which can more easily form compounds in its +4 O.S.

Sol. Thermodynamic stability of the transition elements and their compounds can be evaluated in terms of magnitude of IE's of metals. The smaller the IE of the metal, the stable is its compound.

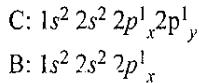
a. Ni = +2 and Pt = +4.

Since $(IE_1 + IE_2) (2.5 \times 10^3)$ of Ni is less than $(IE_1 + IE_2)$ of Pt, so, the most common oxidation states of Ni = +2. Similarly $(IE_3 + IE_4)$ of Pt is less than $(IE_3 + IE_4)$ of Ni, so, the most common oxidation state of Pt = +4.

- b. Pt forms more stable complexes in +4 state due to its higher stability than +2 state.

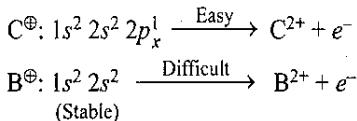
Illustration 1.36 The IE_1 of C atom is greater than that of boron (B) atom, whereas the reverse is true for IE_2 . Explain?

Sol. The electronic configuration of C and B are as follows.



Due to the higher nuclear charge (Z) in C, the force of attraction towards valency electrons is more in C atom and hence IE_1 of C > IE_1 of B.

After loss of one electron, the configuration of C^{\oplus} and B^{\oplus} is as follows:



The B^{\oplus} configuration is stable hence the removal of the 2nd electron is difficult in comparison to C^{\oplus} . Hence, IE_2 of B > IE_2 of C.

Illustration 1.37 The second IE for alkali metals shows a jump while the third IE for alkaline earth metals shows a jump. Explain.

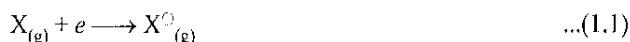
Sol. The alkali metals have ns^1 configuration while alkaline earth metals have ns^2 configuration.

So after IE_1 , the alkali metals attain the inert gas configuration while the alkaline earth metals attain it after IE_2 . Now the removal of electron from a noble gas configuration requires high IE_1 so there is a jump in the IE_2 for alkali and IE_3 for alkaline earth metals.

1.15 ELECTRON GAIN ENTHALPY ($\Delta_{eg} H^{\ominus}$) AND ELECTRON AFFINITY (EA)

When an electron is added to a neutral gaseous atom (X) to convert it into a negative ion, the enthalpy change accompanying

the process is defined as the **electron gain enthalpy** ($\Delta_{eg} H^{\ominus}$). Electron gain enthalpy provides a measure of the ease with which an atom adds an electron to form anion as represented by Eq. (1.1).



Depending on the element, the process of adding an electron to the atom can be either endothermic or exothermic. For many elements energy is released when an electron is added to the atom and electron gain enthalpy is negative. For example, the halogens (group 17) have very high negative electron gain enthalpies because they can attain stable noble gas electronic configurations by picking up an electron.

On the other hand, noble gases have large positive electron gain enthalpies because the electron has to enter the next higher principal quantum level leading to a very unstable electronic configuration.

The electron gain enthalpies have large negative values towards the upper right of the periodic table preceding the noble gases.

1.15.1 Difference Between Electron Gain Enthalpy ($\Delta_{eg} H^{\ominus}$) and Electron Affinity

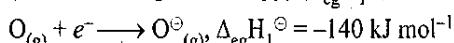
In many books, the negative of the enthalpy changed for the process depicted in Eq. (1.1) is defined as the **electron affinity** (EA) of the atom under consideration. If energy is released when an electron is added to an atom, the electron affinity is taken as positive, contrary to thermodynamic convention. If energy has to be supplied to add an electron to an atom, then the electron affinity of the atom is assigned a negative sign. However, *electron affinity is defined at absolute zero* and therefore at any other temperature heat capacities of the reactants and products have to be taken into account in $\Delta_{eg} H^{\ominus} = -EA - \frac{5}{2}RT$.

1.15.2 Successive Electron Gain Enthalpies

After the addition of one electron the atom becomes negatively charged and the second electron is to be added to a negatively charged ion. But the addition of the second electron is opposed by the electrostatic repulsion and hence the energy is required for the addition of second electron.

Thus, the second electron gains enthalpy of an element is positive. For example, when an electron is added to oxygen atom to form O^{\ominus} ion, energy is released. But when another electron is added to O^{\ominus} ion to form O^{2-} ion, energy is required or absorbed to overcome the strong electrostatic repulsion between the negatively charged O^{\ominus} ion and the incoming electron being added. Thus,

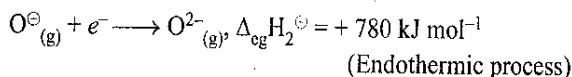
(First electron gain enthalpy) ($\Delta_{eg} H_1^{\ominus}$):



(Exothermic process)

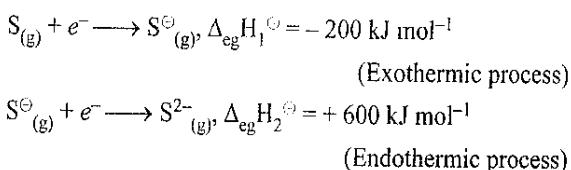
(Second electron gain enthalpy) ($\Delta_{eg} H_2^{\ominus}$):

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Likewise $\Delta_{\text{eg}} H_2^{\ominus}$ of S is also positive.

For example,



1.15.3 Units of $\Delta_{\text{eg}} H^{\ominus}/\text{EA}$

Like IE, $\Delta_{\text{eg}} H^{\ominus}$ or EA is measured either in eV atom⁻¹ or kJ mol⁻¹.

1.15.4 Variation of $\Delta_{\text{eg}} H^{\ominus}$ in the Periodic Table

- Generally, $\Delta_{\text{eg}} H_1^{\ominus}$ decreases (less negative) down the group (\downarrow).
- Generally, $\Delta_{\text{eg}} H_1^{\ominus}$ increases (more negative) along the period (\rightarrow).

But from Table 1.15, it is evident that $\Delta_{\text{eg}} H^{\ominus}$ does not show perfectly regular trend along the period (\rightarrow) and down the group (\downarrow) because of a number of exceptions.

2. Variation of $\Delta_{\text{eg}} H^{\ominus}$ along the period (\rightarrow):

Generally, $\Delta_{\text{eg}} H^{\ominus}$ increases (more -ve) along the period (\rightarrow).

Explanation: The Z_{eff} increases and atomic sizes decrease along the period (\rightarrow) and consequently it will be easier to add an electron to a smaller atom since the added electron on an average would be closer to the positively charged nucleus. Hence, $\Delta_{\text{eg}} H^{\ominus}$, in general, increases (more and more -ve) along the period (\rightarrow).

3. Variation of $\Delta_{\text{eg}} H^{\ominus}$ down the group (\downarrow):

Generally, $\Delta_{\text{eg}} H^{\ominus}$ decreases (less negative) down the group (\downarrow).

Explanation: Both the atomic size and Z_{eff} increase down the group (\downarrow). But the effect of atomic size is much more predominating than Z_{eff} . Thus, with increases in atomic size, the attraction between the nucleus and incoming electron decreases and hence the $\Delta_{\text{eg}} H^{\ominus}$ decreases (becomes less negative).

1.15.5. Factors on Which the $\Delta_{\text{eg}} H^{\ominus}$ Depends

It depends on the following factors.

- Size of atom:** In general, the $\Delta_{\text{eg}} H^{\ominus}$ value decreases (less negative) with increasing atomic radius or size of an atom.

$$\Delta_{\text{eg}} H^{\ominus} \text{ or EA} \propto \frac{1}{\text{Atomic radius}}$$

Explanation: The larger the size of an atom, the larger is the distance between the nucleus and the last shell which receives the incoming electron. As a result, force of attraction between the nucleus and the incoming electron

decreases and hence $\Delta_{\text{eg}} H^{\ominus}$ decreases (less negative value, i.e. energy released is lesser) (see Table 1.15).

Table 1.15 $\Delta_{\text{eg}} H^{\ominus}$ of some elements in kJ mol⁻¹

| Pe- ri- od | Group → | | | | | | | Note the trend |
|------------------|-------------------|-----------|------------|------------|------------|--------------|-------------|----------------|
| | 1 | 2 | 13 | 14 | 15 | 16 | 17 | |
| 1 | H -73 | | | | | | | He (+48) |
| 2 | Li -60 (~0) | Be -23 | B -122 | C +20.1 | N -74 | O -141 | F -32 | Ne (+116) |
| 3 | Na -53 (~0) | Mg -44 | Al -119 | Si -74 | P -200 | S -349 | Cl (+96) | Ar |
| 4 | K -49 (~0) | Ca -36 | Ga -116 | Ge -77 | As -195 | Se -324.5 | Br (+96) | Kr |
| 5 | Rb -47 (~0) | Sr -34 | In -120 | Sn -101 | Sb -190 | Te -295 | I (+77) | Xe |
| 6 | Cs -46 (~0) | Ba -30 | Tl -101 | Pb -110 | Bi -174 | Po -270 | At (+68) | Rn |

2. Effective nuclear charge (Z_{eff}): The higher the Z_{eff} , the greater is the tendency of the atom to attract the incoming electron towards itself and hence the higher the amount of energy is released (i.e. $\Delta_{\text{eg}} H^{\ominus}$ becomes more -ve).

3. Electronic configuration: Elements with half-filled or full-filled orbitals are more stable. As a result, energy is required to add an incoming electron, since they do not accept the incoming electron so easily.

Hence, $\Delta_{\text{eg}} H^{\ominus}$ have high positive value. The effect of this factor on the magnitude of $\Delta_{\text{eg}} H^{\ominus}$ of an element can be understood by the following examples:

- $\Delta_{\text{eg}} H^{\ominus}$ values of the 2nd groups:** ns -orbital of the valence shell of the atoms of the 2nd group is completely filled and the addition of an extra electron to this ns -orbital is not possible. Consequently, the elements of the 2nd group have practically zero $\Delta_{\text{eg}} H^{\ominus}$.

- $\Delta_{\text{eg}} H^{\ominus}$ values of N and P:** The valence shell of N and P are:

$$N = 2s^2 2p^3; P = 3s^2 3p^3$$

$2p$ - and $3p$ -orbitals in N and P respectively are half-filled, and hence are extraordinary stable. Thus, the addition of an extra electron to these orbitals is not possible. Consequently, N and P have low $\Delta_{\text{eg}} H^{\ominus}$ values (N = + 20.1 and P = -74 kJ mol⁻¹).

- $\Delta_{\text{eg}} H^{\ominus}$ of halogens:** The valence shell configuration of halogens ($ns^2 np^5$) requires one electron to stabilise its configuration by attaining stable noble gas configuration ($ns^2 np^6$).

Thus, halogens have a strong tendency to accept one

electron. Consequently, they have very high negative values of $\Delta_{eg}H^\ominus$.

However, from Cl to I, $\Delta_{eg}H^\ominus$ decreases, i.e. becomes less and less negative (Fig. 1.11) due to the corresponding increase in the size of the atoms. In Cl, the incoming electron is added in $3p$ -subshell, in Br it adds in $4p$ -subshell while in I it adds to the $5p$ -subshell.

As the distance between the nucleus and the sub-shell increases, the attraction between the incoming electron and nucleus decreases, hence $\Delta_{eg}H^\ominus$ decreases (i.e. less negative) along the period (\rightarrow) from Cl to Br to I.

Exception (I): Generally, $\Delta_{eg}H^\ominus$ decreases (i.e. becomes less and less -ve) down the group (\downarrow). So, the decreasing order of $\Delta_{eg}H^\ominus$ should be F > Cl > Br > I.

But the *actual order* observed is as follows Cl > F > Br > I.

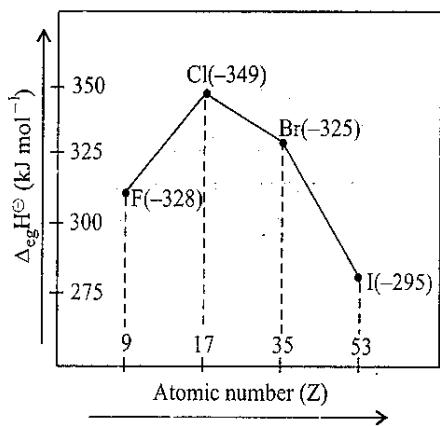


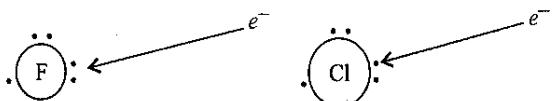
Fig. 1.11 Variation of $\Delta_{eg}H^\ominus$ of halogens

Note: $\Delta_{eg}H^\ominus$ of F is lower (i.e., less negative) than that of Cl.

It is due to the very small size of F atom. There is strong electron-electron repulsion in the relatively small $2p$ orbitals of F and thus, the incoming electron does not experience much attraction. Hence, the incoming electron is not added easily as it is added in large $3p$ -orbitals of Cl.

Consequently, the $\Delta_{eg}H^\ominus$ of F is less negative than that of Cl.

Note: Among halogens, Cl has the highest (most -ve) $\Delta_{eg}H^\ominus$. Alternatively:



Due to the very small size of F atom, the incoming electron experiences a strong repulsion between the seven non-bonding electrons on the F atom and incoming electron. So, the incoming electron is added with difficulty. However, due to the large size of Cl atom the incoming electron experiences very less repulsion between the seven non-bonding electrons and incoming electron. Consequently, the $\Delta_{eg}H^\ominus$ of F is less negative than that of Cl.

Exception (II): Similarly, $\Delta_{eg}H^\ominus$ of some of the elements of the 2nd period have less (-ve) value than the corresponding elements of the 3rd period. For example,

$\Delta_{eg}H^\ominus$ of some elements are as follows: (see Table 1.15)

$$\left(\begin{array}{l} B < Al, \\ -23 < -44 \end{array} \right) \left(\begin{array}{l} N < P, \\ +20 < -74 \end{array} \right) \left(\begin{array}{l} O < S, \\ -141 < -200 \end{array} \right)$$

$$\text{and } \left(\begin{array}{l} F < Cl \\ -322 < -349 \end{array} \right) \text{ in kJ mol}^{-1}$$

The same explanation as given in exception (I).

1.15.6 $\Delta_{eg}H^\ominus$ of Noble Gases

Inert gases have completely filled subshells ($ns^2 np^6$), therefore the incoming electron has to enter the next higher principle quantum level leading to a very unstable electronic configuration. As a result, energy is required to add an additional electron. That is why $\Delta_{eg}H^\ominus$ of noble gases have large positive values.

Down the group (\downarrow), the size of the atom increases and hence $\Delta_{eg}H^\ominus$ have lower positive values.

$\Delta_{eg}H^\ominus$ of Ar (+ 96) is lower than that of Ne (+ 116).

However, $\Delta_{eg}H^\ominus$ of He is the lowest (+ 48) of all the inert gases. This unexpected behaviour is due to its smallest size so it has much higher tendency to accept an incoming electron than any other inert gases.

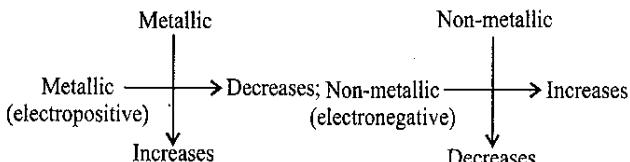
1.15.7 Importance of Electron Gain Enthalpy

Certain properties of the elements are predicted on the basis of values of electron gain enthalpy.

1. The elements having high (-ve) values of electron gain enthalpy are capable of accepting electron easily. They form anions and electrovalent compounds. These elements are electronegative in nature.
2. The elements having high (-ve) values of electron gain enthalpy act as strong oxidising agents, for example, F, Cl, Br, O, S etc.

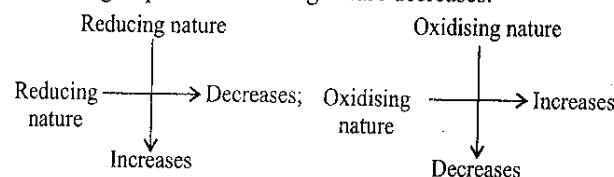
On the basis of the general trend of ionisation potential and electron gain enthalpy, the following properties can be predicted:

- a. Metallic nature decreases in a period while non-metallic nature increases. Metallic nature increases in a group while non-metallic nature decreases. The arrow (\downarrow) represents a group and (\rightarrow) represents a period.

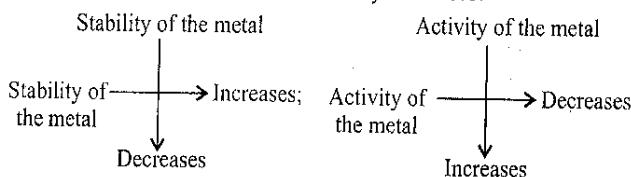


- b. Reducing nature decreases in a period while oxidising

nature increases. The reducing nature increases in a group while oxidising nature decreases.



- c. Stability of the metal increases while the activity of the metal decreases in a period and in a group stability decreases while the activity increases.



This trend is observed especially in 1, 2 and 13 group elements.

- d. The basic nature of the oxides decreases in a period while acidic nature increases. In a group, basic nature increases while acidic nature decreases.

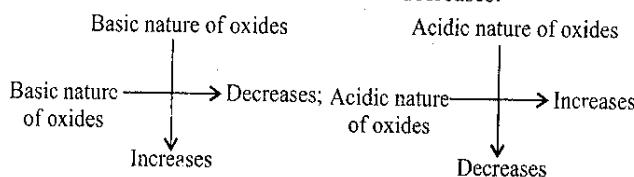
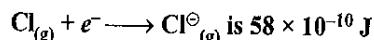


Illustration 1.38 Which of the following will have the most negative electron gain enthalpy and which the least negative?

P, S, Cl, F. Explain your answer. (NCERT Example 3.6)

Sol. Electron gain enthalpy generally becomes more negative across a period as we move from the left to the right. Within a group, electron gain enthalpy becomes less negative down a group. However, adding an electron to the $2p$ -orbital leads to the greater repulsion than adding an electron to the larger $3p$ -orbital. Hence, the element with the most negative electron gain enthalpy is chlorine; and the one with the least negative electron gain enthalpy is phosphorus.

Illustration 1.39 The amount of energy released when 10^{12} atoms of Cl vapours are converted to Cl^{\ominus} ions, according to the equation:



Calculate the $\Delta_{eg}H^{\ominus}$ of Cl atom in kJ mol^{-1} and eV atom^{-1} .

Sol. The amount of energy released when 1 mol ($\approx 6.0 \times 10^{23}$ atoms) of Cl are converted to Cl^{\ominus} ions according to the above equation is $\Delta_{eg}H^{\ominus}$ of Cl vapours.

$\therefore \Delta_{eg}H^{\ominus}$ of Cl vapours

$$= \frac{-58 \times 10^{-10} \text{ J} \times 6 \times 10^{23}}{10^{12}}$$

$$= -348 \times 10 \text{ J mol}^{-1}$$

$$= -3.48 \text{ kJ mol}^{-1}$$

We know that

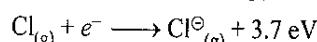
$$1 \text{ eV atom}^{-1} = 96.49 \text{ kJ mol}^{-1}$$

Therefore, $\Delta_{eg}H^{\ominus}$ of Cl vapours in eV is

$$\frac{-3.48}{96.49} = -0.036 \text{ eV atom}^{-1}$$

Illustration 1.40 The electron gain enthalpy of chlorine is 3.7 eV. How much energy in kJ and kcal is released when 1 g of chlorine is converted completely to Cl^{\ominus} ion in the gaseous state. ($1 \text{ eV} = 96.3 \text{ kJ mol}^{-1}$)

Sol. a. The electron gain enthalpy in kJ is represented as



$$\text{Now, } 1 \text{ eV atom}^{-1} = 96.3 \text{ kJ mol}^{-1}$$

$$\therefore 3.7 \text{ eV} = 3.7 \text{ eV} \times 96.3 \text{ kJ mol}^{-1}$$

Energy released when 35.5 g (1 mole) of chlorine is completely converted to $\text{Cl}^{\ominus}_{(g)}$ ion = $3.7 \times 96.3 \text{ kJ}$

Energy released when 1 g of chlorine is completely

$$\text{converted to } \text{Cl}^{\ominus}_{(g)} \text{ ion} = \frac{3.7 \times 96.3}{35.5} = 10.04 \text{ kJ}$$

b. $\Delta_{eg}H^{\ominus}$ in kcal

$$(1 \text{ eV} = 23.06 \text{ kcal mol}^{-1})$$

$$\therefore \Delta_{eg}H^{\ominus} = \frac{3.7 \times 23.06}{35.5} = 2.4 \text{ kcal}$$

Illustration 1.41 Write the electronic configuration of the element with atomic number of 9, 11, 21 and 36. Predict the following from these configurations:

- Which of them has the lowest ionisation potential?
- Which of them has the highest electron gain enthalpy?
- Which of them are non-metals?
- Which of them has zero electron gain enthalpy?

Sol. The electronic configuration of the given elements are

Atomic number

9 : $1s^2 2s^2 2p^5$

11 : $1s^2 2s^2 2p^6 3s^1$

21 : $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^1$

36 : $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 4d^{10} 4p^6$

- The element with atomic number 11 has the lowest ionisation potential.

Reason: Because after losing the most loosely bound electron it acquires a stable configuration.

- The element with atomic number 9 has the highest electron gain enthalpy.

Reason: Tendency to acquire stable configuration on receiving an electron.

- c. The element with atomic numbers 9 and 36 are non-metals.
- d. The elements with atomic number 36 has zero electron gain enthalpy.

Illustration 1.42 Which of the following has the highest electron gain enthalpy. Give reasons.

- a. $[\text{Ne}]3s^23p^3$
- b. $[\text{Ne}]3s^23p^4$
- c. $[\text{Ne}]3s^23p^5$
- d. $[\text{Ne}]3s^23p^6$

Sol. Atomic number (Z) of (a), (b), (c) and (d) respectively are:

- a. $Z = 10 + 5 = 15$, Element is P.
- b. $Z = 10 + 6 = 16$, Element is S.
- c. $Z = 10 + 7 = 17$, Element is Cl.
- d. $Z = 10 + 8 = 18$, Element is Ar.

The element chlorine corresponding to electronic configuration (c) has the highest electronic affinity. Halogens have $ns^2 np^5$ configurations due to which halogens show a strong tendency to accept an electron to acquire inert gas configuration ($ns^2 np^6$). Therefore, (c) the highest (-ve) electron gain affinity value due to its very small size.

Illustration 1.43 Arrange the elements with the following electronic configuration of valence electron in decreasing order of $\Delta_{eg}H^\ominus$.

- a. $3s^23p^4$
- b. $2s^22p^4$
- c. $2s^22p^3$
- d. $2s^22p^5$

Sol. c > b > a > d ($N > O > S > F$)

Elements (b), (c) and (d) are of the 2nd period namely O, N and F respectively, whereas element (a) is of the 3rd period and is S atom.

Out of F, O, N and S, only N has (+ve) $\Delta_{eg}H^\ominus$ because of its stable half-filled electronic configuration. F, O and S have (-ve) $\Delta_{eg}H^\ominus$. But F has the most -ve $\Delta_{eg}H^\ominus$, since it requires one electron to acquire the nearest inert gas configuration.

Out of O and S, O has the less - ve $\Delta_{eg}H^\ominus$ than S because of electron-electron repulsion present in its small and compact $2p$ -orbital.

Thus decreasing order of $\Delta_{eg}H^\ominus$ is
c > b > a > d ($N > O > S > F$)

Illustration 1.44 Which one of the following pairs has higher $\Delta_{eg}H^\ominus$?

- a. S^\ominus, O
- b. N^\ominus, P
- c. S, O^\ominus
- d. O^\ominus, S^\ominus

Sol. a. $S^\ominus > O$

Due to repulsion between the electrons on S^\ominus and the

additional incoming electrons $\Delta_{eg}H^\ominus$ of S^\ominus is + ve unlike that of O is -ve.

- b. $N^\ominus > P$

Due to repulsion between the electrons on N^\ominus and the addition incoming electron $\Delta_{eg}H^\ominus$ of N^\ominus = + ve while that of P is - ve.

- c. $O^\ominus > S$. (Same explanation as in (a) and (b).)
- d. $O^\ominus > S^\ominus$

Due to small size of O atom, repulsion between the electrons on O^\ominus and the additional incoming electron is much more than in S^\ominus .

Hence, $\Delta_{eg}H^\ominus$ of O^\ominus is more +ve than that of S^\ominus .

Illustration 1.45 Give the decreasing order of $\Delta_{eg}H^\ominus$ of the following elements: B, C, N, O.

Sol. $N > B > C > O$

Explanation: N has +ve $\Delta_{eg}H^\ominus$ because of its stable half-filled electronic configuration. Whereas in case of B, C and O, since the size decreases along the period (\rightarrow) i.e., from B to C and to O, thus $\Delta_{eg}H^\ominus$ becomes more and more -ve from $B \rightarrow C \rightarrow O$.

Thus, the overall decreasing order of $\Delta_{eg}H^\ominus$ is
 $N > B > C > O$.

Illustration 1.46 How many Cl atoms can you ionise in the process $\text{Cl} \rightarrow \text{Cl}^\oplus + e^-$ by the energy liberated for the process $\text{Cl} + e^- \rightarrow \text{Cl}^\ominus$ for one Avogadro number of atoms. Given $\text{IP} = 13.0 \text{ eV}$ and $\text{EA} = 3.60 \text{ eV}$.

Sol. Let n atoms be ionised.

$$6.02 \times 10^{23} \times \text{EA} = n \times \text{IP}$$

$$n = \frac{6.02 \times 10^{23} \times 3.60}{13} = 1.667 \times 10^{23} \text{ atoms}$$

1.16 ELECTRONEGATIVITY AND ELECTROPOSITIVITY

Electronegativity (EN) is defined as the tendency of an atom to attract shared pair of electrons towards itself in a covalently bonded molecules. It is represented as χ (pronounced as (chi) or EN).

It may be noted that both IE and $\Delta_{eg}H^\ominus$ relate to atoms in their gaseous isolated state, whereas EN is a property of an atom in the bonded state.

Unlike IE and $\Delta_{eg}H^\ominus$, it is not a measurable quantity. However, a number of numerical scales of EN of elements, e.g. Pauling scale, Mulliken-Jaffe scale, Allred-Rochow scale and Sanderson's have been developed. The most widely used is the Pauling scale. Linus Pauling, an American scientist in 1922 assigned arbitrarily a value of 4.0 to F (fluorine), which has the

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greatest ability to attract electrons. EN's of a few elements are given in Tables 1.16 and 1.17.

The EN of any element is not constant. It varies depending on the element to which it is bound. Although it is not a measurable quantity, yet it provides a means of predicting the nature of force that holds a pair of atoms together.

Electropositivity (EP) is a measure of an element's ability to donate electrons, and therefore form positive ions; thus, it is opposed to electronegativity. Mainly, this is an attribute of metals, meaning that for the most part, the greater the metallic character of an element, the greater the electropositivity. Therefore, the alkali metals are most electropositive of all. This is because they have a single electron in their outer shell and as this is relatively far from the nucleus of the atom, it is easily lost; in other words, these metals have low ionisation energies.

While, electronegativity increases along periods in the periodic table, and decreases down groups, electropositivity decreases along periods (from the left to the right) and increases down the groups.

Electropositive shark repellent utilises electropositive metals as shark repellents, since they generate measurable voltages in a seawater electrolyte relative to a shark.

Table 1.16 Electronegativity values (on Pauling scale) along the periods (\rightarrow)

| Atom (period II) | Li | B | C | N | O | F |
|-------------------|-----|-----|-----|-----|-----|-----|
| Electronegativity | 1.0 | 1.5 | 2.0 | 2.5 | 3.0 | 4.0 |
| Atom (period III) | Na | Mg | Al | Si | P | Cl |
| Electronegativity | 0.9 | 1.2 | 1.5 | 1.8 | 2.1 | 2.5 |

Table 1.17 Electronegativity values (on Pauling scale) down the family (\downarrow)

| Atom (group 1) | Electronegativity value | Atom (group 17) | Electronegativity value |
|----------------|-------------------------|-----------------|-------------------------|
| Li | 1.0 | F | 4.0 |
| Na | 0.9 | Cl | 3.0 |
| K | 0.8 | Br | 2.8 |
| Rb | 0.8 | I | 2.5 |
| Cs | 0.7 | At | 2.2 |

1.16.1 Variation of EN in the Periodic Table

- EN generally increases along the period (\rightarrow), i.e. from lithium (Li) to fluorine (F) in the periodic table.
- EN generally decreases down the group (\downarrow), i.e. from fluorine (F) to astatine (At) in the periodic table.

Note: F is the most EN element with a value of (4.0) (Pauling scale) and Cs is the least EN element.

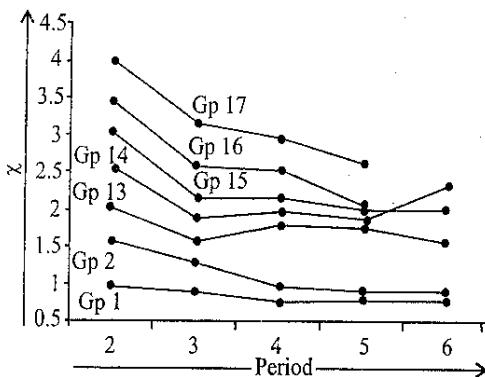


Fig. 1.12. The variation of Pauling electronegativity (y -axis) as one descends the main groups of the periodic table from the second period to the sixth period

There are some exceptions to this general rule:

- Gallium and germanium have higher electronegativities than aluminium and silicon respectively because of the d -block contraction.
- Elements of the fourth period immediately after the first row of the transition metals have unusually small atomic radii because the $3d$ -electrons are not effective at shielding the increased nuclear charge, and smaller atomic size correlates with higher electronegativity (see Allred-Rochow electronegativity).
- The anomalously high electronegativity of lead, particularly when compared to thallium and bismuth, appears to be an artifact of data selection /and data availability)—methods of calculation other than the Pauling method show the normal periodic trends for these elements.

1.16.2 Group Electronegativity

In organic chemistry, electronegativity is associated more with different functional groups than with individual atoms. The terms **group electronegativity** and **substituent electronegativity** are used synonymously. However, it is common to distinguish between the inductive effect and the resonance effect, which might be described as σ - and π -electronegativities respectively. There are a number of linear free-energy relationships which have been used to quantify these effects, of which the Hammett equation is the best known. Kabachnik parameters are group electronegativities for use in organophosphorus chemistry.

1.16.3 Factors Affecting the Magnitude of Electronegativity

- Atomic radius:** As two atomic radius of the element increases the EN value decreases.

$$EN \propto \frac{1}{\text{Atomic radius}}$$

Explanation: Atomic radii tend to decrease along the period (\rightarrow) and increases down the group (\downarrow). The attraction between the outer (or valence) electrons and the nucleus increases as the atomic radius decreases in a period. Therefore, EN also increases. Likewise, EN values decrease with the increase in atomic radii down a group. This trend is similar to that of IE.

2. **Effective nuclear charge (Z_{eff}):** The EN value increases as the Z_{eff} on the atomic nucleus increases.

$$\therefore \text{EN} \propto Z_{\text{eff}}$$

3. **Number of inner shells:** The atom with greater number of inner shells has less value of EN than the atom with smaller number of inner shells.

$$\therefore \text{EN} \propto \frac{1}{\text{Number of inner shells}}$$

For example, EN values of halogens decrease from F ($Z = 9$) to At ($Z = 85$), since the number of inner shell increases in the same order. Decreasing order of EN of halogens is

$$\therefore \text{F (4.0)} > \text{Cl (3.0)} > \text{Br (2.8)} > \text{I (2.5)} > \text{At (2.2)}$$

4. **Charge on the ion or oxidation state of the atom:** The EN increases as the oxidation state (OS), i.e. the number of positive charge of the atom increases. But the EN decreases as the negative charge of the atom increases.

$$\left(\begin{array}{l} \text{EN} \propto +\text{ve charge} \\ \text{and } \text{EN} \propto \frac{1}{-\text{ve charge}} \end{array} \right)$$

Explanation: A cation attracts the electron pair more rapidly towards itself than its parent atom. This is due to smaller size of the cation as compared to its parent atom (i.e. size of M^{\oplus} < size of M). Thus a cation has higher EN than its parent atom. (EN of M^{\oplus} > EN of M), e.g.

Decreasing order of EN = $M^{3+} > M^{2+} > M^{1+} > M \dots$

Order of size = $M > M^+ > M^{2+} > M^{3+}$ for example, the decreasing order of EN of some atoms and their ions.

- a. $\text{Fe}^{3+} (1.96) > \text{Fe}^{2+} (1.83) > \text{Fe} (1.8)$
- b. $\text{Pb}^{4+} (2.33) > \text{Pb}^{2+} (1.87) > \text{Pb} (1.80)$.

An anion has less tendency to attract the electron pair than its parent atom. This is due to larger size of the anion as compared to its parent atom (i.e. size of X^{\ominus} > size X) thus an anion has less EN than its parent atom.

\therefore Decreasing order of EN = $X > X^{\ominus} > X^{2-}$

Decreasing order of size = $X^{2-} > X^{\ominus} > X$

For example, F^{\ominus} ion has less EN value (0.8) than F atom (4.0).

| Acid | Formula | Chlorine oxidation state | pK_a |
|-------------------|-----------------|--------------------------|--------|
| Hypochlorous acid | HClO | +1 | +7.5 |
| Chlorous acid | HClO_2 | +3 | +2.0 |
| Chloric acid | HClO_3 | +5 | -1.0 |
| Perchloric acid | HClO_4 | +7 | -10 |

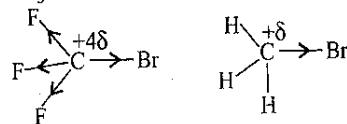
The chemical effects of this increase in electronegativity can be seen both in the structure of oxides and halides and in the acidity of oxides and oxoacids. Hence CrO_3 and Mn_2O_7 are acidic oxides with low melting points, while Cr_2O_3 is amphoteric and Mn_2O_3 is a completely basic oxide.

The effect can also be clearly seen in the dissociation constants of the oxoacids of chlorine. The effect is much larger than could be explained by the negative charge being shared among a larger number of oxygen atoms, which would lead to a difference in pK_a of $\log_{10}(1/4) = -0.6$ between hypochlorous acid and perchloric acid. As the oxidation state of the central chlorine atom increases, more electron density is drawn from the oxygen atoms on to the chlorine, reducing the partial negative charge on the oxygen atoms and increasing the acidity.

5. **Nature and number of atoms (i.e. substituent attached to the atom):** It is evident that EN of an atom is not the property of this atom in its isolated state but it depends on the number and nature of the atoms to which it is bonded. For this reason EN value of an atom is not constant.

For example, EN of P atom in PCl_3 molecule is less than that in PF_5 molecule.

Similarly, EN of C atom in CF_3Br is more than in CH_3Br , because C-atom in CF_3Br acquires greater positive charge than in CH_3Br .



6. **State of hybridisation:** The magnitude of EN increases as the s-character in the hybrid orbitals increases because s-electrons are comparatively near to the nucleus, and are more attracted or penetrated into the nucleus.

For example, the EN values of C-atom in CH_4 (sp^3), ethene (sp^2) and ethyne or acetylene (sp) are shown below in increasing order,

| | | | |
|------------------------|---------------|-----------------------------|------------------------------|
| a. Hydrocarbon | CH_4 | $\text{CH}_2 = \text{CH}_2$ | $\text{HC} \equiv \text{CH}$ |
| b. Hybridisation state | sp^3 | sp^2 | sp |
| c. s-character | 25% | 33.33% | 50% |
| d. EN values of C | 2.48 | 2.75 | 3.25 |

Increasing order of EN

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It implies that CH_4 is unreactive, ethene is more reactive while ethyne is highly reactive.

Moreover, the highest value of EN of C-atom in ethyne also accounts for its highly acidic hydrogen atom, i.e. acidic properties of ethyne.

7. **Ionisation energy (IE) and electron gain enthalpy ($\Delta_{eg}H^\ominus$):** Higher IE of an atom means that it is difficult to remove the most loosely bonded electron from the atom which also means that $\Delta_{eg}H^\ominus$ of that atom will also be greater.

Thus, the atoms which have high positive values of IE and $\Delta_{eg} H^\ominus$ also have higher values of EN.

For example, halogens (group 17) which have the highest IE and $\Delta_{ca}H^\ominus$ also have highest values of EN.

Similarly, alkali metals (group 1) which have the lowest IE and $\Delta_{\text{ep}} H^\ominus$ have the lowest values of FN.

1.16.4 Application of EN

The concept of EN is used to predict the metallic, non-metallic character of elements and polarity of bonds.

1.16.4.1 Metallic and Non-metallic Properties

- Non-metallic elements have strong tendency to gain electrons.

$$\text{OR} \quad \text{EN} \propto \frac{1}{\text{Metallic properties of elements}}$$

2. Thus, the increase in EN along the period (\rightarrow) increases the non-metallic character (or decreases the metallic character) of elements.

3. Similarly, the decrease in EN down the group (\downarrow) decreases the non-metallic character (or increases metallic character) of elements.

All these periodic trends are summarised in Fig. 1.13

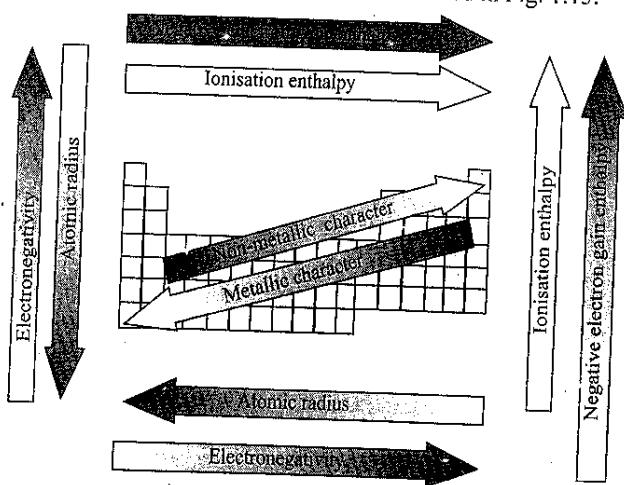
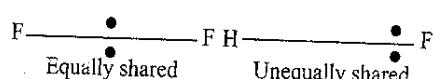


Fig. 1.13 The periodic trends of elements in the periodic table

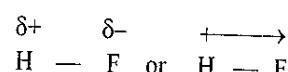
1.16.4.2 Polarity of Covalent Bond

In all homonuclear diatomic molecules such as hydrogen molecule (H_2), chlorine molecule (Cl_2), fluorine molecule (F_2), oxygen molecule (O_2), the electron pair or pairs is shared equally between the two atoms. This means that the shared electrons are equally attracted to both the nuclei and therefore spend equal amounts of time near each nucleus. As a result, the molecule is neutral non-polar.

In the heteronuclear diatomic molecule the bonding is different. Electronegative is defined as the tendency of an atom to attract electrons towards itself in a chemical bond. Thus, in heteronuclear diatomic molecule, both the atoms joined by the covalent bond possess different electronegativities. As a result, the atom having higher value of electronegativity attracts the shared electron pair much more strongly than the other atom. For example, in HF the electron pair is more attracted towards F as it is more electronegative than hydrogen. Due to this, the fluorine end of the molecule appears negative and the hydrogen end positive. Such molecules having two oppositely charged poles are called polar molecules and the bond is said to be a polar covalent bond.



A covalent bond, in which electrons are shared unequally and the bonded atoms acquired a partial positive and negative charge, is called a polar covalent bond or a covalent bond between two dissimilar atoms is a polar covalent bond. Two kinds of notation are used to indicate a polar covalent bond.



Polar covalent bonds may be thought of as being intermediate between the non-polar bond and the pure ionic bond.

1.16.4.3 Characteristics of Polar Bond

1. The polarity of the molecule is determined from their dipole moment (μ) values. Higher the difference in EN of two bonded atoms, the higher is the dipole moment (μ) of the molecule.

For example, the μ values of some molecules are given below. The μ value is usually expressed in Debye units. (D).

| Molecule | $\mu(D)$ |
|----------|----------|
| HF | 1.86 |
| HCl | 1.11 |
| HBr | 0.79 |
| HI | 0.38 |

- 2. Ionic character in a polar covalent bond:** The concept of EN is also used to know the nature of bond and to calculate

the percentage of ionic character in a polar covalent bond.

These trends are summarised below:

(where χ_A and χ_B are the EN values of atoms A and B in AB molecule)

- When $\chi_A = \chi_B$, then A–B bond is non-polar covalent bond or simply covalent bond, e.g. H₂, Cl₂ and N₂ molecules.
- Where $\chi_A > \chi_B$ i.e. $\chi_A - \chi_B$ is small, then A–B bond is polar covalent bond and is represented as A ^{$\delta-$} B ^{$\delta+$} , since $\chi_A > \chi_B$.

For example, both O–H covalent bonds in H₂O molecule are polar covalent bonds and are represented as O ^{$\delta-$} H ^{$\delta+$} . Since $\chi_O > \chi_H$ and $\chi_O - \chi_H$ is small.

- When $\chi_A \gg \chi_B$ i.e. $\chi_A - \chi_B$ is very large, A–B bond is an ionic or polar bond and is represented as A ^{\ominus} –B ^{\oplus} , since $\chi_A \gg \chi_B$. For example, NaCl molecule is an ionic bond and is represented as Na ^{\oplus} Cl ^{\ominus} (here Cl = A and Na is B).

1.16.4.4 Percentage of Ionic Character in Polar Covalent Bond

If two atoms A and B are linked by a polar covalent bond, the percentage of ionic character in this bond depends on the difference of EN values of A and B.

- Greater the difference ($\chi_A - \chi_B$), greater is the percentage of ionic character in A–B bond.
- When ($\chi_A - \chi_B$) = 1.7, the bond is 50% ionic and 50% covalent.
- When ($\chi_A - \chi_B$) < 1.7, the ionic character in A ^{$\delta-$} –B ^{$\delta+$} is less than 50% and that of covalent character is more than 50%. Thus A ^{$\delta-$} –B ^{$\delta+$} is **predominantly covalent**.
- When ($\chi_A - \chi_B$) > 1.7, the ionic character in A ^{$\delta-$} –B ^{$\delta+$} is more than 50% and that of covalent character is less than 50%, hence A ^{$\delta-$} –B ^{$\delta+$} bond is **predominantly ionic**.

Bond polarity is described in terms of ionic character which usually increases with increasing difference in the electronegativity (EN) between the bonded atoms.

| EN | H–F | H–Cl | H–Br | H–I |
|------------------|---------|---------|---------|---------|
| | 2.1–4.0 | 2.1–3.0 | 2.1–2.8 | 2.1–2.5 |
| Difference in EN | 1.9 | 0.9 | 0.7 | 0.4 |

Ionic character and stability of bond decreases as difference in electronegativity decreases →

SiH₄, NCl₃, PH₃ and AsH₃ are unstable. Their EN differences are given below:

EN differences in SiH₄ = ($\chi_H - \chi_{Si}$) = 2.1 – 1.8 = 0.3

EN differences in NCl₃ = ($\chi_N - \chi_{Cl}$) = 3.0 – 3.0 = 0.0

EN differences in PH₃ = ($\chi_P - \chi_H$) = 2.1 – 2.1 = 0.0

EN differences in AsH₃ = ($\chi_H - \chi_{As}$) = 2.1 – 2.0 = 0.1

- Pauling has estimated the approximate percentage of ionic character in various A–B covalent bonds from the ($\chi_A - \chi_B$) values, i.e. electronegativity difference of the two atoms forming the covalent bond.

| $\chi_A - \chi_B$ | Percentage of ionic character | Nature of A–B bond |
|-------------------|-------------------------------|----------------------------|
| 0 | 0 | Purely covalent |
| 0.1 to 0.8 | 0.5–15 | Covalent |
| 0.9 to 1.6 | 19–47 | Polar covalent |
| 1.7 | 50 | 50% ionic and 50% covalent |
| 1.8 to 3.2 | 55–93 | Ionic |

- Hannay and Smith gave the following equation for calculating the percentage of ionic character in A–B bond on the basis of the values of electronegativity of the atoms A and B.

$$\text{Percentage of ionic character} = [16(\chi_A - \chi_B) + 3.5](\chi_A - \chi_B)^2]$$

This equation gives approximate calculation of percentage of ionic character, e.g. 50% ionic character corresponds to ($\chi_A - \chi_B$) equal to 2.1.

- ($\chi_O - \chi_A$) difference predicts the nature of the oxides formed by the element A. χ_O is the EN of oxygen.
 - If ($\chi_O - \chi_A$) is large, the oxide shows basic nature, e.g. Na₂O.
 - If ($\chi_O - \chi_A$) is small, the oxide shows acidic nature, e.g. SO₂.
- Ionic compounds having character < 20%, the compounds were found to be coloured, e.g.

| | | | | |
|---------------------|---------------------|--------|-------------|-------------------|
| Compound ⇒ | AgCl | AgBr | AgI | Ag ₂ S |
| % ionic character ⇒ | 22% | 18% | 11% | 8% |
| Colour ⇒ | White or colourless | Yellow | Dark yellow | Black |

Lesser the percentage of ionic character, darker will be the colour.

Illustration 1.7 Calculate the percentage of ionic character in Cs–Cl bond in CsCl molecule. The electronegativity values of Cs and Cl are 0.7 and 3.0 respectively.

$$\text{Sol. } \chi_A - \chi_B = \chi_{Cl} - \chi_{Cs} = (3.0 - 0.7) = 2.3$$

Percentage of ionic character in Cs–Cl bond

$$= [16 \times 2.3 + 3.5 \times (2.3)^2] = (36.8 + 18.51) = 55.31$$

Illustration 1.43 Arrange the molecules, HF, HCl, HBr and HI in the decreasing order of the percentage of ionic character. Electronegativity values are as follows:

$$H = 2.1 \quad F = 4.0 \quad Cl = 3.0 \quad Br = 2.8 \quad I = 2.5$$

Sol. Percentage of ionic character in H–F

$$\begin{aligned} (\chi_F - \chi_H) &= 4.0 - 2.1 = 1.9 \\ &= [16 \times 1.9 + 3.5 \times (1.9)^2] = 43 \end{aligned}$$

% ionic character in H–Cl

$$\begin{aligned} (\chi_{Cl} - \chi_H) &= 3.0 - 2.1 = 0.9 \\ &= [16 \times 0.9 + 3.5 \times (0.9)^2] = 17.2 \end{aligned}$$

% of ionic character in HBr

$$\begin{aligned} (\chi_{Br} - \chi_H) &= 2.8 - 2.1 = 0.7 \\ &= [16 \times 0.7 + 3.5 \times (0.7)^2] = 12.9 \end{aligned}$$

% ionic character in HI

$$\begin{aligned} (\chi_I - \chi_H) &= 2.5 - 2.1 = 0.4 \\ &= [16 \times 0.4 + 3.5 \times (0.4)^2] = 7.0 \end{aligned}$$

% of ionic character = HF > HCl > HBr > HI

1.16.4.5 Scales of EN (Measurement of EN)

A number of scales have been developed to measure EN of the atoms. These scales are arbitrary and are based on various types of experimental data such as bond energy, dipole moment, IE and EA. Some of them are explained below:

1. Pauling scale (1932): This scale gives a dimensionless quantity, commonly referred to as the **Pauling scale**, on a relative scale running from around 0.7 to 3.98 (hydrogen = 2.20). This scale is based on an empirical relation between the bond energy and EN of the two atoms bonded together (A–B) is given by the relation.

The difference in EN between atoms A and B is given by

$$(\chi_A - \chi_B) = (eV)^{-1/2} \sqrt{E_{A-B} - \frac{1}{2}[E_{A-A} + E_{B-B}]} \quad \dots(1.2)$$

Note: $1 \text{ eV atom}^{-1} = 23.06 \text{ kcal mol}^{-1}$

$$\therefore (23.06)^{-1/2} = \frac{1}{\sqrt{(23.06)^{1/2}}} = 0.208$$

Therefore, changing the value of eV in kcal mol^{-1} , Eq. (1.2) becomes

$$(\chi_A - \chi_B) = 0.208 \sqrt{E_{A-B} - \frac{1}{2}[E_{A-A} + E_{B-B}]} \text{ kcal mol}^{-1} \quad \dots(1.3)$$

Another form of the equation can be written as

$$\begin{aligned} (\chi_A - \chi_B) &= (eV)^{-1/2} \left[E_{A-B} - \sqrt{E_{A-A} \times E_{B-B}} \right]^{\frac{1}{2}} \text{ kcal mol}^{-1} \quad \dots(1.4) \\ &= 0.208 \left[E_{A-B} - \sqrt{E_{A-A} \times E_{B-B}} \right]^{\frac{1}{2}} \quad \dots(1.5) \end{aligned}$$

where χ_A and χ_B are the EN's of two atoms A and B and E_{A-B} , E_{A-A} and E_{B-B} are bond energies of molecules A–B, A_2 and B_2 respectively in kcal mol^{-1} .

In Eqs. (1.4) and (1.5), $[E_{A-B} - \sqrt{E_{A-A} \times E_{B-B}}]$ is known as **ionic resonance energy** of A–B bond and is denoted by Δ_{A-B} . Thus,

$$\Delta_{A-B} = [E_{A-B} - \sqrt{E_{A-A} \times E_{B-B}}]$$

Substituting the value of Δ_{A-B} in Eq. (1.4), we get
 $(\chi_A - \chi_B) = 0.208 \sqrt{\Delta_{A-B}}$ in kcal mol^{-1} ... (1.6)

Note: Converting the value of $eV \text{ atom}^{-1}$ into kJ mol^{-1} (SI unit, we know

$$1 \text{ eV atom}^{-1} = 96.49 \text{ kJ mol}^{-1}$$

$$\therefore (eV)^{-1/2} = \frac{1}{(96.49)^{1/2}} = 0.017$$

Therefore, substituting the value of $eV \text{ atom}^{-1}$ into kJ mol^{-1} in Eq. (1.2) and (1.4).

From Eq. (1.2), we get

$$(\chi_A - \chi_B) = 0.107 \sqrt{E_{A-B} - \frac{1}{2}[E_{A-A} + E_{B-B}]} \text{ kJ mol}^{-1} \quad \dots(1.7)$$

From Eq. (1.4), we get

$$\begin{aligned} (\chi_A - \chi_B) &= 0.107 \left[E_{A-B} - \sqrt{E_{A-A} \times E_{B-B}} \right]^{\frac{1}{2}} \text{ kJ mol}^{-1} \\ &= 0.107 \sqrt{\Delta_{A-B}} \text{ kJ mol}^{-1} \quad \dots(1.9) \end{aligned}$$

Equations (1.7), (1.8) and (1.9) in kJ mol^{-1} can be used and they give approximately the same result.

Note: The dissociation energies of the A–B, A–A and B–B bonds are expressed in eVs, the factor $(eV)^{-1/2}$ is included to ensure a dimensionless result.

2. Mulliken's scale (1934):

- Mulliken proposed that EN of an atom is equal to the average of its ionisation potential (IP) and electron affinity (EA) values, when IP and EA of the atom are in eV atom^{-1} .

$$\chi_A = \frac{(IP)_A + (EA)_A}{2} \quad \dots(1.10)$$

If the values of IP and EA are taken in kcal mol^{-1} , then

$$\chi_A = \frac{(IP)_A + (EA)_A}{2 \times 62.5} = \frac{(IP)_A + (EA)_A}{125} \quad \dots(1.11)$$

If the value of IP and EA are taken in kJ mol^{-1} , then

$$\chi_A = \frac{(IP)_A + (EA)_A}{540} \quad \dots(1.12)$$

Alternatively: However, it is more usual to use a linear transformation to transform these absolute values into values which resemble the more familiar Pauling values. For IP and EA in eV's,

$$\chi_A = 0.187 (\text{IP} + \text{EA}) + 0.17 \quad \dots(1.13)$$

and for IP and EA in kJ mol^{-1} ,

$$\chi_A = (1.97 \times 10^{-3}) (\text{IP} + \text{EA}) + 0.19 \quad \dots(1.14)$$

- b. Mulliken's values of EN are about 2.8 times more than the Pauling's values. Hence to make the Mulliken's values approximately equal to the Pauling's values, then Eq. (1.11) becomes

$$\chi_{\text{Pauling}} = \frac{(\text{IP})_A + (\text{EA})_A}{2 \times 2.8} = \frac{(\text{IP})_A + (\text{EA})_A}{5.6} \quad \dots(1.15)$$

OR

$$\chi_{\text{Pauling}} = \frac{\chi_{\text{Mulliken}}}{2.8} \quad \dots(1.16)$$

The constant 1/56 is called scale adjustment factor. This factor is used when IP and EA are taken in eV.

- c. In terms of electron gain enthalpy ($\Delta_{eg} H^\ominus$), Mulliken scale can be written as

$$\chi_A = \left[\frac{\Delta_i H^\ominus - \Delta_{eg} H^\ominus}{2} \right]$$

where $\Delta_i H^\ominus$ represents ionisation energy.

- d. The Mulliken EN values are scaled down to match the Pauling values by dividing $\left(\frac{\text{IP} + \text{EA}}{2} \right)$ in eV by 3.17, as shown in Table 1.18

Table 1.18 Electronegativity values (shown in italics) on Pauling and Mulliken scales

| H | | | | | | | |
|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|
| 2.20 | | | | | | | |
| <i>3.06</i> | | | | | | | |
| Li | Be | B | C | N | O | F | Nc |
| 0.98 | <i>1.57</i> | <i>2.04</i> | <i>2.55</i> | <i>3.04</i> | <i>3.44</i> | <i>3.92</i> | — |
| <i>1.28</i> | <i>1.98</i> | <i>1.83</i> | <i>2.67</i> | <i>3.08</i> | <i>3.22</i> | <i>4.43</i> | <i>4.60</i> |
| Na | Mg | Al | Si | P | S | Cl | Ar |
| 0.93 | <i>1.31</i> | <i>1.61</i> | <i>1.90</i> | <i>2.19</i> | <i>2.58</i> | <i>3.16</i> | — |
| <i>1.21</i> | <i>1.63</i> | <i>1.37</i> | <i>2.03</i> | <i>2.39</i> | <i>2.65</i> | <i>3.54</i> | <i>3.36</i> |
| K | Ca | Ga | Ge | As | Se | Br | Kr |
| 0.82 | <i>1.00</i> | <i>1.81</i> | <i>2.01</i> | <i>2.18</i> | <i>2.55</i> | <i>2.96</i> | 3.0 |
| <i>1.03</i> | <i>1.30</i> | <i>1.34</i> | <i>1.95</i> | <i>2.26</i> | <i>2.51</i> | <i>3.24</i> | <i>2.98</i> |
| Rb | Sr | In | Sn | Sb | Tc | I | Xe |
| 0.82 | <i>0.95</i> | <i>1.78</i> | <i>1.96</i> | <i>2.05</i> | <i>2.10</i> | <i>2.66</i> | 2.6 |
| <i>0.99</i> | <i>1.21</i> | <i>1.30</i> | <i>1.83</i> | <i>2.06</i> | <i>2.34</i> | <i>2.88</i> | <i>2.59</i> |
| Cs | Ba | Tl | Pb | Bi | | | |
| 0.79 | <i>0.89</i> | <i>2.04</i> | <i>2.33</i> | <i>2.02</i> | | | |

The Mulliken EN can only be calculated for an element for which EA is known. The Mulliken EN of an atom is sometimes said to be the negative of the chemical potential. By inserting the energetic definitions of the IP and EA into the Mulliken EN, it is possible to show that the Mulliken chemical potential (μ_M) is a finite difference approximation of electronic energy with respect to the number of electrons, i.e.

$$\mu_M = -\chi_M = \frac{-(\text{IP} + \text{EA})}{2}$$

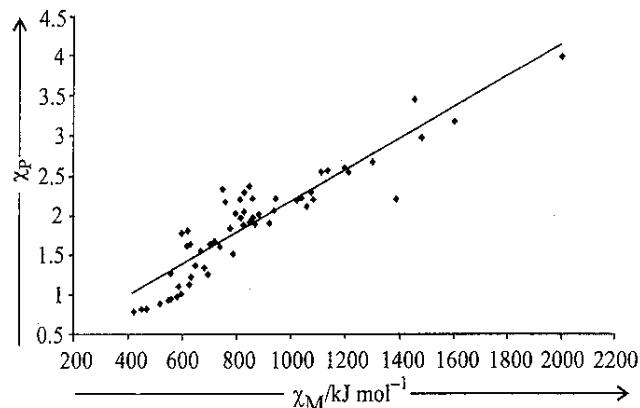


Fig. 1.14. The correlation between Mulliken EN's (x-axis, in kJ mol^{-1}) and Pauling EN's (y-axis)

3. Allred-Rochow's scale (1958): This scale is based on covalent radii. According to this scale, EN of an atom is the force of attraction between the nucleus of one atom and an electron of an adjacent atom bonded to it and separated from the nucleus by the covalent radius. Thus,

$$\text{EN or } (\chi_A) = 0.359 \times \frac{Z_{\text{eff}}}{r^2} + 0.744 \quad \dots(1.17)$$

where r is the radius of an atom in angstrom units (\AA). The value of Z_{eff} is calculated on the basis of Slater's rule taking all the electrons.

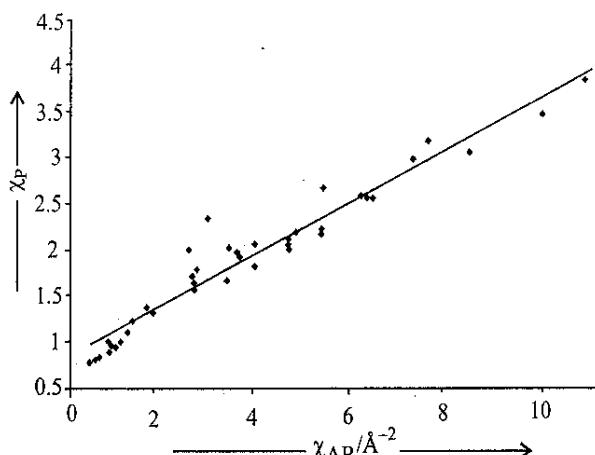


Fig. 1.15. The correlation between Allred-Rochow EN's (x-axis, in \AA^{-2}) and Pauling EN's (y-axis)

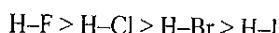
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Illustration 1.49 The ionic resonance energy of C–H bond is $\approx 6.0 \text{ kcal mol}^{-1}$. The EN of H is 2.1. Calculate EN of carbon ?
Given: $\Delta_{\text{C}-\text{H}} \approx 6.0 \text{ kcal mol}^{-1}$

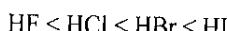
$$\begin{aligned}\text{Sol. } (\chi_{\text{C}} - \chi_{\text{H}}) &= 0.208 \left[E_{\text{A-B}} - \sqrt{E_{\text{A-A}} \times E_{\text{B-B}}} \right]^{\frac{1}{2}} \\ &= 0.208 \times \left(\Delta_{\text{C}-\text{H}} \right)^{\frac{1}{2}} \\ &= 0.208 \times (6.0)^{\frac{1}{2}} = 0.208 \times 2.5 = 0.52 \\ \chi_{\text{C}} - \chi_{\text{H}} &= 0.52 \\ \therefore \chi_{\text{C}} &= 0.52 + 2.1 = 2.62\end{aligned}$$

1.16.4.6 Bond Strength

If the EN difference of a covalently bonded atom ($\Delta\chi$) increases, the bond energy of the covalent bond also increases. For example, the decreasing order of the H–X bond strength is



As the bond strength is decreasing the acid strength is increasing. So the other increasing acid strength is

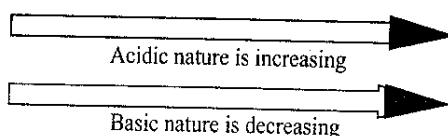


1.16.4.7 Acidic and Basic Nature of Oxides of Normal Elements in a Period

1. The acidic nature of the oxides of normal elements increases along the period (\rightarrow), due to the increase of EN of the elements from the left to the right in a period.

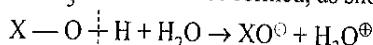
The order of acidic or basic nature of the oxides of the 3rd period is given as under.

| Group | 1 | 2 | 14 | 15 | 16 | 17 |
|-------|-----------------------|--------------|----------------|------------------------|---------------|-------------------------|
| | Na_2O | MgO | SiO_2 | P_2O_5 | SO_3 | Cl_2O_7 |



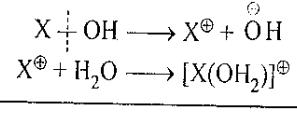
2. Acidic and basic character of XOH molecule in aqueous solution: Whether a given compound of XOH type ($X = \text{metal or non-metal}$) will behave as an acid or a base in aqueous solution is explained by considering the ionisation of XOH molecule in aqueous solution as follows:

a. If $\chi_{\text{O}} - \chi_{\text{H}} > \chi_{\text{O}} - \chi_x$; then O–H bond will be more polar than O–X bond and hence the ionisation of XOH molecule in aqueous solution will take place at O–H bond and $\text{H}_3\text{O}^{\oplus}$ ions will be formed, as shown:



The formation of $\text{H}_3\text{O}^{\oplus}$ shows that XOH will behave as an acid in its aqueous solution.

b. If $\chi_{\text{O}} - \chi_{\text{H}} < \chi_{\text{O}} - \chi_x$, then X–O bond will be more polar than O–H bond and hence the ionisation of XOH molecule in aqueous solution will take place at X–O bond and OH^- ions will be formed as shown:



The formation of OH^- ions shows that XOH will behave as a base in its aqueous solution.

c. From the above discussion and Illustration 1.51 it is evident that hydroxy compounds of metals such as groups 1 and 2 behave as bases in aqueous solution (except $\text{Be}(\text{OH})_2$, which is amphoteric in nature) while those of non-metals like halogens behave as acids.

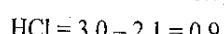
Illustration 1.50 Arrange the following compounds in order of their decreasing stabilities:



(Given EN values of elements as below)



Sol. EN differences for:



The greater the differences in EN, the greater is the bond energy of the covalent bond and the greater is the stability of the covalent bond.

So, the order of decreasing stability is

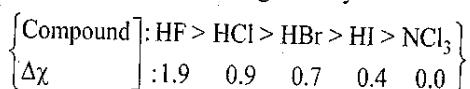
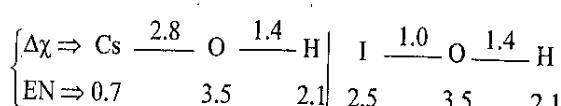


Illustration 1.51 Predict which of the following hydroxy compounds is acidic and which is basic in aqueous solution:

- i. CsOH
- ii. IOH .

EN values are: $\text{Cs} = 0.7, \text{O} = 3.5, \text{H} = 2.1, \text{I} = 2.5$.

Sol. The EN values of different elements present in CsOH and IOH and those of $\chi_{\text{O}} - \chi_{\text{H}}$, $\chi_{\text{O}} - \chi_{\text{Cs}}$ and $\chi_{\text{O}} - \chi_{\text{I}}$ are given below:



Here $\chi_{\text{O}} - \chi_{\text{Cs}} (2.8) > \chi_{\text{O}} - \chi_{\text{I}} (1.0)$, so CsOH will give OH^- ions while IOH will give $\text{H}_3\text{O}^{\oplus}$ ions, consequently CsOH behaves as a base while IOH behaves as an acid.

Illustration 1.53 NaOH behaves as a base while Zn(OH)₂ is amphoteric why?

Sol. In $\text{Na} + \text{O} - \text{H}$, $\chi_{\text{O}} - \chi_{\text{Na}} > \chi_{\text{O}} - \chi_{\text{H}}$, therefore it is the Na–O bond breaks and releases OH ions. So, NaOH is basic.

But in $\text{Zn} + \text{O} + \text{H}$, $\chi_{\text{O}} - \chi_{\text{Zn}} = \chi_{\text{O}} - \chi_{\text{H}}$, therefore there is equal probability that the bond breaks in both ways (releasing both H_3O^+ and OH^- in aqueous solution). So, Zn(OH)₂ is amphoteric.

1.16.5 Differences Between $\Delta_{\text{eg}} \text{H}^\ominus$ and EN

These are summarised below:

| $\Delta_{\text{eg}} \text{H}^\ominus$ | EN |
|--|--|
| 1. It is the tendency of an isolated gaseous atom to attract an electron. | 1. It is the tendency of an atom in a molecule to attract the shared pair of electrons. |
| 2. It can be measured experimentally and is usually expressed in eV atom ⁻¹ or kJ mol ⁻¹ . | 2. It cannot be measured experimentally. It is only a relative number with respect to Γ taken as 4.0. |
| 3. $\Delta_{\text{eg}} \text{H}^\ominus$ of an atom is constant. | 3. EN of an atom is not constant. It depends on the state of hybridisation of the atom, e.g. EN of sp hybridised atom $>$ sp^2 hybridised atom $>$ sp^3 hybridised atom. It also depends on oxidation state (OS) of an element. $\text{EN} \propto \text{OS}$. It also depends on the nature of substituent attached to it. EN of C in CF_3 , Br $>$ EN of C in CH_3Br . |
| 4. It is the property of an isolated atom. | 4. It is property of bonded atom. |
| 5. It does not change regularly in a period or group. | 5. It changes regularly in a period and there are certain exception in a group. |

1.17 SOME IMPORTANT BOND CHARACTERISTICS

- Bond length:** The equilibrium distance between the centres of the nuclei of the two bonded atoms is called its bond length.

It is expressed in terms of Angstrom ($1\text{\AA} = 10^{-10}\text{ m}$) or

picometer ($1\text{ pm} = 10^{-12}\text{ m}$). It is determined experimentally by the X-ray diffraction or electron diffraction methods or spectroscopic methods.

a. Factors affecting bond length:

i. **Size of the atoms:** Bond length increases with the increase in the size of the atoms, e.g. bond lengths of H–X are in the order as H–I $>$ H–Br $>$ H–Cl $>$ H–F.

ii. **Multiplicity of bond:** The bond length decreases with multiplicity of bond, e.g. bond length of $\text{C} \equiv \text{C}$ is $< \text{C} = \text{C} < \text{C} - \text{C}$.

iii. **Types of hybridisation:** Since s -orbital is smaller in size, the greater the s -character, the shorter is the hybrid orbitals and hence shorter is the bond length, e.g. bond lengths of sp^3 , sp^2 and sp hybrid orbitals of C–H bond are in the order as:

$$sp^3 (\text{C}-\text{H}) > sp^2 (\text{C}-\text{H}) > sp (\text{C}-\text{H}).$$

The bond lengths of a few common bonds are given in Table 1.19.

Table 1.19

| Bond | Bond length (pm) |
|-------|------------------|------------------|------------------|------------------|------------------|
| H–H | 74 | C=C | 134 | H–Cl | 127 |
| Cl–Cl | 199 | C≡C | 120 | H–Br | 141 |
| C–C | 154 | O–O | 120 | H–I | 161 |
| | | | | O–H | 96 |

b. **Calculation of bond length:** Generally in case of heteroatomic molecule of AB type, bond length, $d_{(\text{A}-\text{B})}$ is equal to the sum of covalent radii of A and B atoms

$$d_{(\text{A}-\text{B})} = r_{\text{A}} + r_{\text{B}} \quad \dots(1.18)$$

Although Eq. (1.18) holds good in most of the heteroatomic molecules, yet the experimental value of $d_{(\text{A}-\text{B})}$ is found to be slightly less than the sum of r_{A} and r_{B} . The decrease in bond length is due to the ionic character in A–B bond. The increase in ionic character of A–B bond decreases the bond length, $d_{(\text{A}-\text{B})}$.

Schomarkar and Stevenson (1941) proposed the following formula for the calculation of bond length.

$$d_{(\text{A}-\text{B})} = r_{\text{A}} + r_{\text{B}} - 0.09 (\chi_{\text{A}} - \chi_{\text{B}}) \quad \dots(1.19)$$

(χ_{A} and χ_{B} are the EN's of A and B elements.)

$$\therefore d_{(\text{A}-\text{B})} \propto \frac{1}{(\chi_{\text{A}} - \chi_{\text{B}})} \propto \text{Stability of AB molecule} \quad \dots(1.20)$$

i.e. lesser is the value of $(\chi_{\text{A}} - \chi_{\text{B}})$, more will be the bond length and thus less will be the stability of AB molecule.

Illustration 1.53 Calculate the $d_{(\text{N}-\text{C})}$ in $(\text{CH}_3)_3\text{N}$ molecule by using Eqs. (1.18) and (1.19) above and show from which equation $d_{(\text{N}-\text{C})}$ closely resembles with the experimental value of $d_{(\text{N}-\text{C})} = 1.47\text{ \AA}$.

Given: $r_{\text{N}} = 0.75\text{ \AA}$, $r_{\text{C}} = 0.77\text{ \AA}$, $\chi_{\text{A}} = 3.0$, $\chi_{\text{C}} = 2.5$

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Sol. Using Eq. (1.18), we get

$$d_{(N-C)} = r_N + r_C = (0.75 + 0.77) \text{ \AA} = 1.52 \text{ \AA}$$

Using Eq. (1.19), we get

$$\begin{aligned} d_{(N-C)} &= r_N + r_C - 0.09 (\chi_N - \chi_C) \\ &= 0.75 + 0.77 - 0.09 (3.0 - 2.5) \\ &= 1.475 \text{ \AA} \end{aligned}$$

The value of $d_{(N-C)}$ closely resembles the experimental value by using Eq. (1.19).

- 2. Bond strength or bond energy or bond enthalpy:** It is the amount of energy required to break one mole of bonds of a particular type so as to separate them into gaseous atoms.

It is expressed in kJ mol^{-1} .

a. Factors affecting bond strength:

- i. **Size of the atoms:** The greater the size of the atoms, the greater is the bond length and less is the bond dissociation energy or bond strength.
- ii. **Multiplicity of bonds:** The bond strength increases with the multiplicity of the bond, e.g. bond dissociation energy are in the order:

$$N \approx O > O = O > H - H.$$

- iii. **Number of lone pairs of electrons present:** The greater is the number of lone pairs of electrons present on the bonded atoms, the greater is the repulsion between the atoms and hence the less is the bond dissociation energy, e.g. for a few single bond, bond energy is as given below:

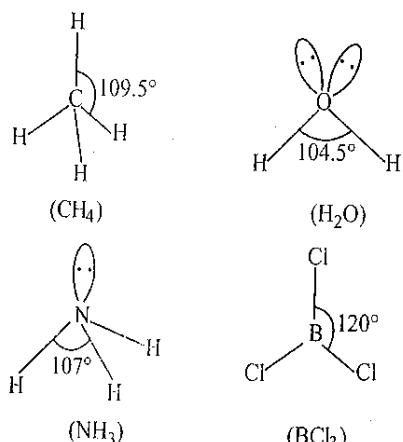
| Bond | C-C | N-N | O-O | F-F |
|--------------------------------------|-----|-----|-----|-----|
| Lone pairs of electrons on each atom | 0 | 1 | 2 | 3 |
| Bond energy (kJ mol^{-1}) | 348 | 163 | 146 | 139 |

- 3. Bond angle:** A bond is formed by the overlap of atomic orbitals. The direction of an overlap gives the direction of the bond.

The angle between the lines representing the direction of the bonds, i.e. the orbitals containing the bonding electrons, is called the bond angle.

Alternatively: It is the angle between the orbitals containing bonding electron pairs around the central atom in a molecule/complex ion.

It is expressed in degree, minutes and second. For example, H-C-H bond angle in CH_4 , H-O-H bond angle in H_2O , H-N-H bond angle in NH_3 and Cl-B-Cl bond angle in BCl_3 are shown as:



a. Calculation of bond angles:

- i. The concept of EN has been found to be very useful to explain the variation of bond angle.

For example, for AB_x type molecule (A is the central atom, B are the atoms attached with atom A and x is the number of B atoms), the B-A-B bond angle is changed with the change of EN of central atom or with change of size of central atom

Rule (i): If the EN of central atom decreases or/and size increases bond angle decreases.

Bond angle ($\text{B}-\text{A}-\text{B}$) \propto EN of central atoms and

$$\propto \frac{1}{\text{Size of central atom}}$$

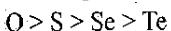
Table 1.20 Change of bond angle of hydrides of groups 15 and 16 with change of EN and size of central atom

| (Hydrides of group 15) (A = N, P, As, Sb) | EN of central atom A | H-A-H bond angle | Bond angle decreases as EN of central atom decreases or size of central atom increases |
|---|----------------------|--|--|
| NH_3 | N = 3.0 | $\text{H}-\text{N}-\text{H} = 107.5^\circ$ | |
| PH_3 | P = 2.1 | $\text{H}-\text{P}-\text{H} = 93.3^\circ$ | |
| AsH_3 | As = 2.0 | $\text{H}-\text{As}-\text{H} = 91.8^\circ$ | |
| SbH_3 | Sb = 1.9 | $\text{H}-\text{Sb}-\text{H} = 91.3^\circ$ | |

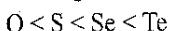
Decreasing order of EN of central atom A: N > P > As > Sb.
Increasing order of size of central atom A: N < P < As < Sb.

| (Hydrides of group 16) (A = O, S, Se, Te) | EN of central atom A | H-A-H bond angle | Bond angle decreases as EN of central atom decreases or size of A increases |
|---|----------------------|--|---|
| H_2O | O = 3.5 | $\text{H}-\text{O}-\text{H} = 104.5^\circ$ | |
| H_2S | S = 2.5 | $\text{H}-\text{S}-\text{H} = 92.3^\circ$ | |
| H_2Se | Se = 2.4 | $\text{H}-\text{Se}-\text{H} = 91^\circ$ | |
| H_2Te | Te = 2.1 | $\text{H}-\text{Te}-\text{H} = 90^\circ$ | |

Decreasing order of EN of central atom A:



Increasing order of size of central atom A:



Explanation: For example, the angle of $\text{H}_2\text{O} > \text{H}_2\text{S}$ (Figs. 1.16(a) and 1.16(b)).

The outer shell electronic configuration of group 16 elements is $ns^2 np^4$ or $ns^2 np_x^2 np_y^1 np_z^1$. They undergo sp^3 hybridisation, containing 2 lone pairs. The expected bond angle is $109^\circ, 28'$. But due to greater $lp-lp$ repulsion as compared to $lp-bp$ repulsion, bond angle decreases.

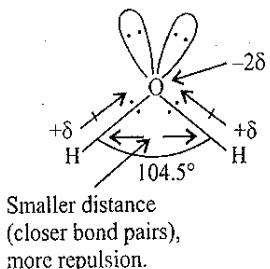


Fig. 1.16(a)

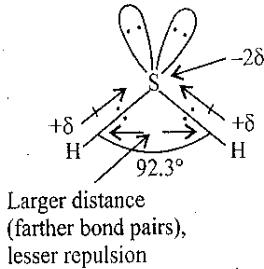


Fig. 1.16(b)

Note: Charge -2δ on O $>$ Charge -2δ on S.

