

Chemistry 1st Paper



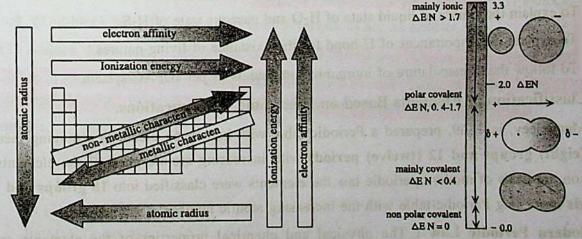
Theoretical Lectures = 21 Class Activities = 9 Total Periods = 30

Chapter-3 **Periodic Properties And Bonding in Elements**

Introduction: In second chapter we have known from electron distribution of atoms that the properties of the elements depend on their electron distributions with gradational periodic repetitions, So those properties of the elements which periodically change with their electron distributions, are called periodic properties. Depending on ionisation energy and electron affinity, metal atom binds with non-metal atom with ionic bond and co-valent bond

forms with non-metal atoms. Again due polarity formation in covalent opposite and compounds mixed properties appear in the both classes of compounds carefully.

Key Words: Electron distribution, transitional to polarization in ionic compounds and elements, alkali metals, periodicity, ionisation energy, electron affinity, pH of solution, periodicity of oxides, orbital hybridization, sigma shape, Ione-pair bond, pi-bond, molecular compounds. We shall observe these electrons. covalent bond, polarization, dipole, characteristics in elements and their Vander Waal's force, H-bond, importance of Hbond, IUPAC system for nomenclature.



After Reading this Chapter, Students will be able -

- 1. To classify the elements into s, p, d and f-blocks on the basis of electron distributions.
- 2. To know and describe common properties of elements of different blocks.
- 3. To explain the periodicity of different properties of the elements.
- 4. To know and describe the affect of the factors (atomic size, sub-orbit electron distribution etc.) on ionisation energy, electron affinity and electronegativity.

- 5. To explain the properties of oxides of different elements (such as elements of 2nd and 3rd periods) of periodic table.
- Practical: To determine experimentally p^H value of water soluble oxides and can explain their acid-base characters.
- 7. To find relation between chemical bonds and periodic properties of elements.
- 8. To explain the classification of covalent bonds on orbital overlapping.
- 9. To explain the concept of orbital hybridization and their different hybrid orbitals.
- 10. To explain the relation between covalent molecular shaves and hybrid orbitals.
- 11. To explain the affect of lone-pair of electrons on safe of molecule and bond angle.
- 12. To prepare molecular models of different compounds with different sized small potatoes or with similar vegetables and can demonstrate.
- 13. To explain the mode of formation of coordinate covalent bond.
- 14. To prove the coordinate covalent bond as a special case of covalent bond.
- 15. To explain the covalent properties in ionic compounds with Fajan's rules.
- 16. Practical: To prove the existance of dipoles in water molecules.
- 17. To explain Vander Waal's forces.
- 18. To explain the formation of hydrogen bond.
- 19. To explain the causes of liquid state of H₂O and gaseous state of H₂S.
- 20. To explain the importances of H-bond for the existance of living natures.
- 21. To follow the nomenclature of inorganic compounds as per IUPAC system.

3.1 Classification of Elements Based on Electronic Configurations.

Mendeleev, in 1869, prepared a Periodic table with known 63 elements arranging them in 8 (eight) groups and 12 (twelve) periods with increasing atomic mass of the elements.

Later on the basis of modern periodic law the elements were classified into 18 groups and 7 periods in a Long Periodic table with the increasing atomic number of elements.

Modern Periodic Law: The physical and chemical properties of the elements are periodic function of their atomic numbers. Among the different scientists Bohr's contribution was more than others in preparing modern long periodic table. Hence long periodic table is also known as Bohr's Periodic Table.

Long Form Periodic Table: Bohr prepared a long periodic table on the basis of electron distribution of the elements. This is known as Long Periodic Table or Bohr's

Periodic Table. The long periodic table contains 18 groups and 7 periods for the elements. In long periodic table, each long period contains 10 elements of d-block at the middle. At the end of each period inert gases or noble gases are placed. Lanthanides and actinides elements are placed in group—3 of period 6th and 7th). This is the modern periodic table.

The basis of Modern Periodic Table: The basic principle of classification of elements in periodic table is their electron distributions. Again all the elements are classified into four blocks on the basis of electron accommodation capacity of different orbitals in their electron distributions. This classification is shown in fig-3.1 below. Elements are arranged into 187 vertical columns or groups and 7 horizontal rows or periods.

Total Number of elements discovered till 10.11.2016 and recognized by **IUPAC** association is 118. With recognised 4 elements of atomic number 113, 115, 117 and 118 period 7th is filled up now.

According to Aufbau rule the gradational order of entry of electrons in different orbitals of atoms of the elements starting from left most towards right side in the periodic table is: $1s\rightarrow 2s\rightarrow 2p\rightarrow 3s\rightarrow 3p\rightarrow 4s\rightarrow 3d\rightarrow 4p\rightarrow 5s\rightarrow 4d\rightarrow 5p\rightarrow 6s\rightarrow 4f\rightarrow 5d\rightarrow 6p\rightarrow 7s\rightarrow 5f\rightarrow 6d\rightarrow 7p.$

On the basis of electron distribution, four blocks of the elements such as (1) s-block, (2) p-block, (3) d-block and (4) f-block and their descriptions are as follows:

(1) s-block Elements: The elements of s-block contain ns¹ or ns² electron in their outermost orbit or valence shell. The s-block elements include those of group 1 and 2 (1A) and 2A) and He of the periodic table. The total s-block elements are 14 in number.

Example:

$$H(1) = 1s^{1}$$

He (2) =
$$1s^2$$

$$Li(3) = 1s^2 2s^1$$

Be (4) =
$$1s^2 2s^2$$

$$Mg (12) = 1s^2 2s^2 2p^6 3s^2$$

The outermost energy level of valence shell of s-block elements contain ns^1 or, ns^2 electrons; here n = 1, 2, 3 etc. means number of orbit.

(2) p-block Elements: The elements of p-block contain np¹ to np⁶ electron in their outermost orbit or valence shell. This block includes the elements of groups 13, 14, 15, 16, 17

and 18 (i.e. 3A, 4A, 5A, 6A, 7A and 8A) except He. Besides these, including newly discovered six elements like Nihonium (113Nh), Flerovium (114Fl), Moscovium (115Mc), and Livermorium (116Lv), Tennessine (117Ts), Oganesson (118Og) total number of p-bolck elements are 36 in number.

Example: B (5) =
$$1s^2 2s^2 2p^1$$

C (6) = $1s^2 2s^2 2p^2$
A1 (13) = $1s^2 2s^2 2p^6 3s^2 3p^1$
C1 (17) = $1s^2 2s^2 2p^6 3s^2 3p^5$
Ar (18) = $1s^2 2s^2 2p^6 3s^2 3p^6$

The outermost energy level or valence shell of p-block elements contain $ns^2 np^1$ to $ns^2 np^6$; electrons; here n = 2, 3, 4 etc. means outermost orbit.

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Fig-3.1: Four blocks (s,p, d, f) of elements in Periodic Table.

(3) d-block Elements: In d-block elements, last electron enters into d-orbital. In 4th period, Scandium, Sc (21) to Zinc, Zn (30) and in 5th period Yttrium, Y (39) to Cadmium, Cd (48) are d-block elements. Besides these two periods, 6th and 7th period include d-block elements. All d-block elements are metals. In the periodic table group -3 to group-12 that is elements of B-sub groups are d-block elements. By this time, d-block included elements are 141 (fourty one) in number. Their atoms contain (n-1)d1 to (n-1) d10 electrons.

Example;

Sc (21) =
$$1s^2 2s^2 2p^6 3s^2 3p^6 3d^1 4s^2$$

Fe (26) = $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$
Zn (30) = $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2$

The outermost two sub-shell or valence shell of d-block elements contain $(n-1)d^{1-10}$ ns¹⁻² electrons; here n = 4, 5, 6, 7 etc. means outermost orbit.

Some of the d-block elements with special properties are called transition elements.

Definition of Transition Elements: The transition elements are those d-block elements which contain at least one stable positive ion with partly filled d-orbital containing d¹-d⁹ electron distributions. Transition elements have special properties such as:

(i) variable valencies or oxidation numbers; (ii) they can form coloured compounds; (iii) they can form complex compounds; (iv) they can act as catalysts; (v) they show paramagnetic property. In 4th period, except Sc and Zn, the rest eight elements are transition elements.

As per definition of trensition elements, two elements of d-block like Sc (21) and Zn (30) of 4th period are not transition elements. Because they form only Sc³⁺ ion and Zn²⁺ ion. In Sc³⁺ ion there is no electron in 3d orbital and Zn²⁺ ion has fully filled 3d¹⁰ orbital.

$$Sc^{3+}$$
 (21) = 1s² 2s² 2p⁶ 3s² 3p⁶ 3d°

$$Zn^{2+}$$
 (30) = 1s² 2s² 2p⁶ 3s² 3p⁶ 3d¹⁰

On the otherhand, Fe(26) is a d-block element and transition element both. Because its two cations like Fe²⁺ ion and Fe³⁺ ion have partially filled 3d orbital.

$$Fe^{2+}$$
 (26) = 1s² 2s² 2p⁶ 3s² 3p⁶ 3d⁶

$$Fe^{3+}$$
 (26) = 1s² 2s² 2p⁶ 3s² 3p⁶ 3d⁵

For this reason it is called, all transition elements are d-block elements but all d-block elements are not transition elements.

(4) f-block Elements: In f-block elements, the last electron enters into f-orbital of the atom. In 6th period, Lanthanum, La (57) to Lutetium, Lu (71) the total 15 (fifteen) elements are called. 'Lanthanoids' or Lanthanide series. Similarly Actinium, Ac (89) to Lawrencium, Lr (103) the total 15 (fifteen) elements are called 'Actinoids' or Actinide series. Of these two periods total 30 (thirty elements) are placed below the others in most modern periodic table. It is important to mention that first element of the Lanthanoids, i.e. Lanthanum, La (57) atom contains last electron as 5d¹ and actinium Ac (89) and Thorium (90) of actinoids have their last electron as 6d¹ and 6d². So these three elements are not f-block elements but d-block elements. Hence total number of f - block elements are [27 (twenty seven)]. [Follow the periodic table].

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Inner-transition Elements: Inner-transition elements are those f-block elements which contain at least one stable positive ion with partially filled f-orbital containing f^{1-13} electron distribution. In Lanthanide series included inner-transition elements contain incomplete 4f orbital and in actinide series include inner transition elements contain incomplete 5f orbital. Example of such inner transition element is cerium ($_{58}$ Ce) = [Xe] $_{58}$ Ce. Because its stable ion $_{58}$ Ce contains partially filled $_{58}$ Ce elements.

Know More:

(1) Group number for s block elements : Electron number in outermost orbit (valence

electron)

(2) Group number for p-block elements: 10 + valence electron (ns + np)

(3) Group number for d-block elements: (n-1) d + ns electron number

(4) Group number for f-block elements : all f-block elements are in group-3 of

periodic table.

By this discussion, the total 118 elements including Nh (113), Fl (114) Mc(115), Lv (116), Ts(117) and Og(118) are classified into 4 blocks such as s, p, d and f-blocks. Now we shall come to know the common properties of the elements of these blocks.

The two groups of s-block on the left and the six group of p-block on the right are the main groups. These s-block and p-block elements are called **Ideal elements** or, **Representative elements**; because they follow the general rules in filling their orbitals with electrons without any exception. Some of the d-block elements are called **transition metals**. Similarly, some of the f-block elements are called **inner-transition metals**. Two systems for numbering the groups are shown above the top row and are explained in modern IUPAC Periodic Table of elements in inner page of cover of this book.

Students' Work: 3.1: Identification of elements from electron distribution.:

Problem - 3.1: Write the electron distribution of the following elements and explain which element belongs to which group: C (6), Na (11), P (15), Ca (20), Cr (24), Fe (26).

Problem - 3.2: Sc (21) and Zn (30) are d-block elements; but not transition metals; xplain.

4524p6 6s²6p⁶ 35-3p6 88 88 5825p6 6s26p5 3s²3p⁵ 88 ¥ 2s22p4 3s23p4 6s26p4 2 0 Se 3 28 p-ব্ৰক মোল 6s²6p³ B:33 2s²2p² 6826p2 14 Si 35²3p² P 22 6d57s2 6d67s2 6d77s2 6d97s1 6d107s1 6d107s2 7s27p1 13 3s23p1 6826p1 252p1 Bo **A** 4d105s2 5d106s2 Metal = 90 Non metal = 17 [11 gass, 5 solid, 1 liquid (Br_2)] Metalloid = 7 (B, Si, Ge, As, Sb, Te, At) 23 5d¹⁰6s¹ 3d104s1 673 Au Au 5d96s1 4 P 8 with valence electrons] IUPAC Most Periodic Table 8Z 5d76s2 3d74s2 4d85s1 62 **25** - d-block elements 3d64s2 5d66s2 4d75s1 E 29 valence electron - atomic number 5456s2 107 Bb 7 25 MM - symbol 5d46s2 5d36s2 6d'7s2 6d27s2 6d37s2 Fe 4 36454 5 E 5d26s2 5d16s2 82 Yc 4 C 2 3 3 4 56 83 652 88 72 72 S5 Sr 38 61 X 18 35-Z 37 Ss.1 SS 25 87 Fr elements -s block [Ne(10)] [Ar(18)] [He(2)] [Xe(54)] [Kr(36)] **Group** → pericd [Rn(86)] 9

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and detect 21 elements which do not have their valence electron distributions Problem: Observe the valence electrons of the elements in the above periodic table according to general rules of electron distributions.

Look at the valence electron of the elements with atomic numbers: 24, 29, 41, 42, 44, 45, 46, 47, 57, 58, 64, 78, 79, 89, 90, 91, 92, 93, 96, 110, 111. Hints:

3.1.1 Position of Element in Periodic Table from Electron Configuration

As the primary basis of Periodic table is the electronic configuration, so the position of an element in the periodic table is determined from its electron distribution. When actual electron distribution of an element is not known; then from atomic number of that element, after writing electron configuration as per Aufbau principle, one can determine the position of the element in periodic table. Here following rules are followed:

- (a) Period Number Determination: In electron distribution of an element the maximum value of 'n' indicates period number. For example, electron distribution of Na(11) is as follows: Na(11) = $1s^2 2s^2 2p^6 3s^1$. In this maximum value of 'n' = 3. So element Na is in 3rd period.
- (b) Group Number Determination: To known the group of an element, its valence electron number and its block are to know. For example.
 - (i) For s-block element ns¹⁻² electron distribution is considered.

 Here ns¹ indicates group-1 and ns² indicates group-2.
 - (2) For p-block element (10 + ns²np¹-6) formula is considered.
 Here ns²np¹ valence electrons indicates group number (10 + 2 + 1) = 13;
 Similarly, ns²np² valence electrons indicates group number (10 + 2 + 2) = 14.
 - (3) For d-block element total electrons of two orbitals (n-1)d ns indicates group number.
 - For all f-block elements, valence shell contain f-electron and are in group number 3.

 Above rules are explained with 7 examples below:

Na (11
$$\rightarrow$$
1s² 2s² 2p⁶ 3s¹ : Here period = 3; group =1
Cl (17) \rightarrow 1s² 2s² 2p⁶ 3s² 3p⁵ : Here period = 3; group = (10 + 7) = 17
Ar (18) \rightarrow 1s² 2s² 2p⁶ 3s² 3p⁶ : Here period = 3; group = (10 + 8) = 18
Cr (24) \rightarrow 1s² 2s² 2p⁶ 3s² 3p⁶ 3d⁵ 4s¹ : Here period = 4; group = 6
Ni (28) \rightarrow 1s² 2s² 2p⁶ 3s² 3p⁶ 3d⁸ 4s² : Here period = 4; group = 10
Cu (29) \rightarrow 1s² 2s² 2p⁶ 3s² 3p⁶ 3d¹⁰ 4s¹ : Here period = 4; group = 11
Ce (58) \rightarrow [Xe (54)] 4f² 6s² : Here period = 6; group = 3

Worked Example - 3.1: Determine the position of elements in periodic table with following atomic numbers: (a) 18, (b) 22, (c) 29, (d) 16, (e) 48, (f) 59.

Solution : (a) Electron distribution of element with atomic number 18 is $Z(18) = 1s^2 2s^2 2p^6 3s^2 3p^6$. So it is an inert gas element because it has full octet set. Hence its group is 18. Again here maximum value of 'n' = 3. group = 18 and period = 3

- (b) Electron distribution of element with atomic number 22 is $Z(22) \rightarrow 1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 4s^2$. Here maximum value of n = 4; so its period is 4th. From incomplete d orbital $(3d^2)$ it indicates d-block element. Total electrons of 3d and 4s = (2 + 2) = 4; so its group = 4. So the element's position is period = 4; group = 4.
- (c) Electron distribution of element with at. no. 29 is $Z(29) \rightarrow 1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$. Here maximum value of n = 4; so its period = 4th. It has ndns electrons so its group = (10 + 1) = 11. So the element's position is period = 4; group = 11.
- (d) Electron distribution of element with at no. 16 is $Z(16) = 1s^2 2s^2 2p^6 3s^2 3p^4$. Here n = 3; so its period = 3rd. It is a representative element and its group = (10 + 2 + 4) = 16. S the element's position is period = 3; group = 16.
- (e) Electron distribution of element with at. no. 48 is $Z(48) \rightarrow 1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2$. Here n = 5, so period = 5th and its ndns electrons = (10 + 2) = 12. So the element's position is period = 5; group = 12.
- (f) Electron distribution of element with at. no. 59 is $Z(59) \rightarrow 1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$ $4s^2 4p^6 4d^{10} 4f^3 5s^2 5p^6 6s^2$. Here n = 6; so its period = 6th; it has partially filled $4f^3$ electrons; so its group = 3. So the element's position is period = 6; group = 3;

3.2 General Properties of Different Block Elements

s-block Elements:

s-block Elements: The elements whose last electron enters into s orbital, are called s-block elements. Total s-block elements are 14 including group-1 group-2 total 13 elements and with He(2) of inert gas. Their outermost orbit or valence shell contains ns¹ or, ns² electron

s-block metals are speciall known by two names; such as :

- (i) alkali. metals and (2) alkaline earth metals.
- (i) Alkali Metals: s-block elements of group -1 such as Li, Na, K, Rb, Cs and Fr are called alkali metals. Because these elements react with water vigorously to produce strong alkali and H₂ gas. Example.

$$2\text{Li}(s) + 2\text{H}_2\text{O}(l) \rightarrow 2\text{LiOH}(aq) + \text{H}_2(g)$$

$$2 \text{ Na(s)} + 2\text{H}_2\text{O}(l) \rightarrow 2\text{NaOH (aq)} + \text{H}_2(g)$$

$$2 \text{ K (s)} + 2\text{H}_2\text{O (l)} \rightarrow 2\text{KOH (aq)} + \text{H}_2 \text{ (g)}$$

(2) Alkaline Earth Metals: s-block elements of group-2 such as Be, Mg, Ca, Sr, Ba and Ra are called alkaline earth metals. Because oxides and carbonates of Mg and Ca metals are found in soil or earth. Alkaline earth metals react with water slowly to form weak alkali like $Ca(OH)_2$ etc. $Ca(s) + 2H_2O(l) \rightarrow Ca(OH)_2(aq) + H_2(g)$

$$CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(aq)$$

s-block elements' electron distributions with their valence electrons & symbols of inert gases are shown below: [See it in Periodic table printed on inner cover.]

| Group-1 | H(1) | Li(3) | Na (11) | K(19) | Rb(37) | Cs (55) | Fr (87) |
|---------|------|------------------------------|----------------------------|----------------------------|-------------------------------|----------------------------|----------------------------|
| | 1s1 | [He] 2s ¹ | [Ne] 3s1 | [Ar] 4s1 | [Kr]5s1 | [Xe]6s1 | [Rn]7s1 |
| Group-2 | | Be(4) [He]2s ¹ | Mg(12) [Ne]3s ² | Ca(20) [Ar]4s ² | Sr(38) [Kr]5s ² | Ba(56) [Xe]6s ² | Ra(88) [Rn]7s ² |

| Period ↓ Group→ | <u> </u> | m.p°C | 2 (2A) | m.p °C |
|------------------------|-----------------|---------|------------------|--------|
| 2 | ₃ Li | 180.5 | ₄ Be | 128 |
| 3 | 11Na | 97.7 | ₁₂ Mg | 650 |
| 4 | 19K | 63.3 | ₂₀ Ca | 842 |
| 5 | 37Rb | 39.3 | 38Sr | 777 |
| 6 | 55Cs | 28.4 | ₅₆ Ba | 727 |
| 7 | 87Fr | etg sød | 88Ra | 700 |
| /alence Electron Set : | ns ¹ | 67 10 1 | ns ² | |

MCQ-3.1: Which of the followings are metalloids:

(a) Si, Ge, As,

(b) Na, K, Rb

(c) Mg, Al, Sb;

(d) B, Fe, Ni

* * Remember :

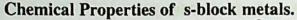
Most strong alkalies are KOH, NaOH and LiOH solutions.