Similarly charge $+2\delta$ on H in NH_3 $>$ charge $+2\delta$ on H in H_2S .

ii. Effect of EN: As O-atom has higher EN than S atom, O-H bond is sufficiently polar i.e. there is a significant more positive charge ($+2\delta$) on H-atoms in H_2O than on H-atoms in H_2S . So, there is greater repulsion between H-atoms in H_2O and H_2S .

Hence $\text{H}-\text{O}-\text{H}$ bond angle $>$ $\text{H}-\text{S}-\text{H}$ bond angle.

iii. Effect of size: O-atom is smaller in size than S-atom. So, the bond length of (O-H) in H_2O is less than the bond length of (S-H) in H_2S . As a result H-atoms in H_2O are quite close so that they repel each other and the bond angle ($\text{H}-\text{O}-\text{H}$) increases to 104.5° and the bond angle ($\text{H}-\text{S}-\text{H}$) decreases to 92.3° .

Alternatively: With the decrease of EN from O (3.5) to Te (2.1), the A-H bonding electron pairs in AH_3 molecules are drawn farther away from the central atom (A) but nearer to H-atom. The effect of this shifting of bonding electron pairs (bp) towards H-atom is that the repulsion between the bonding electron pairs (bp) and lone pairs (lp) on central atom [($bp-lp$) repulsion] increases. The increase in ($bp-lp$) repulsion results in that bonding electron pair come still close to each other and hence the bond angle progressively decreases from H_2O to H_2Te .

Similarly, the decrease in bond angle of the hydrides of group 15 can also be explained.

iv. For AB_x type molecule, the B-A-B bond angle is changed with the change of EN of atom B.

Rule (ii): If the EN of atom B decreases, the bond angle (B-A-B) increases.

$$\text{Bond angle (B-A-B)} \propto \frac{1}{\text{EN of atom B}}$$

This is evident from the data given in Table 1.21.

Table 1.21 Change of bond angle of AB_x molecules with the change of EN of atom B

| | AB_x molecules | EN of B atom | B-A-B angle |
|-----|-------------------------|--------------|----------------------|
| 1. | PF_3 | 4.0 | $\approx 98.5^\circ$ |
| 2. | PCl_3 | 3.0 | 100° |
| 3. | PBr_3 | 2.8 | 101.5° |
| 4. | PI_3 | 2.5 | 102° |
| 5. | AsF_3 | 4.0 | $\approx 90.0^\circ$ |
| 6. | AsCl_3 | 3.0 | 98.4° |
| 7. | AsBr_3 | 2.8 | 100.5° |
| 8. | AsI_3 | 2.5 | 101.5° |
| 9. | NF_3 | 4.0 | 102° |
| 10. | NH_3 | 2.1 | 107° |
| 11. | OF_2 | 4.0 | 103° |
| 12. | OH_2 | 2.1 | 104.5° |

Explanation: The decrease in bond angle, with increase of EN of atom B, the electron pair is attracted more towards more EN atom B, so the bond pairs of electron are away from central atom A, or in other words, the distance between bond pairs is more. As a result the repulsion between the bond pairs in AB_x molecule (with more EN of atom B) is less and the bond angle is less.

For example, bond angle of $\text{NH}_3 > \text{NF}_3$ [see Figs. 1.17(a) and 1.17(b)].

Both NH_3 and NF_3 are pyramidal in shape with one lone pair on N. Since the EN of F $>$ EN of H, the electron pair is attracted more towards F in NF_3 , i.e. bond pairs of electrons are away from N or in other words, the distance between bond pairs is more.

As a result, the repulsion between the bond pairs in NF_3 is less than in NH_3 .

Due to the greater repulsion between the bond pairs in NH_3 than in NF_3 , the bond angle in NH_3 (107°) is greater than that in NF_3 (102°).

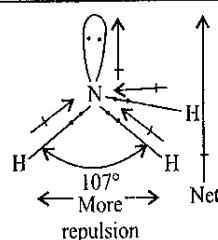


Fig. 1.17(a) NH_3 molecule

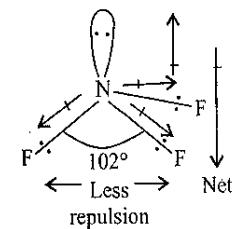


Fig. 1.17(b) NF_3 molecules

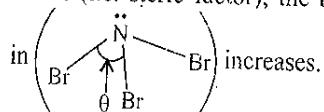
Exception: (i) Bond angle of $\text{NBr}_3 > \text{NH}_3$

(ii) Bond angle of $\text{NMe}_3 > \text{NH}_3$

- i. Expected Bond angle of NH_3 should be greater than NBr_3 but observed bond angle is $\text{NBr}_3 > \text{NH}_3$.

According to Rule (ii), If the EN of atom B decreases, the bond angle increases (EN of H = 2.1, EN of Br = 2.8).

Since size of Br-atom is very large in comparison to the size of H-atom, so due to repulsion between Br atoms (i.e. steric factor), the bond angle $\text{Br}-\text{N}-\text{Br}$



- ii. Similarly, expected bond angle of NH_3 should be greater than NMe_3 but observed bond angle is $\text{NMe}_3 > \text{NH}_3$.

Same explanation as in (i), that is due to steric factor.

Rule iii: Molecules or ions without non-bonding electrons on central atom and having regular geometry, the change in EN of the central atom or the surrounding atom has no effect on the bond angle.

For example, BF_3 , BCl_3 , BBr_3 , etc. all have the same bond angle of 120° . Similarly, CH_4 , CBr_4 , CCl_4 , NH_4^+ etc. have the same bond angle of $109^\circ, 28'$.

Rule iv: For the molecule with same central atom with vacant d -orbitals, and with different B atom, the bond angle increases with the increase of EN of B atom having lone pairs of electrons.

Explanation: For example, bond angle of $\text{PF}_3 > \text{PH}_3$ (opposite to NH_3 and NF_3) (opposite of Rule (ii)).

This is due to back bonding or ($p\pi-d\pi$) multiple bond character. Due to this, PF_3 molecule shows resonance leading to partial bond character as shown in Figs. 1.18 and 1.19.

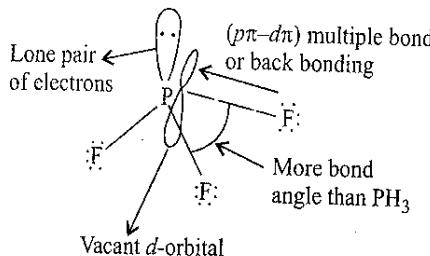
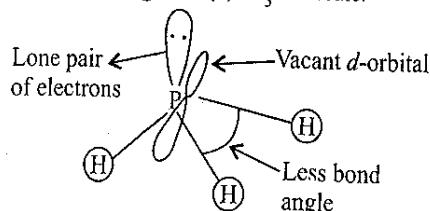


Fig. 1.18 (a) PF_3 molecule.



(Here H-atoms do not have lone pair of electrons for the formation of $p\pi-d\pi$ bond)

Fig. 1.18 (b) PH_3 molecule

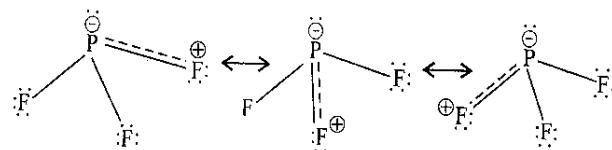


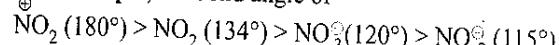
Fig. 1.19 Resonance structures of PF_3 molecule

Due to this, the repulsion between P and F bonds is large and hence the bond angle is large. There is no possibility for the formation of double bonds in PH_3 , although P-atoms have vacant d -orbitals but H-atom does not have lone pair of electron for back donation or for the formation of ($p\pi-d\pi$) multiple bond.

v. State of hybridisation:

Rule v: State of hybridisation (sp , sp^2 , sp^3) is also used to determine the bond angle, since sp , sp^2 and sp^3 hybridisation have 180° , 120° and $109^\circ 28'$ bond angle respectively.

For example, the bond angle of



Explanation:

- NO_2^+ : It has sp hybridisation with bond angle of 180° , as shown below:

Ist formula:

$$\text{Hybridisation (H)} = \frac{1}{2} (V + M - \text{number of +ve charge})$$

where V = number of valence e^- 's (For $N = 2s^2 sp^3$, $\therefore V = 5 e^-$)

M = number of monovalent atom attached to central atom = zero.

$$\therefore H = \frac{1}{2} (5 + 0 - 1) = 2 = sp$$

Alternatively:

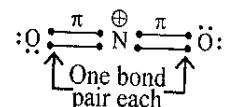
$$H = \text{Number of bond pairs (bp)} + \text{number of lone pairs (lp)}$$

OR

$$= \text{Number of bond pairs (bp)} + \text{number of odd electrons (one unshared } e^-)$$

$$\therefore H = 2 + 0 = 2 = sp$$

Hence the shape of NO_2 is linear with bond angle of 180° .



Note: π bond is excluded in bond pairs

NO_2 : It has sp^2 hybridisation with expected angle of 120° but observed angle is 134° .

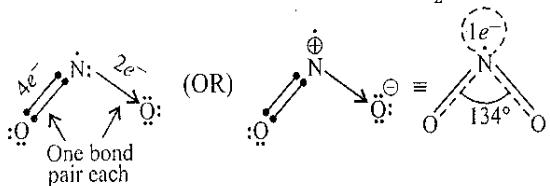
Hybridisation = Number of bond pairs + number of odd e^- s

$$= 2 + 1 = 3 = sp^2$$

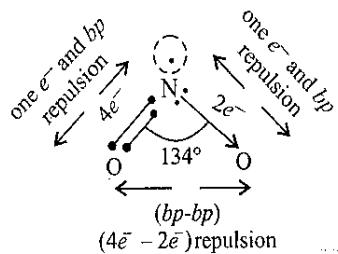
OR

$$\text{Hybridisation} = \frac{1}{2} (V + M + \text{Number of odd } e^-)$$

$$= \frac{1}{2} (5 + 0 + 1) = 3 = sp^2$$

Structure and resonance structures of NO_2 

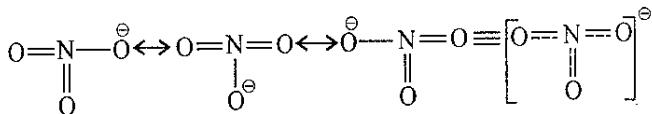
Due to $hp-hp$ repulsion ($4e^- - 2e^-$ repulsion), the bond angle is slightly increased from 120° to somewhat greater than 134° . But there is also a repulsion between one odd electron (or one unshared e^- or one non-bonding e^-) and the bp (i.e. $4e^-$ and $1e^-$ respectively). The bond angle decreases to 134° .



Note: (one $e^- - bp$) repulsion > ($bp - bp$) repulsion.

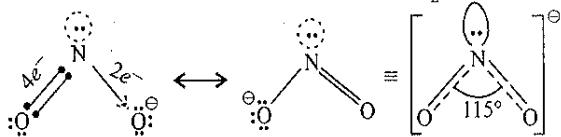
NO_3^{\ominus} : It is sp^2 hybridised with bond angle of 120° . It shows three resonating structures.

$$\begin{aligned} H &= \frac{1}{2} (V + M + \text{number of } -\text{ve charge}) \\ &= \frac{1}{2} (5 + 0 + 1) = 3 = sp^2 \text{ hybrid} \end{aligned}$$



NO_2^{\ominus} : It is sp^2 hybridised with expected bond angle of 120° but observed angle is 115° .

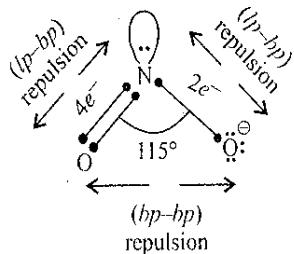
$$\begin{aligned} H &= \frac{1}{2} (V + M + \text{number of } -\text{ve charge}) \\ &= \frac{1}{2} (5 + 0 + 1) = 3 = sp^2 \text{ hybrid} \end{aligned}$$

Structure and resonance structure of NO_2^{\oplus} :

Due to $bp-bp$ repulsion ($4e^- - 2e^-$ repulsion), bond angle is slightly increased from 120° to somewhat greater than 120° . But there is also repulsion between lp and bp repulsion, which decreases the bond angle to 115° .

Note: Here ($lp-bp$) repulsion >> ($bp-bp$) repulsion and also, as in case of NO_2 , ($lp-bp$) repulsion > (one $e^- - bp$) repulsion.

This repulsion produces bending effect in the molecules.



Comparison of bond angle of NO_2 and NO_2^{\oplus} : NO_2 has one non-bonding (or one unshared e^-) whereas NO_2^{\oplus} has one lone pair of electrons (or two non-bonding e^- 's). Hence, ($lp-bp$) repulsion in NO_2^{\oplus} is greater than (one $e^- - bp$) repulsion in NO_2 , hence repulsion on the bond pairs is more and the bond angle is less in NO_2^{\oplus} as compared to bond angle in NO_2 .

Note:

- NO_2^{\oplus} is sp hybridised and linear, bond angle is 180° .
- NO_2 is bent, due to (one $e^- - bp$) repulsion, bond angle is 134° .
- NO_3^{\ominus} is sp^2 hybridised and planar, bond angle is 120° .
- NO_2^{\oplus} is bent, due to ($lp-bp$) repulsion, bond angle is 115° .

Therefore, decreasing order of bond angle is

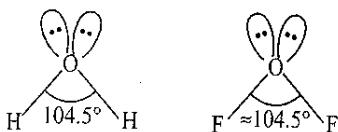
$$\text{NO}_2^{\oplus} > \text{NO}_2 > \text{NO}_3^{\ominus} > \text{NO}_2^{\oplus}$$

QUESTION PAPER

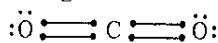
- In which of the following triatomic molecules, the observed bond angle is $116^\circ, 49'$?
 - H_2O
 - OF_2
 - CO_2
 - O_3
- In which of the following molecules, bond angle is the maximum?
 - Be Br_2
 - H_2O
 - H_2S
 - CH_4
- In which of the following molecules, bond angle between two adjacent covalent bonds is smallest?
 - Be H_2
 - BF_3
 - NH_3
 - CCl_4
- Bond angle ($\text{H}-\text{S}-\text{H}$) in H_2S is close to
 - 109°
 - 107°
 - 105°
 - 90°
- The hybridisation of B in BF_3 is sp^2 . The bond angle in BF_4^{\ominus} will be
 - 107°
 - 109°
 - 120°
 - 180°
- Which of the following molecules contains a bond angle which is smaller than the bond angle in CH_4 ?
 - SF_6
 - SO_2
 - O_3
 - NH_4^{\oplus}

Sol. I. (d)

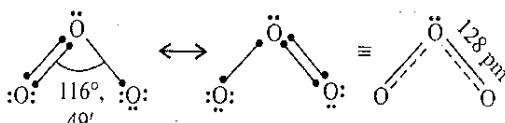
For (a) and (b): $\text{H}_2\ddot{\text{O}}$ and $\ddot{\text{O}}\text{F}_2$ both are bent molecules in which O-atom is sp^3 hybridised. Due to ($lp-lp$), ($lp-bp$) and ($bp-bp$) repulsion, the bond angle is close to 104° .



- c. In CO_2 , C is sp hybridised and it is linear molecule with bond angle of 180° .

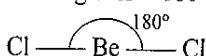


- d. Only in O_3 , bond angle is close to $116^\circ 49'$, because the central O atom is sp^2 hybridised. Hence the answer is (d).



II (a)

- a. In BeCl_2 , Be is sp hybridised and it is linear molecule so the bond angle is $= 180^\circ$.



- b. In $\text{H}_2\ddot{\text{O}}$, O is sp^3 hybridised and due to repulsion between ($lp-lp$), ($lp-bp$) and ($bp-bp$), the bond angle is 104.5° .

- c. In $\text{H}_2\ddot{\text{S}}$, S is sp^3 hybridised but according to rule (i), the bond angle is 92.3° .

- d. In CH_4 , C is sp^3 hybridised, since there is no lone pair of electrons, thus only ($bp-bp$) repulsions. Hence the bond angle is $109^\circ 28'$.

Thus the answer is (a).

III (c)

- a. Be H_2 is linear, the bond angle is 180° .

- b. BF_3 is trigonal planar, the bond angle is 120° .

- c. In $\ddot{\text{N}}\text{H}_3$, N is sp^3 hybridised and due to greater repulsion between ($lp-bp$) and ($bp-bp$) the bond angle is reduced to 107° .

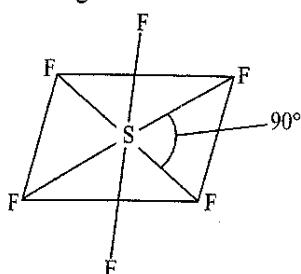
- d. In CCl_4 , C is sp^3 hybridised, the bond angle is $109^\circ 28'$ as explained above for CH_4 .

IV (d): Refer to Section 1.17, Point 3(a).

V (b): In BF_4^- , B is sp^3 hybridised and the bond angle is $109^\circ 28'$.

VI (a)

- a. In SF_6 , S is sp^3d^2 hybridised having octahedral shape, each bond angle is 90° .



- b. In $\ddot{\text{S}}\text{O}_2$ ($\text{O}=\ddot{\text{S}}=\text{O}$), S is sp^2 hybridised but due to greater repulsion between ($lp-bp$) and ($bp-bp$), the angle is reduced to 118° .

- c. O_3 is sp^2 hybridised and the bond angle is 116° as explained above in Illustration 1.54 (I) (d).

- d. $\ddot{\text{NH}}_4^+$ is sp^3 hybridised, since due to the absence of lone pair electrons on N atom, thus only ($bp-bp$) repulsions, so bond angle is $109^\circ 28'$.

Hence the answer is (a).

1.18 PERIODIC TRENDS IN CHEMICAL PROPERTIES (SOME OTHER PERIODIC PROPERTIES)

Some of the trends in chemical properties of elements are described below.

1.18.1 Periodicity of Valence or Oxidation States

The valence or oxidation state is very important property of elements and can be understood in terms of their electronic configuration.

The electrons present in the outermost shell of an atom are called **valence electrons**, and their numbers determine the valence or valency of the atom.

The valence of the s and p block (representative) elements is usually equal to the number of electrons in the outermost orbitals and/or equal to eight minus the number of the outermost electrons as shown below:

| Group | 1 | 2 | 13 | 14 | 15 | 16 | 17 | 18 |
|----------------------------|---|---|----|----|------|------|------|------|
| Number of valence electron | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
| Valence | 1 | 2 | 3 | 4 | 3, 5 | 2, 6 | 1, 7 | 0, 8 |

However, transition and the inner transition elements show variable valence due to the participation of not only the valence electrons but *d*- and *f*-electrons also in the bond formation. But their most common valence are 2 and 3.

- 1. Variation of valence in period:** Along the period (\rightarrow) the number of valence electrons increases from 1 to 18. But the valence of elements, w.r.t. H or O first increases from 1 to 4 and then decreases to zero. These trends are observed in the valence of hydrides and oxides and are shown in Table 1.22.

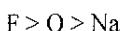
Table 1.22 Periodic trends in valence of elements as shown by the formulas of their compounds

| Group | 1 | 2 | 13 | 14 | 15 | 16 | 17 |
|----------------------------|--------------|----------------|------------------------|---------------|---------------|----------------------|-------------|
| For- mula of hydride | LiH | CaH_2 | B_2H_6 | CH_4 | NH_3 | H_2O | HF |

| | | | | | | | | | | |
|--------------------------|-----------------------|--------------|-------------------------|----------------|--|-------------------------|---|----------------|-----|-------------------------|
| For- mula of oxide | Li_2O | MgO | B_2O_3 | CO_2 | $\text{N}_2\text{O}_3, \text{N}_2\text{O}_5$ | SiO_2 | $\text{P}_4\text{O}_6, \text{P}_4\text{O}_{10}$ | SO_3 | ... | Cl_2O_7 |
| | Na_2O | CaO | Al_2O_3 | GeO_2 | $\text{As}_2\text{O}_3, \text{As}_2\text{O}_5$ | SnO_2 | $\text{Sb}_2\text{O}_3, \text{Sb}_2\text{O}_5$ | SeO_3 | ... | |
| | K_2O | SrO | Ga_2O_3 | PbO_2 | $\text{Bi}_2\text{O}_3 \dots$ | In_2O_3 | | TeO_3 | ... | |
| | | | | | | | | | | |

To explain the concept of valence or oxidation state, consider the two compounds containing oxygen, OF_2 and Na_2O .

The decreasing order of EN of F, O and Na are



Outer electronic configuration of F = $2s^2 2p^5$.

Each of the atom of F shares one electron with oxygen in the OF_2 molecule. Being the highest electronegative element, fluorine is given oxidation state -1. Since there are two fluorine atoms in this molecule, oxygen with the outer electronic configuration $2s^2 2p^4$ shares two electrons with fluorine atoms and thereby exhibits oxidation state +2.

In Na_2O , oxygen being more electronegative accepts two electrons, one from each of the two sodium atoms and, thus, shows oxidation state -2. On the other hand, sodium with electronic configuration $3s^1$ loses one electron to oxygen and is given oxidation state +1.

Thus, the oxidation state of an element in a particular compound can be defined as the charge acquired by its atom on the basis of electronegative consideration from other atoms in the molecule.

2. Variation of valence in a group: Down the group (\downarrow), the number of valence electrons remains the same, so all the elements in the same group exhibit the same valence.

Illustration 1.55: Using the periodic table, predict the formulas of compounds which might be formed by the following pairs of elements: (a) silicon and bromine (b) aluminium and sulphur. (NCERT Example 3.7)

Sol.

- Silicon is group 14 element with a valence of 4; bromine belongs to the halogen family with a valence of 1. Hence, the formula of the compound formed would be SiBr_4
- Aluminium belongs to group 13 with a valence of 3; sulphur belongs to group 16 elements with a valence of 2. Hence, the formula of the compound formed would be Al_2S_3 .

1.19 TYPICAL ELEMENTS

Elements of third period are also called as **typical elements**. These include Na, Mg, Al, Si, P, S, Cl. The properties of all elements belonging to a particular group resemble the properties of the corresponding typical element of that group. For example, the general properties of alkali metal can be predicted from the behaviour of Na, not Li, the first member of the family.

The typical elements (all having $n = 3$) can take up 18 electrons. Note that for these elements $3d$ sub-shell is available

but it is not filled, i.e. these have vacant d sub-shell. This is not the case with second period elements, hence they have somewhat different properties than the rest of the group or we can say that it is the typical element, which in true sense represents a group.

1.20 BRIDGE ELEMENTS

Elements of the IIInd period are also called as **bridge elements**. The properties of these elements resemble the properties of elements of the IIIrd period placed diagonally, as shown.

| IIInd period | Li | Be | B | C | |
|---|----|----|----|----|---|
| IIIrd period | Na | Mg | Al | Si | P |
| | 1 | 2 | 3 | 4 | |
| Number of group = 4 | | | | | |
| Number of periods = 2 | | | | | |
| Pairs of elements diagonally placed = 3 | | | | | |

1.21 ANOMALOUS PROPERTIES OF THE IIIND PERIOD ELEMENTS (DIAGONAL RELATIONSHIP)

The first element of each of the groups 1 (lithium) and 2 (beryllium) and groups 13–17 (boron to fluorine) differs in many respects from the other members of their respective groups.

For example, lithium unlike other alkali metals, and beryllium unlike other alkaline earth metals, form compounds with significant covalent character, the other members of these groups mainly form ionic compounds. The behaviour of lithium and beryllium is more similar with the second element of the following group, i.e. Mg and Al respectively. This is called **diagonal relationship** in the periodic properties.

| Property | Element | | |
|---|---------------------------|--------------------------|-----------|
| | Li | Be | B |
| Metallic radius (M/pm) | 152 | 111 | 88 |
| | Na 186 | Mg 160 | Al 142 |
| Ionic radius ($\text{M}^\oplus/\text{pm}$) | Li^\oplus 76 | Be^\oplus 31 | |
| | Na^\oplus 102 | Mg^\oplus 72 | |

The anomalous behaviour is due to the

- small size
- high charge density (charge/radius) ratio
- high polarising power [Ionic charge/(Ionic radius) 2]
- high EN of the element

Explanation:

- Along the period (\rightarrow), EN of the element increases while down the group (\downarrow) electropositivity of the elements increases or EN decreases.

These two effects tend to cancel each other in moving diagonally from the top left to the bottom right. Therefore, the elements diagonally related in this way tend to have similar properties. They form similar compounds though the valency is different. Sometimes the diagonal relationship is explained in terms of polarising power $\left[\frac{\text{Ionic charge}}{(\text{Ionic radius})^2} \right]$. On moving along a period, the charge

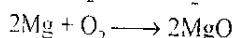
on the ions increases while ionic size decreases hence polarising power increases. On moving down the group the ionic size increases and hence polarizing power decreases. On moving diagonally these two effects cancel each other to some extent and hence properties remain similar.

- The first member of the group has only four valence orbitals ($2s$ and $2p$) available for bonding, whereas the second member of the groups has nine valence orbitals ($3s$, $3p$ and $3d$). As a consequence of this, the maximum covalency of the first member of each group is 4, e.g. boron can only form $[\text{BF}_4^-]$, whereas the other members of the groups can expand their valence shell to accommodate more than four pairs of electrons, e.g. aluminium forms $[\text{AlF}_6]^{3-}$.
- Because of the smaller size and the higher EN, the first member of p -block elements displays greater ability to form $p\pi-p\pi$ multiple bonds to itself (e.g. $\text{C}=\text{C}$, $\text{C}\equiv\text{C}$, $\text{N}=\text{N}$, $\text{N}\equiv\text{N}$) and to the other second period elements (e.g. $\text{C}=\text{O}$, $\text{C}=\text{N}$, $\text{C}\equiv\text{N}$, $\text{N}=\text{O}$) compared to subsequent members of the same group.

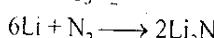
1.21.1 Diagonal Relationship Between Lithium and Magnesium (Chemical Properties)

As an illustration, let us consider diagonal relationship between lithium and magnesium.

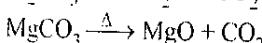
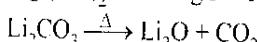
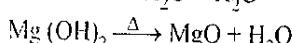
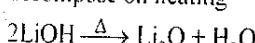
- Ionic radius of Li^+ is 0.60 \AA and that of Mg^{2+} is 0.65 \AA .
- Li and Mg react with oxygen to form normal oxides.



- Both of them react with nitrogen to form nitrides, Li_3N and Mg_3N_2



- Their hydroxides and carbonates are unstable and decompose on heating



- Their halides and alkyls being covalent in character are soluble in organic solvents.

1.21.2 Similarities Between Lithium and Magnesium

- Both combine directly with nitrogen and their nitrides with water give ammonia.
- Both do not form solid bicarbonates.
- Hydroxides of both give oxides on heating.
- Their fluoride carbonates and phosphates are less soluble.

1.21.3 Similarities Between Beryllium and Aluminium

- Both are silvery white, good conductors of electricity.
- Both become passive with conc. HNO_3 .
- Their hydroxides are amphoteric.
- They liberate hydrogen from acids and alkalis.
- Both combine with nitrogen, carbon, silicon and boron.

Illustration 1.56 Are the oxidation state and covalency of Al in $[\text{AlCl}(\text{H}_2\text{O})_5]^{2+}$ same? (NCERT Example 3.8)

Sol. No. The oxidation state of Al is +3 and the covalency is 6.

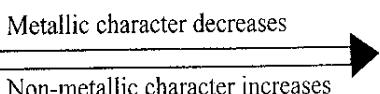
1.22 PERIODIC TRENDS AND CHEMICAL REACTIVITY

It has been observed that there is a periodic trend in certain fundamental properties such as atomic and ionic radii, ionisation enthalpy, electron gain enthalpy and valence, and the periodicity is related to electronic configuration. That is, all chemical and physical properties depend on the electronic configuration of elements.

- Relationships between these fundamental properties of elements with their chemical reactivity:** The atomic and ionic radii generally decrease along the period (\rightarrow). As a consequence, the ionisation enthalpies generally increase (with some exceptions) and electron gain enthalpies become more negative across a period. In other words, the ionization enthalpy of the extreme left element in a period is the least and the electron gain enthalpy of the element on the extreme right is the highest negative. (It is noted that noble gases having completely filled shells have rather positive electron gain enthalpy values.) This results into high chemical reactivity at the two extremes and the lowest in the centre. Thus, the maximum chemical reactivity at the extreme left (among alkali metals) is shown by the loss of an electron leading to the formation of a cation and at the extreme right (among halogens) shown by the gain of an electron forming an anion.

This property can be related with the reducing and oxidising behaviour of the elements.

It can be directly related to the metallic and non-metallic character of elements. Thus, the metallic character of an element, which is highest at the extremely left decreases and the non-metallic character increases along the period.



The chemical reactivity of an element is shown by its reactions with oxygen and halogens. Elements on two extremes of a period easily combine with oxygen to form oxides.

The normal oxide formed by the element on extreme left is the most basic (e.g. Na_2O), whereas that formed by the element on extreme right is the most acidic (e.g. Cl_2O_7).

Oxides of elements in the centre are amphoteric (e.g. Al_2O_3 , As_2O_3) or neutral (e.g. CO , NO , N_2O). Amphoteric oxides behave as acidic with bases and as basic with acids, whereas neutral oxides have no acidic or basic properties.

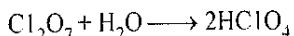
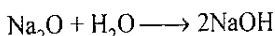
2. Among transition metals ($3d$ series), the change in atomic radii is much smaller as compared to those of representative elements across the period. The change in atomic radii is still smaller among inner-transition metals ($4f$ -series). The ionisation enthalpies are intermediate between those of s - and p -blocks. As a consequence, they are less electropositive than group 1 and 2 metals.

In a group, the increase in atomic and ionic radii with the increase in atomic number generally results in a gradual decrease in ionisation enthalpies and a regular decrease (with exception in some third period elements) in electron gain enthalpies in the case of main group elements.

Illustration 1.57 Show by a chemical reaction with water that Na_2O is a basic oxide and Cl_2O_7 is an acidic oxide.

(NCERT Ex. 3.10)

Sol. Na_2O with water forms a strong base whereas Cl_2O_7 forms strong acid.



Their basic or acidic nature can be qualitatively tested with litmus paper.

Illustration 1.58 Predict the formulae of the stable binary compounds that would be formed by the following pairs of compounds:

- a. Al and Cl
- b. Mg and I
- c. Element 113 and F
- d. Si and S
- e. Element 119 and oxygen.

Sol. a. Al is an element of group 13 with $3e^-$ in its valence shell. Therefore, its valence = 3.

Cl is an element of group 17, with $> 7e^-$ in its valence shell therefore its valence = $8 - 7 = 1$.

$$\therefore \text{Formula} = \text{AlCl}_3$$

b. Mg is an element of group 2, with $2e^-$ in its valence shell. Therefore, its valence = 2.

I is an element of group 17, with $> 7e^-$ in its valence shell. Therefore, its valence = $8 - 7 = 1$.

$$\therefore \text{Formula} = \text{MgCl}_2$$

c.

| | | | |
|-------------------|----------------------|---------|------------|
| Lanthanide series | Atomic number 57–71 | Group 3 | 6th Period |
| Actinide series | Atomic number 89–103 | Group 3 | 7th Period |

Element (X) (At. no. = 113) lies in group 13, and 7th period. Hence, its outer shell electronic configuration is $7s^27p^1$, therefore its valence = 3.

F belongs to group 17 with $7e^-$ in its valence shell. Therefore, its valence = $8 - 7 = 1$.

$$\therefore \text{Formula} = \text{XF}_3$$

d. Si is an element of group 14 with $4e^-$ in its valence shell. Therefore, its valence = 4.

S is an element of group 16 with $6e^-$ in its valence shell. Therefore, its valence = $8 - 6 = 2$.

$$\therefore \text{Formula} = \text{SiS}_2$$

e. Element (X) (Z = 119) lies in group 1, and 8th period. Hence its outer shell electronic configuration is $8s^1$. Therefore, its valence = 1.

O is an element of group 16 with $6e^-$ in its valence shell. Therefore, its valence = $8 - 6 = 2$.

$$\therefore \text{Formula} = \text{X}_2\text{O}$$

| | | | | | | | | | | | | | | | | | | |
|---------------|-----|-----|---|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Group | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 |
| Atomic number | | | | 104 | 105 | 106 | 107 | 108 | 109 | 110 | 111 | 112 | 113 | 114 | 115 | 116 | 117 | 118 |
| | 119 | 120 | | | | | | | | | | | | | | | | |

$\leftarrow s\text{-block}$ $d\text{-block}$ \star $\rightarrow p\text{-block}$

1.23 MAGNETIC PROPERTIES OF ELEMENTS

Each element has some kind of magnetic properties associated with it. These properties are direct consequence of the electronic configuration of the atom. When a magnetic field is applied to substances, mainly two types of magnetic behaviour are

observed: (i) Diamagnetism and (ii) Paramagnetism.

1. Diamagnetic substances are weakly repelled by the magnetic applied field and have all the electrons paired in their atoms, e.g. NaCl and H_2O .
2. Paramagnetic substances are attracted by the magnetic

applied field and has one or more unpaired electrons in their atoms, e.g. Cu^{2+} , Fe^{3+} , Cr^{3+} and O_2^- .

Substances which are strongly attracted by the magnetic applied field are said to be **ferromagnetic**. In fact, ferromagnetism is an extreme form of paramagnetism.

3. Ferromagnetic substances keep their magnetism even after the field is removed while paramagnetic and diamagnetic substances fail to do so. Fe, Co and Ni are some examples of ferromagnetic substances.
4. Paramagnetism is due to the presence of unpaired electrons. An electron in an atom which has two types of motion, one of its motion is about the nucleus (orbital angular momentum), and the other is its spin about its own axis (spin angular momentum).
- A single electron spinning about its own axis generates a magnetic field. For two electrons in an orbital, the spins are opposite and hence the fields cancel each other, hence they have zero magnetic moment value.
5. When there are one or more unpaired electrons in them, the unpaired electron gives rise to a magnetic field on account of its spin and because of the angular orbital moment.
6. Magnetic moment (μ_{S+L}) of the first row of transition metal ions is given by general formula:

$$\mu_{S+L} = \sqrt{4S(S+1) + L(L+1)}$$

where, S is the sum of spin quantum numbers and L = sum of the orbital angular momentum quantum numbers.

For an electron, spin quantum number, $S = \pm 1/2$. Hence, $S = s \times n$ (n = number of unpaired electrons).

For the compounds of the first series of transition metals, the contribution of the orbital angular momentum is effectively quenched and hence is of no significance. For these the magnetic moment is determined by the number of unpaired electrons and is calculated by using ‘spin only’ formula. Taking $L = 0$, the magnetic moment is given as

$$\mu_s = \sqrt{4S(S+1)}$$

In terms of n (number of unpaired electrons), μ_s is given by

$$\mu_s = \sqrt{n(n+2)} \text{ BM (Bohr magneton)}$$

7. It is measured in Bohr magneton (BM).

$$1 \text{ BM} = \frac{e\hbar}{4\pi mc} = 9.27 \times 10^{-21} \text{ ergs gauss}^{-1}$$

or $9.27 \times 10^{-24} \times \text{J Tesla}^{-1}$ or $9.27 \times 10^{-24} \text{ A m}^2$

where \hbar is the Planck’s constant, e is the electronic charge, c is the velocity of light and m is the mass of electrons.

Note: The orbital motion in $4f$ orbitals is not quenched, as in the case of d -block elements. Hence the observed paramagnetism in $4f$ -block elements is due to both orbital motion of the electron and its spinning round its axis.

$$\text{When } n = 1, \mu_s = \sqrt{1(1+2)} = \sqrt{3} = 1.73 \text{ BM}$$

$$n = 2, \mu_s = \sqrt{2(2+2)} = \sqrt{8} = 2.83 \text{ BM}$$

$$n = 3, \mu_s = \sqrt{3(3+2)} = \sqrt{15} = 3.87 \text{ BM}$$

and so on.

$\therefore \mu_s \propto n$ (number of unpaired e^- s).

1.23.1 Experimental Verification of Diamagnetic and Paramagnetic Nature of Substances

It is found by weighing the substance, first in the air and then in the presence of magnetic field. If the weight of the substance is less in the magnetic field, it shows that it is repelled by the magnetic field and hence it is diamagnetic.

If the weight of the substance is more in the magnetic field, it shows that it is attracted by the magnetic field and hence it is paramagnetic, as shown in Figs. 1.20(a), 1.20(b) and 1.20(c).

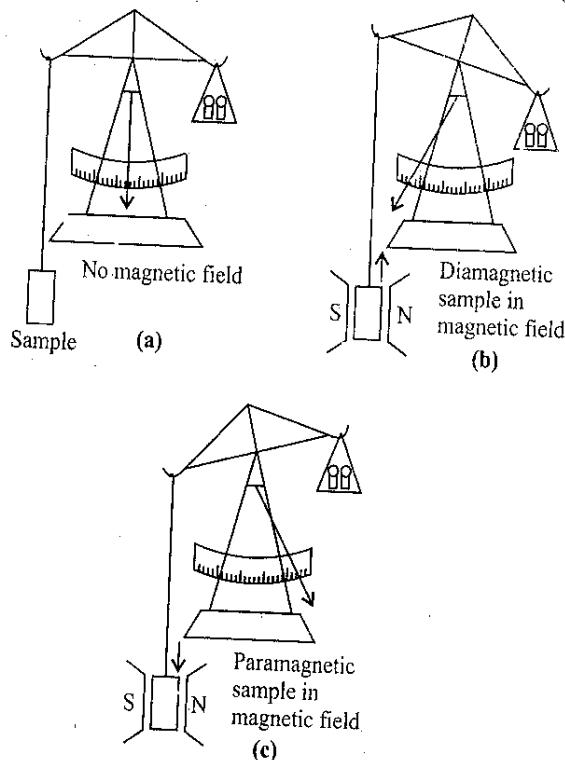


Fig. 1.20 (a) Weight of the substance in the absence of magnetic field.

(b) Substance repelled by the magnetic field—Diamagnetic.

(c) Substance attracted by magnetic field—Paramagnetic.

The magnetic moments calculated from the ‘spin-only’ formula and those derived experimentally for some of the ions of the first row transition elements are given in Table 1.23. The experimental data are mainly for hydrated ions in solution or in the solid state.

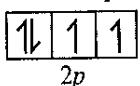
Table 1.23 Magnetic moments of some ions of 3d series

| Ion | Configuration | Unpaired electron(s) | Magnetic moment (BM) | |
|------------------------------|--|----------------------|------------------------------------|----------|
| | | | Calculated | Observed |
| Sc ³⁺ (Z = 21) | Sc = 3d ¹ 4s ² ⇒ Sc ³⁺ = 3d ⁰ 4s ⁰ | 0 | $\mu_s = \sqrt{n(n+2)} = 0$ | 0 |
| Ti ³⁺ (Z = 22) | Ti = 3d ² 4s ² ⇒ Ti ³⁺ = 3d ¹ 4s ⁰ | 1 | $\sqrt{1(1+2)} = \sqrt{3} = 1.73$ | 1.75 |
| Ti ²⁺ (Z = 22) | Ti ²⁺ = 3d ² 4s ⁰ | 2 | $\sqrt{2(2+1)} = \sqrt{8} = 2.84$ | 2.76 |
| V ²⁺ (Z = 23) | V = 3d ³ 4s ² V ²⁺ = 3d ³ 4s ⁰ | 3 | $\sqrt{3(3+2)} = \sqrt{15} = 3.87$ | 3.86 |
| Cr ²⁺ (Z = 24) | Cr = 3d ⁵ 4s ¹ Cr ²⁺ = 3d ⁴ 4s ⁰ | 4 | $\sqrt{4(4+2)} = \sqrt{24} = 4.90$ | 4.80 |
| Mn ²⁺ (Z = 25) | Mn = 3d ⁵ 4s ² Mn ²⁺ = 3d ⁵ 4s ⁰ | 5 | $\sqrt{5(5+2)} = \sqrt{35} = 5.92$ | 5.96 |
| Fe ²⁺ (Z = 26) | Fe = 3d ⁶ 4s ² [1] [1] [1] [1] [1] [1] Fe ²⁺ = 3d ⁶ 4s ⁰ | 4 | $\sqrt{4(4+2)} = \sqrt{24} = 4.90$ | 5.3–5.5 |
| Co ²⁺ (Z = 27) | Co = 3d ⁷ 4s ² [1] [1] [1] [1] [1] [1] [1] Co ²⁺ = 3d ⁷ 4s ⁰ | 3 | $\sqrt{3(3+2)} = \sqrt{15} = 3.87$ | 4.4–5.2 |
| Ni ²⁺ (Z = 28) | Ni = 3d ⁸ 4s ² [1] [1] [1] [1] [1] [1] [1] [1] Ni ²⁺ = 3d ⁸ 4s ⁰ | 2 | $\sqrt{2(2+2)} = \sqrt{8} = 2.84$ | 2.9–3.4 |
| Cu ²⁺ (Z = 29) | [1] [1] [1] [1] [1] | 1 | $\sqrt{1(1+2)} = \sqrt{3} = 1.73$ | 1.8–2.2 |
| Zn ²⁺ (Z = 30) | [1] [1] [1] [1] [1] | 0 | $\sqrt{0(0+2)} = 0$ | 0 |

Illustration 1.59 Give the decreasing order of magnetic moment of the following:

- a. Ca b. Al c. N d. O

- Sol. a. Electronic configuration of Ca = 4s²; n = 0, $\mu = 0$.
 b. Electronic configuration of Al = 3s² 3p¹; n = 1, $\mu = \sqrt{3}$.
 c. Electronic configuration of N = 2s² 2p³; n = 3, $\mu = \sqrt{15}$.
 d. Electronic configuration of O = 2s² 2p⁴; n = 2, $\mu = \sqrt{8}$



Hence, the decreasing order of magnetic moment or paramagnetism is

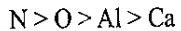


Illustration 1.60 Which element in 3d, 4d and 5d transition series has the highest paramagnetism in

- a. elemental form b. +1 O.S.

c. +2 O.S. d. +3 O.S.
[O.S. = oxidation state]

Sol.

| Group | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
|-------|----|----|----|----|----|----|----|----|----|----|
| 3d | 21 | 22 | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 |
| Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn | |
| 4d | 39 | 40 | 41 | 42 | 43 | 44 | 45 | 46 | 47 | 48 |
| Y | Zr | Nb | Mo | Tc | Ru | Rh | Pd | Ag | Cd | |
| 5d | 57 | 72 | 73 | 74 | 75 | 76 | 77 | 78 | 79 | 80 |
| La | Hf | Ta | W | Re | OS | Ir | Pt | Au | Hg | |

- a. In elemental form:

$$\begin{aligned} \text{3d series: Cr } (Z=24) \Rightarrow 3d^5 4s^1; n=6, \mu &= \sqrt{6+(6+2)} \\ &= \sqrt{48} \text{ BM} \end{aligned}$$

$$\text{4d series: Mo } (Z=42) \Rightarrow 4d^5 5s^1; n=6, \mu = \sqrt{48} \text{ BM}$$

$$\text{5d series: W } (Z=74) \Rightarrow 5d^4 6s^2; n=4, \mu = \sqrt{24} \text{ BM}$$

But Re has the highest number of unpaired e⁻, as shown:

$$\text{Re } (Z=75) \Rightarrow 5d^6 6s^2; n=5, \sqrt{35} \text{ BM}$$

b. In +1 oxidation state:

3d series: Mn ($Z = 25$) $\Rightarrow 3d^5 4s^2$, $Mn^{1+} = 3d^5 4s^1$; $n = 6$, $\mu = \sqrt{48}$ BM

4d series: Tc ($Z = 43$) $\Rightarrow 4d^5 5s^2$, $Tc^{1+} = 4d^5 5s^1$; $n = 6$, $\mu = \sqrt{48}$ BM

5d series: Re ($Z = 75$) $\Rightarrow 5d^5 6s^2$, $Re^{1+} = 5d^5 6s^1$; $n = 6$, $\mu = \sqrt{48}$ BM

c. In +2 oxidation state:

3d series: Mn ($Z = 25$) $\Rightarrow 3d^5 4s^2$, $Mn^{2+} = 3d^5 4s^0$; $n = 5$, $\mu = \sqrt{35}$ BM

4d series: Tc ($Z = 43$) $\Rightarrow 4d^5 5s^2$, $Tc^{2+} = 4d^5 5s^0$; $n = 5$, $\mu = \sqrt{35}$ BM

5d series: Re ($Z = 75$) $\Rightarrow 5d^5 6s^2$, $Re^{2+} = 5d^5 6s^0$; $n = 5$, $\mu = \sqrt{35}$ BM

d. In +3 oxidation state:

3d series: Fe ($Z = 26$) $\Rightarrow 3d^6 4s^2$, $Fe^{3+} = 3d^5 4s^0$; $n = 5$, $\mu = \sqrt{35}$ BM

4d series: Ru ($Z = 44$) $\Rightarrow 4d^7 5s^1$ (exception electronic configuration).

$$\therefore Ru^{3+} = 4d^5 5s^0; n = 5, \mu = \sqrt{35} \text{ BM}$$

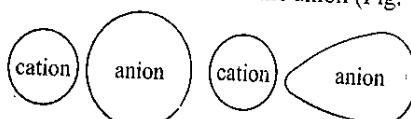
5d series: Os ($Z = 76$) $\Rightarrow 5d^6 7s^2$, $Os^{3+} = 5d^5 7s^0$; $n = 5$, $\mu = \sqrt{35}$ BM

Note:

- From the above calculation it is clear that in the elemental form (zero OS), group 6 has the highest μ , except W, in 5d series, but it is Re of group 7.
- In +1 OS, group 7 has the highest μ .
- In +2 OS, again group 7 has the highest μ .
- In +3 OS, group 8 has the highest μ .

1.24 FAJANS' RULE AND CHANGE OF IONIC CHARACTER TO COVALENT CHARACTER

When two oppositely charged ions of unequal size approach each other closely (during formation of an electrovalent bond), the ion smaller in size attracts the outermost electrons of the other ion and repels its nuclear charge. The net result is distortion or polarisation of the bigger ion. This distortion is usually done by the cation as its size is smaller than the anion (Fig. 1.21).



(a) No polarisation (b) Polarised anion

Fig. 1.21 Representation of polarisation

The electron cloud of anion no longer remains symmetrical but is elongated towards the cations. The ability of a cation to polarise the nearby anion is called its **polarising power** and the tendency of an anion to get distorted or deformed or polarised by

the cation is called its **polarisability**. Due to polarisation, sharing of electrons occurs between two ions to some extent and the bond shows some covalent character. This is shown in Fig. 1.21.

Polarising power of cation (ϕ) is calculated as

$$\phi = \frac{\text{Ionic charge}}{(\text{Ionic radius})^2}$$

The magnitude of polarisation depends upon a number of factors or the increased covalent character is favoured by a number of factors. These factors were suggested by Fajans' and are known as **Fajans' rules**.

1.24.1 Fajans' Rules

1. Charge on the cation: As the charge on the cation increases, its tendency to polarise the anion increases. This brings more and more covalent nature in the electrovalent compound.

For example, in the case of $NaCl$, $MgCl_2$ and $AlCl_3$ charge of cation increases and polarisation increases, thereby covalent character becomes more and more as the charge on the cation increases.

| Cation | Cation charge | Formula of the chloride | Melting point of the chloride, °C |
|-----------|---------------|-------------------------|-----------------------------------|
| Na^{+} | +1 | $NaCl$ | 800 Covalent |
| Mg^{2+} | +2 | $MgCl_2$ | 712 Character |
| Al^{3+} | +3 | $AlCl_3$ | Sublimes Increases |

Similarly, lead forms two chlorides $PbCl_2$ and $PbCl_4$ having charges +2 and +4 respectively. $PbCl_4$ shows covalent nature.

In general, if a metal forms more than one halide, the halide having higher charge on the cation (i.e. higher oxidation state) is usually more covalent in nature in comparison to halide having a cation with lower charge, i.e. lower oxidation state or in other words, the melting point of the halide having higher oxidation state is less than the melting point of halide having lower oxidation state.

2. Size of the cation: Polarisation of the anion increases as the size of the cation decreases, i.e. the electrovalent compounds having smaller cations show more of the covalent nature. For example, in the case of halides of alkaline earth metals, the covalent character decreases.

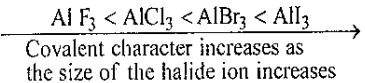
| Cation | Radius of the cation (Å) | Formula of the chloride | Melting point of the chloride, °C |
|-----------|--------------------------|-------------------------|---------------------------------------|
| Be^{2+} | 0.31 | $BeCl_2$ | 405 ↑ Covalent character increases |
| Mg^{2+} | 0.65 | $MgCl_2$ | 712 ↑ Melting point decreases |
| Ca^{2+} | 0.99 | $CaCl_2$ | 772 |
| Sr^{2+} | 1.13 | $SrCl_2$ | 872 |
| Ba^{2+} | 1.35 | $BaCl_2$ | 960 |

Low melting point indicates more covalent nature.

- 3. Size of the anion:** The larger the size of the anion, more easily it will be polarised by the cation, i.e. as the size of the anion increases for a given cation, the covalent character increases. For example, in the case of halides of calcium, the covalent character increases from F^- anion to I^- anion.

| Cation | Anion | Anion size (\AA) | Formula of the halide | Melting point of the halide, $^{\circ}\text{C}$ | | |
|------------------|---------------|-----------------------------|-----------------------|---|---|--|
| Ca^{2+} | F^- | 1.36 | CaF_2 | 1932 | ↓ Covalent character increases ↓ Melting point decreases | |
| | Cl^- | 1.81 | CaCl_2 | 772 | | |
| | Br^- | 1.95 | CaBr_2 | 730 | | |
| | I^- | 2.16 | CaI_2 | 575 | | |

Similarly, in the case of trihalides of aluminium, the covalent character increases with the increase in size of the halide anion.



- 4. Configuration of the cation:** The cations with 18 electrons in the outermost shell bring greater polarisation of the anion than those with inert gas configuration, even if both the cations have same size and same charge. For example, CuCl is more covalent than NaCl .

| Ion | Cu^{2+} | Na^{+} |
|---------------|------------------------|------------------------|
| Size | 0.96 \AA | 0.95 \AA |
| Compound | CuCl | NaCl |
| Melting point | 442 $^{\circ}\text{C}$ | 800 $^{\circ}\text{C}$ |

In general, all those electrovalent compounds having high values of polarisation (more covalent character) are found to be less soluble in water but more soluble in organic solvents.

The following examples support this view:

- Sulphides are less soluble in water than oxides of the same metal.
- Lithium salts are soluble in organic solvents.
- Beryllium compounds are less soluble than the corresponding other alkaline earth metal compounds.
- The solubility of aluminium halides decreases from AlF_3 to AlI_3 .

Points to remember:

- On moving down a group, the polarising power of the cations goes on decreasing.
- Polarising power of the cations increases in moving from the left to the right in a period.
- The polarisability of the anions by a given cation decreases in moving from the left to the right in a period.
- The polarisability of the anions by a given cation increases moving down a group.

5. Increase of polarisation brings more of covalent character in a compound. The increased covalent character is indicated by the decrease in melting point of the compound.

Examples:

Polarisation increases →

Covalent character increases →

Melting point decreases →

| | | |
|----|------------------------------|--|
| a. | m.pt. ($^{\circ}\text{C}$) | $\text{NaF} < \text{NaCl} < \text{NaBr} < \text{NaI}$ (Size of anion increases) $988 > 801 > 755 > 651$ |
| b. | m.pt. ($^{\circ}\text{C}$) | $\text{CaF}_2 < \text{CaCl}_2 < \text{CaBr}_2 < \text{CaI}_2$ (Size of anion increases) $1392 > 772 > 730 > 575$ |
| c. | m.pt. ($^{\circ}\text{C}$) | $\text{BaCl}_2 < \text{SrCl}_2 < \text{CaCl}_2 < \text{MgCl}_2 < \text{BeCl}_2$ (Size of cation decreases) $960 > 872 > 772 > 712 > 405$ |
| d. | m.pt. ($^{\circ}\text{C}$) | $\text{NaCl} < \text{MgCl}_2 < \text{AlCl}_3$ (Charge on the cation increases) $801 > 712 >$ sublimes |
| e. | | $\text{LiCl} < \text{BeCl}_2 < \text{BCl}_3 < \text{CCl}_4$ (Size of the cation decreases) |
| f. | | $\text{GeCl}_2 < \text{GeCl}_4; \text{SnCl}_2 < \text{SnCl}_4; \text{PbCl}_2 < \text{PbCl}_4$ |
| g. | | $\text{HF} < \text{H}_2\text{O} < \text{NH}_3 < \text{CH}_4$ |
| h. | | $\text{HF} < \text{HCl} < \text{HBr} < \text{HI}$ |
| i. | | $\text{NaCl} < \text{CuCl}; \text{NaI} < \text{AgI}$ |

1.24.2 Comparison in the Properties of Covalent and Ionic Compounds

| Covalent character increases | Ionic character increases |
|--|--|
| 1. Melting point decreases | 1. Melting point increases |
| 2. Solubility in polar solvent decreases | 2. Solubility in polar solvent increases |
| 3. Solubility in non-polar solvent increases | 3. Solubility in non-polar solvent decreases |
| 4. Acidic property of oxides increases | 4. Basic property of oxides increases |
| 5. Non-metallic character increases | 5. Metallic character increases |

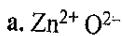
Illustration 1.61 Give the decreasing order of the acidic properties of oxides.



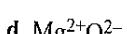
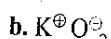
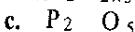
Sol. Since the anions are same, so first check the charges on the cations.

The higher the charge on the ions, the more covalent or more acidic is the nature.

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$+5 \times 2 - 2 \times 2$



Since the charge on MgO and ZnO is same but the size of Zn^{2+} < the size of Mg^{2+} (small cation).

OR

Zn^{2+} has d -orbitals, so more covalent.

So, decreasing order of acidic character is :

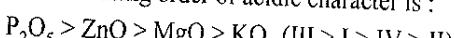
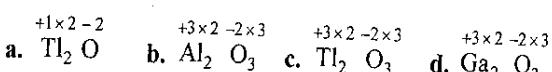


Illustration 1.62 Give the decreasing order of the basic properties of oxides.

- a. $Tl_2 O$ b. $Al_2 O_3$ c. $Tl_2 O_3$ d. $Ga_2 O_3$

Sol. Anions are same, so check the charges on the cation. The lesser the charge on the ions, the more ionic or more basic in the nature.



Charges on the cations in b., c., and d. are same so check the sizes of the cations. Large cation, more ionic and more basic. All of them belong to group 13. Therefore, size of $Tl^{3+} > Ga^{3+} > Al^{3+}$.

Hence decreasing basic oxides :

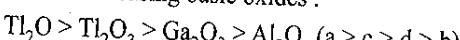


Illustration 1.63 Give the increasing order of melting points of the following compounds:

- | | | | |
|----------------|--------------|---------------|--------------|
| a. I. NaF | II. $NaCl$ | III. $NaBr$ | IV. NaI |
| b. I. CaI_2 | II. $CaBr_2$ | III. $CaCl_2$ | IV. CaF_2 |
| c. I. $BaCl_2$ | II. $SrCl_2$ | III. $CaCl_2$ | IV. $MgCl_2$ |
| V. $BeCl_2$ | | | |
| d. I. $NaCl$ | II. $MgCl_2$ | III. $AlCl_3$ | |
| e. I. CCl_4 | II. BCl_3 | III. $BeCl_2$ | IV. $LiCl$ |

Sol. a. $NaF < NaCl < NaBr < NaI$

m.pt. ($^{\circ}C$) $988 < 801 < 755 < 651$

$\therefore I < II < III < IV$

[Size of anion increases, covalent character increases and m.pt. decreases]

b. $CaF_2 < CaCl_2 < CaBr_2 < CaI_2$ (IV < III < II < I)

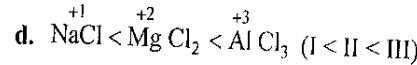
m.pt. ($^{\circ}C$) $1392 < 772 < 730 < 575$

Since cation is same the charges on the ions are also same. So, the size of anion increases (group 17 ions), covalent character increases and m.pt. decreases.

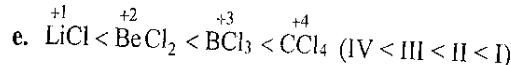
c. $BaCl_2 < SrCl_2 < CaCl_2 < MgCl_2 < BeCl_2$ (I < II < III < IV < V)

m.pt. ($^{\circ}C$) $960 < 872 < 772 < 712 < 405$

Since anion is same the charges on the ions are also same. So, the size of cation decreases (group 2 ions), covalent character of cation decreases and m.pt. increases.



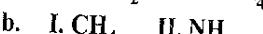
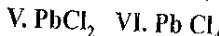
The charge on the cation increases, covalent character increases and m.pt. decreases.



The charge on the cation increases, covalent character increases and m.pt. decreases.

Illustration 1.64 Give the decreasing order of covalent character of the following compounds.

- a. I. $GeCl_2$ II. $GeCl_4$ III. $SnCl_2$ IV. $SnCl_4$

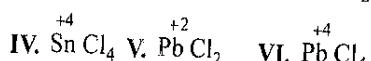
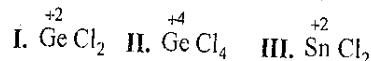


- b. I. CH_4 II. NH_3 III. H_2O IV. HF

- c. I. HF II. HCl III. HBr IV. HI

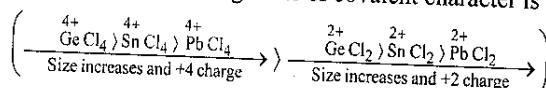
- d. I. AgI II. NaI III. CuI IV. $NaCl$

Sol. a. First check the charge, higher the charge on the ions, more is the covalent character (since anion is same)



So, group compounds of higher charges appear first and then come the lower charges. All the compounds belong to group 14. Now check the sizes of the cation, the small cation shows more covalent character.

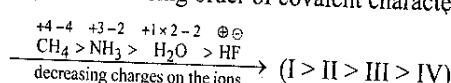
Hence the decreasing order of covalent character is



i.e. (II > IV > VI > I > III > V)

b. Check the charges on the ions. Higher the charge on the ions, more is the covalent character.

So, the decreasing order of covalent character is



decreasing charges on the ions

c. Since charges on the ions (cation and anion) are same and cation (H^+ ion) is also same. So, check the size of anion.

Large anion, more is the covalent character (all anions of group 17).

So, the decreasing order of covalent character is $HI > HBr > HCl > HF$ (IV > III > II > I)

d. Charges on the ions are same.

Size of $Cu^{\oplus} \approx$ Size of Na^{\oplus}

Moreover, Ag^{\oplus} and Cu^{\oplus} have d configuration.

Size of $Ag^{\oplus} >$ Size of Cu^{\oplus}

Small cation, with d configuration is more covalent. Large anion with d configuration is more covalent.

So, the decreasing order of covalent character is

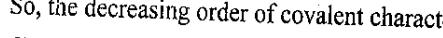
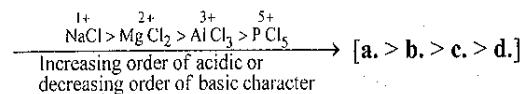


Illustration 1.65 Give the decreasing pH of aqueous solution of the following compounds:

- a. NaCl b. Mg Cl₂ c. AlCl₃ d. PCl₅

Sol. Since anions are same, so higher the charge on the ions, more covalent and more acidic and hence less pH.

So, the decreasing order of pH is



1.25 INERT PAIR EFFECT

In groups 13–16 as we move down the group the stability of lower oxidation state increases. For example in group 13, Tl is more stable in +1 OS than +3. Similarly in groups 14 and 15, Pb and Bi are more stable in +2 and +3 OS than +4 and +5 OS. This is because as we move down the group, the tendency of *s*-electron of the valence shell to participate in bond formation decreases. This reluctance of the *s*-electron to unpair and participate in bond formation is called inert pair effect. This is due to poor or ineffective shielding of *ns*² electrons of valence shell by intervening *d* and *f* electrons.

The inert pair effect becomes more predominant as we move down the group because of the increased nuclear charge which outweighs the effect of the corresponding increase in atomic size and therefore *ns*² electrons become more reluctant to participate in bond formation.

Note: OS in circle is more predominant in bond formation.

| Electronic configuration | Group 13 | OS |
|--|-------------|-----------|
| [He] 2s ² 2p ¹ | B | +3 |
| [Ne] 3s ² 3p ¹ | Al | +3 |
| [Ar] 3d ¹⁰ 4s ² 4p ¹ | Ga | (+1) (+3) |
| [Kr] 4d ¹⁰ 5s ² 5p ¹ | In | (+1) +3 |
| [Xe] 4f ¹⁴ 5d ¹⁰ 6s ² 6p ¹ | Tl | (+1) |
| | Group 14 | OS |
| [He] 2s ² 2p ² | C | +4 |
| [Ne] 3s ² 3p ² | Si | +4 |
| [Ar] 3d ¹⁰ 4s ² 4p ² | Ge | (+4) (+2) |
| [Kr] 4d ¹⁰ 5s ² 5p ² | Sn | (+2) +4 |
| [Xe] 4f ¹⁴ 5d ¹⁰ 6s ² 6p ² | Pb | (+2) |

| | Group 15 | OS |
|--|-------------|-----------|
| [He] 2s ² 2p ³ | N | +3 |
| [Ne] 3s ² 3p ³ | P | +5 |
| [Ar] 3d ¹⁰ 4s ² 4p ³ | As | (+3) (+5) |
| [Kr] 4d ¹⁰ 5s ² 5p ³ | Sb | (+3) +5 |
| [Xe] 4f ¹⁴ 5d ¹⁰ 6s ² 6p ³ | Bi | (+3) |

1.26 FACTORS WHICH DETERMINES THE FORMATION (OR STABILITY) OF COMPOUNDS

It may be noted that some compounds are stable while others are not. In other words, some compounds are formed easily some or not, e.g.

- NH₃ exists, but NH₅ does not exist.
- NCl₃ exists, but NCl₅ does not exist.
- PCl₅ exists, but PBr₅ or PI₅ does not exist.
- PH₃ exists, but PH₅ does not exist.
- TICl, PbCl₂ and BiCl₃ are more stable than TICl₃, PbCl₄ and BiCl₅.
- IF₇ exists, but ICl₇ does not exist.
- AlCl₃ exists as bridged dimer, but BCl₃ does not exist.

Formation or stability of compounds can be explained by the following factors:

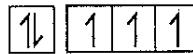
- High EN of the element to excite electrons from central atom to vacant orbitals
- Presence of vacant orbitals
- Inert pair effect
- Sizes of the cation and anion

Explanation:

- NH₃ exists, but NH₅ does not exist.

Valence electronic configuration of N:

$$2s^2 \quad 2p^3$$



N atom does not have vacant *d* orbitals. Moreover, the EN of H atom is not sufficient to excite the 2s electrons to vacant orbitals. So, NH₅ does not exist.

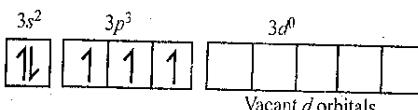
However, NH₃ exists since N atom can form 3 covalent bonds with 3H atoms by sharing 3 electrons from 3H atom to complete its octate.

- NCl₃ exists, but NCl₅ does not exist.

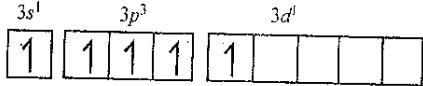
Although EN of Cl atom is very high, it can excite 2s electrons to vacant orbitals. But N atom does not have vacant *d* orbitals so NCl₅ does not exist.

- PCl₅ exists, but PBr₅ and PI₅ do not exist. Valence electronic configuration of P \Rightarrow 3s² 3p³

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Although P atom has vacant 3d orbitals and EN of Cl is sufficiently high to excite 3s electrons to 3d orbitals as



So, PCl_5 can form five covalent bonds with 5 Cl atoms by formation of sp^3d hybridisation.

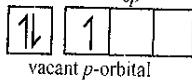
But EN of Br and I atoms are not so high to excite 3s electrons to 3d orbitals, so PBr_5 and PI_5 do not exist.

4. PH_3 exists but PH_5 does not exist.

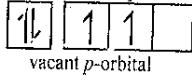
Although P atom has vacant 3d orbitals but EN of H atom is not sufficient to excite 3s electrons to 3d orbitals. So, PH_5 does not exist.

5. TlCl , PbCl_2 and BiCl_3 exist, but TlCl_3 , PbCl_4 and BiCl_5 do not exist.

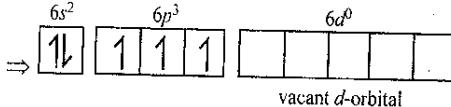
Valence electronic configuration of Tl = $6s^2 6p^1 \Rightarrow$



Valence electronic configuration of Pb $\Rightarrow 6s^2 6p^2 \Rightarrow$



Valence electronic configuration of Bi $\Rightarrow 6s^2 6p^3 6d^0$

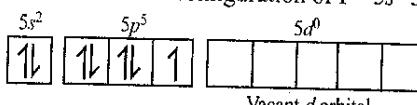


Although both factors, i.e. (i) high EN of Cl atom to excite 6s electrons to 6p orbitals in Tl and Pb and to 6d orbitals in Bi and (ii) vacant orbitals to accommodate the excited 6s electrons, are present in all the compounds, yet TlCl_3 , PbCl_4 and BiCl_5 are not stable compounds.

This is due to the **inert pair effect** (refer to Section 1.25).

6. IF_7 exists, but ICl_7 does not exist.

Valence electronic configuration of I = $5s^2 5p^5 5d^0$



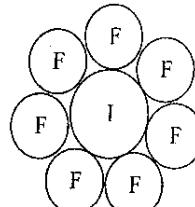
Both factors, i.e. (i) high EN of F and Cl atoms and (ii) vacant 5d orbitals are present.

High EN of F and Cl can excite 5s and 5p electrons to 5d orbitals as

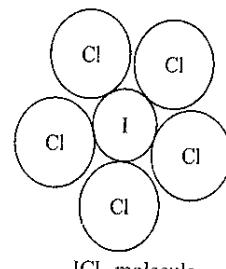


So, both IF_7 and ICl_7 can form 7 covalent bonds with 7F or 7 Cl atoms by formation of sp^3d^1 hybridisation. But ICl_7 does not exist due to the following reason:

- a. Size of F^- ion is very small and I can accommodate 7 F^- ions around it, but it cannot accommodate 7 large size Cl^- ions around it, as shown.



IF_7 molecule

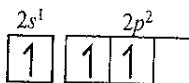


ICl_5 molecule

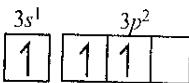
7. AlCl_3 exists as bridged dimer (e.g. Al_2Cl_6), but BCl_3 does not exist.

Valence electronic configuration of B in the ground state = $2s^2 2p^1$

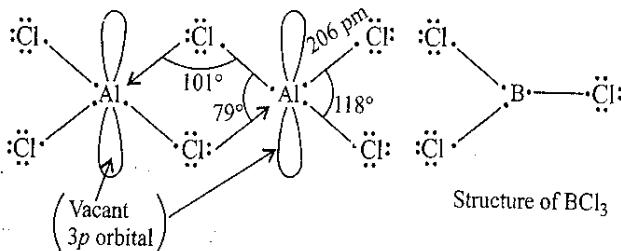
Valence electronic configuration of B in the excited state



Valence electronic configuration of Al in the excited state



Bridged dimer structure of AlCl_3 is formed by the donation of lone pair electrons to the vacant 3p orbitals as shown:



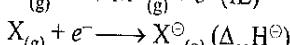
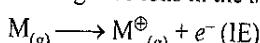
(Structure of bridged dimer of AlCl_3)

Although B atom also has vacant 2p orbitals, it should also form bridged dimeric structure of BCl_3 .

But boron halides exist as monomer because boron (B) atom is so small that it cannot accommodate four large sized halide ions around it with 2 coordinate and 2 covalent bonds.

1.27 IONIC BOND

Kossel and Lewis explained that the formation of ionic bond primarily depends upon (i) The ease of formation of positive and negative ions from the respective neutral atoms, and (ii) The lattice of the compound, i.e. the arrangement of positive and negative ions in the solid, e.g.



It is evident that the ionic bond will be formed more easily between elements with comparatively low IE and elements with comparatively low (negative) $\Delta_{eg} \text{H}^\ominus$.

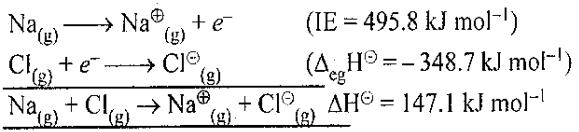
Most ionic compounds have cations derived from metallic elements and anions from non-metallic elements.

The NH_4^+ ion is made up of two non-metallic elements which is an exception.

Ionic compounds in the crystalline state consist of orderly three-dimensional arrangement of cations and anions held together by coulombic interaction energies. These ionic compounds crystallise in different crystal structures. This is due to the difference in the size of the ions, their packing arrangements and other factors.

In ionic compounds, the sum of IE and $\Delta_{eg}H^\ominus$ may be positive but the crystal structure gets stabilised due to the energy released in the formation of the crystal lattice.

Example:

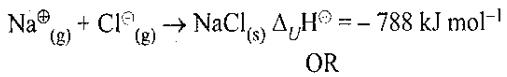


The sum of the above two (i.e. $147.1 \text{ kJ mol}^{-1}$) is more than compensated for by the enthalpy of lattice formation of NaCl which is equal to 788 kJ mol^{-1} .

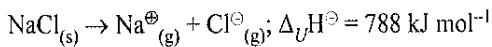
Thus, a qualitative measure of the stability of an ionic compound is provided by the enthalpy of lattice formation.

1.27.1 Lattice Enthalpy

Lattice enthalpy (Δ_UH^\ominus) is the amount of energy released when crystal lattice of one mole of solid ionic compound is formed from their gaseous constituent ions. For example,



Lattice enthalpy (Δ_UH^\ominus) is the amount of energy required to completely separate one mole of solid ionic compound into its gaseous constituent ions. For example,



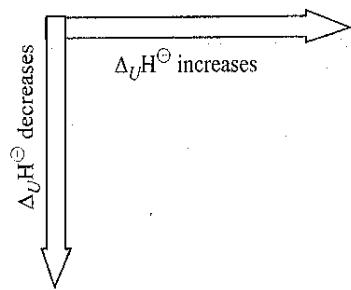
This process involves both the attractive forces between ions of opposite charges and the repulsive forces between ions of like charges.

Since the solid crystal is three dimensional, therefore, lattice enthalpy cannot be calculated directly from the interaction of forces of attraction and repulsion only. Hence, factors associated with the crystal geometry have to be included.

Lattice enthalpy depends on the following factors:

- It depends on the size of the ions. If the sizes of cations and anions are comparable, then a strong lattice is formed and more (negative) energy is released.
- It depends on the magnitude of charges on the ions. If the charges on the ions are greater, than a strong lattice is formed and more (negative) energy is released.

- It increases from uni-univalent ionic solid (e.g. NaCl) to uni-bivalent (e.g. MgCl₂) and then to bi-bivalent ionic solid (e.g. MgO).
- The larger the magnitude of lattice energy, the greater will be the stability of ionic solid.
- Ionic solids having higher value of lattice energies have higher melting, boiling points and are very hard.
- Ionic solids with high value of lattice energies have low solubility in water (polar solvents).
- Generally the lattice energy decreases down the group and increases along the period.



The first theoretical interpretation of lattice energy was given by Born and Lande as

$$U_0 = \frac{A N_A |Z^\oplus| |Z^\ominus| e^2}{4\pi \epsilon_0 r_0} (1 - 1/n)$$

OR

$$U_0 \propto \frac{|Z^\oplus| |Z^\ominus|}{r_0}$$

Where U_0 is the lattice energy and A = Madelung constant.

[The above equation helps to interact with all the other ions besides the nearest neighbours]

N_A = Avogadro's constant

$|Z^\oplus|$ = Charge on the positive ion (only magnitude value)

$|Z^\ominus|$ = Charge on the negative ion (only magnitude value)

e = Charge on the electron

π = Constant (3.14159)

ϵ_0 = Vacuum permittivity

r_0 = Inter-ionic distances

n = Born exponent in the repulsive terms

Other variables such as van der Waals forces, zero point energy and heat capacity are included for more accurate calculations.

- It is evident that the lattice energy becomes stronger (i.e. more negative value) as r_0 , the inter-ionic distance decreases, i.e.

$$U_0 \propto \frac{1}{r_0}$$

Example:

| | r_0 (Å) | U_0 (kJ mol ⁻¹) |
|-----|-----------|-------------------------------|
| LiF | 2.01 | -1004 |
| CsI | 3.95 | -527 |

9. The lattice energy depends on the product of the ionic charges, i.e.

$$U_0 \propto |Z^\oplus| |Z^\ominus|$$

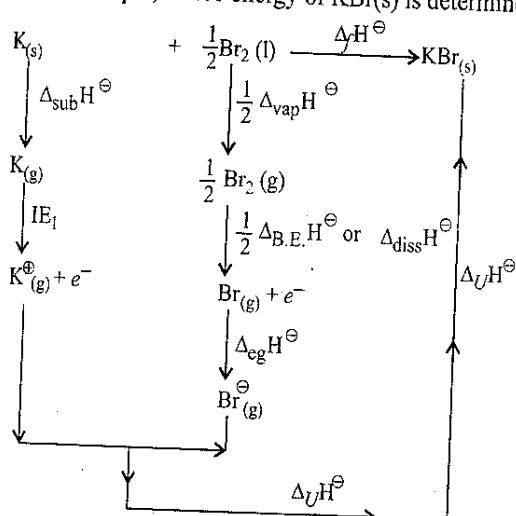
Example:

| | r_0 (Å) | $ Z^\oplus Z^\ominus $ | U_0 (kJ mol ⁻¹) |
|-----|-----------|--------------------------|-------------------------------|
| LiF | 2.01 | 1 × 1 | -1004 |
| MgO | 2.10 | 2 × 2 | -3933 |

1.27.2 Determination of Lattice Energy

It is determined by the use of Born–Haber cycle, which is based on the Hess's law of heat summation.

For example, lattice energy of KBr(s) is determined as:



$$\therefore \Delta_f H^\ominus = \Delta_{\text{sub}} H^\ominus + \text{IE}_1 + \frac{1}{2} \Delta_{\text{vap}} H^\ominus + \frac{1}{2} \Delta_{\text{B.E.}} H^\ominus + \Delta_{\text{eg}} H^\ominus + \Delta_U H^\ominus$$

$$\therefore \Delta_U H^\ominus = \Delta_f H^\ominus - \Delta_{\text{sub}} H^\ominus - \text{IE}_1 - \frac{1}{2} \Delta_{\text{vap}} H^\ominus - \frac{1}{2} \Delta_{\text{B.E.}} H^\ominus - \Delta_{\text{eg}} H^\ominus$$

1.27.3 Application of Lattice Energy

Formation of oxides, peroxides and superoxides of group 1 and group 2 elements: When heated with excess of O₂, Li forms monoxides (Li₂O), Na forms peroxides (Na₂O₂) and K, Rb and Cs form superoxides having general formula (MO₂).

Similarly, when heated with oxygen, Be, Mg and Ca form monoxide (MO) while Sr and Ba form peroxide (MO₂).

Explanation: This is due to the comparable sizes of cation and anion, which forms the strongest lattice with the release of high energy.

Example:

1. 4Li + O₂ $\xrightarrow{\Delta}$ 2Li₂O [size of 2 Li[⊕] ion is comparable with the size of O²⁻ (oxide) ion].

2. 2Na + O₂ $\xrightarrow{\Delta}$ Na₂O₂ [size of 2 Na[⊕] ion is comparable with the size of O₂²⁻ (peroxide) ion].

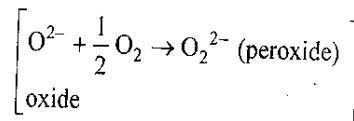
3. K + O₂ $\xrightarrow{\Delta}$ KO₂ [size of K[⊕] ion is comparable with the size of O₂[⊖] (superoxide) ion].

4. Similarly, sizes of Be²⁺, Mg²⁺ and Ca²⁺ ions are comparable with O²⁻ (oxide) ion in MO, where M = Be, Mg and Ca.

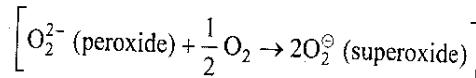
5. Sizes of Sr²⁺ and Ba²⁺ ions are comparable with O₂²⁻ (peroxide) ion in MO₂, where M = Sr and Ba.

Alternative explanation: Due to high charge density ($\frac{\text{charge ratio}}{\text{size}}$) of Li[⊕], it attracts the negative charge so strongly that it does not allow the oxide anion (O²⁻) to combine with another oxygen atom to form peroxide ion, O₂²⁻.

Whereas Na[⊕] ion has comparatively less charge density than Li[⊕] ion, so it cannot prevent O²⁻ ion to combine with another oxygen atom to form peroxide ion.



On the other hand, larger K[⊕], Rb[⊕] and Cs[⊕] ions have still lesser charge density which cannot prevent even peroxide ion (O₂²⁻) to combine with another oxygen atom to form superoxide (O₂[⊖]) ion.



Superoxide ion $[\ddot{\text{O}} \cdots \ddot{\text{O}} \cdots \ddot{\text{O}}]^\ominus$ has three electron bonds (having one unpaired electron) and is coloured and paramagnetic. For example, LiO₂, NaO₂ are yellow, KO₂ is orange, RbO₂ is brown and CsO₂ is orange. Na₂O₂ (sodium peroxide) is yellow in colour probably due to the presence of a small amount of superoxide in it. The normal oxides of group 1 are however, colourless and diamagnetic.

Illustration 1.66: Calculate the ratio of lattice energies of CaCl_{2(s)} and NaCl_(s), if the inter-ionic distance in CaCl_{2(s)} is twice that of NaCl_(s).

$$\text{Sol. } r_0(\text{NaCl}) = r; r_0(\text{CaCl}_2) = 2r.$$

$$U_{(\text{NaCl})} \propto \frac{|Z^\oplus| |Z^\ominus|}{r_0} \propto \frac{1 \times 1}{r} \propto \frac{1}{r}$$

$$U_{(\text{CaCl}_2)} \propto \frac{2 \times 1}{2r} \propto \frac{1}{r}$$

$$\therefore \frac{U_{(\text{CaCl}_2)}}{U_{(\text{NaCl})}} = 1 : 1$$

Illustration 1.07

- a. Give the decreasing order of melting points of the following compounds:

i. NaF ii. BeO iii. MgO iv. SrO

Given: The inter-ionic distances in Å as

NaF = 2.31, BeO = 1.65, MgO = 2.106, SrO = 2.58

- b. Give the decreasing order of hardness of the following compounds:

i. CaO ii. BeO iii. TiC

Given: The inter-ionic distances in Å as

CaO = 2.405, BaO = 2.762, TiC = 2.159

$$\text{Sol. a. } U_0 \propto \frac{|Z^+| |Z^-|}{r_0}$$

i. Smaller the inter-ionic distance and high charges on ions, higher the lattice energy and high is the melting point.

ii. Increasing order of inter-ionic distance with same $|Z^+| = 2$ and $|Z^-| = 2$ is Be O < Mg O < Sr O.

iii. Charge in NaF is $|Z^+| = 1$, $|Z^-| = 1$.

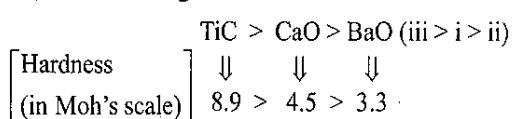
So, the decreasing order of melting point is
BeO > MgO > SrO > NaF (ii > iii > iv > i)
m.pt. (°C) 2930 > 2800 > 2430 > 990

- b. i. Higher the lattice energy, higher is the hardness.

Charge in Ti C is the highest; $|Z^+| = 4$, $|Z^-| = 4$

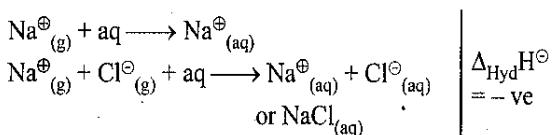
ii. Increasing order of inter-ionic distance with same charge, $|Z^+| = 2$, and $|Z^-| = 2$ is CaO < BaO.

So, the decreasing order of hardness is



1.28 HYDRATION ENERGY

The amount of energy released when one mole of gaseous ions is dissolved in excess of H₂O to give its constituent aqueous ion, e.g.



Generally the hydration energy decreases down the group (↓) and increases along the period (→).

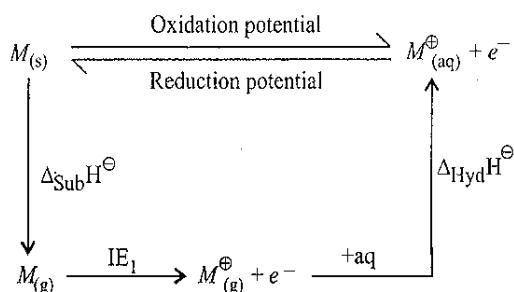
The hydration energy depends on charge density, i.e. $\left(\frac{\text{Ionic charge}}{\text{Ionic radius}} \right)$. Greater is the charge density, more easily it attracts the lone pair of oxygen atom in H₂O molecule and more easily it is hydrated and hence more (negative) energy is released. Down the group (↓), charge density decreases and hence hydration energy decreases.

1.28.1 Application of Hydration Energy ($\Delta_{\text{Hyd}} \text{H}^{\ominus}$)

1. **Lithium is the strongest reducing agent in aqueous solution:** Because of its very high IE, Li should be the weakest reducing agent. But Li is the strongest reducing agent and Na is the least.

Reducing character order in aqueous solution is
Li > Cs > Rb > K > Na

The standard reduction potential [$E^{\ominus}_{M^{\oplus}(\text{aq})/M(s)}$] which measures the reducing power represents the overall change.



Due to high charge density (charge size ratio), Li has the highest hydration enthalpy which compensates its high IE₁ value, thereby accounts for its high negative E^{\ominus} value and its high reducing power.

$E^{\ominus}_{M^{\oplus}(\text{aq})/M(s)}$ in volts are given for alkali metals as

| | Li | Na | K | Rb | Cs |
|-----------------|-------|--------|--------|--------|--------|
| E^{\ominus}/V | -3.04 | -2.714 | -2.925 | -2.930 | -2.927 |

2. **Ionic mobilities in electric field of s-block ions:** Charge densities of (groups I and 2) ions decrease down the group (↓), so their mobilities in electric field **should be** in the order:

$\text{Li}^{\oplus} > \text{Na}^{\oplus} > \text{K}^{\oplus} > \text{Rb}^{\oplus} > \text{Cs}^{\oplus}$

$\text{Be}^{2+} > \text{Mg}^{2+} > \text{Ca}^{2+} > \text{Sr}^{2+} > \text{Ba}^{2+}$

But the **observed order** of ionic mobilities in aqueous solution is reversed, i.e.

$\text{Cs}^{\oplus} > \text{Rb}^{\oplus} > \text{K}^{\oplus} > \text{Na}^{\oplus} > \text{Li}^{\oplus}$

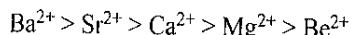
$\text{Ba}^{2+} > \text{Sr}^{2+} > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{Be}^{2+}$

Explanation: Li⁺ and Be²⁺ ions, being heavily hydrated, move very slowly under the effect of electric current and are thus the poorest conductors of electricity as compared to other ions of s-block elements. Thus, it is the degree of hydration of ions, rather than their size or charge density that determines the electrical conductivity or ionic mobility of the s-block element salt solutions.

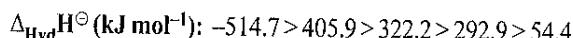
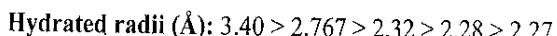
3. **Ionic radii in aqueous solution of ions of s-block elements:**

Smaller the size of a cation, greater is its charge density and hence greater is its tendency to draw electrons from molecules which are thus polarised. Lithium ion and Be²⁺ being the smallest in size among ions of s-block

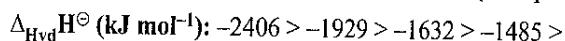
elements, they are most extensively hydrated while Cs^+ and Ba^{2+} ions, the largest ions of *s*-block elements are the least hydrated. So, ionic radii of Li^+ and Be^{2+} in aqueous solution are the highest and that of Cs^+ and Be^{2+} ions are the lowest, i.e. the **expected relative ionic radii should be**



The observed relative ionic radii in water and relative degree of hydration are reverse of the above order (Fig. 1.22):



(Group 2)



-1276

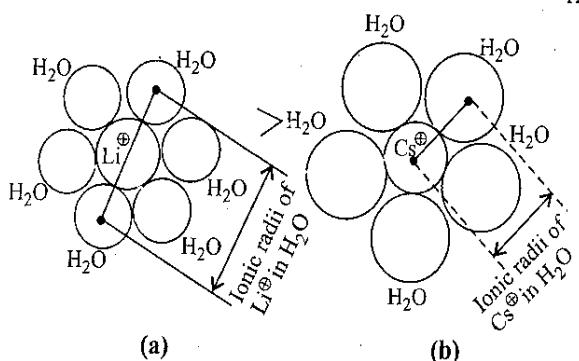


Fig. 1.22 (a) Ionic radii of Li^+ and (b) Ionic radii of Cs^+ in H_2O

Li^+ has maximum degree of hydration and for this reason lithium salts are mostly hydrated (e.g. $\text{LiCl}\cdot 2\text{H}_2\text{O}$) while other alkali metal ions are not hydrated, but NaCl is hygroscopic (absorb moisture).

4. Reducing nature in aqueous solution of group 2 elements: Group 2 elements are also strong reducing agent but their reducing power is less than those of their corresponding group 1 elements.

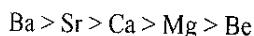
Be is not the strongest reducing agent in group 2 element unlike Li is the strongest reducing agent in group 1 elements.

Reducing power increases down the group (\downarrow) as evident from their $E^\ominus_{M^{2+}(\text{aq})/M(s)}$ values.

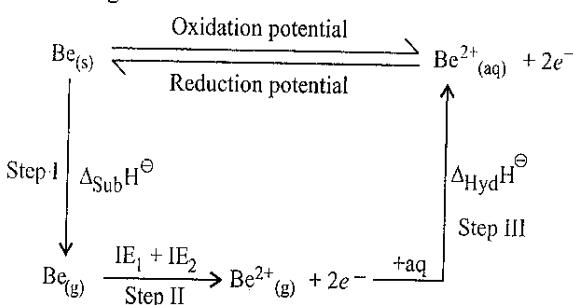
Be has less negative value of E^\ominus_{red} compared to other alkaline earth metals, as shown:

| Group 2 | Be | Mg | Ca | Sr | Ba | Ra |
|---------------------|-------|-------|-------|-------|-------|-------|
| E^\ominus / V for | -1.97 | -2.36 | -2.84 | -2.89 | -2.92 | -2.92 |

Therefore, decreasing order of reducing power in aqueous solution is



Explanation: The standard reduction potential $E^\ominus_{M^{2+}(\text{aq})/M(s)}$, which measures the reducing power represents the over all change.



As a result the overall tendency for the change depends on the net effect of these three steps.

Due to high charge density of Be^{2+} ion, a large amount of hydration energy released in step III does not compensate for the relatively large value of sublimation energy (or atomisation enthalpy) in step I of Be metal plus high ($IE_1 + IE_2$) value of Be in step II.

Hence, Be is the least reducing agent in aqueous solution among group 2 elements.

5. Hydrated salt of group 2 elements: The hydration enthalpies of group 2 metal ions are larger than those of group 1 ions. Thus, compounds of alkaline earth metals are more extensively hydrated than those of alkali metals, e.g. MgCl_2 and CaCl_2 exist as $\text{MgCl}_2\cdot 6\text{H}_2\text{O}$ and $\text{CaCl}_2\cdot 6\text{H}_2\text{O}$ while LiCl exists as $\text{LiCl}\cdot 2\text{H}_2\text{O}$. NaCl and KCl do not form such hydrates.

6. Dipositive oxidation state (M^{2+}): The chemistry of alkaline earth metals is dominated by the dipositive (M^{2+}) oxidation state just as the unipositive (M^+) oxidation state is the predominant oxidation state of group 1 elements. Alkaline earth metals always form divalent cations.

Explanation: In view of the lower value of first ionisation energy, it would appear that the alkaline earth metals should prefer to form $+1$ ions (M^+ rather than $+2$ ions e.g. Mg^{2+} , Ca^{2+} etc. If ionisation energy were the only factor involved, we would have got the monovalent ions, i.e. Mg^+ , Ca^+ etc. rather than the divalent ions, i.e. Mg^{2+} , Ca^{2+} etc. But actually we get divalent ions. This anomaly is explained as follows:

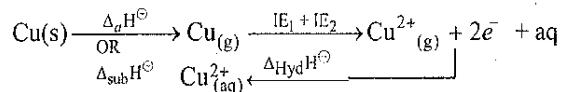
- The $+2$ ions are extensively hydrated and a large amount of energy known as hydration energy is released in the process which counterbalances the higher value of second ionisation energy. Compared to the heats of hydration (hydration energy) of alkali metal ions of comparable size, the heats of hydration

of alkaline earth metal ions are approximately four times greater [e.g. $\Delta_{\text{Hyd}}H^\ominus$ for Na^\oplus (size 102 pm) = -397 kJ mol^{-1} , $\Delta_{\text{Hyd}}H^\ominus$ for Ca^{2+} (size 100 pm) = $-1650 \text{ kJ mol}^{-1}$.] The larger hydration energy is due to the fact that the alkaline earth metal ions, because of their much larger charge density, exert a much stronger electrostatic attraction on the lone pairs on the oxygen of water molecule surrounding them.

- b. The $+2$ cations of alkaline earth metals acquire stable inert gas configuration.
7. **Lanthanides and actinides show in general $+3$ oxidation state:** Their positive high IE_3 value is compensated (or counter balanced) by negative high hydration enthalpies. That is why they generally show $+3$ OS.

8. **The $E_{M+2(\text{aq})/M(\text{s})}^\ominus$ value for copper is positive ($+0.34 \text{ V}$). Why?**

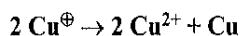
Explanation : $E_{(\text{Cu}^{+2}(\text{aq})/\text{Cu}(\text{s}))}^\ominus$ is related to sum of the enthalpy changes taking place as shown below:



Copper has high positive enthalpy of atomisation or sublimation enthalpy and low (negative) enthalpy of hydration.

The high energy required to convert $\text{Cu}_{(\text{s})}$ to $\text{Cu}^{+2}_{(\text{aq})}$ is not compensated by its low hydration energy. Hence, $E_{(\text{Cu}^{+2}(\text{aq})/\text{Cu}(\text{s}))}^\ominus$ is positive.

9. **Cu^\oplus compounds are unstable in aqueous solution and undergo disproportionation**



Explanation: The stability of $\text{Cu}^{2+}_{(\text{aq})}$ rather than Cu^\oplus is due to the much more negative $\Delta_{\text{Hyd}}H^\ominus$ of $\text{Cu}^{2+}_{(\text{aq})}$ than $\text{Cu}^\oplus_{(\text{aq})}$, which more than compensates for the IE_2 of Cu.

10. Solubility in water:

- a. The solubility of a salt in water depends upon (i) lattice energy and (ii) hydration energy.

In general, if hydration energy > lattice energy, salt dissolves. If hydration energy < lattice energy, salt is insoluble.

- b. **Solubilities in water of hydroxides and fluorides of alkaline earth metal increase down the group (\downarrow).**

Explanation: Generally both the lattice and the hydration energy decrease down the group (\downarrow). Lattice energy depends on the comparable size of cations and anions. If sizes of cations and anions are comparable, a strong lattice is formed and a large amount of energy is released.

Alternatively, lattice energy depends on the sizes of the ions whichever is larger.

However, hydration energy depends on the size of the cations or on the charge density (charge/size ratio) of the cations.

Smaller is the size or higher the charge density of the cation, more (negative) is the hydration energy, i.e. more energy is released.

| Approximate sizes of group 2 ions | Approximate size of F^\ominus ion in fluorides | Approximate size of OH^\ominus ion in hydroxides |
|-----------------------------------|---|---|
| Be^{+2} ○ | BeF_2 ● | $\text{Be}(\text{OH})_2$ ● |
| Mg^{+2} ○ | MgF_2 ● | $\text{Mg}(\text{OH})_2$ ● |
| Ca^{+2} ○ | CaF_2 ● | $\text{Ca}(\text{OH})_2$ ● |
| Sr^{+2} ○ | SrF_2 ● | $\text{Sr}(\text{OH})_2$ ● |
| Ba^{+2} ○ | BaF_2 ● | $\text{Ba}(\text{OH})_2$ ● |

↓ Size increases ↓ Size of F^\ominus ion is constant ↓ Size of OH^\ominus ion is constant

Since the sizes of F^\ominus and OH^\ominus ions are very small and are not comparable with sizes of any cations. Lattice energy depends on the size of cations which are larger than anions, so lattice energy depends on the size of cations only which increase down the group (\downarrow). Hence, lattice energy decreases more rapidly down the group (\downarrow).

Similarly, charge density of cations i.e. from Be^{+2} to Ba^{+2} also decreases down the group.

But decrease in lattice energy is more than the decrease in hydration energy from Be^{+2} to Ba^{+2} .

In other words, hydration energy > lattice energy.

Hence, solubilities of hydroxides and fluorides of alkaline earth metals increase down the group (\downarrow).

- c. **Solubilities in water of carbonates, bicarbonates and sulphates of alkaline earth metals decrease down the group (\downarrow).**

Explanation: Since the sizes of CO_3^{2-} , HCO_3^\ominus and SO_4^{2-} ions are so large and are not comparable with the size of any cations. As we know, lattice energy depends on the size of ions whichever is larger, hence it depends on the size of CO_3^{2-} , HCO_3^\ominus and SO_4^{2-} ions.

Therefore, the magnitude of lattice energy remains almost constant down the group (\downarrow). As the size of anions are so large that a small increase in the size of the cations from Be^{+2} to Ba^{+2} does not make any difference.

However, the hydration energy decreases (i.e. from Be^{+2} to Ba^{+2}) appreciably as the size of the cation increases down the group (\downarrow).

In other words, hydration energy < lattice energy. Hence, **solubilities of carbonates, bicarbonates and sulphates of alkaline earth metals decrease down the group (\downarrow).**

The high solubility of carbonates, bicarbonates and sulphates of Be and Mg is due to their high hydration energies since Be^{+2} and Mg^{+2} ions have smaller size.

| Approximate sizes of group 2 ions | Approximate sizes of CO_3^{2-} , HCO_3^- and SO_4^{2-} in their compounds |
|-----------------------------------|--|
| Be^{2+} ○ | BeCO_3 ○ $\text{Be}(\text{HCO}_3)_2$ ○ BeSO_4 ○ |
| Mg^{2+} ○ | MgCO_3 ○ $\text{Mg}(\text{HCO}_3)_2$ ○ MgSO_4 ○ |
| Ca^{2+} ○ | CaCO_3 ○ $\text{Ca}(\text{HCO}_3)_2$ ○ CaSO_4 ○ |
| Sr^{2+} ○ | SrCO_3 ○ $\text{Sr}(\text{HCO}_3)_2$ ○ SrSO_4 ○ |
| Ba^{2+} ○ | BaCO_3 ○ $\text{Ba}(\text{HCO}_3)_2$ ○ BaSO_4 ○ |

Note: Sizes of CO_3^{2-} , HCO_3^- and SO_4^{2-} ions are taken nearly equal only for understanding the concept.

1.29 FLAME COLOURATION

When s-block elements or their salts (especially chlorides due to its more volatile nature in a flame) are heated in a bunsen flame, they give characteristic colour in the flame.

Principle: Since the energy of bunsen flame is constant, different elements are excited to different levels due to difference in their IE's

Explanation:

- When the elements or their salts are heated in a bunsen flame, the electrons of the elements get energy and are excited to higher energy levels. When these excited electrons return to their original (ground) energy level, they emit the same amount of energy as absorbed during excitation in the form of electromagnetic radiation which appears in the visible region of the spectrum, thereby imparting a characteristic colour to the flame.

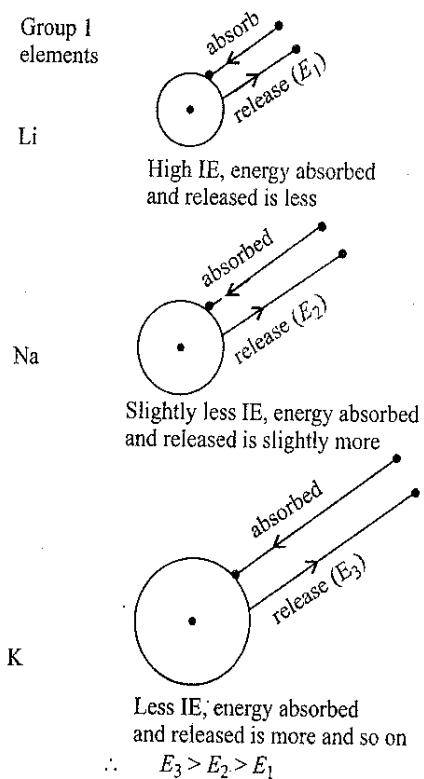
Thus, the following characteristic colours are given:

| Group 1 | Li | Na | K | Rb | Cs | |
|---------------------|---------|---------------|-----------|---------|-------------|---------|
| Colour | Crimson | Golden yellow | Violet | Violet | Blue | |
| λ/nm | 670.8 | 589.2 | 766.5 | 780.0 | 455.5 | |
| Group 2 | Be | Mg | Ca | Sr | Ba | Ra |
| Colour | | | Brick red | Crimson | Apple green | Crimson |

2. Flame colouration in alkali metals: For the same excitation energy, the energy level to which the electron in Li will rise is lower than that to which the electron in Na will rise, this in turn, is lower than the level to which the electron in K will rise and so on. These differences are due to differences in their ionisation energies.

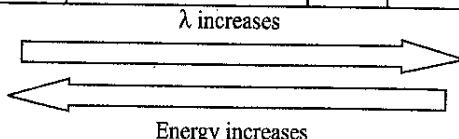
Consequently, when the electron returns to the ground state, energy released will be lowest in Li^\oplus and will increase in the order: Li^\oplus , Na^\oplus , K^\oplus , Rb^\oplus and Cs^\oplus .

As a result of this, the frequency of light emitted in the bunsen flame is minimum in lithium and corresponds to the red region of visible spectra. In potassium, the frequency of the light emitted corresponds to violet region of visible spectra.



(VISIBLE REGION)

| V | I | B | G | Y | O | R |
|----|---|---|---|----|---|----|
| K | - | - | - | Na | - | Li |
| Rb | - | - | - | - | - | - |
| Cs | - | - | - | - | - | - |



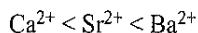
3. Flame colouration in alkaline earth metals: Be and Mg atoms are smaller in size and have high IE's so their electrons are strongly bonded to the nucleus. They need large amounts of energy for excitation to higher energy

levels which is not available in bunsen flame (because energy of bunsen flame is constant), so they do not impart colour to the bunsen flame.

For the same excitation energy, the energy level to which the electrons in Ca will rise is lower than that to which the electrons in Sr will rise, this in turn, is lower than that of the level to which the electrons in Ba will rise and so on.

These differences are due to differences in their IE's.

Consequently, when the electrons return to the ground state, energy released will be lowest in Ca^{2+} ion and will increase in the order:



As a result of this, the frequency of light emitted is minimum in Ca and corresponds to brick red region of visible spectra. In Ba the frequency of the light emitted corresponds to apple green region of visible spectra.

Cu and Pb and their compounds impart characteristic flame colouration, as

$\text{Cu} \Rightarrow$ Deep bluish green

$\text{Pb} \Rightarrow$ Pale blue grey

1.30 COLOUR OF A SUBSTANCE IN VISIBLE LIGHT

Most of the transition metal compounds (ionic as well as covalent), halogens and other compounds or ions are coloured in the solid state and in aqueous solution in visible light.

Explanation: Colour of a substance is due to the absorption of light at a specific wavelength in the visible part of the electromagnetic spectrum (400 to 700 nm or 4000 to 7000 Å) and transmission or reflection of the rest of the wavelengths. An object that absorbs all visible light appears black and the object which reflects all visible light appears white.

This means that some of the visible spectrum is being removed from the white light as it passes through the sample, so the light that emerges is no longer white. The colour of the substance is complementary to that which is absorbed.

The complementary colour is the colour generated from the wavelength left over, for example, if blue green light is absorbed by the substance or complex, it appears red.

Table 1.24(a) gives the approximate (just for understanding) while Table 1.24(b) gives the exact relationship of different wavelength (or colour) absorbed and the complementary colour observed.

Table 1.24(a) Approximate or (theoretical) (for memorising) relationship between the colour absorbed and complementary colour [convert VIBGYOR \rightarrow YORGVIB]

| Colour the light absorbed (VIBGYOR) | Visible spectra | | | | | | |
|--|-----------------|------|-------|--------|--------|--------|-----|
| | V | I | B | G | Y | O | R |
| Violet | Indigo | Blue | Green | Yellow | | Orange | Red |
| Y | O | R | G | V | I | B | |
| Yellow | Orange | Red | Green | Violet | Indigo | Blue | |

↓ Primary colour

400 nm λ → increases 700 nm

← Energy (E) increases

Note: Green is a primary colour, hence its absorbed and complementary colour is same

Table 1.24(b) Observed or (exact) relationship between the colour absorbed and the complementary colour

| Wavelength and colour of the light absorbed in nm | Visible spectra | | | | | |
|---|------------------|---------------|---------------|--------|------|-----|
| | 410 | 475 | 498 | 500 | 535 | 600 |
| Ultra-violet | Blue | Blue green | Blue green | Yellow | | Red |
| Pale Yellow orange | Yellow orange | Purple | Red | Violet | Blue | |

Note: Difference between (i) flame colouration and (ii) colour of the substance in visible light.

- i. In the first case, the colour is observed in the visible spectra corresponding to the energy released.
- ii. In the second case, the observed colour is the complementary colour of the absorbed colour.

1.31 MECHANISM OF ABSORBED COLOUR

When molecules absorb light of a specific wavelength (λ) in the visible region of electromagnetic spectrum, the outer (valence) electrons are excited to higher energy levels. When these excited electrons return to their original (ground) energy levels, they emit radiations in the visible region corresponding to the energy absorbed and gives complementary colour.

1.31.1 Application

- 1. Halogens are coloured:** All halogens are coloured as shown.

| Halogens | Observed (complementary) colour |
|-------------|---------------------------------|
| $F_{2(g)}$ | Yellow |
| $Cl_{2(g)}$ | Greenish yellow |
| $Br_{2(l)}$ | Red or brown or orange |
| $I_{2(s)}$ | Violet |

This is due to absorption of radiation in visible region which results in the excitation of outer electrons to higher energy level. By absorbing different quanta of radiation, they display different colour as shown above.

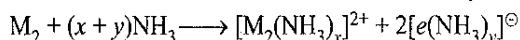
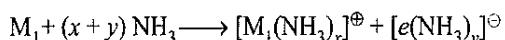
The amount of energy required for excitation decreases progressively down the group (\downarrow), as the IE decreases from F_2 to I_2 .

F_2 absorbs violet light (higher excitation energy) and hence gives complementary pale yellow colour while I_2 absorbs yellow and green (lower excitation energy) and appears deep violet. Similarly, greenish yellow colour of Cl_2 and orange red colour of Br_2 can be explained as shown below:

| Absorbed colour | V | I | B | G | Y | O | R |
|----------------------|-------|--------|--------|-------|---|---|---|
| Complementary colour | Y | O | R | G | V | I | B |
| | ↓ | ↓ | ↓ | ↓ | | | |
| | F_2 | Cl_2 | Br_2 | I_2 | | | |

← Energy increases and IE of halogens increases

- 2. Blue solution of alkali metals and deep blue black colour of alkaline earth metals in NH_3 :** The colour solution of group 1 and group 2 metals in NH_3 is due to the formation of ammoniated metal cations and ammoniated electrons in the metal ammonia solution as



where M_1 is the alkali metals and M_2 is the alkaline earth metals.

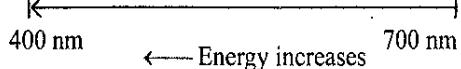
Explanation:

- a. The blue colour of the solution is due to the ammoniated electron which absorbs energy corresponding to red region of visible light and thus imparts complementary blue colour of the solution, as shown

Visible spectrum

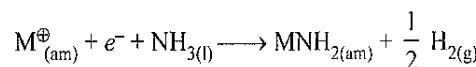
| Absorbed colour | V | I | B | G | Y | O | R |
|----------------------|---|---|---|---|---|---|---|
| Complementary colour | Y | O | R | G | V | I | B |
| | | | | | | | |

Absorbs energy in red region and gives complementary blue colour.



- b. The solutions are paramagnetic and has high electrical conductivity due to the presence of unpaired electron or ammoniated electron present in the cavities formed by the electronic polarisation between the electrons and NH_3 molecules. Consequently, the metal solution occupies large volume and has lower density than solvent itself.

- c. On standing, the solution slowly liberates $H_{2(g)}$ resulting in the formation of amide.



where 'am' denotes solution in NH_3 .

- d. In concentrated solution, the blue colour changes to bronze colour and becomes diamagnetic, due to the formation of metal ion clusters.

In other words, ammoniated metal ions are bound by free unpaired electrons which has been described as 'expanded metals.'

- e. However, under anhydrous conditions and in the absence of catalytic impurities such as transition metal ions, solutions can be stored for several days.

- 3. The colour in the coordination compounds:** It is explained in terms of crystal field theory (CFT).

Explanation: Colour is due to the presence of incomplete d -subshell. Further, when the anions approach the transition metal ions their d -orbitals do not remain degenerate. They split into two sets, one with lower energy and the other with higher energy. This is called **crystal field splitting**. Thus, the electrons can jump from lower energy d -orbitals to higher energy d -orbitals. The required amount of energy to do this is obtained by absorption of the light of a particular wavelength in the region of visible light. One or more electrons from a lower to a higher level within the same d -subshell are promoted.

Since the different d -orbitals belonging to the same subshell have slightly different energies, the energy required to promote such an electron is very small. Radiations of light corresponding to such small amount of energy are available within the visible light and appear coloured due to emission of the remainder as coloured light.

If a substance absorbs wavelength corresponding to red light the transmitted light will consist of wavelengths corresponding to the complementary colours especially greenish blue colour and the substance will appear greenish blue in colour.

Thus, Cu^{2+} salts look blue due to the absorption of the red wavelength. (Red and greenish blue are said to be complementary colours. Complementary colours are those which when mixed together produce white light.)

Anhydrous cobalt (II) compounds also absorb red light and appear blue. An octahedral complex of titanium $[Ti(H_2O)_6]^{3+}$ is purple in colour. It can be explained on the basis of crystal field theory as follows.

In case of complex ions, d -orbitals are split into two different sets due to crystal field effect, one consisting of lower energy orbitals (t_{2g}) and the other consisting of higher energy orbitals (e_g). In $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$, Ti has d^1 configuration and this electron is present in t_{2g} orbital in ground state of the complex.

On absorption of yellow green wavelength, the electron is excited to the green next higher state available for the electron is the empty e_g level.

Since the yellow green wavelength is absorbed from the visible region of light it would excite the electron from t_{2g} level to the e_g level ($t_{2g}^1 e_g^0 \rightarrow t_{2g}^0 e_g^1$). Consequently, the blue and red light will be transmitted and solution of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ will appear purple which is the mixed effect of blue and red colours (Fig. 1.23). The CFT attributes the colour of coordination compounds to $d-d$ transition of the electron.

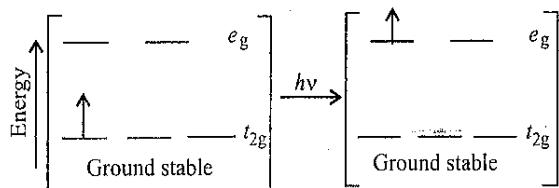


Fig. 1.23 Transition of an electron in $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$

Sc^{3+} and Ti^{4+} have completely empty d -orbitals and are colourless. Cu^{+} and Zn^{2+} have completely filled d -orbitals for promotion of electrons, hence they are also colourless.

In the absence of strong ligand, crystal field splitting does not occur and the substance is colourless.

For example, removal of water from $[\text{Ti}(\text{H}_2\text{O})_6] \text{Cl}_3$ on heating renders it colourless. Similarly, CuSO_4 is white but $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ [i.e. $[\text{Cu}(\text{H}_2\text{O})_4]^{2+} \text{SO}_4^{2-} \cdot \text{H}_2\text{O}$] is blue in colour.

In case of a tetrahedral complex, the electron will be excited from lower level, i.e. (e) level to the next higher state, i.e. t_2 empty level.

4. Colour in lanthanides and actinides: The source of colour in the lanthanides and the actinides is due to $f-f$ transitions. In lanthanides, $4f$ -orbitals are deeply embedded inside the atom and are well shielded by the $5s$ and $5p$ electrons. The f -electrons are practically unaffected by complex formation, hence the colour remains almost constant for a particular ion, regardless of the ligand.

5. Colour of some gem stones: Ruby is Al_2O_3 containing about 0.5–1% Cr^{3+} ions (d^3), which are randomly distributed in positions normally occupied by Al^{3+} . These Cr^{3+} species are octahedral Cr^{3+} complexes incorporated into the alumina lattice; $d-d$ transitions at these centres give rise to the colour.

In emerald, Cr^{3+} ions occupy octahedral sites in the mineral beryl $[\text{Be}_3 \text{Al}_2 \text{Si}_6 \text{O}_{18}]$. The absorption bands seen in the ruby shifts to longer wavelength, namely yellow-red and blue, causing emerald to transmit light in the green region.

6. Colour of compounds having d^0 configuration, i.e.

d -level is empty (charge transfer theory): In the series Sc^{3+} , Ti^{4+} , V^{5+} , Cr^{6+} and Mn^{7+} , these ions have empty d -shell, i.e. d^0 configuration, hence $d-d$ spectra (or ligand field type) are impossible and they **should be colourless**.

However, as the oxidation number increases these states become increasingly covalent. Rather than forming highly charged simple ions, oxoions are formed.

Examples:

- TiO^{2+} , VO_2^+ , VO_4^{3-} , CrO_4^{2-} and VO_4^{\ominus} are pale yellow.
- CrO_4^{2-} is strongly yellow coloured.
- MnO_4^{\ominus} has intense purple colour in solution though the solid is almost black.
- $\text{K}_2\text{Cr}_2\text{O}_7$ has orange colour.

The colour arises by charge transfer transitions.

Explanation: As the term implies, these transitions involve electron transfer from part of the complex to another. More specifically, an electron moves from an orbital that is mainly ligand in character to one that is mainly metal in character (i.e. ligand-to-metal charge transfer, LMCT) or vice versa (metal-to-ligand charge transfer, MLCT). Unlike $d-d$ transitions, those involving charge transfer are fully allowed and hence give rise to much more intense absorptions. When these absorptions fall in the visible region, they produce complementary colours.

For example, in MnO_4^{\ominus} an electron is momentarily transferred from oxygen to a metal (LMCT), thus momentarily changing O^{2-} to O^{\ominus} and reducing the oxidation state of the metal from Mn^{7+} to Mn^{6+} . Charge transfer requires that the energy levels on the two different atoms are fairly close and fall in the visible region and produce complementary colour.

Thus, KMnO_4 is purple colour in solution, $\text{K}_2\text{Cr}_2\text{O}_7$ is orange coloured and K_2CrO_4 is yellow in colour, due to charge transfer transitions.

Many iodide salts are also coloured because of charge transfer transitions. For example, HgI_2 (red), BiI_3 (orange red), PbI_2 (yellow). The metal ions in these substances certainly are not outstanding oxidising agents, but the transitions occur because the I^{\ominus} ion is easily oxidised. Likewise, V_2O_5 is red or orange, NbCl_5 is yellow, NbBr_5 is orange and NbI_5 is brass coloured.

7. Compounds of s - and p -block elements are not coloured: They do not have a partially filled d -shell so

there cannot be any $d-d$ transitions. The energy to excite an s or a p electron to a higher energy level is much greater and corresponds to ultraviolet light being absorbed. Thus, the compounds will not be coloured.

8. Colour due to defects in the solid state: The colour in solid state is due to the following defects.

Non-stoichiometric defects: If an imperfection causes the ratio of cations and anions to become different from that indicated by the ideal chemical formula, the defect is called non-stoichiometric. Non-stoichiometric defects are of two types: (a) metal excess defects and (b) metal deficiency defects.

- a. **Metal excess defects:** Metal excess defects may occur in either of the following two ways:

- i. **By union vacancies or F-centre:** Negative ion may be missing from its lattice site, leaving a hole, which is occupied by an electron thereby maintaining an electrical balance. The trapped electrons are called F-centres (from the German word Farbenzenter for colour centres) because they are responsible for imparting colour to the crystal (Fig. 1.24). This defect is similar to Schottky defect and is found in crystals having Schottky defects.

Example: NaCl when heated in Na vapour atmosphere, the excess Na atom is deposited on the surface. Now Cl^\ominus diffuse to the surface where they combine with Na atoms which lose the electrons. The electrons diffuse into the vacant sites created. The electrons absorb some energy from the visible light and re-emit the complementary yellow colour to NaCl crystal. Excess of Li in LiCl gives a pink colour. Excess of K in KCl make it violet.

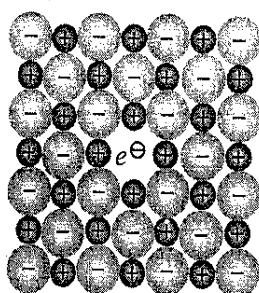


Fig. 1.24 An F-centre in a crystal

- ii. **By the presence of extra cations in interstitial sites:** Extra cations occupying interstitial sites with electrons present in another interstitial site to maintain electrical neutrality causes metal excess defects (Fig. 1.25). This defect is similar to Frenkel defect and is formed in crystals having Frenkel defects.

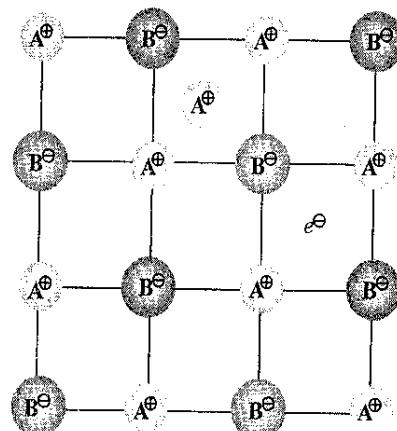
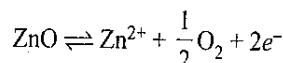


Fig. 1.25 Metal excess defect caused by extra cation in interstitial position

Example: If ZnO is heated, it loses oxygen and turns yellow.



Now there is excess of Zn^{2+} in the crystal and its formula becomes $\text{Zn}_{(1+x)}\text{O}$.

The excess Zn^{2+} ions thus formed get trapped into the vacant interstitial sites, while electrons are entrapped in the neighbouring interstitial sites. These entrapped electrons increase the electrical conductivity of ZnO and turn yellow. On cooling, they again turn into white due to the reverse reaction as shown above.

Note: Crystals with either type of metal excess defect act as semiconductors.

9. Certain substances change their colour when they are hot and revert to their original colour in cold.

Example:

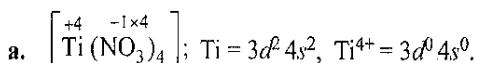
| Observation | Compound suspected |
|--|--|
| a. Yellow when hot and white in cold again | i. ZnO |
| b. Yellowish brown in hot and yellow in cold | ii. Bi_2O_3 and SnO_2 |
| c. Black or red in hot and brown in cold | iii. Fe_2O_3 |
| d. Yellow in hot and yellow in cold | iv. PbO |

Illustration 1.68 Identify the complexes which are expected to be coloured.

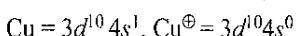
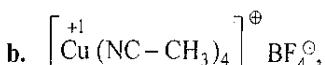
- a. $[\text{Ti}(\text{NO}_3)_4]$
- b. $[\text{Cu}(\text{NC CH}_3)_4]^\oplus \text{BF}_4^\ominus$
- c. $[\text{Cr}(\text{NH}_3)_6]^{3+} 3\text{Cl}^\ominus$
- d. $\text{K}_3[\text{VF}_6]$

[IIT-1994]

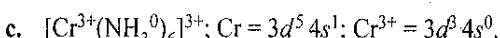
Sol. (c) and (d) are coloured.



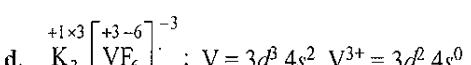
There is no unpaired electron in Ti^{4+} ion, hence no $d-d$ transition occurs, so colourless.



d^{10} configuration of Cu^{\oplus} ion have no unpaired electron, hence colourless.



Cr^{3+} has d^3 configuration, thus have three unpaired electrons, $d-d$ transition occurs, hence coloured.



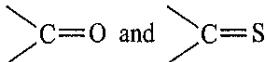
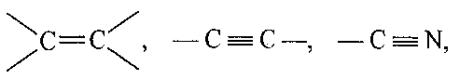
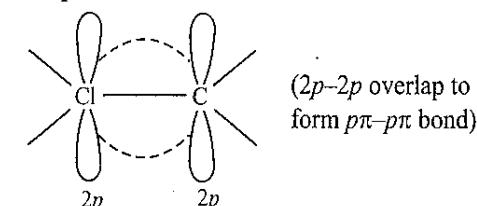
V^{3+} has d^2 configuration, thus have two unpaired electrons, $d-d$ transition occurs, hence coloured

1.32 $p\pi-p\pi$ MULTIPLE BONDING

First element of groups 14, 15 and 16 shows considerable differences in its chemical properties from that of other members of their respective groups, due to (i) their smaller size, (ii) high IE₁, (iii) high EN and (iv) non-availability of d -orbitals.

Carbon (C), nitrogen (N) and Oxygen (O) have unique ability to form $p\pi-p\pi$ multiple bonds with itself and with other elements having (i) small size and (ii) high EN.

Example:



Heavier elements of these groups do not form $p\pi-p\pi$ bonds as their atomic orbitals are so large and diffuse that they cannot have effective overlapping.

Thus, nitrogen exists as a diatomic molecule (N_2) with a triple bond (one s and two p) between the two atoms. Consequently, its bond enthalpy (941.4 kJ mol⁻¹) is very high. On the contrary, phosphorous, arsenic and antimony form single bond as P-P, As-As and Sb-Sb while bismuth forms metallic bonds in elemental state.

However, single N-N bond is weaker than the single P-P bond because of high interelectronic repulsion of the non-bonding electrons, owing to the small bond length. As a result the catenation tendency is weaker in nitrogen. Another factor which affects the chemistry of nitrogen is the absence of d -orbitals in its valence shell.

Besides restricting its covalency to four, nitrogen cannot form $p\pi-d\pi$ bond as the heavier elements can, e.g. $\text{R}_3\text{P} = 0$ or $\text{R}_3\text{P} = \text{CH}_2$ (R = alkyl group).

Phosphorous and arsenic can form $d\pi-d\pi$ bond also with transition metals when their compounds like $\text{P}(\text{C}_2\text{H}_5)_3$ and $\text{As}(\text{C}_6\text{H}_5)_3$ act as ligands.

Tendency of carbon to form $p\pi-p\pi$ multiple bonds is found in the structure of its allotropic modification, graphite.

Elemental silicon exists only in the diamond structure. This clearly indicates the reluctance of silicon to form $p\pi-p\pi$ multiple bond.

Illustration 1.69 ($p\pi-p\pi$) back bonding occurs in the halides of boron but not in those of aluminium. Explain.

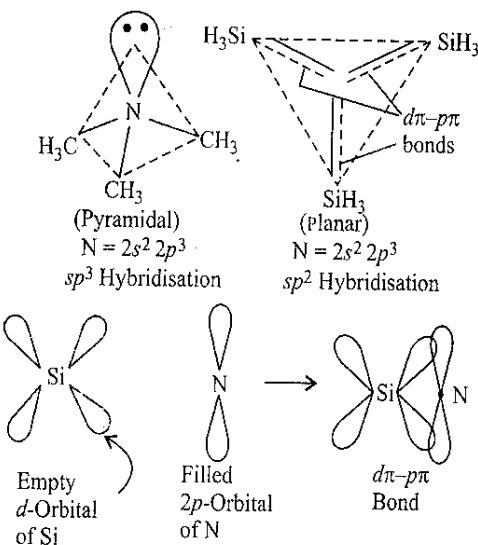
Sol. The tendency of the central atom (A) in AX_3 molecules (A = B or Al, X = halogens) to form ($p\pi-p\pi$) back bonding depends on the size of central atom (A). Smaller is the size of the central atom, greater is the tendency to form ($p\pi-p\pi$) back bonding. Since boron (B) atom is smaller in size than aluminium (Al) atom, BX_3 molecules have ($p\pi-p\pi$) back bonding while AlX_3 molecules do not have this type of bonding.

Illustration 1.70 The Lewis acid character of boron trihalides decreases as: $\text{BBr}_3 > \text{BCl}_3 > \text{BF}_3$. Explain?

Sol. According to the EN order (F > Cl > B), the Lewis acid character should be $\text{BF}_3 > \text{BCl}_3 > \text{BBr}_3$ but it is observed to be reverse, this can be explained by ($p\pi-p\pi$) back bonding that occurs in the given halides.

1.33 $p\pi-d\pi$ MULTIPLE BONDING

Though the tendency to form $p\pi-p\pi$ multiple bonds is not common with silicon and other heavier members of this group, multiple bonding involving d -orbitals has been reported. This tendency is particularly in the case of silicon linked to oxygen and nitrogen. The geometry around the nitrogen atom in trimethylamine $\text{N}(\text{CH}_3)_3$ is pyramidal (sp^3 -hybridisation of nitrogen atom), whereas in the case of similar silicon compound, $\text{N}(\text{SiH}_3)_3$, called trisilylamine, it is planar arrangement of its three bonds (sp^2 hybridisation of N atom). In the latter case, the lone pair on nitrogen is transferred to the empty d -orbital of silicon ($p\pi-d\pi$ overlapping) leading to the planar structure of $\text{N}(\text{SiH}_3)_3$. For the same reason $\text{N}(\text{CH}_3)_3$ is more basic than $\text{N}(\text{SiH}_3)_3$.

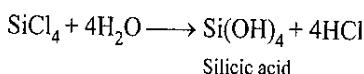


- All the elements of group 14 form tetrahalides of the formula MX_4 , $PbCl_4$ and $PbBr_4$ are unstable and PbI_4 is not known.
- All these halides are covalent compounds and have tetrahedral shapes.

1.33.1 Hydrolysis of SiX_4

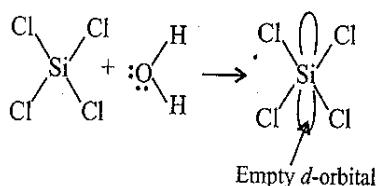
The tetrachloride of carbon (CCl_4) is not hydrolysed by water. However, the tetrachlorides of all the remaining elements are easily hydrolysed.

CCl_4 is not hydrolysed by water because carbon has no d -orbitals and hence cannot expand its coordination number beyond 4. However, silicon can expand its octet (coordination number beyond 4) due to the availability of energetically suitable vacant d -orbitals in its atom.



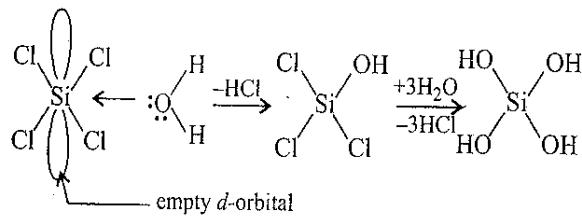
The mechanism of hydrolysis of $SiCl_4$ involves two steps:

- The first step involves the attack of oxygen atom of water molecule on the metal atom forming a coordinate bond between the metal and oxygen atom of water.



- The second step involves the loss of HCl. During this step one Cl atom on silicon in $SiCl_4$ is replaced by an OH group. This process continues till all the four Cl

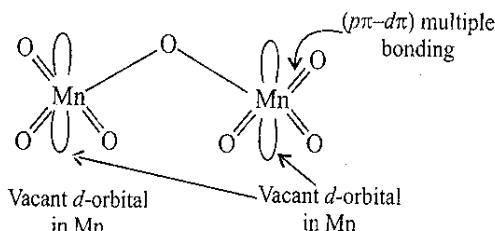
atoms are replaced by OH groups yielding $Si(OH)_4$, i.e. silicic acid.



1.33.2 MnF_4 and Mn_2O_7 Exists but MnF_7 Does Not

The highest Mn fluoride is MnF_4 , whereas the highest oxide is Mn_2O_7 . In other words in Mn fluoride the highest oxidation state of Mn is +4 but in oxides it is +7, although F is more EN than oxygen.

Thus, the ability of oxygen to stabilise these high oxidation states exceeds that of fluorine. This is due to the ability of oxygen to form $p\pi-d\pi$ multiple bonds to metals. Vacant $3d$ -orbitals of Mn overlap with $2p$ -orbitals of oxygen to form ($p\pi-d\pi$) multiple bonds as shown:



1.34 OXIDES

Properties of representative elements along the period (\rightarrow) can be compared from the study of the properties of their oxides. The oxides of elements of the 3rd period are Na_2O , MgO , Al_2O_3 , SiO_2 , P_4O_{10} , SO_3 and Cl_2O_7 .

The tendency of oxygen to form oxide ion is greatly favoured when oxygen combines with metals having low IE's such as group 1 and 2 elements, and aluminium (Al). Thus, Na_2O , MgO and Al_2O_3 are ionic compounds having extensive three-dimensional (3D) structures in which each cation is surrounded by a specific number of anions and vice versa. Silicon is a metalloid whose oxide (SiO_2) has a giant 3D network, although no ions are present.

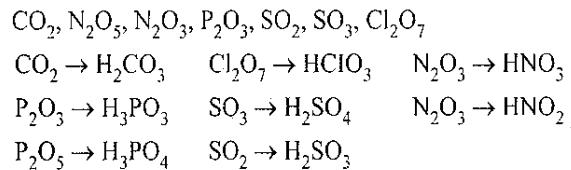
The oxides of P and S and molecular compounds are composed of small discrete units.

1.34.1 Properties of Oxides

Oxygen reacts with almost all elements (except noble gases, Au, Pd, Pt) to form oxides. In general, metallic oxides (O^{2-}), peroxides (O_2^{2-}) and superoxides (O_2^{\bullet}) are ionic solids. For example, Li_2O , Na_2O_2 (Na forms peroxide with O_2 , rather than oxide), KO_2 , RbO_2 . The tendency of group 1 metals to form

oxygen rich compounds increases upon descending the group, i.e. with increasing cation radii and decreasing charge density on the metal ion. A similar trend is observed in the reaction of group 2 metals. Except Be, group 2 metals react with oxygen at normal conditions to form normal ionic oxides and at high pressure of O₂, they form peroxides (CaO₂, SrO₂, BaO₂).

1. Metals that show variable oxidation states react with a limited amount of oxygen to form lower oxidation state oxides (FeO, Cu₂O) while reacting with an excess of oxygen gives higher oxidation state oxides (Fe₂O₃, CuO).
2. Oxides of metals are called as basic anhydrides as many of them combine with water to form hydroxides with no changes in oxidation state of metals. Oxides of groups 1 and 2 dissolve in water to give basic solutions whereas other oxides are insoluble in water.
3. Oxygen combines with many non-metals to form covalent oxides (such as CO, CO₂, SO₂, SO₃, P₄O₆, Cl₂O₇, N₂O₅ etc.). The reaction of non-metals with a limited amount of oxygen usually gives product that contains non-metals in lower oxidation states, while with excess of oxygen, higher oxidation state oxides are formed. Oxides of non-metals are called **acid anhydrides**, as many of them dissolve in water to form acids and oxyacids. Some of such oxides are as follows:



Note: CO, N₂O, NO and H₂O are neutral oxides.

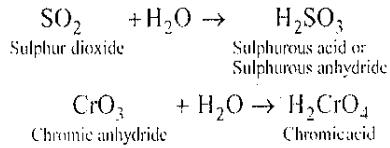
Table 1.25 Periodic trends in valence of electrons shown by the formula of these oxides

| | Group (→) | 1 | 2 | 13 | 14 |
|-------------------|---------------|---|--------------|--------------------------------|--------------------------------|
| | Period (↓) | | | | |
| Formula of oxides | 2 | Li ₂ O, oxide | BeO | B ₂ O ₃ | CO ₂ |
| | 3 | Na ₂ O ₂ , peroxide | MgO | Al ₂ O ₃ | SiO ₂ |
| | 4 | KO ₂ | Super oxides | CaO | Ga ₂ O ₃ |
| | 5 | RbO ₂ | | SrO | In ₂ O ₃ |
| | 6 | CsO ₂ | | BaO | PbO ₂ |

1.34.2 Classification of Oxides Based on Their Chemical Behaviour

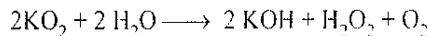
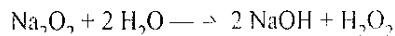
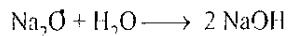
Based on their chemical behaviour, the oxides have been classified as:

1. **Acidic oxides:** Oxides which dissolve in water forming acids and neutralise alkalis are called acidic oxides. They are also called acid anhydrides and are generally the oxides of non-metals (e.g. B₂O₃, SiO₂, CO₂, N₂O₃, N₂O₅, P₂O₅, SO₂, SO₃, Cl₂O₇ and I₂O₅ or metallic oxides of high oxidation state (e.g. Mn₂O₇, CrO₃ and V₂O₅)



2. **Basic oxides:** These may be

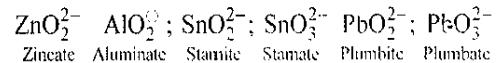
- a. **Essentially covalent:** Oxides of transition metals MO and M₂O₃ are essentially covalent. These are non-volatile (giant molecule structure) insoluble in water and not attacked by it.
- b. **Essentially ionic:** These are attacked by water to give alkalis. These are oxides of metals, e.g. Na₂O, CaO, BaO (normal) oxides containing O²⁻ ion; Na₂O₂, BaO₂ (peroxide containing O₂²⁻ ion); and KO₂, RbO₂ (superoxides containing O₂⁻ ion).



3. **Amphoteric oxides:** A few metallic oxides exhibit a dual behaviour. These dissolve in both acids and alkalis.

- a. ZnO gives zinc salts, Zn²⁺ and Zn(OH)₄²⁻.
- b. Al₂O₃ gives aluminium salts, Al³⁺ and aluminates, Al(OH)₄⁻.
- c. SnO gives stannous salts, Sn²⁺ and stannites, Sn(OH)₄²⁻.
- d. SnO₂ gives stannic salts, Sn⁴⁺ and stannates Sn(OH)₆²⁻.

The above formulae for hydroxyl complexes are correct for the ions in solution. If the solution, say sodium zincate is evaporated, it loses water.



4. **Neutral oxides:** Those oxides which are neutral towards litmus are called neutral oxides. Examples of neutral oxides are carbon monoxide (CO), water (H₂O), nitrous oxide (N₂O) and nitric oxide (NO).

The two systems for classification of oxides are quite independent of each other. For example, sodium oxide (Na₂O) is a **basic oxide as well as normal oxide**. Similarly, nitrous oxide (N₂O) is a **neutral oxide as well as suboxide**.

Examples:

Basic oxides: $\text{Cs}_2\text{O} > \text{Rb}_2\text{O} > \text{K}_2\text{O} > \text{Na}_2\text{O} > \text{Li}_2\text{O} > \text{BaO} > \text{SrO} > \text{CaO} > \text{MgO}$

Amphoteric oxides: $\text{BeO} > \text{Al}_2\text{O}_3 > \text{Ga}_2\text{O}_3 > \text{ZnO}$
(Table 1.26)

Table 1.26 Elements forming amphoteric oxides are shown in circles

| Acidic character increases → | | | | | | | | | | | | | | | | | | | | | |
|------------------------------|----|---------|---|--|--|--|--|--|--|--|--|--|--|--|----|---------|-----|----|-----|----|----|
| s-Block | | d-Block | | | | | | | | | | | | | | p-Block | | | | | |
| 1s | 1 | 2 | H | | | | | | | | | | | | 13 | 14 | 15 | 16 | 17 | He | |
| 2s | Li | Be | | | | | | | | | | | | | 2p | B | C | N | O | F | Ne |
| 3s | Na | Mg | | | | | | | | | | | | | 3p | Al | Si | P | S | Cl | Ar |
| 4s | K | Ca | | | | | | | | | | | | | 4p | Ga | Ge | As | Sc | Br | Kr |
| 5s | Rb | Sr | | | | | | | | | | | | | 5p | In | Sn | Sb | Te | I | Xe |
| 6s | Cs | Ba | | | | | | | | | | | | | 6p | Tl | Pb | Bi | Po | At | Rn |
| 7s | Fr | Ra | | | | | | | | | | | | | 7p | — | Uuq | — | Uuh | — | — |

1.34.3 Trends of Oxides**1. Trends of oxides in periodic table:**

a.

| Along the period, oxides show basic to acidic character | | |
|---|---------------------------|----------------------|
| Group | Example | Nature |
| 1 | Na_2O | Strongly basic |
| 2 | MgO | Basic |
| 13 | Al_2O_3 | Amphoteric |
| 14 | SiO_2 | Weakly acidic |
| 15 | P_4O_{10} | Acidic |
| 16 | SO_3 | Acidic |
| 17 | Cl_2O_7 | Very strongly acidic |

2. In a group, basic nature increases or acidic nature decreases. Oxides of metals are generally basic and oxides of non-metals are acidic. The oxides of metalloids are amphoteric. The oxides of Al, Zn, Sn, As and Sb are amphoteric.

- a. Among s-block elements, on moving down a group the basic character increases.

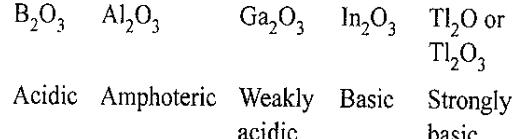
| | | | |
|-----------------------|-----------------------|----------------------|---|
| Li_2O | Na_2O | K_2O | $\text{Rb}_2\text{O},$ Cs_2O |
| Weakly basic | Basic | More strongly basic | Very strongly basic |

- b. Among p-block elements, on moving down the group the acidic character of oxides decreases while the basic

Acidic oxides: $\text{Cl}_2\text{O}_7 > \text{SO}_3 > \text{N}_2\text{O}_5 > \text{P}_2\text{O}_5 > \text{CO}_2 > \text{B}_2\text{O}_3$

Group 17 16 15 15 14 13

Neutral oxides: $\text{H}_2\text{O}, \text{CO}, \text{N}_2\text{O}$ and NO



3. In case when an element forms a number of oxides, the acidic nature increases as the percentage of oxygen increases.

Note: For molecules having $\frac{\text{O}}{\text{M}} \geq 1.5$, they are acidic, others are neutral.

a.

| N_2O | NO | N_2O_3 | NO_2 | N_2O_5 |
|---|---|---|---|---|
| Neutral | Neutral | Acidic | Acidic | Acidic |
| $\frac{\text{O}}{\text{M}} = \frac{1}{2} = 1.5$ | $\frac{\text{O}}{\text{M}} = \frac{1}{1} = 1.0$ | $\frac{\text{O}}{\text{M}} = \frac{3}{2} = 1.5$ | $\frac{\text{O}}{\text{M}} = \frac{2}{1} = 2.0$ | $\frac{\text{O}}{\text{M}} = \frac{5}{2} = 2.5$ |
| (Exception) | | | | |

b.

| P_2O_3 | P_2O_4 | P_2O_5 |
|---|---|---|
| Acidic | Acidic | Acidic |
| $\frac{\text{O}}{\text{M}} = \frac{3}{2} = 1.5$ | $\frac{\text{O}}{\text{M}} = \frac{4}{2} = 2.0$ | $\frac{\text{O}}{\text{M}} = \frac{5}{2} = 2.5$ |
| | | |

c.

| MnO | Mn ₂ O ₃ | MnO ₂ | MnO ₃ | Mn ₂ O ₇ |
|--|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|
| Neutral | Neutral | Acidic | Acidic | Acidic |
| $\frac{O}{M} = \frac{1}{1} = 1.0$ (Exception) | $\frac{O}{M} = \frac{3}{2} = 1.5$ | $\frac{O}{M} = \frac{2}{1} = 2.0$ | $\frac{O}{M} = \frac{3}{1} = 3.0$ | $\frac{O}{M} = \frac{7}{2} = 3.5$ |

Note: The acidity increases as the oxidation state of N, P or Mn increases to more positive oxidation states.

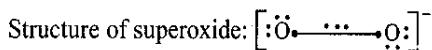
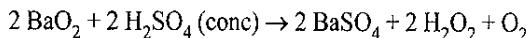
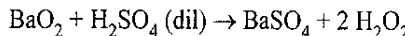
1.34.4. Classification of Oxides Based on Their Oxygen Content

A binary compound of oxygen with another element is called an oxide. Based on their chemical behaviour or oxygen content, chief classes of oxides are given below:

1. **Normal oxides:** Oxides which contain just as much oxygen as permitted by the normal oxidation number of M are called normal oxides. A few examples of normal oxides are H₂O, MgO, Al₂O₃. These contain only M–O bonds.

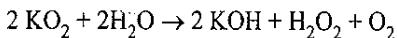
2. **Polyoxides:** Oxides containing more oxygen than allowed by normal oxidation number of M are termed as polyoxides. They involve O–O bonds as well as M–O bonds. These have been further classified as given below:

a. **Peroxides:** These contain O₂²⁻ ion and are derivatives of H₂O₂ (H–O–O–H). These produce hydrogen peroxide with dilute acids and liberate oxygen with concentrated acids. A few examples of true peroxides are sodium peroxide and barium peroxide.

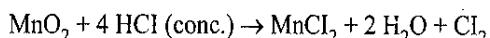
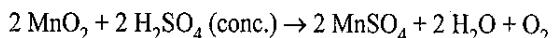


Superoxides have 3e⁻ bond and are paramagnetic and coloured due to the presence of unpaired e⁻.

b. **Superoxides:** These contain O₂²⁻ ion. The superoxides known are KO₂, RbO₂ and CsO₂. These react with water to give hydrogen peroxide and oxygen.



c. **Dioxides:** Polyoxides which contain higher percentage of oxygen such as peroxides but do not give any hydrogen peroxide with dilute acids are termed dioxides. These oxidise conc. HCl to Cl₂ and yield O₂ when heated with conc. H₂SO₄. Manganese dioxide (MnO₂) and lead dioxide (PbO₂) are examples of dioxides.



3. **Suboxides:** Oxides which contain a lower percentage of oxygen than expected by the oxidation number of M are

called suboxides, e.g. nitrous oxide, N₂O, carbon suboxide (C₃O₂).

They involve M–M bonds in addition to M–O bonds, for example O=C=C=O (carbon suboxide).

4. **Mixed oxides:** Some oxides may be considered to be made of two simpler oxides. Their chemical behaviour confirms this view. These oxides are also called compound oxides, e.g.

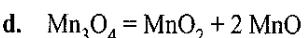
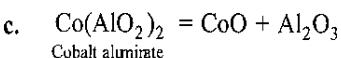
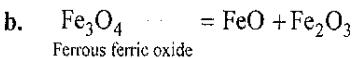
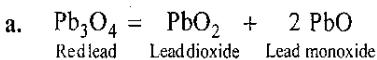


Illustration 1.71 The correct order of relative basic character of NaOH, Mg(OH)₂ and Al(OH)₃ is

- a. Al(OH)₃ > Mg(OH)₂ > NaOH
- b. Mg(OH)₂ > NaOH > Al(OH)₃
- c. NaOH > Mg(OH)₂ > Al(OH)₃
- d. Al(OH)₃ > NaOH > Mg(OH)₂

Sol. c. Basic strength decreases along the period (→).

Illustration 1.72 Which of the oxides behave both as neutral oxide and suboxide?

- a. N₂O
- b. NO
- c. C₃O₂
- d. CO

Sol. a. N₂O acts both as neutral oxide and suboxide.

- b. NO is neutral oxide.
- c. C₃O₂ is suboxide.
- d. CO is neutral oxide.

Illustration 1.73 Which of the following is not amphoteric oxide?

- a. ZnO
- b. BeO
- c. Al₂O₃
- d. CrO₃

Sol. d. CrO₃ is acidic oxide while others are amphoteric oxide.

Illustration 1.74 Which of the following is superoxide?

- a. Na₂O₂
- b. BaO₂
- c. CsO₂
- d. MnO₂

Sol. c. CsO₂ is superoxide (Cs⁺ and O₂²⁻)

(a) and (b) are peroxide.

Illustration 1.75 Which of the oxides is coloured and contains 3e⁻ bond?

- a. MgO
- b. Na₂O
- c. KO₂
- d. Mn₃O₄

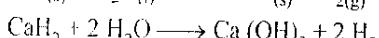
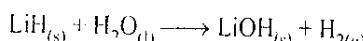
Sol. c. KO₂ is superoxide and is coloured and contains 3e⁻ bond.

(a) and (b) are oxides while (d) is mixed oxide of (2MnO + MnO₂).

1.35 PERIODICITY IN HYDRIDES OF ELEMENTS

- Hydrides:** Hydrogen forms binary compounds with metals and non-metals and are called hydrides.
- Ionic hydrides:** Hydrogen with active metals of groups 1 and 2 forms ionic hydrides. These contain hydride ion $H^{(1)}$ formed by gaining one electron per atom from an active metal.

These ionic hydrides are basic in nature as hydride ions reduce water to form OH ions and H_2 , e.g.

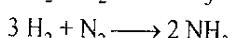
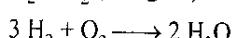
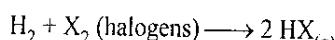


- The hydrides BeH_2 and MgH_2 are not strongly ionic (intermediate character).

| Group (\rightarrow) | 1 | 2 |
|-------------------------|-----|---------|
| Period (\downarrow) | | |
| 2nd | LiH | BeH_2 |
| 3rd | NaH | MgH_2 |
| 4th | KH | CaH_2 |
| 5th | RbH | SrH_2 |
| 6th | CsH | BaH_2 |

4. Covalent hydrides:

- These are formed by sharing its electron with an atom of another non-metal to form a single covalent bond.
- Hydrogen reacts with non-metals to form binary covalent hydrides



- Most of the covalent (non-metal) hydrides are acidic in nature. Their aqueous solution produce H^+ ions in H_2O , e.g. HF, HCl, HI, H_2O , H_2S etc.

1.35.1 Nature of Hydrides

- The nature of hydrides changes from basic to acidic in a period from the left to the right.

| | | | |
|------------|-----------------|------------------|-------------|
| 2nd Period | NH ₃ | H ₂ O | HF |
| | Weak base | Neutral | Weak acid |
| 3rd Period | PH ₃ | H ₂ S | HCl |
| | Very weak base | Weak acid | Strong acid |

- In a group, the acidic nature of the hydrides of non-metal increases. The reducing nature also increases but the stability decreases down the group (\downarrow).

1.35.2 Stability of Covalent Hydrides

The stability of the hydrides of groups 13 to 17 decreases down the group (\downarrow) due to corresponding decreases in the strength of M-H bond as the size of the M atom increases and bond length of M-H bond increases.

Thus, TlH_3 , PbH_4 , BiH_5 and H_2P_0 are quite unstable.

| Group (\rightarrow) Period (\downarrow) | 13 | 14 | 15 | 16 | 17 |
|--|----|------------------|------------------|------------------|-------------------|
| Period | 2 | BH ₃ | CH ₄ | NH ₃ | H ₂ O |
| | 3 | AlH ₃ | SiH ₄ | PH ₃ | H ₂ S |
| | 4 | GaH ₃ | GeH ₄ | AsH ₃ | H ₂ Se |
| | 5 | InH ₃ | SnH ₄ | SbH ₃ | H ₂ Te |
| | 6 | TlH ₃ | PbH ₄ | BiH ₅ | |

1.35.3 Reducing Character of Covalent Hydrides

Since down the group, the stability of hydrides of above group decreases, the ability to give H-atom increases (i.e. ability of oxidation increases). Thus, the heavier hydrides have more reducing character.

In other words, the reducing character of the hydrides of the above group increases down the group (\downarrow).

ILLUSTRATION 1.7.1 The least stable hydride is

- a. Stannane b. Silane c. Plumbane d. Germane

Sol. c. Stability order of carbon family hydride is Silane (SiH_4) > Stannane (SnH_4) > Plumbane (PbH_4)

Hence the answer is (c).

ILLUSTRATION 1.7.2 The most stable hydride is

- a. B_2H_6 b. AlH_3 c. GaH_3 d. InH_3

Sol. a. BH_3 or B_2H_6 is the most stable since the stability of hydrides decreases down the group (\downarrow).

ILLUSTRATION 1.7.3 The strongest reducing hydride is

- a. NH_3 b. PH_3 c. AsH_3 d. SbH_3

Sol. Reducing character of hydrides increases down the group (\downarrow).

1.36 ARRHENIUS CONCEPT OF ACIDS AND BASES

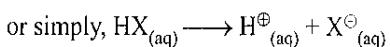
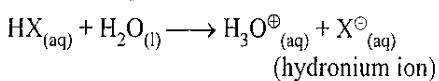
According to this concept, an acid and a base can be defined as follows:

Acid: It is a substance that produces hydrogen ions (H^+) in water, e.g. HCl, H_2SO_4 , HNO_3 etc.

Base: It is a substance that produces hydroxyl ion (OH^-) in water. NaOH, KOH, $Mg(OH)_2$ etc. are the examples of Arrhenius bases.

Let us represent an acid as HX and a base as BOH .

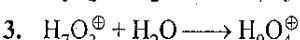
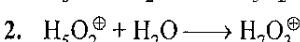
The ionisation of acid as (HX) can be represented by the following equation:



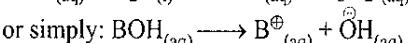
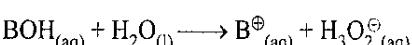
Hydronium ion ($\text{H}_3\text{O}^{\oplus}$) is used to represent a hydrated H^{\oplus} ion, i.e. H^{\oplus} ion surrounded by water molecules.

General formula of a hydronium ion is $\text{H}_{2n+1}\text{O}_n^{\oplus}$.

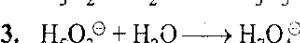
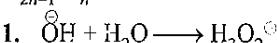
Thus, $\text{H}_9\text{O}_4^{\oplus}$ is a hydronium H^{\oplus} ion surrounded by four water molecules.



Similarly, the ionisation of a base (BOH) is represented by the following equation:



The hydroxyl is hydrated to give species of general formula $\text{H}_{2n-1}\text{O}_n^{\ominus}$.



Note: The Arrhenius concept of acids and bases is only limited to aqueous solutions.

1.36.1 Limitations of Arrhenius Concept

- It is applicable only to the aqueous solutions. For the acidic or basic properties, the presence of water is absolutely necessary. Dry HCl shall not act as an acid.
- The concept does not explain the acidic or basic properties of acids or bases in non-aqueous solvents respectively.
- It fails to explain the acidic nature of the non-protic compounds such as SO_2 , NO_2 , CO_2 , P_2O_5 etc., which do not have hydrogen for furnishing H^{\oplus} ions.
- It fails to explain the basic nature of compounds such as NH_3 , Na_2CO_3 etc., which do not have OH in the molecules to furnish OH^- ions.
- It fails to explain the acidic nature of certain salts such as AlCl_3 in aqueous solution.

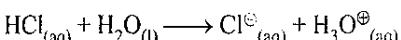
1.37 BRONSTED-LOWRY ACIDS AND BASES

According to this concept, an acid and a base can be defined as follows:

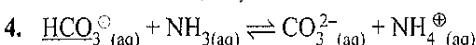
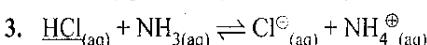
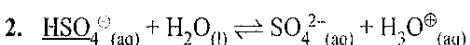
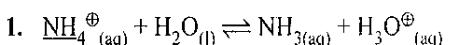
Acid: It is a substance that can donate a proton.

Base: It is a substance that can accept a proton.

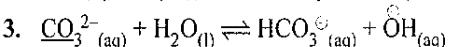
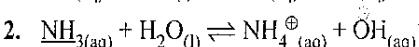
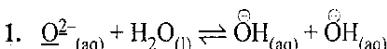
Example: When HCl is dissolved in water, it donates a proton to H_2O which behaves as a base.



Other examples of Bronsted-Lowry acids (underlined) are:



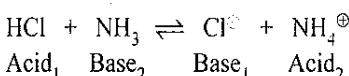
Some examples of Bronsted-Lowry bases (underlined) are:



Note:

- This theory states that an acid must contain transferable hydrogen and it offers great freedom in defining what constitutes a base.
- When an acid has donated its proton, the remaining portion of the molecule or ion is a base.
- When a base accepts a proton, it forms an acid.
- The base must have an unshared pair of electrons so as to accept a proton.

The base formed from an acid is known as the *conjugate base of the acid*. Correspondingly, the acid formed from a base is called the *conjugate acid of the base*.



In the above reaction, Cl^{\ominus} is the conjugate base of HCl and NH_4^{\oplus} is the conjugate acid of NH_3 .