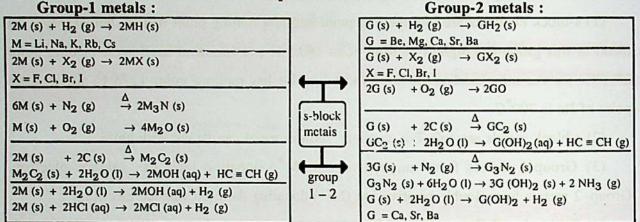
3.2.1 General Properties of s-block Metals

- (1) s-block elements are low melting point and low boiling point metals. For example, Li metal of this group has highest melting point 180.5°C and Cs metal has lowest melting point 28.4°C. On the otherhand group-2 element like Be has melting point 1278°C, the melting point of Ra is 700°C.
 - (2) s-block metals are soft. For example, sodium metal can be cut with knife.
- Group-1 metals form unipositive ion (M⁺) donating their ns¹ valence electron. Group-2 metals form double positive ion (M²⁺) donating their ns² valence electrons.
- (4) Group-1 and Group-2 metal ions have no unpaired electron, So their compounds are colourless. But exceptions are those which contain coloured negative ions like dichromate, (K₂C₂O₇) chromate, (K₂CrO₄), manganate (K₂MnO₄) and permanganate (KMnO₄).
- (5) s-block metal cations, having no unpaired electron, are diamagnetic, that is they are repelled by magnetic field.
- (6) The ionisation energy of group-1 metals are lowest and comparatively metals of group-2 have higher ionisation energy.
- (7) s-block metals are most electropositive and their reactivity increases from upwards to downwards in a group. For example, ; Cs is the most reactive metal. [Fr' is a radioactive unstable metal.]
 - (8) s-block metals act as most powerful reducing agents.
 - (9) Except Be and Mg, other s-block metals form characteristic colour in bunsen flame.
 - (10) Except Be, other s-block metals can form ionic compounds with non-metals.

Due to smaller size Be²⁺ ion never forms. Although Li atom forms, Li⁺ ion, yet due to more charge density its ionic compounds are converted into covalent compounds with polarization. For this, Li-salts are less soluble in water. LiCl, LiBr, LiI etc. are more soluble in organic solvent like polar liquid alcohol and acetone for same reason.

Worked Example 3.2: Be and Mg can not form any special colour in flame tests explain. The atomic sizes of Be and Mg are comparatively smaller and their ionisation energy values are higher, the available heat energy of Bunsen Burner cannot excite their valence electrons. So Be and Mg can not form coloured flame in Bunsen burner flame.





Chemical Reactions of s-block Elements & Rule to Remember:

Ionic compounds with non-metals: All the elements of group -1 and group -2 of s-block of the periodic table react with non-metals H_2 , halogens $(X_2 = F_2, Cl_2, Br_2, I_2)$, O_2 , N_2 and C etc. to form ionic compounds. [Follow above table].

(2) Nitrides & Carbides hydrolyse: Metallic nitrides (M₃N, G₃N₂) of s-block elements get hydrolyzed in contact of water to produce respectively NH₃ and acctylene (HC≡CH) gas together with metal hydroxide.

For example, when Mg metal is heated with N_2 gas then ionic compound magnesium nitride (Mg₃N₂) is formed. Here nitride ion of Mg₃N₂ is being polarised by Mg²⁺ ion, Mg₃N₂ is hydrolysed in hot water like a covalent compound to form Mg(OH)₂ and NH₃ gas.

$$Mg(s) + N_2(g) \xrightarrow{\Delta} Mg_3 N_2 (s)$$

 $Mg_3N_2 (s) + 6H_2O(l) \longrightarrow 3Mg(OH)_2 (s) + 2NH_3 (g)$

Similarly magnesium carbide (MgC₂) is hydrolysed in hot water to form Mg(OH)₂ and acetylene gas.

$$Mg(s) + 2C(s) \xrightarrow{\Delta} MgC_2(s)$$

 $MgC_2(s) + 2H_2O(l) \longrightarrow Mg(OH)_2(s) + HC \equiv CH(g)$

3. Reaction with water: Group-1 metals being more reactive, react with water vigorously to produce strong alkali NaOH. KOH and H₂. So group -1 metals are called alkali metals. But group-2 metals, being less reactive, react with water slowly to produce metal hydroxide and H₂ gas. Besides this, group-2 metal compounds are being the components of soil, group-2 metals are called alkaline earth metals.

Worked Example-3.3: Na metal is preserved in kerosene; explain why.

Solution: Sodium metal is a very reactive group-1 metal. Na metal can not left in air and water. Because in contact with air Na metal reacts with O₂ to form sodium oxide (Na₂O). Later Na₂O reacts with CO₂ gas of air to form sodium carbonate.

$$4Na + O_2 \longrightarrow 2Na_2O;$$
 $Na_2O + CO_2 \longrightarrow Na_2CO_3$

Again Na metal can not be kept in water. Because in contact with water, Na reacts with water vigorously to produce NaOH alkali and H₂ gas. It is an exothermic reaction; so H₂ gas sets fire in O₂ of the air to form H₂O.

$$2Na + 2H_2O \longrightarrow 2NaOH + H_2 + heat;$$
 $2H_2 + O_2 \longrightarrow 2H_2O$

So sodium metal is preserved in inactive or inert liquid kerosene.

4. Replacement of H from acid: Both group-1 and group-2 metals react with HCl acid vigorously to produce H₂ gas and metal chorides. [Follow above table]

3.2.2 General Properties of p-block Elements

p-block Elements:

Representative Elements: \$-block and p-block elements are called representative elements; because these elements follow Aufbau rule in filling their orbitals with electrons.

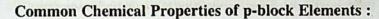
In periodic table, the elements of p-block begins from group-13 with electron distribution ns² np¹and continues with group-14, 15, 16, 17 and ends at group-18 elements with electror distribution ns² np⁶. For example:

| $\mathbf{Period} \downarrow \mathbf{Group} \longrightarrow$ | 13) | 14) | 15) | 16) | 17) | 18 |
|---|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
| 2 12 2 13 10 10 10 10 | 5B | ₆ C | ₇ N | ₈ O | 9F | 10Ne |
| all 3 gasonets ar | 13Al | ₁₄ Si | 15P | 16S | 17Cl | 18Ar |
| 4 discontinua | 31Ga | ₃₂ Ge | 33As | 34Se | 35Br | 36Kr |
| o m 5 maga (ist i | 49In | ₅₀ Sn | 51Sb | ₅₂ Te | 531 | ₅₄ Xe |
| anim 6 a sero abilique | 81Tl | 82Pb | 83Bi | 84Po | 85At | 86Rn |
| Valence Electron Set : | ns ² np ¹ | ns ² np ² | ns ² np ³ | ns ² np ⁴ | ns ² np ⁵ | ns ² np ⁶ |

General Properties of p-block Elements:

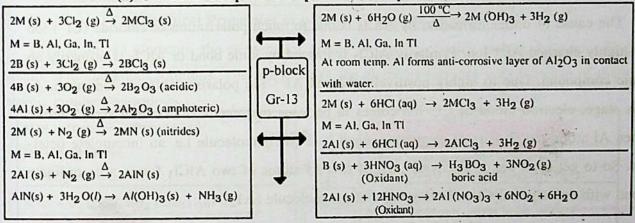
(1) Total number of p-block elements together with newly discovered Nh(113), Fl (114), Mc(115), Lv (116), Ts(117) and Og(118) are 36. These p-block elements include 08 metals (Al, Ga, In, Tl, Sn, Pb, Bi. Po except six radioactive elements) 7 metalloids or semi metals (B, Si, Ge, As, Sb, Te, At) and 15 non metals (C, N, P, O, S, Se, F, Cl, Br, I, Ne, Ar, Kr, Xe, Rn). Chemistry—First—32

- (2) Metals (12 in number) and graphite (allotrope of carbon) are good conductors of heat and electricity; and the rests are bad conductors of heat and electricity. Among these 7 metalloids (B,Si, Ge, As, Sb, Te, At) all are semiconductors.
 - (3) Most of the p-block elements are electronegative non metals.
- [4] In a period from left to right, with the increase of atomic no. of the elements valence electron also increases in the atoms; but energy level or orbit remains same. As a result elements' atomic sizes gradually decrease.
 - (5) In a period from left to right reducing property of the element decreases gradually.
- 6 In a period from left to right, oxidising property of the element increases gradually. But in a group from upwards to downwards the oxidizing property of the element decreases.
- In a group, the atomic sizes of the elements increase gradually, the ionisation energy, of an element decreases and metallic property increases.
- (8) In a same group from upwards to downwards the reducing property of the element increases.
- p-block elements form covalent bonds among themselves and form ionic bonds with different metal atoms.
- Variable oxidation numbers in p-block elements are shown in their different compounds.
- * Group-17 of the periodic table, having valence electrons ns²np⁵ are called 'halogens' These elements are F, Cl, Br I and At etc. Halogen means 'sea salt' producers; such as NaCl, NaBr, NaI salt are present in saline-water of the sea. Again Group-18 elements like. He, Ne, Ar, Kr, Xe, Rn are called inert gases. Becauses they are chemically inactive due to their more stable octet set valence electrons (except 'He' having 1s² electron set). Again most of the metals of group-16 are found in nature as metal-oxide and metal sulphide ores in mines. So group-16 elements like O, S, Se, Te are called 'Chalcogens' or 'ore-forming elements'. Most of p-blocks elements are non-metals. Among p-block elements seven elements like B, Si, Ge, As, Sb, Te and At are called metalloides due to having their mixed properties of metal and non-metal. In periodic table, right side of 'zig-zag' line in middle of p-block elements contains all nonmetals and the left side of it contains metals.



There are six groups in p-block elements. In these six groups of p-block elements, from left to right, each element adds up one electron more gradually upto six electrons at the last element. The common electron distribution of p-block elements is ns² np¹⁻⁶. The chemical properties of six groups of p-block elements are shown separately as follows:

(1) Chemical Properties of p-block Group-13 Elements:



Chlorides and nitrides are covalent in nature. So they are hydrolysed with water to form their hydroxides.

$$AlCl_3(s) + 3H_2O(l) \longrightarrow Al(OH)_3(s) + 3HCl(aq)$$

 $AlN(s) + 3H_2O(l) \longrightarrow Al(OH)_3(s) + NH_3(g)$

- * Chemical Reactions of Group-13 of p-block Elements & Rule to Remember:
- 1. Formation of binary Compounds: Boron, the 1st element of group -13, is a metalloid, but Al, Ga, In, Tl are metals. They are less reactive, so they react with Cl₂, O₂, N₂ at high temperature to form chloride, oxide and nitride. [Follow above table]
- 2. Formation of Acidic oxide: Boron oxide (B₂O₃) is acidic. So B₂O₃ reacts with water to form orthoboric acid H₃BO₃ or B₂O₃.3H₂O and metaboric acid HBO₂ (or B₂O₃. H₂O)
 - (i) $B_2O_3(s) + H_2O(l) \rightarrow 2HBO_2(s)$ [with less water]
 - (ii) $B_2O_3(s) + 3H_2O(l) \rightarrow 2H_3BO_3(s)$ [with more water]
- 3. Formation of Amphoteric oxide: A12O3 is amphoteric, So A12O3 reacts separately
 with acid (HCl) and conc. alkali (NaOH) to form salt and water in each case.

$$Al_2O_3$$
 (s) + 6HCl(aq) \rightarrow 2AlCl₃ (aq) + 3H₂O (l)
Al₂ O₃ (s) + 2NaOH(aq) \rightarrow 2NaAlO₂ (aq) + H₂O (l)

4. Hydrolysis of nitrides & Chlorides: Due to maximum polarisation in metal chloride (AlCl₃) and metal nitride (AlN), (see article-3.15.2) both AlCl₃ and AlN, like covalent compounds are hydrolyzed by water to form Al(OH)₃, HCl and NH₃ gas.

$$AlCl_3(s) + 3H_2O \Longrightarrow Al(OH)_3(s) + 3HCl(aq)$$

Al N (s) +
$$3H_2O \rightleftharpoons Al (OH)_3$$
 (s) + NH_3 (g)

Know More: AlCl3 forms dimer molecule (Al2Cl6)

The cause of dimer formation by AlCl₃ is due to much polarisation of chloride (Cl⁻) ion by highly charged Al³⁺ ion. Primarily AlCl₃ is formed by ionic bond or AlCl₃ is primarily an ionic compound. Due to highly positively charged Al³⁺ ion polarises chloride ion much. At this stage, electron cloud of Cl⁻ ion comes in between two nuclie of Al atom and Cl atom. Then Al atom gets 3 pairs of electrons around it in AlCl₃ molecule i.e. an incomplete octet-set. So to get octet set of electrons each of two Al atoms of two AlCl₃ forms a co-ordinate bond with the adjacent Cl atom forming a dimer molecule (Al₂Cl₆).

In solid state these dimer molecules form tetrahedral structure approximately and attracted by weak Vander Waal's force forming sheet structure.

5. Replacement of H of acid: Being less reactive, metals of group-13 can replace H from H₂O at 100°C to form metal hydroxide and H₂ gas. Besides this, these metal replace H from acid like HCl acid [Follow above table].

2Al (s) + 6 H₂O(g)
$$\rightarrow$$
 2Al(OH)₃ (s) + 3H₂ (g)
2Al (s) + 6 HCl(aq) \rightarrow 2AlCl₃ (aq) + 3H₂ (g)

6. Reaction with Oxidising acids: In oxidising acid like conc. HNO₃ acid, B is oxidised to B₂O₃ and HNO₃ is reduced to NO gas. Again acidic B₂O₃ forms H₃BO₃ acid with water, Similarly, Al metal reacts with HNO₃ to form first Al₂O₃ and NO₂ gas and then reacts with more HNO₃ to form Al(NO₃)₃ salt and water. [Follow above table]

At first HNO₃ dissociates into H₂O, brown NO₂ gas and nascent oxygen atom [O].

Reaction with 'B':
$$2HNO_3$$
 (conc.) $\rightarrow H_2O + 2NO_2 + [O].....\times 3$

$$2B + 3[O] \rightarrow B_2O_3$$

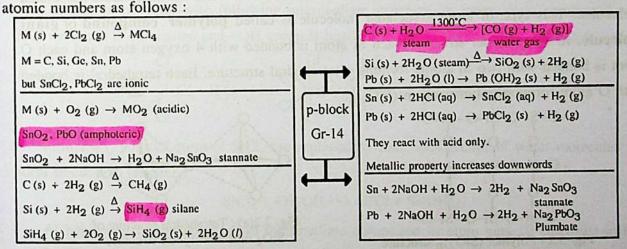
$$B_2O_3 + 3H_2O \rightarrow 2H_3BO_3$$
 [boric acid]

Reaction with 'Al': $2HNO_3$ (conc) $\rightarrow H_2O + 2NO_2 + [O]....\times 3$

$$2Al + 3[O] \rightarrow Al_2O_3$$

$$Al_2O_3 + 6HNO_3 \rightarrow 2Al(NO_3)_3 + 3H_2O$$
(2) Chemical Properties of p-black Group-14 Elements:

Like group-13 elements, the elements of group-14 also react with oxygen, halogens, H₂, steam, acid and alkali solutions. The reactivity of the elements increase with increase of their



* Chemical Reactions of group-14 of p-block elements & Rule to Remember :

- (1) Reaction with Cl₂: Non-metal C and Si and metal Sn and Pb each reacts with Cl₂ at high temperature to form tetrachloride, But Sn and Pb form dichloride salts which mostly ionic. [Follow above table]
- (2) Reaction with O₂: All elements of group-14 react with O₂ at high temperature with tetra-valency. For example, acidic CO₂, SiO₂ and oxidising againts like SnO₂, PbO act as amphoteric and react separately with conc. NaOH and HCl acid forming salt and water.

$$SnO_2$$
 as base : SnO_2 (s) + 4HCl (aq) \rightarrow $SnCl_4$ (aq) + 2H₂O (l)
 SnO_2 as acid : SnO_2 (s) + 2NaOH (aq) \rightarrow Na_2SnO_3 (aq) + H₂O (l)
 SnO_2 as base : PbO (s) + 2HNO₃ (aq) \rightarrow Pb(NO₃)₂ (aq) + H₂O (l)
PbO as acid : PbO(s) + 2NaOH (aq) \rightarrow Na_2PbO_2 (aq) + H₂O (l)
 SnO_2 as base : PbO(s) + 2NaOH (aq) \rightarrow $SnCl_4$ (aq) + H₂O (l)
 SnO_2 as acid : PbO(s) + 2NaOH (aq) \rightarrow $SnCl_4$ (aq) + H₂O (l)

Know More: At room temp. CO2 is a gas; but SiO2 is solid substance.

Here CO₂ is a simple molecule. In CO₂ molecule two O atoms are bonded with one C atom sharing two pairs of electrons forming double bonds. Structure of CO₂ molecule is linear; such as -

CO₂ molecules are attracted by weak Van-der-Waal's force only. So at room temp. CO₂ is a gas.

On the otherhand silicon dioxide (SiO₂) is a polymer compound i. e. large number of SiO₂ molecules are bonded among themselves with covalent bonds forming stable associated molecules. This type of large associated molecule is called polymer compound or giant molecule. In the polymer structure each Si atom is bonded with 4 oxygen atom and each O atom is bonded with two Si atoms forming a tetrahedral structure. Each tetrahedral is bonded with O atom forming polymer-chain (SiO₂)_n.

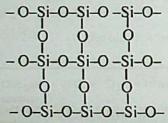


Fig- 3.2: Polymer (SiO₂)_n structure

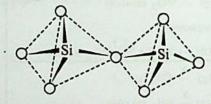


Fig- 3.2(a): Tetrahedral structure of SiO₂ unit in Polymer structure

During melting of polymer $(SiO_2)_n$, many covalent bonds are to break and much heat energy is used for this. Hence melting point and boiling point of polymer silicon dioxide $(SiO_2)_n$ is much high; Such as m.p = 1610°C and b. p. = 2230°C. At room temp. silicon dioxide $(SiO_2)_n$ is a solid crystalline substance

- (3) Formation of hydride: The elements of group-14 react with H₂ to form tetrahydrides called silane. [Follow above table]
- (4) Replacement of H from water: C, Si, Pb react with steam at high temperature to form H₂ gas. This reaction proves those metals are more reactive than H.
 - (5) Replacement of H from HCl: Metal Sn and Pb can replace H from HCl acid.

 ydrolysis of Halides: Except CCl₄, other covalent halides of group-14 like SiCl₄

 plysed in contact of water. The first condition for hydrolysis of a compound, the

central atom of covalent compound must contain a d-orbital vacant. With that vacant d-orbital, a co-ordinate bond is formed with lone-pair of O atom of H₂O. The C-atom of 2nd period element has no d-orbital, So CCl₄ is not hydrolysed in water.