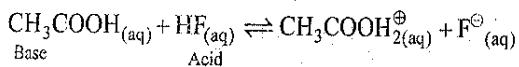
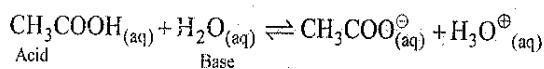
Note:

- The conjugate acid always has one or more proton than its conjugate base.
- To obtain a conjugate acid of a compound, remove a proton (H^{\oplus}) from it and to obtain the conjugate base of the same, add a proton to the compound, e.g. conjugate acid of NH_3 is NH_4^{\oplus} while the conjugate base of NH_3 is NH_2^{\ominus} .

iii. This concept has the advantage that it can be applied to a solvent other than water, having the tendency to accept or lose a proton.

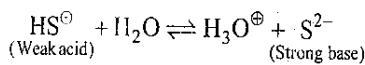
iv. The terms acid and base are comparative. A substance can behave as an acid in one solvent and as a base in another.

For example, acetic acid (CH_3COOH) behaves as an acid in water and as a base in HF.



1.37.1 Strength of Bronsted-Lowry Acids and Bases

The strength of an acid or a base is measured by its tendency to lose or gain proton. A strong acid is a substance which loses a proton easily to a base. Consequently, the conjugate base of a strong acid is a weak base.



The ability of an acid to lose proton is experimentally measured by its equilibrium constant known as K_a .

The larger the value of K_a , the more complete a reaction or higher the concentration of $\text{H}_3\text{O}^{\oplus}$ and the stronger is the acid.

Similarly, for bases, we have the equilibrium constant K_b which determines the extent of the completion of the reaction.

Reaction of common ions with water:

| No reaction | Weak reaction | Strong reaction |
|--|--|---|
| Basic | | |
| $\text{Cl}^{\ominus}, \text{Br}^{\ominus}, \text{I}^{\ominus}$ | $\text{CH}_3\text{COO}^{\ominus}, \text{F}^{\ominus}$ | $\text{PO}_4^{3-}, \text{S}^{2-}, \text{CO}_3^{2-}$ |
| $\text{NO}_3^{\ominus}, \text{ClO}_4^{\ominus}$ | $\text{NO}_2^{\ominus}, \text{HCO}_3^{\ominus}$ | |
| | $\text{CN}^{\ominus}, \text{SO}_4^{2-}$ | |
| | SO_3^{2-} | |
| Acidic | | |
| $\text{Li}^{\oplus}, \text{Na}^{\oplus}, \text{K}^{\oplus}$ | $\text{NH}_4^{\oplus}, \text{Be}^{2+}, \text{Zn}^{2+}$ | $\text{Fe}^{3+}, \text{Bi}^{3+}, \text{Sn}^{4+}$ |
| $\text{Mg}^{2+}, \text{Ca}^{2+}$ | $\text{Cu}^{2+}, \text{Fe}^{2+}, \text{Sn}^{2+}$ | Al^{3+} |
| Ag^{\oplus} | Cd^{2+} | |

Table 1.27 Acid-base table containing some common conjugate acid-base pairs

| Acid | Conjugate base | K_a | pK_a |
|-------------------------------|-----------------------------------|-----------------------|--------|
| HI | I^{\ominus} | 10^{11} | -11 |
| HClO_4 | ClO_4^{\ominus} | 10^{10} | -10 |
| HBr | Br^{\ominus} | 10^9 | -9 |
| HCl | Cl^{\ominus} | 10^7 | -7 |
| H_2SO_4 | HSO_4^{\ominus} | 10^2 | -2 |
| $\text{H}_3\text{O}^{\oplus}$ | H_2O | 1 | 0.0 |
| H_2SO_3 | HSO_3^{\ominus} | 1.5×10^{-2} | 1.81 |
| HSO_4^{\ominus} | SO_4^{2-} | 1.20×10^{-2} | 1.92 |
| H_3PO_4 | $\text{H}_2\text{PO}_4^{\ominus}$ | 7.5×10^{-3} | 2.12 |
| HF | F^{\ominus} | 2.5×10^{-4} | 3.45 |
| CH_3COOH | $\text{CH}_3\text{COO}^{\ominus}$ | 1.80×10^{-5} | 4.7 |
| H_2S | HS^{\ominus} | 1.0×10^{-7} | 7.0 |
| NH_4^{\oplus} | NH_3 | 5.6×10^{-10} | 9.3 |
| HCN | CN^{\ominus} | 4.0×10^{-10} | 9.4 |
| H_2O | OH^{\ominus} | 1.0×10^{-14} | 14.0 |
| CH_3OH | $\text{CH}_3\text{O}^{\ominus}$ | Very small | Large |
| NH_3 | NH_2^{\ominus} | Very small | Large |

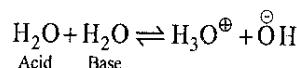
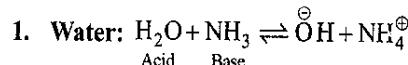
Note: CH_3OH is a stronger acid than H_2O .

Note: In general, solvents can be of four types:

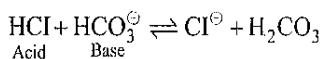
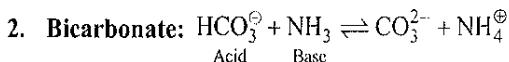
- Protophilic:** Solvents having a tendency to accept protons. For example, water, alcohol, liquid ammonia etc.
- Protogenic:** Solvents having a tendency to donate protons. For example, water, liquid HF, liquid HCl etc.
- Amphiprotic:** Solvents having a tendency to accept or donate protons. For example, water, liquid ammonia etc.
- Aprotic:** Solvents which neither accept nor donate protons. For example, benzene, carbon tetrachloride etc.

1.37.2 Amphoteric Compounds

The compounds which can act either as acids or as bases, H_2O , NH_3 and CH_3COOH are some of the examples.



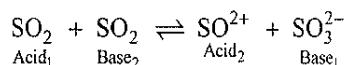
In the first reaction, H_2O is behaving as an acid while in the second one it is behaving as a base.



Note: The reaction $H_2O + H_2O \rightleftharpoons H_3O^{\oplus} + OH^{\ominus}$ is known as auto-ionisation of water.

Limitations of Bronsted concept:

1. A substance is termed as an acid or a base if it reacts with some other substance, i.e. if it donates proton to other substance, it is an acid and if it accepts proton from other substance, it is a base.
2. There are a number of acid-base reactions in which no proton transfer takes place, e.g.

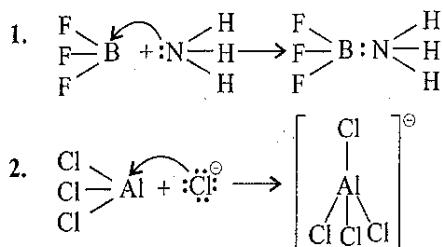


Thus, the protonic definition cannot be used to explain the reactions occurring in non-protonic solvents such as COC_2 , SO_2 , N_2O_4 etc.

1.38 LEWIS ACIDS AND BASES

Acid: It is a substance that can form a bond by accepting a shared pair of electrons.

Base: It is a substance that possesses at least one unshared pair of electrons.



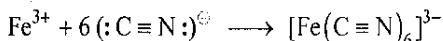
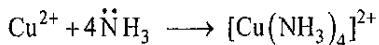
Monoprotic acids: Acids that give up one proton per molecule.

Polyprotic acids: Acids that can give up more than one proton per molecule.

Substances that are bases in the Bronsted system are also bases according to the Lewis concept. However, the Lewis definition of an acid considerably expands the number of substances that are classified as acids. A Lewis acid must have an empty orbital capable of receiving the electron pair of the base.

Lewis acids include molecules or atoms that have incomplete octets. For example, molecules such as BF_3 , $AlCl_3$ etc. act as Lewis acid.

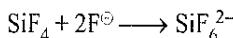
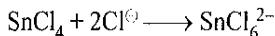
Many simple cations can act as Lewis acids:



Some metal atoms can function as acids in the formation of compounds such as



Compounds that have central atoms capable of expanding their valence shells are Lewis acids in reaction in which this expansion occurs.



Some compounds have an acidic site because of one or more multiple bonds in the molecule.

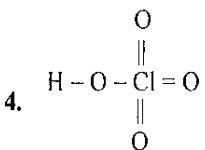
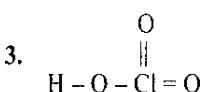
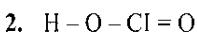
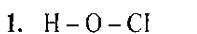
1.39 OXYACIDS

Acids that contain oxygen are called oxyacids.

Acidity of oxyacids increases with increasing oxidation number of the central atom, the atom to which oxygen atoms are attached.

| Acid | Formula | Oxidation number of chlorine |
|--------------|----------|------------------------------|
| Hypochlorous | $HClO$ | +1 |
| Chlorous | $HClO_2$ | +3 |
| Chloric | $HClO_3$ | +5 |
| Perchloric | $HClO_4$ | +7 |

Structures of the above oxyacids are



Due to resonance, the electron density decreases as the number of oxygen atoms in the oxyacids increases.

Note:

i. For monatomic anions of similar charge, base strength decreases with increasing size.

For example, S^{2-} is a weaker base than O^{2-} as the size of S^{2-} ion is greater than that of O^{2-} .

(Consequently, H_2S is a stronger acid than H_2O .)

ii. The base strength of anions is also influenced by the charge on them.

Thus, the base strength of the monatomic anions of the

elements of the second period $N^{3-} > O^{2-} > F^-$ decrease with increasing EN and with decreasing negative charge on the ion.

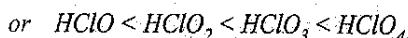
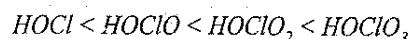
iii. For acids with structure: $H-O-Z$, the acid strength increases with increasing EN of Z.

The higher the EN of Z, the more the electrons of the molecule are displaced toward Z and the more proton is removed.

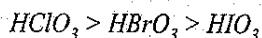
However, for the oxyacids of phosphorus, the oxidation number fails to give a true indication of the acid strength.

Thus, H_3PO_2 , H_3PO_3 and H_3PO_4 are approximately of equal strength although the oxidation state of P in these three oxyacids are +1, +3 and +5 respectively.

The number of O atom bonded to the central atom but not bonded to H atoms influence the formal charge of the central atom and thus provides a qualitative indication of the strength of acids of the general formula $(HO)_xZO_y$ (x and y are positive integers).



For the variations in the same groups (i.e. compounds with x and y), the acidic character increases with increasing EN of the central atom.



1.39.1 Strength of Binary Acids and Oxyacids

They are composed of hydrogen and a non-metallic elements.

| Increasing acidity | | | | | |
|--------------------|-----------------|-------------------|-----|--|--|
| CH ₄ | NH ₃ | H ₂ O | HF | | |
| | | H ₂ S | HCl | | |
| | | H ₂ Se | HBr | | |
| | | | HI | | |

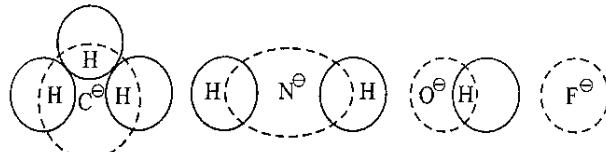
The following factors influence the acid strength:

- Too many factors influence the acid strength, making the predictions impossible.
- The acid strength order will be explained on one main assumption of charge density.
- Basicity of an ion is related to the volume available to the electron, i.e. the volume over which the electron can spread. The greater the volume available for a given series of basic ions, the smaller is the electron density. The smaller the electron density, the smaller is the attraction for the proton and weaker the base. The weaker the base, the stronger is the conjugate acid.

Illustration 1.79 Arrange the following acids in the decreasing order of their acid strength:

CH₄, NH₃, H₂O, HF

Sol. The conjugate bases are CH₃⁻, NH₂⁻, OH⁻ and F⁻



| | | |
|--|--|---|
| Nearly 3/4th of the volume of C is overlapped by H-atoms | Half of the volume of N is overlapped by H-atoms | Less than half the volume of O is overlapped by H-atoms |
|--|--|---|

Increasing volume available to electron →
 Decreasing electron density →
 Decreasing electron donating tendency →
 Decreasing basicity of conjugate bases →
 Increasing acidity of corresponding acids →
 ∴ HF > H₂O > NH₃ > CH₄

Illustration 1.80 Arrange the following acids in the decreasing order of their acid strength:

HF, HCl, HBr, HI

Sol. F⁻, Cl⁻, Br⁻ and I⁻ are the conjugate bases of HF, HCl, HBr and HI respectively.

Sizes of conjugate bases are as shown:



Increasing volume available to electron →
 Decreasing electron density →
 Decreasing electron donating tendency →
 Decreasing basicity of conjugate bases →
 Increasing acidity of corresponding acids →
 ∴ HI > HBr > HCl > HF

1.40 TRENDS IN ACIDIC AND BASIC PROPERTIES BASED ON ARRHENIUS AND BRONSTED-LOWRY CONCEPTS

1. **Covalent hydrides:** In these the proton is directly attached with the central atom of the molecule.

HX (X = F, Cl, Br, I), H₂O, CH₄, H₂S etc. These are also called hydracids or hydroacids.

Two factors influence the acid strength of the hydride of an element are the EN of the element and the atomic size

of the element. The first of these factors is best understood by comparing the hydrides of the elements of a period of the periodic table. The second is important when group comparisons of the periodic table are made.

- a. **Hydrides of the element of a period:** The acid strengths of the hydrides of the elements of a period increase from the left to the right in the same order as EN increases. Highly EN element withdraws electrons from the hydrogen easily and facilitate the release of hydrogen as proton. The EN of the following second and third period elements fall in the order: F > O > N and Cl > S > P.

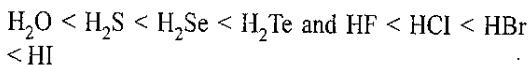
The acid strength of the hydrides increases in the same order: $\text{NH}_3 < \text{H}_2\text{O} < \text{HF}$ and $\text{PH}_3 < \text{H}_2\text{S} < \text{HCl}$.

The increase in acidic nature is also due to the fact that the solubility of their conjugate bases increases in the order: $\text{NH}_2^- < \text{OH}^- < \text{F}^-$.

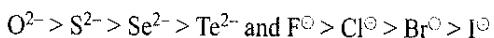
The increase in the acidic properties is supported by successive increase in the dissociation constant.

$$\text{NH}_3 (=10^{-35}) < \text{H}_2\text{O} (=10^{-14}) < \text{HF} (=10^{-4})$$

- b. **Hydrides of the elements of a group:** The acidity of the hydrides of the elements of group increases with increasing size of the central atom. For example, in the hydrides of groups 16 and 17, the acidic nature increases as the atomic number of the central element increases.

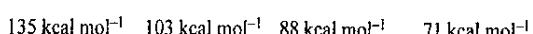
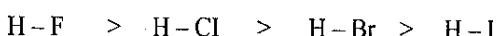


The two factors which influence acid strength work against each other in these hydrides. The effect of atomic size outweighs the electronegativity effect. A proton is more easily removed from a hydride in which the central atom is large than from the one in which the central atom is small. The charge density on the conjugate base is in the order:



Greater charge density on the conjugate base will result in greater proton attraction.

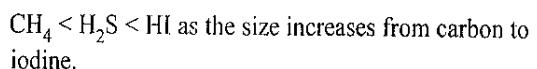
The acidic nature of the hydrides of group 17 elements is also explained by the fact that bond energies decrease.



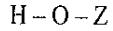
Due to large electronegativity, hydrogen bonding exists in the hydrides of oxygen and fluorine which also decrease their acid strength.

In the hydrides of the elements having nearly the same electronegativity, the acidic nature increases as the size of the central element increases. C, S and I possess

same electronegativity, the acidic nature follows the following order:



2. **Oxyacids:** In these the proton is attached to an oxygen atom, the latter being bonded to the central atom. For example, H_2SO_3 , HNO_3 , H_2SO_4 , HClO_4 etc.



The main factors which affect the strength of an oxyacid are

- The size of the central atom
- The electronegativity of the central atom
- The number of other electronegative atoms attached to the central atom

Smaller the size and greater the electronegativity of Z make the oxyacid stronger. These factors will shift the electron pair between Z and O towards Z and this displacement will in turn cause a shifting of electron pair between oxygen and hydrogen towards oxygen. Thus, O-H bond is weakened and proton is easily released in the series, $\text{HOI} < \text{HOBr} < \text{HOCl}$.

The electronegativity increases and size decreases of the central element. Same trend is observed in the oxyacid of different elements in the same oxidation state $\text{HClO}_4 > \text{HBrO}_4 > \text{HIO}_4$.

Greater the number of negative atoms present in the oxyacid make the acid stronger. In general, the strengths of acids that have general formula $(\text{HO})_x\text{ZO}_y$ can be related to the value of y.

If $y = 0$, the acid is very weak. HOCl , $(\text{OH})_3\text{B}$ or H_3BO_3 , $(\text{OH})_4\text{Si}$ or H_4SiO_4 .

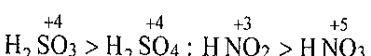
If $y = 1$, the acid is weak, HClO , HONO , $(\text{HO})_2\text{SO}$, $(\text{HO})_2\text{SO}_2$.

If $y = 2$, the acid is strong, HClO_2 , HONO_2 , $(\text{HO})_2\text{SO}_2$.

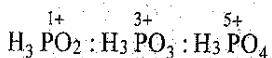
If $y = 3$, the acid is very strong, HClO_3 , HOIO_3 .

The negative atoms draw electrons away from the Z-atom and make it more positive. The Z-atom, therefore, becomes more effective in withdrawing electron density away from the oxygen atom that is bonded to hydrogen. In turn, the electrons of H-O bond are drawn more strongly away from the H-atom. The net effect makes it easier for the proton release and increases the acid strength.

This effect is illustrated by the following series of acids:



Note: In the above examples, it is evident that strength of the acid increases as the oxidation number of the central atom increases. However, this rule fails in oxyacids of phosphorus.



As all are weak acids, i.e. about the equal strength. Thus, prediction on the basis of oxidation number is incorrect. Formal charge on the central atom gives more reliable prediction. The strength of the acid increases as the formal charge on the central atom increases.

Formal charge = [Group number - number of bonds - number of unshared electrons]

| | |
|--|---|
| $\begin{bmatrix} \text{Formal} \\ \text{charge} \\ \text{on Cl} \end{bmatrix}$ | $\text{HOCl} < \text{HOCIO} < \text{HOClO}_2 < \text{HOClO}_3$ |
| | $0 \quad +1 \quad +2 \quad +3$ |
| | $\text{H}_3\text{PO}_2; \quad \text{H}_2\text{PO}_3; \quad \text{H}_3\text{PO}_4$ |
| | $\begin{array}{c} \text{H} \\ \\ \text{HO} - \text{P} \rightarrow \text{O} \\ \\ \text{H} \end{array} \quad \begin{array}{c} \text{H} \\ \\ \text{HO} - \text{P} \rightarrow \text{O} \\ \\ \text{OH} \end{array} \quad \begin{array}{c} \text{OH} \\ \\ \text{HO} - \text{P} \rightarrow \text{O} \\ \\ \text{OH} \end{array}$ |
| $\begin{bmatrix} \text{Formal} \\ \text{charge} \\ \text{on P} \end{bmatrix}$ | $+1 \quad +1 \quad +1$ |

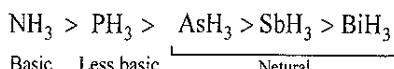
As the formal charge is same, all the above oxyacids of phosphorus are nearly of equal strength.

1.40.1 Strength of Bases

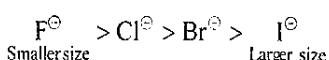
1. Among alkali and alkaline earth metal oxides and hydroxides, the basic nature increases as the size of the central atom increases, i.e. electropositive nature increases.



2. Among the hydrides of the same group, the basic nature decreases with increase in the size of central atom as the tendency to accept proton decreases due to decrease in electron density (or ability to donate electron pair decrease).

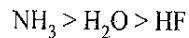


3. The larger the size of the atom holding the unshared electrons, the lesser is the availability of the electrons, i.e. the basic strength of halide ions follow the following order:

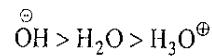


Similarly, $O^{2-} > S^{2-} > Se^{2-} > Te^{2-}$

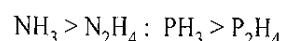
4. The basic nature of a substance decreases with the increase of the electronegativity of the atom holding the lone pair of electrons, i.e. the tendency to donate the electron pair to proton decreases with increase of electronegativity



5. The presence of a positive charge on the atom holding the lone pair decreases the base strength while a negative charge increase the base strength.



6. Base strength increases with decrease in oxidation state of the central atom.



Oxidation number -3 -2 -3 -2

1.41 SOFT AND HARD ACIDS AND BASES

Lewis acids and bases are classified as hard and soft acids and bases. A firmly held electron cloud with low polarisability makes a species 'hard', whereas an easily polarisable electron cloud characterises the species as 'soft'. A third category with intermediate character appears in the border line. Thus, we have the following cases:

- 1. Hard acid:** Those species in which the electron-accepting atom is small with a high positive charge and there are no electrons which are easily polarised or removed.
 - 2. Soft acid:** Those species in which the acceptor atom is large, carries a low positive charge or has electrons in orbitals which are easily polarised or distorted.
 - 3. Hard base:** The Lewis base which holds its electrons strongly.
 - 4. Soft base:** The Lewis base in which the position of the electrons is easily polarised or removed.
 - 5. SHAB (soft and hard acid base) principle:** Soft bases (nucleophiles) bind best with soft acids (electrophiles) and hard bases with hard acids. This is known as SHAB principle.

The smallest M^+ is the ‘hardest’ acid and smallest X^- is the hardest base. They combine to form the strongest bonding of the most effective ion pairs, which is a good application of SHAB principle.

The comparison between hard and soft acids and between hard and soft bases is given in Tables 1.28 and 1.29, respectively.

Table 1.28 Comparison between hard and soft acids

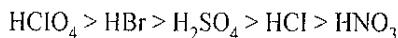
| Hard acids | Soft acids |
|---|---|
| i. Small size | i. Large size |
| ii. Absence of any outer electron which is easily excited to higher states | ii. Several easily excitable valence electrons |
| iii. High positive oxidation state | iii. Zero or low positive oxidation state |
| iv. Low polarisability | iv. High polarisability |
| v. High electronegativity | v. Low electronegativity |
| vi. H^{\oplus} , Li^{\oplus} , Na^{\oplus} , K^{\oplus} | vi. Cu^{\oplus} , Ag^{\oplus} , Hg^{\oplus} |
| vii. Al^{3+} , Fe^{3+} , Co^{3+} , Cr^{3+} | vii. I^{\oplus} , I_2 , Br_2 , Br^{\oplus} |
| viii. Be^{2+} , Mg^{2+} , Ca^{2+} , Sr^{2+} | viii. Cd^{2+} , Pt^{2+} , Hg^{2+} , Pt^{4+} |
| ix. CO_2 , SO_3 | ix. Cl, Br, I, N |
| HX (hydrogen-bonding molecules) | M° (metal atoms) and bulk metals |

Table 1.29 Comparison between hard and soft bases

| Hard bases | Soft bases |
|---|--|
| i. High electronegativity | i. Low electronegativity |
| ii. Presence of filled orbitals | ii. Partially filled orbitals |
| iii. Low polarisability | iii. High polarisability |
| iv. Empty orbitals may exist at high energy level | iv. Empty orbitals are low lying |
| $\text{CH}_3\text{CO}^{\ominus}$, PO_4^{3-} , SO_4^{2-} | SCN^{\ominus} , CN^{\ominus} , $\text{S}_2\text{O}_3^{2-}$ |
| H_2O , OH^{\ominus} , F^{\ominus} , Cl^{\ominus} | H^{\oplus} , I^{\ominus} |
| NH_3 , N_2H_4 , RNH_2 | R_3P , R_3As |
| NO_3^- , CO_3^{2-} , ClO_4^{\ominus} | R_2S , RSH , RS^{\ominus} |

Levelling solvents: Whenever an acid is dissolved in water, it acts as an acid only if the solvent acts as a base. That is, if we dissolve acids such as HCl, HNO_3 , etc. in water, their acidic strength is almost the same, since water acts as a base for both these acids. In fact, it is known that all strong acids show equal acidic strength when dissolved in water. This is because water acts as a base to all these acids and thus forces them to donate almost the same amount of protons irrespective of their chemical nature. Since water levels the acidic strength of strong acids, it is

referred to as a levelling solvent. In order to measure the strength of strong acids, they are dissolved in glacial acetic acid and the amount of protons is measured by conductometry. It is found that the strength of acids varies as

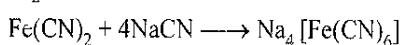
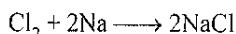
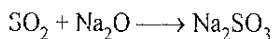


Amphiprotic species: Many molecules and ions can behave like water and may either gain or lose a proton under the appropriate conditions. Such species are said to be amphiprotic, e.g.

| Acid ₁ | Base ₂ | Acid ₂ | Base ₁ |
|-------------------------------|--------------------------|-------------------------|----------------------|
| HBr | HS^{\ominus} | H_2S | Br^{\oplus} |
| HS^{\ominus} | OH^{\ominus} | H_2O | S^{2-} |
| $\text{H}_3\text{O}^{\oplus}$ | HCO_3^{\ominus} | H_2CO_3 | H_2O |
| HCO_3^{\ominus} | CN^{\ominus} | HCN | CO_3^{2-} |

1.42 USANOVICH CONCEPT OF ACIDS AND BASES

According to Usanovich an acid is a chemical species which reacts with bases, gives up cations or accepts anions or electrons, and conversely a base is any chemical species which reacts with acids, gives up anions or combines with cation. For example,



We will discuss Hydrogen Bonding; Geometry, Shape, Hybridisation and Dipole Moment of Compounds and Ions; and Lanthanides and Actinides Contraction in Chapter 2.

Illustration 1.31 Arrange the order of decreasing/increasing properties given below:

1. Decreasing order of atomic and ionic radii

- Mg^{2+} , O^{2-} , Na^{\oplus} , F^{\ominus}
- Cl^{\ominus} , S^{2-} , Ca^{2+} , Ar
- N^{3-} , Na^{\oplus} , F^{\ominus} , O^{2-} , Mg^{2+}
- S, O, Se, C
- B, Be, Li, Na
- Li^{\oplus} , Na^{\oplus} , K^{\oplus} , Rb^{\oplus} , Cs^{\oplus} (in aqueous solution)
- Cl^{7+} , Si^{4+} , Mg^{2+} , Na^{\oplus}
- H^{\oplus} , Li, H^{\ominus}
- O^{2-} , B^{3+} , Li^{\oplus} , F^{\ominus}
- Br^{\ominus} , I, I^{\oplus} , I^{\ominus}
- I^{\oplus} , I, I^{\oplus}
- K^{\oplus} , Ca^{2+} , Ti^{3+} , Ti^{4+}

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- m. Ce, Sn, Yb, Lu
- n. F, F^\ominus , O, O^{2-}
- o. Ar, Br, Ca^{2+} , Mg^{2+}

2. Decreasing order of IE

- a. Mg, Al, Si, Na
- b. Decreasing IE_1 of the following:
Ar, Cl, P, S, Si, Mg, Al, Na
- c. Decreasing IE_2 of the following:
Na, Ar, Cl, S, P, Al, Si, Mg
- d. IE of completely filled, half filled and incompletely filled orbitals.
- e. N, O, F
- f. B, C, N, O
- g. F, Cl, Br, I
- h. Ne, O, Na, Na^\oplus
- i. Cu, Ag, Au
- j. Na, K, Mg, Kr
- k. F, Cl, O, N
- l. Li, Na, K
- m. Be, Mg, Ca
- n. B, C, N
- o. Ge, Si, C
- p. Ti, V, Cr, Mn
- q. B, Al, Ga, In, Tl
- r. IE_2 of 2nd period elements

3. Decreasing order of $\Delta_{eg}H^\ominus$

- a. F, Cl, Br, I
- b. N and P
- c. B, Al
- d. O, S
- e. O, N, F, S
- f. B, C, N, O
- g. Cl, F, Br, I, S, Si
- h. S^\ominus , O
- i. N^\ominus , P
- j. S, O^\ominus
- k. O^\ominus , S^\ominus
- l. O, O^\oplus , O^{2+} , O^{2-}
- m. Li, Be, Na, Ne
- n. C, N, Be, F, O, Cl

4. Decreasing order of EN

- a. As, P, S, Cl
- b. O^\oplus , O, O^\ominus

- c. H, O, Al, F
- d. F, N, O, Cl, S
- e. M^\oplus , M^{2+} , M^{3+} , M^{4+}
- f. F, Cl, Br, I
- g. N, P, C, Si
- h. P, S, N, O
- i. Zn, Cd, Hg
- j. H, P, S, Te
- k. X^\ominus , X, X^{2-}
- l. Decreasing order of EN of carbon in the following:
 CH_4 , $CH_2 = CH_2$, $HC = CH$

5. Decreasing order of acidic property/strength

- a. ZnO , Na_2O_2 , P_2O_5 , MgO
- b. CO_2 , N_2O_5 , SiO_2 , SO_3
- c. $HClO$, $HClO_2$, $HClO_3$, $HClO_4$
- d. HNO_3 , H_3PO_4 , H_3AsO_4 , H_3SbO_4
- e. H_2O , H_2S , H_2Te , H_2Se
- f. H_2SO_3 , H_2SeO_3 , H_2TeO_3
- g. SO_4 , H_2SeO_4 , H_2TeO_4
- h. HF, HCl, HBr, HI
- i. HOCl, HOBr, HOI
- j. Al_2O_3 , MgO , SiO_2 , P_4O_{10}
- k. Increasing pH of aqueous solution of
 $LICl$, $BeCl_2$, $MgCl_2$, $AlCl_3$

6. Decreasing order of basic property/strength

- a. MgO , SrO , K_2O , NiO , Cs_2O
- b. $LiOH$, $NaOH$, KOH , $RbOH$, $CsOH$
- c. $Be(OH)_2$, $Mg(OH)_2$, $Ca(OH)_2$, $Ba(OH)_2$
- d. NH_3 , AsH_3 , SbH_3 , PH_3
- e. Li_2O , BeO , B_2O_3 , CO_2
- f. F^\ominus , Cl^\ominus , Br^\ominus , I^\ominus
- g. F^\ominus , $\overset{\ominus}{OH}$, $\overset{\ominus}{NH}_2$, $\overset{\ominus}{CH}_3$
- h. Al_2O_3 , Tl_2O_3 , Tl_2O , Ga_2O_3

7. Decreasing order of ionic character

- a. $CaCl_2$, $BeCl_2$, $MgCl_2$, $BaCl_2$, $SrCl_2$
- b. BCl_3 , $AlCl_3$, $GaCl_3$
- c. VCl_2 , VCl_3 , VCl_4 , $VOCl_3$
- d. $LiBr$, $NaBr$, KBr , $RbBr$, $CsBr$
- e. LiF , K_2O , ClF_3 , SO_3 , N_2
- f. P_2O_5 , CrO_3 , MnO , Mn_2O_7

8. Decreasing order of covalent character

- a. $LiCl$, $LiBr$, LiI

- b. TiCl_2 , TiCl_3 , TiCl_4
 c. NaCl , MgCl_2 , AlCl_3 , SiCl_4 , PCl_5 , SF_6 , IF_7
 d. CCl_4 , SiCl_4 , GeCl_4 , SnCl_4 , PbCl_4
 e. CCl_4 , CBr_4 , Cl_4
 f. LaCl_3 , CeCl_3 , GdCl_3 , LuCl_3
- 9. Decreasing order of melting and boiling points**
- Melting points of Li, Na, K, Rb, Cs
 - Melting and boiling points of hydrides of group 15
 - Melting and boiling points of hydrides of group 16
 - Melting and boiling points of hydrides of group 17
 - Melting and boiling points of H_2O , HF and NH_3
 - Melting points of KCl , KBr , KF , KI
 - Melting points of CaF_2 , CaCl_2 , CaBr_2 , CaI_2
 - Melting points of LiBr , BeBr_2 , BBr_3 , LiI
- 10. Decreasing order of magnetic moment and also mention whether they are coloured or colourless**
- Ti^{3+} , Ni^{2+} , Cr^{2+} , Co^{2+} , Zn^{2+}
 - Ca , A, N, O
 - Sc, Ti, V, Cr, Mn, Fe
 - Sc^{\oplus} , Ti^{\oplus} , V^{\oplus} , Cr^{\oplus} , Mn^{\oplus} , Fe^{\oplus}
 - Sc^{2+} , Ti^{2+} , V^{2+} , Cr^{2+} , Mn^{2+} , Fe^{2+}
 - Sc^{3+} , Ti^{3+} , V^{3+} , Cr^{3+} , Mn^{3+} , Fe^{3+}
 - Al, Si, P, S, Cl
- 11. Decreasing order of bond angles**
- NH_3 , PH_3 , AsH_3
 - H_2O , H_2S , H_2Se
 - NF_3 , PH_3 , AsF_3
 - NF_3 , NCl_3
 - NO_2^{\oplus} , NO_2 , NO_2^{\ominus}
 - NH_3 , NF_3
 - PH_3 , PF_3
 - CH_4 , NH_3 , H_2O , BF_3 , C_2H_2
 - H_2O , CO_2 , NH_3 , CH_4
 - NH_3 , $\overset{\oplus}{\text{NH}}_4$, PCl_5 , SCl_2
 - NO_3^{\ominus} , NO_2^{\ominus} , NO_2^{\oplus} , NO_2
 - BF_3 , NH_3 , SiH_4 , H_2S
 - Cl_2O , ClO_2 , Cl_2O_7 , I_3^{\ominus}
- 12. Decreasing order of solubility**
- BeF_2 , MgF_2 , CaF_2 , BaF_2
 - Be(OH)_2 , Mg(OH)_2 , Ca(OH)_2 , Ba(OH)_2
 - BeCO_3 , MgCO_3 , CaCO_3 , BaCO_3
 - BeSO_4 , MgSO_4 , CaSO_4 , BaSO_4
 - $\text{Be}(\text{HCO}_3)_2$, $\text{Mg}(\text{HCO}_3)_2$, $\text{Ca}(\text{HCO}_3)_2$, $\text{Ba}(\text{HCO}_3)_2$
- f. NaCl , MgCl_2 , AlCl_3 , CCl_4
 g. NaCl , CuCl (note the size of Na^{\oplus} = size of Cu^{\oplus})
 h. HNO_3 , H_3PO_4 , H_3AsO_4 , H_3SbO_4
 i. H_2SO_3 , H_2SeO_3 , H_2TeO_3
- 13. Decreasing order of bond strength or bond dissociation enthalpy and bond length**
- Bond length and bond strength of F_2 , N_2 , Cl_2 , O_2
 - Single bond strength: N_2 , O_2 , F_2
 - Bond dissociation enthalpy: F_2 , Cl_2 , Br_2 , I_2
 - Bond strength and thermal stability: HCl , HBr , HF , HI
 - Thermal stability: HClO , HClO_2 , HClO_3 , HClO_4
 - Thermal stability: LiOH , NaOH , KOH , RbOH , CsOH
 - Thermal stability and reducing character: NH_3 , AsH_3 , SbH_3 , PH_3
 - Thermal stability and reducing character: H_2O , H_2S , H_2Se , H_2Te
 - Thermal stability: H_2SO_3 , H_2SeO_3 , H_2TeO_3
 - Thermal stability: H_2SO_4 , H_2SeO_4 , H_2TeO_4
 - Thermal stability: HFO_3 , HClO_3 , HBrO_3 , HIO_3
 - Thermal stability: LiH , NaH , KH , CsH
 - Thermal stability: BeCO_3 , MgCO_3 , CaCO_3 , BaCO_3
 - Stability: Li^{\ominus} , Be^{\ominus} , B^{\ominus} , C^{\ominus}
- (IIT-2002)
- 14. Decreasing order of extent of hydrolysis, hydration of ions and hydration energy**
- Extent of hydrolysis: CCl_4 , MgCl_2 , AlCl_3 , PCl_5 , SiCl_4
 - Extent of hydrolysis: NCl_3 , PCl_3 , AsCl_3 , SbCl_3 , BiCl_3
 - Hydration of ions: Be^{+2} , Mg^{+2} , Ca^{+2} , Sr^{+2} , Ba^{+2}
 - Hydration energy: Li^{\oplus} , Na^{\oplus} , K^{\oplus} , Rb^{\oplus} , Cs^{\oplus}
 - Hydration energy: K^{\oplus} , Cs^{\oplus} , Ca^{2+} , Ba^{2+}
- 15. Decreasing order of strength of Lewis acids**
- BF_3 , ECl_3 , BBr_3
 - AlCl_3 , GaCl_3 , InCl_3
- 16. Decreasing order of oxidising/reducing power**
- Decreasing oxidising power:
- GeCl_4 , SnCl_4 , PbCl_4
 - F, Cl, Br, I
 - O, S, Se, Te
 - BrO_4^{\ominus} , ClO_4^{\ominus} , IO_4^{\ominus}
 - ClO^{\ominus} , BrO^{\ominus} , IO^{\ominus}
- Decreasing reducing power:
- GeCl_2 , SnCl_2 , PbCl_2
 - HF, HCl, HBr, HI

17. Decreasing order of miscellaneous properties as indicated.

- a. Decreasing strength of hydrogen bonding (X H - X) O, S, F, Cl, N

Decreasing reactivity with water:

- b. Li, Na, K, Rb, Cs
- c. Be, Mg, Ca, Sr, Ba
- d. Decreasing reactivity with hydrogen: Li, Na, K, Rb, Cs
- e. Decreasing reactivity towards air: Be, Mg, Ca, Sr, Ba
- f. Decreasing number of hybrid orbitals: C, Si, Sn
- g. Decreasing oxidation number of iodine: I₂, HI, HIO₄, ICl
- h. Decreasing order of +5 oxidation state: N, P, As, Sb, Bi
- i. Decreasing poisonous nature: H₂O, H₂S, H₂Se, H₂Te, H₂Po
- j. Decreasing affinity for hydrogen: F₂, Cl₂, Br₂, I₂
- k. Decreasing electropositivity: Fe, N, Cu, Li
- l. Decreasing density: Fe, Pb, Al, Au
- m. Decreasing density: H₂S, O₂, CO₂, NH₃, H₂

Sol.

1. a. O⁻² > F⁰ > Na⁺ > Mg²⁺

| Z | O = 8 | F = 9 | Na = 11 | Mg = 12 | |
|---------------------|------------------|------------------|-------------------|-------------------|---------------------------------|
| \bar{e} | 8 + 2 = 10 | 9 + 1 = 10 | 11 - 1 = 10 | 12 - 2 = 10 | (All species are isoelectronic) |
| $\frac{Z}{\bar{e}}$ | 8 10 = 0.8 | 9 10 = 0.9 | 11 10 = 1.1 | 12 10 = 1.2 | |

Smaller the value of $\frac{Z}{\bar{e}}$, larger is the size.

Hence the order is as given above.

b. $S^{2-} > Cl^0 > Ar > \underbrace{Ca^{2+}}_{\text{All belong to 3rd period}} \quad \left(\begin{array}{l} \text{All species are} \\ \text{isoelectronic} \end{array} \right)$

- i. Size of element decreases along the same period (\rightarrow) but the size of noble gas is maximum in that period (due to greater electron-electron repulsion).
- ii. Size of Ca (4th period) > size of Ar (3rd period), but the size of Ar > size of Ca²⁺. Therefore, Size of dinegative ion > size of mononegative ion > noble gas (of the same period) > size of dipositive cation.

Hence the order is as given above.

c. N³⁻ > O⁻² > F⁰ > Na⁺ > Mg²⁺ (All species are isoelectronic)

| Z | N = 7 | O = 8 | F = 9 | Na = 11 | Mg = 12 |
|-----------|---------------|---------------|---------------|----------------|----------------|
| \bar{e} | 7 + 3 = 10 | 8 + 2 = 10 | 9 + 1 = 10 | 11 - 1 = 10 | 12 - 2 = 10 |

Same explanation as in parts (a) and (b) above

d. $\frac{\text{Se}}{\text{4th Period}} > \frac{\text{S}}{\text{3rd Period}} > \frac{\text{C}}{\text{2nd Period}} > \frac{\text{O}}{\text{2nd Period}}$

Size of atom increases down the group because of addition of new shell (or increase in principal quantum number n).

Size of atom decreases along the period (\rightarrow), i.e. decreases from C to O.

e. $\frac{\text{Na}}{\text{3rd Period}} > \frac{\text{Li}}{\text{2nd Period}} > \frac{\text{Be}}{\text{2nd Period}}$

Same explanation as in part (d) above.

f. Li⁺ > Na⁺ > K⁺ > Rb⁺ > Cs⁺ (in aqueous solution)

The ions in solution are present as hydrated ions. The smaller the size of the ion, greater is the charge density and hence greater is the extent of hydration. So, the size of hydrated ions becomes larger for the smaller sized ion and vice versa.

g. Na⁺ > Mg²⁺ > Si⁴⁺ > Cl⁷⁺ (All species are isoelectronic)

| Z | Na = 11 | Mg = 12 | Si = 14 | Cl = 17 |
|-----------|----------------|----------------|----------------|----------------|
| \bar{e} | 11 - 1 = 10 | 12 - 2 = 10 | 14 - 4 = 10 | 17 - 7 = 10 |

Smaller the charge on the cation, larger is the size and vice versa.

h. H⁺ > Li > H⁰ (The species are not isoelectronic)

| Z | H = 1 | Li = 3 | H = 1 |
|---------------------|---------------------|---------------------|-----------|
| \bar{e} | 1 + 1 = 2 | 3 + 0 = 3 | 1 - 1 = 0 |
| $\frac{Z}{\bar{e}}$ | $\frac{1}{2} = 0.5$ | $\frac{3}{8} = 1.0$ | — |

Smaller the value of $\frac{Z}{\bar{e}}$, larger is the size.

i. O²⁻ > F⁰ > Li⁺ > B³⁺ (All species are not isoelectronic, but all of them belong to the same 2nd period)

| Z | O = 8 | F = 9 | Li = 3 | B = 5 |
|-----------|---------------|---------------|--------------|--------------|
| \bar{e} | 8 + 2 = 10 | 9 + 1 = 10 | 3 - 1 = 2 | 5 - 3 = 2 |

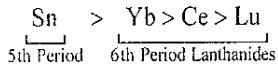
Higher the -ve charge, larger is the size and higher the +ve charge, smaller is the size of an ion.

j. $\frac{I^0}{\text{5th period}} > \frac{I^{\ominus}}{\text{5th period}} > \frac{Br^{\oplus}}{\text{4th period}}$ [All the species are not isoelectronic]

| Z | I = 53 | I = 53 | I = 53 | Br = 35 |
|-----------|----------------|----------------|----------------|----------------|
| \bar{e} | 53 + 1 = 54 | 53 + 0 = 53 | 53 - 1 = 52 | 35 + 1 = 36 |

Same explanation as in (a) and (b) above.

- k. $I^{\ominus} > I > I^{\oplus}$ [Same explanation as in (j)]
- l. $K^{\oplus} > Ca^{2+} > Ti^{3+} > Ti^{4+}$ [Same explanation as in (g)]
- m. (Z for Ce = 58, Sn = 60, Yb = 70 and Lu = 71)



In lanthanides, the size decreases from La to Lu ($Z = 57$ to 71) due to lanthanide contraction. Although Sn belongs to the 5th period but its size is larger than lanthanides.

- n. $O^{2-} > F^{\ominus} > O > F$
(The species are not isoelectronic)
[Same explanation as in parts (a) and (d) above]
- o. $Br > Ar > Ca^{2+} > Mg^{2+}$
[Refer to solved example 1.5 (b)]

2. a. $Si > Mg > Al > Na$

(All of them belong to the same 3rd period)

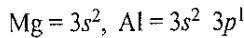
$IE (kJ mol^{-1}) 1577 > 737 > 577 > 496$

IE increases along the period (\rightarrow)

But there is an exception, IE_1 of Mg $>$ IE_1 of Al.

This is due to penetration effect.

The valence electronic configurations of Mg and Al are



It is easier to remove electron from $3p$ orbital than $2s$ orbital, since $2s$ is more penetrated towards nucleus. Hence the order is as given above.

- b. $Ar > Cl > [P > S] > Si > [Mg > Al] > Na$

All of them belongs to 3rd period

3rd period element

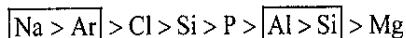
| Group | 1 | 2 | — | 13 | 14 | 15 | 16 | 17 | 18 |
|---------|----|----|---|----|----|----|----|----|----|
| Element | Na | Mg | | Al | Si | P | S | Cl | Ar |

Generally IE_1 increasing along the period.

With an exception, IE_1 of Mg $>$ IE_1 of Al (due to penetration effect).

Similarly, there is an exception, IE_1 of P $>$ IE_1 of S [due to stable half filled orbitals in P]

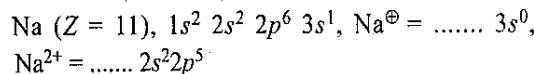
- c. IE_2 : All of these elements belong to 3rd period



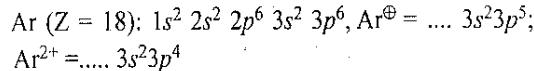
Generally IE_2 also increases along the period, but there are two exceptions as marked in the box.

1st exception: IE_2 of Na $>$ IE_2 of Ar

Electronic configuration:

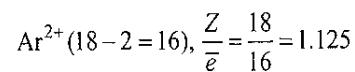
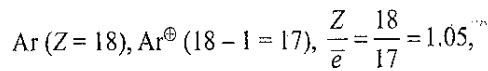
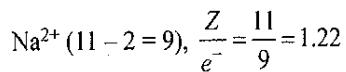
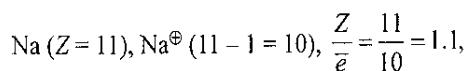


IE_1 of Na is very low. IE_2 is the highest among the given elements, since it is very difficult to remove electron from inner ($2p$) orbitals.



IE_1 of Ar is very high since it is very difficult to remove electron from stable full-filled configuration ($3s^2 3p^6$). But IE_2 of Ar is less than IE_2 of Na, since in case of Na, electron has to be removed from the inner $2p$ orbital, whereas in the case of Ar, it has to be removed from the valence $3p$ orbital.

Alternatively: Larger the value of $\frac{Z}{e^-}$, smaller is the size and high is the IE and vice versa.



$\frac{Z}{e^-}$ for both Na^{\oplus} and Na^{2+} $>$ $\frac{Z}{e^-}$ for both Ar^{\oplus} and Ar^{2+}

Hence IE_2 of Na $>$ IE_2 of Ar

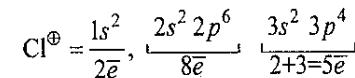
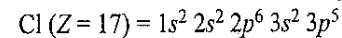
| | | |
|--------------|--------|---------------|
| IE_2 of Cl | $>$ | IE_2 of S |
| (2298) | (2252) | $kJ mol^{-1}$ |

Note: From the electronic configuration and $\frac{Z}{e^-}$ value, IE_2 of S should be $>$ IE_2 of Cl, but the observed values are reversed.

Therefore, this discrepancy has to be explained by calculating Z_{eff} (effective nuclear charge) using Slater rule. Higher the Z_{eff} , higher is the IE_2 .

- i. Z_{eff} for last electron in Cl^{\oplus} :

Electron configuration of Cl and Cl^{\oplus}



- ii. σ for last electron in Cl^{\oplus}

$$\begin{aligned} & \left[0.35 \times \text{No. of electrons left in the } n^{\text{th}} \text{ shell} \right. \\ & \quad \left. + (0.85 \times \text{No. of electrons in } (n-1)^{\text{th}} \text{ shell}) \right. \\ & \quad \left. + (1.00 \times \text{Total no. of electrons in the inner shells}) \right] \end{aligned}$$

$$= 0.35 \times 5 + 0.85 \times 8 + 1.00 \times 2 = 10.55$$

$$Z_{\text{eff}} \text{ for } Cl^{\oplus} = Z - \sigma = 17 - 10.55 = 6.45$$

ii. Z_{eff} for last electron in S^{\oplus} :Electron configuration of S and S^{\oplus}

$$\text{S} (Z=16) = 1s^2 2s^2 2p^6 3s^2 3p^4$$

$$\text{S}^{\oplus} = \frac{1s^2}{2e^-} \quad \frac{1s^2 2p^6}{8e^-} \quad \frac{3s^2 3p^3}{2+2=4e^-}$$

 $\therefore \sigma$ for last electron in S^{\oplus}

$$= (0.35 \times 4 + 8 \times 0.85 + 1.00 \times 2) = 10.2$$

$$Z_{\text{eff}} \text{ for } \text{S}^{\oplus} = Z - \sigma = 16 - 10.2 = 5.8$$

$$\therefore Z_{\text{eff}} \text{ for } \text{Cl}^{\ominus} > Z_{\text{eff}} \text{ for } \text{S}^{\oplus}$$

Hence IE_2 of Cl > IE_2 of S**2nd exception:** IE_2 of Al > IE_2 of Si

Electronic configuration:

$$\text{Al} (Z=13), 1s^2, 2s^2 2p^6, 3s^2 3p^1$$

$$\text{Al}^{\oplus} = \dots 3s^2 3p^0, \quad \text{Al}^{2+} = \dots 3s^1$$

$$\text{Si} (Z=14), 1s^2, 2s^2 2p^6, 3s^2 3p^2$$

$$\text{Si}^{\oplus} = \dots 3s^2 3p^1, \quad \text{Si}^{2+} = \dots 3s^2 3p^0$$

IE_2 of Al > IE_2 of Si, since in case of Al, the second electron has to be removed from $3s$ orbital (which is more penetrated toward nucleus) whereas in case of Si, the second electron has to be removed from $3p$ orbital (which is less penetrated than s -orbital) (Penetration effect). Hence IE_2 of Al > IE_2 of Si.

Alternatively: Larger the value of $\frac{Z}{e^-}$, smaller is the size and high is the IE_2 and vice versa.

d. IE of completely filled > half filled > incompletely filled orbitals.

Since completely filled orbitals are more stable (due to high release of exchange energy) than half-filled orbitals which in turn more stable than incompletely filled orbitals.

$$\text{Al} (Z=13), \text{Al}^{\oplus} (13-1=12), \frac{Z}{e^-} = \frac{13}{12} = 1.083$$

$$\text{Al}^{2+} (13-2=11), \frac{Z}{e^-} = \frac{13}{11} = 1.18$$

$$\text{Si} (Z=14), \text{Si}^{\oplus} (14-1=13), \frac{Z}{e^-} = \frac{14}{13} = 1.076$$

$$\text{Si}^{2+} (14-2=12), \frac{Z}{e^-} = \frac{14}{12} = 1.166$$

$\therefore \frac{Z}{e^-}$ for both Al^{\oplus} and Al^{2+} > $\frac{Z}{e^-}$ for both Si^{\oplus} and Si^{2+}

Hence IE_2 of Al > IE_2 of Sie. $F > \boxed{N > O}$ IE increases along the period (\rightarrow).But there is exception, IE_1 of N > IE_1 of O.

This is due to half-filled stable configuration in N.

f. $\text{N} > \text{O} > \text{C} > \text{B}$ (same explanation as in part (b) above)g. $\text{F} > \text{Cl} > \text{Br} > \text{I}$ (generally IE decreases down the group (\downarrow))h. $\frac{\text{Ne}}{\text{2nd period}} > \frac{\text{Na}^{\oplus}}{\text{3rd period}} > \frac{\text{O}}{\text{2nd period}} > \frac{\text{Na}}{\text{3rd period}}$
For explanation refer to solved example 1.5 (f).i. $\text{Cu} > \boxed{\text{Ag} < \text{Au}}$ (Cu, Ag and Au belongs to $3d$, $4d$ and $5d$ transition element series).Generally IE decreases from Cu \rightarrow Ag \rightarrow Au. But there is an exception, IE_1 of Au > IE_1 of Ag.

Explanation: In all the 3 cases an s -electron in the unpaired state is to be removed. In the case of Cu a $4s$ electron is to be removed which is closer to the nucleus than the $5s$ electron of Ag. So IE decreases from Cu to Ag. However from Ag to Au, the $14f$ -electrons are added which provide very poor shielding effect. The nuclear charge is thus enhanced and therefore the outer electron of Au is more tightly held and so the IE_1 of Au is high.

j.

| Element | Kr > | Mg > | Na > | K |
|---------------------------------|--------|-------|------|-----|
| IE_1 (kJ mol $^{-1}$) | 1351 > | 737 > | 496 | 419 |
| Group | 18 | 2 | 1 | 1 |

Generally IE decreases down the group (\downarrow) and IE_1 of group 2 > IE_1 of group 1.Kr being inert gas has the maximum IE_1 as the process involves removal of electron from the stable $4s^2 4p^6$ configuration.

k.

| Elements | F > | N > | O > | Cl |
|---------------------------------|--------|--------|--------|------|
| IE_1 (kJ mol $^{-1}$) | 1680 > | 1402 > | 1314 > | 1256 |
| Period | 2 | 2 | 2 | 3 |

 IE_1 of 2nd period > IE_1 of 3rd period. So IE_1 of Cl is the least [i.e. IE decreases down the group (\downarrow)]IE increases along the period, so IE_1 of F is the highest. There is an exception; IE_1 of N > IE_1 of O.

This is due to the stable half-filled orbitals in N.

l. $\text{Li} > \text{Na} > \text{K}$ [All of them belong to group 1 and IE decreases down the group (\downarrow)]m. $\text{Be} > \text{Mg} > \text{Ca}$ [All of them belong to group 2 and IE decreases down the group (\downarrow)]

- n. N > C > B [All of them belong to 2nd period and IE increases along the period (\rightarrow)]
 o. C > Si > Ge [All of them belong to group 14 and IE decreases down the group (\downarrow)]

p.

| Element | Mn > | Cr > | V > | Ti |
|--|-------|-------|-------|-----|
| Z | 25 | 24 | 23 | 22 |
| IE ₁ (kJ mol ⁻¹) | 717 > | 653 > | 650 > | 646 |

[All of them belong to 3d transition element series and IE increases along the period]

- q. IE₁ should be B > Al > Ga > In > Tl (IE₁ decreases down the group).

But the observed order is

| IE ₁ (kJ mol ⁻¹) | B > | Tl > | Ga > | Al > | In |
|--|-------|-------|-------|------|----|
| 800 > | 590 > | 579 > | 577 > | 558 | |

Note: There is a deviation from general trend.

This is due to the inert pair effect and which is due to the imperfect (or poor) screening effect of d- and f-electrons.

- i. In Ga, due to the poor screening effect of 3d electrons, size of Ga⁺ < size of Al⁺, so the IE₁ of Ga > IE₁ of Al.
 ii. In Tl, due to poor screening effect of 4f-electrons (screening effect of s > p > d > f orbitals).
 \therefore IE₁ of Tl > Ga > Al > In

Hence the order is as given above.

- r. 2nd period elements from left to right are

Li, Be, B, C, N, O, F, Ne

The electronic configuration of these elements and their ions in +1 oxidation states are as

- i. Li (Z = 3), $\rightarrow 2s^1$, Li⁺ $\Rightarrow 2s^0$ [stable noble gas configuration and IE₂ is the highest in 2nd period]
 ii. Be (Z = 4) $\Rightarrow 2s^2$, Be⁺ $\Rightarrow 2s^1$, Be²⁺ $\Rightarrow 2s^0$.
 [Most stable]

Therefore, IE₂ of Be is lower than of B.

- iii. B (Z = 5), $\Rightarrow 2s^2 2p^1$, B⁺ $\Rightarrow 2s^2 2p^0$

[Stable noble gas configuration]

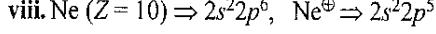
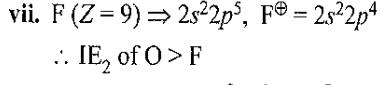
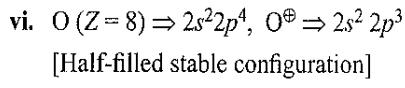
\therefore IE₂ of B > Be

- iv. C (Z = 6) $\Rightarrow 2s^2 2p^2$, C⁺ $\Rightarrow 2s^2 2p^1$

Due to penetration effect, i.e. it is easier to remove an 2p electron from C⁺ than from 2s electron from B⁺

\therefore IE₂ of B > C

- v. From C to N to O, nuclear charge increases by one unit at a time. Therefore, their IE₂ also increases accordingly, i.e. IE₂ of O > N > C



Since Ne, has the highest nuclear charge in 2nd period, therefore IE₂ of Ne is expected to be much higher than that of O and F,

\therefore IE₂ of Ne > O > F

Hence decreasing order of IE₂ of 2nd period is
 Li > Ne > O > F > N > B > C > Be

3. a. $\boxed{\text{Cl} > \text{F}}$ $\boxed{\text{Br} > \text{I}}$

$[\Delta_{\text{eg}} H^\ominus$ decreases down group (\downarrow) but there is an exception in $\Delta_{\text{eg}} H^\ominus$ of Cl and F]

$\Delta_{\text{eg}} H^\ominus$ of Cl > $\Delta_{\text{eg}} H^\ominus$ of F.

It is due to very small size of F atom. There are strong electron-electron repulsion in the relatively small 2p orbitals of F and thus, the incoming electron does not experience much attraction. Hence, the incoming electron is not added easily as it is added in large 3p orbitals of Cl. Consequently, $\Delta_{\text{eg}} H^\ominus$ of F is less negative than that of Cl.

b. $N = 2s^2 2p^3$, $P = 3s^2 3p^3$

$\Delta_{\text{eg}} H^\ominus$ of P (more -ve value, -74 kJ mol^{-1}) > N ($+20.1 \text{ kJ mol}^{-1}$). In both N and P, 2p and 3p orbitals are half-filled respectively. Thus the addition of extra electron to these orbitals is not possible. But an extra electron is added much more easily in 3p orbitals of P than that of 2p orbital of N.

Consequently, $\Delta_{\text{eg}} H^\ominus$ of P is more negative than that of N.

- c. $\Delta_{\text{eg}} H^\ominus$ of Al (more -ve, -44 kJ mol^{-1}) > B (less -ve, -23 kJ mol^{-1}).

Note: $\Delta_{\text{eg}} H^\ominus$ of 2nd period have negative value than the corresponding of 3rd period.

Valence shell configuration of B and Al is as

$B = 2s^1 2p^1$, $Al = 3s^2 3p^1$

Same explanation as in part (b) above.

- d. $\Delta_{\text{eg}} H^\ominus$ of S (-200 kJ mol^{-1}) > O (-141 kJ mol^{-1})

Valence shell electronic configuration of O and S is as:

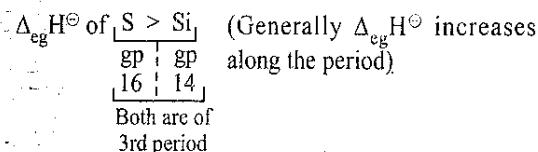
$O = 2s^2 2p^4$, $S = 3s^2 3p^4$

Same explanation as in part (b) above.

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- e. $N > O > S > F$ (from +ve value to increasing -ve values). (Refer to Illustration 1.43.)
- f. $N > B > C > O$ (from +ve value to increasing -ve values) (Refer to Illustration 1.45).
- g. $Cl > F > Br > I > S > Si$

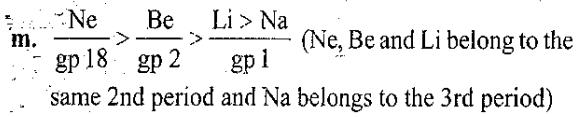
For explanation of $\Delta_{eg}H^\ominus$ of $Cl > F > Br > I$, [Refer to part (a) above.]



Hence the order is as given above.

For part (h) to (k), refer to Illustration 1.44.

- h. $S^\ominus > O$
- i. $N^\ominus > P$
- j. $O^\ominus > S$
- k. $O^\ominus > S^\ominus$
- l. $O^{+2} > O^\ominus > O > O^{2-}$ (Greater the +ve charge, greater is the tendency to attract electron)



$\Delta_{eg}H^\ominus$ of inert gases is the highest because of the stable completely filled ($2s^2 2p^6$) configuration. So, energy is required to add extra electron.

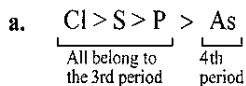
$\Delta_{eg}H^\ominus$ of Be is comparable with Ne, because of the stable completely filled ($2s^2$) configuration.

Down the group (\downarrow), $\Delta_{eg}H^\ominus$ decreases, so $\Delta_{eg}H^\ominus$ of Li $>$ $\Delta_{eg}H^\ominus$ of Na.

Hence the order is as given above.

- n. $Cl > F > O > C > N > Be$ [refer to solved example 1.5(c)].

4.

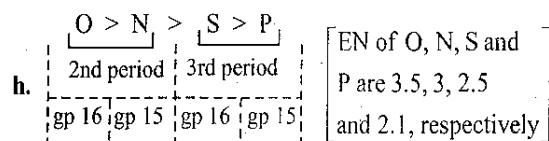
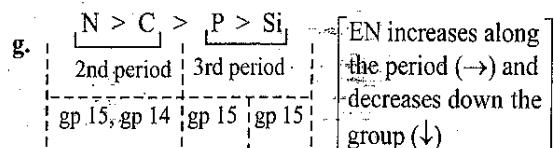


EN increases along the period (\rightarrow) and decreases down the group (\downarrow).

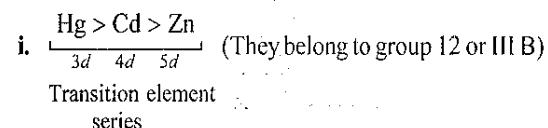
- b. $O^\oplus > O > O^\ominus$

The positive charge on the atoms increases its EN while negative charge decreases its EN.

- c. $F > O > Al > H$ [refer to solved example 1.5(a)]
- d. $F > O > Cl > S > N$ [refer to solved example 1.5(e)]
- e. $M^{+4} > M^{+3} > M^{+2} > M^\ominus$ (As the polarising power increases, EN increases)
- f. $F > Cl > Br > I$ [EN decreases down the group (\downarrow)]



Same explanation as in part (g) above.



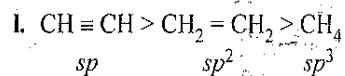
In case of Zn, Cd and Hg, EN increases down the group.

- j. $S > H = P = Te$

Note: EN of H, P and Te are 2.1 each.

EN of S = 2.6. It is an experimental fact.

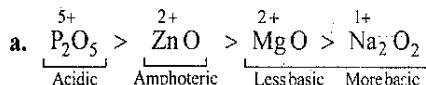
- k. $X > X^\ominus > X^{-2}$ [Higher the positive charge or lower the negative charge, higher is the EN. Refer to Section 1.16.3, Point (4)]



[Refer to Section 1.16.3, Point (6)]

More the s-character in hybrid orbital, higher the EN.

5.

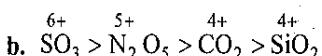


Acidic character of oxides increases along the period (\rightarrow). According to Fajans' rule, higher the oxidation state of the atom, more is the covalent character and more is the acidic character.

In case of ZnO and MgO, both have +2 charge on the atom. But the size of $Mg^{2+} >$ size of Zn^{2+} . The smaller the cation, the more covalent and more acidic the solution.

Zn belongs to 3d transition element series, so the size decreases along the 3d series (\rightarrow).

Alternatively: Oxides of electropositive elements are alkaline while those of electronegative elements are acidic. Alkaline property will increase with the increase of electropositive character of metal and acidic characteristic increase with the increase of electronegative characteristics of non-metals. Since the electronegativity decrease in the order P > Zn > Mg > Na the acidic character of oxide will also decrease in the same order.



In case of CO_2 and SiO_2 both have +4 charge on the atom. But the size of $Si^{4+} >$ size of C^{4+} (size increases down the group, and both belong to group 14).

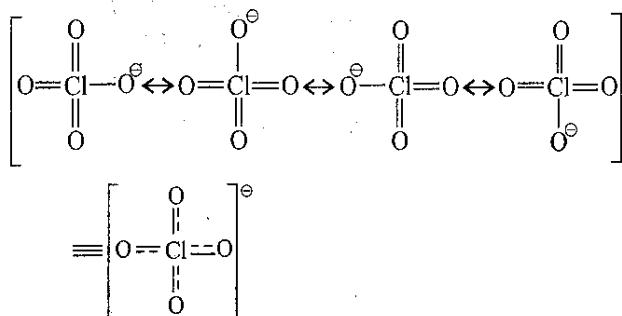
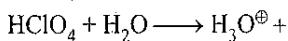
Rest is same explanation as in part (a) above.

c. $\text{HClO}_4 > \text{HClO}_3 > \text{HClO}_2 > \text{HClO}$.

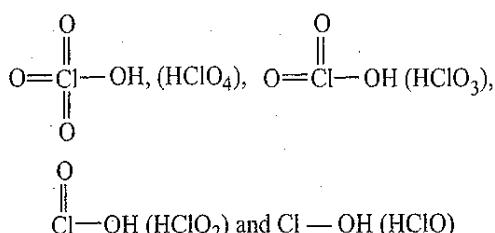
The more stronger the acid, the weaker will be its conjugate base. In HClO_4 , ClO_4^- is the conjugate base and therefore it is stabilised by four resonating structure. Hence more acidic.

Similarly, ClO_3^- , ClO_2^- and ClO^- will have 3, 2 and 1 resonating structure. Hence the order is as given above.

For example,



Alternatively: These acids are oxoacids and are represented as



The larger number of O-atoms attached to Cl, the greater the pull towards O-atom, hence it is more easy to remove hydrogen from acid.

d. $\text{HNO}_3 > \text{H}_3\text{PO}_4 > \text{H}_3\text{AsO}_4 > \text{H}_3\text{SbO}_4$ (All are oxo-acids)

All of them belong to group 15. Size of central atom increases down the group. According to Fajans' rule, smaller is the size of cation, more covalent character and thus more acidic. Hence the order is as given above.

e. $\text{H}_2\text{Te} > \text{H}_2\text{Se} > \text{H}_2\text{S} > \text{H}_2\text{O}$

Note: These are not oxoacids but are hydrides of group 16.

The acidic strength depends on M-H bonds. The larger the size of M (O, S, Se, Te) the weaker its bonds with hydrogen and more easily H^+ gets released in aqueous solution.

f. $\text{H}_2\text{SO}_3 > \text{H}_2\text{SeO}_3 > \text{H}_2\text{TeO}_3$

[All are oxoacids of group 16]

Same explanation as in part (d) above.

Alternatively: Increasing size and decreasing EN from S to Te, withdraws electron from O-H bond towards itself (more in H_2SO_3), thus facilitating the release of proton.

g. $\text{H}_2\text{SO}_4 > \text{H}_2\text{SeO}_4 > \text{H}_2\text{TeO}_4$

[All are oxoacids of group 16]

Same explanation as in part (f) above.

h. $\text{HI} > \text{HBr} > \text{HCl} > \text{HF}$ [These are hydrogen halides]

According to decreasing order of EN, $\text{F} > \text{Cl} > \text{Br} > \text{I}$, the acidic strength should be $\text{H}-\text{F} > \text{HCl} > \text{H}-\text{Br} > \text{HI}$. The more the EN of the central atom, the more is the withdrawal of electrons from H to X towards itself, thus facilitating the release of proton.

But the observed order of the acidic strength is as given above, i.e. $\text{HI} > \text{HBr} > \text{HCl} > \text{HF}$.

The larger the size of X (I, Br, Cl, F), the weaker its bonds with hydrogen and more easily H^+ ion is released in aqueous solution. Hence the order is as given as above.

i. $\text{HO}-\text{Cl} > \text{HO}-\text{Br} > \text{HO}-\text{I}$. [All are oxoacids of group 17]

Decreasing order of EN of halogens is as

$$\text{F} > \text{Cl} > \text{Br} > \text{I}$$

More the EN of the halogens, more is the withdrawal of electrons from O to H bonds towards itself, thus facilitating the release of proton.

j. $\text{P}_4\text{O}_{10} > \text{SiO}_2 > \text{Al}_2\text{O}_3 > \text{MgO}$

Same explanation is in part (a) above.

k. $\text{AlCl}_3 > \text{BeCl}_2 > \text{MgCl}_2 > \text{LiCl}$

Increasing pH

Decreasing acidic character

According to Fajans' rule, higher the charge (+ve or -ve), more is the covalent, more is the acidic character, and less is its pH.

In case of BeCl_2 , both have +2 or -2 charge, but the size of $\text{Be}^{2+} <$ size of Mg^{2+} , so BeCl_2 is more covalent than MgCl_2 , and hence more acidic. Thus pH of $\text{BeCl}_2 <$ pH of MgCl_2 .

Hence the order is as given above.

6. a. $\underbrace{\text{Cs}_2\text{O} > \text{K}_2\text{O}}_{\text{Group 1}} > \underbrace{\text{SrO} > \text{MgO}}_{\text{Group 2}} > \underbrace{\text{NiO}}_{\substack{\text{Group 10} \\ \text{Transition element}}}$

Generally basic strength increases down the group (\downarrow) and decreases along the period (\rightarrow).

Therefore, oxides of group 1 elements are more basic than that of group 2 elements.

Alternatively: According to Fajans' rule, small charge on the ions (+ve or -ve), large cation and small anion, the more is the ionic compound (reverse of covalent nature) and thus more basic is the compound.

Both MgO and NiO have same charge, but size of $Mg^{2+} >$ size of Ni^{2+} .

Alternatively: Increasing electropositive nature of the element makes their oxides more basic. Mg is more electropositive than Ni (*s*-block elements are more electropositive than transition elements).

b. $CsOH > RbOH > KOH > NaOH > LiOH$

All of these hydroxides belong to group 1, and basic character increases down the group (\downarrow).

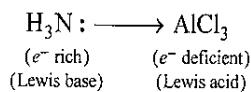
c. $Ba(OH)_2 > Ca(OH)_2 > Mg(OH)_2 > Be(OH)_2$

All of these hydroxides belong to group 2, and the basic character increases down the group (\downarrow).

d. $\ddot{N}H_3 > \ddot{P}H_3 > \ddot{As}H_3 > \ddot{Sb}H_3$

Note: These are not oxides or hydroxides but hydrides of group 15.

The basic character of these hydrides is based on the availability of lone pair electron on the central atom for donation to the electron-deficient compounds (Lewis acid), e.g.,



The basic character of the hydrides decreases down the group (\downarrow). Since the size of N atom is small, the lone pair of electrons is distributed over a small volume. As a result, electron density on N is high and hence $\ddot{N}H_3$ is strongly basic.

Down the group, the size of the atoms (P, As, Sb and Bi) goes on increasing and the lone pair of electrons is distributed over a large volume. As a result, electron density decreases and therefore the basic strength of their respective hydrides keeps on decreasing.

e. $\frac{Li_2O}{\text{Group 1}} > \frac{BeO}{\text{Group 2}} > \frac{B_2O_3}{\text{Group 3}} > \frac{CO_2}{\text{Group 4}}$

(All belong to the 2nd period)

Basic character decreases along the period (\rightarrow).

Alternatively: For explanation of basic character/acidic character by Fajans' rule, refer as given in part (b) above.

f. $F^\ominus > Cl^\ominus > Br^\ominus > I^\ominus$

The stronger the acid, the weaker is its conjugate base and vice versa.

Acidic strength: $HI > HBr > HCl > HF$ [refer to Question 5 (h) above].

Basic strength: $I^\ominus < Br^\ominus < Cl^\ominus < F^\ominus$.

Hence the order is as given above.

g. $\overset{\ddot{\circ}}{C}H_3 > \overset{\ddot{\circ}}{N}H_2 > \overset{\ddot{\circ}}{O}H > \overset{\ddot{\circ}}{F}$

Acidic strength: $HF > H_2O > NH_3 > CH_4$

Basic strength: $F^\ominus < OH^\ominus < NH_2^\ominus < CH_3^\ominus$

Alternatively: The more EN the atom, the lesser is its tendency to give a lone pair of electrons.

Decreasing order of EN: $F > O > N > C$.

Hence the order is as given above.

h. $\overset{1+}{Tl}_2O > \overset{3+}{Tl_2}O_3 > \overset{3+}{Ga_2}O_3 > \overset{3+}{Al_2}O_3$ [All belong to group 13]

According to Fajans' rule, small charge, large cation and small anion, the more the ionic character and thus the more basic is the compound.

Hence the order is as given above.

7. a. $\overset{2+}{Ba}Cl_2 > \overset{2+}{Sr}Cl_2 > \overset{2+}{Ca}Cl_2 > \overset{2+}{Mg}Cl_2 > \overset{2+}{Be}Cl_2$

[All belong to group 2]

According to Fajans' rule, small charge, large cation and small anion, the more is the ionic character.

Thus ionic character increases down the group (\downarrow).

Alternatively: Increase in electropositivity of the element increases the ionic character.

b. $\overset{3+}{Ga}Cl_3 > \overset{3+}{Al}Cl_3 > \overset{3+}{BCl_3}$ [All belong to group 13]

Same explanation as in part (a) above.

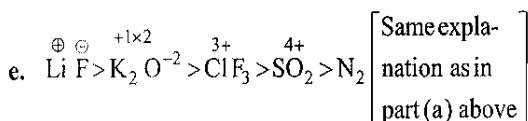
c. $\overset{2+}{V}Cl_2 > \overset{3+}{V}Cl_3 > \overset{4+}{V}Cl_2 > \overset{5+}{VO}Cl_3$

Same explanation as in part (a) above.

d. $\overset{1+}{Cs}Br > \overset{1+}{Rb}Br > \overset{1+}{K}Br > \overset{\oplus}{Na}Br > \overset{\oplus}{Li}Br$

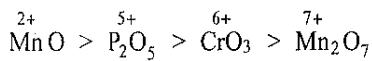
[All belong to group 1]

Same explanation as in part (a) above.



f. MnO is the most ionic. Apply Fajans' rule.

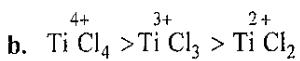
The lesser the charge, the more is the ionic character. Therefore, decreasing order of ionic character:



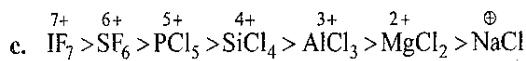
8. a. $\text{LiI}^{1+} > \text{LiBr}^{1+} > \text{LiCl}^{1+}$ [All belong to group 1]

According to Fajans' rule, high charge on the ions, small cation, large anion, the more is the covalent character.

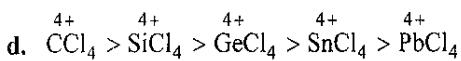
Hence the order is as given above.



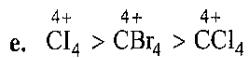
Same explanation as in part (a) given above.



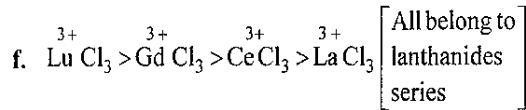
Same explanation as in part (a) given above.



Same explanation as in part (a) given above.



Same explanation as in part (a) given above.



In lanthanides, the size of cation decreases in that series (due to lanthanide contraction).

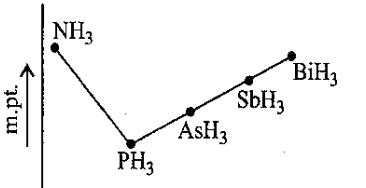
\therefore Size of $\text{La}^{3+} > \text{Ce}^{3+} > \text{Gd}^{3+} > \text{Lu}^{3+}$

Hence according to Fajans' rule, the order is as given above.

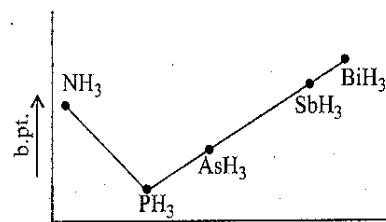
9. a. $\text{Li} > \text{Na} > \text{K} > \text{Rb} > \text{Cs}$ [All belong to group 1]

The melting (or boiling) point decreases down group 1, since the metallic bonding decreases but metallic character increases down the group (\downarrow).

- b. Hydrides of group 15.



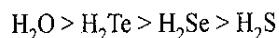
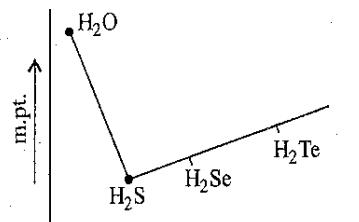
m.pt. (K) 195.2 — 185 156.7 139.5



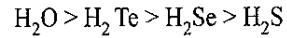
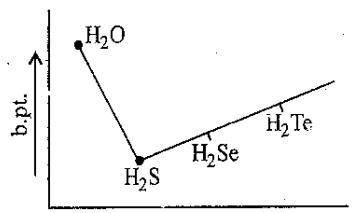
b.pt. (K) 290 254.6 238.6 210.6 185

For explanation, refer to Chapter 2.

- c. Hydrides of group 16



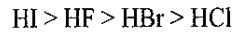
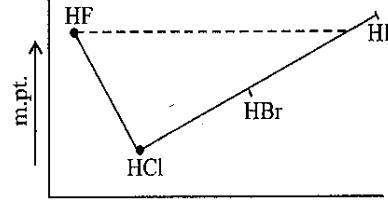
m.pt. (K) 273 > 222 > 208 > 188



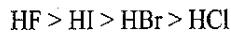
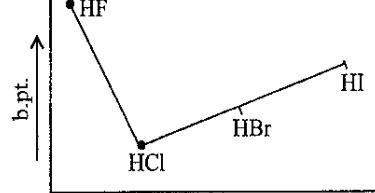
b.pt. (K) 373 > 269 > 232 > 213.

For explanation, refer to Chapter 2.

- d. Hydrides of group 17



m.pt. (K) 222 > 190 > 185 > 159



b.pt. (K) 293 > 238 > 206 > 189

For explanation, refer to Chapter 2.

- e. Melting point of $\text{H}_2\text{O} > \text{NH}_3 > \text{HF}$

m.pt. (K) 273 > 195.2 > 190

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Boiling point of $\text{H}_2\text{O} > \text{HF} > \text{NH}_3$

b.pt. (K) $373 > 293 > 238.5$

For explanation, refer to Chapter 2.

f. m.pt. $\text{KF} > \text{KCl} > \text{KBr} > \text{KI}$

The more ionic a compound, the higher is the m.pt. Therefore according to Fajans' rule, the more in the ionic character. Hence the m.pt. are as given above.

g. m.pt. $\text{CaF}_2 > \text{CaCl}_2 > \text{CaBr}_2 > \text{CaI}_2$

Same explanation as given in part (f) above.

h. $\begin{array}{ccccccc} \text{Li}^+ & \text{Br}^- & \text{Li}^+ & \text{I}^- & \text{Be}^{2+} & \text{Br}_2^- & \text{B}^{3+} \\ \text{Li Br} > \text{Li I} > \text{Be Br}_2 > \text{B Br}_3 \end{array}$

Same explanation according to Fajan's rule.

10. a. All of them belong to $3d$ series of transition element.

$\text{Cr}^{2+} > \text{Co}^{2+} > \text{Ni}^{2+} > \text{Ti}^{3+} > \text{Zn}^{2+}$

(The more the number of unpaired e^- 's, the higher is the magnetic moment) and are coloured also.

| Valence electronic configuration | $n =$ unpaired e^- | Colour |
|---|----------------------------|--------------|
| $\text{Ti} (\text{Z} = 22) \dots 3d^2 4s^2 \quad \text{Ti}^{3+} = 3d^1 4s^0$ | $n = 1$ | All coloured |
| $\text{Cr} (\text{Z} = 24) \dots 3d^5 4s^1 \quad \text{Cr}^{2+} = 3d^4 4s^0$ | $n = 4$ | |
| $\text{Co} (\text{Z} = 27) \dots 3d^7 4s^2 \quad \text{Co}^{2+} = 3d^6 4s^0$ | $n = 3$ | |
| $\begin{array}{ c c c c c c } \hline & 1 & & 1 & & 1 & & 1 & & 1 \\ \hline \end{array}$ | | |
| $\text{Ni} (\text{Z} = 28) \dots 3d^8 4s^2 \quad \text{Ni}^{2+} = 3d^8 4s^0$ | $n = 2$ | |
| $\begin{array}{ c c c c c c } \hline & 1 & & 1 & & 1 & & 1 & & 1 \\ \hline \end{array}$ | | |
| $\text{Zn} (\text{Z} = 30) \dots 3d^{10} 4s^2 \quad \text{Zn}^{2+} = 3d^{10} 4s^0$ | $n = 0$ | Colourless |

b. $\text{N} > \text{O} > \text{Al} > \text{Ca}$ ($n = 3, 2, 1, 0$)

| Valence electronic configuration | | |
|---|---------|--------------|
| $\text{Ca} (\text{Z} = 20) \dots 4s^2$ | $n = 0$ | Colourless |
| $\text{Al} \dots 3s^2 3p^1$ | $n = 1$ | All coloured |
| $\text{N} (\text{Z} = 7) \dots 2s^2 2p^3$ | $n = 3$ | |
| $\text{O} (\text{Z} = 8) \dots 2s^2 2p^4$ | | |
| $\begin{array}{ c c c } \hline & 1 & & 1 \\ \hline \end{array}$ | $n = 2$ | |

c. All of them belong to $3d$ transition element.

$\text{Cr} > \text{Mn} > \text{Fe} > \text{V} > \text{Ti} > \text{Sc}$ ($n = 6, 5, 4, 3, 2, 1$)

Valence electronic configuration:

$\text{Sc} (\text{Z} = 21) \dots 3d^1 4s^2 \Rightarrow n = 1$

$\text{Ti} (\text{Z} = 22) \dots 3d^2 4s^2 \Rightarrow n = 2$

$\text{V} (\text{Z} = 23) \dots 3d^3 4s^2 \Rightarrow n = 3$

$\text{Cr} (\text{Z} = 24) \dots 3d^5 4s^1 \Rightarrow n = 6$

$\text{Mn} (\text{Z} = 25) \dots 3d^6 4s^2 \Rightarrow n = 5$

$\text{Fe} (\text{Z} = 26) \dots 3d^6 4s^2 \Rightarrow n = 4$

$$\begin{array}{|c|c|c|c|c|c|} \hline & 1 & | & 1 & | & 1 & | & 1 & | & 1 \\ \hline \end{array} \Rightarrow n = 4$$

d. $\text{Mn}^\oplus > \text{Cr}^\oplus > \text{Fe}^\oplus > \text{V}^\oplus > \text{Ti}^\oplus > \text{Sc}^\oplus$

($n = 6, 5, 4, 3, 2$)

Valence electronic configuration [as given in part (c) above]

$\text{Sc}^\oplus = \dots 3d^1 4s^1 \Rightarrow n = 2$

$\text{Ti}^\oplus = \dots 3d^2 4s^1 \Rightarrow n = 3$

$\text{V}^\oplus = \dots 3d^3 4s^1 \Rightarrow n = 4$

$\text{Cr}^\oplus = \dots 3d^5 4s^0 \Rightarrow n = 5$

$\text{Mn}^\oplus = \dots 3d^5 4s^1 \Rightarrow n = 6$

$\text{Fe}^\oplus = \dots 3d^6 4s^1 \Rightarrow n = 5$

($n = 4$) ($n = 1$)

All are coloured

e. $\text{Mn}^{2+} > \text{Cr}^{2+} > \text{Fe}^{2+} > \text{V}^{2+} > \text{Ti}^{2+} > \text{Sc}^{2+}$

($n = 5, 4, 4, 3, 2, 1$)

Valence electronic configuration as given in part (c) above

$\text{Sc}^{2+} = \dots 3d^1 4s^0 \Rightarrow n = 1$

$\text{Ti}^{2+} = \dots 3d^2 4s^0 \Rightarrow n = 2$

$\text{V}^{2+} = \dots 3d^3 4s^0 \Rightarrow n = 3$

$\text{Cr}^{2+} = \dots 3d^4 4s^0 \Rightarrow n = 4$

$\text{Mn}^{2+} = \dots 3d^5 4s^0 \Rightarrow n = 5$

$\text{Fe}^{2+} = \dots 3d^6 4s^0 \Rightarrow n = 4$

All are coloured

f. $\text{Fe}^{3+} > \text{Mn}^{3+} > \text{Cr}^{3+} > \text{V}^{3+} > \text{Ti}^{3+} > \text{Sc}^{3+}$ ($n = 5, 4, 3, 2, 1, 0$)

Valence electronic configuration as given in part (c) above

$\text{Sc}^{3+} = \dots 3d^0 4s^0 \Rightarrow n = 0$

Colourless

$\text{Ti}^{3+} = \dots 3d^1 4s^0 \Rightarrow n = 1$

$\text{V}^{3+} = \dots 3d^2 4s^0 \Rightarrow n = 2$

$\text{Cr}^{3+} = \dots 3d^3 4s^0 \Rightarrow n = 3$

$\text{Mn}^{3+} = \dots 3d^4 4s^0 \Rightarrow n = 4$

$\text{Fe}^{3+} = \dots 3d^5 4s^0 \Rightarrow n = 5$

All are coloured

g. $\text{P} > \text{Si} = \text{S} > \text{Al} = \text{Cl}$

Valence electronic configuration:

$\text{Al} (\text{Z} = 13) \dots 3s^2 3p^1 \quad n = 1$

$\text{Si} (\text{Z} = 14) \dots 3s^2 3p^2 \quad n = 2$

$\text{P} (\text{Z} = 15) \dots 3s^2 3p^3 \quad n = 3$

$\text{S} (\text{Z} = 16) \dots 3s^2 3p^4 \quad n = 2$

$$\begin{array}{|c|c|c|} \hline & 1 & | & 1 & | & 1 \\ \hline \end{array} \quad n = 2$$

$\text{Cl} (\text{Z} = 17) \dots 3s^2 3p^5 \quad n = 1$

$$\begin{array}{|c|c|c|} \hline & 1 & | & 1 & | & 1 \\ \hline \end{array} \quad n = 1$$

All are coloured

11. a. $\text{NH}_3 > \text{PH}_3 > \text{AsH}_3$ For explanation, refer to $107.5^\circ > 93.3^\circ > 91.8^\circ$] Section 1.17.(3)(a).

- b. $\text{H}_2\text{O} > \text{H}_2\text{S} > \text{H}_2\text{Se}$ For explanation, refer to
 $104.5^\circ > 92.5^\circ > 91^\circ$ Section 1.17, Point 3(a)
 (Explanation) and Table 1.20.
- c. $\text{NF}_3 > \text{PH}_3 > \text{AsF}_3$
 $102^\circ > 93.3^\circ > 90^\circ$

The increasing size (from N \rightarrow P \rightarrow As) and decreasing EN (from N \rightarrow P \rightarrow As) of the central atom, permit the bonding electrons to be drawn out further, thus decreases repulsion between bonding pairs.

- d. $\text{NCl}_3 > \text{NF}_3$

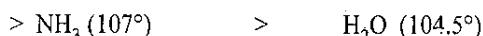
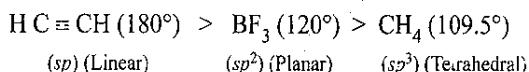
For explanation, refer to Section 1.17, Point 3(a)(ii).

- e. $\text{NO}_2^+ > \text{NO}_2 > \text{NO}_2^-$ For explanation, refer to
 $180^\circ > 134^\circ > 115^\circ$ Section 1.17, Point 3(a)(v).

- f. $\text{NH}_3 > \text{NF}_3$. For explanation, refer to Section 1.17, Point 3(a)(iii).

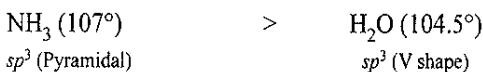
- g. $\text{PF}_3 > \text{PH}_3$. For explanation, refer to Section 1.17, Point 3(a)(iii).

- h. State of hybridisation is also used for determination of bond angle, refer to Section 1.17, Point 3(a)(v).



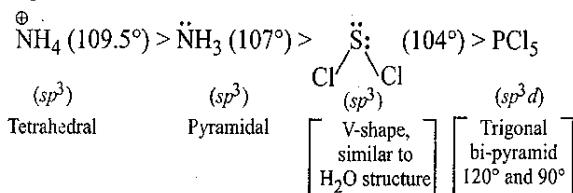
Pyramidal, sp^3 but there is repulsion between lone pair and bond pair.

V shape, sp^3 but more repulsion between lone pair and bond pair.



Same explanation as given in part (h) above.

j.



Same explanation as given in part (h) above.

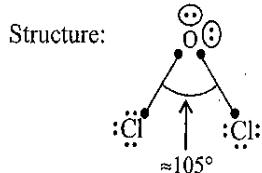
- k. $\text{NO}_2^+ (180^\circ) > \text{NO}_2 (134^\circ) > \text{NO}_3^- (120^\circ) > \text{NO}_2^- (115^\circ)$
 Linear, One unshared sp^2 and have one lone
 (sp) electron, sp^2 3 resonating pair, sp^2 structure

For explanation, refer to Section 1.17, Point 3(a)(v).

- l. $\text{BF}_3 > \text{SiH}_4 > \ddot{\text{N}}\text{H}_3 > \text{H}_2\ddot{\text{S}}$
 $\text{sp}^2 \quad \text{sp}^3 \quad \text{sp}^3 \quad \text{sp}^3$
 $\left(\begin{array}{c} \text{Planar} \\ 120^\circ \end{array} \right) \left(\begin{array}{c} \text{sp}^3 \\ \text{Tetrahedral} \\ 109.5^\circ \end{array} \right) \left[\begin{array}{c} \text{sp}^3 \\ \text{Tetrahedral} \\ 107^\circ \\ \text{Due to repulsion} \\ \text{between} \\ \text{lp and bp} \end{array} \right] \left[\begin{array}{c} \text{sp}^3 \\ \text{Tetrahedral} \\ 104.5^\circ \\ \text{Due to repulsion} \\ \text{between} \\ \text{lp and lp} \end{array} \right]$

- m. i. $\text{Cl}_2\ddot{\text{O}}$: \Rightarrow Hybridisation = $2 \text{ bp} + 2 \text{ lp} = 4 = \text{sp}^3$
 OR

$$\text{Hybridisation} = \frac{1}{2}(V + M) = \frac{1}{2}(6 + 2) = 4 = \text{sp}^3$$

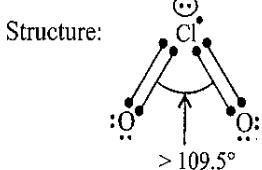


Due to lp-lp repulsion the bond angle decreases from the expected 109.5° to $\approx 105^\circ$ (like H_2O).

- ii. $\text{Cl}\ddot{\text{O}}_2 \Rightarrow$ Hybridisation = $2 \text{ bp} + 1 \text{ lp} + 1e^- = 4 = \text{sp}^3$

OR

$$\begin{aligned} \text{Hybridisation} &= \frac{1}{2}(V + M + \text{unpaired } e^-) \\ &= \frac{1}{2}(7 + 01) = 4 = \text{sp}^3 \end{aligned}$$

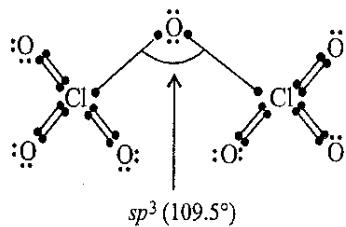


Since there are only three non-bonding e^- 's on the central atom in ClO_2 , the repulsion for the bonded pairs is less than that in Cl_2O and the angle between the bonds is greater in ClO_2 .

Moreover, the resonance of single electron among the bonding and non-bonding orbitals on the central atom lead to angle somewhat greater than the tetrahedral angle (i.e. $> 109.5^\circ$).

The shorter bond length ($\text{O}-\text{Cl}$) in ClO_2 results from resonance, with the unpaired e^- 's on the Cl or O atom.

- iii. Cl_2O_7 structure:



The tetrahedral angle about the Cl atoms is as expected (109.5°).

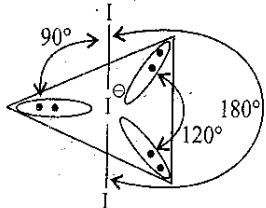
The angle about the central O atom is also expected for an sp^3 hybridised central atom with two of the pairs of electrons bonded to other atoms.

- iv. I_3^- OR
- Central atom

$$\text{Hybridisation} = 2 \text{ bp} + 3 \text{ lp} = 5 = sp^3d$$

OR

$$\begin{aligned}\text{Hybridisation} &= \frac{1}{2}(V + M + (\text{negative charge})) \\ &= \frac{1}{2}(7+2+1) = 5 = sp^3d \\ &\Rightarrow \text{Trigonal bipyramidal (Tbp)}\end{aligned}$$



The linear orientation of I_3^- results from the five pairs of electrons being oriented in Tbp geometry about the central atom. The two bonding pairs repel less than the non-bonding pairs (i.e. lp's) and so are most stable at the **apical positions** (90° from three other pairs). Bond angle between $I-I^-I$ is 180° . So, the decreasing order of bond angle is $I_3^- (180^\circ) > ClO_2 (>109.5^\circ) > Cl_2O_7 (109.5^\circ) > Cl_2O (\approx 105^\circ)$

12. a. $BaF_2 > CaF_2 > MgF_2 > BeF_2$

b. $Ba(OH)_2 > Ca(OH)_2 > Mg(OH)_2 > Be(OH)_2$

For explanation of (a) and (b), refer to Section 1.28.1, Point 10(b).

Note: Lattice energy variation is more dominating than the variation in hydration energy.

c. $BeCO_3 > MgCO_3 > CaCO_3 > BaCO_3$

d. $BeSO_4 > MgSO_4 > CaSO_4 > BaSO_4$

e. $Be(HCO_3)_2 > Mg(HCO_3)_2 > Ca(HCO_3)_2 > Ba(HCO_3)_2$

Note: Down the group (↓), the lattice energies of carbonates, sulphates and bicarbonates do not decrease much while the degree of hydration of the metal ions decreases significantly leading to decreased solubility.

For detailed explanation of (c), (d) and (e), refer to Section 1.28.1, Point 10 (c).

f. $NaCl > MgCl_2 > AlCl_3 > CCl_4$

According to Fajans' rule, the more ionic a compound the more is soluble in water.

Hence, the order is as given above.

g. $NaCl > CuCl$

According to Fajans' rule, NaCl is more ionic than CuCl (which is covalent).

Both have same charge, sizes of cation and anion are

also same.

But Cu^{+2} have d -orbitals. So $CuCl$ is covalent and $NaCl$ is ionic.

The more the ionic, the more is the solubility in water. Hence, the order is as given above.

h. $HNO_3 > H_3PO_4 > H_3AsO_4 > H_3SbO_4$

(All of them belong to group 15)

According to Fajans' rule, the acidic character is given as above (Refer to solution of Question 5 (d)).

The more is the acidic character, the more is the solubility in water

i. $H_2SO_3 > H_2SeO_3 > H_2TeO_3$ [All are oxoacids of group 16]

Refer to solution of Question 5 (f).

13. a. Bond length: $Cl-Cl > F-F > O=O > N \equiv N$

Bond strength: $N \equiv N > O=O > F-F > Cl-Cl$

Fluorine and chlorine contain a single bond each. Chlorine involves overlap of $3p$ orbitals while fluorine involves overlap of $2p$ orbitals. Overlap of $2p-2p$ orbitals is stronger than $3p-3p$ overlap. So bond strength of $F_2 > Cl_2$ and bond length of $Cl_2 > F_2$.

Nitrogen contains triple bond and oxygen contains double bond. Triple bond is stronger than double bond.

$$\text{Bond strength} \propto \frac{1}{\text{Bond length}}$$

Hence, the order is as given above.

b. $F-F > O-O > N-N$

Same explanation as given in part (a) above.

c. $Cl_2 > Br_2 > F_2 > I_2$ (observed trend)

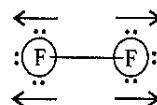
Bond enthalpy (kJ mol^{-1}) $242.6 > 192.8 > 158.8 > 151.1$

The expected trend in the bond dissociation energy should be:

$$F_2 > Cl_2 > Br_2 > I_2$$

Enthalpy of dissociation decreases as the bond distance increases from F_2 to I_2 , due to a corresponding increase in the size of the atom down the group from F to I.

But the bond dissociation enthalpy of F_2 is however smaller than that of Cl_2 and even smaller than that of Br_2 . This is due to the reason that F atom is very small and hence the electron-electron repulsions between the lone pairs of electrons are very large, e.g.



Hence, the order is as given above.

- d. HF > HCl > H Br > H I (Hydrides of group 17)

As the size of halogen atom increases, the strength of HX bond increases. Besides this, the decreasing per cent of ionic character from HF to HI makes the bond less stable.

- e. $\text{HClO}_4 > \text{HClO}_3 > \text{HClO}_2 > \text{HClO}$

The stability is explained by increasing the number of electrons involved in the formation of σ and π bonds is going from HClO to HClO_4 . In ClO_4^- ion, all the valence orbitals and electrons of chlorine are involved in the formation of bonds.

- f. $\text{CsOH} > \text{RbOH} > \text{KOH} > \text{NaOH} > \text{LiOH}$

Down the group, according to Fajans' rule, the ionic character of hydroxides of group 1 and group 2 increases. Therefore, the more ionic a compound, the more is the thermal stability.

- g. $\text{NH}_3 > \text{PH}_3 > \text{SbH}_3 > \text{BiH}_3$ (Hydrides of group 15)

Stability of hydrides of groups 15, 16 and 17 decreases down the group (\downarrow). SbH_3 and BiH_3 are thermally unstable whereas BiH_3 has been obtained in traces only.

Since the size of element (M) in M–H increases down the group (\downarrow), the bond length between M and H in MH increases and the bond strength decreases down the group.

Reducing the character of hydrides of groups 15, 16 and 17 increases down the group.

Down the group (\downarrow) the removal of H-atom increases, so the reducing character order is as given below:

Reducing character: $\text{BiH}_3 > \text{SbH}_3 > \text{AsH}_3 > \text{PH}_3 > \text{NH}_3$.

- h. Thermal stability: $\text{H}_2\text{O} > \text{H}_2\text{S} > \text{H}_2\text{Se} > \text{H}_2\text{Te}$.

Reducing character: $\text{H}_2\text{Te} > \text{H}_2\text{Se} > \text{H}_2\text{S} > \text{H}_2\text{O}$.

Same explanation as in part (g) above.

- i. $\text{H}_2\text{SO}_3 > \text{H}_2\text{SeO}_3 > \text{H}_2\text{TeO}_3$ (All are oxoacids).

Same explanation as in part (g) above.

- j. $\text{H}_2\text{SO}_4 > \text{H}_2\text{SeO}_4 > \text{H}_2\text{TeO}_4$ (All are oxoacids).

Same explanation as in part (g) above.

- k. $\text{HIO}_3 > \text{HBrO}_3 > \text{HClO}_3 > \text{HFO}_3$

Ions of these acids are stabilised due to strong $p\pi-d\pi$ multiple bonding between full $2p$ orbitals on oxygen and empty d -orbitals on the halogen atom. Fluorine has no d -orbitals and can not form $p\pi-d\pi$ bonds. Thus oxoacids of fluorine are not known.

- l. $\text{LiH} > \text{NaH} > \text{KH} > \text{CsH}$ (All hydrides of groups 1 and 2)

According to Fajans' rule, hydrolysis of cations depends on two factors: larger charge and smaller size favour more hydrolysis, hence, more free H^+ ions.

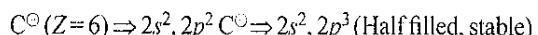
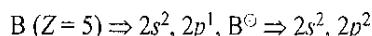
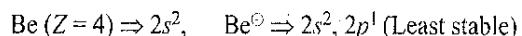
- m. $\text{BaCO}_3 > \text{CaCO}_3 > \text{MgCO}_3 > \text{BeCO}_3$

Increasing size of cation decreases its polarising ability towards carbonate ion, (CO_3^{2-}) , and thus making the compound more stable. Hence stability of carbonates of group 2 elements decreases down the group.

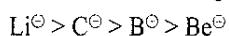
For more explanation, refer to Chapter 4, Section 4.6.7.1.

- n. $\text{Li} (Z=3) \Rightarrow 2s^1, \quad \text{Li}^\ominus \Rightarrow 2s^2$

(Full filled, most stable)



Therefore, decreasing order of stability:



14. a. $\text{PCl}_5 > \text{SiCl}_4 > \text{AlCl}_3 > \text{MgCl}_2 > \text{CCl}_4$

| | | | | |
|----------|----------|----------|---------|----------|
| group 15 | group 14 | group 13 | group 2 | group 14 |
|----------|----------|----------|---------|----------|

In covalent halides, hydrolysis occurs as a result of coordination of a water molecule to the less EN element. CCl_4 does not undergo hydrolysis as carbon cannot expand its octet to accommodate water molecules.

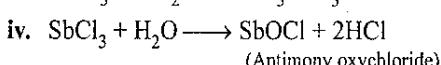
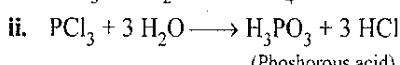
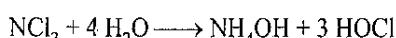
- b. $\text{BiCl}_3 > \text{SbCl}_3 > \text{AsCl}_3 > \text{PCl}_3 > \text{NCl}_3$ (All belong to group 15)

Hydrolysis increases down the group (\downarrow).

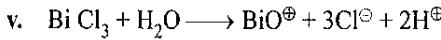
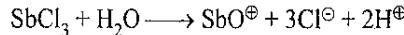
These trihalides are predominantly covalent with ionic character increasing down the group (\downarrow) (Fajans' rule). The trihalides undergo hydrolysis but the product of hydrolysis depends upon the nature of the element. For example,



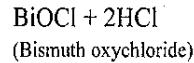
OR



OR



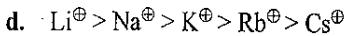
OR



- c. $\text{Be}^{2+} > \text{Mg}^{2+} > \text{Ca}^{2+} > \text{Sr}^{2+} > \text{Ba}^{2+}$

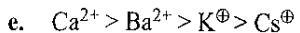
Hydration of ions \propto charge density $\left(\frac{\text{Charge}}{\text{Size}} \right)$

Hydration of ions decreases down the group (\downarrow) and increases along the period (\rightarrow).

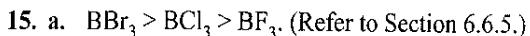


Same explanation as given in part (c) above.

The more is the extent of hydration, the more negative hydration energy is released.

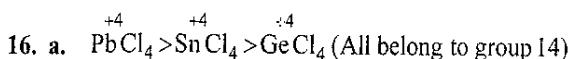
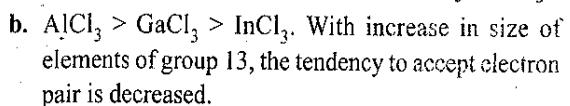


Hydration energy of group 2 ions > Hydration energy of group 1 ions [as explained in part (c) above].

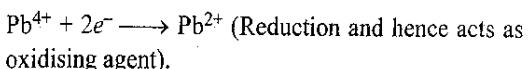


Besides σ bond between boron and halogen atoms, there exists additional $p\pi-p\pi$ bond between the two atoms resulting from back-donation of electrons from fluorine to boron (back bonding).

The tendency to form $p\pi-p\pi$ bond is maximum in BF_3 ($2 p\pi - 2 p\pi$ back bonding) and falls rapidly on passing to BCl_3 ($2 p\pi - 3 p\pi$ back bonding) and BBr_3 ($2 p\pi - 4 p\pi$ back bonding). The tendency to accept electron pair, therefore increases from BF_3 to BBr_3 .



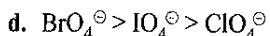
Due to inert pair effect, the stability of element in group 14, from +4 oxidation state to +2 oxidation state increases down the group (\downarrow), e.g.



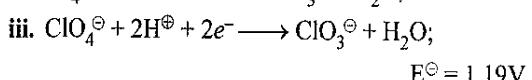
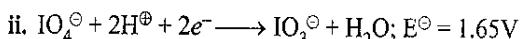
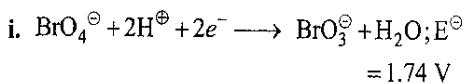
Reduction potential $[E_{\text{F}/\text{F}^{\oplus}(\text{aq})}]$ of halogens decreases down the group, so oxidising power also decreases.



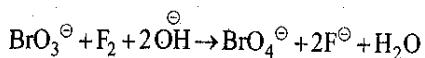
Same explanation as given in part (b) above.



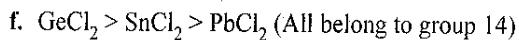
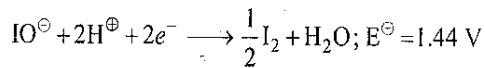
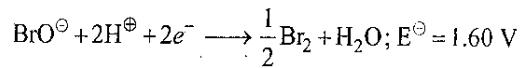
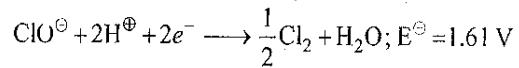
This is due to their reduction potential values.



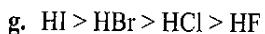
Although among perhalates, BrO_4^{\ominus} is the strongest oxidising agent, yet it is a weaker oxidising agent than F_2 . This is because BrO_4^{\ominus} (perbromate) and HBrO_4 (per bromic acid) can be obtained by the oxidation of bromates (BrO_4^{\ominus}) by F_2 in alkaline solution



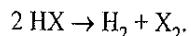
As the size of the halogen increases, the thermal stability of the O-X bond increases and the oxidising power of XO^{\ominus} decreases, as shown by their reduction potential values.



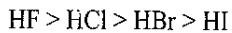
The stability of element in +2 oxidation state increases down the group 14 (\downarrow). This is due to inert pair effect [As explained in part (a) above].



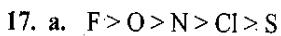
The reducing power of HX acids depends upon the ease with which it decomposes to give H_2 and X_2 .



Greater the bond dissociation energy, the more stable is the HX acid and hence weaker is the reducing agent. Bond dissociation energy of HX is as:



and hence the reducing power of HX is as shown above.



H-bonding \propto EN of the element and

$$\text{H-bonding} \propto \frac{1}{\text{size of the element}}$$

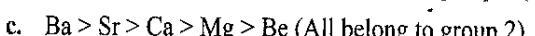
The decreasing order of EN is $\text{F} > \text{O} > \text{N} > \text{Cl} > \text{S}$.

The decreasing order of size is $\text{F} < \text{O} < \text{N} < \text{Cl} < \text{S}$.

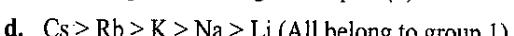
High EN and small size of the element makes hydrogen bonding more strong.



The reactivity increases down the group 1 (\downarrow) due to decrease in ionisation energy down the group 1 (\downarrow).



Same explanation as given in part (b) above.



The ease of formation of hydrides increases down the group 1 (\downarrow).

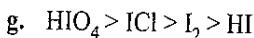


The ease of formation of oxides increases down the group 2 (\downarrow).

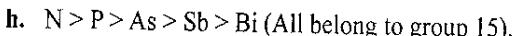


The number of hybrid orbitals and ease with which

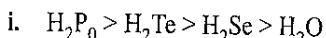
these are formed decreases down the group 14 (\downarrow), i.e. from C to Pb.



The oxidation of iodine in HIO_4 , ICl , I_2 and HI are +7, +1, 0 and -1 respectively

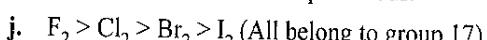


Stability of lower oxidation state (i.e. from +5 to +3 in group 15) increases down the group 15 (\downarrow). This is due to inert pair effect.



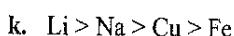
(All belong to group 16)

Poisonous nature increases down the group 16 (\downarrow). Po is radioactive and is most poisonous.



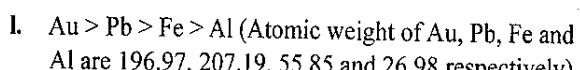
F_2 is most reactive of all the halogens, because F_2 has higher reduction potential than other halogens. The

reduction potential $\left[E_{X_2/2X^{(aq)}}^{\ominus} \right]$ decreases down the group 17 (\downarrow).



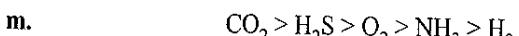
(s-block) (d-block)

s-block elements are more electropositive than d-block elements. But the electropositive character in s-block elements increases down the group. So the electropositive character of Na should be more than Li. But this is an exceptional case, Li is more electropositive in aqueous solution (refer to Section 1.28.1).



Increasing atomic mass increases the density.

So, the density of Pb should be greater than that of Au. But Au belongs to 4d-transition element series and the size is less than that of Pb. So, the density of Au > the density of Pb.



[Molecular weight

(g mol^{-1})] 44 34 32 17 2

Increasing molecular masses increases the density.

CONCEPT APPLICATION EXERCISE 1.2

Solutions on page 1.146

1. Answer the following:

- Why inert gases are monoatomic?
- Potassium (K) is strongly metallic, while Cl is strongly non-metallic. Explain.
- Why metals are good conductors of electricity?

- Comment on 'Iodine possesses some metallic lusture'.
- Of all noble metals, gold (Au) has a relatively high EA. Explain.
- In alkali metal which element is the strongest reducing agent in aqueous solution and why?
- Cl can be converted to Cl^{\ominus} ion easily than F to F^{\ominus} ion. Explain.
- Why Al(OH)_3 is amphoteric in nature?
- Why Be and Mg do not impart flame colouration?
- The IE of K is same as EA of K^{\oplus} ion. Explain.
- Explain the large atomic radii of noble gases.

Objective Type

- Which has maximum polarising power in cation?
 - O^{2-}
 - Al^{+3}
 - Li^+
 - Mg^{+2}
- Which has the maximum IE?
 - O^{\oplus}
 - N
 - O
 - Na
- Which of the following ions has the highest heat of hydration?
 - Na^{\oplus}
 - Li^{\oplus}
 - Cs^{\oplus}
 - K^{\oplus}
- Inert pair effect is shown by
 - s-block
 - p-block
 - d-block
 - f-block
- Which is/are amphoteric oxide?
 - ZnO
 - BeO
 - SnO
 - All of these
- EA is positive when
 - O^{\ominus} is formed from O
 - O^{\oplus} is formed from O
 - O^{2-} is formed from O
 - EA is always a negative value
- Which has the maximum covalent character?
 - MgCl_2
 - NaCl
 - SiCl_4
 - AlCl_3
- In which solvent KBr has maximum solubility?
 - $\text{C}_2\text{H}_5\text{OH}$
 - CH_3COCH_3
 - $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$
 - H_2O
- Lattice energy of BeCO_3 (I), MgCO_3 (II) and CaCO_3 (III) is in order.
 - I > II > III
 - III > II > I
 - II > III > I
 - III > I > II
- NO_2 and N_2O_4 are two forms of nitrogen dioxide. One exists in gaseous state while other in liquid state. The nature of NO_2 and N_2O_4 forms are
 - Both are diamagnetic
 - Both are paramagnetic
 - NO_2 is diamagnetic while N_2O_4 is paramagnetic
 - NO_2 is paramagnetic while N_2O_4 is diamagnetic

12. Magnetic moments of V ($Z = 23$), Cr ($Z = 24$) and Mn ($Z = 25$) are x, y and z respectively, hence
 a. $x = y = z$ b. $x < y < z$ c. $x < z < y$ d. $z < y < x$
13. 'Solubility of groups 1 and 2 fluorides increases down the group'. Which of the following is correct explanation for the above given statement?
 a. Both the hydration and lattice energies decrease down the group (\downarrow) but decrease in lattice energy is rapid.
 b. Both the energies increase down the group but increase in hydration energy is rapid.
 c. Both the energies decrease down the group but decrease in hydration energy is rapid.
 d. Hydration energy increases and lattice energy decreases down the group.
14. Which of the following molecule is theoretically not possible?
 a. OF_4^- b. O_2F_2 c. OF_2 d. SF_4
15. Which of the following triads have approximately equal size?
 a. $\text{Na}^{\oplus}, \text{Mg}^{2+}, \text{Al}^{3+}$ (isoelectronic)
 b. $\text{Mn}^{\oplus}, \text{Fe}^{2+}, \text{Cr}$ (isoelectronic)
 c. $\text{F}^{\ominus}, \text{Ne}, \text{O}^{2-}$ (isoelectronic)
 d. $\text{Fe}, \text{Co}, \text{Ni}$
16. Which pair is different from the others?
 a. Na-K b. Ca-Mg c. Li-Mg d. B-Al
17. Compound XY is predominantly ionic as $X^{\oplus} Y^{\ominus}$ if
 a. $(\text{IE})_X < (\text{IE})_Y$ b. $(\text{EA})_X < (\text{EA})_Y$
 c. $(\text{EN})_X < (\text{EN})_Y$ d. $(\text{IE})_Y < (\text{IE})_X$.
18. (X), (Y), (Z) are elements in third short period. Oxide of (X) is ionic, (Y) is amphoteric and (Z) is a giant molecule. (X), (Y) and (Z) will have atomic number in the order:
 a. $(X) < (Y) < (Z)$ b. $(Z) < (Y) < (X)$
 c. $(X) < (Z) < (Y)$ d. $(Y) < (X) < (Z)$
19. Which of the following species have correct order of size?
 a. $\text{O}^{2-} > \text{O}^{\ominus} > \text{F}^{\ominus} > \text{F}$ b. $\text{O}^{\ominus} > \text{O}^{2-} > \text{F}^{\ominus} > \text{F}$
 c. $\text{O}^{2-} > \text{F}^{\ominus} > \text{O}^{\ominus} > \text{F}$ d. $\text{O}^{2-} > \text{F}^{\ominus} > \text{F} > \text{O}^{\ominus}$
20. F has the highest electronegativity among the group 17 elements (i.e. $ns^2 np^5$ type), on the Pauling scale, but the EA of F is less than that of Cl because
 a. F being the first member of the family behaves in an unusual manner.
 b. The atomic number of F is less than that of Cl.
 c. Cl can accommodate an electron better than F by utilising its vacant $3d$ orbital.

- d. Small size, high EN and an increased electron-electron repulsion makes addition of an electron to F less favourable.
21. The correct order of decreasing ionic character is
 a. $\text{BaCl}_2 > \text{CaCl}_2 > \text{MgCl}_2 > \text{BeCl}_2$
 b. $\text{BaCl}_2 > \text{MgCl}_2 > \text{CaCl}_2 > \text{BeCl}_2$
 c. $\text{BeCl}_2 > \text{MgCl}_2 > \text{CaCl}_2 > \text{BaCl}_2$
 d. $\text{BaCl}_2 > \text{BeCl}_2 > \text{CaCl}_2 > \text{MgCl}_2$
22. The correct order of decreasing polarisability of ion is
 a. $\text{Cl}^{\ominus} > \text{Br}^{\ominus} > \text{I}^{\ominus} > \text{F}^{\ominus}$ b. $\text{F}^{\ominus} > \text{I}^{\ominus} > \text{Br}^{\ominus} > \text{Cl}^{\ominus}$
 c. $\text{I}^{\ominus} > \text{Br}^{\ominus} > \text{Cl}^{\ominus} > \text{F}^{\ominus}$ d. $\text{F}^{\ominus} > \text{Cl}^{\ominus} > \text{Br}^{\ominus} > \text{I}^{\ominus}$
23. Which of the following has the smallest bond length?
 a. O_2 b. N_2 c. Cl_2 d. HCl

ANSWER KEYS

- | | | | |
|-------|-------|-------|-------|
| 2. b | 3. a | 4. b | 5. b |
| 6. d. | 7. c | 8. c | 9. d |
| 10. a | 11. d | 12. c | 13. a |
| 14. a | 15. d | 16. c | 17. c |
| 18. a | 19. a | 20. d | 21. a |
| 22. c | 23. b | | |

CONCEPT APPLICATION EXERCISE 1.3*Solutions on page 1.148*

- Arrange the following in order of decreasing ionic character.
 a. $\text{ClF}_3, \text{SO}_2, \text{N}_2, \text{K}_2\text{O}$ and LiF
 b. C – H, F – H, Br – H, Na – I, K – F and Li – Cl
 c. $\text{AlF}_3, \text{AlCl}_3, \text{AlBr}_3$
- Arrange the following in order of decreasing bond angle.
 a. $\text{CO}_2, \text{H}_2\text{O}, \text{CH}_4$
 b. $\text{SO}_4^{2-}, \text{SO}_3^{2-}$
- Ca CO_3 dissolves in HCl but not in water. Why?
- Why MgO exist as $\text{Mg}^{2+}\text{O}^{2-}$ not as $\text{Mg}^{\oplus}\text{O}^{\ominus}$ whereas the formation of Mg^{2+} from Mg requires more energy than formation of Mg^{\oplus} and formation of O^{\ominus} from O is exothermic whereas the formation of O^{2-} is endothermic.
- Anhydrous AlCl_3 is covalent from the data given below, predict whether it would remain covalent or become ionic in aqueous solution
 IE_1 of Al = 5140 kJ mol^{-1}
 $\Delta_{\text{hyd}}\text{H}^{\ominus}(\text{Al}^{3+}) = -4665 \text{ kJ mol}^{-1}$
 $\Delta_{\text{hyd}}\text{H}^{\ominus}(\text{Cl}^{\ominus}) = -380 \text{ kJ mol}^{-1}$
- Which compound for each of the following pairs is more ionic and why?

- a. BeBr_2 or MgBr_2 b. PbCl_2 or PbCl_4
 c. AgBr or AgI d. CuO or CuS

7. NaBr gives pale yellow precipitate with AgNO_3 solution but CBr_4 does not. Why?
8. Copper is conducting as such while Cu SO_4 is conducting only in molten state or in aqueous solution. Why?
9. Explain the observed bond angle order.
 $\text{Cl}_2\text{O} (110.8^\circ) > \text{H}_2\text{O} (104.5^\circ) > \text{F}_2\text{O} (103.2^\circ)$
10. NH_4^+ has bond angle identical to CH_4 but NH_3 has different bond angle. Why?
11. Electronegativities of F, O, N, Cl, H are 4.0, 3.5, 3.2 and 2.1 respectively. In which atoms there is strongest bond.
12. The IE_1 of Li is 5.4 eV and IE_1 of H is 13.6 eV. Calculate the charge acting on the outermost electron of Li atom.
13. a. The melting point of KBr is higher than that of AgBr though the crystal radii of Ag^+ and K^+ ions are almost the same. Explain.
 b. SnCl_2 is solid but SnCl_4 is liquid. Why?

Objective Type

14. The correct order of IE_2 of C, N, O and F is
 a. O > F > N > C b. F > O > N > C
 c. C > N > O > F d. O > N > F > C
15. The least stable ion among the following is
 a. Li^\ominus b. B^\ominus c. C^\ominus d. Be^\ominus
16. Which has the most stable +2 oxidation state?
 a. Sn b. Fe c. Pb d. Ag
17. Among the following elements (whose electronic configuration are given below) the one having the highest IE is
 a. [Ne] $3s^2 3p^3$ b. [Ne] $3s^2 3p^1$
 c. [Ne] $3s^2 3p^2$ d. [Ar] $3d^{10} 4s^2 4p^3$
18. The magnitude of lattice energy of a solid increases if
 a. The ions are large
 b. The ions are small
 c. The ions are of equal sizes
 d. Charges on the ions are small
19. Bond angle in PH_3 is
 a. Much less than NH_3
 b. Much less than PF_3
 c. Slightly more than NH_3
 d. Much more than PF_3
20. The correct order of decreasing bond angles in H_2S , NH_3 , BF_3 and SiH_4 is
 a. $\text{BF}_3 > \text{SiH}_4 > \text{H}_2\text{S} > \text{NH}_3$
 b. $\text{BF}_3 > \text{SiH}_4 > \text{NH}_3 > \text{H}_2\text{S}$

- c. $\text{BF}_3 > \text{NH}_3 > \text{SiH}_4 > \text{H}_2\text{S}$
 d. $\text{SiH}_4 > \text{BF}_3 > \text{NH}_3 > \text{H}_2\text{S}$

21. The bond angle around central atom is maximum for
 a. H_2O b. H_2S c. H_2Se d. H_2Te

Multiple Correct Answers Type

22. Which of the following can conduct electricity in?
 a. MgBr_2 b. CaBr_2 c. BaBr_2 d. BeBr_2
23. Which of the following are expected to be covalent?
 a. BeCl_2 b. SnCl_4 c. CuS d. CaCl_2
24. Which of the following does not exist?
 a. HS_6 b. HPO_4 c. FeI_3 d. HClO_4
25. Which of the following relation is/are correct?
 a. Covalent character \propto Pseudo inert configuration
 b. Ionic character \propto Inert configuration
 c. Covalent character $\propto \frac{1}{\text{Dipole moment}}$
 d. Ionic character $\propto \frac{1}{\text{Dipole moment}}$

26. Which of the following are correct?

- a. As^{5+} salts are better oxidising agents
 b. Tl^{3+} salts are better oxidising agents
 c. Ga^\oplus salts are better reducing agents
 d. Pb^{4+} salts are better oxidising agents

Integer Type

27. On the basis of quantum number, which period of the periodic table should have 32 elements.
28. What is the atomic number of the element present in the second period and group 15.
29. ΔH^\ominus of hypothetical MX is -150 kJ mol^{-1} and for MX_2 is -600 kJ mol^{-1} . The enthalpy of disproportionation of MX is $= -100x \text{ kJ mol}^{-1}$. Find the value of x .

Assertion Reasoning Type

- a. If both A and R are correct and R is the correct explanation for A.
 b. If both A and R are correct and R is not the correct explanation for A.
 c. If A is correct and R is incorrect
 d. If A is incorrect and R is correct
30. **Assertion (A):** IE_1 of Mg is greater than that of Al.
Reason (R): It is easier to remove an electron from $3s$ orbital than from $3p$ orbital.
31. **Assertion (A):** s-block elements can form ionic hydrides, which on electrolysis in fused state give H_2 gas at cathode.
Reason (R): s-block elements have low IE and low EN as compared to p-block elements.

ANSWER KEYS**Objective Type**

14. a 15. d 16. c 17. a
 18. b 19. a 20. b 21. a

Multiple Correct Answers Type

22. a, b, c 23. a, b 24. a, b, c 25. a, b, c
 26. b, c, d

Integer Type

27. (6) 28. (7) 29. (3)

Assertion Reasoning Type

30. c 31. d

SOLVED EXAMPLES

Example 1.1 Predict the group number and block to which the given elements belong.

A ($Z = 9$), B ($Z = 20$), C ($Z = 29$), D ($Z = 36$) and E ($Z = 58$).

$$\text{Sol. A} = 1s^2, [2s^2, 2p^5] \quad (Z = 9)$$

The last electron is in the $2p$ -orbital, therefore it belongs to p -block elements.

$$\therefore \text{Group number} = 10 + 7 = 17$$

$$\begin{array}{l} \text{Period of the element} = 2\text{nd} \\ \left[\begin{array}{l} \text{Number of the} \\ \text{principal quantum} \\ \text{number of the} \\ \text{valence shell} \end{array} \right] \end{array}$$

Hence A = group 17 and 2nd period.

$$\text{B} = 1s^2, 2s^22p^6, 3s^23p^6, [4s^2] \quad (Z = 20)$$

The last electron is in the $4s$ -orbital, therefore it belongs to s -block elements.

$$\therefore \text{Group number} = 2 \quad (\text{Number of electrons in the valence shell})$$

Period = 4th (Number of the principal quantum number of the valence shell!)

$$\text{C} = 1s^2, 2s^22p^6, 3s^23p^6, [4s^1, 3d^{10}] \quad (Z = 29)$$

The last electron is in the $3d$ -orbital, therefore it belongs to d -block elements.

$$\therefore \text{Group number} = 11\text{th} \quad \left[\begin{array}{l} \text{Number of electrons in} \\ \text{the penultimate shell} \\ (\text{i.e. in } 3d) \text{ and valence} \\ \text{shell (i.e. in } 4s) = 10 + 1 \\ = 11 \end{array} \right]$$

Period = 4th (Number of the principal quantum number of the valence shell)

$$\text{D} = 1s^2, 2s^22p^6, 3s^23p^6, 3d^{10}, [4s^24p^6] \quad (Z = 36)$$

The last electron is in the $4p$ -orbital, therefore it belongs to p -block elements.

$$\therefore \text{Group number} = 10 + 8 = 18$$

Period = 4th (Number of the principal quantum number of the valence shell)

$$\text{E} = 1s^2, 2s^22p^6, 3s^23p^6, 3d^{10}, 4s^24p^6, 4d^{10}, 5s^25p^6, [6s^2, 4f^2] \quad (Z = 58)$$

The last electron is in the $4f$ -orbital, therefore it belongs to f -block elements.

Note: The filling of $4f$ -orbitals occurs only when one electron has already entered $5d$ -orbital. Therefore, E belongs to f -block elements and not to d -block elements.

Since it belongs to lanthanides series, therefore as such it does not have any group number.

Note: But all lanthanides and actinides belong to group 3 (or III B).

However, its period = 6th Number of the principal quantum number of the valence shell

Example 1.2 IE₁ (first ionisation energy) and IE₂ (second ionisation energy) of a few elements are given below:

| Elements | A | B | C | D |
|--|------|------|------|------|
| IE ₁ (kJ mol ⁻¹) | 2370 | 520 | 900 | 1680 |
| IE ₂ (kJ mol ⁻¹) | 5250 | 7300 | 1760 | 3380 |

Which of the above elements is likely to be:

- a reactive metal
- a reactive non-metal
- a noble gas
- a metal forming binary halide (MX_2)

- Sol.**
- B is reactive metal since it has minimum IE₁.
 - D is reactive non-metal since it has second minimum IE₁.
 - A is noble gas since it has maximum IE₁.
 - C forms MX_2 . Since IE₂ of C is the least.

Example 1.3 Identify the three elements A, B and C from the data given below:

- The elements have successive atomic numbers.
- B forms a stable anion, A^\ominus
- C forms a stable cation, C^\oplus

- Sol.** Let the atomic number of A is Z, and B must be $(Z + 1)$ and C must be $(Z + 2)$ since A, B and C have successive atomic numbers.

Halogens form the most stable halide anions as their octet is complete. But in halogens Cl^- is the most stable.

Whereas alkali metals form the most stable cations.

The atomic number of Cl = 17

- $\therefore A = \text{Chlorine } (Z = 17)$
- $B = \text{Argon } (Z = 17 + 1 = 18)$
- $C = \text{Potassium } (Z = 17 + 2 = 19)$

Note: 17, 18 and 19 are successive numbers.

Example 1.4 Among the elements, Ar, Si, Na and Cl. Select an element with

- a. Highest IE
- b. Highest EA
- c. Smallest size
- d. Highest electrical conductivity

Sol. All of them belongs to the same 3rd period.

- a. Highest IE = Ar (Since it is a noble gas)
- b. Highest EA = Chlorine
[since EA or $\Delta_{eg}\text{H}^\ominus$ increases along the period (\rightarrow)
(EA of Cl > F > Br > I)]
- c. Smallest size = Chlorine (since size decreases along the same period (\rightarrow))
- d. Highest electrical conductivity = Sodium [alkali metals have highest conductivity]

Example 1.5 Arrange the following in decreasing order as directed.

- a. Decreasing order of EN: H, O, Al, F
- b. Decreasing order of radii: Ar, Br, Ca^{2+} , Mg^{2+}
- c. Decreasing order of EA: C, N, Be, F, O, Cl
- d. Decreasing order of IE and EA: F, Cl, Br, I
- e. Decreasing order of EN: F, N, O, Cl, S
- f. Decreasing order of IE: Ne, O, Na, Na^\oplus
- g. Decreasing electropositive character: Na, Cu, Zn

Sol. a. EN: $\underset{\text{2nd period}}{\text{F}} > \underset{\text{3rd period}}{\text{O}} > \underset{\text{3rd period}}{\text{Al}} > \underset{\text{1st period}}{\text{H}}$

[EN increases along the period, \therefore EN of F > O]

Aluminium (Al) belongs to 3rd period. [EN decreases down the group (\downarrow)]

b. Radii: $\underset{\text{4th period}}{\text{Br}} > \underset{\text{3rd period}}{\text{Ar}} > \underset{\text{4th period}}{\text{Ca}^{2+}} > \underset{\text{3rd period}}{\text{Mg}^{2+}}$

Although size of an atom decreases along the period (\rightarrow) but in a period, size of noble gas is highest.

Ar belongs to 3rd period whereas Br belongs to 4th period.

\therefore Size of Br > Size of Ar

Similarly, although both Ca^{2+} and Mg^{2+} ions have same charge, but Ca belongs to 4th period and Mg belongs to 3rd period.

\therefore Size of Ca^{2+} > Size of Mg^{2+}

- c. EA: Cl > F > O > C > N > Be

Among halogens decreasing order of EA or $\Delta_{eg}\text{H}^\ominus$ = Cl > F > Br > I

Generally EA increases along the period (\rightarrow)

Therefore, order of EA should be O > $\boxed{\text{N} > \text{C}}$

But there is exception in the EA of N and C. Since N has half-filled stable configuration, so it is difficult to add electron to N as compared to C.

\therefore EA of C > N

Among Be, $\boxed{\text{C}; \text{N}}$, O and F (all of them belong to 2nd period), EA of Be is the least.
Hence the order is as given above.

d. IE: F > Cl > Br > I [Generally IE decreases down the group (\downarrow)]

EA: $\boxed{\text{Cl} > \text{F}} > \text{Br} > \text{I}$ [Exception in case of Cl > F]

e. EN: $\underset{\text{2nd period}}{\text{F}} > \underset{\text{3rd period}}{\text{O}} > \underset{\text{3rd period}}{\text{Cl}} > \underset{\text{2nd period}}{\text{S}} > \boxed{\text{N}}$

Generally EN increases along the same period (\rightarrow).
Therefore, EN of 2nd period > EN of 3rd period. But EN of N (2nd period) is the least, and is an exception due to half-filled stable configuration.

f. IE: $\underset{\text{2nd period}}{\text{Ne}} > \underset{\text{3rd period}}{\text{Na}^\oplus} > \underset{\text{2nd period}}{\text{O}} > \underset{\text{3rd period}}{\text{Na}}$

IE increases along the same period (\rightarrow) and IE of noble gas (Ne) is the highest.

IE of alkali metal (Na) is less as compared to Na^\oplus ion, since it is very difficult to remove an electron from a positive ion.

Generally, IE decreases down the group (\downarrow), so IE of O > Na.

Hence the order is as given above.

g. Electropositive character: Na > Zn > Cu

Group 1 is more metallic (or electropositive character) than group 2. So, Na is most metallic than Zn and Cu. Similarly, d-block elements have more electropositive character than p-block elements.

Hence the electropositive character is as given below.

Note: In the metallic character series, the electropositive character (or reducing character) is in the order

$\text{Na} > \text{Mg} > \text{Zn} > \text{Fe} > \text{Ni} > \text{Cu} > \text{Ag}$

Note that in metallic character series, PSBC MAZINTL CHAAP, Zn comes after s-block elements.

Example 1.6 Predict from each set, the atom/ion which has the greatest IE₁ with explanation:

- | | |
|---|--------------------------|
| a. Cl or F | b. S or Cl |
| c. Ar or K | d. Xe or Kr |
| e. O or N | f. Na ⁺ or Na |
| g. Be ²⁺ or Mg ²⁺ | h. I ⁻ or I |
| i. B or C | j. Ne or F |
| k. N, O, F | l. P, Ar, Mg |
| m. B, Al, Ga | |

Sol. a. F [Small size, more Z_{eff}, less shielding effect, high IE₁ of F]

- b. Cl [Cl has high IE₁ due to small size, high nuclear charge]
- c. Ar [Ar has high IE, due to stable configuration K has low IE than Ar, because K has one more electron than Ar, and hence can easily lose this electron to acquire stable Ar configuration]
- d. Kr [Kr has high IE, because of smaller size than that of Xe, and weaker shielding effect in Kr]
- e. N [N has high IE₁, because an electron has to be lost from a stable half-filled electronic configuration. In case of O, loss of electron gives O²⁻ which has stable exactly half-filled electronic configuration]
- f. Na⁺ [Na⁺ has high IE₁, since an electron has to be lost from a stable inert gas configuration but in case of Na, loss of electron gives stable inert gas configuration]
- g. Mg²⁺ [In case of Mg²⁺, the electron has to be lost from the stable gas inert gas configuration, while in case of Be²⁺, the loss of an electron gives a stable inert gas configuration. Hence IE of Mg²⁺ > Be²⁺]
- h. I⁻ [IE of I⁻ > I, because in case of I⁻ an electron has to be lost from inert gas configuration]
- i. C [IE of C > B, because of higher nuclear charge in C]
- j. Ne [IE of Ne > F, because of stable inert gas configuration in Ne]
- k. F [All belong to 2nd period. IE of F > N > O since F has the highest nuclear charge, and the smallest size among them]
- l. Ar [All belong to 3rd period, IE of Ar > P > Mg. Ar has stable inert gas configuration]
- m. B [All belong to group 13. IE₁ of B > Ga > Al (800 > 578 > 577), because of the smallest size and weaker shielding effect of B]

Example 1.7

- a. The Δ_{eg}H[⊖] of Br is 3.4 eV. How much energy in kcal is released when 0.8 g of Br (g) is completely

converted to Br[⊖](g) ions. (1 eV = 23.06 kcal mol⁻¹)

- b. The energy released when 10⁷ atoms of I (g) is converted to I[⊖] (g) ions, is 5 × 10⁻¹³ J. Calculate Δ_{eg}H[⊖] of I (g) in (i) eV atom⁻¹ and (ii) kJ mol⁻¹.

Sol. a. Moles of Br = $\frac{\text{Mass}}{\text{Atomic mass}} = \frac{0.8}{80} = 10^{-2}$

Energy released = $10^{-2} \times 3.4 \text{ eV} \times 23.06$
= 0.784 kcal

b. i. $\Delta_{\text{eg}}H^{\ominus} = \frac{6.023 \times 10^{23} \times 5 \times 10^{-13}}{10^7} = 30.115 \times 10^3$
= 30115 kJ mol⁻¹

ii. 96.49 kJ mol⁻¹ = 1 eV atom⁻¹
 $\therefore \Delta_{\text{eg}}H^{\ominus} = (30115/96.49) \text{ eV atom}^{-1}$
= 312.104 eV atom⁻¹

Example 1.8 Predict from each set, the element which has the more negative electron gain enthalpy (Δ_{eg}H[⊖]). Give reasons:

- a. C or Si b. F or Cl c. N or O d. O or S
- e. F, Cl, S, P
- f. (i) [Ne] 3s² 3p⁵ (ii) [Ne] 3s² 3p⁴ (iii) [Ne] 3s² 3p³

Sol. a. Δ_{eg}H[⊖] of C > Si (more negative), due to small size of C than Si. [Since they contain only 4e⁻s in the outermost shell, so electron repulsion in these atoms are not very large and therefore are not considered.]

b. Δ_{eg}H[⊖] of Cl > F (more negative). Because adding an electron to the larger 3p-orbitals of Cl leads to lesser interelectronic repulsion than adding an electron to smaller 2p-orbitals of F.

c. Δ_{eg}H[⊖] of O > N

Note: Δ_{eg}H[⊖] of O is highly negative, while that of N is slightly positive.

Since N is quite stable due to half-filled 2p-orbitals, therefore it is difficult to add an extra electron to N and thus energy is required to add an extra electron.

Whereas O atom has smaller size and higher nuclear charge than N and therefore it has a high tendency to accept an extra electron. Thus energy is released.

d. Δ_{eg}H[⊖] of S > O [Same explanation as in part (b) above].

e. $\Delta_{\text{eg}}H^{\ominus} \text{ of } \frac{\text{Cl} > \text{F}}{\text{Group 17}} > \frac{\text{S}}{\text{Group 16}} > \frac{\text{P}}{\text{Group 15}}$

Δ_{eg}H[⊖] of Cl > F [as explained in part (b) above]

Δ_{eg}H[⊖] becomes more and more negative along the period (→).

$\therefore \Delta_{\text{eg}}H^{\ominus} \text{ of S} > \text{P}$

f. Electronic configuration of (i) corresponds to Cl ($Z = 17$).

Electronic configuration of (ii) corresponds to S ($Z = 16$).

Electronic configuration of (iii) corresponds to P ($Z = 15$).

All of them belong to the 3rd period and $\Delta_{eg}H^\ominus$ becomes more and more negative along the period (\rightarrow).

$$\therefore \Delta_{eg}H^\ominus \text{ of Cl} > \text{S} > \text{P}$$

Cl contains one electron less than the stable inert gas configuration, i.e. $[\text{Ne}] 3s^2 3p^6$ and hence has a strong tendency to accept an electron to acquire the stable inert gas configuration so the highest energy is released (more negative value).

- Example 3**
- The EN of cesium (Cs) is 0.7 and that of chlorine (Cl) is 3.5. Predict the bond formed between them.

- The X-X bond length is 100 pm and C-C bond length is 154 pm. If EN of 'X' and 'C' are 3.0 and 2.0 respectively, calculate the C-X bond length.

- 127 pm
- 118 pm
- 108 pm
- 128 pm

- Which of the properties can be predicted by EN values?
- If a , b and c are EN, IE and EA respectively. What is the formula of EA (c) in the terms of EN (a) and IE (b)?

Sol. a. EN difference between Cs and Cl = $(3.5 - 0.7) = 2.8$. Thus the bond between the two is ionic or electrovalent since $(\chi_{\text{Cs}} - \chi_{\text{Cl}}) > 1.7$.

b. ii. Atomic radius of X = $\frac{\text{Bond length}}{2} = \frac{100}{2} = 50 \text{ pm}$

$$\text{Atomic radius of C} = \frac{\text{Bond length}}{2} = \frac{154}{2} = 77 \text{ pm}$$

$$\text{C-X bond length} = 50 + 77 = 127 \text{ pm}$$

As there is EN difference ($\chi_X - \chi_C = 3.0 - 2.0 = 1.0$), the extent of overlapping of orbitals will be more.

Therefore, the bond length will be slightly less than 127 pm i.e. 118 pm.

- Bond energy of a molecule
 - Polarity of a molecule
 - Nature of an oxide.
 - Metallic and non-metallic character of elements.
 - Percentage of ionic or covalent character of a molecule.
- d. EN = a , IE = b , EA = c

$$\text{EN} = \frac{\text{IE} + \text{EA}}{2} \Rightarrow \text{EA} = 2\text{EN} - \text{IE}$$

$$\Rightarrow c = 2a - b$$

Example 4 Among the elements with $Z = 9, 12$ and 36 , identify by atomic number of an element which is

- Highly electropositive
- Highly EN
- An inert gas

Sol. a. $Z = 12$ (Mg)

- $Z = 9$ (F)
- $Z = 36$ (Kr)

Example 5 Explain the following questions (based on ionisation energy):

- Why IE_1 of N is higher than that of O atom?
- Why IE_1 of Mg is higher than that of Al atom?
- Why IE_1 of C is greater than that of B atom whereas IE_2 is reverse?
- In general, IE increases along the period (\rightarrow). Explain why the IE_2 of Cr is higher than that of Mn (Manganese)?
- The IE_1 and IE_2 of K are 420 and 3050 kJ mol^{-1} respectively and those of Ca are 560 and 1140 kJ mol^{-1} respectively. Compare their values and comment on the differences.
- The IE of Li, Be and C are 5.5 , 9.3 and 11.3 eV . What would be the IE's of B and N?
- Arrange the species in each group in the order of decreasing IP in each case and explain.

| | |
|---|---|
| i. K, Ca, Sc | ii. N, O, F |
| iii. K^+ , Ar, Cl^\ominus | iv. Fe^{2+} , Fe^{3+} |
| v. C, N, O | vi. Cu, Ag, Au |
| vii. K, Rb, Cs | viii. Be, B, C |
| ix. Na, Mg, Al | |
- Explain why Fe^{2+} is more easily oxidised to Fe^{3+} than Mn^{2+} to Mn^{3+} .
- Explain whether IE_1 of two isotopes of the same element would be same or different.
- What are the factors on which IE of main group elements tends to decrease down the group (\downarrow)?

Sol. a. N has half-filled configuration, hence stable. Therefore IE_1 of N $>$ IE_1 of O.

b. This is due to penetration effect. It is difficult to remove an electron from $3s$ orbital in comparison to $3p$ orbital. Hence IE_1 of Mg $>$ IE_1 of Al.

c. Refer to Illustration 1.36.

d. Valence electronic configuration of Cr = $3d^5 4s^1$ and that of Cr^\oplus is $3d^5 4s^0$ (stable half-filled configuration).

e. Valence electronic configuration of Mn = $3d^5 4s^2$ and that of Mn^\oplus is $3d^5 4s^1$ (less stable configuration than that of Cr $^\oplus$).

$\therefore \text{IE}_2$ of Cr > IE_2 of Mn

f. Valence electronic configuration of K = $4s^1$.

Valence electronic configuration of Ca = $4s^2$.

Therefore, the removal of the second electron from K is extremely difficult because K acquires noble gas configuration after the removal of one electron while the removal of both electrons from Ca is comparatively easy, as it requires stable configuration after the removal of the second electron.

f.

| Group | 1 | 2 | 13 | 14 | 15 |
|------------|----|----|----|----|----|
| 2nd period | Li | Be | B | C | N |

Generally IE increases along the period (\rightarrow). But there is an exception in IE_1 of Be and B (due to penetration effect).

Therefore, IE_1 of B should be greater than that of Be. But actually, IE_1 of Be > IE_1 of B.

Therefore, IE_1 of N (half-filled configuration) > IE_1 of C > IE_1 of Be > IE_1 of B > IE_1 of Li

g. i. Sc > Ca > K (IE of 3d block > group 2 > group 1).

ii. F > N > O [IE of group 17 > group 15 (half-filled configuration) > group 16]

iii. $\text{K}^\oplus > \text{Ar} > \text{Cl}^\ominus$ [IE of group 1 (+ve charge) > Inert gas > group 17 (-ve charge)]

iv. $\text{Fe}^{3+} > \text{Fe}^{2+} > \text{Fe}$ [IE of +3 charge > +2 charge > neutral element]

Valence electronic configuration of Fe, Fe^{2+} and Fe^{3+} are $3d^6 4s^2$, $3d^6 4s^0$ and $3d^5 4s^0$ respectively.

v. N > O > C [IE of half filled configuration of N of group 15 > IE of group 16 > IE of group 14]

vi. Au > Cu > Ag.

$5d > 3d > 4d$

IE should decrease from $3d \rightarrow 4d \rightarrow 5d$
 $(3d > 4d > 5d)$ transition element series. But due to imperfect screening effect of $4f$ orbitals in $5d$ transition series, the IE of $5d > 3d > 4d$.

vii. K > Rb > Cs [IE of group 1 decreases down the group (\downarrow)]

viii. $\text{C} > \text{Be} > \text{B}$

Group \Rightarrow 14 2 13

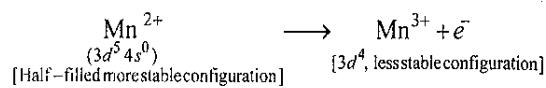
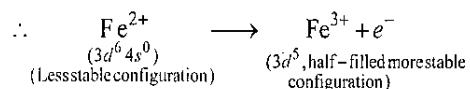
[Generally IE increases along the period, i.e. from group 2 < group 13 < group 14. But there is exception in the IE of Be and B due to penetration effect, therefore, IE_1 of Be > IE_1 of B]

ix. Al > Mg > Na

[IE of group 13 > group 2 > group 1]

h. Valence electronic configuration of Fe and Fe^{2+} are $3d^6 4s^2$ and $3d^6 4s^0$ respectively.

Valence electronic configuration of Mn and Mn^{2+} are $3d^5 4s^2$ and $3d^5 4s^0$ respectively.



Fe^{2+} is easily oxidised to Fe^{3+} , since valence electronic configuration changes from less stable $3d^6$ configuration to more stable half-filled $3d^5$ configuration, whereas it is reverse in the case of Mn^{2+} to Mn^{3+} .

i. Same, since the number of protons and electrons are same but neutrons are different in isotopes of same element. Therefore, Z_{eff} and size remains same in the isotopes. Neutrons have no effect on Z_{eff} and size of isotopes.

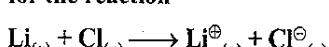
j. i. Increase in size.

ii. Increase in screening effect.

iii. Decrease in Z_{eff} .

Example 1.2 Answer the following questions (Based on EA, $\Delta_{\text{eg}} H^\ominus$ and IE).

a. IE_1 of Li is 5.4 eV atom^{-1} and the EA of Cl is 3.6 eV atom^{-1} . Calculate $\Delta_{\text{eg}} H^\ominus$ in kcal mol $^{-1}$ and kJ mol $^{-1}$ for the reaction



formed at such a low pressure that resulting ions do not combine with each other.

b. The IE of atoms X and Y are 400 and $300 \text{ kcal mol}^{-1}$ respectively. EA's of these atoms are 80.0 and $85.0 \text{ K cal mol}^{-1}$. Explain as which of the atoms has higher EN.

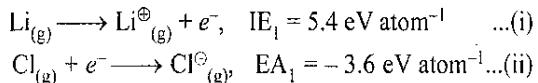
c. Explain why EA of S is -200 kJ mol^{-1} but the second EA is $+649 \text{ kJ mol}^{-1}$?

d. Which of the following pairs of elements would have more negative electron gain enthalpy ($\Delta_{\text{eg}} H^\ominus$)?

i. F or Cl ii. O or F

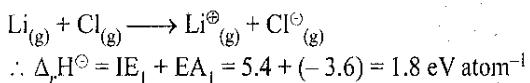
- e. What would be the second electron gain enthalpy ($\Delta_{eg}H_2^\ominus$) of oxygen as positive, more negative or less negative than the first ($\Delta_{eg}H_1^\ominus$)? Explain.
- f. Which has less negative $\Delta_{eg}H^\ominus$ oxygen or sulphur?

Sol. a.



Note: EA₁ is negative.

Adding Eqs. (i) and (ii), we get



We know 1 eV atom⁻¹ = 23.06 kcal mol⁻¹ and 1 eV atom⁻¹ = 96.49 kJ mol⁻¹

$$\therefore \Delta_rH^\ominus (\text{in kJ mol}^{-1}) = 1.8 \times 23.06 \\ = 41.508 \text{ kJ mol}^{-1}$$

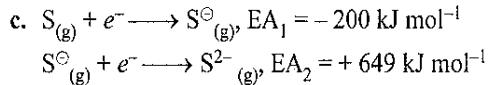
$$\therefore \Delta_rH^\ominus (\text{in kcal mol}^{-1}) = 1.8 \times 96.49 \\ = 173.682 \text{ kcal mol}^{-1}$$

b. EN of $X = \frac{\text{IE} + \text{EA}}{125}$ (when IE and EA values are in kcal mol⁻¹)

$$= \frac{400 + 80}{125} = 3.84$$

$$\text{EN of } Y = \frac{300 + 85}{125} = 3.08$$

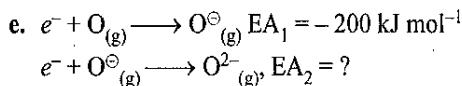
$\therefore \text{EN of } X > \text{EN of } Y$



The addition of the second electron to $\text{S}_{(g)}^\ominus$ experience repulsion from the already present electrons.

- d. i. Cl. When electron is added to F, the added electron goes to smaller $n = 2$ (i.e. $2p$ orbital) quantum level and suffers significant repulsion from the other electrons present in that shell. So, electron is being added with difficulty in F than in Cl. Hence less negative energy is released in F than in Cl. So, $\Delta_{eg}H^\ominus$ of F is less negative than Cl.

- ii. F. $\Delta_{eg}H^\ominus$ of F is more negative than O due to the small size of F than O. Moreover, $\Delta_{eg}H^\ominus$ increases (more negative) along the period (\rightarrow).



EA_2 is positive due to more electron-electron repulsion.

- f. Due to the compact nature of oxygen atom it has less negative $\Delta_{eg}H^\ominus$ (-141 kJ mol^{-1}) than S (-200 kJ mol^{-1}). [Same explanation as in $\Delta_{eg}H^\ominus$ of F and Cl, refer to the above part (d) (i).]

Example 13 Explain the following questions (based on size of atoms or ions and other periodic properties):

- a. Arrange the following species in decreasing order of their sizes/ionic radii.
- $\text{Ar}, \text{K}^\oplus, \text{Cl}^\ominus, \text{S}^{2\ominus}$ and Ca^{2+}
 - $\text{Al}^{3+}, \text{Mg}^{2+}, \text{Na}^\oplus, \text{Cl}^\ominus, \text{N}^{3-}$ and O^{2-}
- b. What are isoelectronic species? Name the species which are isoelectronic with each of the following atoms or ions.
- Rb^\oplus
 - F^\ominus
 - Mg^{2+}
 - Ar
- c. Arrange the following species/atoms in decreasing order of reducing character.
- Na, Mg and Al
 - Mg, Ca and Sr
 - Na, K and Rb
 - $\text{F}^\ominus, \text{Cl}^\ominus, \text{Br}^\ominus$ and I^\ominus
- d. The decreasing order of reactivity of group 1 elements is $\text{Cs} > \text{Rb} > \text{K} > \text{Na} > \text{Li}$ whereas that of group 17 elements is $(\text{Cl} > \text{F} > \text{Br} > \text{I})$. Explain.
- e. Predict the formula of the stable binary compounds that would be formed by the combination of the following pairs of elements:
- Mg and N
 - Si and O
 - Element with $Z = 71$ and F
 - P and F
 - Al and I
 - Li and O
- f. Answer the following by the use of periodic table.
- Identify the element that would tend to gain two electrons.
 - Identify the group having metal, non-metal, liquid as well as gas at the room temperature.
 - Identify the element with five electrons in the outer shell.
 - Identify the element that would tend to lose two electrons.