But central atom of SiCl₄ is Si atom is a non-metal included in 3rd period, and it has vacant 3d orbital. So the Si atom of SiCl₄ can form coordinate bond with O atom of water and then gets hydrolysed.

SiCl₄ + 4H-OH
$$\longrightarrow$$
 4HCl + Si(OH)₄ [silicic acid]
CCl₄ + H₂O \longrightarrow no reaction

Explanation: The hydrolysis of SiCl₄ occurs with formation of a co-ordinate bond with Si and O atom of water with following intermediate structure. In intermediate compound one HCl molecule is eliminated and -OH group is bonded with Si atom with covalent bond.

In this way four Cl atom of SiCl₄ are replaced by four -OH groups of water molecules t form silicic acid (H₄SiO₄).

At beginning of the reaction, in intermediate compound Si atom gets 10 electrons in its valence shell. Among these electrons, 4 pairs in four Si-Cl bond and one pair electrons, from co-ordinate bond of $Si \leftarrow OH_2$. As Si is the element of 3rd period; it has vacant 3d orbital at which electron-pair can be supplied by H_2O to form co-ordinate bond; and thus octeve expansion for Si atom is possible. Later in final product $Si(OH)_4$ molecule Si atom gets back octet set of electrons.

But carbon is an element of 2nd period. In 2nd orbit of any atom has no d-orbital. So C atom has no possibility to expand its octet. Hence water molecule (H₂O) can not get opportunity to form intermediate compound with co-ordinate bond between C atom and O atom of H₂O. Thus CC1₄ is not hydrolysed.

(3) Chemical Properties of p-block Group-15 Elements:

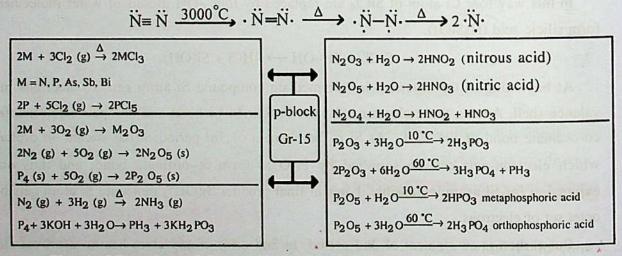
Like group-14 elements, the elements of group-15 also react with halogens, oxygen and H₂ gas. N₂ and Cl₂ react to form NCl₃ only, but other elements form pentachloride with octet expansion using their d-orbitals, N forms 5 oxides, P forms 4 oxides. Oxides of the both

elements N, P with oxidation number + 3 and higher are acidic which form oxoacids with water forming HNO₂, HNO₃, H₃PO₃ and H₃PO₄ acids.

Know More: Next to inert gases, N2 is an inert gas; so N2 gas is used as inert medium.

Explanation: From electron distribution of N atom, $N(7) \rightarrow 1s^2 2s^2 2p_x^{-1} 2p_y^{-1} 2p_z^{-1}$, it is known that it has three half filled p-orbitals which are symmetrical and more stable. Again its valence electrons are in 2nd orbit; hence size of N atom is small. So during formation of diatomic molecule (N_2) , after formation of nitrogen-nitrogen sigma bond, each of two remaining p-orbitals of one N atom can overlap side-wise with similar p-orbital of other N atom to form two pi-bonds $(N\equiv N)$. Thus triple bond formed in nitrogen molecule $(N\equiv N)$ becomes more stable. Bond-strength of this triple bond is 945 kJmol⁻¹ and bond length is 0.1098 nm.

For this reasons, N₂ molecule is chemically inert much. Actually next to inert gases of group-18, nitrogen molecule is inert. So N₂ gas is used as inert medium. But at high temp like 3000°C the triple bond of N₂ molecule breaks stepwise to form atomic nitrogen and then it becomes chemically active.



- * Chemical Reactions of Group-15 of p-block Elements & Rule to Remember.
- (1) Chloride formation: Trivalent N forms NCl₃ with Cl₂. But P, a member of 3rd period, at excited state can transfer one electron of 3s² orbital to vacant 3d orbital to get five unpaired electrons. Then P atom can form PCl₅ in addition to PCl₃. It is called expansion of octet by P atom.

For example, electron distribution of N(7) = $1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$. Then N atom having three unpaired electrons, can react with halogen atoms (F, Cl, Br, I) to form trihalides like NF₃, NCl₃, NBr₃ and NI₃ with covalent bonds. Here N atom shows co-valency 3.

$$N_2(g) + 3Cl_2(g) \rightarrow 2NCl_3(l)$$

Here NF₃ is stable much and NCl₃, NBr₃ and NI₃ are somewhat explossive.

Similarly, phosphorus atom having 3 unpaired valence electrons, can show co-valency 3. But at excited state of P atom one electron from 3s² can jump to vacant 3d orbital to get 5 unpaired electrons. Then P atom can show co-valency 5.

$$P(15) = 1s^2 2s^2 2p^6 3s^2 3p_x^1 3p_y^1 3p_z^1 3d^\circ$$

$$\mathring{p} (15) = 1s^2 2s^2 2p^6 3s^1 3p_x^1 3p_y^1 3p_z^1 3d_{xy}^1$$

So phosphorus can form pentahalides together with trihalides. But with iodine PI₃ is formed but PI₅ is not formed. Phosphorus with limited Cl₂ can form PCl₃ and with excess Cl₂ forms PCl₅.

$$P_4(s) + 6Cl_2(g) \rightarrow 4PCl_3(l)$$

$$P_4(s) + 10Cl_2(g) \rightarrow 4PCl_5(l)$$

But N atom has no 2d orbital in 2nd orbit; hence N atom has no capacity to increase its covalency. So NCl₅ is not formed.

- (2) Oxide formation: Non-metal N has five different oxides like nitrous oxide (N_2O) , nitric oxide (NO). dinitrogen trioxide (N_2O_3) , dinitrogen tetraoxide (N_2O_4) or nitrogen dioxide (NO_2) and dinitrogen pentoxide (N_2O_5) . Here N_2O and NO are neutral oxide. Other three oxides are acidic. They form oxoacids with water. [Follow above table].
- * Acid anhydride like P₂O₅ combines with less number of water to form metaphosphoric acid (HPO₃) and with more water to form orthophosphoric acid (H₃PO₄) or Phosphoric acid.
- (3) Hydride formation: At high temp. 500°C and high pressure (200 atm) in presence of catalyst iron powder, N₂ gas and H₂ gas react to form ammonia (NH₃).

But with conc. alkali (NaOH), white phosphorus on heating, forms phosphine (PH₃) gas and sodium hypophosphite (NaH₂PO₂).

$$N_2(g) + 3H_2(g) = \frac{500^{\circ}\text{C, Fe}}{200 \text{ atm}} 2NH_3(g)$$

$$P_4(s) + 3 \text{ NaOH(aq)} + 3H_2O(l) \xrightarrow{\Delta} PH_3(g) + 3NaH_2PO_2(aq)$$

Basic Property of NH₃ and PH₃: Ammonia (NH₃) and phosphine (PH₃) molecules both contain lone pair electron which can donate to proton to form co-ordinate bond with proton. So as proton acceptor or electron pair donor both NH₃ and PH₃ are bases.

H₃N: + H⁺
$$\longrightarrow$$
 [H₃N: \rightarrow H⁺] or, NH₄⁺ (ammonium ion) mistry—First—33

.
$$H_3P$$
: + $H^+ \longrightarrow [H_3P : \rightarrow H^+]$ or, PH_4^+ (phosphonium ion)

But NH3 is more basic than PH3. It has following two causes-

- (1) First cause is that electronegativity of N atom (3.0) is more than that of P atom (2.1). Due to more electro-negativity, in comparison to P-H bond, here N-H bond electron cloud is attracted more towards N atom.
- (2) Second cause is that comparatively atomic size of N atom (0.075 nm) is smaller than that of P atom (0.11nm). Due to smaller atomic size of N atom than P atom, the net electron density of that covalent bond and lone-pair electron over N atom is more than P atom. As a result comparatively N atom of NH₃ has more capacity to donate electron pair or accept proton than P atom of PH₃. So ammonia is more basic than phosphine.
- (4) Hydrolysis of Halides: Except NF₃ other halides of group-15 elements are hydrolysed in contact of water. For example, NCl₃ is hydrolysed in contact of water to produce NH₃ gas and HOCl acid (hypochlorous acid).

During hydrolysis to form a co-ordinate bond the group-15 element or related halogen atom of halide must have a vacant d-orbital. It is to be noted, none of N atom and F atom in NF₃, has any vacant d-orbital; so NF₃ is not hydrolysed by water. On the otherhand, in NCl₃ molecule Cl atom has vacant d-orbital, although N atom has no vacant d-orbital. So O atom of H₂O can make co-ordinate bond with Cl atom of NCl₃ as follows and finally after bond dissociation NH₃ gas and HOCl acid are produced.

$$Cl_{2}N - Cl + H_{2}O \longrightarrow \downarrow \uparrow \uparrow \xrightarrow{-HOCl} Cl_{2}NH \xrightarrow{2H_{2}O} NH_{3} + 2HOCl$$

$$H - \ddot{O} - H$$

PCl₃ in contact with water (like NCl₃) is hydrolysed to form HCl acid and H_3PO_3 (phosphorus acid). $PCl_3 + 3H_2O \rightarrow 3HCl + H_3PO_3$

During hydrolysis of PCl₃ both P atom and Cl atom are capable to form co-ordinate bond with lone-pair electron of H₂O and PCl₃ gets hydrolyzed as follows:

$$CLP - Cl + HQ \rightarrow \uparrow \downarrow \downarrow \\ H - \ddot{O} + H \qquad H - O - P \stackrel{Cl}{\longleftarrow} 2H_2O \rightarrow H - O - P \stackrel{OH}{\longleftarrow} + 2HCl$$

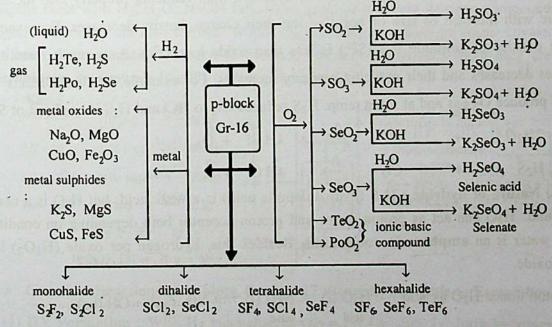
Again PCl₅ is hydrolysed to form H₃PO₄ and HCl. This hydrolysis occurs in two steps. At first step phosphorus oxychloride (POCl₃) and HCl and at 2nd step POCl₃ is hydrolysed to form H₃PO₄ and HCl acid.

$$PCl_5 + H_2O \rightarrow POCl_3 + 2HCl$$

 $POCl_3 + 3H_2O \rightarrow H_3PO_4 + 3HCl$

(4) Chemical Properties of p-block Group-16 Elements:

First element of group-16 is oxygen which is second highest electronegative element. With oxygen, the other elements of the same group and all the less electronegative elements placed on left side of oxygen, react to form different oxides. Most of the metals remain in earth surface as metal oxide and metal sulphide as their ores in mines. So elements of group -16 (like O, S, Se, Te etc.) are called ore-forming elements or `Chalcogens' Other reactions of this group elements are shown below:



- * Chemical Reactions of Group-16 of p-block Elements & Rule to Remember:
- (1) Hydride formation: Elements of group-16 form oxides with oxidation number-2; such as H₂O, H₂S etc. Again with oxidation number -1, oxygen forms H₂O₂ (hydrogen peroxide).

Characteristics of hydrides:

(i) At room temp. among different hydrides of group-16, only hydride of oxygen or weater (H₂O) is liquid. Hydride of sulphur (H₂S) is a gas. Cause of this is smaller size of

O atom and O atom is being more electronegative, H₂O is a polar compound. So the molecules of H₂O are bonded with H-bond among themselves forming cluster-molecules. Hence at room temp. water is a liquid.

$$H \longrightarrow \ddot{Q} : \cdots \longrightarrow H \longrightarrow \ddot{Q} : \cdots \longrightarrow H \longrightarrow \ddot{G} : \cdots \longrightarrow H \longrightarrow \r{G} : \cdots \longrightarrow H \longrightarrow$$

Inter molecular H-bond (----) among water (H2O) molecules.

But sulphur and next elements of sulphur in group-16 have less electronegativity. So their hydrides like H₂S is non-polar. They do not form H-bonds among themselves and are attracted by weak Van-der Waal's force. So they are gases at room temperature.

Similarly tellurium hydride (H₂Te), selenium hydride (H₂Se), polonium hydride (H₂Po) etc. are gases.

(11) Reducing property of hydrides (H_2O , H_2S): H_2O , H_2S have reducing property and with increase of size of central atom of hydrides, their reducing property also increases. Because with increase of size of negative ion their charge density decreases. For example, charge density of sulphide ion (S^{2-}) is less than oxide ion (O^{2-}). As a result stability of hydrides decreases and their reducing property increases. For example, hot water reacts with $C1_2$ to produce O_2 gas and at room temp. H_2S reduces $C1_2$ to HC1 and H_2S is oxidised of S.

$$2H_{2}\overrightarrow{O} + 2\overset{\triangle}{C}l_{2} \xrightarrow{\Delta} 4H\overset{-1}{C}l + \overset{\triangle}{O}_{2}$$

$$H_{2}\overrightarrow{S} + \overset{\triangle}{C}l_{2} \xrightarrow{\Delta} 4H\overset{-1}{C}l + \overset{\triangle}{S}$$

(iii) Nature of hydride: H_2S (hydrosulphuric acid) is a weak acid; but H_2O is a neutral compound. H_2O can act as proton donor and proton acceptor both depending on condition. Hence water is an amphoteric compound. Besides this, hydrogen per oxide (H_2O_2) is an acidic oxide.

Proton donor H₂O as acid : H₂O (l) + NH₃ (l)
$$\longrightarrow$$
 NH₄⁺ (aq) + OH̄ (aq)
acid base

Proton acceptor H₂O as base : H₂O (l) + HCl (g) \longrightarrow H₃O⁺ (aq) + \overline{Cl} (aq)

(2) Metal oxide & Metal sulphide formation: Different metals form metal oxides when they are heated with oxygen; such as Na₂O, MgO, CuO, Fe₂O₃ etc. Similarly metals form sulphides on heating with sulphur.

$$4Na + O_2 \xrightarrow{\Delta} 2Na_2O;$$
 $Mg + S \xrightarrow{\Delta} MgS$
 $2Cu + O_2 \xrightarrow{\Delta} 2CuO;$ $Fe + S \xrightarrow{\Delta} FeS$

(3) Non-metal oxides acidic: Oxides of sulphur and selenium non-metals are acidic; so they form oxo-acids with water and with alkali form salts of oxoacids.

$$SO_2 + H_2O \longrightarrow H_2SO_3$$
 [sulphurous acid]
 $SO_2 + 2KOH \longrightarrow H_2O + K_2SO_3$ [potassium sulphite]
 $SeO_2 + H_2O \longrightarrow H_2SeO_3$ [selenus acid]
 $SeO_2 + 2KOH \longrightarrow H_2O + K_2SeO_3$ [potassium selenite]

(4) Halide formation: On heating sulphur with halogens monohalides (S₂F₂, S₂Cl₂), dihalides (SCl₂, SeCl₂), tetrahalides (SF₄, SCl₄) and hexahalides (SF₆, SCl₆) etc. are formed.

(5) Chemical Properties of p-block Group-17 Elements:

Group-17 elements are strong oxidising agents. Of this groups 'F' is the most electronegative reactive non-metal element. This group elements are also called **halogens** which react with all the elements placed on left side of halogens in the periodic table. Halogens react with H₂, H₂O, NaOH (alkali) to produce different halogen compounds. Inter halogen compounds are also formed. When less eletronegative halogen forms covalent bond with more electronegative halogen to produce covalent compounds, then they are called inter-halogen compounds like IF₅ (iodine penta fluoride).

- * Chemical Reactions of p-block Group -17 Elements and Rule to Remember:
- (1) HX Formation: With H_2 gas halogens ($X_2 = F_2$, Cl_2 , Br_2 , I_2) form hydrogen halide (HX) gas. Except HF, other halides HCl, HBr, HI remain as diatomic molecules; but due to H-bond between HF molecules, HF molecules remain as associated molecules (HF)_n and its b.p. is 19.5° C. Aqueous solution of HX gas is called halogen hydracid HX(aq). Gradational strength of different halogen hydracids is HI(aq)> HBr(aq)> HCl> (aq)> HF(aq). From the value of acid dissociation constant K_a , it becomes clear. The values of K_a are shown in above table at the side of each acid.

(2) F₂ is the most reactive element: F₂ and Cl₂ are stronger than O₂. Hence F₂ can oxidise H₂O completely by forming O₂ gas and HF(aq) acid.

$$2F_2(g) + 2H_2O(l) \rightarrow 4HF(aq) + O_2(g)$$

(3) Disproportionation Reaction of halogens: With water Cl₂ reacts slowly to form hydrochloric acid HCl (aq) and hypochlorous acid or chloric(I)acid [HOCl(aq]. Here between two Cl atoms one is oxidised and other Cl atom is reduced, so this type of reaction is called disproportionation reaction.

$$O_{Cl_2(g)} + H_2O(l) \rightarrow HCl(aq) + HOCl(aq)$$

In product HCl, the oxidation number of Cl is - 1; so here reduction of Cl atom occurs and in HOCl, the oxidation number of Cl atom is +1; so here oxidation of Cl atom occurs. In elementary Cl₂, its oxidation number is 0 (zero).

Similarly with KOH solution Cl₂ gives disproportionation reaction of Cl atom to form potassium chloride (KCl) and potassium chlorate (I) salt and water.

$$Cl_2(g) + 2KOH(aq) \xrightarrow{25^{\circ}C} KCl(aq) + KOCl(aq) + H_2O(l)$$

(6) Chemical Properties of p-block Group-18 Elements :

Group-18 elements have their outer most energy level filled with octet set of electrons in s and p orbitals like ns² np⁶; hence these elements have no tendency to combine with any other element generally. Yet Xe element can react with most electronegative F₂ at high temperature in presence of catalyst Ni-powder to form xenon difluoride (XeF₂), xenon tetrafluoride (XeF₄) and hexa fluoride (XeF₆).

* Inert element xenon (Xe) reacts with flourine to form xenon fluorides.

Its Explanation: The atomic size of xenon, the element in 5th period, is larger than other 4 inert gases (except Rn and Og). Due to larger atomic size, the nuclear attraction on valence electrons of xenon becomes weak generally. At high temp, and in presence of Ni-catalyst, the paired up electron of 5p orbital becomes unpaired and replaced to 5d orbital. Then two unpaired electrons of Xe atom can combine with reactive F atoms to form xenon diflouride.