Sol. a. i. All of them are isoelectronic species, with 18 electrons.

\therefore Size of more negative ion $>$ size of inert gas $>$ size of less positive $>$ size of more positive ion.

$$\therefore \text{S}^{2\ominus} > \text{Cl}^\ominus > \text{Ar} > \text{K}^\oplus > \text{Ca}^{2+}$$

ii. $\text{N}^{3-} > \text{O}^{2-} > \text{F}^\ominus > \text{Na}^\oplus > \text{Mg}^{2+} > \text{Al}^{3+}$

(All of them are isoelectronic species with 10 electrons)

b. Isoelectronic species have same number of electrons.

- Rb^\oplus ($Z = 37$, No. of e^- 's = $37 - 1 = 36$) is isoelectronic with Sr^{2+} ($Z = 38$, No. of e^- 's = $38 - 2 = 36$).

- ii. F^\ominus ($Z = 9$, No. of e^- 's = $9 + 1 = 10$) is isoelectronic with Ne ($Z = 10$).
 - iii. Mg^{2+} ($Z = 12$, No. of e^- 's = $12 - 2 = 10$) is isoelectronic with Na^\oplus ($Z = 11$, No. of e^- 's = $11 - 1 = 10$) and with Ne ($Z = 10$).
 - iv. Ar ($Z = 18$), is isoelectronic with Ca^{2+} ($Z = 20$, No. of e^- 's $20 - 2 = 18$).
 - c. Elements with low IE and large size have more tendency to undergo oxidation and thus acts as stronger reducing agent.
 - i. Na (group 1) > Mg (group 2) > Al (group 13 elements). [IE increases along the period (\rightarrow). All of them belong to the 3rd period].
 - ii. $\text{Sr} > \text{Ca} > \text{Mg}$ [All of them belong to group 2 and IE decreases down the group (\downarrow)].
 - iii. $\text{Rb} > \text{K} > \text{Na}$ [Group 1 elements. IE decreases down the group (\downarrow)].
 - iv. $\text{I}^\ominus > \text{Br}^\ominus > \text{Cl}^\ominus > \text{F}^\ominus$ [Group 17, size increases and IE decreases down the group (\downarrow)].
 - d. The reactivity of group 1 element is the tendency to lose electrons easily, i.e., to undergo oxidation easily. Low IE and large size of group 1 elements, so more reactive is the element. Hence reactivity order of group 1 elements is $\text{Cs} > \text{Rb} > \text{K} > \text{Na} > \text{Li}$ [IE decreases down the group (\downarrow)]
- The reactivity of group 17 element is the tendency to accept electrons easily, i.e. to undergo reduction easily. High is the negative EA or $\Delta_{\text{eg}}H^\ominus$ of group 17 elements so more reactive is that element (or magnitude of EA or $\Delta_{\text{eg}}H^\ominus$ decreases down the group except in case of F and Cl).
- Therefore, reactivity order of group 17 elements is $\text{Cl} > \text{F} > \text{Br} > \text{I}$ ($\Delta_{\text{eg}}H^\ominus = -349 > -333 > -325 > -296 \text{ kJ mol}^{-1}$)
- e. i. Mg^{2+} and N^3- give Mg_3N_2 (Magnesium nitride)
 - ii. Si^{4+} and O^{2-} give $\text{Si}_2\text{O}_4 \Rightarrow \text{SiO}_2$ (Silicon dioxide)
 - iii. Element with $Z = 71$ is lutetium (Lu) and general oxidation states (OS) of lanthanides and actinides is +3.
 - iv. Lu^{3+} and F^\ominus give Lu F_3 (Lutetium trifluoride)
 - v. P^{5+} and F^\ominus give PF_5 (Phosphorous pentafluoride)
 - vi. Al^{3+} and I^\ominus give AlI_3 (Aluminium triiodide)
 - f. i. Only oxygen atom in group 16 has OS of -2 (except in case of peroxides and OF_2).

The other element of group 16 (e.g. S, Se, Te, Po), besides -2 OS, they also show +2, +4 and +6 OS.

So, oxygen tends to gain two electrons to attain noble gas stable configuration.

- ii. Group 17 elements Metal is At (Astatine), non-metal is Cl (Chlorine), liquid is Br_2 (Bromine) and gas is F_2 and Cl_2 .
- iii. Group 15 elements. The valence electronic configuration of N is $2s^22p^3$.
- iv. Group 2 elements, e.g. $\text{Mg} \rightarrow \text{Mg}^{2+}(g) + 2e^-$

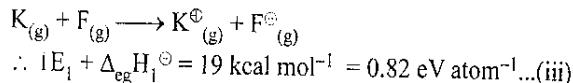
Example 1.14 For the gaseous reaction



$\Delta H = 19 \text{ kcal mol}^{-1}$ under the conditions when cations and anions are prevented by electrostatic separation from combining with each other. The $1E_1$ of K is 4.3 eV. Calculate $\Delta_{\text{eg}}H^\ominus$ of F.

$$\begin{aligned} \text{Sol. } \text{K}_{(g)} &\longrightarrow \text{K}_{(g)}^\oplus + e^- & 1E_1 = 4.3 \text{ eV atom}^{-1} & \dots(i) \\ e^- + \text{F}_{(g)} &\longrightarrow \text{F}_{(g)}^\ominus & \text{Let } \Delta_{\text{eg}}H_1^\ominus = y \text{ eV atom}^{-1} & \dots(ii) \end{aligned}$$

Adding Eqs. (i) and (ii), we get



Note: Use direct relation: $1 \text{ eV} = 23.06 \text{ kcal mol}^{-1}$

$$\therefore 19 \text{ kcal mol}^{-1} = \frac{19.0}{23.06} = 0.82 \text{ eV atom}^{-1}$$

Alternatively:

Convert 19 kcal mol⁻¹ in eV atom⁻¹ as follows:

$$(1 \text{ eV} = 1.6 \times 10^{-10} \text{ J})$$

$$\begin{aligned} 19 \text{ kcal mol}^{-1} &= 19 \times 10^3 \text{ cal mol}^{-1} \\ &= 19 \times 10^3 \times 4.18 \text{ J mol}^{-1} \\ &= \frac{19 \times 10^3 \times 4.18}{1.6 \times 10^{-10}} \text{ eV mol}^{-1} \end{aligned}$$

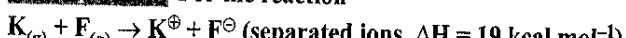
$$\begin{aligned} &= \frac{19 \times 10^3 \times 4.18}{1.6 \times 10^{-10}} \times \frac{1}{6.023 \times 10^{23}} \text{ eV atom}^{-1} \\ &= 0.82 \text{ eV atom}^{-1} \end{aligned}$$

Substituting the value of $1E_1$ in Eq. (iii), we get

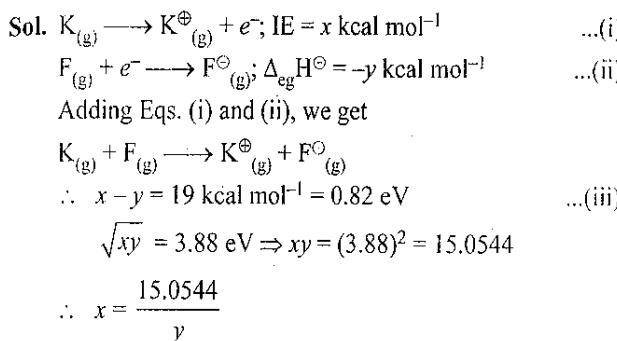
$$4.3 \text{ eV atom}^{-1} + \Delta_{\text{eg}}H_1^\ominus = 0.82 \text{ eV atom}^{-1}$$

$$\therefore \Delta_{\text{eg}}H_1^\ominus = (0.82 - 4.3) = -3.48 \text{ eV atom}^{-1}$$

Example 1.15 For the reaction



If the $1E_1$ of K and $\Delta_{\text{eg}}H_1^\ominus$ of F[⊖] have a geometric mean of 3.88 eV and $1E_1 > \Delta_{\text{eg}}H_1^\ominus$. Calculate the value of $1E_1$ and $\Delta_{\text{eg}}H_1^\ominus$. Given: $19 \text{ kcal mol}^{-1} = 0.82 \text{ eV atom}^{-1}$ (as in Example 1.14 above)



Substituting the value of x in Eq. (iii), we get

$$\frac{15.0544}{y} - y = 19$$

Solving, we get

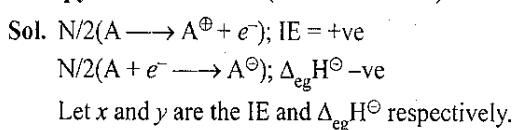
$$y = 3.48 \text{ eV}$$

$$x + y = 7.48 \text{ eV}; \quad x - y = 0.82 \text{ eV}$$

$$\therefore IE = x = 4.313 \text{ eV}$$

$$\Delta_{eg}H^{\ominus} = -y = -3.48 \text{ eV}$$

Example 1.16 From N atoms of an element A, when half the atoms transfer one electron to the another atom, 405 kJ mol^{-1} of energy was found to be consumed. An additional energy of 745 kJ mol^{-1} was further required to convert all the A^{\ominus} ions to A^{\oplus} . Calculate the ionisation energy and the electron gain enthalpy of atom A in eV ($1 \text{ eV} = 96.48 \text{ kJ}$).



$$\therefore \frac{1}{2}(x - y) = 405 \text{ kJ}$$

$$\frac{1}{2}(x + y) = 745 \text{ kJ}$$

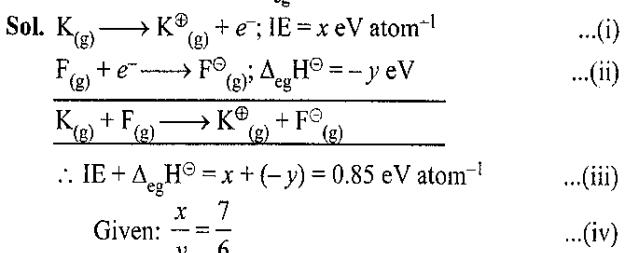
$$\text{On solving } x = 1150 \text{ and } y = 340 \text{ kJ}$$

$$\text{or } 1150 \text{ kJ} = 11.91 \text{ eV}$$

$$\text{Similarly, } 340 \text{ kJ} = 3.52 \text{ eV}$$

$$IE = 11.9 \text{ eV} \text{ and } \Delta_{eg}H^{\ominus} = -3.5 \text{ eV}$$

Example 1.17 The conversion of gaseous atoms K and F to K^{\oplus} and F^{\ominus} absorbs 0.85 eV of energy. If the IE and $\Delta_{eg}H^{\ominus}$ of K and F have magnitudes in the ratio of $7 : 6$, what is the electron gain enthalpy ($\Delta_{eg}H^{\ominus}$) of fluorine?



From Eqs. (iii) and (iv), solve for x and y ,

$$y = 5.10 \text{ eV atom}^{-1}$$

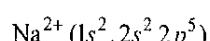
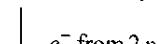
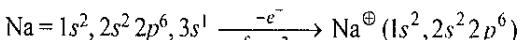
$$\therefore \Delta_{eg}H^{\ominus} = -y = -5.10 \text{ eV atom}^{-1}$$

Example 1.18 Explain the following:

- Which of the elements Na, Mg, Si and P would have the greatest difference between the IE_1 and IE_2 ? Explain?
- The EN's of B, Al and Ga are 2.0, 1.5 and 1.6 respectively. The trend is not regular. Explain?
- Li_2CO_3 decomposes on heating but other alkali metal carbonate (e.g. Na_2CO_3) does not. Explain?
- Explain why Cu^{\oplus} is found only in solid state and not in solutions.
- Be of N have extremely low value of EA (i.e. less negative value) against the trend. Explain?
- Arrange the following in decreasing order of their properties indicated:
 - i. Ionic mobility in H_2O
 - ii. Size of ions
 - iii. Standard reduction potential ($E^{\ominus}_{M^{x+}(aq) / M_s}$)
 - iv. Extent of hydration
 - v. Hydration energy
 - vi. Size of hydrated ions
- In iodometry, why KI is not added dropwise to an acidified solution of $KMnO_4$ but reverse is done?
- Why the decrease in size between Li and Be is much greater than that between Na and Mg or K and Ca?
- K_2CO_3 is less soluble than Cs_2CO_3 or Rb_2CO_3 while among group 2 elements $MgCO_3$ is more soluble than $BaCO_3$.
- Explain the decreasing order of solubility of sulphate of group 2 element.
- 'EA of Cl is the highest among the halogens, yet F is the strongest oxidising agent'. Why?

Sol. a. Elements having stable noble gas configuration after removal of one electron will have the maximum difference between IE_1 and IE_2 so the element is Na.

Electronic configuration of Na, Na^{\oplus} and Na^{2+} ion

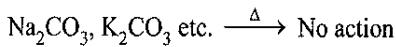
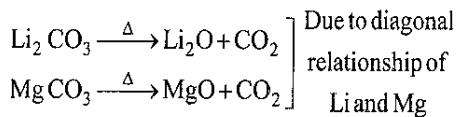


A jump in IE is noticed only when the valence shell changes during the successive removal of electrons.

- B, Al and Ga belong to group 13, and down the group (\downarrow), EN decreases. But after Al, due to the imperfect (minimum) shielding effect of d electrons, the nuclear charge increases and hence EN also increases.

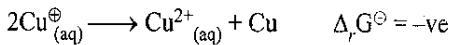
| Group 13 | EN |
|----------|-----|
| B | 2.0 |
| Al | 1.5 |
| Ga | 1.6 |
| In | 1.7 |
| Tl | 1.8 |

- c. Comparable sizes of the ions form the strongest lattice, so crystal lattice of Li_2CO_3 is not so strong due to small size of Li^{\oplus} and larger size of CO_3^{2-} . So Li_2CO_3 decomposes on heating. But other alkali metal carbonates (e.g. Na_2CO_3), have strong crystal lattice, due to comparable size of cation (e.g. Na^{\oplus} ion and CO_3^{2-} ion). So they are stable to heat.



Note: The crystal lattice of Li_2O is stronger due to comparable sizes of Li^{\oplus} and O^{2-} ions.

- d. In solution Cu^{\oplus} disproportionate to Cu^{2+} and Cu, but in solid state it does not. So, Cu^{\oplus} ion is found only in solid state.



- e. Valence electronic configuration of Be and N:

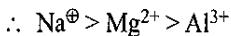


In Be, the incoming electron has to be added in $2p$ orbitals because $2s$ orbital is completely filled and in N, it is to be added to half-filled $2p$ orbitals. Since half-filled and full-filled orbitals are more stable, therefore incoming electron will be added with difficulty. Hence Be and N have low value of EA (i.e. less negative value).

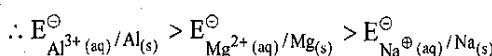
- f. i. Hydration energy or extent of hydration increases along the period (\rightarrow). Greater the extent of hydrations, lesser is the ionic mobility in aqueous solution:



- ii. The greater the positive charge, the lesser is the size,



- iii. The greater the positive charge, the higher is the reduction potential value.



- iv. Extent of hydration increases along the period due to increase in charge density $\left(\frac{\text{charge}}{\text{size}} \right)$



- v. Same explanation as in part (iv) above

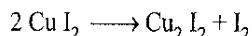
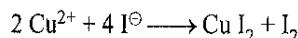
The greater the extent of hydration the more (negative) energy is released



- vi. The greater the extent of hydration, the larger is the size of that ion (reverse of the size of ions).

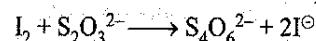


- g. **Iodometry:** The estimation of oxidising substance involving the liberation of I_2 and subsequent volumetric estimation of I_2 is called iodometry, e.g.



If KI is added dropwise to acidic KMnO_4 solution, then MnO_4^{\ominus} will oxidise I^{\ominus} to IO_3^{\ominus} and IO_4^{\ominus} instead of I_2 .

Note: Iodometry is the estimation of reducing substance by use of standard I_2 , e.g.



- h. From Li ($2s^1$) to Be ($2s^2$), the additional electron is added to the $2s$ orbital or (L shell) which is quite closer to nucleus whose charge is also increased by 1 unit. So, greater force is experienced by the electron and size decreases.

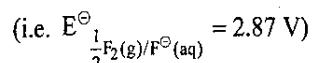
From Na ($3s^1$) to Mg ($3s^2$) and K ($4s^1$) to Ca ($4s^2$), the electrons are added in $3s$ and $4s$ orbitals (or M and N shell) respectively, which are away from nucleus. So, lesser force of attraction is experienced by the electrons and decrease in size is less than that of decrease in size between Li and Be. Moreover, screening effect also contributes in the small decreases in the sizes of Na and K and K and Ca.

- i. K_2CO_3 is less soluble than Cs_2CO_3 or Rb_2CO_3 because IE factor out weighs hydration energy factor (K has high IE and high hydration energy and Cs and Rb have low IE and low hydration energy).

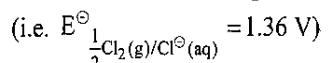
But it is reverse for group 2 element carbonates (refer to Section 1.28.1, Point 10(c)).

- j. For explanation, refer to Section 1.28.1, Point 10(c).

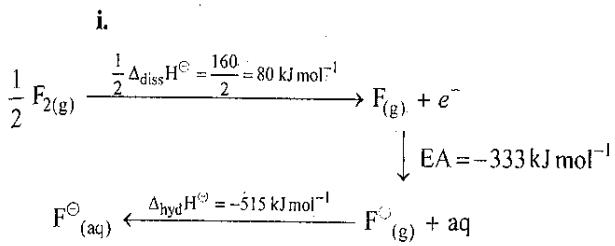
- k. EA of Cl is more negative (-349 kJ mol^{-1}) than that of F (-333 kJ mol^{-1}). But the reduction potential value or oxidising ability of F_2



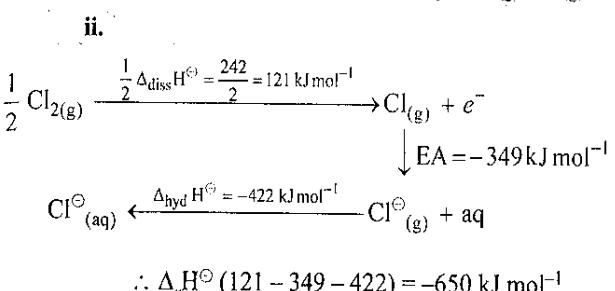
is greater than that of Cl₂



as shown by Born–Haber cycle.



Note: $\Delta_{\text{diss}} \text{H}^\ominus$ of $\text{Cl}_{2(\text{g})} > \text{Br}_{2(\text{g})} > \text{F}_{2(\text{g})} > \text{I}_{2(\text{g})}$



F has low $\Delta_{\text{diss}} \text{H}^\ominus$, high (negative) $\Delta_{\text{hyd}} \text{H}^\ominus$ and less negative EA than that of Cl. Thus overall position is that F has the largest negative $\Delta_r \text{H}^\ominus$ value (i.e. -768 kJ mol^{-1}) than that of Cl (i.e. -650 kJ mol^{-1}).

So, reaction $\left(\frac{1}{2} \text{F}_{2(\text{g})} \text{ to } \text{F}_{(\text{aq})}^\ominus \right)$ is more feasible than that of $\left(\frac{1}{2} \text{Cl}_{2(\text{g})} \text{ to } \text{Cl}_{(\text{aq})}^\ominus \right)$. Therefore, the more is the negative $\Delta_r \text{H}^\ominus$ value of a reaction the more positive will be its reduction potential value. Hence, F is the strongest oxidising agent among halogens.

Example 1.19 Classify the following oxides as

- | | | | |
|---------------------------|--------------------|-----------------------------|------------------------------|
| a. Strongly acidic | b. Weakly acidic | | |
| c. Neutral | d. Amphoteric | | |
| e. Weakly basic and | f. Strongly basic | | |
| i. SnO_2 | ii. SnO | iii. CO | iv. PbO |
| v. MnO_2 | vi. RaO | vii. N_2O | viii. FeO |
| ix. Ag_2O | x. OsO_4 | xi. Al_2O_3 | xii. Fe_2O_3 |
| xiii. CeO_2 | xiv. CO_2 | xv. MgO | xvi. K_2O |

Sol:

| Strongly acidic | Weakly acidic | Neutral | Amphoteric | Weakly basic | Strongly basic |
|-----------------|--------------------|-------------------|---|--|--|
| None | (x) OsO_4 | (iii) CO | (i) SnO_2 (ii) SnO (xi) Al_2O_3 | (iv) PbO (viii) FeO (xii) Fe_2O_3 (xv) Moderately strongly basic MgO | (vi) RaO (ix) Ag_2O (xiii) CeO_2 (xvi) K_2O |

Example 1.20 Select the strongest and weakest acid in each of the following sets:

- $\text{HBr}, \text{HF}, \text{H}_2\text{Te}, \text{H}_2\text{Se}, \text{PH}_3, \text{H}_2\text{O}$
- $\text{HClO}, \text{HIO}, \text{H}_3\text{PO}_3, \text{H}_2\text{SO}_3, \text{H}_2\text{AsO}_3$

- Sol.** a. HBr, a strong acid, is the strongest in the given set. PH_3 , which has weakly basic properties, is least acidic.
b. H_2SO_3 , which is farthest to the right in the periodic table and has the most oxygen atoms, is the most acidic.
HClO, with the fewest oxygen atoms and the farthest up in the periodic table, is the weakest.

Example 1.21 A 0.10 M aqueous solution of which salt in each of the following pairs would have the higher pH?

- NaNO_2 or NaAsO_2
- NaF or NaCN
- Na_2SO_3 or Na_2TeO_3
- NaOCl or NaOBr

Sol. The stronger the acid, the weaker is its conjugate base. The oxyacids are stronger towards the top of the periodic table.

- HNO_2 is a stronger acid; hence, NO_2^\ominus is a weaker base. Therefore, AsO_2^\ominus has a higher pH (Note: Higher pH means more basic, and lower pH means more acidic).
- HF is a stronger acid; hence, F^\ominus is a weaker base. Therefore, CN^\ominus has a higher pH.
- H_2SO_3 is a stronger acid; SO_3^{2-} is a weaker base; TeO_3^{2-} has a higher pH.
- HOCl is a stronger acid; OCl^\ominus is a weaker base; OBr^\ominus has a higher pH.

Example 1.22 Identify:

- The good oxidising agent(s)
- The good reducing agent
- The good dehydrating agent(s) among the following substances:

$\text{H}_2\text{SO}_3, \text{HNO}_3, \text{P}_4\text{O}_{10}, \text{H}_3\text{PO}_4, \text{H}_2\text{S}, \text{H}_2\text{SO}_4$.

- Sol.** a. Good oxidising agents: HNO_3 and H_2SO_4 (Conc.)
b. Good reducing agent: H_2S
c. Good dehydrating agents: H_2SO_4 and P_4O_{10}

Example 1.23 Answer the following:

- Which of the following has the greatest affinity for water: $\text{P}_4\text{O}_{10}, \text{Cl}_2\text{O}, \text{I}_2\text{O}_5$.
- Which of the following is the most basic: $\text{Al}_2\text{O}_3, \text{Ti}_2\text{O}_3, \text{Ti}_2\text{O}$.
- Which of the following has the lowest melting point: $\text{LiBr}, \text{BeBr}_2, \text{BBr}_3$.

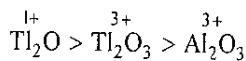
- d. Which of the following has highest EN: Li, Be, Mg.
e. Which of the following is most stable towards oxidation: GeCl_2 , SnCl_2 , PbCl_2 .
f. Which of the following is the strongest oxidising agent: CrO_4^{2-} , MoO_4^{2-} , WO_4^{2-} .

Sol. a. P_4O_{10} . It is more powerful as a dehydrating agent than Cl_2O_7 since the latter is the product of dehydration of HClO_4 by P_4O_{10} . Reverse reaction does not proceed so well.

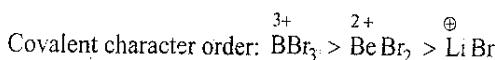
Since I_2O_5 can be prepared by heating HIO_3 , it cannot have too great an affinity for water. In fact, P_4O_{10} is one of the most powerful dehydrating agents known.

- b. Apply Fajans' rule, more ionic a compound more basic is it (large cation and less charge). So, Ti_2O is more basic.

Therefore, basic or ionic order is



- c. Apply Fajans' rule, more covalent a compound, lesser is the melting point (small cation and high charge). So, BBr_3 is having the lowest melting point.



- d. EN increases along the period, i.e. from Li to Be (2nd period) but decreases down the group. So, Be is the most EN element. Order of EN: Be (1.5) > Mg (1.2) > Li (1.0)
- e. PbCl_2 . The inert pair effect of the 6th period element is more stable than those of the 5th period elements and far more stable than the analogous pair in the 4th period.

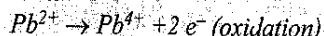
Alternatively:

Down the group; inert pair effect is more stable.

| Group 14 | Stable OS |
|----------|-------------|
| C | + 4 |
| Si | + 4 |
| Ge | (+ 4) (+ 2) |
| Sn | (+ 4) (+ 2) |
| Pb | - (+ 2) |

Note: OS in circle is more stable.

So, Pb^{2+} is difficult to oxidise to Pb^{4+} ion



∴ Therefore, order of stability towards oxidation:



- f. CrO_4^{2-} . The higher oxidation states of the 2nd and 3rd transition series elements are more stable.

Order of oxidising agent: $\text{CrO}_4^{2-} > \text{MoO}_4^{2-} > \text{WO}_4^{2-}$
Transition element series 1 2 3

Example 1.21 Explain the following:

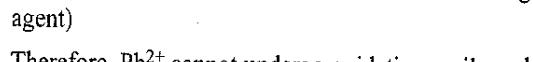
- The formation of Cs_2O from its element is less exothermic than the formation of ZnO from its element.
- On the basis of appropriate Born–Haber cycle, state what factor(s) is (are) responsible for the fact that lithium nitride (Li_3N) is more stable while potassium nitride (K_3N) is unstable.
- Why Al^{3+} is the only stable oxidation state of Al in its compounds while Tl has +1 and +3 oxidation states?
- Pb^{4+} is a powerful oxidising agent. What is the reducing ability of Pb^{2+} ?
- Which is more soluble in water LiI or KI ?

- Sol. a. The lattice energy of ZnO must be greater since it is the major contribution to the exothermic nature of each reaction.
- b. The lattice energy of Li_3N is higher than that of K_3N , due to the large difference in ionic size between Li^+ and K^+ ions.

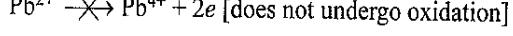
Note: Comparable size of the ions forms the strongest lattice, so sizes of Li^+ and N^{3-} are comparable.

The difference in IE, sublimation energy and other factors of the Born–Haber cycle are relatively small between the two compounds.

- Tl has an inert pair of electrons ($6s^2$); Al has no corresponding inert pair.
- Due to the inert pair effect Pb^{2+} is more stable than Pb^{4+} . Therefore, Pb^{4+} can undergo reduction easily and acts as powerful oxidising agent.



Therefore, Pb^{2+} cannot undergo oxidation easily and hence acts as a relatively poor reducing agent.



- LiI . According to Fajans' rule, LiI is less ionic than KI and therefore KI should be more soluble in H_2O than LiI .

But the lattice energy of LiI (small cation and large anion) is less than that of KI , due to comparable sizes of K^+ and I^- ions. Thus the energy required to break up the lattice of LiI is lower and is easily provided by hydration energy. So, LiI is more soluble in H_2O than KI .

Example 1.25 Give the name and atomic number of the inert gas atom in which the total number of *d*-electrons is equal to the difference in number to the total *p*- and *s*-electrons.

Sol. The first inert gas which contains *d*-electron is in 4th period (or from 3*d* transition element series), i.e. Kr ($Z = 36$).

Electronic configuration of Kr:

$$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^2 4p^6.$$

Total number of *d*-electrons = 10

Total number of *p*-electrons = $6 + 6 + 6 = 18$

Total number of *s*-electrons = $2 + 2 + 2 + 2 = 8$

Difference in total number of *p*- and *s*-electrons = $(18 - 8) = 10$

Thus, the inert gas is Kr (krypton).

Example 1.26 Classify the elements having atomic numbers (9, 12, 16, 34, 53, 56) into three separate pairs on the basis of similar chemical properties.

Sol. 2nd period ends with $Z = 10$

3rd period ends with $Z = 10 + 8 = 18$

4th period ends with $Z = 18 + 18 = 36$

5th period ends with $Z = 36 + 18 = 54$

Note: Magic numbers are 8, 18, 18 and 32.

- $Z = 9$ ($10 - 1$) (group 18 – 1) = group 17, 2nd period, element is F.
- $Z = 12$ ($10 + 2$) (group 2), 3rd period, element is Mg.
- $Z = 16$ ($18 - 2$) (group 18 – 2) = group 16, 3rd period, element is S.
- $Z = 34$ ($36 - 2$) (group 18 – 2) = group 16, 4th period, element is Se.
- $Z = 53$ ($54 - 1$) (group 18 – 1) = group 17, 5th period, element is I.
- $Z = 56$ ($54 + 2$) (group 2), 5th period and element is Ba.
 - Therefore, elements with atomic number 9 (F) and 53 (I) belong to group 17, i.e. halogens.
 - Elements with atomic number 12 (Mg) and 56 (Ba) belong to group 2, i.e. alkaline earth metals.
 - Elements with atomic number 16(S) and 34 (Se) belongs to group 16, i.e. oxygen family.

Example 1.27 Calculate the electronegativity of fluorine from the following data:

$$E_{H-H} = 104.2 \text{ kcal mol}^{-1}, E_{F-F} = 36.6 \text{ kcal mol}^{-1}$$

$$E_{H-F} = 134.3 \text{ kcal mol}^{-1}, \chi_H = 2.1$$

Sol. Let the electronegativity of fluorine be χ_F .

Applying Pauling's equation

$$\chi_F - \chi_H = 0.208 [E_{H-F} - (E_{F-F} \times E_{H-H})^{1/2}]^{1/2}$$

In this equation, dissociation energies are taken in kcal mol^{-1}

$$\chi_F - 2.1 = 0.208 [134.3 - (36.6 \times 104.2)^{1/2}]^{1/2}$$

$$\chi_F = 3.87$$

Example 1.28 Calculate the electronegativity of carbon from the following data:

$$E_{H-H} = 104.2 \text{ kcal mol}^{-1}, E_{C-C} = 83.1 \text{ kcal mol}^{-1}$$

$$E_{C-H} = 98.8 \text{ kcal mol}^{-1}, \chi_H = 2.1$$

Sol. Let the electronegativity of carbon be χ_C .

Applying Pauling's equation.

$$\chi_C - \chi_H = 0.208 [E_{C-H} - (E_{C-C} \times E_{H-H})^{1/2}]^{1/2}$$

$$\chi_C - 2.1 = 0.208 [98.8 - (83.1 \times 104.2)^{1/2}]^{1/2}$$

$$\chi_C = 2.59$$

Example 1.29 Ionisation potential and electron affinity of fluorine are 17.42 and 3.45 eV respectively. Calculate the electronegativity of fluorine.

Sol. According to Mulliken's equation

$$\chi = \frac{IP + EA}{5.6} \quad \text{when both IP and EA are taken in eV}$$

$$\chi_F = \frac{17.42 + 3.45}{5.6} = 3.726$$

Example 1.30 Calculate the EN of silicon using Allred–Rochow method. Covalent radius of silicon is 1.75 Å.

Sol. Allred–Rochow equation is

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

(Z_{eff} is calculated on the basis of Slater's rules taking all the electrons.)

Electronic configuration of Si ($Z = 14$) is

$$1s^2, 2s^2 2p^6, 3s^2 3p^2$$

$$Z_{\text{eff}} = 14 - (0.35 \times 4 + 0.85 \times 8 + 2 \times 1) = 3.80$$

$$\chi = 0.359 \times \frac{3.80}{(1.175)^2} + 0.744 = 1.73$$

Example 1.31 Calculate the electronegativity value of chlorine on Mulliken's scale, given that IP = 13.0 eV and EA = 4.0 eV.

$$\text{Sol. } \chi_{Cl} = \frac{(IP)_{Cl} + (EA)_{Cl}}{5.6} = \frac{13 + 4}{5.6} = 3.03$$

Example 1.32 Find the electronegativity of lead with the help of the given values. Screening constant (σ) of Pb = 76.70, atomic number of lead = 82 and covalent radius of Pb = 5.3 Å

Sol. Substituting the value of σ , Z and r in Allred–Rochow's scale

$$Z_{\text{eff}} = Z - \sigma = 82 - 76.70 = 5.3.$$

$$\chi_{Pb} = 0.359 \times \frac{Z_{\text{eff}}}{r^2} + 0.744$$

$$= 0.359 \times \frac{5.3}{(5.3)^2} + 0.744 \\ = 1.55$$

Example 1.33 The ionisation potentials of atoms A and B are 400 and 300 kcal mol⁻¹ respectively. The electron gain enthalpy of these atoms are 80.0 and 85.0 kcal mol⁻¹ respectively. Which of the atoms has higher electronegativity.

Sol. Substituting the value of IP, EA (or $\Delta_{eg} H^\ominus$) in Eq. (ii) of Mulliken's scale, we get

$$\chi_A = \frac{400 + 80}{2 \times 62.5} = 3.84$$

$$\chi_B = \frac{300 + 85}{2 \times 62.5} = 3.08$$

Hence atom A has higher EN.

Example 1.34 Give the names of seven *f*-orbitals and how they are represented.

Sol. A complete set of seven *f*-orbitals is shown in the table and the figure given here.

As with *d*-orbitals, there is no unique way of representing them, nor is there even a way which is optimum for all problems.

The figure presents two sets, a 'General set' and a 'cubic set'. The latter is advantageous in considering the properties of the orbitals in cubic (i.e. octahedral and tetrahedral fields).

Table: Names and shapes of *f*-orbitals

| The general set | The cubic set |
|----------------------------|---|
| 1. xz^2 | 5. z^3 or x^3 or y^3 . |
| 2. $x(x^2 - 3y^2)$ | i. x^3 same as z^3 except lies along the <i>x</i> -axis. |
| 3. $y(3y^2 - x^2)$ | ii. y^3 same as z^3 except lies along the <i>y</i> -axis. |
| | Same as $x(x^2 - 3y^2)$ except lies along the <i>y</i> -axis. |
| 4. $z(x^2 - y^2)$ or xyz | 6. xyz |
| | Same as the corresponding orbitals in the cubic set |
| | 7. $z(x^2 - y^2)$ |
| | or $y = (z^2 - x^2)$ $z = (x^2 - y^2)$ |
| | Same as xyz but rotated 45° about the <i>x</i> , <i>y</i> , <i>z</i> axes |

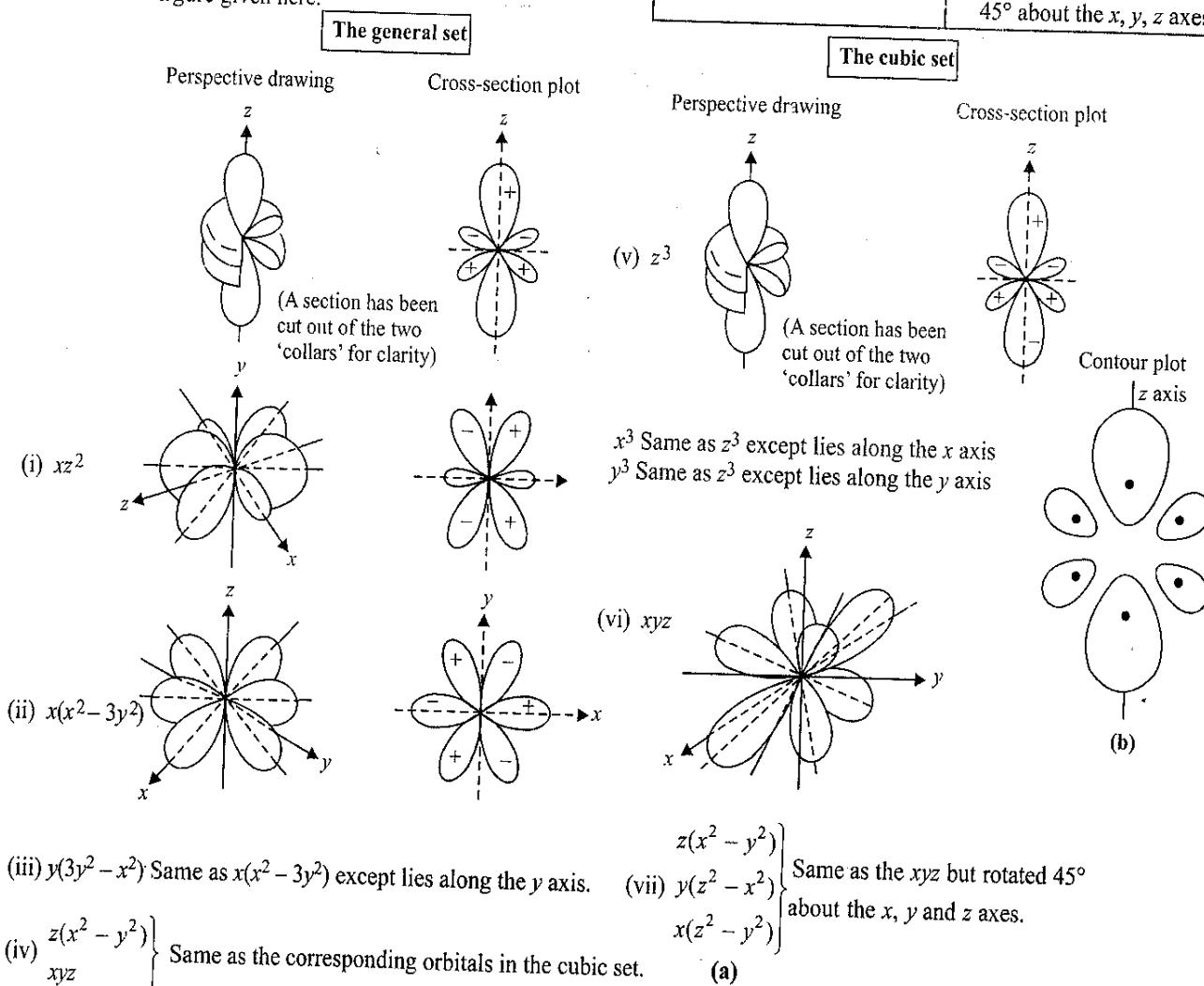


Figure: The *f*-orbitals: (a) Plots of the angular part of the wave functions of the *f* orbital; (b) contours of a 4*f* orbital. Dots indicate maxima in electron density. The lines are drawn for densities which are 10% of maximum.

EXERCISES

Linked Comprehension Type
Solutions on page 1.150

This section contains five paragraphs. Based on each paragraph four to six single choice questions have to be answered. Each question has four options (a), (b), (c) and (d), out of which one or more may be correct.

Paragraph 1

Effective nuclear charge (Z_{eff}) is the net attractive force on electrons under consideration and is equal to:

$Z_{\text{eff}} = Z - \sigma$ (nuclear charge – screening constant). Z_{eff} or σ is calculated by Slater's formula, as given.

If one electron is present in the outermost orbit, there will be no screening in that orbital. Each electron contributes 0.35 (total electrons minus one electron) present in the outermost shell.

A contribution of 0.85 for each electron is taken in the $(n-1)$ th shell.

1. The screening constant (σ) for $4s$ electron of Mn ($Z=25$) will be

a. 18.00 b. 4.25 c. 18.35 d. 22.6

2. Which of the following statement is wrong?

- a. IE_1 of Ga > Al, due to imperfect shielding of $3d$ -orbitals in Ga.
- b. IE_1 of Ga < Al, due to perfect shielding of $3d$ -orbitals in Ga.
- c. The atomic size of Ga and Al are almost same because of poor shielding effect of electrons in d -orbitals as the effective nuclear charge increases in Ga.
- d. IE_1 of group 16 elements is less than that of group 15 elements.

3. Which of the following statement is wrong?

- a. The number of lobes in f -orbitals are 8.
- b. IE_1 of elements increases along the period.
- c. IE_1 of the group 3 elements is more than that of the group 2 elements.
- d. IE_1 , IE_2 and IE_3 of an element are 9.5, 18.5 and 154.4 eV. Predict that the element has either two s -electrons or two p -electrons in the valence shell.

Paragraph 2

In the long or modern form of the periodic table, the elements in the periodic table have been divided into four blocks, s -, p -, d -, and f . Each period begins with the filling of new energy shell. Two series of f -block elements are placed at the bottom of the periodic table.

4. The element with $Z=39$ belongs to

| | |
|---------------|---------------|
| a. s -block | b. p -block |
| c. d -block | d. f -block |

5. The element with $Z=113$ has been discovered. Its block, group number, period and outermost shell electronic configuration are

- a. s -block, group 2, period 7, $7s^2$
- b. p -block, group 13, period 7, $7s^2 7p^1$
- c. p -block, group 13, period 6, $6s^2 6p^1$
- d. d -block, group 12, period 6, $5d^{10}, 6s^2$

6. Which of the element whose atomic numbers are given below cannot be accommodated in the present set-up of the modern periodic table?

a. 109 b. 118 c. 120 d. 125

7. What is the maximum number of electrons that can be accommodated with $n=5$ (n = principal quantum number)?

a. 10 b. 18 c. 36 d. 54

8. Which of the following ions is most stable?

a. Li^\ominus b. Be^\ominus c. B^\ominus d. C^\ominus

9. The last element of the p -block in the present periodic table is represented by the configuration, where [X] represents inert gas is

- a. $[\text{X}] 7s^2 7p^6$
- b. $[\text{X}] 5f^{14}, 6d^{10}, 7s^2 7p^5$
- c. $[\text{X}] 4f^{14}, 5d^{10}, 6s^2 6p^6$
- d. [X] None of the above

10. If the elements were discovered in future in which the electrons would be present in g -orbitals. Then g -orbital starts and ends up with what atomic number?

a. 121, 139 b. 121, 138
c. 122, 140 d. 122, 139

Paragraph 3

The energy required to remove an electron from the outermost shell of an isolated gaseous atom is known as IE_1 of that atom. Similarly, the energy required for the removal of the electron from the unipositive ion, dipositive ion and tripositive ion are known as IE_2 , IE_3 and IE_4 , respectively, and are called successive ionisation energies. The magnitude of the charge depends on the size of the orbital of electron. Electrons in smaller orbitals are on average close with each other and have more repulsion. Thus for Be ($2s^2$), the IE_1 and IE_2 are 9.3 and 18.2 eV atom $^{-1}$, whereas for Ca ($4s^2$), the values are 6.1 and 11.9 eV.

11. The correct order of arrangement of the first ionisation energies of C, N, O and F (in decreasing values) is

| | |
|------------------|------------------|
| a. C > N > O > F | b. O > N > F > C |
| c. O > F > N > C | d. F > N > O > C |

12. Four elements have the following first ionization energies in kJ mol^{-1} : 762, 709, 59 and 558. The elements are Ga,

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- Ge, In and Sn (not in order). Which of these elements has the ionisation energy of 762 kJ mol^{-1} ?
- In
 - Ga
 - Sn
 - Ge
13. Which of the following are isoelectronic species?
 I $\rightarrow \text{CH}_3^+$, II $\rightarrow \text{NH}_2^+$, III $\rightarrow \text{NH}_4^+$, IV $\rightarrow \text{NH}_3^-$
- I, II and III
 - II, III and IV
 - I, II and IV
 - II and I
14. Among the following ionisation reactions, which one will have the maximum value of ionisation energy?
- $\text{Be} \rightarrow \text{Be}^\oplus$
 - $\text{Be}^\oplus \rightarrow \text{Be}^{2+}$
 - $\text{Sr} \rightarrow \text{Sr}^\oplus$
 - $\text{Sr}^\oplus \rightarrow \text{Sr}^{2+}$
15. Consider the IE_1 of the elements whose electronic configurations correspond to the following:
- $[\text{He}] 2s^2 2p^3$
 - $[\text{He}] 2s^2 2p^4$
 - $[\text{Ne}] 3s^2 3p^1$
 - $[\text{Ar}] 3d^{10} 3s^2 3p^1$
- Which of the above have almost same IE_1 ?
- i and ii
 - i and iii
 - iii and iv
 - ii and iv
16. The relationship between IE_4 and IE_2 of an element is
- $\text{IE}_4 > \text{IE}_2$
 - $\text{IE}_4 < \text{IE}_2$
 - $\text{IE}_4 = \text{IE}_2$
 - None of the above
- Paragraph 4**
- Energy is released when an electron is added to neutral isolated gaseous atom in its ground state to give monoanion and this is known as EA, or $\Delta_{\text{eg}}\text{H}_1^\ominus$. The greater the amount of energy released the greater is the EA. EA is expressed in eV atom $^{-1}$ or kcal or kJ mol $^{-1}$.
17. The EA values of elements depends on the following:
- Nuclear charge
 - Electronic configuration
 - Atomic size
 - Chemical environment
- i, iii, iv
 - i, ii, iii
 - ii, iii, iv
 - All
18. EA values of N and P are exceptionally low, because
- Both N and P have half-filled p -orbitals in the valence shell.
 - The atom is more stable than the corresponding anion.
 - The electronic configuration of the anion N^\ominus and P^\ominus is relatively more stable than the corresponding atom.
 - Both (b) and C.
19. Select the correct statements (**more than one correct**)
- EA and $\Delta_{\text{eg}}\text{H}_1^\ominus$ of an atom of element have same magnitude
 - $\Delta_{\text{eg}}\text{H}_1^\ominus$ of Al $>$ B
 - $\Delta_{\text{eg}}\text{H}_1^\ominus$ of P $>$ N
 - $\Delta_{\text{eg}}\text{H}_1^\ominus$ of S $>$ O
20. Select the correct statements (**more than one correct**)
- $\Delta_{\text{eg}}\text{H}^\ominus$ of noble gases have large positive values.
 - $\Delta_{\text{eg}}\text{H}^\ominus$ of noble gases have large negative values.
 - $\Delta_{\text{eg}}\text{H}^\ominus$ of helium (He) is the lowest of all the noble gases.
 - $\Delta_{\text{eg}}\text{H}^\ominus$ of Ar is lower than that of Ne.
- Paragraph 5**
- Along the period (\rightarrow) atomic/ionic radii and metallic character decreases while IE, EN, non-metallic character and oxidising power increases. Down the group (\downarrow), atomic/ionic radii, metallic character and reducing character increase while IE and EN decrease. However, $\Delta_{\text{eg}}\text{H}^\ominus$ becomes less negative down a group but more negative along a period.
- Which of the following isoelectronic species has lowest IE_1 ?
 - K^\oplus b. Ca^{2+} c. S^{2-} d. Cl^\ominus
 - If the ionic radii of M^\oplus and X^\ominus are about 135 pm, then expected values of metallic radii of M and X should be respectively.
 - 65 and 230 pm b. 230 and 60 pm
c. 230 and 135 pm d. 135 and 135 pm
 - In which of the following pairs, both species have nearly the same size? (**more than one correct**)
 - $\text{Mg}^{2+}, \text{Al}^{3+}$ b. $\text{K}^\oplus, \text{F}^\ominus$
c. $\text{Li}^\oplus, \text{Mg}^{2+}$ d. $\text{Rb}^\oplus, \text{O}^{2-}$
 - Correct order of IE_2 of the following is
 - a. F $>$ O $>$ N $>$ C b. O $>$ N $>$ F $>$ C
c. O $>$ F $>$ N $>$ C d. C $>$ N $>$ O $>$ F.
 - Which of the following are correct statements? (**more than one correct**)
 - IE and EA are defined at absolute zero temperature. At any other temperature, heat capacities for the reactants and products have to be taken into account.
 - The ionisation enthalpy ($\Delta_i\text{H}^\ominus$) and IE are related to each other by the equation:

$$\Delta_i\text{H}^\ominus(\text{ionisation enthalpy}) = [\text{IE} (\text{ionisation energy}) + \frac{5}{2}RT]$$
 - The electron gain enthalpy ($\Delta_{\text{eg}}\text{H}^\ominus$) and EA are related to each other by the equation:

$$\Delta_{\text{eg}}\text{H}^\ominus(\text{electron gain enthalpy}) = [(-\text{EA} (\text{electron affinity}) - \frac{5}{2}RT)]$$
 - The value of C_p (heat capacity at constant pressure and C_v (heat capacity at constant volume) are $\frac{3}{2}R$ and $\frac{5}{2}R$ respectively)

Matching Column Type
Solutions on page 1.152

1. Match the following statements with law and their discoverer.

| | Statement | Law | Discoverer |
|-----|--|----------------------------------|---------------------|
| (a) | Middle element of each of triads had an atomic weight half way between the atomic weights of the other two. | (i) Law of triads | (p) de Chancourtois |
| (b) | Arrangement of known elements in order of increasing atomic weights in a cylindrical table of elements to display the periodic recurrence of properties. | (ii) Telluric screw or Helix law | (q) Dobereiner |
| (c) | Arrangement of the lighter elements in increasing order of their atomic weights and noted that every eighth element had properties similar to the first element. | (iii) Law of octaves | (r) Newlands |

2. Match the following:

| | X | Y |
|----|--------------------|--------------|
| a. | Transition element | p. Thorium |
| b. | Noble gas | q. Cerium |
| c. | Lanthanides | r. Krypton |
| d. | Actinides | s. Potassium |
| e. | Normal element | t. Manganese |

3.

| | X | Y |
|----|--------------------------|-------------|
| a. | <i>s</i> -block elements | p. Selenium |
| b. | <i>p</i> -block elements | q. Chromium |
| c. | <i>d</i> -block elements | r. Francium |
| d. | <i>f</i> -block elements | s. Radon |
| e. | Rare gas | t. Uranium |

4.

| | X | Y | Z |
|----|-----------------------|-------------|----------------|
| a. | Liquid metal | i. Carbon | p. Halogen |
| b. | Graphite | ii. Mercury | q. Lubricant |
| c. | Liquid non-metals | iii. II A | r. Amalgam |
| d. | Alkaline earth metals | iv. Bromine | s. $6s^2 6p^4$ |

| | | | | | |
|----|--------------------|------|--------------------------|----|---------------------------|
| e. | Polonium | v. | <i>d</i> -block elements | t. | ns^2 |
| f. | Noble metal | vi. | Group 16 (or VI A) | u. | Coinage metal |
| g. | Transition element | vii. | Gold | v. | variable oxidation states |

5.

| | Column I | Column II |
|----|-----------------|------------------|
| a. | $Cl > Ar$ | p. Atomic size |
| b. | $S > O$ | q. IE |
| c. | $Mg > Al$ | r. EA |
| d. | $Zn > Cu$ | s. EN |

6.

| | Column I (Ions) | Column II (Magnetic moment in Bohr Magneton) |
|----|------------------------|---|
| a. | Fe^{3+} | p. $\sqrt{24}$ BM |
| b. | Fe^{2+} | q. $\sqrt{8}$ BM |
| c. | Ti^{3+} | r. $\sqrt{35}$ BM |
| d. | Ni^{2+} | s. Zero BM |
| e. | Sc^{3+} | t. $\sqrt{3}$ BM |

7.

| | Column I | Column II |
|----|---|----------------------------------|
| a. | $\chi_{Pauling} = \frac{\chi_{Mulliken}}{y}$ | p. Alfred-Rochow scale |
| b. | $\chi_A = 0.744 + \frac{0.359 Z_{eff}}{r^2}$ | q. Mulliken scale |
| c. | $\chi_A = \frac{(IP)_A + (EA)_A}{540} \text{ kJ mol}^{-1}$ | r. $y = 2.8$ |
| d. | $\chi_A - \chi_B = \frac{1}{(\Delta_{A-B})^2}$ (where Δ_{A-B} is in kJ mol^{-1}) $= E_{A-B} - \sqrt{E_{A-A} \times E_{B-B}}$ | s. Pauling scale t. $y = 1.4$ |

8.

| | Column I | Column II |
|----|----------------------|----------------------|
| a. | Covalent radius | p. Diatomic molecule |
| b. | Crystal radius | q. Halogens |
| c. | Leonard radius | r. Metals |
| d. | van der Waals radius | s. Inert gases |

9.

| | Column I | Column II |
|----|---|----------------------------|
| a. | $\text{Na} > \text{Mg} > \text{Al} > \text{B}$ | p. Oxidising nature |
| b. | $\text{F} > \text{N} > \text{C} > \text{B} > \text{Si}$ | q. Lowest IE ₁ |
| c. | $\text{F} > \text{O} > \text{Cl} > \text{N}$ | r. Metallic character |
| d. | Out of B, C Al and SiC have | s. Non-metallic |
| | | t. Highest IE ₁ |

10.

| | Column I | Column II |
|----|-------------------------|---------------------|
| a. | N_2O | p. Normal oxide |
| b. | Na_2O | q. Neutral oxide |
| c. | Ga_2O_3 | r. Suboxide |
| d. | C_3O_2 | s. Basic oxide |
| e. | Mn_3O_4 | t. Amphoteric oxide |
| f. | SnO_2 | u. Mixed oxide |

11.

| | Column I | Column II |
|----|--|-------------------------------|
| | Ions | Soft and hard acids and bases |
| a. | $\text{Li}^{\oplus}, \text{Mg}^{2+}, \text{Al}^{3+}$ | p. Soft acids |
| b. | $\text{Cu}^{\oplus}, \text{Cd}^{2+}, \text{Pt}^{4+}$ | q. Soft bases |
| c. | $\text{OH}^{\ominus}, \text{NO}_3^{\ominus}, \text{CO}_3^{2-}$ | r. Hard acids |
| d. | $\text{H}^{\ominus}, \text{I}^{\ominus}, \text{CN}^{\ominus}$ | s. Hard bases |

12.

| | Column I | Column II |
|----|--|-------------------------------|
| | Property | Soft and hard acids and bases |
| a. | High electronegativity and low polarisability | p. Soft bases |
| b. | Low electronegativity and high polarisability | q. Hard bases |
| c. | Small size with high positive oxidation state | r. Soft acids |
| d. | Large size with zero or low positive oxidation state | s. Hard acids |

**Multiple Correct
Answers Type**

*Solutions on page 1.153***General Electronic Configuration and Periodicity**

1. Which of the following statement(s) is/are correct?
- Mendeleev's periodic law was based on atomic numbers of the element.
 - Zero group was not present in the periodic table when Mendeleev presented it.

c. The effective nuclear charge (Z_{eff}) is the atomic number minus shielding effect.

d. There are four transition series in the periodic table each one consists of 10 elements.

2. Which of the following statement(s) is/are correct?

a. Similar electronic configuration is repeated after intervals of 2, 8, 8, 18 and 32 in the extended form of periodic table.

b. In a period from right to left (\leftarrow), reducing nature increases.

c. Along the period (\rightarrow) the number of valency electrons increases from 1 to 8.

d. The first member of lanthanide series is lanthanum.

3. Which of the following statement(s) is/are correct?

a. All the members of the actinide series are man made.

b. Zero group elements are paramagnetic.

c. Third group of the periodic table accommodates maximum number of elements.

d. All members of zero groups are non-metals.

4. Which of the following statements(s) is/are correct?

a. In Mendeleev periodic table, all groups are divided into two subgroups.

b. There is no relationship between electronic configuration of the elements and their position in the extended form of periodic table.

c. s-block elements have one or two electrons in their outermost shell.

d. Osmium has the maximum density among metals.

5. Which of the following statement(s) is/are correct?

a. The last member of the 7th period of the periodic table will have atomic number 118 if discovered.

b. All the transition elements are metals and paramagnetic.

c. The maximum number of elements are present in the 5th period of the periodic table.

d. Every period of the periodic table starts with a member of alkali group.

Atomic and Ionic Radii

6. Which of the following is correct in order of increasing size?

a. $\text{I}^{\ominus} < \text{I} < \text{I}^{\oplus}$

b. $\text{Fe} < \text{Fe}^{2+} < \text{Fe}^{3+}$

c. $\text{Fe}^{3+} < \text{Fe}^{2+} < \text{Fe}$

d. All of the above

7. Reason for diagonal relationship is

a. Same size

b. Same electronegativity

c. Same electron affinity

d. Same polarisability

8. Which of the following pairs of elements have almost similar atomic radii?

- a. Zr, Hf
- b. Mo, W
- c. Co, Ni
- d. Nb, Ta

9. Which of the following statements is/are correct?

- a. An anion is larger than a cation if they are isoelectronic.
- b. Out of Na^+ and Al^{3+} , Na^+ has the largest size.
- c. The ionic radii of trivalent lanthanides [La^{3+} , Ce^{3+} , Pr^{3+} , ...] decreases with increasing atomic number.
- d. Out of P^{3-} , S^{2-} , and $\text{Cl}^{(-)}$, $\text{Cl}^{(-)}$ ion has the largest size.

Effective Nuclear Charge (Z_{eff})

10. Which of the following statement(s) is/are correct?

- a. Z_{eff} of elements increases along the period (\rightarrow).
- b. Z_{eff} of elements increases down the group (\downarrow).
- c. Isoelectronic species have the same nuclear charge.
- d. Screening constant (σ) increases down the group (\downarrow).

Ionisation Energy (IE)

11. Which of the following statement(s) is/are correct?

- a. Successive IE's are lower.
- b. Less energy is required to remove an electron from a half-filled shell or completely filled shell.
- c. IE_1 of Al < IE_1 of Mg
- d. IE_1 of Be > IE_1 of B

12. The factors that influence the ionisation energies are

- a. Size of the atom
- b. Charge on the nucleus
- c. The inner electrons which effectively screen the nuclear charge
- d. Atomic number of the element

13. Which is the correct increasing order of ionisation energy?

- a. Li < B < Be
- b. Be < B < Li
- c. Li < Na < K
- d. O < N < F

14. Which is correct about ionisation potential?

- a. IE_1 of O > IE_1 of N
- b. IE_2 of N > IE_2 of O
- c. IE_2 of Li > IE_2 of Ne
- d. IE_1 of Al > IE_1 of Ca

15. The first eight ionisation energies for a particular neutral atom is as given below. All values are expressed in kJ mol^{-1} . Which oxidation state(s) is/are not possible of the atom?

| 1st | 2nd | 3rd | 4th | 5th | 6th | 7th | 8th |
|-------|-------|-------|------|-------|-------|-------|-------|
| 1.31 | 3.39 | 5.30 | 7.47 | 10.99 | 13.33 | 71.33 | 84.01 |
| a. -2 | b. -3 | c. -6 | d. 6 | | | | |

16. IE_2 for an element is invariably higher than IE_1 because

- a. The size of cations is smaller than its atom.
- b. It is difficult to remove electron from cations.

c. Ionisation energy is endothermic.

d. All of the above.

17. Which sequence is correct regarding the first ionisation potential of coinage metals?

- a. Cu > Ag > Au
- b. Cu < Ag < Au
- c. Cu > Ag < Au
- d. Ag > Cu < Au

18. Mark the correct statements out of the following:

- a. He has highest IE_1 in the periodic table.
- b. Cl has the highest EA out of all elements in the periodic table.
- c. Hg and Br are liquid at room temperature.
- d. In any period, the atomic radius of the noble gas is lowest.

19. Ionisation energy is influenced by

- a. Size of atom
- b. Charge of nucleus
- c. Electrons present in inner shells
- d. None of the above

Electron Affinity (EA)

20. Which of the following statement(s) is/are correct?

- a. The element which has higher EA acts as a strong oxidising agent.
- b. The element with higher EA has higher IE.
- c. Along a period halogen has maximum EA.
- d. The decreasing order of EA is F > Cl > Br.

21. Which of the following process do not involve absorption of energy?

- a. $\text{Cl}(g) + e^- \longrightarrow \text{Cl}^\ominus(g)$
- b. $\text{S}(g) + e^- \longrightarrow \text{S}^\ominus(g)$
- c. $\text{O}(g) + e^- \longrightarrow \text{O}^\ominus(g)$
- d. $\text{O}^\ominus + e^- \longrightarrow \text{O}^{2-}(g)$

Electronegativity (EN)

22. Which of the following properties can be determined by using Born-Haber cycle?

- a. $\Delta_{\text{hyd}}\text{H}^\ominus$
- b. $\Delta_{\text{eg}}\text{H}^\ominus$
- c. $\Delta_u\text{H}^\ominus$
- d. EN

23. Select the correct statement(s).

- a. On Mulliken scale, the average of IP and EA (in eV atom^{-1}) is known as EN.
- b. The maximum EN is shown by Cl.
- c. H, P and Te have similar value of EN.
- d. H, S and Te have similar value of EN.

24. Select the correct statement(s).

- a. Mulliken's values of EN are about 2.8 times more than the Pauling scale.

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b. Mulliken's values of EN are about 2.8 times less than the Pauling scale.

c. On Mulliken's scale if IP and EA are in kJ mol^{-1} , then

$$\text{EN} = \frac{\text{IP} + \text{EA}}{540}.$$

d. On Mulliken's scale if IP and EA are in kcal mol^{-1} , then

$$\text{EN} = \frac{\text{IP} + \text{EA}}{2 \times 62.5}.$$

25. Select the correct statement(s).

a. On Pauling scale, the difference in EN of two atoms A and B in SI units is.

$$(\text{EN}_A - \text{EN}_B) = 0.1017 \sqrt{\Delta_{A-B}}$$

b. On Pauling scale, the difference in EN of two atoms A and B in kcal mol^{-1} is

$$(\text{EN}_A - \text{EN}_B) = 0.208 \sqrt{\Delta_{A-B}}$$

c. The Mulliken's EN values are scaled down to match the Pauling value by dividing $\left(\frac{\text{IP} + \text{EA}}{2} \right)$ in eV by 3.17.

d. The Mulliken's EN values are scaled down to match the Pauling value by multiplying $\left(\frac{\text{IP} + \text{EA}}{2} \right)$ in eV by 3.17.

26. Select the correct statement(s).

a. EN of Ga and Ge > EN of Al and Si, due to *d*-block contraction.

b. EN of Ga and Ge < EN of Al and Si, due to *d*-block contraction.

c. EN of Pb > EN of Tl and Bi, due to *d*-block contraction.

d. EN of Pb < EN of Tl and Bi, due to *d*-block contraction.

Miscellaneous

27. Transition metals are characterised by which of the following properties?

a. Variable valency

b. Coloured compounds

c. High melting and boiling points

d. Tendency to form complexes

28. Which is correct statement regarding BOH (where χ is electronegative)?

a. If $\chi_O - \chi_B > \chi_O - \chi_H$ will be basic.

b. If $\chi_O - \chi_B < \chi_O - \chi_H$ will be acidic.

c. If $\chi_O - \chi_B > \chi_O - \chi_H$ will be acidic.

d. If $\chi_O - \chi_B < \chi_O - \chi_H$ will be basic.

29. The elements which are radioactive and have been named after the names of planet are

a. Hg (Mercury) (Hergentium)

b. Np (Neptunium)

c. Pu (Plutonium)

d. Ra (Radium)

30. The properties which are common to the elements belonging to groups 1 and 17 of periodic tables are

a. Electropositive character increases down the group.

b. Reactivity decreases from top to bottom.

c. Atomic radii increase as atomic number increases.

d. Electronegativity decreases on moving down a group.

31. The number of which subatomic particle is same in case of chlorine atom and chloride ion?

a. Electron

b. Proton

c. Neutrons

d. All of the above

32. Which of the following show amphoteric behaviour?

a. $\text{Zn}(\text{OH})_2$

b.

BeO

c. Al_2O_3

d.

$\text{Pb}(\text{OH})_2$

33. Which is correct in increasing order of ionic character?

a. $\text{AlCl}_3 < \text{MgCl}_2 < \text{NaCl}$

b. $\text{LiI} < \text{LiBr} < \text{LiCl} < \text{LiF}$

c. $\text{NaCl} > \text{MgCl}_2 < \text{AlCl}_3$

d. None of the above

34. Highly pure dilute solution of sodium in ammonia

a. Shows blue colouration due to solvated electrons

b. Shows electrical conductivity due to both solvated electrons and solvated sodium ions

c. Shows red colouration due to solvated electrons but a bad conductor of electricity

d. Produces hydrogen gas or carbonate

35. Which of the following are ionic carbides?

a. CaC_2

b.

Al_4C_3

c.

SiC

d. Be_2C

36. Which of the following substance(s) is/are used in laboratory for drying purposes?

a. Anhydrous P_2O_5

b.

Graphite

c. Anhydrous CaCl_2

d.

Na_3PO_4

37. Born-Haber cycle cannot be used to estimate

a. Electronegativity

b. Hydration energy

c. Lattice energy of ionic crystals

d. Binding energy of electrons

38. The compound(s) which have $-\text{O}-\text{O}-$ bond(s) is/are

a. BaO_2

b.

Na_2O_2

c.

CrO_5

d.

Fe_2O_3

39. Which of the following compounds are paramagnetic in nature?

a. KO_2

b.

K_2O_2

c.

Na_2O_2

d.

RbO_2

40. Select the correct statement(s).

a. Cr^{2+} compounds are ionic.

b. They are oxidised to Cr^{3+} by air.

- c. They are reducing agent in aqueous solution.
d. None is correct.
41. On moving down the group from F to I, which of the following properties decreases?
a. Ionic radius b. IE
c. Oxidising power d. EN
42. Select the correct statement(s).
a. Alkali metals have lowest IE in respective period.
b. Noble gas have highest IE in respective period.
c. EA_1 of N < EA_1 of O.
d. F^\ominus is the strongest reducing agent among halide ions.
43. The electronic configuration of given species (X) is $1s^2$, $2s^2 2p^6$, $3s^2 3p^6 3d^5$, $4s^1$. This can be its
a. Cationic form X^\oplus b. Anionic form X^\ominus
c. Excited state d. Ground state
44. Which of the following sets contain only isoelectronic species?
a. K^\oplus , Ca^{2+} , Sc^{3+} , Cl^\ominus b. Zn^{2+} , Ca^{2+} , Ga^{3+} , Al^{3+}
c. Ti , Ar , Cr^{6+} , V^{5+} d. P^{3-} , S^{2-} , Cl^\ominus , K^\oplus
45. In which of the following arrangements, the order is according to the property indicated against it?
a. IE_1 : O > N > C > B
b. $\Delta_{eg} H^\oplus$ (with -ve sign): Cl > F > Br > I
c. Metallic radius: Rb > K > Na > Li
d. Ionic size: F^\ominus > Na^\oplus > Mg^{2+} > Al^{3+}
46. In which of the following arrangements, the order is according to the property indicated against it?
a. Basic strength: SbH_3 > AsH_3 > PH_3 > NH_3
b. IE_1 : N > O > C > B.
c. Oxidising power: PbO_2 > SnO_2 > SiO_2 > CO_2
d. Acid strength: HI > HBr > HCl > HF
47. The bond dissociation energy of B–F in BF_3 is 646 kJ mol⁻¹ whereas that of C–F in CF_4 is 515 kJ mol⁻¹. The correct reason for higher B–F bond dissociation energy as compared to that of C–F in CF_4 is
a. Lower degree of $p\pi-p\pi$ interaction between B and F in BF_3 than that between C and F in CF_4
b. Significant $p\pi-p\pi$ interaction between B and F in BF_3 whereas there is no possibility of such interaction between C and F in CF_4
c. Smaller size of B-atoms as compared to that of C-atom and the stronger bond between B and F in BF_3 as compared to that between C and F in CF_4
d. Lewis acid character of boron trihalides is as:
 BBr_3 > BCl_3 > BF_3

Single Correct

Answer Type

Solutions on page 1.156

General Electronic Configuration and Periodicity

- According to modern periodic law, the chemical properties of elements are the periodic functions of their
a. Atomic mass b. Atomic number
c. Density d. Mass number
- Newlands' law of octave applies to which of the following set of elements?
a. Be, Mg, Ca b. As, K, Ca
c. B, N, C d. None of these
- The element whose electronic configuration is $1s^2$, $2s^2 2p^6$, $3s^2$ is a/an
a. Metal b. Metalloid
c. Inert gas d. Non-metal
- The number of periods and groups in the long form of periodic table are
a. 7 and 9 b. 8 and 18 c. 7 and 18 d. 6 and 10
- The elements of group 1, 2, 13, 14, 15, 16, 17, 18 are collectively called
a. Noble elements b. Typical elements
c. Transition elements d. Representative elements
- The statement that is **false** regarding the long form of the periodic table is
a. It reflects the sequence of filling the electrons in the order of sub-energy levels s, p, d and f.
b. It helps to predict the stable valency states of the elements.
c. It reflects trends in physical and chemical properties of the elements.
d. It helps to predict the relative ionic character of the bond between any two elements.
- In the periodic table, going down in group 17
a. Reactivity will increase
b. Electronegativity will increase
c. Ionic radius will increase
d. Ionisation potential will increase
- In the long form of periodic table all the non-metals are placed under
a. s-block b. p-block
c. d-block d. f-block
- Alkali metals in each period have
a. Smallest size b. Highest EN
c. Lowest IE d. Highest IE
- Which one pair of atoms or ions will have same configuration?

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- a. F^{\oplus} and Ne b. Li^{\oplus} and He^{\ominus}
 c. Na and K d. Cl^{\ominus} and Ar
11. In the modern periodic table, the period indicates the value of
 a. Atomic number
 b. Atomic mass
 c. Principal quantum number
 d. Azimuthal quantum number
12. Which of the following does not reflect periodicity of elements?
 a. Bonding behaviour b. EN
 c. IE d. Neutron/proton ratio
13. The 3rd period of the periodic table contains
 a. 8 elements b. 32 elements
 c. 3 elements d. 18 elements
14. Which of the following set contains pair of elements that do not belong to same group but show chemical resemblance?
 a. Hf, Zr b. K, Rb c. Be, Al d. B, Al
15. Which of the following belongs to the category of transition metal?
 a. K b. Ra
 c. Fe d. All of the above
16. Without looking at the periodic table, select the elements belonging to same group from the following list.
 a. $Z = 12, 38, 4, 88$ b. $Z = 9, 16, 3, 35$
 c. $Z = 5, 11, 27, 19$ d. $Z = 24, 47, 42, 55$
17. The elements of same group of the periodic table have
 a. Same number of protons
 b. Same valence shell
 c. Same valence electrons
 d. Same electron affinity
18. The elements which are characterised by the outer shell configuration ns^1 to $ns^2 np^6$ are collectively called
 a. Transition elements
 b. Representative elements
 c. Lanthanides
 d. Inner transition elements
19. The outer most electronic configuration of transition elements is
 a. $ns^2 nd^{1-10}$ b. $(n-1)d^{1-10} ns^{1-2}$
 c. $(n-1)d^2 ns^{0-2}$ d. $(n-1)d^{1-10} ns^2$
20. An element with atomic number 20 is placed in which period of the periodic table?
 a. 4 b. 3 c. 2 d. 1
21. The statement that is **not correct** for periodic classification of elements is
- a. The properties of elements are the periodic functions of their atomic numbers.
 b. Non-metallic elements are less in number than metallic elements.
 c. The first ionisation energies of elements along a period do not vary in a regular manner with an increase in atomic number.
 d. For transition elements the ionisation energies increase gradually with increase in atomic number.
22. In the modern periodic table, elements are arranged in
 a. Increasing mass
 b. Increasing volume
 c. Increasing atomic number
 d. Alphabetically
23. The heaviest element among the following is
 a. U b. Ra c. Pb d. Hg
24. The screening effect of d -electron is
 a. Equal to p -electron
 b. Much more than p -electron
 c. Same as f -electrons
 d. Less than p -electrons
25. Which of the following represents the electronic configuration of the most electropositive element?
 a. $[\text{He}]2s^1$ b. $[\text{Xe}]6s^1$ c. $[\text{He}]2s^2$ d. $[\text{Xe}]6s^2$
- Atomic and Ionic Radii**
26. Which of the following has the largest ionic radius?
 a. Be^{2+} b. Mg^{2+} c. Ca^{2+} d. Sr^{2+}
27. The size of species I , I^{\oplus} and I^{\ominus} decreases in the order
 a. $\text{I}^{\oplus} > \text{I}^{\ominus} > \text{I}$ b. $\text{I}^{\ominus} > \text{I} > \text{I}^{\oplus}$
 c. $\text{I}^{\oplus} > \text{I} > \text{I}^{\ominus}$ d. $\text{I} > \text{I}^{\oplus} > \text{I}^{\ominus}$
28. Which of the following is smallest in size ?
 a. Na^{\oplus} b. N^{3-} c. O^{2-} d. F^-
29. Which of the following represent increasing order of size of 4th period element?
 a. K, Kr, Ca, Br b. Kr, Br, Ca, K
 c. K, Ca, Br, Kr d. Br, Kr, Ca, K
30. Which of the following van der Waals radii is the largest?
 a. Ne b. Cl c. O d. F
31. The correct order of the size of C, N, P and S is
 a. $\text{N} < \text{C} < \text{P} < \text{S}$ b. $\text{C} < \text{N} < \text{P} < \text{S}$
 c. $\text{N} < \text{C} < \text{S} < \text{P}$ d. $\text{C} < \text{N} < \text{S} < \text{P}$
32. The correct order of the size of Be, C, F and Ne is
 a. $\text{Be} > \text{C} > \text{F} > \text{Ne}$ b. $\text{Be} < \text{C} < \text{F} < \text{Ne}$
 c. $\text{F} < \text{Ne} < \text{Be} < \text{C}$ d. $\text{Be} > \text{C} > \text{F} < \text{Ne}$
33. The correct order of increasing radii are
 a. $\text{Be}^{2+}, \text{Mg}^{2+}, \text{Na}^{\oplus}$ b. $\text{K}^{\oplus}, \text{Ca}^{2+}, \text{S}^{2-}$
 c. $\text{O}^{2-}, \text{F}^{\ominus}, \text{N}^{3-}$ d. $\text{S}^{2-}, \text{O}^{2-}, \text{As}^{3-}$
34. The correct arrangement of decreasing order of atomic radius among Na, K, Mg and Rb is

- a. $\text{Rb} > \text{Na} > \text{K} > \text{Mg}$ b. $\text{K} > \text{Rb} > \text{Na} > \text{Mg}$
 c. $\text{Rb} > \text{K} > \text{Na} > \text{Mg}$ d. $\text{Mg} > \text{Rb} > \text{K} > \text{Na}$
35. Which of the following pairs of elements have almost similar atomic radii?
 a. Zr, Hf b. Cu, Ag c. Sc, Ti d. Pd, Pt
36. The radius of isoelectronic species
 a. Increases with increase in nuclear charge
 b. Decreases with increase in nuclear charge
 c. Same for all
 d. First increases and then decreases
37. Atomic radii of fluorine and neon (\AA) respectively are given as
 a. 0.72, 1.60 b. 1.60, 1.60
 c. 0.72, 0.72 d. 1.60, 0.72
38. Anything that influences the valence electrons will affect the chemistry of the element. Which one of the following factors does not affect the valence shell?
 a. Valence principal quantum number (n)
 b. Nuclear charge (Z)
 c. Nuclear mass
 d. Number of core electrons
39. The size of isoelectronic species F^\ominus , Ne and Na^\oplus is affected by
 a. Nuclear charge (Z)
 b. Valence principal quantum number (n)
 c. Electron-electron interaction in the outer orbitals
 d. None of the factors because their size is the same
40. Ionic radii of
 a. ${}^{35}\text{Cl}^\ominus > {}^{37}\text{Cl}^\ominus$ b. $\text{Mn}^{7+} > \text{Ti}^{4+}$
 c. $\text{K}^\oplus > \text{Cl}^\ominus$ d. $\text{P}^{3+} > \text{P}^{5+}$
- Effective Nuclear Charge (Z_{eff})**
41. Which of the following statement is most correct? Effective nuclear charge of atom depends on
 a. The charge on the ion
 b. The atomic number of an atom
 c. The screening effect
 d. Both (a) and (c)
42. The shielding effect of d -electrons is
 a. More than s -electrons b. More than p -electrons
 c. Less than s -electrons d. Same as f -electrons
43. The chemistry of lithium is very similar to that of magnesium even though they are placed in different groups. Its reason is
 a. Both are found together in nature
- b. Both have nearly the same size
 c. Both have similar electronic configuration
 d. The ratio of their charge and size (i.e. charge density) is nearly the same
44. In a given energy level, the order of penetration effect of different orbitals is
 a. $f < d < p < s$ b. $s = p = d = f$
 c. $s < p < d < f$ d. $p > s > d > f$
45. Which one of the following group of atoms or ions is not isoelectronic?
 a. $\text{He}, \text{H}^\ominus, \text{Li}^\oplus$ b. $\text{Na}^\oplus, \text{Mg}^{2+}, \text{Al}^{3+}$
 c. $\text{F}^\ominus, \text{O}^{2-}, \text{N}^\oplus$ d. $\text{K}^\oplus, \text{Ca}^{2+}, \text{Ne}$
46. The correct order of relative stability of half filled and completely filled sub-shell is
 a. $p^3 > d^5 < d^{10} < p^6$ b. $d^5 > p^3 < d^{10} < p^6$
 c. $d^5 < p^3 < d^{10} < p^6$ d. $p^3 > d^{10} < d^5 < p^6$
- Ionisation Energy (IE)**
47. From the ground state electronic configurations of the elements given below, pick up the one with the highest value of second ionisation energies
 a. $1s^2, 2s^2 2p^6, 3s^2$ b. $1s^2, 2s^2 2p^6, 3s^1$
 c. $1s^2, 2s^2 2p^6$ d. $1s^2, 2s^2 2p^5$
48. Which of the following process refers to IE_2 ?
 a. $\text{X}_{(\text{g})} \rightarrow \text{X}^{2+}_{(\text{g})}$ b. $\text{X}^\oplus_{(\text{g})} \rightarrow \text{X}^{2+}_{(\text{g})}$
 c. $\text{X}^\oplus_{(\text{aq})} \rightarrow \text{X}^{2+}_{(\text{g})}$ d. $\text{X}_{(\text{g})} \rightarrow \text{X}^\oplus_{(\text{g})}$
49. Which of the following statement concerning ionisation energy is not correct?
 a. The IE_2 is always more than the first.
 b. Within a group, there is a gradual increase in ionisation energy because nuclear charge increases.
 c. Ionisation energies of Be is more than B.
 d. Ionisation energies of noble gases are high.
50. The graph of IE_1 or $\Delta_1 \text{H}_1^\ominus$ versus atomic number (Z) is given below:
-
- | Element | Atomic Number (Z) | Ionization Energy (IE_1) or $\Delta_1 \text{H}_1^\ominus$ (kJ/mol) |
|---------|-----------------------|---|
| H | 1 | ~2400 |
| Li | 3 | ~600 |
| Na | 11 | ~600 |
| K | 19 | ~600 |
| Ar | 18 | ~1500 |
| Rb | 37 | ~600 |
| Kr | 36 | ~1500 |
| Xe | 54 | ~1200 |
| Cs | 55 | ~600 |

1.134 Inorganic Chemistry

- Which of the following statement is correct?
- Alkali metals are at the maxima and noble gases at the minima.
 - Noble gases are at the maxima and alkali metals at the minima.
 - Transition elements are at the maxima.
 - Minima and maxima do not show any regular behaviour.
51. Which of the following isoelectronic ions have the lowest ionisation enthalpy?
- K^{\oplus}
 - Ca^{2+}
 - Cl^{\ominus}
 - S^{2-}
52. For any given element, the second ionisation potential will be — the first ionisation potential
- less than
 - higher than
 - same
 - depends on the element
53. Which of the following process requires the largest amount of energy?
- $Al_{(g)} \longrightarrow Al^{\oplus} + e^-$
 - $Al^{2+}_{(g)} \longrightarrow Al^{3+} + e^-$
 - $Al^{\oplus}_{(g)} \longrightarrow Al^{2+} + e^-$
 - All require same amount of energy
54. Which of the following is an energy consuming process?
- $O_{(g)} + e^- \longrightarrow O^{\ominus}_{(g)}$
 - $Na^{\oplus}_{(g)} + e^- \longrightarrow Na_{(g)}$
 - $O^{\ominus}_{(g)} + e^- \longrightarrow O^{2-}_{(g)}$
 - $O^{2-}_{(g)} \longrightarrow O^{\ominus} + e^-$
55. Arrange S, P and As in order of increasing ionisation energy.
- $S < P < As$
 - $P < S < As$
 - $As < S < P$
 - $As < P < S$
56. The five successive ionisation energies of an element are 800, 2427, 3658, 25024 and 32824 kJ mol⁻¹ respectively. The number of valence electron is
- 3
 - 5
 - 1
 - 2
57. Which of the following transitions involve maximum amount of energy?
- $M^{\ominus}_{(g)} \longrightarrow M_{(g)}$
 - $M^{\ominus}_{(g)} \longrightarrow M^{\oplus}_{(g)}$
 - $M^{\oplus}_{(g)} \longrightarrow M^{2+}_{(g)}$
 - $M^{2+}_{(g)} \longrightarrow M^{3+}_{(g)}$
58. Which of the elements show least values of ionisation within their periods?
- Alkaline earth metals
 - Alkali metals
 - Noble gases
 - Chalcogens
59. Which one of the following has the largest ionisation energy.
- $_{11}Na$
 - $_{19}K$
 - $_{12}Mg$
 - $_{37}Rb$
60. Which one of the following elements has the highest ionisation energy?
- [Ne] $3s^2 3p^1$
 - [Ne] $3s^2 3p^3$
 - [Ne] $3s^2 3p^2$
 - [Ar] $3d^{10} 4s^2 4p^2$
61. The correct order of the second ionisation potential of carbon, nitrogen, oxygen and fluorine is
- $C > N > O > F$
 - $O > N > F > C$
 - $O > F > N > C$
 - $F > O > N > C$
62. Which has the largest first ionisation energy?
- Na
 - K
 - Rb
 - Li
63. Which of the following element has the highest ionisation energy?
- Carbon
 - Boron
 - Oxygen
 - Nitrogen
64. The ionisation potential of nitrogen is more than that of oxygen molecules because of
- Greater attraction of electrons by the nucleus
 - Extra stability of the half-filled p -orbitals
 - Smaller size of nitrogen
 - More penetrating effect
65. The set representing the correct order of the first ionisation potential is
- $K > Na > Li$
 - $Be > Mg > Ca$
 - $B > C > N$
 - $Ge > Si > C$
66. The first ionisation potential of which of the element is highest
- Na
 - Mg
 - Al
 - Si
67. Highest ionisation potential in a period is shown by
- Alkali metals
 - Transition elements
 - Halogens
 - Alkaline earth metals
68. The first ionisation energy is maximum for
- Na
 - Mg
 - K
 - Kr
69. What is the order of ionisation energies of the coinage metal
- $Cu > Ag < Au$
 - $Cu > Ag > Au$
 - $Cu < Ag < Au$
 - $Au > Ag < Cu$
70. The second ionisation potentials in electron volts of oxygen and fluorine atoms are respectively given by
- 35.1, 38.3
 - 38.3, 38.3
 - 38.3, 35.1
 - 35.1, 35.1
71. The value of IE_1 , IE_2 , IE_3 and IE_4 of an atom are respectively 7.5 eV, 25.6 eV, 48.6 eV and 170.6 eV. The electronic configuration of the atom will be
- $1s^2 2s^2 2p^6 3s^1$
 - $1s^2 2s^2 2p^6 3s^2 3p^1$
 - $1s^2 2s^2 2p^6 3s^2 3p^3$
 - $1s^2 2s^2 2p^6 3s^2$

72. IE_1 , IE_2 and IE_3 values are 100, 150 and 1500 eV respectively. The element can be

- a. Na b. B c. Be d. F

73. $N_0/2$ atoms of $X_{(g)}$ are converted into $X^{\oplus}_{(g)}$ by energy E_1 , $N_0/2$ atoms of $X_{(g)}$ are converted into $X^{\ominus}_{(g)}$ by energy E_2 . Hence ionisation potential and electron affinity of $X_{(g)}$ per atom are

a. $\frac{2E_1}{N_0}, \frac{2(E_2 - E_1)}{N_0}$

b. $\frac{2E_1}{N_0}, \frac{2E_2}{N_0}$

c. $\frac{(E_1 - E_2)}{N_0}, \frac{2E_2}{N_0}$

d. None is correct

74. Which of the following ionisation energy values for calcium show a sudden increase?

- a. Third b. Second c. First d. Fourth

75. Which one of the following statements is incorrect in relation to ionisation enthalpy?

- a. Ionisation enthalpy increases for each successive electron
 b. The greatest increase in ionisation enthalpy is experienced on removal of electron from core noble gas configuration.
 c. End of valence electrons is marked by a big jump in ionisation enthalpy.
 d. Removal of electron from orbitals bearing lower n value is easier than from orbital having higher n value.

76. IE_2 for an element is invariably higher than IE_1 because

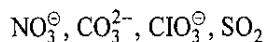
- a. It is difficult to remove electron from cation
 b. The size of the cation is smaller than its atoms
 c. Z_{eff} is more for cation
 d. All the above

77. Which of the following metal requires radiation of the lowest wavelength to cause emission of electrons?

- a. Na b. K c. Mg d. Ca

Isoelectronic Species

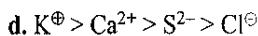
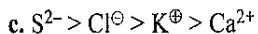
78. Which of the following are isoelectronic?



- a. $\text{NO}_3^{\ominus}, \text{CO}_3^{2-}, \text{ClO}_3^{\ominus}$ b. $\text{NO}_3^{\ominus}, \text{CO}_3^{2-}, \text{SO}_2$
 c. $\text{CO}_3^{2-}, \text{ClO}_3^{\ominus}, \text{SO}_2$ d. None of these

79. Consider the isoelectronic series, $\text{K}^{\oplus}, \text{S}^{2-}, \text{Cl}^{\ominus}, \text{Ca}^{2+}$, the radii of the ions decrease as

- a. $\text{Ca}^{2+} > \text{K}^{\oplus} > \text{Cl}^{\ominus} > \text{S}^{2-}$
 b. $\text{Cl}^{\ominus} > \text{S}^{2-} > \text{K}^{\oplus} > \text{Ca}^{2+}$



80. Which of the following are isoelectronic species?



- a. II, III and IV b. I, II and III
 c. I, II and IV d. II and I

81. Two p -block elements x (outer configuration $ns^2 np^3$) and z (outer configuration $ns^2 np^4$) occupy neighbouring positions in a period. Using this information which of the following is correct with respect to their ionisation potential I_x and I_z .

- a. $I_x > I_z$
 b. $I_z > I_x$
 c. $I_z = I_x$
 d. Relation between I_x and I_z is uncertain

Metallic-Non-metallic Character

82. Considering the elements B, Al, Mg and K, the correct order of their metallic character is

- a. B > Al > Mg > K
 b. Al > Mg > B > K
 c. Mg > Al > K > B
 d. K > Mg > Al > B

83. IE_1 and IE_2 of Mg are 178 and 348 kcal mol⁻¹. The energy required for the reaction $\text{Mg} \rightarrow \text{Mg}^{2+} + 2 e^-$ is

- a. +170 kcal b. +526 kcal
 c. -170 kcal d. -526 kcal

84. Considering the elements B, C, N and Si, the correct order of their non-metallic character is?

- a. B > C > Si > N > F b. Si > C > B > N > F
 c. F > N > C > B > Si d. F > N > C > Si > B

Electron Affinity (EA) and Electron Gain Enthalpy ($\Delta_{eg}H^{\ominus}$)

85. Which of the following have least electron affinity?

- a. Oxygen b. Fluorine
 c. Nitrogen d. Carbon

86. Second and successive electron affinity of an element

- a. is always successive (energy is released)
 b. is always positive (energy is absorbed)
 c. can be positive or negative
 d. is always zero

87. Which one of the following statements is incorrect?

- a. Greater is the nuclear charge, greater is the electron affinity.
 b. Neon has zero electron affinity.

- c. Electron affinity decreases from fluorine to iodine in the group.
 d. Electron affinity decreases in going down a group and increases across period from the left to the right (\rightarrow).
88. The lower electron affinity of fluorine than that of chlorine is due to
 a. Smaller size
 b. Smaller nuclear charge
 c. Difference in their electronic arrangement
 d. Its highest reactivity
89. The EA order for halogen is
 a. F > Cl > Br > I b. F < Cl < Br < I
 c. F < Cl > Br > I d. F > Cl < Br < I
90. The EA for inert gases is likely to be
 a. High b. Small
 c. Zero d. Positive
91. Ionisation of energy F^\ominus is 320 kJ mol^{-1} . The electron gain enthalpy of fluorine would be
 a. -320 kJ mol^{-1} b. -160 kJ mol^{-1}
 c. $+320 \text{ kJ mol}^{-1}$ d. $+160 \text{ kJ mol}^{-1}$
92. Which of the following represents the correct order of electron affinities?
 a. F > Cl > Br > I b. C < N < O < F
 c. N < C < O < F d. C < Si < P < N
93. Fluorine has the highest electronegativity among the group on the Pauling scale, but the electron affinity of fluorine is less than that of chlorine because
 a. The atomic number of fluorine is less than that of chlorine
 b. Fluorine being the first member of the family behaves in an unusual manner
 c. Chlorine can accommodate an electron better than fluorine by utilising its vacant $3d$ orbital
 d. Small size, high electron density and an increased electron repulsion make addition of an electron to fluorine less favourable than that in the case of chlorine
- Electronegativity (EN)**
94. Which is true about the electronegativity order of the following elements?
 a. P > Si b. C > N c. Br > Cl d. Sr > Ca
95. The electronegativity of the following elements increases in the order
 a. C, N, Si, P b. N, Si, C, P
 c. Si, P, C, N d. P, Si, N, C
96. An atom with high EA generally has
 a. Tendency to form +ve ions
 b. High ionisation energy
 c. Large atomic size
 d. Low electron affinity
97. The electronegativity of the following elements increases in the order
 a. S < P < N < O b. P < S < N < O
 c. N < O < P < S d. N < P < S < O
98. Downwards in a group, the electropositive character of elements
 a. Increases b. Decreases
 c. Remains same d. None
99. What is the correct order of electronegativity?
 a. $M^{1-} < M^{2-} < M^{3-} < M^{4-}$
 b. $M^{1-} > M^{2-} > M^{3-} > M^{4-}$
 c. $M^{1-} < M^{2-} > M^{3-} < M^{4-}$
 d. $M^{4-} < M^{2-} < M^{3-} < M^{1-}$
100. Due to screening effect of electrons in an atom
 a. IE decreases
 b. IE increases
 c. No change in IE
 d. Attraction of nucleus on the valence electron increases
101. Select the group where EN increases down the group
 a. F, Cl, Br b. Li, Na, K
 c. Ca, Sr, Ba d. Zn, Cd, Hg
102. Which of the following element has the highest EN?
 a. As b. Sb c. P d. S
103. The electronegativity values of C, N, O and F
 a. Increases from carbon to fluorine
 b. Decreases from carbon to fluorine
 c. Increases up to oxygen and is minimum at fluorine
 d. Is minimum at nitrogen and then increases continuously
- Acidic, Basic and Amphoteric Character**
104. Among the following oxides, which is least acidic?
 a. Al_2O_3 b. B_2O_3 c. CO_2 d. NO_2
105. Which of the following oxides is most basic?
 a. Na_2O b. MgO c. Al_2O_3 d. CuO
106. The order of which of the following oxides is arranged according to decreasing basic nature?
 a. $\text{Na}_2\text{O}, \text{MgO}, \text{Al}_2\text{O}_3, \text{CuO}$
 b. $\text{CuO}, \text{Al}_2\text{O}_3, \text{MgO}, \text{Na}_2\text{O}$
 c. $\text{Al}_2\text{O}_3, \text{CuO}, \text{MgO}, \text{Na}_2\text{O}$
 d. $\text{CuO}, \text{MgO}, \text{Na}_2\text{O}, \text{Al}_2\text{O}_3$
107. The correct order of acidic strengths of the following is
 a. $\text{CaO} < \text{CuO} < \text{H}_2\text{O} < \text{CO}_2$

- b. $\text{CaO} < \text{H}_2\text{O} < \text{CuO} < \text{CO}_2$
 c. $\text{H}_2\text{O} < \text{CuO} < \text{CaO} < \text{CO}_2$
 d. $\text{H}_2\text{O} < \text{CO}_2 < \text{CaO} < \text{CuO}$
108. What is the nature of Al_2O_3 and B_2O_3 ?
 a. Acidic, acidic
 b. Acidic, amphoteric
 c. Amphoteric, amphoteric
 d. Amphoteric, acidic
109. Which of the following oxides is neutral?
 a. SiO_2 b. CO c. ZnO d. SnO_2
110. Which of the following oxides is amphoteric in nature?
 a. CaO b. CO_2 c. SnO_2 d. SiO_2
111. The correct order of acidic strength of the following is
 a. $\text{SO}_2 > \text{P}_2\text{O}_3 > \text{SiO}_2 > \text{Al}_2\text{O}_3$
 b. $\text{P}_2\text{O}_3 > \text{SO}_2 > \text{SiO}_2 > \text{Al}_2\text{O}_3$
 c. $\text{P}_2\text{O}_3 > \text{Al}_2\text{O}_3 > \text{SO}_2 > \text{SiO}_2$
 d. $\text{Al}_2\text{O}_3 > \text{SiO}_2 > \text{P}_2\text{O}_3 > \text{SO}_2$
112. Which of the oxides behaves both as suboxide and as neutral oxide?
 a. CO b. CO_2 c. C_3O_2 d. N_2O
113. Which of the oxides is not a mixed oxide?
 a. $\text{Co}(\text{Al}_2\text{O}_2)_2$ b. Mn_3O_4
 c. Pb_3O_4 d. C_3O_2
114. Which of the oxides is basic as well as normal oxide?
 a. N_2O b. Na_2O c. NO d. H_2O
- Bond Angle**
115. Decreasing order of bond angle of $(\text{NH}_3, \text{PH}_3, \text{AsH}_3)$ is
 a. $\text{NH}_3 > \text{PH}_3 > \text{AsH}_3$ b. $\text{NH}_3 > \text{AsH}_3 > \text{PH}_3$
 c. $\text{PH}_3 > \text{NH}_3 > \text{AsH}_3$ d. $\text{AsH}_3 > \text{PH}_3 > \text{NH}_3$
116. Decreasing order of bond angle of $(\text{NO}_2^\oplus, \text{NO}_2, \text{NO}_2^\ominus)$ is
 a. $\text{NO}_2^\ominus > \text{NO}_2 > \text{NO}_2^\oplus$
 b. $\text{NO}_2^\oplus > \text{NO}_2 > \text{NO}_2^\ominus$
 c. $\text{NO}_2^\ominus > \text{NO}_2^\oplus > \text{NO}_2$
 d. $\text{NO}_2 > \text{NO}_2^\ominus > \text{NO}_2^\oplus$
117. Decreasing order of bond angle of $(\text{NH}_3, \overset{\oplus}{\text{NH}}_4, \text{PCl}_5, \text{SCl}_2)$ is
 a. $\text{NH}_3 > \text{SCl}_2 > \text{PCl}_5 > \overset{\oplus}{\text{NH}}_4$
 b. $\text{NH}_3 > \text{SCl}_2 > \overset{\oplus}{\text{NH}}_4 > \text{PCl}_5$
 c. $\overset{\oplus}{\text{NH}}_4 > \text{NH}_3 > \text{SCl}_2 > \text{PCl}_5$
 d. $\overset{\oplus}{\text{NH}}_4 > \text{NH}_3 > \text{PCl}_5 > \text{SCl}_2$
118. Increasing order of bond angle of $(\text{Cl}_2\text{O}, \text{ClO}_2, \text{Cl}_2\text{O}_7, \text{I}_3^\ominus)$ is
 a. $\text{Cl}_2\text{O} < \text{ClO}_2 < \text{Cl}_2\text{O}_7 < \text{I}_3^\ominus$
 b. $\text{Cl}_2\text{O} < \text{ClO}_2 < \text{I}_3^\ominus < \text{Cl}_2\text{O}_7$
 c. $\text{I}_3^\ominus < \text{Cl}_2\text{O}_7 < \text{ClO}_2 < \text{Cl}_2\text{O}$
 d. $\text{Cl}_2\text{O} < \text{Cl}_2\text{O}_7 < \text{ClO}_2 < \text{I}_3^\ominus$
- Lattice and Hydration Energy**
119. Decreasing order of hydration energy of the following is
 a. $\text{Li}^\oplus > \text{Na}^\oplus > \text{K}^\oplus > \text{Cs}^\oplus$
 b. $\text{Cs}^\oplus > \text{K}^\oplus > \text{Na}^\oplus > \text{Li}^\oplus$
 c. $\text{Li}^\oplus > \text{K}^\oplus > \text{Na}^\oplus > \text{Cs}^\oplus$
 d. $\text{Cs}^\oplus > \text{Na}^\oplus > \text{K}^\oplus > \text{Li}^\oplus$
120. Extent of hydrolysis of the following is
 a. $\text{PCl}_5 > \text{SiCl}_4 > \text{MgCl}_2 > \text{AlCl}_3$
 b. $\text{AlCl}_3 > \text{MgCl}_2 > \text{SiCl}_4 > \text{PCl}_5$
 c. $\text{SiCl}_4 > \text{PCl}_5 > \text{MgCl}_2 > \text{AlCl}_3$
 d. $\text{PCl}_5 > \text{SiCl}_4 > \text{AlCl}_3 > \text{MgCl}_2$
121. Give the decreasing order of thermal stability of the following.
 a. $\text{Be CO}_3 > \text{Mg CO}_3 > \text{Ca CO}_3 > \text{Ba CO}_3$
 b. $\text{Ba CO}_3 > \text{Ca CO}_3 > \text{Mg CO}_3 > \text{Be CO}_3$
 c. $\text{Be CO}_3 > \text{Ca CO}_3 > \text{Ba CO}_3 > \text{Mg CO}_3$
 d. $\text{Mg CO}_3 > \text{Ca CO}_3 > \text{Ba CO}_3 > \text{Be CO}_3$
122. Lattice energy of an ionic compound depends on
 a. Charge density of the ion
 b. Packing of ions only
 c. Size of the ion only
 d. Charge on the ions only
123. Na_2SO_4 is soluble in water while BaSO_4 is insoluble. Which of the reason is correct about the above statement.
 a. Lattice energy of BaSO_4 exceeds its hydration energy.
 b. Hydration energy of BaSO_4 exceeds its lattice energy.
 c. The solubility in H_2O of a compound depends only on its hydration energy.
 d. The solubility in H_2O of a compound depends only on its lattice energy.
124. Calculate the lattice energy from the following data (given $1 \text{ eV} = 23.0 \text{ kcal mol}^{-1}$)
 i. $\Delta_f H^\ominus (\text{KI}) = -78.0 \text{ kcal mol}^{-1}$
 ii. $\text{IE}_1 \text{ of K} = 4.0 \text{ eV}$
 iii. $\Delta_{\text{diss}} H^\ominus (\text{I}_2) = 28.0 \text{ kcal mol}^{-1}$
 iv. $\Delta_{\text{sub}} H^\ominus (\text{K}) = 20.0 \text{ kcal mol}^{-1}$
 v. $\text{EA of I} = -70.0 \text{ kcal mol}^{-1}$
 vi. $\Delta_{\text{sub}} H^\ominus \text{ of I}_2 = 14.0 \text{ kcal mol}^{-1}$

- a. +14.1 kcal mol⁻¹ b. -14.1 kcal mol⁻¹
 c. -141 kcal mol⁻¹ d. +141 kcal mol⁻¹
125. Calculate the EA of O atom to O²⁻ ion from the following data:
- $\Delta_f H^\ominus [MgO(s)] = -600 \text{ kJ mol}^{-1}$
 - $\Delta_u H^\ominus [MgO(s)] = -3860 \text{ kJ mol}^{-1}$
 - $IE_1 + IE_2 \text{ of Mg(g)} = 2170 \text{ kJ mol}^{-1}$
 - $\Delta_{\text{diss}} H^\ominus [O_2(g)] = +494 \text{ kJ mol}^{-1}$
 - $\Delta_{\text{sub}} H^\ominus \text{ of Mg(s)} = +150 \text{ kJ mol}^{-1}$
- a. +693 kJ mol⁻¹ b. -693 kJ mol⁻¹
 c. +69.3 kJ mol⁻¹ d. -69.3 kJ mol⁻¹
- Miscellaneous**
126. Which of the following is correct?
- With increase in atomic size, ionisation energy increases
 - With increase in atomic size, electron affinity increases
 - With increase in atomic size, metallic character increases
 - With increase in atomic size, electronegativity increases
127. Which of the following is incorrect?
- An element which has high electronegativity always has high electron gain enthalpy.
 - Electron gain enthalpy is the property of an isolated atom.
 - Electronegativity is the property of bonded atom.
 - Both electronegativity and electron gain enthalpy are usually directly related to nuclear charge and inversely related to atomic size.
128. The ionisation of hydrogen atom would give rise to
- Hydride ion
 - Hydronium ion
 - Proton
 - Hydroxyl ion
129. Chloride of an element A gives neutral solution in water. In the periodic table, the element A belongs to
- First group
 - Third group
 - Fifth group
 - First transition series
130. In a period, density first ___ then ___ and in a group it ___ down the group
- Decreases, increases, remains constant
 - Increases, decreases, decreases
 - Increases, remains constant, increases
 - Increases, decreases, increases
131. In the transformation of Na(s) → Na⁺(g), the energies involved are
- Ionisation energy
 - Sublimation energy
 - Ionisation energy and sublimation energy
 - Bond dissociation energy

132. Beryllium and aluminium exhibit many properties which are similar. But the two elements differ in
- Forming covalent halides
 - Forming polymeric hydrides
 - Exhibiting maximum covalency in compounds
 - Exhibiting amphoteric nature in their oxides
133. Among LiCl, BeCl₂, BCl₃ and CCl₄ the covalent bond character follows the order
- LiCl > BeCl₂ > BCl₃ > CCl₄
 - LiCl < BeCl₂ < BCl₃ < CCl₄
 - LiCl > BeCl₂ > CCl₄ > BCl₃
 - BeCl₂ > LiCl > BCl₃ > CCl₄

134. The correct order of polarisability of ion is
- Cl[⊖] > Br[⊖] > I[⊖] > F[⊖]
 - F[⊖] > I[⊖] > Br[⊖] > Cl[⊖]
 - I[⊖] > Br[⊖] > Cl[⊖] > F[⊖]
 - F[⊖] > Cl[⊖] > Br[⊖] > I[⊖]

135. Diagonal relationship is shown by
- All elements with their diagonally opposite elements.
 - All elements of 3rd and 4th periods
 - Some of the elements of 2nd and 3rd periods
 - Elements of *d*-block

**Assertion Reasoning
Type**

Solutions on page 1.161

- a. If both Assertion (A) and Reason (R) are correct and Reason (R) is the correct explanation of Assertion (A).
 b. If both (A) and (R) are correct but (R) is not the correct explanation for (A).
 c. If (A) is correct but (R) is not correct.
 d. If (A) is incorrect but (R) is correct.
 e. If both (A) and (R) are incorrect
- Assertion (A):** He and Be have similar electronic configuration of the type ns^2 .
Reason (R): Both are chemically inert.
 - Assertion (A):** EA of O is less than that of F but greater than that of N.
Reason (R): IE is as follows: N > O > F.
 - Assertion (A):** IE₁ of N is lower than O.
Reason (R): Across a period Z_{eff} decreases.
 - Assertion (A):** IE₂ of Li is the highest in the second period.
Reason (R): Li⁺ has noble gas, i.e. Ne gas configuration.
 - Assertion (A):** IE₂ of C is greater than that of B.
Reason (R): Due to penetration effect.
 - Assertion (A):** In the modern periodic table period indicates the value of azimuthal quantum number.

- Reason (R):** Each period begins with the filling of new shell.
7. **Assertion (A):** Anything that influences the valence electrons will affect the chemistry of the element. So, the nuclear mass does not affect the valence shell.
- Reason (R):** Nucleus contains protons and neutrons, whereas protons i.e. nuclear charge affects the valence shell but neutrons do not.
8. **Assertion (A):** Metallic character order is
 $K > Mg > Al > B$.
- Reason (R):** Along the period (\rightarrow) metallic character increases and decreases down the group (\downarrow).
9. **Assertion (A):** When the transition element ionises, the $4s$ -orbital electrons are removed before the $3d$ -orbital electrons.
- Reason (R):** The energy of $3d$ -orbital electrons is lower than that of $4s$ -orbital electrons.
10. **Assertion (A):** Mercurous ion is paramagnetic.
- Reason (R):** It contains one unpaired electron.
11. **Assertion (A):** LiCl is predominantly a covalent compound.
- Reason (R):** EN difference between Li and Cl is too small.
7. How many of the following energies are involved in the transformation of $Na(s) \longrightarrow Na^{\oplus}(aq)$?
a. IE b. $\Delta_{\text{Sub}}H^{\ominus}$ c. $\Delta_{\text{diss.}}H^{\ominus}$ d. $\Delta_{\text{hyd.}}H^{\ominus}$
e. $\Delta_u H^{\ominus}$
8. Among the following oxides how many of them are mixed oxides?
a. H_2O b. C_3O_2 c. Fe_3O_4 d. Fe_2O_3
e. Pb_3O_4 f. PbO_2 g. $Co(AlO_2)_2$ h. Mn_3O_4
9. Number of species that are isoelectronic with Ar is.
10. Among the following oxides, how many of them are amphoteric oxides?
a. B_2O_3 b. Al_2O_3 c. CaO d. ZnO
e. Ga_2O_3 f. SnO_2 g. PbO_2 h. BeO
i. CuO j. Fe_2O_3
11. Among the following elements how many of them are inner transition elements?
a. Sg b. Bk c. Er d. Em
e. Fe f. Pb g. Cr h. Ca
i. Ar j. Zr k. Ce
12. How many number of pairs of elements exhibit diagonal relationship.
13. Among $BeCO_3$, $CaCO_3$, $SrCO_3$ and $BaCO_3$, how many number of these compounds are thermally more stable than $MgCO_3$?

Integer Type*Solutions on page 1.161*

1. Among the following oxides how many of them are suboxides?
a. C_3O_2 b. N_2O c. NO_2 d. CO
e. Fe_3O_4 f. KO_2
2. The number of factors that influence the IE are
a. Size of the atom b. Charge on the nucleus
c. Shielding effect d. The atomic mass
3. The number of process(es) requiring the absorption of energy is/are
a. $Cl \longrightarrow Cl^{\ominus}$ b. $O^{\ominus} \longrightarrow O^{2-}$
c. $Fe^{+3} \longrightarrow Fe^{+2}$ d. $Ar \longrightarrow Ar^{\ominus}$
4. For an element (X) the successive ionisation energies, IE₁, IE₂, IE₃, IE₄ and IE₅ are 800, 2427, 3658, 25024 and 32824 kJ mol^{-1} respectively, then what is the number of valence electrons present in the element?
5. The diagonal relationship is shown by the elements upto how many groups only?
6. The number of the following pairs contains elements with similar atomic radii
a. Co, Ni b. Zn, Mo c. Rh, Ir d. Hf, Ti

Fill in the Blanks Type*Solutions on page 1.162*

1. IUPAC name for the element with $Z=117$ is _____ and its symbol is _____.
2. In the long form of the periodic table, physical and chemical properties of the elements are a periodic function of their _____.
3. The property used by Mendeleev to classify the elements in his periodic table is _____.
4. The elements which constitute $5f$ -block are called _____ with atomic numbers from _____ to _____.
5. Elements of s and p blocks are collectively called _____.
6. The group all members of which are in gaseous state under ordinary conditions is a _____ group.
7. Lather Meyer drew a graph showing the relation between atomic _____ and atomic _____.
8. Ionic radii _____ with increase in atomic number in a period and _____ in a group.
9. The electron gain enthalpy of oxygen is _____ that of sulphur.
10. On Mulliken scale the average of IP and EA is known as _____.

11. On the Pauling's EN scale, the element next to F is _____.
12. The IE of Be is _____ than that of B.
13. The bond angle in SO_4^{2-} ion is _____.
14. The angle between two covalent bonds is maximum for $(\text{CH}_4, \text{H}_2\text{O}, \text{CO}_2)$ _____.
15. Second element of group I shows diagonal relationship with the first element of group _____.
16. The EN of the elements C, N, Si and P increases in the order of _____.
17. The decreasing order of IE for elements Li, Be, C, B is _____.
18. The type of magnetism exhibited by $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ ion is _____.
19. Among the ions Cl^\ominus , S^{2-} and Na^\oplus , the largest ion is _____.
20. The inner electrons are shielded to a _____ extent than the outer electrons.

True/False Type*Solutions on page 1.162*

1. Number of species that are isoelectronic with F^\ominus ion are five.
2. Number of species that are isoelectronics with Sr^{2+} ion are four.
3. Among the elements, Li, K, Ca, Cl and Kr, the element K has the lowest IE and Kr has the highest IE.
4. Be and Mg atoms do not impart colour to the flame.
5. Energy is released when electron is added to an isolated gases anion.
6. van der Waals radius of chlorine is less than that of covalent radius.
7. The oxides and hydroxides of alkali metals are strong bases.
8. Lithium is the lightest metal.
9. As the s character of the hybrid orbital decreases, the EN increases.
10. Ionic bonds are non-directional while covalent bonds are directional.

Archives*Solutions on page 1.162***Multiple Correct Answers Type**

1. Which of the following statements is/are true for the long form of the periodic table?
 - a. It reflects the sequence of filling the electrons in the order of sub-energy level s, p, d and f.
 - b. It helps to predict the stable valency states of the elements.

- c. It reflects trends in physical and chemical properties of the elements.
 - d. It helps to predict the relative ionicity of the bond between any two elements. (IIT-JEE, 1981)
2. Sodium sulphate is soluble in water, whereas barium sulphate is sparingly soluble because
 - a. the hydration energy of sodium sulphate is more than its lattice energy.
 - b. the lattice energy of barium sulphate is more than its hydration energy.
 - c. the lattice energy has no role to play in solubility.
 - d. the hydration energy of sodium sulphate is less than its lattice energy. (IIT-JEE, 1989)
 3. Ionic radii of

| | |
|--|--|
| a. $\text{Ti}^{4+} < \text{Mn}^{7+}$ | b. ${}^{35}\text{Cl}^\ominus < {}^{37}\text{Cl}^\ominus$ |
| c. $\text{K}^\oplus > \text{Cl}^\ominus$ | d. $\text{P}^{3+} > \text{P}^{5+}$ |
- (IIT-JEE, 1999)

Single Correct Answer Type

1. The correct order of the second ionisation potential of carbon, nitrogen, oxygen and fluorine is

| | |
|--|--|
| a. $\text{C} > \text{N} > \text{O} > \text{F}$ | b. $\text{O} > \text{N} > \text{F} > \text{C}$ |
| c. $\text{O} > \text{F} > \text{N} > \text{C}$ | d. $\text{F} > \text{O} > \text{N} > \text{C}$ |

(IIT-JEE, 1981)

2. The element with the highest first ionisation potential is

| | | | |
|----------|-----------|-------------|-----------|
| a. boron | b. carbon | c. nitrogen | d. oxygen |
|----------|-----------|-------------|-----------|

(IIT-JEE, 1982)

3. The first ionisation potential (in electron volts) of nitrogen and oxygen atoms are, respectively, given by

| | |
|---------------|---------------|
| a. 14.5, 13.6 | b. 13.6, 14.6 |
| c. 13.6, 13.6 | d. 14.6, 14.6 |

(IIT-JEE, 1987)

4. Atomic radii of fluorine and neon (in Angstrom units) are, respectively, given by

| | |
|---------------|------------------|
| a. 0.72, 1.60 | b. 1.60, 1.60 |
| c. 0.72, 0.72 | d. None of these |

(IIT-JEE, 1987)

5. The electronegativity of the following elements increases in the order

| | |
|----------------|----------------|
| a. C, N, Si, P | b. N, Si, C, P |
| c. Si, P, C, N | d. P, Si, N, C |

(IIT-JEE, 1987)

6. The first ionisation potential of Na, Mg, Al and Si is in the order

| | |
|--|--|
| a. $\text{Na} < \text{Mg} > \text{Al} < \text{Si}$ | b. $\text{Na} > \text{Mg} > \text{Al} > \text{Si}$ |
| c. $\text{Na} < \text{Mg} < \text{Al} > \text{Si}$ | d. $\text{Na} > \text{Mg} > \text{Al} < \text{Si}$ |

(IIT-JEE, 1988)

7. Which of the following is the smallest in size?
 a. N^{3-} b. O^{2-} c. F^\ominus d. Na^\oplus
 (IIT-JEE, 1989)

8. Among the following elements (whose electronic configurations are given below) the one having the highest ionisation energy is
 a. $[\text{Ne}]3s^23p^1$ b. $[\text{Ne}]3s^23p^3$
 c. $[\text{Ne}]3s^23p^2$ d. $[\text{Ne}]3d^{10}4s^24p^3$
 (IIT-JEE, 1990)

9. Which of the following statements is **not correct** for the periodic classification of elements?
 a. The properties of elements are the periodic functions of their atomic numbers.
 b. Non-metallic elements are lesser in number than metallic elements.
 c. The first ionisation energies of elements along a period do not vary in a regular manner with the increase in atomic number.
 d. For transition elements, the *d*-subshells are filled with electrons monotonically with the increase in atomic number.
 (IIT-JEE, 1992)

10. Which of the following has the most stable +2 oxidation state?
 a. Sn b. Pb c. Fe d. Ag
 (IIT-JEE, 1995)

11. Which of the following has the maximum number of unpaired electrons?
 a. Mg^{2+} b. Ti^{3+} c. V^{3+} d. Fe^{2+}
 (IIT-JEE, 1996)

12. Which of the following statement is **wrong**?
 a. The first ionisation potential of Al is less than the first ionisation potential of Mg.
 b. The second ionisation potential of Mg is greater than the second ionisation potential of Na.
 c. The first ionisation potential of Na is less than the first ionisation potential of Mg.
 d. The third ionisation potential of Mg is greater than the third ionisation potential of Na.
 (IIT-JEE, 1997)

13. The correct order of acidic strength is
 a. $\text{Cl}_2\text{O}_7 > \text{SO}_2 > \text{P}_4\text{O}_{10}$ b. $\text{CO}_2 > \text{N}_2\text{O}_5 > \text{SO}_3$
 c. $\text{Na}_2\text{O} > \text{MgO} > \text{Al}_2\text{O}_3$ d. $\text{K}_2\text{O} > \text{CaO} > \text{MgO}$
 (IIT-JEE, 2000)

14. The correct order of radii is
 a. $\text{N} < \text{Be} < \text{B}$ b. $\text{F}^\ominus < \text{O}^{2-} < \text{N}^{3-}$
 c. $\text{Na} < \text{Li} < \text{K}$ d. $\text{Fe}^{3+} < \text{Fe}^{2+} < \text{Fe}^{4+}$
 (IIT-JEE, 2000)

15. Which of the following has the highest boiling point?
 $\text{H}_2\text{O}, \text{H}_2\text{S}, \text{H}_2\text{Se}$ and H_2Te
 a. H_2O because of hydrogen bonding
 b. H_2Te because of higher molecular weight

- c. H_2S because of hydrogen bonding
 d. H_2Se because of lower molecular weight
 (IIT-JEE, 2000)

16. The set representing the correct order of first ionisation potential is
 a. $\text{K} > \text{Na} > \text{Li}$ b. $\text{Be} > \text{Mg} > \text{Ca}$
 c. $\text{B} > \text{C} > \text{N}$ d. $\text{Ge} > \text{Si} > \text{C}$
 (IIT-JEE, 2001)
17. Which of the following represent the correct order of increasing IE_1 for Ca, Ba, S, Se and Ar?
 a. $\text{S} < \text{Se} < \text{Ca} < \text{Ba} < \text{Ar}$ b. $\text{Ba} < \text{Ca} < \text{Se} < \text{S} < \text{Ar}$
 c. $\text{Ca} < \text{Ba} < \text{S} < \text{Se} < \text{Ar}$ d. $\text{Ca} < \text{S} < \text{Ba} < \text{Se} < \text{Ar}$
 (JEE Advanced, 2013)

Assertion Reasoning Type

Read the following questions and answer as per the directions given below:

- a. Statement-I is true; Statement-II is true; Statement-II is the correct explanation for Statement-I.
 b. Statement-I is true; Statement-II is true; Statement-II is not the correct explanation for Statement-I.
 c. Statement-I is true; Statement-II is false.
 d. Statement-I is false; Statement-II is true.
1. **Statement-I:** F atom has a less negative electron affinity than Cl atom.
Statement-II: Additional electrons are repelled more effectively by 3p electrons in Cl atom than by 2p electron in F atom.
 (IIT-JEE, 1998)
2. **Statement-I:** The first ionisation energy of Be is greater than that of B.
Statement-II: 2p-orbital is lower in energy than 2s.
 (IIT-JEE, 2000)

Fill in the Blanks Type

1. The energy released when an electron is added to a neutral gaseous atom is called _____ of the atom.
 (IIT-JEE, 1982)
2. On Mulliken scale, the average of ionisation potential and electron affinity is known as _____.
 (IIT-JEE, 1985)
3. Ca^{2+} has a smaller ionic radius than K^\oplus because it has _____.
 (IIT-JEE, 1993)
4. Compounds that formally contain Pb^{4+} are easily reduced to Pb^{2+} . The stability of the lower oxidation state is due to _____.
 (IIT-JEE, 1997)

True/False Type

1. The softness of group IA metals increases down the group with increasing atomic number.
 (IIT-JEE, 1986)

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2. In group IA of alkali metals, the ionisation potential decreases down the group. Therefore, lithium is a poor reducing agent. (IIT-JEE, 1987)
3. The decreasing order of electron affinity of F, Cl and Br is F > Cl > Br. (IIT-JEE, 1993)
4. The basic nature of the hydroxides of group 13 (III B) decreases progressively down the group. (IIT-JEE, 1993)

Subjective Type

1. Arrange the following in the given order.
 - a. Decreasing ionic size: Mg^{2+} , O^{2-} , Na^+ , F^- (IIT-JEE, 1985)
 - b. Increasing first ionisation energy: Mg, Al, Si, Na (IIT-JEE, 1985)

c. Increasing bond length: F_2 , N_2 , Cl_2 , O_2 (IIT-JEE, 1985)

d. The order of their increasing size:

Cl^- , S^{2-} , Ca^{2+} , Al^{3+} (IIT-JEE, 1986)

2. Explain the following statement:

'The first ionisation energy of carbon atom is greater than that of boron atom, whereas the reverse is true for the second ionisation energy.' (IIT-JEE, 1989)

3. Arrange the following as stated: Increasing order of ionic size
 N^{3-} , Na^+ , F^- , O^{2-} , Mg^{2+} (IIT-JEE, 1991)
4. Arrange the following ions in order of their increasing radii:
 Li^+ , Mg^{2+} , K^+ , Al^{3+} (IIT-JEE, 1997)

ANSWER KEYS

Linked Comprehension Type

Paragraph 1

1. d 2. b 3. c

Paragraph 2

4. c 5. b 6. d 7. c 8. a
9. c 10. b

Paragraph 3

11. d 12. d 13. b 14. b 15. c
16. a

Paragraph 4

17. b 18. a 19. a, b, c, d 20. a, c, d

Paragraph 5

21. c 22. b 23. b, c, d 24. c 25. a, b, c

Matching Column Type

| Q. No. | a | b | c | d | e | f | g |
|-----------|--------|--------|---------|---------|--------|---------|-------|
| 1. | i → q | ii → p | iii → r | — | — | — | — |
| 2. | t | r | q | p | s | — | — |
| 3. | r | p | q | t | s | — | — |
| 4. | ii → r | i → q | iv → p | iii → t | vi → s | vii → u | v → v |
| 5. | r, s | p, r | p, q | p, q | — | — | — |
| 6. | r | p | t | q | s | — | — |
| 7. | r | p | q | s | — | — | — |
| 8. | q | r | s | p | — | — | — |
| 9. | r | s | p | t | — | — | — |
| 10. | q, r | p, s | t | r | u | t | — |
| 11. | r | p | s | q | — | — | — |
| 12. | q, s | p, r | s | r | — | — | — |

Multiple Correct Answers Type

General Electronic Configuration and Periodicity

1. b, c, d 2. a, b, c, d 3. c, d 4. c, d
5. a, b

Atomic and Ionic Radii

6. a, c 7. a, b, d 8. a, b, c, d 9. a, b, c

Effective Nuclear Charge (Z_{eff})

10. a, d

Ionisation Energy (IE)

11. c, d 12. a, b, c 13. a, d 14. a, c
15. b, c 16. a, b 17. c 18. a, b, c
19. a, b, c

Electron Affinity (EA)

20. a, b, c 21. a, b, c

Electronegativity (EN)

22. b, c 23. a, c 24. a, c, d 25. a, b, c
26. a, c

Miscellaneous

27. a, b, c, d 28. a, b 29. b, c 30. a, c, d
31. b, c 32. a, b, c, d 33. a, b 34. a, b
35. a, b, d 36. a, c 37. a, b, d 38. a, b, c
39. a, d 40. a, b, c 41. b, c, d 42. a, b, c
43. a, d 44. a, c, d 45. b, c, d 46. b, c, d
47. b, d

Single Correct Answer Type

General Electronic Configuration and Periodicity

1. b 2. a 3. a 4. c 5. d
6. d 7. c 8. b 9. c 10. d

11. c 12. d 13. a 14. c 15. c
 16. a 17. c 18. b 19. b 20. a
 21. d 22. c 23. a 24. d 25. b

Atomic and Ionic Radii

26. d 27. b 28. a 29. d 30. b
 31. c 32. d 33. a 34. c 35. a
 36. b 37. a 38. c 39. c 40. d

Effective Nuclear Charge (Z_{eff})

41. d 42. c 43. d 44. a 45. d
 46. c

Ionisation Energy (IE)

47. b 48. b 49. b 50. b 51. d
 52. b 53. b 54. c 55. c 56. a
 57. d 58. b 59. c 60. b 61. c
 62. d 63. d 64. b 65. b 66. d
 67. c 68. d 69. a 70. c 71. b
 72. c 73. a 74. a 75. d 76. d
 77. c

Isoelectronic Species

78. b 79. c 80. a 81. a

Metallic–Non-metallic Character

82. d 83. b 84. c

Electron Affinity (EA) and Electron Gain Enthalpy $\Delta_{eg}H^\ominus$

85. c 86. b 87. c 88. a 89. c
 90. c 91. a 92. c 93. d

Electronegativity (EN)

94. a 95. c 96. b 97. b 98. a
 99. b 100. a 101. d 102. d 103. b

Acidic, Basic and Amphoteric Character

104. a 105. a 106. a 107. b 108. d
 109. b 110. c 111. a 112. d 113. d
 114. b

Bond Angle

115. a 116. b 117. c 118. d

Lattice and Hydration Energy

119. a 120. d 121. b 122. a 123. a
 124. c 125. a

Miscellaneous

126. c 127. a 128. c 129. a 130. d
 131. c 132. c 133. b 134. c 135. c

Assertion Reasoning Type

1. c 2. c 3. e 4. c 5. d
 6. d 7. a 8. c 9. a 10. e
 11. c

Integer Type

1. (2) 2. (3) 3. (2) 4. (3) 5. (4)
 6. (1) 7. (3) 8. (4) 9. (5) 10. (6)
 11. (4) 12. (3) 13. (1)

Fill in the Blanks Type

- | | |
|---|--|
| 1. Ununseptium, Uus | 2. Atomic numbers |
| 3. Atomic masses | 4. Actinoids, 90 to 103 |
| 5. Normal or representative | 6. Zero or 18 |
| 7. Mass, volume | 8. Decrease, increase |
| 9. Lower | 10. EN |
| 11. Oxygen | 12. Greater |
| 13. $109^\circ, 28'$ | 14. CO_2 |
| 15. Group 2 | 16. $\text{Si} < \text{P} < \text{C} < \text{N}$ |
| 17. $\text{C} > \text{Be} > \text{B} > \text{Li}$ | 18. Paramagnetic |
| 19. S^{2-} | 20. Lesser |

True/False Type

- | | | | | |
|------|------|------|------|-------|
| 1. T | 2. F | 3. T | 4. T | 5. F |
| 6. F | 7. T | 8. T | 9. F | 10. T |

Archives**Multiple Correct Answers Type**

1. a, c, d 2. a, b 3. d

Single Correct Answer Type

- | | | | |
|-------|-------|-------|-------|
| 1. c | 2. c | 3. a | 4. a |
| 5. c | 6. a | 7. d | 8. b |
| 9. d | 10. b | 11. d | 12. b |
| 13. a | 14. b | 15. a | 16. b |
| 17. b | | | |

Assertion Reasoning Type

1. c. 2. c

Fill in the Blanks Type

1. Electron gain enthalpy
 2. EN
 3. Higher charge density
 4. Inert pair effect

True/False Type

- | | | | |
|------|------|------|------|
| 1. T | 2. F | 3. F | 4. F |
|------|------|------|------|

Subjective Type

1. a. $\text{O}^{2-} > \text{F}^\ominus > \text{Na}^\oplus > \text{Mg}^{2+}$
- b. $\text{Na} < \text{Mg} > \text{Al} < \text{Si}$
- c. $\text{N}_2 < \text{O}_2 < \text{F}_2 < \text{Cl}_2$
- d. $\text{Ca}^{2+} < \text{Ar} < \text{Cl}^\ominus < \text{S}^{2-}$
3. $\text{Mg}^{2+} < \text{Na} < \text{F}^\ominus < \text{O}^{2-} < \text{N}^{3-}$
4. $\text{Al}^{3+} < \text{Mg}^{2+} < \text{Li}^\oplus < \text{K}^\oplus$

HINTS AND SOLUTIONS

Concept Application

Exercise 1.1

- In $3d$, $4d$ and $5d$ series, the differentiating electron enters to $(n-1)d$ -subshell. The maximum capacity of d -subshell is to accommodate 10 electrons. Thus, there are 10 elements each in $3d$, $4d$ and $5d$ series [$(n-1)d^{1-10}$].
- The differentiating electron enters to $(n-2)$ subshell and thus f -block elements are called inner transition elements.
- Transition elements, due to shielding effect acquire almost similar size to last five elements to show horizontal relationship. Vertical relationship is due to similar electronic configuration.
- It is due to diagonal relationship. On moving across a period the charge on the ions increases and the size decreases, causing the polarising power to increase. On moving down a group the size increases and polarising power decreases. On moving diagonally, i.e. from Be to Al these two effects partly cancel each other and so there is no marked change in properties of diagonal elements as shown below:

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

- d -block
 - f -block
 - s -block
 - d -block
 - p -block
6. $K > Mg > Al > B$
7. Isoelectronic species have same number of electrons.

a. Ca^{2+} has $18 e^-$'s ($Z = 20, 20 - 2 = 18 e^-$)

P^{3-} ($Z = 15, 15 + 3 = 18 e^-$)

S^{2-} ($Z = 16, 16 + 2 = 18 e^-$)

Ar ($Z = 18$)

K^{\oplus} ($Z = 19, 19 - 1 = 18 e^-$'s)

Hence, all are isoelectronic with Ca^{2+} .

b. Ne has $10 e^-$'s.

Therefore, the following species are isoelectronic with it.

N^{3-} ($Z = 7, 7 + 3 = 10 e^-$)

O^{2-} ($Z = 8, 8 + 2 = 10 e^-$)

F^{\ominus} ($Z = 9, 9 + 1 = 10 e^-$)

Na^{\oplus} ($Z = 11, 11 - 1 = 10 e^-$)

Mg^{2+} ($Z = 12, 12 - 2 = 10 e^-$)

Al^{3+} ($Z = 13, 13 - 3 = 10 e^-$)

c. Cl^{\ominus} has $18 e^-$'s ($Z = 17, 17 + 1 = 18 e^-$)

Therefore, the following species are isoelectronic with it. P^{3-} , S^{2-} , Ar , K^{\oplus} and Ca^{2+} , all have $18 e^-$'s.

d. Rb^{\oplus} has $36 e^-$'s ($Z = 37, 37 - 1 = 36 e^-$).

Therefore, the following species are isoelectronic with it.

Br^{\ominus} ($Z = 35, 35 + 1 = 36$)

Kr ($Z = 36$)

Sr^{2+} ($Z = 38, 38 - 2 = 36$)

8. a. Mg^{2+}

Both Na^{\oplus} and Mg^{2+} are isoelectronic species with $10 e^-$'s each.

Effective nuclear charge (Z_{eff}) of Mg^{2+} is greater than that of Na^{\oplus} . Hence ionic radius of Mg^{2+} is less than the ionic radii of Na^{\oplus} ion.

b. F^{\ominus}

Both O^{2-} and F^{\ominus} are isoelectronic species with $10 e^-$'s each. Z_{eff} of F^{\ominus} is greater than Z_{eff} of O^{2-} . Hence ionic radius of F^{\ominus} is less than that of O^{2-} ion.

c. P.

Both P and As belong to the same 15 group. P is in the 3rd period and As is in the 4th period. Hence, the atomic size of P is less than that of As.

9. All of them are not isoelectronic species.

So, the smaller the $\left(\frac{\text{Charge}}{\text{No. of electrons}} \right)$ ratio, i.e. $\left(\frac{Z}{e^-} \right)$, the larger is the ionic radii.

For Li^{\oplus} , $\frac{Z}{e^-}$ ratio = $\frac{3}{2} = 1.5$

K^{\oplus} , $\frac{Z}{e^-}$ ratio = $\frac{19}{18} = 1.055$

Mg^{2+} , $\frac{Z}{e^-}$ ratio = $\frac{12}{10} = 1.2$

Al^{3+} , $\frac{Z}{e^-}$ ratio = $\frac{13}{10} = 1.3$

So, the order of decreasing ionic radii is as:

$K^{\oplus} > Mg^{2+} > Al^{3+} > Li^{\oplus}$

10. Atomic masses (i.e. mass numbers).

11. $Z = 107$, General configuration = 2, 18, 18, 32, 13, 2.

Electronic configuration for the last two shells is

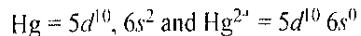
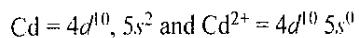
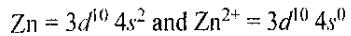
$6s^2 6p^6 6d^6, 7s^2$ i.e. $(n-1)d^5, ns^2$ type.

So, element $Z = 107$ belongs to group 7 and elements

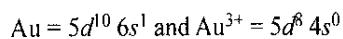
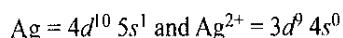
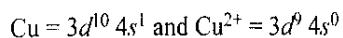
$Z = 108$ and 109 belong to groups 8 and 9 respectively.

12. Transition elements have incomplete d -orbitals. Zn, Cd and Hg are the end members of the first three series of the transition elements. The electronic configuration of Zn, Cd and Hg are represented by general formula $(n-1)d^{10} ns^2$.

Since in these elements and their ions in stable state, the d -orbitals are completely filled hence they do not show general properties of transition elements, e.g.



13. These elements have completely filled d -orbitals but their ions in their stable oxidation state have incomplete d -orbitals. Hence they show general properties of transition elements, e.g.



14. Because of higher exchange energy (i.e. energy released due to exchange of electrons in orbitals of same shell) and symmetry involved in these configuration.

Very Short Answer Type

15. Elements with $Z > 100$ have high densities and are called super heavy elements.

16. Four anomalous pairs (Ar, K), (Co, Ni), (Te, I) and (Th, Pa).

17. Hydrogen (13), alkali metals (6), alkaline earth element (6).

18. p -block elements

19. Carbon (diamond)

20. Mercury (Hg)

21. Tungsten (W)

22. Bromine (Br)

23. Ag and Pb

24. Osmium (Os)

25. Plutonium (Pu)

26. Uranium (U)

27. Francium (Fr)

28. Cesium (Cs)

29. Boron (B)

30. Carbon (C)

31. Iodine (I)

32. Tellurium (Te)

33. Sulphur (S)

34. Fluorine (F) and chlorine (Cl) respectively.

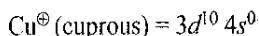
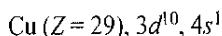
35. Gallium (Ga). Since it has low melting point (29.8°C) and high boiling point.

36. Germanium (Ge). Since it is transparent in the infrared region, hence used in making IR windows, prism and lenses.

Objective Type

37. a. Statement (a) is wrong. The number of transition elements is five (Mn, Fe, Cu, Os, Y).

38. d. Statement (d) is wrong.



Cu^{2+} (cupric) = $3d^9 4s^0$ (one unpaired electron and hence is coloured).

39. c. Triads of group VIII (groups 8, 9 and 10) have approximately the same size, e.g.

Ist triad, Fe, Co, Ni

IIInd triad, Ru, Rh, Pd

IIIrd triad, Os, Ir, Pt

40. a. The more the negative charge, the larger the size of anion.

Moreover along the period (\rightarrow) size of atom decreases.

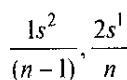
\therefore Size of $\text{O}^\ominus > \text{F}^\ominus$

Size of atom is less than its anion. Hence the order is

$\text{O}^{2-} > \text{O}^\ominus > \text{F}^\ominus > \text{F}$

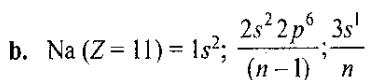
41. d. Moseley found a plot of \sqrt{v} against atomic number (Z) gave a straight line.

42. a. Electronic configuration of Li ($Z = 3$) is



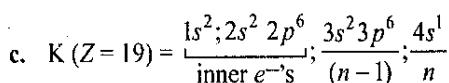
$$(\sigma)_{2s^1} = [0.85 \times \text{No. of electrons in } (n-1)\text{th shell}]$$

$$= 0.85 \times 2 = 1.7$$



$$(\sigma)_{3s^1} = \left[\begin{array}{l} (0.85 \times \text{No. of electrons in } (n-1)\text{th shell}) \\ + 1.00 \times \text{Total no. of electrons} \\ \text{in the inner shell} \end{array} \right]$$

$$= (0.85 \times 8) + (1.00 \times 2) = 8.8$$



$$(\sigma)_{4s^1} = \left[\begin{array}{l} (0.85 \times \text{No. of electrons in } (n-1)\text{th shell}) \\ + 1.00 \times \text{Total no. of electrons} \\ \text{in the inner shell} \end{array} \right]$$

$$= (0.85 \times 8) + (1.00 \times 10) = 16.8$$

d. Rb ($Z = 37$) = $\frac{1s^2; 2s^2 2p^2; 3s^2 3p^6 3d^{10}}{\text{inner } e^- \text{'s}};$
 $\frac{4s^2 4p^6}{(n-1)}; \frac{5s^1}{n}$

$$(\sigma)_{5s^1} = \left[(0.85 \times \text{No. of electrons in } (n-1)\text{th shell}) + (1.00 \times \text{Total no. of electrons in the inner shell}) \right]$$

$$= (0.85 \times 8) + (1.00 \times 28) = 34.8$$

e. Cs ($Z = 55$) = $\frac{1s^2; 2s^2 2p^6; 3s^2 3p^6 3d^{10}; 4s^2 4p^6 4d^{10}}{\text{inner } e^- \text{'s}}$

$$\frac{5s^2 5p^6}{(n-1)}; \frac{6s^1}{n}$$

$$(\sigma)_{6s^1} = \left[(0.85 \times \text{No. of electrons in } (n-1)\text{th shell}) + (1.00 \times \text{Total no. of electrons in the inner shell}) \right]$$

$$= (0.85 \times 8) + (1.00 \times 46) = 52.8$$

43. a. Li ($Z = 3$): $1s^2 2s^1$

$$(\sigma)_{2s^1} = [(0.85 \times \text{No. of electrons in } (n-1)\text{th shell})]$$

$$= 0.85 \times 2 = 1.7$$

b. Be ($Z = 4$) = $1s^2 2s^2$ (one electron is left in $2s$ shell)

$$(\sigma)_{2s^1} = \left[(0.35 \times \text{No. of electrons left in the } n\text{th shell}) + (\text{shell i.e. in } 2s \text{ orbital} + 0.85 \times \text{No. of electrons in } (n-1)\text{th shell}) \right]$$

$$= (0.35 \times 1) + (2 \times 0.85) = 2.05$$

c. B ($Z = 5$) = $1s^2 2s^2 2p^1$

$$(\sigma)_{2p^1} = \left[(0.35 \times \text{No. of electrons left in } n\text{th shell}) + (\text{nth shell} + 0.85 \times \text{No. of electrons in } (n-1)\text{th shell}) \right]$$

$$= (0.35 \times 2) + (0.85 \times 2) = 2.40$$

d. C ($Z = 6$) = $1s^2 2s^2 2p^2$ (one electron in $2p$ and 2 electrons in $2s$ are left)

$$(\sigma)_{2p^1} = \left[(0.35 \times \text{No. of electrons left in } n\text{th shell}) + (0.85 \times \text{No. of electrons in } (n-1)\text{th shell}) \right]$$

$$= (0.35 \times 3) + (0.85 \times 2) = 2.75$$

e. N ($Z = 7$) = $1s^2 2s^2 2p^3$ (two electrons in each $2p$ and $2s$ are left)

$$(\sigma)_{2p^2} = \left[(0.35 \times \text{No. of electrons left in the } n\text{th shell}) + (\text{nth shell} + 0.85 \times \text{No. of electrons in } (n-1)\text{th shell}) \right]$$

$$= (0.35 \times 4) + (0.85 \times 2) = 3.10$$

f. O ($Z = 8$) = $1s^2 2s^2 2p^4$ (three electrons in $2p$ and two electrons in $2s$ are left).

$$(\sigma)_{2p^3} = \left[(0.35 \times \text{No. of electrons left in the } n\text{th shell}) + (0.85 \times \text{No. of electrons in } (n-1)\text{th shell}) \right]$$

$$= (0.35 \times 5) + (0.85 \times 2) = 3.45$$

g. F ($Z = 9$) = $1s^2 2s^2 2p^5$ (four electrons in $2p$ and two electrons in $2s$ are left).

$$(\sigma)_{2p^4} = \left[(0.35 \times \text{No. of electrons left in the } n\text{th shell}) + (0.85 \times \text{No. of electrons in } (n-1)\text{th shell}) \right]$$

$$= (0.35 \times 6) + (0.85 \times 2) = 3.80$$

h. Ne ($Z = 10$) = $1s^2 2s^2 2p^6$ (five electrons in $2p$ and two electrons in $2s$ are left).

$$(\sigma)_{2p^5} = \left[(0.35 \times \text{No. of electrons left in the } n\text{th shell}) + (0.85 \times \text{No. of electrons in } (n-1)\text{th shell}) \right]$$

$$= (0.35 \times 7) + (0.85 \times 2) = 4.15$$

44. a. Zero group, i.e. noble gases

b. Li and Be

c. Na and Mg

d. Li and Mg; Be and Al

e. Fe and Co

f. La and Ce (lanthanides)

g. Np and Pu (with $Z = 93$ and 94 respectively). Z of U = 92.

h. iv. In CrCl_2 , oxidation state of Cr is +2 which is minimum in all the above compounds and hence it will have the maximum radius.

45. This is due to a pair of electrons remaining paired in -ous form and becoming unpaired in -ic, bonding [e.g. Sn, P, Te etc. (*p*-block)].

But in transition elements different number of *d*-electrons may take part in bonding [e.g. Fe^{2+} , Fe^{3+} and Cu^{+} and Cu^{2+} etc.].

46. In Mn_2O_7 , Mn is in +7 oxidation state, i.e. highly electron deficient. So, its tendency to accept electron increases and therefore it is an acidic oxide.

47. In modern periodic table, elements have been placed in order of their increasing atomic numbers (not atomic masses). The atomic number (i.e. Z) of Ar is 18 and that of potassium (K) is 19. Thus, Ar has been placed before potassium.

48. K is an alkali metal with low IE, and thus forms K^+ readily by losing an electron. But in case of Ag, due to imperfect screening effect of inner $4d$ orbitals, the valence electrons are not lost easily. Thus the IE of Ag is very high. That's why Ag is relatively inert.

Concept Application

Exercise 1.2

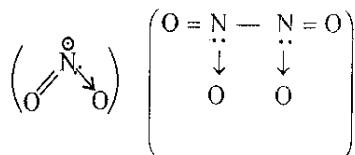
1. a. Inert gas has completely filled orbitals ($ns^2 np^6$) and so does not form bonds.

- b. K ($4s^1$) has low IE and thus possesses strong tendency to lose electron and show strong metallic nature. Whereas Cl ($3s^2 3p^5$) possesses high EA and thus shows more tendency to accept electron and shows non-metallic character.
- c. Metals have low IE and so valence electrons form an ocean of loosely bonded electrons. These loosely bonded electrons are responsible for conduction of current in metals.
- d. I₂ is a violet crystalline solid having metallic lusture and forms ionic compounds like $(CH_3COO)_3I$ in which it forms I³⁺ ion.
- e. Due to imperfect (or poor) shielding effect by the inner 4f and 5d orbitals, the Z_{eff} is increased which increases the attracting ability of incoming electron and hence it has high EA value (i.e. more negative value).
- Electronic configuration of Au (Z = 79) is
 $Au \Rightarrow 1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 5d^{10} 6s^1$
- f. Refer to Section 1.28.1.
- g. Because EA of Cl > F.
- h. Because both Al-O and O-H bond dissociation energies are comparable and hence both can undergo dissociation imparting amphoteric nature
- i. Refer to Section 1.29, Point (3).
- j. $K_{(g)} \rightarrow K_{(g)}^+ + e^- ; IE_1 = x \text{ kJ mol}^{-1}$.
 $K_{(g)}^+ + e^- \rightarrow K_{(g)} ; EA_1 = -x \text{ kJ mol}^{-1}$.
 $K_{(g)}$ is converted to $K_{(g)}^+$ by giving IE_1 . In order to go back to its original state, it will liberate energy equal to $x \text{ kJ mol}^{-1}$, and this is called EA. (IE and EA of the same element are equal in magnitude).
- k. The radii of noble gases are van der Waals radii which are larger than both ionic and covalent radii which is shown by other atoms.

Objective Type

2. b. Small cation has more polarising power. Cation with +3 charge is the smallest.
3. a. Due to the positive charge.
4. b. Due to the small size. All belong to group 1 and the hydration energy decreases down the group.
5. b. Groups 13, 14 and 15 show inert pair effect.
6. d. Refer to Section 1.34.1 (Table 1.25)
7. c. EA is positive due to electron-electron repulsion.
8. c. Due to high charge of +4 on cation, i.e. on Si.
9. d. KBr is ionic and polar compound so it is maximum soluble in highly polar H₂O molecule.

10. a. All of the carbonates are of group 2 element. Lattice energy decreases down the group (↓).
11. d. NO₂ has one unpaired electron while N₂O₄ has paired electrons.



12. c. V (Z = 23) $\Rightarrow 3d^3 4s^2$ ($n = 3$) (n is the number of unpaired electrons) (x).
 $Cr (Z = 24) \Rightarrow 3d^5 4s^1$ ($n = 6$) (y)
 $Mn (Z = 25) \Rightarrow 3d^5 4s^2$ ($n = 5$) (z)
- The more the number of unpaired electrons, the higher is the magnetic moment. So the answer is x < z < y.
13. a. Solubility increases if hydration energy > Lattice energy (for explanation, refer to Section 1.28.1, Point 10(b)).
14. a. Oxygen atom generally has -2 oxidation state (OS). But O has -1 OS (in peroxides and peracids), +1 OS (in O₂F₂) and +2 OS (in OF₂).
In OF₄, OS of O is +4 which is not possible.
15. d. Isoelectronic species does n't have equal size.

16. c.
- a. Both elements belong to group 1.
 - b. Both elements belong to group 2.
 - c. Li is of group 1 element and Mg is of group 2 element, hence different pairs form other pairs.
 - d. Both elements belong to group 13 elements.
17. c. For an ionic compound, EN of Y should be greater than EN of X.

18. a.
- | | Group 1 | 2 | 13 | 14 | 15 | 16 | 17 | 18 | |
|----------------------------|--------------------------|----|-----|---|-------------------------------------|----|----|----|----|
| 3rd Period elements/ | Na | Mg | ... | Al | Si | P | S | Cl | Ar |
| | Forms ionic compound (X) | | | Forms amphoteric oxides (Al ₂ O ₃) | Forms mole-cule (SiO ₂) | | | | |

Hence, the atomic number of (Z) > (Y) > (X).

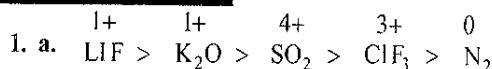
19. a. They are not isoelectronic species. Size of O > size of F, along the 2nd period (→) size decreases. Size of more negatively charged ion is greater than less negatively charged ion and size of neutral atom is greater than positively charged ion. Hence the order is
 $O^{2-} > O^{\ominus} > F^{\oplus} > F$

20. d. Factual statement.

21. a. Apply Fajans' rule, charge on the cation is same and the anion is common in all the compounds, so the size of cation will decide the ionic character or the ionic character down group 2, increases. So, the order is as given in (a).
22. c. The larger the ion, the more is its polarisation.
23. b. N₂ having triple bond will show the smallest bond length while O₂ has double bond, Cl₂ and HCl have single bonds.

Concept Application

Exercise 1.3



Apply Fajans' rule

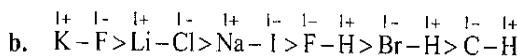
- i. (1) Low charge, (2) large cation and (3) small anion. More is the ionic character.

In LiF and K₂O, charge (+1) is same and size of K⁺ > Li⁺, but size of F⁻ < size of O²⁻.

Hence, LiF is more ionic than K₂O.

- ii. $\text{SO}_2 > \text{ClF}_3$, Although charge on ClF₃ is less than in SO₂. So, ClF₃ should be more ionic than SO₂. But the order is reversed.

This is due to the size of F⁻ < size of O²⁻.



Apply Fajans' rule

Charge (+1) on all the species is same.

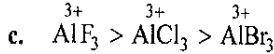
In KF and LiCl, size of K⁺ > size of Li⁺, and size of F⁻ < size of Cl⁻.

In LiCl and NaI, although size of Na⁺ > size of Li⁺ but size of Cl⁻ < size of I⁻.

In NaI and F-H, although size of Na⁺ > size of H⁺ but size of F⁻ < size of I⁻.

In F-H and Br-H, size of F⁻ < size of Br⁻.

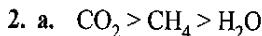
In F-H and C-H, size of F⁻ < size of C⁻.



Apply Fajans' rule

Size of F⁻ < Cl⁻ < Br⁻

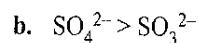
So, AlF₃ is ionic but AlCl₃ and AlBr₃ are covalent.



- i. CO₂ is sp hybridised ($\ddot{\text{O}} = \text{C} = \ddot{\text{O}}$) and is linear, so the bond angle is 180°.

- ii. CH₄ is sp³ hybridised and is tetrahedral so the bond angle is 109.5°.

- iii. H₂O is also sp³ hybridised, but due to two lone pairs it is bent or V-shaped, so the bond angle is 104.5°.



i. SO₄²⁻ is sp³ hybridised $\left(\begin{array}{c} \text{O} \\ || \\ \text{O} - \text{S} - \text{O} \\ || \\ \text{O} \end{array} \right)$, and is tetrahedral so the bond angle is 109.5°.

ii. SO₃²⁻ is also sp³ hybridised $\left(\begin{array}{c} \text{O} \\ || \\ \text{O} - \text{S} - \text{O}^{\cdot} \end{array} \right)$, due to one lone pair, it is pyramidal in shape, so the bond angle is 107°.

3. CaCO₃ reacts with HCl to form CaCl₂ whose lattice energy is greater than hydration energy, so it does not dissolve in water.

4. MgO exists in crystalline state.

Greater the charge density ($\frac{\text{charge}}{\text{size}}$ ratio) on ions the greater is the release of lattice energy. So in MgO, Mg exists as Mg²⁺ and O exists as O²⁻.

$$\begin{aligned} 5. \Delta_{\text{hyd}}\text{H}^\circ(\text{AlCl}_3) &= \Delta_{\text{hyd}}\text{H}^\circ \text{ for } \text{Al}^{3+} + 3 (\Delta_{\text{hyd}}\text{H}^\circ \text{ for } \text{Cl}^{\cdot}) \\ &= -4665 + 3 (-380) \\ &= -5808 \text{ kJ mol}^{-1} \end{aligned}$$

The magnitude of hydration energy of AlCl₃ is greater than IE₁, hence AlCl₃ is ionic in aqueous solution.

6. a. Apply Fajans' rule:

A compound is more ionic if it has (i) large cation, (ii) small anion and (iii) low charge.

Size of Mg²⁺ > Size of Be²⁺

So, MgBr₂ is more ionic.

- b. PbCl₂²⁺ is more ionic than PbCl₄⁴⁺ because of low charge in PbCl₂.

- c. Ag Br is more ionic than AgI (size of Br⁻ < size of I⁻).

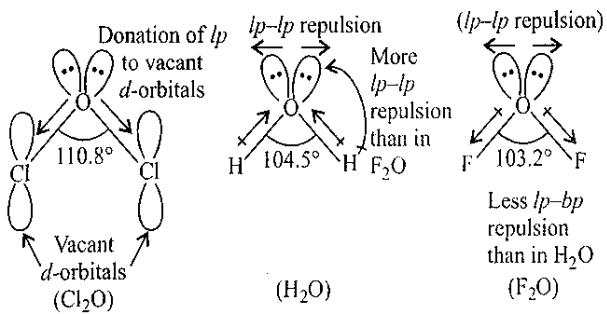
- d. CuO is more ionic than CuS (size of O²⁻ < size of S²⁻)

7. Both NaBr and AgNO₃ are ionic while CBr₄ is covalent.

8. Cu is conducting due to its metallic character while CuSO₄ is conducting in molten or aqueous solution due to the movement of ions (Cu²⁺ and SO₄²⁻ ions).