Ground state electron distribution of Xe is:

$$Xe(54) = 1s^{2} 2s^{2} 2p^{6} 3s^{2} 3p^{6} 3d^{10} 4s^{2} 4p^{6} 4d^{10} \left[5s^{2} 5p_{X}^{2} 5p_{Y}^{2} 5p_{Z}^{2} \right]$$

At 1st excited state, one electron of 5p is transferred to 5d orbital; then electron

distribution of Xe becomes:
$$X^*$$
 (54) =... $5s^2$ $5p_X^2$ $5p_Y^2$ $5p_Z^2$ $5d_{XY}^2$. Here two unpaired

electrons exist. Then before reaction, sp^3d orbital hybridization occurs in Xe atom to form 5 hybrid orbitals $(5\psi_1^2 \ 5\psi_2^2 \ 5\psi_3^2 \ 5\psi_4^1 \ 5\psi_5^1)$. Among these 5 hybrid orbitals two hybrid orbitals with single eletron combine with two F atoms to form XeF₂. Then valency of Xe atom is 2.

$$Xe(g) + F_2(g) \xrightarrow{400^{\circ}C} XeF_2(s)$$

At 2nd excited state, two paired 5p electrons get unpaired and out of 4 electrons, two unpaired electrons are transferred to 5d orbitals; then electron distribution of Xe becomes:

**
$$Xe(54) = \dots$$
 $5s^2 5p_x^2 5p_y^1 5p_z^1 5d_{xy}^1 5d_{yz}^1$ Here 4 unpaired electrons exist.

Then with this electron distribution sp³d² orbital hybridization occurs in Xe atom to form 6 hybrid orbitals $(5 \, \Psi_1^2 \, 5 \, \Psi_2^2 \, 5 \, \Psi_3^1 \, 5 \, \Psi_4^1 \, 5 \, \Psi_5^1 \, 5 \, \Psi_6^1)$. Then 4 hybrid orbitals with single electron combine with four F atoms to form XeF₄ (xenon tetra fluoride) with its valency 4.

$$Xe(g) + 2F_2(g)$$
 $F \longrightarrow Xe \longrightarrow F$
 XeF_2
 XeF_4
 XeF_4
 XeF_6
 XeF_6
 YeF_6
 $YeF_$

Fig-3.2(b): Structures of XeF₂, XeF₄ and XeF₆

Similarly by transfer of 3 unpaired electrons to 5d orbitals and with sp³d³ hybridization Xe atom gets valency 6 to form XeF₆. Again by transfer of 4 electrons to 5d orbitals and with sp³d⁴ hybridization Xe atom gets valency 8.

Again Xe atom can be excited, but smaller atom like Kr, Ne etc. can not be easily excited. For this reason Ne can not form flouride.

Student's Work-3.2: Problems Based on s-block and p-block Elements:

Problem-3.2.1: Be and Mg do not form any special colour in flame test; explain.

Problem-3.2.2: Sodium metal is preserved in kerosene; explain why.

Problem-3.2.3: Explain what happens when Mg metal is heated with N₂ gas and the product is mixed with hot water.

Problem-3.2.4: Explain what happens when Ca metal is heated with C-powder and the product is mixed with water.

Problem-3.2.5: Explain what happens when B is heated with oxygen and the product is mixed with water.

Problem- 3.2.6: Al₂O₃ is an amphoteric oxide; establish it with related chemical reactions.

Problem-3.2.7: Explain with equations what happens when Al metal is dissolved in conc. HNO₃ acid.

Problem-3.2.8: Explain what happens when Al metal is heated with N₂ gas and the product is mixed with hot water.

Problem-3.2.9: Explain CCl₄ is not hydrolysed in water; but SiCl₄ is hydrolysed.

Problem-3.2.10: SnO₂ is an amphoteric oxide; establish it with chemical reactions.

Problem- 3.2.11: PbO is an amphoteric oxide; prove it with related reactions.

Problem-3.2.12: With Cl₂ gas N₂ forms only NCl₃; but P can form PCl₃ and PCl₅; explain why.

Problem-3.2.13: NCl₃ is hydrolysed with water; but NF₃ is not hydrolysed; explain why.

Problem-3.2.14: PCl₃ is hydrolysed with water; explain with equation.

Problem-3.2.15: Comparatively PCl₃ is hydrolysed rapidly than NCl₃; explain why.

Problem-3.2.16: NH₃ and PH₃ both show basic property; explain why.

Problem-3.2.17: NH3 is more basic than PH3; explain why.

Problem-3.2.18: H₂O is a liquid, but H₂S is a gas; explain why.

Problem- 3.2.19: H₂S and H₂O both show reducing property; explain with reactions.

Problem-3.2.20: H₂O is an amphoteric oxide; explain

Problem-3.2.21: Explain the physical states of Group-17(or VIIA) elements.

[Ctg. B. 2017]

Problem-3.2.21(a): What is disproportionation reaction? Cl₂ shows disproportionation reaction; prove it.

Problem-3.2.22: What are inter-halogen compounds? Explain with examples.

Problem-3.2.23: Xe atom has octet valence shell; yet it can form xenon difluoride

(XeF2); explain how it occurs.

3.2.3 General Properties of d-block Elements

The electron distributions of the d-block elements in their outer two energy levels is (n-1) d¹⁻¹⁰ ns¹⁻². That is these elements contain 1 or 2 electrons in s-orbital of outer most n-orbit and 1 to 10 electrons in d-orbital of (n-1) orbit. For example:

$$Sc(21) \rightarrow 1s^2 2s^2 2p^6 3s^2 3p^6 3d^1 4s^2$$
; $Fe(26) \rightarrow 1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$

Classification of d-block Elements:

3d-block elements: Sc(21) - Zn(30); outer two orbits 3d1-10 4s1-2

4d-block elements: Y(39) - Cd(48); outer two orbits 4d¹⁻¹⁰ 5s¹⁻²

5d-block elements: La(57), Hf(72) — Hg(80); outer two orbits 5d¹⁻¹⁰ 6s¹⁻²

6d-block elements: Ac(89), Th (90), Rf(104) - Cn(112); with 6d1-10 7s1-2

| Period ↓ | block | Group> | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | ii - | 12 |
|-------------|-------|--------|------|------------------|--------|------------------|------------------|-------|-------|-------|-------|-------|
| 4 | 3d | All A | 21Sc | ₂₂ Ti | 23 V | ₂₄ Cr | ₂₅ Mn | 26Fe | 27Co | 28Ni | 29Cu | 30Zn |
| 5 | 4d | l ben | 39 Y | 40Zr | 41Nb | 42Mo | 43Tc | 44Tu | 45Rh | 46Pd | 47Ag | 48Cd |
| 6 | 5d | | 57La | 72Hf | 73Ta | 74W | 75Re | 76Os | 77 Ir | 78Pt | 79Au | 80Hg |
| 7 | 6d | | 89Ac | 104Rf | 105Db | 106Sg | 107Bh | 108Hs | 109Mt | 110Ds | 111Rg | 112Cn |
| | | | 90Th | electr | on set | (n-1)d1 | -10 ns1- | -2 | | | | |

General Properties of d-block Elements:

- All the d-block elements are heavy metals. Their density is very high. Among them, density of Sc (21) is minimum like 3.4 g cm⁻³. Iridium. Ir(77) of 5d block has maximum density of 22.61 g cm⁻³, then Osmium Os(76) has second highest density 22.59 g cm⁻³.
- Except gr-12 elements, other d-block elements have partially filled d-orbital and most of them have variable oxidation number.
- (W) has the highest m.p. (3410°C) in 5d-block and highest for Mo (2617°C) in 4 d block and for V (1910°C) in 3d-block elements.
- These d-block metals are hard and strong (except liquid mercury, Hg (melting point is -38.84°C)
- (5) d-block elements are good conductors of heat and electricity.

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- (6) The ionisation energy of d-block element is higher than that of s-block element; but lower than that of p-block elements.
 - (7) d-block metals are less electropositive than s-block metals.
- (8) Most of the d-block metals are paramagnetic, that is they are attracted by magnetic field; the reason is that they contain unpaired electron in d-orbital. Iron and cobalt can be magnetised; hence they are called ferromagnetic metals.

[exception: Sc3+, Ti4+, Zn2+, Cu+ ions]

- (9) Most of the d-block metals can form good metal alloys.
- (10) Most of the d-block metals are called transition metals for their special properties.

[Note: The present syllabus includes only 3d elements. But 4d, 5d, 6d, elements are out of present syllabus.]

Transition metals: Those d-block elements which have at least one stable ion with partly filled d-orbital (like d¹⁻⁹) are called transition metals.

For example iron Fe (26) is both d-block element and transition metal. Firstly the last electron of Fe atom enters into d-orbital; secondly its stable Fe²⁺ and Fe³⁺ ions contain partially filled d-orbitals. Their electronic configurations are as follows:

Fe(26) \rightarrow 1s² 2s² 2p⁶ 3s² 3p⁶ 3d⁶·4s² [d-orbital element] Fe²⁺(26) \rightarrow 1s² 2s² 2p⁶ 3s² 3p⁶ 3d⁶ [Transition metal ions with Fe³⁺(26) \rightarrow 1s² 2s² 2p⁶ 3s² 3p⁶ 3d⁵ partially filled d-orbitals] Transition elements have following characteristic properties:

| | What are the |
|---------------|--------------|
| period and | d group of |
| element 39Y | ? |
| (a) Period-5 | group -1 |
| (b) Period-5. | group -2 |
| (c) Period-5, | group- 3 |
| (d) Period-4 | group -2 |

- (1) Variable oxidation states; (2) Formation of coloured ion,
- (3) Formation of complex ion, (4) Catalytic action, (5) Paramagnetic property.

Similarly like Sc and Zn, 4d-block elements Ag (47), Cd (48) and 5d-elements Hg (80) are not transition elements because their ions Ag⁺, Cd²⁺, Hg²⁺ contain d¹⁰ electronic structures. However the chemistry of these elements are discussed together with the chemistry of transition elements, because some of their properties are similar to those of transition elements.

* All d-block elements are not transition Elements.

The d block elements which have stable cation with partial d¹⁻⁹ electron distribution are called transition elements. But those d-block elements which have cations with d-orbital either

vacant (d°) or fully filled up (d10) are not transition metals. Those d- block elements can not show special properties like variable valency, coloured compound formation, complex compound formation. Hence those d-block elements are not transition elements. For example, Sc (21) and Zn(30) are d-block elements. Here stable Sc3+ ion has vacant d-orbital (d°) and Zn2+ ion has fully filled d10 orbital. So Sc and Zn are not transition elements ?

$$Sc^{3+}(21) \longrightarrow 1s^{2} 2s^{2} 2p^{6} 3s^{2} 3p^{6} 3d^{\circ}$$
 $Z_{n}^{2+}(30) \longrightarrow 1s^{2} 2s^{2} 2p^{6} 3s^{2} 3p^{6} 3d^{10}$

Student's Work: 3.3: d-block Elements & Transition Elements Based.

Problem-3.3(a): Write the electron distributions of following atoms and their ions; and then confirm them which are transitional metals and which are only d-block metals:

Cr. (24), Cr³⁺; Mn (25), Mn²⁺; Ni (27), Ni²⁺; Cu(29), Cu²⁺; Pb(46), Pb²⁺; Cd(48), Cd²⁺

Problem-3.3(b): Cr (24) and Cu(29) have exceptional electron distributions; explain.

[Syl. B. 2015; Din. B. 2015]

Problem-3.3(c): What is transition element? [D.B. 2015; J. B. 2016; B. B. 2017]

Problem-3.3(d): All d-block elements are not transition elements, but all transition [D.B. 2017; R. B. 2017] elements are d-block elements; explain.

[C. B. 2017] Problem-3.3(e): Explain whether Zn is a transition element.

Problem-3.3(f): Which one of Cu and Zn is a transition element; explain.

[Brd. Q. 2018] Problem-3.3(g): Fe is called transition element; explain.

Problem-3.4(a): Write the differences between ideal elements (s and p blocks) and transition elements of periodic table.

Problem-3.4(b): Write the electron distributions of A(24) and D(30) elements; and then [Madrasa B. 2017] determine their position in periodic table.

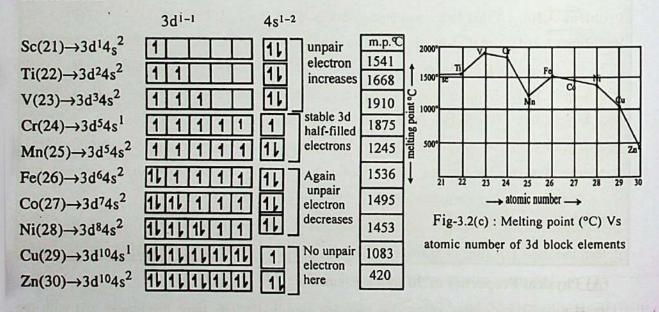
(A) Physical Properties of 3d-block Elements:

The physical properties of 3d-elements are mainly-(i) they have brightness, (ii) with the increase of atomic number or increase of atomic mass but decrease in atomic radius in a period, their density increases. Among 3d-metals scandium [Sc(21)] has minimum density of 3.4g cm⁻³ and Cu has maximum density of 8.9 g cm⁻³ in 3d metals. Of all the metals iridium [Ir (77] has highest density of 22.61g cm⁻³ and next to Ir is Osmium [Os(76)] having density 22.59gcm⁻³; (iii) depending on metallic bond 3d metals have high melting point (m.p.) and high boiling point (b.p); (iv) 3d-metals have special magnetic property and (v) they act as catalyst in chemical reactions.

(1) Explanation for high M.P. and high B.P. of 3d-metals :

The melting points of 3d-metals in 4th period increases gradually from left to right in periodic table with the increase of their atomic number and after three metals again decreases. Of the 3d block metals, Sc(21) has m.p. 1541°C and increases gradually upto vanadium V(23) with highest m.p. 1910°C and then decreases abruptly to manganese Mn(25) at middle of the period with m.p. 1245°C. After that again it increases suddenly to iron Fe(26) with m.p. 1536°C. And then m.p of the rest metals gradually decreases to Cu(29) with m.p. 1083°C and upto last d-block metal Zn(30) with m.p. 420°C.

Melting point of metal depends on magnitude of metallic bond energy among the metal atoms and this bond-energy depends on number of mobile unpaired electrons in metallic bond. So m.p. of the metals with 3d¹ to 3d³ electron distributions like Sc(21) to V(23) increases. But symmetrical d⁵ electron distribution is more stable and remain less mobile. So m.p of Cr(24) and Mn(25) decreases. This will be clear from following box based electron distributions.



Again Fe(26) atom contains 4 mobile unpaired electrons, so m.p. of Fe increases abruptly to 1536°C. After that with decrease of number of unpaired electrons, the metallic bond energy decreases and m.p. of the related metal also decreases gradually upto Cu(29) with m.p. 1083°C having only 4s¹ mobile electron. Zn metal atom has no unpaired mobile electron; so Zn has lowest m.p. 420°C in 3d metal series.

(2) Magnetic Property: We know from spin quantum number of atom, each electron, due to its spin movement, acts as a thin magnet producing poor magnetic field. Some spinning unpaired electrons creates magnetic moment ($\mu = Q \times r$) and shows magnetic

property towards external magnet. On the otherhand magnetic moments of electrons with opposite spins become mutually opposite and their net magnetic moment becomes zero; so that atom or ion has no magnetic property. According to behaviour towards external magnetic field matters are classified into 3 types; such as: (1) paramagnetic, (2) ferromagnetic and, (3) diamagnetic.

- (i) Paramagnetic: The substance attracted by external magnetic field, is called paramagnetic substance. Paramagnetic property is due to unpaired electrons in atom or ion of the substance. How many unpaired electrons are present in an atom or ion can be determined by the magnitude of its paramagnetic attraction. The transition metals' ions with unpaired electrons like Ti³⁺, V³⁺, Cr³⁺, Mn²⁺, Fe²⁺, Fe³⁺, Co²⁺, Ni²⁺, Cu²⁺ are all paramagnetic.
- (ii) Ferro-magnetic: The substances which are attracted much by external magnetic field are called ferro-magnetic substances; such as Fe, Co, Ni etc. Fero-magnetic atoms or ions contain maximum number of unpaired electrons. Ferro-magnetic substance can be magnetised. Basically ferromagnetism is the highest point of paramagnetism.
- (iii) Diamagnetic: The substances which are not attracted by external magnetic field, but repelled mildly, are called diamagnetic substances.

In diamagnetic substances, their atoms or ions contain all paired electrons; so they have no magnetic property. So they are not attracted by any magnet. Ions of group—1 and group—2 metals are all diamagnetic; because they contain full octet set of electrons.

(3) Catalytic Property of Transition Metals: Transition metal atom contains one or more vacant d-orbital; all the transition metals can show more than one oxidation state to form compounds and having more surface area, transition metals can act as catalyst in different chemical reactions.

There are two theories for explanation of catalytic activity of transition metals:

- (i) Catalysis through adsorption and,
- (ii) Catalysis with intermediate compound formation.
- (1) Catalysis through adsorption: According to adsorption theory, on the surface of transition metal, the reactant molecules are adsorbed in single layer in vacant d-orbitals. Then reactant molecules, with following 4 steps, complete the reaction:

$$A(g) + B(g) \xrightarrow{Fe} C(g) + D(g)$$

1st Step: Gaseous reactant molecules (A and B) are adsorbed on the catalyst metal (Fe) surface in proper orientation i. e with weak chemical bond they form one-layer closed arrangement.

2nd Step: In this 2nd step covalent bonds in adsorbed molecules become weak; affective collisions between adsorbed molecules occur in proper orientations, and form activated complex with lower activation energy.

3rd Step: In this 3rd step, the unstable 'activated complex' dissociates to form new product molecules ('C' and 'D') and still remain attached on catalyst surface. The energy produced is absorbed by catalyst and is supplied to reactant molecules next.

4th Step: In this last step, the product molecules (C and D) get free from catalyst surface.

Example: In Haber's process for manufacture of ammonia from N₂ and H₂ gases catalyst iron (Fe) powder is used. At this on the surface of Fe powder H₂ and N₂ molecules are adsorbed. As a result bond strengths in molecules of N≡N and H-H get weakened; hence the molecules can form easily at first NH then NH₂ and finally NH₃ molecule. At last molecule NH₃ leaves the catalyst surface. [See article-4.4.1: Heterogeneous catalysis]

(2) Catalysis with Intermediate Compound Formation:

According to `intermediate compound formation theory' transition metal compound such as vanadium pentaoxide (V_2O_5) combines with reactant to form an unstable intermediate compound which dissociates later. Here catalyst changes into different oxidation states of it and finally returns to its initial oxidation state. Through the formation of intermediate compound catalyst decreases activation energy and thereby can increase rate of reaction. For example, in contact process for H_2SO_4 manufacturing, V_2O_5 is used as catalyst in oxidation of SO_2 into SO_3 gas. Here V_2O_5 forms SO_3 from SO_2 with change its oxidation number + SO_3 to + SO_3 and finally reacts with SO_3 to get SO_3 oxidation state back.

$$SO_2 + V_2O_5 \longrightarrow SO_3 + 2VO_2$$

$$2VO_2 + \frac{1}{2}O_2 \longrightarrow V_2O_5$$

$$SO_2 + \frac{1}{2}O_2 + V_2O_5 \longrightarrow SO_3 + V_2O_5$$
net reaction:

(B) Chemical Properties of d-block Elements

1. Variable Oxidation States:

The general electronic structure of 3d-block elements is (18Ar) 3d¹⁻¹⁰ 4s¹⁻². The energy difference between 4s and 3d orbital electrons is very small and it is much less than that between 3s and 3p orbital electrons. So transition elements can form bond using 4s as well as 3d-orbital electrons. Thus these elements show variable valencies and oxidation states.

For example: Chromium shows + 2, + 3 and + 6 oxidation number in different compounds. Manganese shows + 2, + 3, + 4, + 6 and + 7 oxidation number. Iron shows + 2 and + 3 oxidation number in its compounds:

| (1) | Compounds of Cr : | CrCl ₂ | CrCl ₃ | K ₂ CrO ₄ K-chromate | K ₂ Cr ₂ O ₇ K-dichromat | e |
|-----|---------------------------------------|-------------------|--------------------------------|---|--|--------------------------------------|
| | O. Number of $Cr \longrightarrow : +$ | 2 | + 3 | +6 | +6 | |
| (2) | Compounds of Mn : | MnCl ₂ | Mn ₂ O ₃ | MnO ₂ | K ₂ MnO ₄ K-manganate | KMnO ₄ K-per manganate |
| | O.Number of Mn \longrightarrow : | + 2 | + 3 | + 4 | + 6 | + 7 |
| (3) | Compounds of Fe : | FeCl ₂ | FeCl ₃ | | | |
| | O. Number of Fe \rightarrow : | + 2 | + 3 | | | varion beinger |

The transition elements form different ions by the removal of 4s-orbital electrons first, then by removal of 3d-orbital electrons. The electrons entered lastly in 3d-orbitals repel the electrons of 4s-orbital. So 4s² electrons are removed first and then remove electrons from 3d-orbitals to get stability in electronic structures of ions.

(2) Formation of Coloured Ion: Transition metals and their ions having partially filled d-orbitals, become colourful. Transition metal atom or ion contains five d-orbitals of equal energy. This is called degenerate state of d-orbitals.

Crystal Field Theory: During the formation of complex ion, according to 'Crystal Field Theory' when the ligands with their lone pair electrons come closer to these d-orbitals of metal ion along x, y, z axes then ligand's lone pair electrons forcibly compel the unpaired electrons in 3d-orbitals to be paired up by rearranging them. This repulsive force causes five d-orbitals energy to be divided into two groups with a little energy difference (ΔE). This is called non-degenerate state of d-orbitals. The two higher energy orbitals namely $d_{x^2-y^2}$ and d_{z^2} are called e_g orbital, and the three lower energy orbitals namely d_{xy} , d_{yz} and d_{zx} are called e_g orbitals. Thus the splitting of orbital energies is called the crystal field effect (CFE) and the difference in energy between the e_g and e_g sets of orbitals is the crystal field splitting energy (ΔE). Different ligands creat crystal fields of different strength and thus cause d-

orbital energies to split to different extents; which causes the complex ions coloured. The magnitude of ΔE relates directly to the colour. Strong-field ligands (like NH₃, CN⁻) lead to a larger splitting energy (larger ΔE) makes the dense colour to complex ions; but weak-field ligands (like OH⁻, H₂O) lead to a smaller splitting energy (smaller (ΔE) and makes light or miled colour to complex ions.

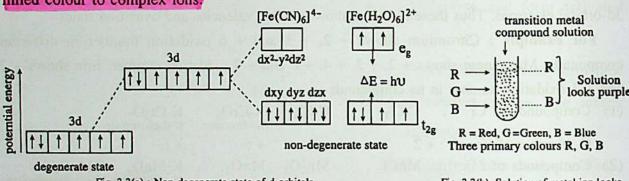


Fig-3.3(a): Non-degenerate state of d-orbitals of Fe²⁺ ion due to ligands' effect

Fig-3.3(b): Solution of metal ion looks purpledue to green colour absorption

Thus there is a little or more change in energy (ΔE) between e_g and t_{2g} sets. If this required energy change equals to particular band of visible light then the unpaired electron or electrons absorb that band of light with same wave lengths. The complementary colour of visible light reflects to our eyes. Thus that transition metal ion gets colour complementary to absorbed colour. When prime green colour is absorbed then the solution of transition metal ions becomes purple (mixture of red and blue). If prime blue colour is absorbed then colour of solution of transition ions becomes orange or purple (mixture of red and green).

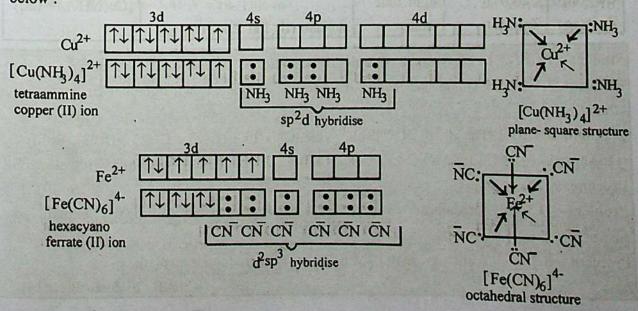
- (3) Formation of Complex ion: The transition metal atoms or ions form co-ordinate bonds with their vacant d-orbitals and lone pairs of electrons supplied by neutral molecules or negative ions known as ligand forming compounds or ions with complex structures. These co-ordinated metal-ligand ions are called complex ions. The compound containing complex ion is called complex compound. During the formation of complex ion or complex compound the lone pair electrons supplying neutral molecules and negative ions are called ligands. Common ligands are neutral molecules like: NH₃, H₂O: and negative ions: Cl ion :CN ion etc. Example,
- (1) Neutral molecule with lone pair electrons like NH₃ can form co-ordinate bonds with Cu²⁺ ion to form a positive complex ion called tetraammine copper (II) ion, [Cu(NH₃)₄]²⁺.
- (2) Again negative cyanide ion (CN-) can form co-ordinate bonds with Fe²⁺ ion to form a negative complex ion called hexacyano ferrate (II) ion. [Fe(CN)₆]⁴⁻.

$$H_3$$
 N: I_3 NC: I_4 NC: I_5 CN I_5 CN I_5 CN I_5 CN I_6 CN

Fig: 3. 4. Structures of positive and negative complex ions.

Co-ordination Number: The number of lone pair of electrons supplied by ligands to transition matal ion to form co-ordinate bonds is called Co-ordination number of transition metal. For example, in formation of [Cu(NH₃)₄]²⁺ ion Cu²⁺ ion accepts 4 lone pair electrons given by 4 NH₃ ligand molecules to form 4 co-ordinate bonds. So co-ordination number of Cu²⁺ ion in complex ion [Cu(NH₃)₄]²⁺ is 4. Similarly in complex ion [Fe(CN)₆]⁴⁻, the co-ordination number of Fe²⁺ ion is 6.

Explanation of Complex ion formation: According to 'Valence' Bond (VB) Theory formation of complex ion by transition metals and their ions with the ligands is discussed here. Due to the influence of lone-pair electrons of ligands the electrons of transition metal atom or its ion get paired up to make their orbitals vacant as possible for the incoming ligands. With these vacant orbitals like 3d, 4s, 4p, 4d etc, the metal atoms or ions can undergo different types of orbital hybridizations like plane-square sp²d (as in Cu²⁺), octahedral d²sp³ (as in Fe²⁺) or, sp³d² etc. forming equivalent hybrid orbitals. Later with these hybrid orbitals ligands get bonded with co-ordinate bonds with their lone-pair electrons to form complex ions or compounds. Here formation of complex ions by Cu²⁺ ion and Fe²⁺ ion are shown below:



Note: In systematic method, the naming process and writing the formula of complex compounds are discussed in article 3.21.1 at the end of this chapter.

(4) Coloured Hydroxides of Transition Metals:

When a solution of NaOH, KOH or NH4OH is added to the different solutions of different transition metal ions, then metal ion reacts with OH- ions with following characteristic colourobservations:

- (i) Coloured metal hydroxides are precipitated; based on characteristic colour, metal ion can be detected.
 - (ii) Some precipitates become jelly like by absorbing water.
- (iii) Some metal hydroxides like Cr(OH)3, Co(OH)2 are amphoteric. These amphoteric hydroxides dissolve in excess NaOH to form soluble salts.

(iv) Some metal hydroxides dissolve in excess NH₄OH to form complex ions.

| Metal cations | Precipitated hydroxide | 2 of mation of amon | | | | |
|---|------------------------|--|--|---|--|--|
| Cr3+(aq) | Cr(OH) ₃ | green | chromate (III) ion CrO ₃ ³ -(aq) | NH ₄ OH | | |
| Mn2+(aq) | Mn(OH) ₂ | ash | in the city and city and city | | | |
| Fe2+(aq) | Fe(OH) ₂ | green | a supplied the supplied by the | | | |
| Fe3+(aq) | Fe(OH) ₃ | brown · | College freshold and an arrange of the | | | |
| Co2+(aq) | Co(OH) ₂ | TO THE STATE OF TH | coholtat : G to | | | |
| Ni ²⁺ (aq) | Ni(OH) ₂ | green | cobaltate (Inion Co(OH) ₄ ² -(aq) | [Co(NH ₃) ₆] ²⁺ (aq) | | |
| Cu ²⁺ (aq) | Cu(OH) ₂ | light blue | se vermina le sonannot atten | [Ni(NH ₃) ₆] ²⁺ (aq) | | |
| Zn ²⁺ (aq) | $Zn(OH)_2$ | | | [Cu(NH ₃) ₄] ²⁺ (aq) | | |
| STATISTICS OF THE PARTY OF THE | (011)2 | wille | zincate (II) ion Zn(OH) ₄ ²⁻ (aq) | A TOTAL CONTRACTOR | | |

Student's Work-3.4: Physical & Chemical Properties of Transition Metals Based:

Problem-3.4 (a): Explain the change of m.p. of 3d elements with gradual change of their

Problem-3.4(b): The m. p. of 3 d-block elements like B (23), C (25), D(28), E(30) are

respectively 1910°C, 1245°C, 1453°C and 420°C. Explain their such m.p with electronic

Problem-3.4 (c): Whether the element Z(28) shows any catalytic property; explain your

Problem - 3.5 (a): Transition metal forms coloured compounds explain. [D. B. 2017]

[R.B. 2015; B. B. 2015]

Problem-3.5 (b): $A = (n-1)d^5 \text{ ns}^1$ and $B = (n-1) d^1 \text{ ns}^2$; here n = 4. Which of A and B elements will form coloured compound; explain. [D. B. 2016]

Problem-3.5 (c): The valence electron of element 'A' included in period 4 is (n-1)d⁶ ns².

Explain whether the [A(CN)₆]⁴ ion will be coloured.

[Ctg. B. 2016]

Problem-3.5 (d): A (3d⁶4s²), B (3d¹⁰ 4s²), C(3s²3p⁵); which of these three elements will form coloured ion; explain. [C.B. 2017]

Problem-3.5 (e): A (24), B (30); - which of the two given elements will form coloured compound; explain. [Madrasa B. 2017]

Problem-3.6 (a): Explain, how transition metal forms a complex compound.

Problem-3.6 (b): Explain the nature of the solution of [29M(NH₃)₄]²⁺ ion. [Syl.B. 2015]

Problem-3.7 (a): Explain, what happens when NH₄OH solution is mixed with aqueous CuSO₄ solution.

Problem-3.7 (b): Write the detection test with equation for M²⁺ ion of [29M (NH₃]₄]²⁺.
[Syl. B. 2015]

Problem-3.8 Write with equations what happen when NH₄OH solution is mixed with solutions of FeSO₄ and FeCl₃ separately.

Problem-3.9 Explain with equations what happens when canc. NaOH solution is mixed slowly with ZnSO₄ solution.

Problem-3.10: A metal of 'M' has its molecular formulae of oxides and chlorides as MO, M₂O₃ and MCl₂, MCl₃. Explain what will be the position of element 'M' in periodic table.

Worked Example-3.4:
$$A = (n-1)d^5 ns^1$$

 $B = (n-1)d^1 ns^2$, here $n = 4$

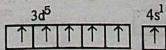
[D.B. 2016]

- (a) Calculate the values of 4 quantum numbers for the last electron of 'A' element.
- (b) Explain which of the elements 'A' and 'B' will form coloured compound?

Solution-(a): Calculation of Values of 4 Quantum NO's for last electron of 'A':

From given stem, $A = (n - 1) d^5 ns^1$, here n = 4

- .. Valence electrons of 'A' element, A = 3d⁵4s¹
- .. The element 'A' is chromium, Cr(24), Electron distribution of Cr(24) in box-form is :



Here last electron means 4s1 electron. For 4s1 electron:

Principal quantum no, n = 4; Subsidiary quantum no. l = 0 (for s orbital);

Magnetic quantum no., m = 0; ... Spin quantum no. $s = +\frac{1}{2}$

Solution-(b): Explanation for Coloured Compound Formation:

From given stem, valence electron of element 'A' = $(n-1)d^5ns^1 = (4-1)d^54s^1 = 3d^54s^1$

:. Element 'A' is Cr(24).

Again, valence electron of element 'B' = $(n-1)d^{1}ns^{2} = (4-1)d^{1}4s^{2} = 3d^{1}4s^{2}$

:. Element 'B' is Sc(21).

Here Cr (24) is a transition element and Sc(21) is a d-block element but not transition element. Because from definition of transition metal, a transition metal must have an ion having partially filled d-orbital liked d ¹⁻⁹. Here Sc(21) has its stable ion Sc³⁺ only and Cr(24) has its stable ion Cr³⁺ ion. Both ions have following electron distributions:

$$Sc^{3+}(21) \longrightarrow 1s^{2} 2s^{2} 2p^{6} 3s^{2} 3p^{6} 3d^{\circ}$$

 $Cr^{3+}(24) \longrightarrow 1s^{2} 2s^{2} 2p^{6} 3s^{2} 3p^{6} 3d^{3}$

From above electron distribution Sc^{3+} ion has no electron in 3d orbital. Hence Sc(21) is not a transition element. But Cr^{3+} ion contains $3d^3$ electrons which supports d^1-d^9 arrangement. Hence Cr(24) is a transition element. One of the characteristics of a transition element is the formation of coloured compound. So Cr(24) can form coloured compound. But Sc(21) can not form any coloured compound.

Transition metal Cr and its ion Cr³⁺ ion both contain partially filled 3d orbital; hence hey are coloured. Besides this, during the formation of complex ion at the approach of the igands five 3d orbitals undergo a slight change in potential energy which is absorbed from visible light energy. So its complex ion becomes coloured.

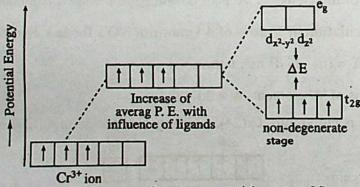


Fig-3.4(a): Increase of average potential energy of five 3 d-orbitals and splitting in ligand field

According to crystal field theory, as the ligands approach towards Cr^{3+} ion their electron pairs repel electrons in five 3d-orbitals of Cr^{3+} ion. When the ligands move along the x, y, and z axes, they approach **directly towards the lobes** of the $d_x^2-y^2$ and d_z^2 orbitals but **between the lobes** of the d_{xy} , d_{yz} and d_{zx} orbitals. Thus electrons in $d_x^2-y^2$ and d_z^2 orbitals experience stronger repulsions than those in the d_{xy} , d_{yz} and d_z^2 orbitals. Then due to the repulsions from approaching ligands, the orbital energies split with two d-orbitals higher in energy than the other three. This is called non-degenerate state of orbitals. The two higher energy orbitals $d_x^2-y^2$ and d_z^2 are called e_g orbitals and three lower energy set orbitals like d_{xy} , d_{yz} and d_{zx} are called d_z^2 orbitals. The splitting of orbital energies is called the **crystal** field effect and the difference in energy between e_g and d_z^2 sets of orbitals is called the **crystal** field splitting energy (ΔE). When Cr^{3+} ion absorbs light in the visible range, electrons are excited (jumped') from lower energy d_z^2 level to the higher e_g level. The difference between two electronic energy levels in the d_z^2 ion is equal to the energy (and inversely related to the wave-length) of the absorbed light.

$$\Delta E_{electron} = E_{photon} = \frac{h \times c}{\lambda}$$

Then complex compound of Cr³⁺ ion becomes colour because only certain wavelengths of the incoming white light are absorbed. So transition metal Cr³⁺ ion complex compound like [Cr(H₂O)₃Cl₃] looks purple.

Worked Example-3.5: Valence electrons of element 'A' of 4th period is (n-1)d⁶ ns².

[Ctg. B. 2016]

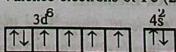
- (a) Calculate values of 4 quantum numbers set for electrons in d-orbitals of 'A'.
- (b) Explain whether [A(CN)₆]⁴⁻ ion will be coloured as per given stem.

Solution -(a): Calculation of 4 quantum no's set for d-electrons of 'A' element.

From question, $A = (n-1)d^6 ns^2$, here n = 4

∴ Valence electrons of 'A' element, A = 3d⁶4s²

So the element 'A' is Fe (26). Valence electrons of Fe (26) in box method is:



| electron | n | l | m | S | orbital |
|----------------|---|---|-----|----------------|-----------------------------|
| e ₁ | 3 | 2 | + 2 | $+\frac{1}{2}$ | d _{xy} |
| e ₂ | 3 | 2 | + 1 | $+\frac{1}{2}$ | d _{yz} |
| ез | 3 | 2 | 0 | $+\frac{1}{2}$ | d _{zx} |
| e ₄ | 3 | 2 | - 1 | $+\frac{1}{2}$ | $d_x^2 - y^2$ |
| e ₅ | 3 | 2 | - 2 | $+\frac{1}{2}$ | d _z ² |
| e ₆ | 3 | 2 | + 2 | $-\frac{1}{2}$ | dxy |

Four quantum numbers set for 3d6 electrons of element 'A' or, Fe(26) are followings:

Solution-(b): Explanation whether [A(CN)₆]⁴⁻ ion will be coloued.

As per given stem, $[A(CN)_6]^{4-}$ ion is $[Fe(CN)_6]^{4-}$ ion and it is a complex ion. In this complex ion the central metal ion is Fe^{2+} ion and ligands are cyanide ions (CN-). Fe metal is a transition element. One of the characteristics of a transition metal is the formation of complex coloured ion. So this ion will be coloured. It is explained with crystal field theory as follows:

According to crystal field theory, as the ligands (CN⁻) approach, their electron pairs repel electrons in 5 d-orbitals of Fe²⁺ ion. Then due to the repulsions from approaching electrons, the orbital energies split, with two d-orbitals higher in energy than other three. This is called non-degenerate state of orbitals. The two higher energy orbitals $d_x^z-y^2$ and d_z^z are called e_g orbitals and three lower energy set orbitals like d_{xy} , d_{yz} and d_{zx} orbitals are called t_{2g} orbitals. The difference in energy between e_g and t_{2g} sets of orbitals is called the crystal field splitting energy (ΔE). When Fe²⁺ ion absorbs light in the visible range, electrons are excited (jumped) from lower energy t_{2g} level to the higher e_g level. The difference between two electronic energy levels in the Fe²⁺ ion is equal to the energy of the absorbed light.

$$\Delta E_{electron} = E_{photon} = \frac{h \times c}{\lambda}$$

Then complex ion of Fe²⁺ ion like [Fe(CN)₆]⁴⁻ becomes yellow colour; because only certain wavelengths of the incoming white light are absorbed.

3.2.4 General Properties of f-block Elements

Of the periodic table, f-block elements' atoms have their fully filled up outermost ns² orbital; but their last electron enters into (n-2)f orbital, keeping unfilled (n-1) d orbital. The

basic cause of this is the vary close up difference in energy levels between d-orbital and f-orbital; there n = 6 and 7.

| Period | Elect | ron dist | ribution | : (n – 2) | f ¹⁻¹⁴ , (1 | n–1) d ^{0'1} | ns ² ; | n = 6, 7 | due | i de sul | South ! | Couried | Lismoi | SUSSET. |
|--------|-------------------|----------|-----------------|------------------|------------------------|-----------------------|-------------------|------------------|------------------|------------------|-------------------|-------------------|-------------------|--------------------|
| 6(4f) | ₅₈ Ce | 59Pr | 60Nd | 61Pm | ₆₂ Sm | ₆₃ Eu | 64Gd | ₆₅ Tb | ₆₆ Dy | ₆₇ Ho | 68Er | ₆₉ Tm | 70 Yb | 71Lu |
| 7(5f) | 1010 -1 016 -1 | 91Pa | ₉₂ U | ₉₃ Np | ₉₄ Pu | 95Am | 96 ^{Cm} | ₉₇ Bk | ₉₈ Cf | ₉₉ Es | ₁₀₀ Fm | ₁₀₁ Md | ₁₀₂ No | 103 ^L w |

f-block elements are divided into two series; such as (i) Lanthanide series or Lanthanoids and (ii) Actinide series or Actinoids.

(1) Lanthanide Series or, lanthanoids: Lanthanum (57La) together with its next 14 elements of 4f-block from Cerium (58Ce) to Lutetium (71Lu), total 15 elements are known as 'Lanthanide series' or, 'Lanthanoids'. These 15 elements, due to their similarities in physical and chemical properties, are included in group-3 (3B) of 6th period in periodic table.

Lanthanoids elements are less available in nature as compounds, hence they are also called 'Rear earth elements'. Lanthanide series has general valence shell electron distribution like (n-2) f¹⁻¹⁴ (n-1)d⁰⁻¹ ns²; here n = 6.