9. Cl₂O, H₂O and F₂O all are sp³ hybridised (2 bond pairs + 2 lone pairs) having tetrahedral geometry but due to the presence of 2 lone pairs (lp) on oxygen atom, all of them have bent shape or V-shape.

Therefore, the expected angle should be 109.5°. But due to repulsion between lp-lp, lp-bp and bp-bp, the angle varies as shown below:



- a. In case of Cl_2O , delocalisation of lone pair (lp) of electrons of oxygen to the vacant d -orbital of chlorine decreases the repulsion by lp and increases the repulsion between bp (bond pairs). The bond angle thus becomes very large (110.8°).
- b. In case of F_2O , because of more electronegative F atom, bond pairs (bp) of electrons in O–F bond are shifted towards F, whereas in H_2O , bp of electrons are drawn towards oxygen atom. So in F_2O , the bond pairs (bp) being displaced away from the central atom has very little tendency to open the angle (i.e. bp – bp repulsion decreases and lp – lp repulsion closes the angle).

But in H_2O , bp of electrons are closer to each other, and have more bp – bp repulsion than that in F_2O , which opens the angle.

That is why, bond angle of F_2O is less than that of H_2O .

Hence, the bond angle order is $\text{Cl}_2\text{O} > \text{H}_2\text{O} > \text{F}_2\text{O}$.

10. NH_4^+ , CH_4 and $\ddot{\text{N}}\text{H}_3$ all are sp^3 hybridised. In NH_4^+ like CH_4 , there are four bond pairs and no lone pairs. However, $\ddot{\text{N}}\text{H}_3$ has only three bond pairs (bp) and one lone pair (lp), hence its bond angle is less due to lp – bp (lone pair–bond pair) repulsion.

11. Between H and F the EN difference is maximum. Hence, HF is the strongest bond.

12. Electronic configuration of Li is $1s^2 2s^2$ ($n = 2$).

$$E_{\text{Li}} = \frac{(Z^2)_{\text{Li}}}{n^2} \times E_{\text{H}} \Rightarrow Z_{\text{Li}} = n \sqrt{\frac{E_{\text{Li}}}{E_{\text{H}}}}$$

$$= 2 \times \left(\frac{5.4}{13.6} \right)^{\frac{1}{2}} = 1.26 \text{ eV}$$

Z_{eff} of Li is 1.26 eV because $2s$ electrons are shielded by $1s^2$ electrons.

13. a. More is the ionic character, higher is the melting point. Applying Fajans' rule for ionic compounds, both compounds have same charge, same anion and size of cations are also same.

Electronic configuration of K^+ and Ag^+ are

K^+ ($Z = 19$); $1s^2 2s^2 2p^6 3s^2 3p^6 4s^0$ or [Ar] (noble gas core)

Ag^+ ($Z = 47$); [Kr] $4d^{10}$ (pseudo noble gas core)

Pseudo noble gas core forms more covalent character in its compounds due to ineffective shielding of d -orbitals. Hence, KBr is more ionic due to which it has higher melting point.

- b. Apply Fajans' rule, SnCl_2 is ionic and SnCl_4 is covalent. Hence, SnCl_2 is solid whereas SnCl_4 is liquid.

Objective Type

14. a. $\text{O} > \text{F} > \text{N} > \text{C}$

i. $\text{O} (2s^2 2p^4) \xrightarrow{-e^-} \text{O}^+ (2s^2 2p^3) \xrightarrow{-e^-} \text{O}^{2+} (2s^2 2p^2)$

\therefore Stable half-filled
 p -shell,
hence IE_2 is
very high Difficult
to remove
 e^-

ii. $\text{F} (2s^2 2p^5) \xrightarrow{-e^-} \text{F}^+ (2s^2 2p^4) \xrightarrow{-e^-} \text{F}^{2+} (2s^2 2p^3)$

\therefore IE_2 is less
than that of
 O Easily to
remove e^- Stable half-filled
 p -shell

iii. $\text{N} (2s^2 2p^3) \xrightarrow{-e^-} \text{N}^+ (2s^2 2p^2) \xrightarrow{-e^-} \text{N}^{2+} (2s^2 2p^1)$

\therefore Stable half-
filled
 p -shell,
hence IE_1 is
higher than
 O and F IE_2 is
less than
 O and F Easy to
remove
 e^-

iv. $\text{C} (2s^2 2p^2) \xrightarrow{-e^-} \text{C}^+ (2s^2 2p^1) \xrightarrow{-e^-} \text{C}^{2+} (2s^2 2p^0)$

\therefore IE_2 is
less than
 O , F and N Very
easy
to remove
 e^- Very
stable
configur-
ation

Hence order of IE_2 is

$\text{O} > \text{F} > \text{N} > \text{C}$

15. d. $\text{Li} = 1s^2 2s^1$, $\text{Be} = 1s^2, 2s^2$, $\text{B} = 1s^2, 2s^2, 2p^1$, $\text{C} = 1s^2, 2s^2 2p^2$.

Be is highly stable due to filled s -orbitals, therefore Be^+ is highly unstable.

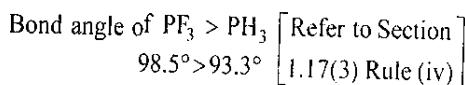
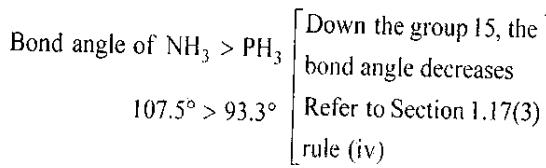
16. c. In the outermost orbit of Pb both s -subshell and p -subshell have two electrons. Due to the inert pair effect s -subshell electrons are unable to take part in bonding.

1.150 Inorganic Chemistry

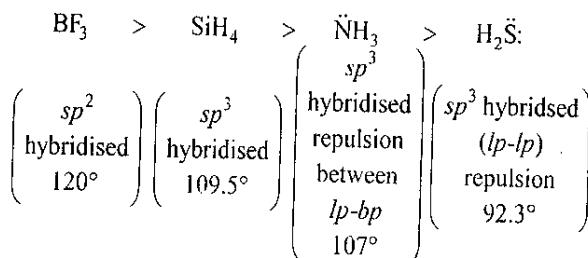
17. a. [Ne] $3s^2 3p^3$ has half-filled p -orbital.

18. b. Lattice energy is directly proportional to charge density ($\frac{\text{Charge}}{\text{Size}}$ ratio), i.e. high charges on the ions, and small sizes of the ions.

19. a.



20. b.



21. a. Bond angle decreases down the group 16.

[Refer to Section 1.17, Point 3, rule (i)]

Multiple Correct Answers Type

22. (a, b, c)

BeBr_2 is covalent, others are ionic and in fused state. BeBr_2 exists in polymeric state.

23. (a, b)

The oxidation state of Be and Sn in BeCl_2 and SnCl_4 are +2 and +4 respectively. Due to the small size of cations the polarising power of cations is very high and thus they are covalent.

24. (a, b, c)

a. $\text{HS}_6 \Rightarrow 1 + 6x = 0 \therefore x = -1/6$

Hence, the oxidation state of S cannot be $-1/6$.

b. $\text{HPO}_4 \Rightarrow 1 + x - 8 = 0 \therefore x = 8$

Hence, the oxidation state of P cannot be 7.

c. Due to more polarisation of electrons in FeI_3 , I^\ominus reduces Fe^{3+} , therefore FeI_3 is not possible.

d. The oxidation state of Cl in HClO_4 is +7. Hence, HClO_4 exists.

25. (a, b, c)

a. Pseudo inert gas configuration has more Z_{eff} .

b. A stable ion must have inert gas configuration.

c. Covalent character is inversely proportional to dipole moment.

d. Ionic character is directly proportional to dipole moment.

26. (b, c, d)

a. As^{5+} is stable, but Sb^{3+} and Bi^{3+} are more stable than $+5$ OS.

b. Due to inert pair effect, TI^\oplus is more stable than Tl^{3+}
 $\text{TI}^{3+} + 2e^- \rightarrow \text{TI}^\oplus$ (reduction acts as oxidising agent)
Hence, TI^\oplus acts as oxidising agent.

c. For the same reason Ga^{3+} is more stable than Ga^\oplus .

d. Pb^{2+} is more stable than Pb^{4+} , due to inert pair effect.
So, Pb^{4+} salts are better oxidising agents.

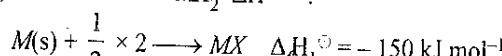
Integer Type

27. 6th Period.

Number of elements in periods 1, 2, 3, 4, 5 and 6 are 2, 8, 8, 18, 18, 32 respectively.

28. $Z = 7$, Element is nitrogen.

29. (3) $2\text{MX} \rightarrow M + \text{MX}_2 \Delta H^\ominus = ?$



$$\therefore \Delta H^\ominus = \Delta H_2^\ominus - 2 \Delta H_1^\ominus$$

$$= -600 - (2 \times 150) = -300 \text{ kJ mol}^{-1}$$

$$\therefore -100x = -300$$

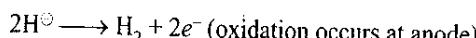
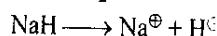
$$\therefore x = 3$$

Assertion Reasoning Type

30. c. IE_1 of Mg $> \text{IE}_1$ of Al. Assertion is correct.

Correct reason: It is easier to remove an electron from $3p$ orbital than from $3s$ orbital (due to penetration effect).

31. d. **Correct assertion:** s-block elements form ionic hydrides but gives H_2 gas at anode, e.g.



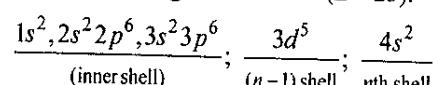
Reason is correct.

Linked Comprehension

• Type

Paragraph 1

1. d. Electronic configuration of Mn ($Z = 25$).



$$(\sigma)_{4s} = \left[(0.35 \times \text{No. of electrons in the } n \text{ th shell}) + (0.85 \times \text{No. of electrons in } (n-1) \text{ th shell}) + (1.00 \times \text{Total no. of electrons in the inner shell}) \right]$$

$$= (0.35 \times 1) + (0.85 \times 5) + (1.00 \times 18)$$

$$= 22.6$$

2. b. Statement (b) is wrong.
 3. c. Statement (c) is wrong. IE_1 of group 3 element is less than that of group 2 elements due to penetration effect.

Paragraph 2

4. c. First transition element series, i.e. $3d$ -block starts from $Z = 21$ to $Z = 30$.
 Second transition element series, i.e. $4d$ -block starts from $Z = (21 + 18) = 39$ to $Z = (30 + 18) = 48$.
 So, the element with $Z = 39$ belongs to d -block.
 5. b. $Z = 113$ means group 13, and it is in p -block, and 7th period. Therefore, electronic configuration is $7s^2 7p^1$.
 6. d. From $Z \geq 121 \leq 138$, the filling up of g -orbitals begins for which there is no provisions in the present form of the periodic table.
 7. c. Magic numbers are 2, 8, 8, 18, 18 and 32 with $n = 1, 2, 3, 4, 5$ and 6 respectively.

| n | No. of electrons |
|-----|------------------|
| 1 | 2 |
| 2 | $2 + 8 = 10$ |
| 3 | $10 + 8 = 18$ |
| 4 | $18 + 18 = 36$ |
| 5 | $36 + 18 = 54$ |

8. a. Refer to solution of Question 13, part (n) of Illustration 1.81.
 $\text{Li} (Z = 3) = 2s^1$
 $\text{Li}^\ominus = 2s^2$ (stable configuration and most stable)
 9. c. Last element of the p -block is Rn with $Z = 86$, group 18, period 6.
 Therefore, its valence electronic configuration is $6s^2 6p^6$.
 10. b. g -orbital will start with $Z = 121$.
 Since g -orbitals will contain $18 e^-$'s. So, it will end at $(121 + 17) = 138$ (because the element with $Z = 121$ is also included in calculation).

Paragraph 3

11. d. $F > \underset{\substack{\uparrow \\ \text{exception}}}{\text{N}} > O > C$ $\left[\begin{array}{l} \text{IE}_1 \text{ of N} > \text{IE}_1 \text{ of O due} \\ \text{to half-filled orbitals} \end{array} \right]$
 12. d. Along the period
 IE increases \rightarrow
Down the group
 (\downarrow) IE decreases \downarrow

| Group 13 | Group 14 |
|----------|----------|
| Ga | Ge |
| In | Sn |

So, Ge has the highest IE of 762 kJ mol^{-1} .

13. b. II, III and IV are isoelectronic species.
 (Refer to solution of Question 80 (Single Correct Answer Type)).

14. b. $\text{IE}_2 > \text{IE}_1$. Therefore, answer can be (b) or (d).

But both Be and Sr belong to group 2; and IE decreases down the group (\downarrow) so answer is (b).

Paragraph 4

15. c.
- $[\text{He}] 2s^2 2p^3$ corresponds to $1s^2, 2s^2 2p^3 (Z = 7)$ and element is N (group 15 and 2nd period).
 - $[\text{He}] 2s^2 2p^4$ corresponds to $1s^2, 2s^2 2p^4 (Z = 8)$ and element is O (group 16 and 2nd period).
 - $[\text{Ne}] 3s^2 3p^1$ corresponds to $1s^2, 2s^2 2p^6, 3s^2 3p^1 (Z = 13)$ and element is Al (group 13 and 3rd period).
 - $[\text{Ar}] 3d^{10}, 3s^2 3p^1$ corresponds to $Z = 18 + 10 + 3 = 31$ and the element is Ga (group 13 and 4th period).
 $\therefore \text{IE}_1$ of Ga (579 kJ mol^{-1}) $\approx \text{IE}_1$ of Al (577 kJ mol^{-1}).
 This is due to the imperfect shielding of $3d$ orbitals in Ga.

16. a. $\text{IE}_4 > \text{IE}_3 > \text{IE}_2 > \text{IE}_1$

Paragraph 5

17. b. Factual statement.
 18. a. Factual statement.
 19. a, b, c, d
- In (b), (c) and (d), all are exceptional cases.
 This is due to the small sizes of B, N and O in comparison to the sizes of Al, P and S respectively, similar to exceptional case of Cl and F ($\Delta_{eg} H^\ominus$ of Cl $>$ F). (Refer to Section 1.15.5, Part (c), exception II).
 20. a, c, d. Refer to Section 1.15.6.

Paragraph 5

21. c. S^{2-} have the largest size among the given isoelectronic ions, so it has the lowest IE_1 .
 22. b. Since size of M $>$ M^\oplus (135 pm) and that of X $<$ X $^\ominus$ (135 pm), therefore answer (b) is correct.
 23. b, c, d.
- Mg^{2+} and Al^{3+} are isoelectronic, so their ionic sizes will be different.
 $\text{Mg}^{2+} = 65$ and $\text{Al}^{3+} = 50 \text{ pm}$
 So, the answer which have same sizes are b, c and d.
 - $\text{K}^\oplus = 133 \text{ pm}$, and $\text{F}^\ominus = 136 \text{ pm}$, nearly the same size.
 - $\text{Li}^\oplus = 60 \text{ pm}$, and $\text{Mg}^{2+} = 65 \text{ pm}$, nearly the same size due to diagonal relationship.
 - $\text{Rb}^\oplus = 148 \text{ pm}$, and $\text{O}^{2-} = 140 \text{ pm}$, nearly the same size.

Note: To solve such tricky questions, it is advised to check the isoelectronic species only because they will have different sizes and others may have same size.

24. c. Refer to solution of Question 2 (r) of Illustration 1.81.

25. a, b, c.

For (a) and (b), refer to Section 1.14 (iii). For (c), refer to Section 1.15.1.

$$\text{d. } C_p = \frac{5}{2}R \text{ and } C_v = \frac{3}{2}R.$$

Matching Column
Type

| Q. No. | a | b | c | d | e | f | g |
|-----------|--------|--------|---------|---------|--------|---------|-------|
| 1. | i → q | ii → p | iii → r | — | — | — | — |
| 2. | t | r | q | p | s | — | — |
| 3. | r | p | q | t | s | — | — |
| 4. | ii → r | i → q | iv → p | iii → t | vi → s | vii → u | v → v |
| 5. | r, s | p, r | p, q | p, q | — | — | — |

5. a. (a → r, s)

i. Atomic size of Ar > Cl (in Ar, van der Waals radii) and (in Cl, covalent radii)

ii. IE of Ar > Cl (due to the stable configuration in Ar)

iii. EA and EN of Cl > Ar. Hence, answers are r, s.

b. (b → p, r)

i. Size of S > O (S is in 3rd period and O is in 2nd period of same group 16)

Therefore, 'p' is correct.

ii. IE of O > S (Down the group IE decreases)

Therefore, 'q' is wrong.

iii. EA of O should be greater than S (since down the group EA decreases). But here is exception, due to very small size of O than S. (Same explanation as in EA of Cl > F)

Therefore, 'r' is correct.

iv. EN decreases down the group. Therefore, 's' is wrong).

Hence answers are 'p' and 'r'.

c. (p, q)

i. Size of Mg > Al (size decreases along the period). Therefore, 'p' is correct.

ii. IE of Al should be greater than Mg. But IE of Mg > Al due to penetration effect.

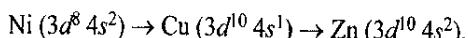
Therefore, 'q' is correct.

iii. Both EA and EN increase along the period.

Therefore, 'r' and 's' are wrong.

d. (p, q)

i. Size of 3d transition series decreases and then increases from



[See Fig. 1.6 (c)]

This is due to repulsion between electrons of fully filled configuration in Zn than Cu.

Therefore, 'p' is correct.

ii. Due to stable fully filled ($3d^{10} 4s^2$) configuration of Zn than Cu ($3d^{10} 4s^1$), IE of Zn > Cu.

Therefore, 'q' is correct.

iii. Both EA and EN increase along the period.

Therefore, 'r' and 's' are wrong.

6. (a → r; b → p; c → t; d → q; e → s)

(a → r), Fe ($Z = 26$) ... $3d^6 4s^2$,

$$\text{Fe}^{3+} = 3d^5, n = 5, \mu_{MM} = \sqrt{5(5+2)} = \sqrt{35} \text{ BM}$$

$$(\text{b} \rightarrow \text{p}), \text{Fe}^{2+} = 3d^6, n = 4, \mu_{MM} = \sqrt{n(n+2)} \text{ BM}$$

$$= \sqrt{4(4+2)} = \sqrt{24} \text{ BM}$$

$$(\text{c} \rightarrow \text{t}), \text{Ti} (Z = 22), \dots 3d^2 4s^2, \text{Ti}^{3+} = 3d^1, n = 1$$

$$\mu_{MM} = \sqrt{3} \text{ BM}$$

$$(\text{d} \rightarrow \text{q}), \text{Ni} (Z = 28), \dots 3d^8 4s^2, \text{Ni}^{2+} = 3d^8, n = 2$$

$$\mu_{MM} = \sqrt{8} \text{ BM}$$

$$(\text{e} \rightarrow \text{s}), \text{Sc} (Z = 21), \dots 3d^1 4s^2, \text{Sc}^{3+} = 3d^0, n = 0$$

$$\mu_{MM} = \text{zero BM}$$

7. (a → r; b → p; c → q; d → s)

[Refer to Section 1.16.3 (5)]

8. (a → q; b → r; c → s; d → p)

Factual statement.

9. (a → r; b → s; c → p; d → t)

(a → r)

Along the period metallic character decreases (\rightarrow).

Therefore, metallic character of Na > Mg > Al (3rd period)

But down the group the metallic character increases (\downarrow).

Therefore, metallic character of Al > B (Group 13). Hence order is: Na > Mg > Al > B [\therefore r is correct]

Note the metallic character series is remembered as:

PSBC MAZINTL CHAAP

(b → s)

Along the period the non-metallic character increases (\rightarrow).

Therefore, the non-metallic character order is

F > N > C > B (2nd period)

But down the group the non-metallic character decreases (\downarrow).

Hence, the non-metallic character of B (group 3, 2nd period) > Si (group 4, 3rd period). Hence option (s) is correct (F > N > C > B > Si)

(c → p)

Along the period, oxidising character increases (\rightarrow).

Therefore, oxidising power of F > O > N (2nd period).

But down the group, oxidising character decreases (\downarrow).

Thus, F is strong oxidising agent than Cl. Further because O is more EN than Cl, therefore O is a stronger oxidising agent than Cl.

Hence the oxidising power is $F > O > Cl > N$.

Option 'p' is correct.

(d \rightarrow t) IE_1 increases along a period but decreases down a group.

| Group | 13 | 14 |
|------------|----|----|
| 2nd period | B | C |
| 3rd period | Al | Si |

Thus C has the highest IE_1 . Therefore, option 't' is correct.

10. (a \rightarrow q, r; b \rightarrow p, s; c \rightarrow t; d \rightarrow r)

e \rightarrow u, f \rightarrow t [Refer to Section 1.34.]

11. (a \rightarrow r; b \rightarrow p; c \rightarrow s; d \rightarrow q)

[Refer to Section 1.41.]

12. (a \rightarrow q, s; b \rightarrow p, r; c \rightarrow s; d \rightarrow r)

[Refer to Section 1.41.]

Multiple Correct Answers Type

General Electronic Configuration and Periodicity

1. Statements (b, c and d) are correct.

a. False. This law was based on atomic masses of the elements.

2. All statements (a, b, c and d) are correct.

b. s-block elements can undergo oxidation easily (i.e. strong reducing nature) because of low IE.

Thus reducing nature increases from the right to the left (\leftarrow) in a period.

3. Statements (c and d) are correct.

a. False. All the transuranium elements from 94 to 102 are man made.

b. False. Zero group elements are diamagnetic because of the presence of paired electrons.

c. True. Group 3, the total contains f-block elements also. Total elements = $4 + 14 + 14 = 32$.

| | Group 3 | Total no. of elements | |
|-----------------------|------------|-----------------------|--------|
| 3d Transition element | 4th Period | Sc (Z = 21) | 1 |
| 4d Transition element | 5th Period | Y (Z = 39) | 1 |
| 5d and 4f -block | 6th Period | 57–71 Lanthanides | 14 + 1 |
| 6d and 5f -block | 7th Period | 89–103 Actinides | 14 + 1 |
| | | | 32 |

- d. Statement (d) is correct.

4. Statements (c and d) are correct.

Statement (a) is false. Except zero and VIII groups, all other groups (I to VII) are subdivided.

Statement (b) is false. The position of element is linked with its electronic configuration in the extended form of the periodic table.

Statement (c) is true. General electronic configuration of s-block elements is ns^{1-2} .

Statement (d) is true and it is a conceptual fact.

5. Statements (a and b) are correct.

a. Learn it as a fact.

| Group | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 |
|------------|---------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|----|
| 7th Period | Z = 104 | 105 | 106 | 107 | 108 | 109 | 110 | 111 | 112 | 113 | 114 | 115 | 116 | 117 | 118 | |
| 89 to 103 | 103 | | | | | | | | | | | | | | | |

b. Statement (b) is correct and all the transition elements are paramagnetic (except Zn, Cd and Hg i.e. they have filled d-orbitals)

c. False. Maximum number of elements present in 6th period are:

s-block = 2, d-block = 10, f-block = 14, p-block = 6, Total = 32 elements

d. False. Except 1st period (H), every period starts with a member of alkali group.

Atomic and Ionic Radii

6. (a, c)

a. Size of negative ion > parent neutral atom > size of positive ion

c. Size of neutral parent atom > size of less positive ion > size of more positive ion

7. (a, b, d)

Conceptual fact.

8. (a, b, c, d)

Refer to solution of Question 35 (Single Correct Answer Type)

9. (a, b, c)

Conceptual fact as explained in Question 6 above.

c. Size of Ln and Ln^{3+} decreases with increasing Z, due to lanthanide contraction.

Effective Nuclear Charge (Z_{eff})

10. (a, d)

Conceptual fact.

Ionisation Energy (IE)

11. (c, d)

a. False. $IE_3 >> IE_2 > IE_1$

Successive IE's are always higher as the force of attraction increases towards nucleus due to lesser number of electrons.

- b. False. More energy is required to remove an electron from an atom which has stable (half-filled or full filled) electronic configuration.
- c and d. True. Due to penetration effect.

12. (a, b, c)

Conceptual fact.

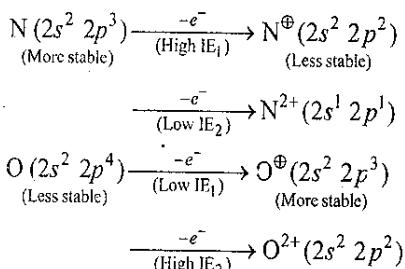
13. (a, d)

- a. True. IE_1 of Be > IE_1 of B, due to penetration effect.
- d. True. IE_1 of N > IE_1 of O, due to half-filled configuration in N.

14. (a, c)

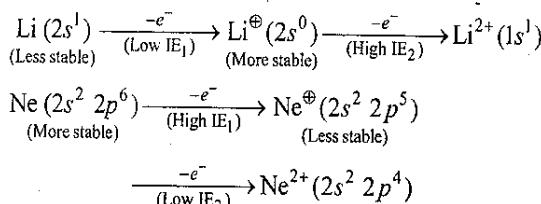
- a. True. IE_1 of N > IE_1 of O, due to half-filled configuration in N.

- b. False.



Hence, IE_2 of O > IE_2 of N

- c. True.



$\therefore \text{IE}_2$ of Li > IE_2 of Ne

- d. False.

IE of Ca > IE of Al, due to stable configuration in Ca ($4s^2$) than in Al ($3s^2 3p^1$).

15. (b, c)

There is a larger jump in the IE_6 to IE_7 , so removal of 7th electron is very very difficult.

Hence, the oxidation state of the neutral atom can be +6 or $(6 - 8) = -2$.

16. (a, b)

Conceptual fact.

17. (c) [Refer to Point 23(c) in the section Overview]

In case of transition elements, IE_1 first decreases from $3d$ series to $4d$ series (i.e. Cu > Ag), due to increase in size from Cu to Ag.

Then IE_1 increases from $4d$ series to $5d$ series (i.e. Au > Ag) due to imperfect screening effect of $4f$ -orbitals in Au. Thus IE_1 of Cu > Ag < Au.

18. (a, b, c)

Conceptual fact.

19. (a, b, c)

Conceptual fact.

Electron Affinity (EA)

20. (a, b, c)

Conceptual fact.

- d. False. The order of EA is Cl > F > Br.

21. (a, b, c)

Addition of the first electron to a gaseous neutral atom involves release of energy, whereas addition of the second electron involves absorption of energy.

Electronegativity (EN)

22. (b, c)

Conceptual fact. (Refer to Section 1.27.2.)

23. (a, c)

$$\text{a. EN} = \frac{\text{IP} + \text{EA}}{2} \text{ in eV atom}^{-1}.$$

- b. False, the maximum EN is shown by F.

- c. True, conceptual fact.

24. (a, c, d)

Refer to the section Overview, Point 31 (b).

25. (a, b, c)

Refer to the section Overview, Point 31 (a and b).

26. (a, c)

Refer to the section Overview, Point (29).

Miscellaneous

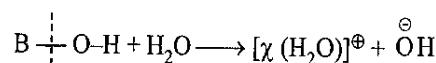
27. (a, b, c, d)

All are properties of transition elements.

28. (a, b)

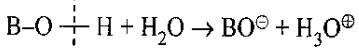
Refer to Section 1.16.4.7, Point (2).

- a. If $\chi_O - \chi_B > \chi_O - \chi_H$, compound BOH will be basic, then B–O bond will be more polar than O–H bond and hence ionisation of BOH molecule in aqueous solution will take place at B–O bond and $\overset{\ominus}{\text{OH}}$ will be formed.



- b. If $\chi_O - \chi_B < \chi_O - \chi_H$, compound BOH will be acidic, then O–H bond will be more polar than B–O bond and hence ionisation of BOH molecule in aqueous solution

will take place at O-H bond and $\text{H}_3\text{O}^\oplus$ ions will be formed.



29. (b, c)

- a. Hg (derived from the word Hergentum) is not radioactive.
- b. Np (Neptunium, $Z=93$) is radioactive and named after the name of a planet.
- c. Pu (Plutonium, $Z=94$) is also radioactive and named after the name of a planet.
- d. Ra (Radium, $Z=88$) is also radioactive but not named after the name of any planet.

30. (a, c, d)

Conceptual fact.

31. (b, c)

Cl ($Z=17$, Aw = 35), No. of e^- 's = 17

No. of proton = 17

No. of neutrons = 18

Cl^\ominus ($Z=17$, Aw = 35), No. of e^- 's = $17 + 1 = 18$

No. of protons = 17

No. of neutrons = 18

32. (a, b, c, d)

Refer to Section 1.34.1 (Table 1.26).

33. (a, b)

Apply Fajans' rule (low charge, large cation, small anion and hence more ionic)

a. $\text{Na}^{+1} \text{Cl} > \text{Mg}^{+2} \text{Cl}_2 > \text{Al}^{+3} \text{Cl}_3$ (Check the charges)

b. $\text{LiF} > \text{LiCl} > \text{LiBr} > \text{LiI}$ (Check the sizes of anion)

34. (a, b)

Refer to Section 1.31.1, Point 2 (a to e).

35. (a, b, d)

Carbides of metals (e.g. Ca, Al and Be) are ionic whereas non-metals and metalloids (e.g. Si) are covalent.

36. (a, c)

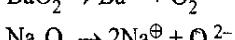
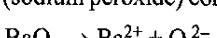
Conceptual fact.

37. (a, b, d)

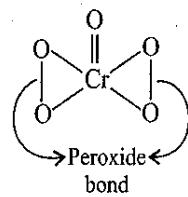
Refer to Section 1.27.2.

38. (a, b, c)

a and b. Both BaO_2 (barium peroxide) and Na_2O_2 (sodium peroxide) contain O_2^{2-} (peroxide ion)



c. CrO_5 (chromium pentaoxide), a compound which have butterfly structure also have peroxide linkage as shown:



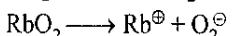
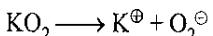
d. It is an oxide.

39. (a, d)

The compounds containing superoxide ion (O_2^\ominus) are paramagnetic and coloured, due to the presence of one unpaired electron. They have three electron bond, as shown:



KO_2 and RbO_2 are superoxides.

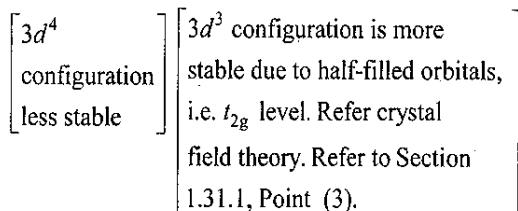
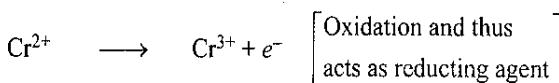


40. (a, b, c)

The variability of oxidation states (OS), a characteristic of transition elements (TE) arises out of incomplete filling of d -orbitals in such a way that their OS differ from each other by unity.

Cr is most stable in +3 and 6 OS.

Lower oxidation states of TE forms mostly ionic compounds. Cr ($Z=24$) $\Rightarrow 3d^5 4s^1$, $\text{Cr}^{2+} \Rightarrow 3d^4$



41. (b, c, d). Fact.

42. (a, b, c). Fact.

43. (a, d)

According to electronic configuration, the element is Cr ($Z=24$).

Valence electronic configuration of Cr in ground state = [Ar] $3d^4 4s^1$.

Valence electronic configuration of Cr in excited state = [Ar] $3d^5 4s^1$.

44. (a, c, d)

a. $\text{K}^\oplus (19 + 1 = 18 e^-)$, $\text{Ca}^{2+} (20 - 2 = 18 e^-)$, $\text{Sc}^{3+} (21 - 3 = 18 e^-)$, $\text{Cl}^\ominus (17 + 1 = 18 e^-)$

Hence isoelectronic.

b. Not isoelectronic: $\text{Zn}^{2+} (30 - 2 = 28 e^-)$, $\text{Ca}^{2+} (20 - 2 = 18 e^-)$, $\text{Ga}^{3+} (31 - 3 = 28 e^-)$, $\text{Al}^{3+} (13 - 3 = 10 e^-)$

1.156 Inorganic Chemistry

- c. Isoelectronic: Ti^{4+} ($22 - 4 = 18 e^-$), Ar ($Z = 18 e^-$), Cr^{6+} ($24 - 6 = 18 e^-$), V^{5+} ($23 - 5 = 18 e^-$)
 - d. Isoelectronic: P^{3-} ($15 + 3 = 18 e^-$), S^{2-} ($16 + 2 = 18 e^-$), Cl^{\ominus} ($17 + 1 = 18 e^-$), K^{\oplus} ($19 - 1 = 18 e^-$)
45. (b, c, d) are correct and factual statement.
In (a), IE_1 order should be $\text{N} > \text{O} > \text{C} > \text{B}$.
46. (b, c, d) are correct and factual statement.
In (a), basic strength order should be

$$\ddot{\text{N}}\text{H}_3 > \ddot{\text{P}}\text{H}_3 > \ddot{\text{A}}\text{sH}_3 > \ddot{\text{BiH}}_3$$
 Basic strength of the hydrides of group 15 decreases down the group (\downarrow).
 Due to small size of N, lone pair electron density on N is very high, so it can donate lone pair electrons very effectively. Therefore as the size of the central atom increases the basic strength decreases.
47. (b, d)
 b. Due to $p\pi-p\pi$ back bonding, BF_3 is the strongest Lewis acid as compared to BCl_3 and BBr_3 . B-F bond is shorter in length causing it to be more stronger.
 In CF_4 , there is no such back bonding possible as there is no vacant p -orbital in cation.
 d. Due to strong $p\pi-p\pi$ back bonding in BF_3 , ($2p-2p$ overlap) its electron deficiency is less, so it is the weakest Lewis acid. Hence, the order of Lewis acid is

$$\text{BBr}_3 > \text{BCl}_3 > \text{BF}_3$$
 $(2p-4p)(2p-3p)(2p-2p)$ overlap.

Single Correct Answer Type

General Electronic Configuration and Periodicity

1. b. Factual statement.
2. a. Newlands arranged the elements in increasing order of their atomic weights and noted that every eighth element had properties similar to the first element (see Table 1.2).
3. a. Metals (groups 1 and 2) have ns^2 configuration.
4. c. Factual statement.
5. d. s- and p-block elements are called representative elements.
6. d. Factual statement.
7. c. Factual statement.
8. b. Non-metals are placed in p-block.
9. c. Factual statement.
10. d. $\text{Cl} = 3s^2 3p^5$, $\text{Cl}^{\ominus} = 3s^2 3p^6$, $\text{Ar} = 3s^2 3p^6$
11. c. Factual statement.
12. d. Factual statement.

| | s-block | | p-block | | | | | |
|------------|---------|----|---------|----|----|----|----|----|
| 3rd Period | 1 | 2 | 13 | 14 | 15 | 16 | 17 | 18 |
| | Na | Mg | Al | Si | P | S | Cl | Ar |

13. a.
14. c. Due to diagonal relationship. Be (group 2), Al (group 13).
15. c. Factual statement.
16. a. Group 2. Li ($Z = 4$), Mg ($Z = 12$), Ca ($Z = 20$), Sr ($Z = 38$), Ba ($Z = 56$), Ra ($Z = 88$)
17. c. Factual statement.
18. b. ns^1 to ns^2 (s-block) and np^6 (p-block) are called representative elements.
19. b. Factual statement.
20. a. Factual statement.
21. d. Factual statement.
22. c. Factual statement.
23. a. U ($Z = 92$, Aw = 238) is the heaviest element among the given elements.
24. d. Order of screening effect is $s > p > d > f$.
25. b. Group 1 elements with ns^1 configuration are more electropositive (EP) than group 2 (ns^2) configuration. Moreover, EP character increases down the group 1 (\downarrow).
 So, Cr ($6s^1$) is the most EP element.

Atomic and Ionic Radii

26. d. Down the group 2, size of dipositive ions, increases.
27. b. Size of negative ion $>$ neutral atom $>$ positive ion of the parent element.
28. a. For the isoelectronic species, positive ion species have smallest size.
29. d. Same solution as in Question 32 below.
30. b. Ne, O and F are of 2nd period elements whereas Cl is of 3rd period. Hence have large van der Waals radii.
31. c. C and N are of 2nd period element. Size decreases from C to N. Therefore, size of N $<$ C.
 P and S are of 3rd period elements. But size of P $>$ S [opposite to the expected trend, i.e. size of S $>$ P].
 Because P has half-filled stable configuration.
 Increase of one electron in S causes repulsion between paired electrons ($3s^2 3p_x^2 3p_y^1 3p_z^1$) and thus size of S is slightly increases from P to S.
 Moreover, size of 3rd period elements is greater than that of 2nd period.

Hence the correct order of sizes is

$$\frac{\text{P} > \text{S}}{\text{3rd period}} > \frac{\text{C} > \text{N}}{\text{2nd period}}$$

32. d. Along the period (\rightarrow), size decreases. But size of noble gases is slightly greater than the preceding element

(i.e. halogens) due to repulsion between all paired electrons ($sn^2 np^6$)

Hence the answer is (d).

33. a. Be^{2+} ion is of 2nd period, whereas Mg^{2+} and Na^+ ions are of 3rd period. Size of 3rd period ions is greater than that of 2nd period. Moreover, more positive charge have lesser size. Therefore, order of sizes is

$$\frac{\text{Be}^{2+}}{\text{2nd period}} < \frac{\text{Mg}^{2+}}{\text{3rd period}} < \text{Na}^+$$

34. c. Na, K and Rb are of group 1 elements and size increase down the group 1 elements (\downarrow).

Na and Mg are of group 1 and 2 elements respectively but both belong to 3rd period. Along the period size decreases (\rightarrow), i.e. size of Na $>$ Mg.

Hence the order of sizes is

| | |
|--------------------------------------|--------------|
| $\text{Rb} > \text{K} > \text{Na} >$ | Mg |
| group 1 | group 2 |
| \Downarrow | \Downarrow |
| Period \Rightarrow 5 | 4 3 3 |

35. a. Refer to Fig. 1.6 (c).

Due to the consequence of lanthanide contraction

Size of Zr = size of Hf

Size of Nb = size of Ta

Size of Mo = size of W

Size of Co = size of Ni (due to imperfect screening effect of $3d$ orbitals)

| Group \Rightarrow | 4 | 5 | 6 |
|------------------------|----|----|----|
| Period \Rightarrow 5 | Zr | Nb | Mo |
| Period \Rightarrow 6 | Hf | Ta | W |

36. b. Factual statement.

37. a. F and Ne belong to the same 2nd period. Size of inert gases is slightly greater than the preceding halogens, due to repulsion between paired electrons ($ns^2 np^6$).

\therefore Size of Ne $>$ size of F ($1.60 \text{ \AA} > 0.72 \text{ \AA}$)

Same explanation as in Question 29 and Question 32 above.

38. c. Factual statement.

39. c. Factual statement.

40. d. Size of less positive charge ion is greater than that of having more positive ion.

Note: Size of isotopes (e.g. $^{35}\text{Cl}^\ominus$ and $^{37}\text{Cl}^\ominus$) is same.

Effective Nuclear Charge (Z_{eff})

41. d. Factual statement.

42. c. Screening effect order is $s > p > d > f$.

43. d. Diagonal relationship.

44. a. Penetration effect order is $s > p > d > f$.

45. d.

K^\oplus , ($Z = 19$), no. of e^- 's = $19 - 1 = 18$] Hence not
 Ca^{2+} , ($Z = 20$), no. of e^- 's = $20 - 2 = 18$] isoelectronic
 Ne , ($Z = 10$), no. of e^- 's = 10

46. c. Full-filled p -orbital is more stable than full-filled d -orbitals, i.e. $p^6 > d^{10}$.

Similarly, half-filled p -orbital is more stable than half-filled d -orbitals, i.e. $p^3 > d^5$.

Hence the order is $p^6 > d^{10} > p^3 > d^5$.

Ionisation Energy (IE)

47. b. Electronic configuration of (b) corresponds to Na ($Z = 11$), so it will have the highest IE_2 among the given configuration. Because the 2nd e^- has to be removed from the full-filled stable $2p^6$ configuration.

48. b. Factual statement.

49. b. Factual statement.

50. b. Noble gases are at the maxima which have closed electron shells and very stable electronic configuration. On the other hand, minima occurs at the alkali metals and their low IE_1 can be correlated with their high reactivity.

51. d. More positively charged ion will require high energy to remove electron than that of more negatively charged ion. Hence, the IE of S^{2-} will be the lowest among the given ions.

52. b. Factual statement

53. b. Since $\text{IE}_3 >> \text{IE}_2 > \text{IE}_1$.

54. c. Second EA of $\text{O}^{2-}_{(g)}$ is positive.

55. c. IE_1 of P $>$ S due to half-filled stable configuration ($3s^2$, $3p^3$) of P. Moreover, P and As both belong to group 15, but P is in the 3rd period and As is in the 4th period and IE_1 decreases down the group (\downarrow). Hence, the answer is (c).

56. a. There is a large jump from IE_3 (3658 kJ mol^{-1}) to IE_4 ($25024 \text{ kJ mol}^{-1}$). Therefore, it is very difficult to remove the 3rd valence electron.

Hence, the answer is (a).

57. d. Since in (d) it is IE_3 and $\text{IE}_3 >> \text{IE}_2 > \text{IE}_1$

58. b. Factual statement.

59. c. Group 2 elements (e.g. Mg) have high IE than group 1 element (e.g. Na, K and Rb)

60. b. Half-filled orbitals have stable configuration and thus required high IE.

61. c. Refer to solution of Question 14, Concept Application Exercise 1.3.

62. d. IE_1 decreases down the group 1 elements.

So IE_1 of Li is high in group 1 elements.

63. d. Due to half-filled stable configuration of N.
64. b. Conceptual fact.
65. b. IE_1 decreases down the group 2 elements.
Hence, IE_1 order is Be > Mg > Ca.
66. d. IE increases along the 4th period elements (\rightarrow) (i.e. from Na < Mg < Ae < Si).
67. c. Conceptual fact.
68. d. IE_1 is maximum for Kr (inert gas) due to the full-filled p -orbitals.
69. a. Cu = $3d^{10} 4s^1$, Ag = $4d^{10} 5s^1$, Au = $4f^{14} 5d^{10} 6s^1$

In all the above given cases, unpaired s -electron has to be removed. In the case of Cu, a $4s$ electron is to be removed which is closer to the nucleus than the $5s$ electron of Ag.

So, IE_1 of Cu > IE_1 of Ag.

However, in case of Au, due to imperfect screening effect of $14 e^-$'s of $4f$ orbitals, the nuclear charge increases and therefore $5s e^-$ of Au is more tightly held. Thus, the order of IE_1 is Cu > Ag < Au.

70. c. IE_2 of O (38.3 eV) > IE_2 of F (35.1 eV). For explanation, refer to solution Question 14. Concept Application Exercise 1.3.
71. b. There is a high jump from IE_3 to IE_4 . Therefore, it is difficult to remove the 4th valence electron. So, electronic configuration of element must have three valence electrons. Hence, the answer is (b).
72. c. There is a high jump from IE_2 to IE_3 . Therefore, it is difficult to remove the 3rd valence electron. So, the element must be of group 2, e.g. Be ($2s^2$).

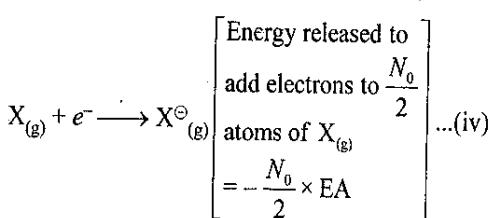
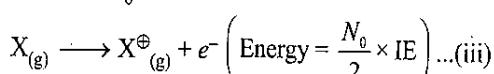
73. a. Let the ionisation energy of $X_{(g)}$ = IE per atom and electron affinity of $X_{(g)}$ = -EA per atom.



$$\text{Energy required to ionise } \frac{N_0}{2} \text{ atoms of } X_{(g)} = \frac{N_0}{2} \times \text{IE}$$

$$\times \text{IE} = E_1 \text{ (given)}$$

$$\therefore \text{IE} = \frac{2E_1}{N_0} \quad \dots(ii)$$



Energy for the process $X_{(g)}$ to $X_{(g)}^{\ominus}$ = E_2 (given).

Therefore, adding Eq. (iii) and (iv), we give

$$\left(\frac{N_0}{2} \times \text{IE} - \frac{N_0}{2} \times \text{EA} \right) = E_2 \text{ (given)} \quad \dots(v)$$

Substitute the value of IE from Eq. (ii) in Eq. (v).

$$\left(\frac{N_0}{Z} \times \frac{Z E_1}{N_0} - \frac{N_0}{2} \times \text{EA} \right) = E_2$$

$$-\frac{N_0}{2} \times \text{EA} = E_2 - E_1$$

$$\therefore -\text{EA} = \frac{2(E_2 - E_1)}{N_0}$$

$$\therefore \text{IE} = \frac{2E_1}{N_0} \text{ atom}^{-1} \text{ and } -\text{EA} = \frac{2(E_2 - E_1)}{N_0}$$

74. a. Ca = $3s^2 3p^6 4s^2$



(Stable noble gas configuration)

Hence, there would be sudden increase in IE_3 value.

75. d. As the value of n increases, the nuclear attraction over the outermost shell decreases, therefore removal of an electron will be easier.
76. d. Statements in a, b and c, all are characteristics to be observed during the removal of the 2nd electron.

77. c. Among Na, K, Mg and Ca, IE of Mg is highest (due to the smallest metal atom) which requires high energy ($E = h\nu = h \times \frac{C}{\lambda}$) or requires radiation of highest frequency (or lower wavelength to cause emission of electrons)

Isoelectronic Species

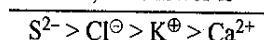
78. b.

$$\begin{aligned} \text{No. of electrons in } \text{NO}_3^{\ominus} &= 7 + 8 \times 3 + 1 = 32 && \text{Hence} \\ \text{No. of electrons in } \text{CO}_3^{2-} &= 6 + 8 \times 3 + 2 = 32 && \text{iso-} \\ \text{No. of electrons in } \text{SO}_2 &= 16 + 8 \times 2 = 32 && \text{electronic} \end{aligned}$$

79. c. Among the isoelectronic species, the ionic radii decreases as

More negative charge > Less negative charge > Neutral atom > Less positive charge > More positive charge.

Hence, the answer is



80. a. No. of electrons in $\overset{\oplus}{\text{CH}}_3$ (I) = $6 + 3 - 1 = 8$

$$\text{No. of electrons in } \overset{\ominus}{\text{NH}}_2 \text{ (II)} = 7 + 2 + 1 = 10 \quad \begin{matrix} \text{II, III and} \\ \text{IV are} \end{matrix}$$

$$\text{No. of electrons in } \overset{\oplus}{\text{NH}}_4 \text{ (III)} = 7 + 4 - 1 = 10 \quad \begin{matrix} \text{iso-} \\ \text{electronic} \end{matrix}$$

$$\text{No. of electrons in } \text{NH}_3 \text{ (IV)} = 7 + 3 = 10$$

81. a. Stable configuration of X (due to half-filled orbitals than that of Z).

$$\therefore I_x > I_z$$

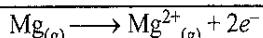
82. d. Metallic character increases down the group (\downarrow) and decreases along the period (\rightarrow).

Therefore, metallic character order is

| | K | > | Mg | > | Al | > | B |
|----------------------|-----|---|-----|---|-----|---|-----|
| Group \Rightarrow | 1 | | 2 | | 13 | | 13 |
| Period \Rightarrow | 4th | | 3rd | | 3rd | | 4th |

83. b. (i) $Mg_{(g)} \longrightarrow Mg_{(g)}^{\oplus} + e^{-}$, $IE_1 = 178 \text{ kcal mol}^{-1}$
(ii) $Mg_{(g)}^{\oplus} \longrightarrow Mg_{(g)}^{2+} + e^{-}$ $IE_2 = 348 \text{ kcal mol}^{-1}$

Adding (i) and (ii), we have



$$\therefore E = IE_1 + IE_2 = 178 + 348 = 526 \text{ kcal}$$

84. c. Non-metallic character decreases down the group (\downarrow) and increases along the period (\rightarrow).

Therefore, non-metallic character order is

| | F | > | N | > | C | > | B | > | Si |
|--------|-----|---|-----|---|-----|---|-----|---|-----|
| Group | 17 | | 15 | | 14 | | 13 | | 14 |
| Period | 2nd | | 2nd | | 2nd | | 2nd | | 3rd |

Electron Affinity (EA) and Electron Gain Enthalpy ($\Delta_{eg}H^{\ominus}$)

85. c. EA increases (more negative value) along the period (\rightarrow). But there is an exception in EA's value of N and C.

Therefore, EA's of N (less negative) $<$ C (more negative) due to half-filled p -orbitals in N. Addition of electron will be difficult. So, less energy is released in comparison to N.

Increasing order of EA is from less negative to more negative.



\Downarrow

(least EA)

86. b. $O_{(g)} + e^{-} \xrightarrow{-EA_1} O_{(g)}^{\ominus} + e^{-} \xrightarrow{+EA_2} O_{(g)}^{2-}$

Energy is required to add an electron to the negatively charged species due to electron-electron repulsion.

87. c. There is an exception in EA values of F and Cl.

Therefore, EA order is Cl $>$ F $>$ Br $>$ I.

(More negative to less negative)

88. a. Conceptual fact.

89. c. As explained in Question 87 above.

90. c. Due to stable full-filled orbitals of noble gases, it is very-very difficult to add electron. Hence, their EA's is almost zero.

91. a. IE and EA of an element are equal in magnitude but opposite in sign.

$$\therefore IE = -EA$$

92. c. As explained in Question 85 above.

93. d. Experimental fact.

Electronegativity (EN)

94. a. P and Si belong to group 4 and group 5 respectively and both of them are in the 3 rd period.

EN increases along the period.

$$\therefore EN \text{ of } P(2.1) > Si(1.8)$$

95. c. EN decreases down the group (\downarrow) but increases along the period (\rightarrow).

Therefore, increasing order of EN's is Si $<$ P $<$ C $<$ N.

| | Si | < | P | < | C | < | N |
|--------|-----|---|-----|---|-----|---|-----|
| Group | 14 | | 15 | | 14 | | 15 |
| Period | 3rd | | 3rd | | 2nd | | 2nd |

96. b. Conceptual fact.

97. b. EN decreases down the group (\downarrow) but increases along the period (\rightarrow)

| | P | < | S | < | N | < | O |
|--------|-----|---|-----|---|-----|---|-----|
| Group | 15 | | 16 | | 15 | | 16 |
| Period | 3rd | | 3rd | | 2nd | | 2nd |

98. a. Trend of EP (electropositive) character is reverse that of EN character of elements.

Thus, EP character increases down the group (\downarrow) but decreases along the period (\rightarrow).

99. b. Higher the positive charge the greater is the EN and higher the negative charge the lesser is the EN. So, EN order is

$$M^{-1} > M^{2-} > M^{3-} > M^{4-}$$

100. a. Conceptual fact.

101. d. Zn, Cd and Hg belong to 3d, 4d and 5d series of transition elements (group 12). Due to imperfect screening effect of d - and f -orbitals in transition elements, EN deceases down the group 12.

102. d. EN down the group (\downarrow) decreases and increases along the period (\rightarrow).

P, As, Sb elements belong to group 15 and EN decreases from P \rightarrow As \rightarrow Sb. But S belongs to group 16 and EN increases from P \rightarrow S.

Hence, S has the highest EN among the above elements.

103. b. EN order of period 2 elements is

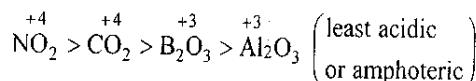
$$C < N < O < F$$

Acidic, Basic and Amphoteric Character

104. a. Applying Fajans' rule, the higher the oxidation state (or charge), the more is the covalent character and the more

is acidic and vice versa. Moreover, the acidic character increases from B to F.

Acidic character order is



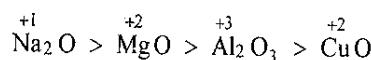
Period \Rightarrow 2nd 2nd 2nd 3rd

Group \Rightarrow 15 14 13 13

105. a. Applying Fajans' rule, the lower the charge; the more is ionic and the more is basic and vice versa.

Moreover, small cation, large anion, high charge and presence of *d* electrons mean more covalent and more acidic.

Therefore, decreasing order of basic nature is



Group \Rightarrow 1 2 13 11

Period \Rightarrow 3rd 3rd 3rd 4th

Size $\text{Al}^{3+} > \text{Cu}^{2+}$ and presence of *d* electron in Cu^{2+} makes it less basic (or more acidic) than Al_2O_3 .

106. a. Same explanation as in Question 105 above.

107. b. Acidic strength: $\text{CaO} < \text{H}_2\text{O} < \text{CuO} < \text{CO}_2$ (same explanation as in Question 105 above).

108. d. $\text{Al}_2\text{O}_3 \Rightarrow$ Amphoteric, $\text{B}_2\text{O}_3 \Rightarrow$ Acidic (same explanation as in Question 105 above).

109. b. Refer to Section 1.34.2, Point (4).

110. c. Refer to Section 1.34.2, Point 3 (Table 1.26).

111. a. Same explanation as in Question 105 above

112. d. Refer to Sections 1.34.2 (Point 4) and 1.34.4 (Point 3).

113. d. Refer to Section 1.34.4, Point (4).

114. b. Refer to Section 1.34.2, Point (2) and Section 1.34.4, Point (1).

Bond Angle

115. a. Refer to Section 1.17, Point 3 (a) (i).

116. b. Refer to Section 1.17, Point 3 (a) (v).

117. c. Refer Illustration 1.81, Question 11, part (j).

118. d. Refer Illustration 1.81, Question 11, part (m).

Lattice and Hydration Energy

119. a. Refer Illustration 1.81, Question 14, part (d).

120. d. Refer Illustration 1.81, Question 14, part (a).

121. b. Refer Illustration 1.81, Question 13, part (m).

122. a. Conceptual fact.

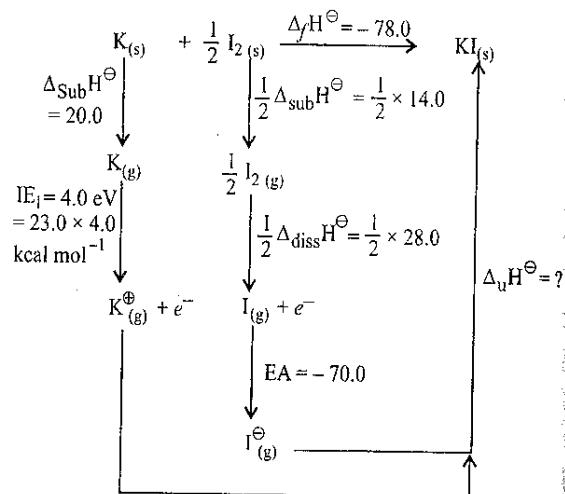
123. a. For ionic compound if lattice energy ($\Delta_u H^\ominus$) $>$ hydration

energy ($\Delta_{\text{hyd}} H^\ominus$) the compound is insoluble and vice versa.

For Na_2SO_4 , $\Delta_u H^\ominus < \Delta_{\text{hyd}} H^\ominus$, thus it is soluble in H_2O .

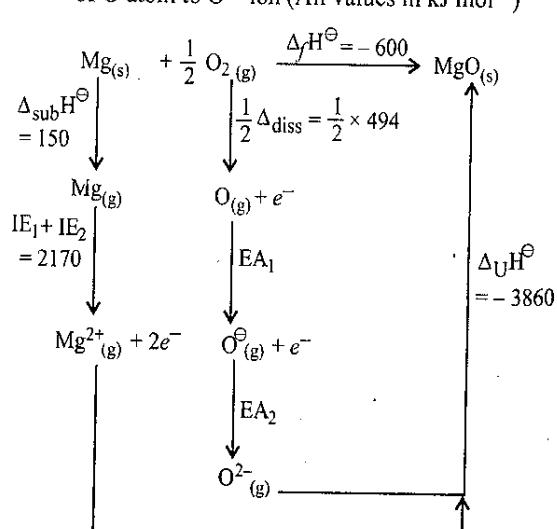
For BaSO_4 , $\Delta_u H^\ominus > \Delta_{\text{hyd}} H^\ominus$, thus it is insoluble in H_2O .

124. c. Using Born–Haber cycle for KI . (All values are in kJ mol^{-1})



$$\begin{aligned}\therefore \Delta_f H^\ominus &= \Delta_{\text{sub}} H^\ominus + \text{IE}_1 + \frac{1}{2} \Delta_{\text{sub}} H^\ominus + \frac{1}{2} \Delta_{\text{diss}} H^\ominus + \text{EA} \\ &\quad + \Delta_u H^\ominus \\ -78 &= 20.0 + 23.0 \times 4.0 + \frac{1}{2} \times 14.0 + \frac{1}{2} \times 28.0 - 70.0 \\ &\quad + \Delta_u H^\ominus \\ \therefore \Delta_u H^\ominus &= -141 \text{ kcal mol}^{-1}\end{aligned}$$

125. a. Using Born–Haber cycle for MgO , calculation of EA of O atom to O^{2-} ion (All values in kJ mol^{-1})



$$\begin{aligned}\therefore \Delta_f H^\ominus &= \Delta_{\text{sub}} H^\ominus + (\text{IE}_1 + \text{IE}_2) + \frac{1}{2} \Delta_{\text{diss}} + (\text{EA}_1 + \text{EA}_2) \\ &\quad + \Delta_u H^\ominus\end{aligned}$$

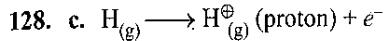
$$-600 = 150 + 2170 + \frac{1}{2} \times 494 + (\text{EA}_1 + \text{EA}_2) - 3860$$

$$\therefore (\text{EA}_1 + \text{EA}_2) = +693 \text{ kJ mol}^{-1}$$

Miscellaneous

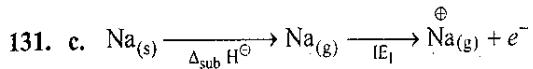
126. c. Conceptual fact.

127. a. Conceptual fact



129. a. Salts of strong acid and strong base (e.g. NaCl) do not hydrolyse, and thus they have pH = 7 (neutral). Group 1 forms salts of strong acid (S_A) and strong base (S_B).

130. d. Conceptual fact.

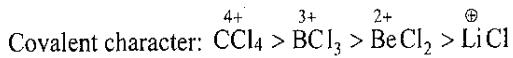


132. c. Both Be and Al show different maximum covalency in compounds.

Maximum covalency of Be = 4 (due to absence of d -orbitals).

Maximum covalency of Al = 6 (due to presence of d -orbitals).

133. b. Apply Fajans' rule (refer Question 105 above).



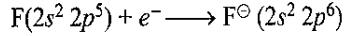
134. c. As the size of anion decreases, the polarisability decreases (small cation, large anion, high charge, more covalent or more polarisability) (Fajans' rule).

135. c. Conceptual fact.

Assertion Reasoning Type

1. c. **Correct reason:** Although He and Be have similar outer electronic configuration (ns^2), only He ($1s^2$) has inert gas configuration and hence is chemically inert. But Be ($2s^2$) does not have inert gas configuration and hence is not chemically inert.

2. c. **Correct reason:** EA of N is essentially zero because of its half-filled electronic configuration.



(More stable configuration)



(Less stable configuration than that of F^{\ominus})

Hence EA_1 of F > EA_1 of O.

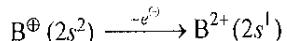
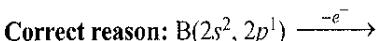
Therefore, EA order is F > O > N.

3. e. **Correct assertion:** IE_1 of N > IE_1 of O, due to stable half-filled configuration of N.

Correct reason: Z_{eff} increases across a period.

4. c. **Correct reason:** Li^{\oplus} has noble gas (e.g. He gas) configuration.

5. d. **Correct assertion:** IE_2 of C < IE_2 of B.



Due to penetration effect, it is easier to remove an electron from $2p$ orbital of C^{\oplus} than from $2s$ electron of B^{\oplus} .

6. d. **Correct assertion:** In the modern periodic table the period indicates the value of principal quantum number.

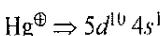
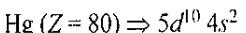
7. a. Both (A) and (R) are correct and factual statements.

8. c. **Correct reason:** Metallic character decreases along the period (\rightarrow) but increases down the group (\downarrow).

Thus Al is more metallic than B (group 13).

9. a. Both (A) and (R) are correct and factual statements.

10. e. **Both (A) and (R) are false.** Mercurous ion is Hg_2^{2+} .



It should be paramagnetic, containing one unpaired electron. But it was observed experimentally to be diamagnetic.

That is why two Hg^{\oplus} ions combine to give Hg_2^{2+} , so it becomes diamagnetic and does not contain any unpaired electron.

11. c. **Correct assertion:** LiCl is a covalent compound due to the large size of the anion (Cl^{\ominus} ion), its Z_{eff} decreases and its valence shell electrons are held less tightly towards its nucleus.

Integer Type

1. (2) C_3O_2 and N_2O (Refer to Section 1.34.)

2. (3) Factors (a), (b) and (c) influence IE of an element.

3. (2) Processes (b) and (d) require absorption of energy.

4. (3) First three IE are small, as compared to IE_4 and IE_5 . So three electrons can be easily lost.

5. (4) It is shown by four groups only, e.g.

| Group | 1 | 2 | 13 | 14 | No. of pairs of elements |
|---------------|----|----|----|----|--------------------------|
| 2nd Period | Li | Be | B | C | |
| 3rd Period | Na | Mg | Al | Si | |
| No. of groups | 1 | 2 | 3 | 4 | = 3 |

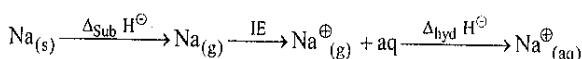
Number of group = 4.

Number of period = 2.

6. (1) Co and Ni have similar atomic radii.

[Refer to the solution of Question 35 (Single Correct Answer Type)]

7. (3)



8. (4) Fe_3O_4 , Pb_3O_4 , $\text{Co}(\text{AlO}_2)_2$ and Mn_3O_4 (Refer to Section 1.34.4).

9. (5) Ar ($Z = 18$)

There are five species which has $18 e^-$'s.

- i. P^{3-} ($15 + 3 = 18$)
- ii. S^{2-} ($16 + 2 = 18$)
- iii. Cl^{\ominus} ($17 + 1 = 18$)
- iv. K^{\oplus} ($19 - 1 = 18$)
- v. Ca^{2+} ($20 - 2 = 18$)

10. (6) Al_2O_3 , ZnO , Ga_2O_3 , SnO_2 , PbO_2 , BeO
(Refer to Section 1.34.2 and Table 1.26)

11. (4) Inner transition elements are Bk, Er, Fm, Ce.

Transition elements are Sg, Fe, Cr, Zr.

p-block elements are Pb and Ar.

s-block element is Ca.

12. (3) Refer to the solution of Question 5 (above).

13. (1) Only BeCO_3 is more stable than MgCO_3 .

Since stability of the carbonates of group 2 decreases down the group.

[Refer Illustration 1.81, Solution of Question 13 (Part m)]

Fill in the Blanks Type

1. Ununseptium, Uus
2. Atomic numbers
3. Atomic masses
4. Actinoids; 90 to 103
5. Normal or representative
6. Zero or 18
7. Mass, volume
8. Decrease, increase
9. Lower
10. EN
11. Oxygen
12. Greater
13. $109^\circ 28'$ (because it is sp^3 hybridised)
14. CO_2 (because it is sp hybridised, bond angle = 180°)
15. Group 2 (Li shows diagonal relationship with Mg)
16. $\text{Si} < \text{P} < \text{C} < \text{N}$
17. $\text{C} > \text{Be} > \text{B} > \text{Li}$
18. Paramagnetic $[\text{Mn}^{2+} (\text{H}_2\text{O})_6]^{2+}$
 $\text{Mn} (Z = 25) \Rightarrow 3s^2 3d^5$
 $\text{Mn}^{2+} = 3d^5 4s^0$
 No. of unpaired e^- 's = 5. Hence paramagnetic
19. S^{2-} [All of them belong to the 3rd period. Hence the more negative charge, the larger is the size].
20. Lesser

True/False Type

1. True. $\text{F}(Z = 9)$, $\text{F}^{\ominus} = 9 + 1 = 10 e^-$'s.

So, the species with $10 e^-$'s are

- 1. N^{3-} ($7 + 3 = 10$)
- 2. O^{2-} ($8 + 2 = 10$)
- 3. $\text{Ne} (Z = 10)$
- 4. Na^{\oplus} ($11 - 1 = 10$)
- 5. Mg^{2+} ($12 - 2 = 10$)

2. False. $\text{Sr} (Z = 38)$, $\text{Sr}^{2+} = 38 - 2 = 36 e^-$'s.

So, the number of species with $36 e^-$'s are only three.

- 1. Br^{\ominus} ($35 + 1 = 36$)
- 2. $\text{Kr} (Z = 36)$
- 3. Rb^{1+} ($37 - 1 = 36$)

3. True. Factual statement.

4. True. Be and Mg have very high IE, so energy of flame is not sufficient to excite the electrons to higher energy level, so they do not import flame colouration.

5. False. For example, $\text{O}_{(g)}^{\ominus} + e^- \rightarrow \text{O}_{(g)}^{2-}$
 EA_2 is always positive, i.e. energy is absorbed.

6. False. Because van der Waals radii > Metallic radii > Covalent radii

7. True. Factual statement.

8. True. Factual statement.

9. False. As the s-character of the hybrid orbital decreases, the EN decreases.

10. True. Factual statement.

Archives

Multiple Correct Answers Type

1. (a, c, d). Only (b) seems to be incorrect because in many cases, stable valency states are difficult to predict on the basis of the periodic table.

2. (a, b). When the hydration energy is more than the lattice energy, the salt is soluble in water and vice versa.

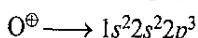
3. (d). $\text{P}^{3+} > \text{P}^{5+}$

Higher the value of positive charge on the cation, the smaller the ionic size.

Single Correct Answer Type

1. c. The order is O > F > N > C

From left to right, the first ionisation potential increases.



After losing one electron, oxygen atom acquires half-filled stable configuration, so its second ionisation potential becomes larger than that for fluorine.

2. c. N : $1s^2 2s^2 2p^3$

From left to right in a period, the first ionisation potential increases. But in nitrogen, half-filled stable configuration is present, therefore its ionisation potential is greater than that of oxygen.

3. a. Same explanation as in Question 2 above.

$$\therefore IE_1 \text{ of N (14.5)} > IE_1 \text{ of O (13.6) eV}$$

4. a. In case of fluorine, it is covalent radius. In case of neon, it is van der Waals radius because it is a noble gas which is monatomic. van der Waals radius is always more than that the covalent radius.

5. c. Si < P < C < N

EN increases from left to right in a period.

EN decreases down the group in the periodic table.

6. a. Refer Question 1(b) (subjective type).

7. d. All of these are isoelectronic ions (10 electrons).

In isoelectronic species, as the number of protons (atomic number) goes on increasing, size goes on decreasing due to stronger attraction on the electrons (Z for N, O, F and Na = 7, 8, 9 and 11)

8. b. $[Ne] 3s^2 3p^3$

From left to right in a period, the first ionisation potential increases. Down the group, ionisation potential decreases.

In option (c), half-filled stable configuration is also present.

9. d. Option (d) is incorrect because for transition elements, the *d*-subshells are filled with electrons regularly with increase in atomic number.

10. b. In the periodic table, inert pair effect increases down the group. So in group 14, the stability of lower oxidation state of +2 goes on increasing down the group. This makes Pb^{2+} a stable oxidation state.

In Fe^{2+} ($3d^6$), the *d*-orbital is not completely filled. Ag^{+} ($4d^{10}$) is the most stable oxidation state of silver because due to fully filled *d*-subshell, removal of the second electron is very difficult.

11. d. The greater the number of unpaired electrons, the higher the magnetic moment.

$$Mg = \dots 3s^2, Mg^{2+} = \dots 3s^0$$

No unpaired electron

$$Ti = 3d^2 4s^2, Ti^{3+} = 3d^1 4s^0$$

One unpaired electron

$$V = 3d^3 4s^2, V^{3+} = 3d^2 4s^0$$

Two unpaired electrons

$$Fe = 3d^6 4s^2, Fe^{2+} = 3d^6 4s^0$$

Four unpaired electrons

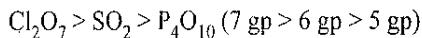
| | | | | |
|----|---|---|---|---|
| 11 | 1 | 1 | 1 | 1 |
|----|---|---|---|---|

12. b. Na ($Z = 1$) : $1s^2 2s^2 2p^6 3s^1$

$$Na^{\oplus} : 1s^2 2s^2 2p^6$$

After losing the first electron, sodium acquires a very stable noble gas configuration. Therefore, its second ionisation potential is very high. So, it is incorrect to say that the second ionisation potential of Mg is greater than the second ionisation potential of Na.

13. a. The correct order of acidic strength is



In the periodic table, acidic nature of oxides increases from left to right. Acidic nature of oxides decreases down the group.

14. b. $F^{\ominus} < O^{2-} < N^{3-}$

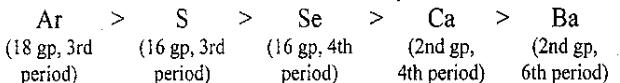
All of these are isoelectronic ions (10 electrons).

In isoelectronic species, as the number of protons (atomic number) goes on increasing, the size goes on decreasing due to stronger attraction on the electrons (Z for N, O and F = 7, 8 and 9).

15. a. In hydrides of group 16, boiling point increases down the group because of increasing molecular mass. But water has an exceptionally high boiling point because it shows intermolecular hydrogen bonding. One H_2O molecule is bonded to four molecules of H_2O .

16. b. From left to right in a period, the first ionisation potential increases. Down the group, ionisation potential decreases.

17. b. IE_1 increases along the period and decreases down the group. Moreover Ar is inert gas, has completely filled \bar{e} 's (Stable structure) hence highest IE_1 .

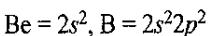


Assertion Reasoning Type

1. c. Statement II is incorrect. In general, the electron affinity decreases down the group but the electron affinity for chlorine is more than that for fluorine, and similarly the electron affinity for sulphur is more than that for oxygen because in F and S, due to very small size of the atom. There are strong electron-electron repulsion in the relatively small $2p$ orbitals of F and thus, the incoming electron does not experience much attraction. Hence, the incoming electron is not added easily as it is added in large $3p$ orbitals of Cl.

Consequently, the $\Delta_{eg} H^{\ominus}$ or EA of F is less negative than that of Cl.

2. c. Statement II is incorrect. The first ionisation energy of Be is greater than that of B because of its relatively stable electronic configuration.



It is easier to remove electron from $2p$ orbitals than $2s$ orbitals since $2s$ is much more penetrated towards nucleus.

Hence IE_1 of Be > IE_1 of B.

Therefore, $2p$ -orbital has rather higher energy than $2s$.

Fill in the Blanks Type

- The energy released when an electron is added to a neutral gaseous atom is called **electron gain enthalpy** of the atom.
- On Mulliken scale, the average of ionisation potential and electron affinity is known as **electronegativity**.
- Ca^{2+} has a smaller ionic radius than K^{\oplus} because it has **higher charge density** ($\frac{\text{charge}}{\text{size}}$ ratio). In isoelectronic species, as the number of protons (atomic number) goes on increasing, size goes on decreasing due to stronger attraction on the electrons.
- Compounds that formally contain Pb^{4+} are easily reduced to Pb^{2+} . The stability of the lower oxidation state is due to **inert pair effect**.

In the periodic table, inert pair effect increases down the group. So in group 14, the stability of smaller oxidation state of +2 goes on increasing down the group. Pb^{4+} has an oxidising nature and Br^{\ominus} and I^{\ominus} have reducing nature, so Pb^{4+} is reduced to Pb^{2+} .



True/False Type

- True.** The softness of group IA metals (alkali metals) increases down the group with increasing atomic number. This is a true statement.
- False.** In group IA of alkali metals, the ionisation potential decreases down the group. But lithium is a very strong reducing agent because of its very high hydration energy.
- False.** The decreasing order of electron affinity of F, Cl and Br is $Cl > F > Br$. In general, the electron affinity decreases down the group but the electron affinity for chlorine is more than that for fluorine, and similarly the electron affinity for sulphur is more than that for oxygen because in F and S, due to very small size of the atom. There are strong electron-electron repulsion in the relatively small $2p$ orbitals of F and thus, the incoming electron does not experience much attraction. Hence, the incoming electron is not added easily as it is added in large $3p$ orbitals of Cl. Consequently, the $\Delta_{eg}H^{\ominus}$ or EA of F is less negative than that of Cl.
- False.** The basic nature of the hydroxides increases progressively down the group.

Subjective Type

- The decreasing order of ionic size is $O^{2-} > F^{\ominus} > Na^{\oplus} > Mg^{2+}$.**

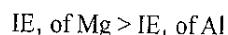
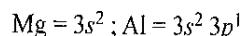
All of these are isoelectronic ions.

In isoelectronic species, as the number of protons (atomic number) goes on increasing, size goes on decreasing due to stronger attraction on the electrons.

- $Na < Mg > Al < Si$

From left to right, IE increases.

But in magnesium, stable configuration is present, therefore its ionisation potential is greater than that of aluminium.



Due to penetration effect. It is easier to remove electron from $3p$ orbital than $3s$ orbital.

- The increasing order of bond length is**



In nitrogen, triple bond is present which has the smallest bond length. In oxygen, double bond is present, which has smaller bond length than single bonds. In chlorine, bond length is larger than in fluorine due to larger size of the atom.

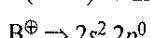
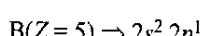
- The increasing order of size is $Ca^{2+} < Ar < Cl < S^{2-}$.**

All of these are isoelectronic ions.

In isoelectronic species, as the number of protons (atomic number) goes on increasing, size goes on decreasing due to stronger attraction on the electrons.

- From left to right in the periodic table, the ionisation energy increases; therefore, the first ionisation energy of carbon atom is greater than that of boron.

The second ionisation energy of boron is greater than that of carbon because after losing one electron, boron acquires a stable electronic configuration.



- The increasing order of ionic sizes is**



All of these are isoelectronic ions.

In isoelectronic species, as the number of protons (atomic number) goes on increasing, size goes on decreasing due to stronger attraction on the electrons.

- $Al^{3+} < Mg^{2+} < Li^{\oplus} < K^{\oplus}$

Al^{3+} and Mg^{2+} are isoelectronic ions.

In isoelectronic species, as the number of protons (atomic number) goes on increasing, size goes on decreasing due to stronger attraction on the electrons. K^{\oplus} is larger than Li^{\oplus} because on moving down the group, size decreases.