Properties of Lanthanoids:

- Lanthanoids are heavy metals. These metals are good conductors of heat and electricity.
 - 2. These metals have higher density, higher melting points and boiling points.
- 3. The ionisation energy of each lanthanoid metal is lower than that of d-block element. So these metals are more electropositive.
- 4. The f-block metals contain inner transition metals. These inner-transition metals have coloured ions and can form complex ions or compounds.
- The prime and more stable oxidation state of the metals of lanthanide series is + 3. Yet +2 and +4 oxidation numbers are also shown by some of the lanthanoids. For example, Eu²⁺ (4f⁷), Tb⁴⁺ (4f⁷).
- 6. The Lanthanide metals can resist UV-rays and IR-rays both. So different metal oxides of Lanthanoids are used in making goggles used as sunglass or for metal welding works.
- 7. The size of the trivalent ion (M³⁺) of Lanthanide metal decreases gradually from La to Lu, this decreasing tendency of the Lanthanide metal ionic radii is known as 'Lanthanide contraction'.

Cause of Lanthanide Contraction: Lanthanoids common electron distribution is

4f²⁻¹⁴ 5s² 5p⁶ 5d⁰⁻¹ 6s². With the increase of atomic number of the elements, the
additional electron enters the 4f- sub-shell but not into the valence shell namely sixth shell.

The shielding of one electron in 4f-sub-shell by another in the same sub-shell (i.e. mutual
shielding effect of 4f-electrons) is very little, being even smaller than that of d-electrons,
because the shape of f-orbitals is very much diffused. Thus the nuclear charge at each
metal atom increases while there is no comparable increase in the mutual shielding effect
of 4f-electrons. This causes a decrease in the size of the 4f- subshell from La to Lu-atoms.

(2) Actinide Series or, Actinoids: Actinium (89Ac) together with thorium (90Th) and next 13 elements of 5f block from protactinium (91Pa) to lowrencium (103Lr), total 15 elements are known as 'Actinide Series' or, 'Actinoids'

These 15 elements, due to their similarities in physical and chemical properties, are included in group-3 (3B) of 7th period in periodic table. General valence shell electronic configuration is 5f¹⁻¹⁴ 6d⁰⁻¹ 7s².

Now according to IUPAC rule, 'Lanthanide Series' is called 'Lanthanoids' and 'Actinide series is called 'Actinoids'. Because the suffix '-ide' is used after the name of negative ion like chloride ion (Cl-), sulphide ion (S²⁻) etc.

Properties of Actinoids:

- 1. Actinoid metals are radioactive elements.
- 2. Actinoid metals have very much high density. (Exception: sp. gr. of Thorium is 10.11)
- 3. These metals have high melting points and high boiling points.
- 4. Actinoid metals are more electropositive. They show + 3, + 4, +5, + 6 oxidation numbers. The ionisation energy of each actinoid metal is low.
- 5. Actinoid metals become fade in colour in contact with air and become less reactive.
- 6. As very fine particles, actinoid metals become very active. They react with water and dilute acid to produce H₂ gas.
- Alkalies have no effect on actinoid metals. Their compounds are more basic in character.
- 8. Thoria (ThO2) and Ceria (CeO2), as fine particles, are used in car head-light and as search light of marine ship and railway engine.

3.3 Periodic Properties of Elements

Periodic Properties: The electronic distributions of the elements change with their increase of atomic numbers and repetition of valence shell electron distributions occur with the rhythm of electron distributions like 2,8,8,18,18,32. Similarly many properties of the elements are repeated. So periodic properties of the elements are repeated. So periodic properties of the elements mean the repetition of similar properties among the elements after a definite intervals according to their increasing atomic numbers. Here some periodic properties of the elements such as (1) Melting point and boiling point, (2) Atomic size, (3) Valency, (4) Ionization energy, (5) Electron affinity, (6) Electronegativity, (7) Metallic property of the elements will be discussed

(A) Melting Point and Boiling Point:

Each of Group-1 alkali metals has only one valence electron, hence metallic bond of alkali metals is very weak. So these metals are soft and have low melting points. In a group

The temperature at which solid substance melts, is called **melting point** of the compound or substance. But the temperature at which liquid at 1 atm pressure, boils with bubble is called **boiling point** of that liquid.

The atomic size of every element increases with the increase of atomic number and electron density in valence-shell decreases. As a result, metallic bond attraction decreases. Hence the melting point of alkali metal decreases gradually with increase of their atomic number. But the atomic size of Li atom is comparatively smaller and its metallic bond is comparatively strong than others. For this reason, melting point and boiling point of Li are higher than those of other alkali metals.

Table-3.1: Melting Point and Boiling Point of Group-1 Metals:

| Metal | Li 1940 | Na | K | Rb | Cs |
|-------------------|---------|------|------|------|-------|
| Melting Point, °C | 180.5 | 97.7 | 63.3 | 39.3 | 28.4 |
| Boiling Point, °C | 1342 | 883 | 759 | 688 | 678.4 |

In a same period, melting point and boiling point of different elements show no regular or gradational change. For example, the melting and boiling points of the elements of 3rd period are as follows:

| Element → | Na | Mg | Al | Si | P | S | CI | Ar |
|-------------------|------|------|------|------|-----|--------|-------|---------|
| Melting point, °C | 97.8 | 649 | 660 | 1410 | 44 | 112.8 | - 101 | - 189.2 |
| Boiling point, °C | 883 | 1090 | 2519 | 2355 | 280 | 444.67 | -34.6 | -185.7 |

Table-3.2: Melting Points and Boiling Points of the Elements of 3rd Period

From sodium to aluminium, metallic bond is present. In sodium crystal, Na⁺ ions are present, the size of sodium ion is large and only one mobile electron attracts this Na⁺ ion with a weak binding. For this to melt the crystalline structure needs only a small heat energy for sodium metal; hence melting point of Na is lower. In crystal of Mg metal double charge Mg²⁺ ion has two mobile electrons and triple charge Al³⁺ ion has three mobile electrons. These metal ions have much attraction on these mobile electrons. For this reason, strength of metallic bond increases with the increase of melting point and boiling point of those metals.

In silicon crystal, giant molecule is present, in which Si-Si bonds form three dimensional network. Here much heat energy is required to break those Si-Si bonds during the melting of silicon crystals. Hence melting point and boiling point of silicon are very much higher.

Next element is phosphorus which exists as white phosphorus allotrope, P₄ molecule. This molecule is covalent in nature. Vander Waals force exists as intermolecular force among these covalent molecules. So phosphorus has low melting and low boiling points.

Next element is sulphur which exists as octa-atomic molecule, S₈. The nonmetal sulphur atoms form covalent bonds among themselves. Here also weak Vander Waals force exists among the sulphur molecules. Hence melting point and boiling point of sulphur are lower.

Chlorine molecule is diatomic. These diatomic molecules are purely covalent and nonpolar. So chlorine molecules remain attracted by weak Vander Waals force. For this C1₂ remains as gas and its melting point and boiling point are lower than 0°C, having negative value like -101°C and -34.6°C.

(B) Atomic Size of the Elements

For the comparison of atomic size of different elements, generally atomic radius which is the distance between the atomic nucleus and outer most electron shell, is considered. Practically determination of atomic radius is very difficult; because the distance of outermost electron cloud from the atomic nucleus is uncertain. So depending on the nature of the different elements, their atomic sizes are expressed in two ways:

(C) Covalent Radius: Half of the distance between the nuclei of two same atoms bonded together by a single covalent bond is called covalent radius of the atom of that element, The covalent rodius is considered as the atomic radius. The sum of covalent radius of two atoms is considered as the bond length of molecule formed by the related two atoms.

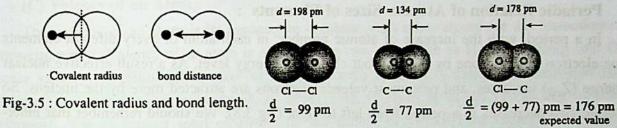


Fig-3.5(a): Calculation of atomic radius.

In diamond, inter nuclei distance of carbon atoms (C-C bond distance) is calculated as 0.154 nm or 154 pm by X-ray diffraction expt. So covalent radius of C-atom is half of that bond distance = 0.154/2nm = 0.077 nm or 77pm (picometre). In Cl₂ molecule the distance between two nuclei of C1 atoms or C1- Cl bond length is 198 pm. So atomic radius of Clatom is half of it $198 \div 2 = 99$ pm.

(2) Metallic Radius: The metal atoms are supposed to touch one another in the crystals. The metallic radius or crystal radius is defined as one-half of the distance between the nuclei of two adjacent metal atoms in the metallic closed packed crystal lattice. Metallic radius is 10—12% more than covalent radius. So; metallic bond is somewhat weaker than that of covalent bond.

The internuclear distance between two adjacent Na atoms in its crystal is 372 pm. So metallic radius of Na-atom is $\frac{372}{2}$ pm = 186 pm.

To get comparative idea, covalent radii and metallic radii of group-1A elements are cited below:

••••

Fig. 3.6: Metallic radius & diameter

235 157 K 203 Rb 216 Cs Covalent radius (pm): Li 123 Na K 227 Rb 248 Cs 263 Metallic radius (pm): Li 152 Na 186

The relative atomic radii of different elements in picometer (pm) are shown in table.3.7.

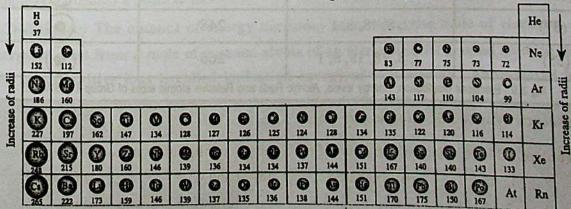


Fig-3.7: Atomic radii of different elements in pm unit. $(1pm = 10^{-12} m)$

Periodic Relation of Atomic Sizes of Elements:

In a period, with the increase of atomic number, in each atom of every different elements one electron is added one by one without change of energy level. As a result effective nuclear charge (Z_{eff}) increases, and outermost valence electrons are attracted more by the nucleus. So atomic size decreases in a period from left to right (fig 3.8). We should remember that innershell electrons pushed away the outer most electrons from the nucleus. That is outermost electrons are shielded from the nucleus by the inner electrons. The nuclear charge actually felt by an electron is called effective nuclear charge, Z_{eff}. Hence effective nuclear charge is substantially lower than the actual nuclear charge, Z.

| :. Effective nuclear charge, $Z_{eff} = Z_{actual} - Electronic Effective nuclear charge, Z_{eff} = Z_{actual} - Electronic Effective nuclear charge nuclear$ | on shielding. |
|---|---------------|
|---|---------------|

| 3rd period Elements | Na(11) | Mg(12) | Al(13) | Si(14) | P(15) | S(16) | CI(17) |
|-----------------------|--------|--------|--------|--------|-------|-------|--------|
| Electron Distribution | 2.8.1 | 2.8.2 | 2.8.3 | 2.8.4 | 2.8.5 | 2.8.6 | 2.8.7 |
| Atomic Radius (pm) | 186 | 160 | 143 | 117 | 110 | 104 | 99 |
| Relative Atomic Size | • | • | • | • | 0 | • | • |

Fig 3.8: Electron distribution, Atomic radii, Relative atomic sizes of 3rd Period Elements.

Group Relation: In a group, from up to down with the increase of atomic number, new energy level or orbit is added for accommodation of electrons. As a result, atomic radius of every atom increases. For example atomic radius of Li = 152 pm, that of Na = 186 pm, that of K = 227 pm, Rb = 248 pm and Cs = 265 pm [Fig-3.9].

| Group-1 Elements | Energy Levels in Atom | Atomic Radius (pm) | Relative Atomic Siz | | |
|-------------------------|-----------------------|--------------------|---------------------|--|--|
| Li (3) | 2, 1 | 152 | 0 | | |
| Na (11) | 2, 8, 1 | 186 | • | | |
| K (19) | 2, 8, 8, 1 | 227 | | | |
| Rb (37) | 2, 8, 18, 8, 1 | 248 | • | | |
| Cs (55) | 2, 8, 18, 18, 8, 1 | 265 | • | | |

Fig 3.9: Electrons distribution, Energy levels, Atomic Radii and Relative atomic sizes of Group-1 Elements

Student's Work- 3.5: Atomic Size Based

Problem-3.11: Explain which atom of each pair is smaller in atomic size:

(a) Mg and Ba (b) Si and Sn (c) Si and Cl (d) Cl and I.

Problem -3.12: Explain how atomic sizes of the following elements change:

Li (3), Be(4), B (5), C(6), N(7), O(8), F(9) [B. B. 2017]

(C) Valency of an Atom

The valency of an atom is its capacity to combine with other atoms for the formation of new compound. Valency of an atom is expressed in two units such as H-scale valency and O-scale valency. Combining capacity of an atom with H-atom is called H-valency of the element and combining capacity of an atom with O-atom is called O-valency of that element. The outermost total electrons of the atoms of Group-1 to Group-4 elements represents the valency of each element; hence outermost total electrons of an atom is called valence electron. Again from Group-5 to Group -7, the H-scale of valency of different elements decreases gradually but O-scale valency of those elements increases. The valency of different elements of 3rd period to form oxide and hydride are shown in Table-3.3.

Table-3.1: Valency of the elements of 3rd period as per O-scale and H-scale

| Compounds | Gr-1 | Gr-2 | Gr-3 | Gr-4 | Gr-5 | Gr-6 | Gr-7 |
|---|------------------------------|-----------------------------------|--|---------------------------------------|---|---|--------------------------------------|
| (i) Oxide formation: Valency of atom [O-scale based] (ii) Hydride formation: Valency of atom: | Na ₂ O 1 NaH 1 | MgO 2 MgH ₂ 2 | A1 ₂ O ₃ 3 A1H ₃ 3 | SiO ₂ 4 SiH ₄ 4 | P ₂ O ₅ 5 PH ₃ 3 | SO ₃ 6 H ₂ S 2 | C1 ₂ O ₇ 7 HCl |
| [H-scale based] | Valence number of | | ermost electron | Valenc | e number | = [8 - T | otal |

(D) Ionisation Energy

We have learnt in second chapter that the valence electron of an atom is promoted to higher energy level (value of n is higher), when that atom absorbs electro magnetic waves of energy. If enough energy is absorbed, the electron can be removed completely from the atom, leaving behind a positive ion.

Definition: The amount of energy necessary to remove one mole of electrons from outermost orbit from a mole of gaseous atoms of an element in its ground state to form a mole of unipositive ions is called ionisation energy of that element, abbreviated by Ei. Ionisation energies differ widely from a low value of 375.7 kJ/mol for Caesium to a high value of 2372 kJ/mol for Helium.

$$Na (g) \longrightarrow Na^{+} (g) + e^{-}$$
 $E_i = +496 \text{ kJ / mol}$ $K (g) \longrightarrow K^{+} (g) + e^{-}$ $E_i = +419 \text{ kJ / mol}$ $E_i = +738 \text{ kJ / mol}$

Again, the amount of energy necessary to remove one mole of electrons from one mole of unipositive gaseous ions to form double positive one mole gaseous ions is called **second** ionisation energy of that element. The second ionisation energy is always higher than that of the first ionisation energy. For example:

The 2nd ionisation energy of Na⁺ ion and K⁺ ion become more than 1st ionisation energy of octet filled Ne (10) atom (Ei = $+2080 \text{ kJ mol}^{-1}$). So Na²⁺ ion and K²⁺ ion are not formed.

Different factors that do effect on ionisation energies of elements :

- (1) Increase of atomic size decreases ionisation energy; it is a group based relation.
- (2) Increase of suborbit increases ionisation energy; it is a period based relation.
- (3) More stable half- or fully filled electron set of an atom disrupts periodic relation.

In a Group: With the increase of atomic number of the elements, energy level of the electrons also increases and outermost electron level gradually goes apart from nucleus decreasing the attraction of nucleus on electron level. So ionisation energy decreases.

For example:
$$Li = 520 \text{ kJ}$$
; $Na = 496 \text{ kJ}$; $K = 419 \text{ kJ}$; $Rb = 403 \text{ kJ}$; $Cs = 376 \text{ kJ}$.

In a Period: With the increase of atomic number of the elements in a period, energy level of the electrons remains same, only sub-energy levels increase. As a result the distance of outermost electrons does not increase but reduce a little. Besides this, the attraction of nucleus, with more nuclear charge, also increases on outermost electrons. That's why, more energy is necessary to remove electron. It is clear that in any period, the element of group-1 has lowest ionisation energy and inert gas member has highest ionisation energy (Fig-3.10).

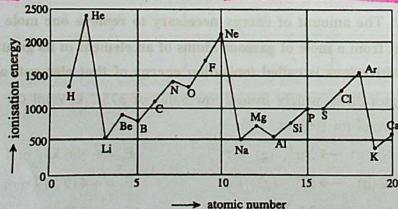


Fig-3.10: Ionisation energies of first 20 elements

★ Less stable electron set containing element has lower ionisation energy than element with more stable electron set. For this B(5) of group-13 in 2nd period and Al(13) of group-13 in 3rd period have sudden lower ionisation energies, instead of gradual normal increase.

★ Similarly O(8) and S(16) of group-16 have lower ionisation energies than their prior N(7) and P(15) of group-15 in 2nd and 3rd period respectively.

Table-3.2: Ionisation energies of elements of 2nd Period.

| 2nd Period Elements | diam'r. | Li(3) | Be(4) | B(5) | C(6) | N(7) | 0(8) | F(9) | Ne(10) |
|------------------------|----------------|--------|--------|------|------|------|------|------|--------|
| Ionisation energy | El | 520 | 899 | 800 | 1086 | 1402 | 1314 | 1681 | 2080 |
| (kJmol ⁻¹) | E ₂ | 7297 | 1757 | 2426 | 2352 | 2855 | 3388 | 3375 | 3963 |
| | E3 | 11,810 | 14,845 | 3659 | 4714 | 4576 | 5296 | 6045 | 6130 |

Table - 3.2(a): Ionisation energies of elements of 3rd and 4th periods (s & p blocks)

| 3rd Period Elements | | Na(11) | Mg(12) | Al(13) | Si(14) | P(15) | S(16) | CI(17) | Ar(18) |
|--|----------------------------------|-------------|-------------|-----------------|----------|--------|--------|--------|--------|
| Ionisation energy (kJmol ⁻¹) | E ₁ E ₂ | 496 4562 | 738 1450 | 578 1882 | 786 | 1062 | 1007 | 1260 | |
| 4th Period Elements | | K(19) | Ca(20) | Ga(31) | Ge(32) | As(33) | Se(34) | Br(35) | Kr(36) |
| Ionisation energy (kJmol ⁻¹) | E ₁ | 419 3051 | 590 1145 | 579 2083 | 760 - | 945. | 948 | 1140 | • |

Ionisation energy depends on electronic configuration of elements. For this reason there are some deviations in the gradual increase of ionisation energy (I.E.) of elements from left to right in a period.

- * (i) The I.E. of boron is less than that of beryllium. [as per fig-3.10]
- * (ii) The I.E. of oxygen is less than that of nitrogen. [as per fig-3.10]

Worked Example-3.6: Ionisation Energy Based:

Problem: Ionisation energy of Boron (5) is 800 kJ mol⁻¹; but that of Beryllium (4) is 899 kJ mol⁻¹ Explain this irregularity.

Strategy: Normally ionisation energies of the elements increase periodically from left to right gradually. But exception in gradational regularity disrupts due to more stable half filled and fully filled electron distributions in the atoms.

Solution: The reason behind these deviations is their electronic distributions. The half-filled and fully filled orbitals with electrons of atoms are more stable. The electronic configurations of Be (4) and B (5) are as follows:

Be (4)
$$\longrightarrow 1s^22s^2$$
 Ei = 899 kJ / mol
B (5) $\longrightarrow 1s^22s^2 2p_X^1 2p_Y^0 2p_Z^0$ Ei = 800 kJ / mol

Here less energy is needed to remove one electron from boron atom, because after then a stable electronic configuration like $1s^22s^2$ is achieved. On the other hand the electronic configuration of beryllium is $1s^2$ $2s^2$; which is stable due to fully filled 2s orbital. To remove one electron from Be-atom more energy is needed, because then the stable $2s^2$ configuration is broken down. For this reason the ionisation energy of beryllium is more than normally expected value and it is more than that of boron.

Problem: 3.7: I. E. of O (8) is less than that of N (7) atom; explain why.

Solution: The electronic configurations of oxygen and nitrogen are as follows:

O (8)
$$\rightarrow 1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$$
 Ei = 1314 kJ / mol
N (7) $\rightarrow 1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$, Ei = 1402 kJ / mol

When one electron is removed from O-atom then electronic configuration like Is²2s² 2p_x¹ 2p_y¹ 2p_z¹ is obtained, which is exactly half filled 2p orbitals. This configuration is relatively more stable and hence less energy than usual is needed to remove one electron from oxygen atom. Then first ionisation energy of oxygen is relatively low.

On the other hand, electronic configuration of nitrogen is N(7)= 1s² 2s² 2p_x¹ p_y¹ 2p_z¹ which is relatively stable due to exactly half filled 2p orbitals. Removal of one electron needs to break this stable configuration and hence relatively more energy is needed. Hence the first ionisation potential of nitrogen is higher than that of oxygen.

Worked Example-3.8: Ionisation Energy based:

Arrange the elements Se, Cl and S in order of increasing ionisation energy.

Strategy: Ionisation energy generally increases from left to right across a row of the periodic table and decreases from top to bottom drown a group. 'Cl' should have a larger E_i than its neighbour 'S', and 'Se' should have a smaller E_i than 'S'.

Solution: The order is Se < S < Cl

Student's Work - 3.6: Ionisation Based:

Problem-3.13: Using the periodic table as your guide, predict which element in each of the following pairs has the larger ionisation energy:

(a) K or Br,

(b) Ne or Sr,

(c) S or Te (d) Be or C

Problem - 3.14: Explain, the changes in ionisation energies of the four elements like [R. B. 2017] A(7), B(8), C(15), D(16) in group and period base.

Problem - 3.15: Explain the exception observed in gradation of change; in ionization energies of Li(3), Be(4), B(5), C(6), N(7), O(8), F(9) etc. [B. B 2017]

Problem - 3.16: Explain the mode of changes in ionization energies of the elements [D. B. 2017] from left to right in 3rd period.

Problem - 3.17(a): Explain: (i) Na+ is formed but Na2+ ion is not formed.

[Ctg. B. 2015]

Problem - 3.17(b): Explain, which will be more between 2nd ionization energy of Na⁺ ion and 1st ionizsation energy of Ne atom?

Problem - 3.17(c): Why is 1st ionization energies of N more than that of O atom?

[Di. B. 2017; Ctg.B. 2016; Syl. B, 2015]

Problem - 3.17(d): Between two elements D (ns2) and G(n + 2)s2, why ionization energy of G is less than that of D element; Explain. [D. B. 2016]

(E) Electron Affinity

In the previous article, we have learnt that it is possible to measure the energy change on removing an electron from an atom to form a cation, which is known as ionisation energy. It is also possible to measure the energy change on adding an electron to an atom to form an anion. This type of energy change of an element is known as electron affinity of the element.

Definition: The amount of energy released, when one mole of electrons is added to one mole of neutral gaseous atoms of an element to produce one mole uninegative gaseous ions. is called the electron affinity of that element; abbreviated by Ee.

Electron affinities, however, are generally negative, because energy is usually released when a neutral atom adds an electron.

$$F(g) + e^- \longrightarrow F^-(g)$$
 $E_{ea} = -328 \text{ kJ / mol}$

Cl (g) + e⁻
$$\rightarrow$$
 Cl⁻(g) $E_{ea} = -349 \text{ kJ/mol}$

Again the value of Eea may not be negative for some elements. Whether the value of Eea may be negative or positive, depends on electron distribution of the element and the stability of the negative ion formed. For example:

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$$\begin{array}{lll} F \ (g) & + \ 1e^- & \longrightarrow F^- \ (... \ 2s^2 2p^6) & E_{ea} = - \ 32.8 \ kJ mol^{-1} \\ H \ (1s^1) & + \ 1e^- & \longrightarrow H^- \ (1s^2) + 72.8 \ kJ mol & E_{ea} = - \ 72.8 \ kJ mol^{-1} \\ Mg \ (... \ 3s^2) & + \ 1e^- & \longrightarrow Mg^- \ (... \ 3s^2 3p^1) & E_{ea} = 0 \ kJ mol^{-1} \end{array}$$

Ne $(1s^2 2s^2 2p^6) + 1e^- + \text{Energy} \longrightarrow \text{Ne}^{-(...3s^1)}$

 $E_{ea} > 0 \text{ kJ mol}^{-1} = + 29 \text{kJ mol}^{-1}$

orbitals can show more affinity to accept electron forming stable negative ions. So values of electron affinity energies (E_{ea}) of those elements are higher. Large negative E_{ea} 's are found for the halogens (F, Cl, Br, I), because each of these elements has both a high Z_{eff} (effective nuclear charge) and room for an additional electron in its valence shell. Halide ions have a stable noble gas electron configuration with filled s and p subshells, and the attraction between the addition electron and the atomic nucleus is high.

| 1A (1) | | | | | | | 8A (18) |
|-------------|--------------|-------------|------------|-------------|------------|------------|-------------|
| H -72.8 | 2A (2) | 3A (13) | 4A (14) | 5A (15) | 6A (16) | 7A (17) | He (0.0) |
| Li | Be | B | C | N | O | F | Ne |
| -59.6 | ≤0 | -26.7 | -122 | +7 | -141 | -328 | (+29) |
| Na | Mg | Al | Si | P | S | Cl | Ar |
| -52.4 | ≤0 | -42.5 | -134 | -72.0 | -200 | -349 | (+35) |
| K | Ca | Ga | Ge | As | Se | Br | Kr |
| -48.4 | -2.37 | -28.9 | -119 | -78.2 | -195 | -325 | (+39) |
| Rb | Sr | In | Sn | Sb | Te | I | Xe |
| -46.9 | -5.03 | -28.9 | -107 | -103 | -190 | -295 | (+41) |
| Cs -45.5 | Ba -13.95 | Tl -19.3 | Pb -35.1 | Bi -91.3 | Po -183 | At -270 | Rn (+41) |

Fig-3.11: Electron affinities of the elements of the main groups.

- (ii) Effective nuclear charge ($Z_{\rm eff}$) of the elements of s-block elements is low. So they have little or a little affinity for electron. So group-IA elements have lower values of electron affinity and group 2A elements have filled s-subshells so additional electron must go into a p-subshell. Because of the higher energy of the p-subshell, together with a relatively low $Z_{\rm eff}$ for group-2A elements $E_{\rm ea}$ values are near about zero; [Fig-3.11].
- (iii) Positive E_{ea} 's are found for the noble gas elements (He, Ne, Ar, Kr, Xe), because the s and p-sublevels in these elements are full, and the additional electron must go to next higher shell, where it is shielded from the nucleus and feels a relatively low Z_{eff} . The attraction of the nucleus for the added electron is small here and is reduced by additional electron-electron repulsions.

Different factors that do effect on Electron affinity

Electron affinity of the elements depend on the following factors:

- Increase of atomic size decreases electron affinity; it is a group based relation.
- Increase of nuclear charge increases electron affinity; it is a period based relation.

(iii) Increase of electron density in valence shell decreases electron affinity; - it is shown in Group-17 (7A). So electron affinity of halogens is Cl > F > Br > I

Worked Example-3.9: Electron Affinity Based:

Problem: Electron affinity of fluorine is less than that of chlorine; - explain.

Strategy: (i) F is an element of 2nd orbit; it has 2s² 2p⁵ valence electrons.

(ii) C1 is an element of 3rd orbit; it has 3s2 3p5 valence electrons.

Solution: The outermost orbit of fluorine atom is second orbit and that of chlorine is third orbit. In both cases seven valence electrons are present. The size of the 2nd orbit is small, hence the seven electrons cloud density in this orbit is high. The electrons of the 2nd orbit repel the incoming electron strongly. Hence the electron affinity of fluorine decreases. On the other hand, the comparatively large third orbit of chlorine atom can accomodate its seven valence electrons easily. Hence electron cloud density in Cl-atom is normal. So incoming electron is attracted by Cl-nucleus more. Hence electron affinity of Cl-atom is higher than that of F-atom.

Worked Example - 3.10: Electron Affinity Based:

Problem: Why does nitrogen have a less favourable (more positive) E_{ea} than its neighbours on its left and right side, C and O?

Strategy: The magnitude of an element's E_{ea} depends on the element's valence-shell electron configuration.

Solution: The electron configurations of C, N, O are as follows:

C (6)
$$\rightarrow$$
 1s² 2s² 2p_x¹ 2p_y¹ p_z⁰
N (7) \rightarrow 1s² 2s² 2p_x¹ 2p_y¹ 2p_z¹
O (8) \rightarrow 1s² 2s² 2p_x² 2p_y¹ 2p_z¹

Carbon has only two electrons in its 2p subshell and can readily accept another in its vacant $2p_z$ orbital. Nitrogen, however, has a half-filled 2p subshell, so the additional electron must pair up in a 2p orbital where it feels a repulsion from the electron already present. Thus, the E_{ea} of nitrogen is less favourable than that of carbon.

Oxygen also must add an electron to an 2p orbital that already has one electron, but the additional stabilizing effect of increased Z_{eff} across the periodic table counteracts the effect of electron repulsion, resulting in a more favourable E_{ea} for O than for N.

Student's Work -3.7: Electron affinity Based:

Problem -3.18: Electron affinity of different elements may be negative, positive and even zero. Explain with examples.

(F) Electronegativity

We know ionic bond is formed between metal atom and non-metal atom by complete transfer of electron. On the otherhand, a pure covalent bond is formed between two same atoms of a nonmetal like H or Cl to form covalent molecule like H_2 or Cl_2 by equal sharing of bond electron pair. But in many covalent compounds like HCl or H_2O , covalent bond is formed between two unlike atoms by unequal sharing of bond electron pair or by partial transfer of electron cloud from one atom to other atom; creating partial positive charge $(\delta +)$ and partial negative charge $(\delta -)$ on the two nonmetal bonded atoms. This type of covalent bond is called **polar covalent bond.** Then partial positive charge or delta plus $(\delta +)$ developes on the atom that has a smaller share of the bonding electrons and the other atom with larger share of bonding electrons gets partial negative charge or delta negative $(\delta -)$. For examples:

| M+ X: | 0+ 0- Y : X | X:X |
|----------------|-------------------|-----------------------------|
| Ionic | Polar covalent | Nonpolar covalent |
| (full charges) | (partial charges) | (electron-pair symmetrical) |

Definition: The electronegativity of an element present in a covalent compound is defined as its relative ability to attract the shared electron pair of the covalent bond towards itself. For example.

In HCl molecule, bond pair electron is unsymmetrically distributed; H atom end gets delta positive (δ^+) charge and Cl atom end gets delta negative (δ^-) charge.

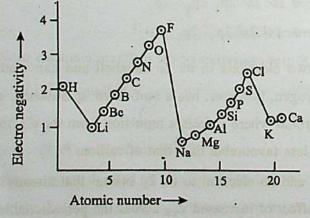


Fig. 3.12: Change in electronegativity with increase of atomic number.

When difference of electronegativities of two bonded atoms is between 0.5 to 1.9; then the two ends of the covalent molecule attain partial positive charge and partial negative charge and the molecule becomes polar. H. Cl \rightarrow H. Cl \rightarrow H. Cl

Effects of Different Factors on Electronegativity:

The electronegativities of different elements depend on following factors:

- (i) Increase of atomic size increases electronegativity, it is a group based relation.
- (ii) Increase of nuclear charge increases electronegativity.- it is a period based relation.

Fluorine, the member of 2nd period and group-17 (7A), being at upper most right end of the periodic table, is smaller in atomic size and most reactive nonmetal. So fluorine atomic nucleus attracts bond pair electrons most. Hence the electronegativity of F atom is the highest. According to Pauling electronegativity (EN) scale, the relative EN value of F is 4.07

| | | | | | Ele | ctrone | gativi | y incr | eases | | | | | | Pim | | → | |
|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|----------|------------------------|
| H 2.1 | | | | | | | | | | | | | | | | | Не | |
| Li 1.0 | Be 1.5 | | | | | | | | | | | B 2.0 | C 2.5 | N 3.0 | O 3.5 | F 4.0 | Ne | (53)(53) |
| Na 0.9 | Mg 1.2 | | | | | ynai | 7054 | nvit | | 311 | 170 | Al 1.5 | Si 1.8 | P 2.1 | S 2.5 | Cl 3.0 | Ar | decreases downwards |
| K 0.8 | Ca 1.0 | Sc 1.3 | Ti 1.5 | V 1.6 | Cr 1.6 | Mn 1.5 | Fe 1.8 | Co 1.9 | Ni 1.9 | Cu 1.9 | Zn 1.6 | Ga 1.6 | Ge 1.8 | As 2.0 | Se 2.4 | Br 2.8 | Kr | top to botton |
| Rb 0.8 | Sr 1.0 | Y 1.2 | Zr 1.4 | Nb 1.6 | Mo 1.8 | Tc 1.9 | Ru 2.2 | Rh 2.2 | Pd 2.2 | Ag 1.9 | Cd 1.7 | In 1.7 | Sn 1.8 | Sb 1.9 | Te 2.1 | I 2.5 | Xe | Musik san |
| Cs 0.7 | Ba 0.9 | Lu 1.1 | Hf 1.3 | Ta 1.5 | W 1.7 | Rc 1.9 | Os 2.2 | Ir 2.2 | Pt 2.2 | Au 2.4 | Hg 1.9 | Tl 1.8 | Pb 1.9 | Bi 1.9 | Po 2.0 | At 2.1 | Rn | - Van |

Fig-3.13: Electronegativity value of different elements and trends in the periodic table.

Electronegativities of the elements in the periodic table increase from left to right in a period due to increase of effective nuclear charge of the atoms of the elements with the increase of atomic numbers. As a result, atomic nuclei of the different atoms attract sharing bond electron pair more showing more electronegativities. According to Pauling electronegativity scale, the electronegativities of the different elements of 2nd period are as follows:

$$Li = 1.0$$
, $Be = 1.5$, $B = 2.0$, $C = 2.5$, $N = 3.0$, $O = 3.5$, $F = 4.0$

Students' Work - 3.8: Electron affinity, Electronegativity Based

Problem-3.19: Use the electronegativity values in Fig-3.13 to predict whether the bonds in the following compounds are polar covalent or ionic.

(a) SiCl₄

(b) CsBr

(c) CH₄

(d) FeBr₃

Problem - 3.19(a): Arrange the following compounds according to the increasing

ionic character of their bonds:

(a) CCl_4 (b) $BaCl_2$ (c) $TiCl_3$ (d) Cl_2O

Problem - 3.20 (a): Why electron affinity of flourine is less than that of chlorine; explain.

[D. B. 2015]

Problem - 3.20 (b): Flourine is the most electronegative element; explain.

[Syl. B. 2016; R. B. 2016, J. B. 2015]

Problem - 3.20 (c): Discuss the gradational electronegativity of four elements;

E (3), R(12), A(6), R(8).

[Ctg. B. 2017]

Problem-3.21(a): Write in tabular form the relation between electron affinity and electronegativity in group and period together with their effects in bond formation.

* With following stem give the answer of related next two questions:

| Elements → | F | Cl · | Br | 1 |
|--------------------------------|-------|-------|-------|-------|
| Electron affinity (kJ mol -1): | - 328 | - 349 | - 325 | - 295 |
| Electronegativity: | 4.0 | 3.0 | 2.8 | 2.5 |

Problem-3.21(b): Explain the such changes of electron affinity of stem elements.

Problem-3.21(c): Explain the influence of different factors on electron affinity and electronegativity of given stem elements.

(G) Metallic Properties

We have learnt upto this discussion that the effective nuclear charge ($Z_{\rm eff}$) on outermost orbit of the atoms of the elements in a period increases gradually from left to right. So the valence electrons of the atoms are attracted more by its nucleus, decreases atomic radii, and increases generally ionisation energy and electronegativity of the elements. Then atoms of the elements of the periodic table in the left side donate electrons, during bond formation, to form positive ions and the elements on right side of the periodic table accept electrons forming negative ions. In this way, metallic properties of the elements decrease from left side towards right side in a period with the increase of nonmetallic properties. For example, in 3rd period of the periodic table Na, Mg, Al are metals; Si is a metalloid or semimetal and P,S and Cl are nonmetals.

Atomic size increases down a group in the periodic table due to addition of new energy level for the electrons. As a result, valence electron shell gets apart from the nucleus of the atom gradually, causing the decrease of ionisation energy and electronegativity of the atom. Then the metallic properties gradually increase down a group and non-metallic properties decrease. On the left most and group-1 downwards most is the 'Fr' which is most reactive but unstable radioactive. So stable most reactive metal is Cs.

In the periodic table, along the staircase zigzag line running from boron (B) to Astatine (At), the adjacent elements seven in total number such as B, Si, Ge, As, Sb, Te, At are metalloids or semimetals having mixed properties of metal and nonmetal.

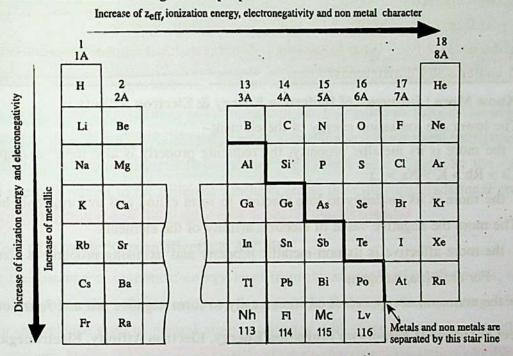


Fig-3.14: Increase of metallic property down a group; and non-metallic property increases in a period left to right.

Worked Example - 3.9.1: Metallic and Nonmetallic Properties

Using periodic table, predict which element in each pair has more metallic character :

(a) P or Bi

(b) As or Ga

(c) Sb or S

(d) Sn or Ba

Strategy: Metallic character increases from right to left and from top to bottom in the periodic table. Look out which element in each pair lies lower in a group and most left in a period.

Solution: (a) Bi lies below P in group 15 (5A). Therefore, Bi is more metallic.

- (b) As and Ga are in the same row of the periodic table, but Ga [group-13 (3A)] lies to the left of As [group -15 (5A)]. Therefore, Ga is more metallic.
- (c) Sb [group-15 (5A) has more metallic character because it lies below and to the left of S [group-16 (6A)].
- (d) Ba [group-2 (2A)] is more metallic because it lies below and to the left of Sn [group-14 (4A)].

Students' Work - 3.9: Metal, Non-metal and Metalloid Based:

Problem-3.22(a): Predict which element in each of the following pairs has more non-metallic character:

(a) B or Al (b) Ge or Br (c) Cl or Te (d) In or Se

Problem-3.22(b): What is metalloid? What is the total number of metalloids? Which period contains more metalloids?

Know More: Influence of Ionisation Energy & Electron Affinity:

- (A) The lower the ionisation energy of the element
 - the more is its metallic property, the reducing property is also more. example Cs > Rb > K > Na > Li
 - the more is its tendency to lose electron to form cation and to form ionic bond.
- (B) The more the negative value of electron affinity of the element
 - the more affective is its non-metallic property and oxidising property is also more.

 For example, halogens.
 - the nonmetal accepts electron more easily to form negative ion and form ionic bond.

3.4 Effect of Different Factors on Ionisation Energy, Electron Affinity, Electronegativity

The effect of different factors such as atomic size, different subshells and electron configurations are very prominent on the three prime periodic properties of the elements like ionisation energy, electron affinity and electronegativity. These are discussed below in short.

3.4.1 Effect of Atomic Size on Ionisation Energy

The size of an atom is mainly understood from the value of principal quantum number (n). The sizes of the different atoms will be increased with the increase of the values of 'n'. With the increasing values of n the atomic nuclear attraction on the valence electrons is gradually decreased. As a result, the ionisation energy of the atom decreases. Hence in a group from up to downwards, the ionisation energies of the elements decrease gradually. For example, in group-1, the ionisation energies of the alkali metals decrease gradually with the increase of their atomic numbers as follows:

Li = 530 kJ, Na = 496 kJ, K = 418 kJ, Rb = 403 kJ, Cs = 376 kJ

Effect of Subshells on Ionisation Energy

Subshells mean s, p, d, f orbitals. In a period for the electron distributions of the different atoms of different elements, the value of principal quantum number or the orbit (n) remains same; but their valence-electrons remain distributed in different subshells or s, p, d, f orbitals.

In a period with the increase of atomic number of the elements positive charge increases in the atomic nucleus. Then nuclear attraction on the p-orbital remains more than s-orbital. Similarly nuclear attraction on d-orbital remains still more than p-orbital and s-orbital. In these cases ionisation energies of the elements with different subsells containing valence electrons are as follows: d-subshell > p-subshell > s-subshell

Effect of Electron Configurations on Ionisation Energy:

When the electron configuration of an atom contains half filled or fully filled degenerate orbitals (such as p³, d⁵ or p⁶, d¹⁰), then that atom gets more stable electron configuration. In those cases, to remove one electron from valence shell needs more energy. So the values of ionisation energies related to the different subshells are in the following gradational order.

fully filled subshell > half filled subshell > partially filled subshell

3.4.2 Effect of Atomic Size on Electron Affinity

When the distance of outermost energy level from the atomic nucleus decreases, then the nuclear attraction on the valence electrons increases. In this case, the incoming additional electron in the valence shell of neutral atom is attracted with more energy. As a result, more energy is evolved. Hence the atom with smaller atomic size shows more electron affinity. As the atomic sizes of different elements in a period gradually decrease with increase of atomic numbers from left to right, then the electron affinities of different elements also increase generally. For example—

In 2nd period O atom has electron affinity, $E_{ea} = -141 \text{ kJmol}^{-1}$ and its right side placed F atom with smaller atomic size, has more electron affinity such as $E_{ea} = -328 \text{kJ} \text{ mol}^{-1}$.

But in group-17 (7A), the electron affinity of fluorine ($E_{ea} = -328 \text{ kJmol}^{-1}$) is less than that of chlorine ($E_{ea} = -349 \text{ kJmol}^{-1}$). This is due to the very smaller atomic size and existance of its valence shell at smaller second orbit. The seven electrons of F atom in smaller second orbit repel the incoming additional electron strongly. Hence the electron affinity of F atom decreases.

Effect of Subshell on Electron Affinity: Shielding Effect

The electron affinity of an element also depends on the presence of valence electrons on different subshell of the atom. The attraction of the atomic nucleus on the outermost electrons is somewhat shielded by the inner subshell electrons' cloud. So with the increase of number of subshells in an atom for the electrons, the attraction of atomic nucleus on the

valence electrons decreases more. Hence electron affinity of that atom will also be decreased. For this reason, the values of electron affinity of the elements of period-4 and 5 are smaller than those of period-2 and 3. This type of effect of subshells on electron affinity is known as the shielding effect of subshells.

Effect of Electron Configurations on Electron Affinity

Electron affinity of an element means the tendency of its atom to fill up the octet set of electrons in its outermost valence-shell. So the smaller the required number of electrons to fill up the octet set of the atom of the element, the greater is the electron affinity of that element. Hence the electron affinity of the member of halogens is the highest in a period.

3.4.3 Effect of Atomic size, Subshells and Electron Configurations on Electronegativity

With the increase of atomic sizes, electronegativity of the elements decreases, it is the periodic ralation. In a group, from up to down, with the increase of atomic numbers of the elements, the number of subshells in an energy level also increases. Then the attraction of the nucleus on the valence-shell of the atom decreases. So electronegativity of the members of halogens of group-17 (7A) decreases in the following order:

$$F = 4.0$$
, $Cl = 3.0$, $Br = 2.8$, $I = 2.5$

Similarly, the effect of electron configuration on electronegativity has the same tendency.

.5 Acid-Base Properties of Oxides of 2nd & 3rd Period's Elements

The acid-base properties of the oxides of the elements of period-2 and 3 of the periodic table depend on the ionisation energies, electron affinities and electronegativities of those elements. We have learnt the following facts from the discussion of these periodic properties:

- (i) Li and Be of 2nd period, Na, Mg and Al of 3rd period are metals. With oxygen these elements form ionic metal oxides by transfer of electrons. The metal oxides are basic in character. Again, from the left to right across the period metallic properties decrease gradually and the last metal on the right side in a period shows mixed properties of metal and nonmetal. This mixed properties of metal and nonmetal will be seen in oxide of Al-metal.
- (2) Again the nonmetals B, C, N of 2nd period have the values of electronegativity more than 2 and nonmetals Si, P, S of 3rd period have the electronegativity values still less than those of 2nd period. So they form covalent oxides by sharing of electrons.

Among the nonmetal oxides with higher oxidation numbers are acidic and they form oxoacids with water. Those oxides are called acid anhydrides.

For example,
$$CO_2 + H_2O \rightarrow H_2CO_3$$
; $N_2O_5 + H_2O \rightarrow 2HNO_3$

But oxides of lower oxidation number are neutral oxides like CO, N2O, NO etc.

Table-3.5: Oxides of elements of 2nd and 3rd periods, with increase of covalent character.

| | O-112-4 | in-084 | Covalent | character incre | ases | LOU. HO. F. | | |
|-----------------|---|--|--------------------------------------|---|--|--|--|--|
| | 0.015 = 21140 | 1 1A | 2 2 2A | 13 3A | 14 4A | 15 5A | 16 6A | 17 7A |
| ionic character | Increase of ionic character Increase of basic properties | Li metal Li ₂ O strong base | Be metal BeO ampho teric | B non metal B ₂ O ₃ acidic | C nonmetal CO ₂ acidic | N nonmetal N ₂ O ₅ more acidic | CH STAN O | New York |
| 1 | Increase of Increase of | Na metal Na ₂ O strong base | Mg metal MgO strong base | Al metal Al 2O 3 ampho teric | Si nonmetal SiO ₂ mild acidic | P nonmetal P ₂ O ₅ P ₂ O ₃ | S nonmetal SO ₃ SO ₂ | Cl nonmetal Cl ₂ O ₇ ClO ₂ |
| | | | | | | Strong a | cidic oxide: | 5 |

* Formation of Alkali and Acid by the Oxides of Elements of Same Period with Water:

(1) By the reactions of oxides of different elements of a period with water proves the gradational change of basic properties to acidic properties of those oxides. For example,

Li₂O of the metal of 2nd period, group-1, forms soluble strong alkali lithium hydroxide (LiOH) with water and Na₂O of the metal of 3rd period, group-1, forms soluble strong alkali sodium hydroxide (NaOH) with water

$$\text{Li}_2\text{O}(s) + \text{H}_2\text{O}(l) \longrightarrow 2\text{LiOH}(aq) \longrightarrow 2\text{Li}^+(aq) + 2\text{OH}^-(aq)$$

 $\text{Na}_2\text{O}(s) + \text{H}_2\text{O}(l) \longrightarrow 2\text{NaOH}(aq) \longrightarrow 2\text{Na}^+(aq) + 2\text{OH}^-(aq)$

(2) Beryllium oxide (BeO) of 2nd period and magnesium oxide of 3rd period of group-2 are water insoluble. They do not react with water to form any alkali. But BeO reacts with acid and strong alkali solutions as an amphoteric oxide to form salt and water. With strong NaOH solution BeO forms beryllate salt and water.

As base: BeO (s) + 2HC1 (aq)
$$\longrightarrow$$
 BeC1₂ (aq) + H₂O(l)
As acid: BeO (s) + 2NaOH (aq) \longrightarrow Na₂BeO₂ (aq) + H₂O(l)
sodium beryllate

On the other hand; MgO of Mg metal of 3rd period is water insoluble and reacts with acid to form salt and water.

$$MgO(s) + H_2SO_4(aq) \longrightarrow MgSO_4(aq) + H_2O(l)$$

(3) B₂O₃ and CO₂ of elements of 2nd period are weak acidic; both the oxides react with water to form unstable acids; and form salt and water with alkali. B₂O₃ form orthoboric acid with water and metaborate salt with alkali like NaOH.

$$B_2O_3(s) + 3H_2O(1) \longrightarrow 2H_3BO_3(aq); H_3BO_3(aq) + NaOH(aq) \longrightarrow NaBO_2(aq) + 2H_2O(l)$$

 $CO_2(g) + H_2O(l) \longrightarrow H_2CO_3(aq); H_2CO_3(aq) + 2NaOH(aq) \longrightarrow Na_2CO_3(aq) + 2H_2O(l)$

(4) The two oxides, N₂O₃ and N₂O₅ of N element of 2nd period, are both acidic oxides. On reaction with water N₂O₃ forms unstable nitrous acid (HNO₂), but forms sodium nitrite (NaNO₂) salt with NaOH solution. On the otherhand, N₂O₅ reacts with water to form strong nitric acid (HNO₃) and with NaOH it forms sodium nitrate salt and water.

$$N_2O_3$$
 (g) $+ H_2O(l) \longrightarrow 2HNO_2$ (aq)
 HNO_2 (aq) $+ NaOH(aq) \longrightarrow NaNO_2$ (aq) $+ H_2O(l)$
 N_2O_5 (s) $+ H_2O(l) \longrightarrow 2HNO_3$ (aq)
 $HNO_3(aq) + NaOH(aq) \longrightarrow NaNO_3(aq) + H_2O(l)$

(5) Al₂O₃ of metal Al, member of 3rd period, group-13, does not react with water; but it reacts separately with acid and alkali to produce salt and water. Hence Al₂O₃ is an amphoteric oxide.

Al₂O₃ as a base: Al₂O₃ + 6HC1
$$\longrightarrow$$
 2AICl₃ + 3H₂O
Al₂O₃ as an acid: Al₂O₃ + 2NaOH \longrightarrow 2NaAIO₂ + H₂O

(6) Silicon dioxide (SiO₂) does not react with water or acid; but it reacts with strong alkali to form silicate salt and water.

$$SiO_2(s) + 2NaOH(aq) \longrightarrow Na_2SiO_3(aq) + H_2O(l)$$

(7) Diphosphorus pentaoxide (P_2O_5) reacts with water to form weak acid phosphoric acid (H_3PO_4). With an alkali NaOH, it forms disodium phosphate and water. So P_2O_5 is an acidic oxide. $P_2O_5 + 3H_2O \longrightarrow 2H_3PO_4$

$$P_2O_5 + 4NaOH \rightarrow 2Na_2HPO_4 + H_2O$$

Another oxide of phosphorus is P_2O_3 which reacts with water to form phosphorous acid (H_3PO_3) . $P_2O_3 + 3H_2O \longrightarrow 2H_3PO_3$.

(8) Sulphur trioxide (SO₃) reacts with water to form strong sulphuric acid (H₂SO₄). With alkali NaOH solution SO₃ reacts to form sulphate salt and water.

$$SO_3 + H_2O \longrightarrow H_2SO_4$$

 $SO_3 + 2NaOH \longrightarrow Na_2SO_4 + H_2O.$

Another oxide of sulphur is sulphur dioxide, (SO₂) which reacts with water to form sulphurous acid (H₂SO₃). With alkali (NaOH) solution, SO₂ forms sodium sulphite salt and water. SO₂ + H₂O \rightarrow H₂SO₃; SO₂ + 2NaOH \rightarrow Na₂SO₃ + H₂O

(9) Dichloroheptaoxide (Cl₂O₇) reacts with water to form parchloric acid (HClO₄). With alkali Cl₂O₇ forms perchlorate salt and water. Hence Cl₂O₇ is an acidic oxide.

$$Cl_2O_7 + H_2O \longrightarrow 2HClO_4;$$
 $Cl_2O_7 + 2NaOH \longrightarrow 2NaClO_4 + H_2O$

Note that metal oxide is basic; nonmetal oxide is acidic. It is the pH periodicity of the oxides of elements. So it is established from the acid-base properties of the oxides of elements of 2nd and 3rd periods that going from left to right across a period metallic property of the elements decreases gradually with the increase of non-metallic property.

Know more: The uses of different oxides depend on their properties such as high thermal stability, mechanical strength, and electrical resistance, MgO and Al₂O₃ are used as high-temperature electrical insulators in products such as electrical heaters and automobile spark plugs. SiO₂ is the main component of the optical fibers used for communications. The acidic oxides of the nonmetals are used for three industrial acids such as H₂SO₄, HNO₃ and H₃PO₄.

At a Glance:

| Periodic Properties | Periodic Tendency | Group Tendency |
|------------------------------|------------------------------|---------------------|
| 1. Atomic radius, Size : | Decreases from left to right | Increases downwards |
| 2. Metallic Property : | Decreases from left to right | Increases downwards |
| 3. Non-metallic Property: | Increases from left to right | Decreases downwards |
| 4. Oxidising Property: | Increases from left to right | Decreases downwards |
| 5. Readucing Property: | Decreases from left to right | Increases downwards |
| 6. Valency: | Increases from left to right | No change |
| 7. Ionisation Energy: | Increases from left to right | Decreases downwards |
| 8. Electron Affinity: | Increases from left to right | Decreases downwards |
| 9. Electronegativity: | Increases from left to right | Decreases downwards |
| 10. Basic property of oxides | Decreases from left to right | Increases downwards |
| 11.Acidic Property of Oxides | Increases from left to right | Decreases downwards |

Worked Example 3.11: Formulas and Properties of oxides based:

Three elements A, B, C are respectively of the 2nd period's groups-15 (5A), 5th period's group-14 (4A), 6th period's group-2 (2A). From these informations-(a) Write the formula of oxide of each element with its highest oxidation number. (b) Which oxide of these is more ionic and more covalent? (c) Classify each oxide as basic, acidic, or amphoteric.

Strategy: (a) The highest oxidation number (O.N) of main group element and the formula of its oxide are determined by location of the element in periodic table. If M is in group-1 (1A). its O. N = + 1 and its oxide has formula M_2O , because the O.N of oxygen in an oxide is -2, and O.N of all atoms in a neutral compound must sum to zero.

- (b) Recall that ionic character of a compound decreases and covalent character increases in the periodic table from left to right and from bottom to top.
- (c) Recall that basic character of oxide decreases and acidic character increases in the periodic table from left to right and from bottom to top.

Solution: (a) Elements A, B, C can be identified as N, Sn and Ba, respectively. Because N, Sn and Ba are in groups 5A, 4A and 2A repectively, their formulas of oxides with highest O.N are N₂O₅, SnO₂ and BaO.

- (b) BaO is the most ionic because Ba is in the lower left region of the periodic table, and N₂O₅ is the most covalent because N is in the upper right region.
- (c) BaO is basic, N₂O₅ is acidic, and SnO₂ is amphoteric. Note that Sn is one of the five main-group elements that form an amphoteric oxide.

(such as BeO, Al₂O₃, Ga₂O₃, SnO₂, PbO₂)

Students' Work- 3.10: Properties of Oxides Based:

Problem-3.23: Write balanced net ionic equations for the following reactions:

- (a) Dissolution of solid Li₂O in water. (b) Dissolution of SO₃ in water.
- (c) Dissolution of amphoteric oxide Cr₂O₃ in strong acid.
- (d) Dissolution of Cr₂O₃ in strong base to give Cr(OH)₄⁻ ions.
- (e) Dissolution of ZnO in strong acid and strong alkali solutions.

Problem-3.24: Discuss the acidic and basic properties of oxides of elements of 3rd

period

[D. B. 2015]

Practical

Students' Work in the Laboratory

3.6 Name of Expt: To Determine Acid-Base nature of Soluble Oxides of Elements

Expt. No. - 11

Time: 2 Period

Date :

Principle: Soluble metal oxides react with water forming metal hydroxides which later ionize to form OH- ions. The OH- ions turn red litmus to blue or turn universal indicator blue or pink. On the other hand, nonmetal oxides react with water forming weak or strong acids which ionize to form hydrogen ions (H⁺) or hydronium ions (H₃O⁺). The produced H⁺ ions or H₃O⁺ ions turn blue litmus red or turn universal indicator to red or yellow.

$$CaO(s) + H_2O(l) \longrightarrow Ca(OH)_2(s)$$

$$SO_2(g) + H_2O(l) \longrightarrow H_2SO_3$$
 (aq)

$$Ca(OH)_2(s) + aq \longrightarrow Ca^{2+}(aq) + 2OH^-(aq)$$
 $H_2SO_3(aq) + aq \longrightarrow H^+(aq) + HSO_3^-(aq)$

$$H_2SO_3$$
 (aq) + aq \longrightarrow H^+ (aq) + HSO_3^- (aq)

$$OH^-(aq) + red litmus \longrightarrow blue litmus$$

$$H^+(aq) + blue litmus \longrightarrow red litmus$$

Required Oxides: (1) Calcium oxide (CaO), (2) Barium Oxide, (BaO),

(3) Carbon dioxide (CO₂) gas, (4) Sulphur dioxide (SO₂) gas

Required Chemicals: (1) Sodium sulphite (Na₂SO₃), (2) Hydrochloric acid (HCl),

(3) Lime stone (CaCO₃), (4) Distilled water.

Required Apparatus: (1) Test tubes, (2) Gas delivery tube with cork,

(3) Litmus papers (red, blue) or Universal indicator.

Procedure:

Expt. No-1: In a test tube a small amount of calcium oxide or lime (CaO) is taken and about 10 mL water is added to dissolve CaO. To the clear solution a red litmus paper is added; the red litmus paper turns blue. Then a blue litmus paper is added, blue litmus remains blue. This indicates calcium oxide solution is basic. Hence the pH of CaO solution or Ca(OH)₂ is more than 7. In the observation data, it is recorded.

Expt.No. 2: Following Expt. No. 1, a small amount of barium oxide is taken in a test tube and is dissolved in water. In the solution, red litmus and blue litmus papers are added. In both cases litmus papers turn blue. It proves barium oxide solution or Ba(OH)2 is basic. The PH value of the solution of BaO is more than 7. In the observation data, it is recorded.

Expt. No. 3: In a test tube small amount of sodium sulphite (Na₂SO₃) is taken and HCl acid is added, then gas delivery tube is fitted with cork at its mouth. The evolved SO₂ gas is passed in water taken in another test tube. Now in SO₂ gas solution, blue litmus and red litmus papers are added. Both the litmus papers become red. This proves that solution of SO₂ gas is acidic. The pH value of this solution is less than 7.

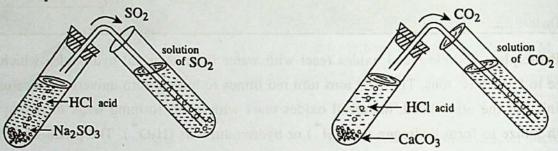


Fig-3.15: Preparation of SO₂ and CO₂ gases.

Expt. No.-4: Similar to Expt. No-3, in a test tube a few pieces of lime stone are taken and HCl acid is added, then gas delivery tube is fitted with cork at its month. The evoled CO₂ gas is passed in water taken in a test tube. Now in CO₂ gas solution, red litmus and blue litmus papers are added. Both the litmus papers become red. This proves that CO₂ gas is acidic. The PH value of this CO₂ gas solution is less than 7.

Table – 3.3 : Expt. Observation data and Conclusion

| Expt-No. | Solution of oxides | | Colour of blue litmus | Conclusion That (1) A studing A beginned |
|-------------|--------------------------|------|-----------------------|--|
| Expt. No1 | CaO solution | blue | blue | 1.Solution of CaO is basic; pH >7 |
| Expt. No- 2 | BaO solution | blue | blue | 2. Solution of BaO is basic; pH >7 |
| Expt. No-3 | SO ₂ solution | red | red | 3. Solution of SO ₂ is acidic; pH < 7 |
| Expt. No4 | CO ₂ solution | red | red | 4. Solution of CO ₂ is acidic; pH < 7 |

3.7 Relation between Periodic Properties and Bond Formation

To mean the relation between periodic properties and bond formation is the scope of formation of ionic compounds and covalent compounds according to octet theory of chemical combination on the basis of electron configurations of the elements of s-block elements and p-block elements. With this concept of chemical combination, two periodic properties like ionisation energy and electron affinity are closely related.